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**From Micro-Structured Materials to Layered
Compounds: Strategies for Thermal Energy
Management**

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From Micro-Structured Materials to Layered Compounds: Strategies for Thermal Energy Management
Sapienza University of Rome

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Introduction

The motivation behind this thesis project is to investigate several materials using various experimental and computational techniques to address the demand for the development of new energy sources and novel materials capable of energy generation/conversion. More broadly, the topic of thermal energy management is addressed in several ways, involving micro-structured and layered materials. The investigation of these processes was made possible thanks to the superposition of several techniques, including near-field and far-field spectroscopic and thermal emission measurements, Seebeck coefficient, and resistivity measurements. The fabrication of high-quality samples via Molecular Beam Epitaxy and the performance of electromagnetic simulations gave a boost to this study.

The fundamental mechanisms responsible for energy generation and transfer are examined, together with their compatibility with the emerging requirement of producing green-nature systems. In fact, the environmental impact of global climate change, resulting from fossil fuel combustion, greenhouse gas emissions, and ozone layer damage, is driving research toward new, environmentally friendly materials, highly efficient in converting energy into other usable forms. One of the major challenges of the last decade concerns the possibility of recovering the employed energy as much as possible, avoiding energy waste in the form of heat. Within this context, the term energy harvesting refers to the set of processes by which useful energy is captured from waste, environmental, or mechanical sources and is converted into a usable form. The discipline of energy harvesting is a broad topic, including established methods and materials, such as photovoltaics and thermoelectrics, as well as more recent technologies that convert mechanical energy, magnetic energy, and waste heat into electricity. Thermoelectric materials are semiconductor systems that can directly convert electricity into thermal energy for cooling or heating, or recover waste heat and convert it into electrical power. Their competition with standard mechanical providers of heating, cooling, and electrical power generation, such as air conditioners, refrigerators, heat pumps, and turbine engines, is still unbalanced, as their conversion efficiency is low; therefore, research on this topic is essential and is object of interest in this work.

The mechanism of heat generation is also considered by studying the emission of thermal radiation. The latter is a powerful and easy way to respond to the demand for new energy sources since it is a photon production process easily generated via the Joule effect by heating conductive materials.

This work is divided into two main research areas, addressing the thermal energy management issue: the first covering the study of one of the heat transfer mechanisms, i.e., the emission of thermal radiation as a function of frequency and temperature from micro-structured materials, both natural and artificially patterned; the second covering instead the development and investigation of exotic epitaxial materials to strongly enhance and improve the thermoelectric performance and boost the research toward the development of devices based on phase-change effects. Micro-structured

materials and layered compounds are considered for the two areas, respectively. The first topic is explored in depth to gain insight into the fundamental physics underlying this heat transfer mechanism, through the investigation of 3D microporous graphene and standard Silicon Carbide (SiC) samples. The microstructures in 3D graphene induce non-trivial optical and thermal behavior, enhancing the emissivity performance of these materials compared to the standard SiC counterpart, paving the way toward the realization of new eco-friendly thermal emitters. Later, the study moves towards the understanding of phonon-polariton excitations in polar materials such as SiC and how they can be exploited to modify far-field optical and thermal emission properties when artificial patterning is introduced.

The second topic is instead addressed through the study of the optical and transport properties of topological insulators, which turn out to be promising candidates for thermoelectricity. Epitaxial thin films of Bi_2Se_3 , Bi_2Te_3 , Sb_2Te_3 , and $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ alloys, grown via Molecular Beam Epitaxy, are presented. Their resistivity, Seebeck coefficient, electronic thermal conductivity, and figure of merit ZT are estimated.

At last, the optical properties of epitaxial $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ layered alloys are presented. These materials belong to the phase-change material class, i.e., a group of semiconducting materials characterized by two allotrope phases, a crystalline and an amorphous one. More specifically, these compounds exhibit reversible and fast phase transitions from amorphous to crystalline phases, characterized by different optical properties. This switching capability can be employed as a storage mechanism for volatile memories. Beyond this functionality, these materials could exhibit interesting thermoelectric properties.

Chapter 1

Heat Transfer and Energy Conversion Mechanisms

In this Chapter, an overview of the physical phenomena describing heat transfer and energy generation mechanisms is given, with the purpose of laying the basics for a theoretical understanding of the investigated experimental aspects of this work. At first, the emission of thermal radiation, that is an energy generation mechanism, is discussed to understand its physical origins, and later on, the possibility of acting and modifying its main features is considered. As a second step, an overview of thermoelectricity, that is a reversible phenomenon of energy conversion, is given, focusing on the strategies and on the materials that are already efficient in performing this kind of process. Finally, epitaxial phase-change materials are considered.

1.1 The emission of thermal radiation

Heat is a transient exchange of energy between two macroscopic objects at different temperatures, typically considered a form of energy dissipation and thus classified as 'useless' energy. Nevertheless, heat transfer control has recently been attracting significant interest because it enables addressing problems such as the heating of smart devices and, more broadly, global warming and the energy crisis. Among the various heat transfer mechanisms, such as conduction, convection, and thermal radiation emission, the latter has gained significant interest due to its potential applications [1, 2, 3, 4, 5, 6].

In this Section, the origin of the emission of thermal radiation is discussed from a macroscopic and microscopic point of view, first explaining the phenomenon through the concept of light quanta, embedded in Planck's law, and then focusing on the microscopic current density correlations existing within material bodies as the trigger mechanism of thermal emission. Finally, the concept of thermal emission engineering is presented as a way to alter this fundamental physical process via the excitation of surface waves.

1.1.1 Macroscopic Interpretation

It is well known that from a macroscopic point of view, any object at a non-zero temperature and in thermal equilibrium emits thermal radiation in the far-field regime according to Planck's law, with universal features such as large spatial and temporal incoherence, translated into unpolarized field distribution, isotropic propagation, and broadband spectrum [7, 8, 9, 10]. However, the mechanism behind

this process was not fully understood until the beginning of the twentieth century. Thanks to Max Planck, the idea of thermal radiation being emitted through discrete energy packets, referred to as photons, took place in 1900, and a universal formula describing the spectral radiance, i.e., the energy emitted per unit of time, frequency, solid angle, and area, was proposed [11]:

$$I(\omega, T) = \frac{\omega^2}{\pi^2 c^3} \hbar \omega \frac{1}{e^{\hbar \omega / k_B T} - 1} = \text{DOS} \cdot \langle E \rangle \quad (1.1)$$

where ω is the frequency, c is the speed of light, $\hbar$ is the Planck constant, k_B is the Boltzmann constant, and T is the temperature. This expression can be read as the product of the photon density of states (DOS) $\frac{\omega^2}{\pi^2 c^3}$ and the average energy $\langle E \rangle$ of the harmonic oscillators that make up the "photon gas" in thermal equilibrium as a function of temperature, weighted with the Bose distribution $\frac{1}{e^{\hbar \omega / k_B T} - 1}$ [12]. The core of this equation is that the emission of thermal radiation depends only on frequency and temperature. Thus, it properly describes the behavior of a black body, an idealized physical body that absorbs all incident electromagnetic radiation, regardless of frequency or angle of incidence, and that has a universal

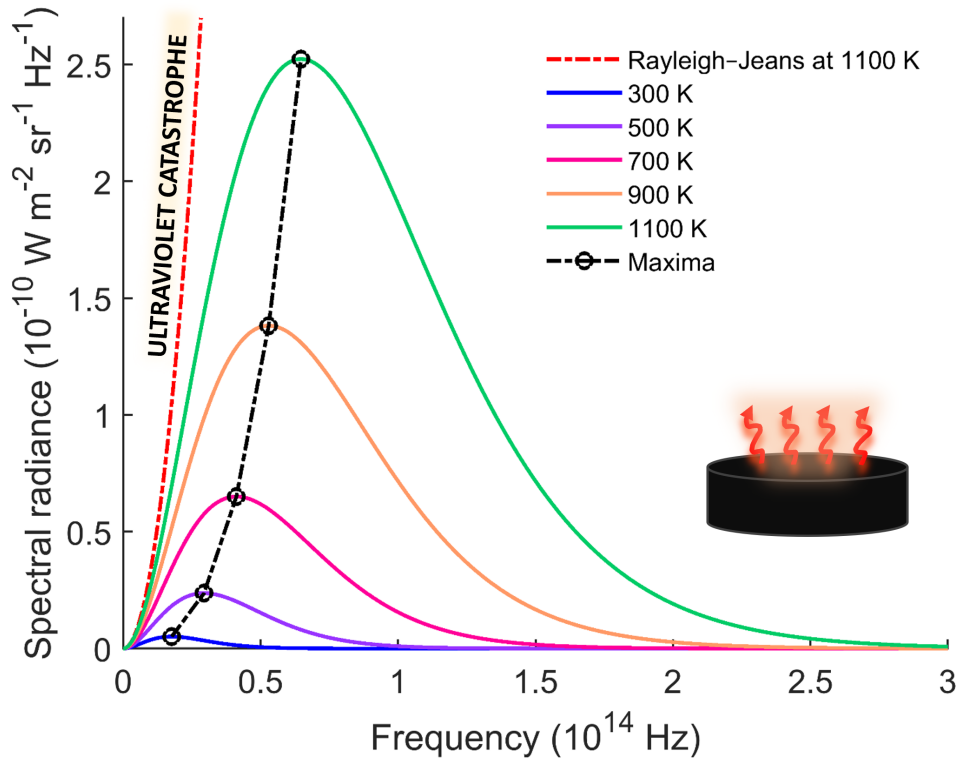


Figure 1.1. Blackbody spectra calculated using Planck's formula (see Equation 1.1) from 300 K (blue curve) to 1100 K (green curve). Black circles correspond to the maxima of the distributions, which depend only on temperature, as predicted by Wien's displacement law. The black dashed curve is a guide for the eye. The red dashed curve is instead the spectral radiance calculated at 1100 K by using the Rayleigh-Jeans formula (see Equation 1.2), displacing the problem of the ultraviolet catastrophe, i.e., of the energy divergence for large frequency values.

temperature-dependent spectrum, independent of the material composition itself.

Real bodies, which are not optically black, deviate from this behavior because their optical properties, such as reflection, transmission, and absorption, exhibit spectral selectivity, and because they thermally emit less than a black body. These discrepancies can be accounted for by multiplying Planck's law for a quantity called emissivity $\varepsilon(\theta, \phi, \nu, T)$, defined as the ratio between the spectral radiance of the real body and that of an ideal black body at the same temperature. This quantity is itself a function of solid angle, frequency, and temperature [13]. Additionally, this formula puts both upper and lower constraints on the emission of thermal radiation versus frequency, showing that it is impossible to emit infinite radiation, both at low and high frequencies, overcoming the ultraviolet catastrophe. The latter was theoretically predicted by the Rayleigh-Jeans formula, which describes the spectral radiance as [11]:

$$I(\omega, T) = \frac{\omega^2 k_B T}{\pi^2 c^2} \quad (1.2)$$

As can be observed, this equation leads to an infinite value for large frequencies, which is in total contradiction with the real physical observations. Figure 1.1 shows the calculation of the spectral radiance for a blackbody using Planck's formula (Equation 1.1), from 300 K, corresponding to the blue curve, to 1100 K, corresponding to the green curve. Compared to the spectral radiance calculated with the Rayleigh-Jeans formula at 1100 K (red dashed curve), the other curves exhibit a bell shape, with a maximum in frequency given by $\omega_{max}/T = \text{const}$, as predicted by the Wien displacement trend, highlighted by the black circles [14]. The red dashed curve, instead, recovers the correct frequency behavior only for small frequency values, diverging as ω increases. In summary, within a far-field macroscopic framework, each body emits thermal radiation due to its finite temperature, with a bell-shaped spectral distribution that shifts its maximum toward larger frequencies and enlarges its area as temperature is increased.

1.1.2 Microscopic Interpretation

On the other side, from a microscopic point of view, the emission of thermal radiation can be explained via a semi-classical approach called *fluctuational electrodynamics* [15]. According to this theoretical model, the emission of thermal radiation from a hot body at temperature T can be understood as a result of the radiation emitted by fluctuating electromagnetic currents, i.e., random thermally activated electric currents inside the body due to the thermally induced motion of particles and quasiparticles. The latter, being random, vanish on average, but their correlations don't, making the emission of radiation on a macroscopic scale possible. Current density correlations can be calculated within the framework of the fluctuation-dissipation theorem (FDT) [16] and show that thermally fluctuating currents at different frequencies and positions are uncorrelated, explaining the stochastic and incoherent nature of thermal fields. More in detail, the FDT relates the correlations of the fluctuating electromagnetic currents $\mathbf{j}(\mathbf{r}; \omega)$ in a given position $\mathbf{r}$ and at a given frequency ω , and the dissipative characteristics associated with the material response function $\epsilon(\omega)$, also named dielectric function [17]:

$$\langle \mathbf{j}^*(\mathbf{r}; \omega) \cdot \mathbf{j}(\mathbf{r}'; \omega') \rangle_{th} = 4\pi\epsilon_0\epsilon_2(\mathbf{r}, \omega)\hbar\omega^2\Theta(\omega, T)\delta[\omega - \omega']\delta[\mathbf{r} - \mathbf{r}'] \quad (1.3)$$

Here, the brackets indicate a thermal ensemble average, ϵ_0 is the vacuum permittivity, $\hbar$ the Planck's constant, ω the frequency, $\Theta(\omega, T) = [e^{\hbar\omega/k_B T} - 1]^{-1}$ is the Bose distribution [12], and $\epsilon(\mathbf{r}, \omega) = \epsilon_1(\mathbf{r}, \omega) + i\epsilon_2(\mathbf{r}, \omega)$ is the linear response function of

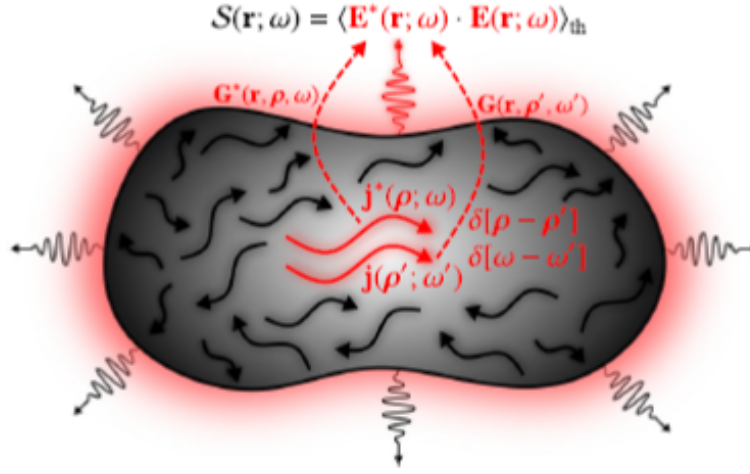


Figure 1.2. Schematic representation of the fluctuating electromagnetic currents $\mathbf{j}(\mathbf{r};\omega)$ moving inside a body at finite temperature T . The solid red arrows represent two particular electric currents that are locally correlated, which release, via the corresponding Green's function (dashed red arrows), the emission of thermal fields out of the material. Obtained from Ref. [17].

the medium, i.e., the dielectric function, composed of a real (ϵ_1) and an imaginary (ϵ_2) part. Therefore, the FDT theorem shows that the current density operator in position $\mathbf{r}$ and at frequency ω and the current density operator in position $\mathbf{r}'$ and at frequency ω' are totally uncorrelated, since their thermal average is null unless $\mathbf{r} = \mathbf{r}'$ and $\omega = \omega'$. From this equation, the spectral energy density $S(\mathbf{r}, \omega) = \langle \mathbf{E}^*(\mathbf{r};\omega) \cdot \mathbf{E}(\mathbf{r};\omega) \rangle_{th}$ [17], which involves the thermal fields $\mathbf{E}(\mathbf{r}; \omega) = i\omega\mu_0 \int_V d^3\mathbf{r}' \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{j}(\mathbf{r}';\omega)$ connected to currents via the dyadic Green's function of the body (see Appendix A), i.e., the response of the medium, can be calculated at a given position $\mathbf{r}$ and frequency ω , obtaining [17]:

$$S(\mathbf{r}, \omega) = 4\pi\mu_0\hbar\omega\Theta(\omega, T)ImTr[G^E(\mathbf{r}, \mathbf{r}', \omega)] \quad (1.4)$$

where the following relation of the dyadic Green's function was used [17]:

$$Im[G(\mathbf{r}, \mathbf{r}', \omega)] = \frac{\omega^2}{c^2} \int_V d^3\rho \epsilon_2(\rho, \omega) G(\mathbf{r}, \rho, \omega) G^*(\mathbf{r}', \rho, \omega) \quad (1.5)$$

The superscript E refers to the electric contribution to the dyadic Green's function. Looking at Equation 1.4, it is understood that the emitted thermal spectrum depends on the characteristics of the emitter, such as its absorptivity, embedded inside the imaginary part of the dielectric function $\epsilon_2(\mathbf{r}, \omega)$, the temperature, embedded inside the Bose distribution $\Theta(\omega, T)$, and the geometry of the emitter, including its shape and size. In the particular case of emission into free space, Equation 1.4 turns into Planck's law, recovering the macroscopic law of thermal emission. Additionally, it is understood that the thermal spectrum emitted from a body at temperature T is given by the sum of the thermal contributions at a given frequency and spatial position, without interference effects, as shown in Figure 1.2. This explains typical characteristics of thermal radiation, such as broadband spectrum, omnidirectional propagation, and unpolarized fields. The same result can be recovered within the *Macroscopic Quantum Electrodynamics* framework, as shown in Appendix A.

Beyond the fundamental mechanism that explains how thermal radiation is emitted, this phenomenon is of interest to many major scientific disciplines, like chemistry, biology, and physics. This is because the spectral features of the thermal spectrum arising solely from the existence of a body at finite temperature are intrinsically determined by the properties of the emitting material itself. A widely spread application dealing with the emission of thermal radiation concerns the building of new broadband radiation sources, mainly in the Infrared (IR) spectral range, which are extremely relevant for IR spectroscopy and photonics [18, 19, 20]. One of the most employed thermal emitters is Silicon Carbide (SiC), due to its chemical and thermal stability at high temperatures [21]. However, most of the thermal emitting materials exhibit spectral features that limit and suppress radiation emission at specific frequencies. This is the case of SiC (see below), which presents some absorption bands in the IR due to phonon excitations [22, 23, 24]. Therefore, the development of novel systems with reduced self-absorption, high efficiency, broadband, and spectrally homogeneous emission is highly desirable in this landscape. Black soot compounds find their place in this framework, being regarded as thermal references thanks to their high and frequency-independent emissivity [3, 4], but the combustion process necessary for their production is harmful to the environment. Moreover, these materials show limited mechanical robustness, since they cannot be fabricated as self-standing structures. Additionally, black soot scatters and absorbs incoming solar radiation, contributing to poor air quality and inducing respiratory and cardiovascular problems [25]. On the other side, graphene nanostructures are good candidates as thermal emitters since they exhibit low reflectance and transmittance and high mechanical resistance to temperature [26, 27]. In general, carbon-family materials have attracted considerable attention in condensed matter research due to their peculiar electronic, optical, thermal, and mechanical properties, such as their high carrier mobilities, quantum effects at high temperatures, and mechanical strength [28, 29, 30]. Within this material group, graphene has been intensively studied due to its intriguing properties, and various applications have been reported, including optical modulators, saturable absorbers, thermoelectric devices, solar cells, and optoelectronic devices [31, 32, 33, 34, 35, 36, 37, 38]. Nevertheless, a single graphene sheet with a single-atomic thickness exhibits some drawbacks, including a low light absorption rate of 2.3 % in the infrared–visible range and difficulty in handling. To overcome these disadvantages, three-dimensional graphene structures have been developed, leading to materials exhibiting properties similar to or beyond those of the 2D sheets, such as unique electrical, thermal, and optical properties [39, 40, 41, 42, 43, 44, 45]. These 3D networks can be obtained in different ways, such as stacking high-quality monolayer graphene sheets and getting complex structures with branches and pores ranging from hundreds of nanometers to hundreds of microns. The innovative way of heat localization close to and around the pores is an interesting key to tune their thermal behavior, since changing the pore size may change the thermal properties, leading to promising interesting applications related to thermal and/or optical functional devices, such as heat storage and photo-detectors [46, 47, 48].

The heat localization around the pores in 3D graphene was investigated, for example, in Ref. [49] with high spatial resolution (~ 20 nm). Figure 1.3 (a) depicts topographic images and third-order near-field images of the IR-induced heat maps acquired by s-SNOM (scattering-type scanning near-field optical microscopy) for three-dimensional bi-continuous nanoporous graphene films with two different pore sizes. Figure 1.3 (b) reports the near-field IR signals along the blue dashed curved lines in panel (a) for both pore sizes, that is, along the edges of the pores. A peak value of 953 nV (370 nV) in the vicinity of the small pores and 2260 nV (643 nV) around the large

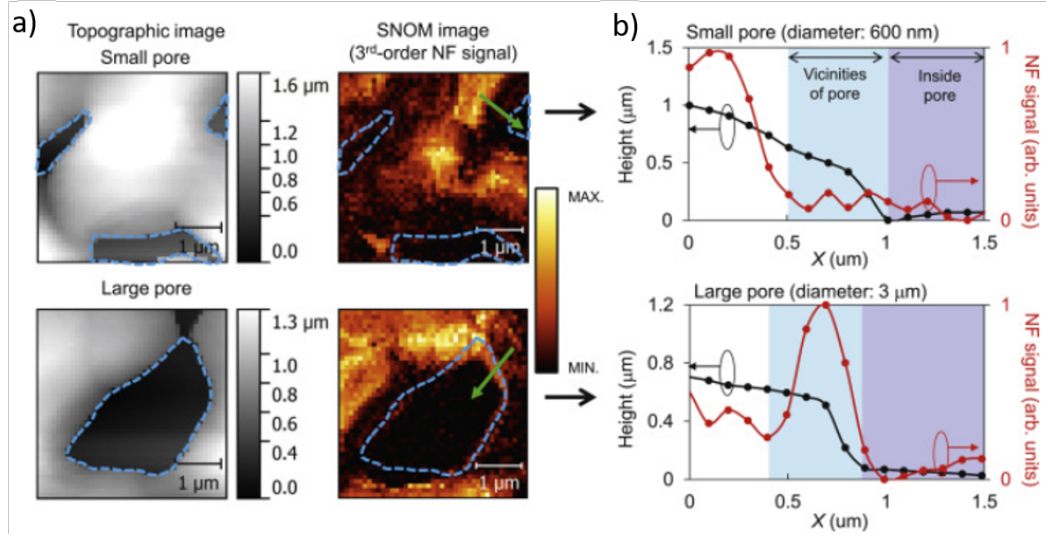


Figure 1.3. (a) Topographic and s-SNOM (scattering-type scanning near-field optical microscopy) images in the IR region for three-dimensional bi-continuous nanoporous graphene films with two different pore sizes. (b) Topographic (black circles) and s-SNOM (red circles) signals obtained along the blue dashed lines tracing the edges of the pores for the two different samples. Obtained from Ref. [49].

pores is detected. The experimental results reveal that the near-field IR signals in the highly curved graphene of the pores were relatively weaker. This weakness is equivalent to a decrease in the near-field IR radiation and originates from the decrease in thermal conductivity, owing to both strain itself and the topological defects geometrically required by the high curvature. Such highly curved graphene with lower thermal conductivity around the pores behaves as a thermal insulator, and consequently, induces the localization of heat in the vicinity of the pores. This interesting feature is expected to strongly depend on the curvature (i.e., the pore size). Similar measurements were carried out on a nanoporous graphene sample containing larger pores (i.e., a typical pore size of 1 μm). Figure 1.3 (a) reveals that the larger-pore graphene generated higher near-field IR radiation than the smaller-pore graphene. The line profiles from the s-SNOM images (Figure 1.3 (b)) clearly illustrate that strong near-field IR radiation occurs in the vicinity of the larger pores, in contrast to the weaker radiation around the smaller pores. This result indicates that the nanoporous graphene containing larger pores tends to strongly radiate heat.

1.1.3 Thermal Emission Engineering

Within this landscape, it appears clear that manipulating thermal radiation, i.e., modifying its incoherent nature, constitutes a challenge. As mentioned above, the finite temperature of a body is responsible for the generation of uncorrelated thermal fluctuating currents, which emit highly incoherent thermal fields, resulting in broadband spectra, omnidirectional field distributions, and unpolarized propagation. Nevertheless, this field has been attracting attention thanks to its strong link with photonics. In fact, thermal radiation is composed of waves like electromagnetic radiation, whose coherence properties can be modified in several ways. The core of this process lies in the strong difference between near- and far-field radiation due to

the existence of evanescent surface modes, dominant in the near-field but suppressed in the far-field regime due to their exponentially decaying nature far from the material medium [50]. Within the generalized plane-wave expansion [51], any electromagnetic field in homogeneous media can be written in terms of elementary plane waves, which can be either propagating or evanescent. Assuming an electromagnetic (either optical or thermal) field propagating along the z axis, and a wavevector $\mathbf{k}=(k_x, k_y, k_z)$, so that $|\mathbf{k}|=k=n\omega/c$, with n the refractive index of the medium, such that $n=\sqrt{\epsilon\mu}$, with ϵ and μ the dielectric function and magnetic permeability, respectively, it can be shown that the field evolution along the z axis can be expressed, in the momentum space, as:

$$\tilde{\Psi}(k_x, k_y; z) = \tilde{\Psi}(k_x, k_y; 0)e^{\pm ik_z z} \quad (1.6)$$

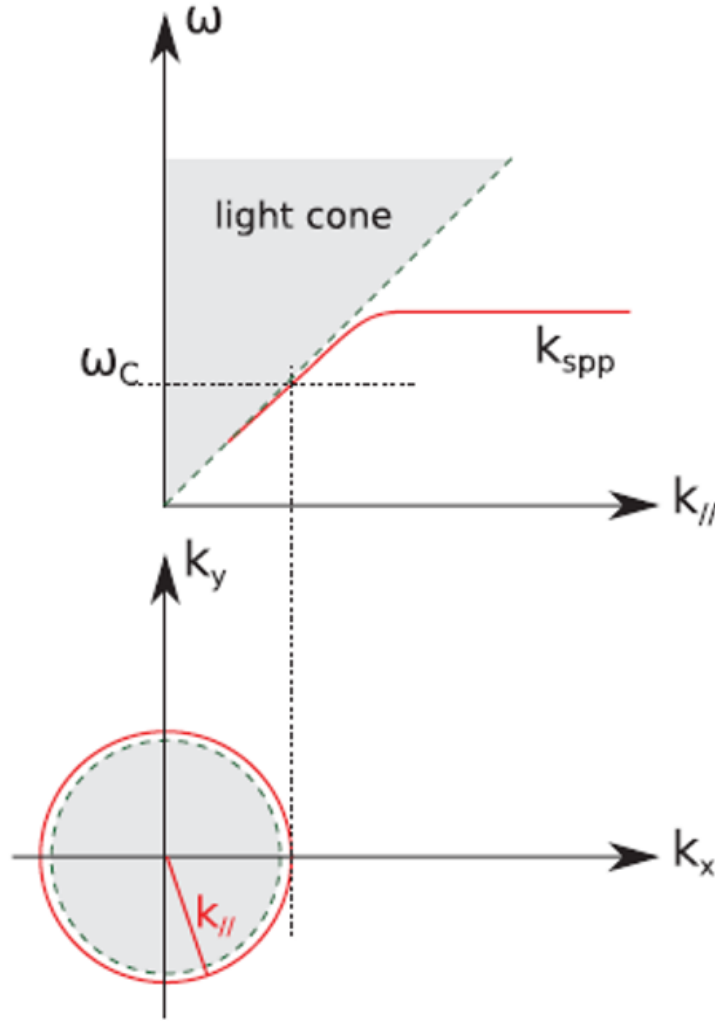


Figure 1.4. Dispersion relation of Surface-Phonon Polaritons (SPPs) and its isofrequency projection on the $(\mathbf{k}_x, \mathbf{k}_y)$ plane at a given frequency ω_c . The gray area identifies the light cone, where propagating modes exist. Obtained from Ref. [52].

In real space, the field evolution is:

$$\Psi(x, y, z) = \int \int dk_x dk_y \tilde{\Psi}(k_x, k_y; 0) e^{i(k_x x + k_y y \pm k_z z)} \quad (1.7)$$

where the $\pm$ sign indicates the sense of propagation along z , and k_z is defined as:

$$k_z = \begin{cases} \sqrt{k^2 - k_R^2}, & k_x^2 + k_y^2 = k_R^2 \leq k^2 \\ i\sqrt{k_R^2 - k^2}, & k_x^2 + k_y^2 = k_R^2 > k^2 \end{cases} \quad (1.8)$$

From this Equation, it is clear that, depending on whether k_z is real or imaginary, the modes are propagating or evanescent, respectively. In this way, it is easy to distinguish between these two types of modes when they are compared with free-space modes propagating in air. The relation between the frequency and the wavevector, named the dispersion relation (see Appendix C), gives a straightforward visual interpretation of this concept.

Figure 1.4 depicts the dispersion relation for a 2D system. The propagating modes lie within the gray area, delimited by the gray dashed line, that represents the dispersion relation of light in air. The red dashed curve depicts the dispersion relation of evanescent modes, in this case, Surface-Phonon Polaritons (SPhPs), which will be discussed later. These modes are exponentially damped when moving outside a material interface. The isofrequency projection on the $(\mathbf{k}_x, \mathbf{k}_y)$ plane is shown in the lower part of the Figure, where a red circle with radius equal to the tangential component of the SPhP wavevector is represented.

The separation between near- and far-field regimes is dictated by the typical wavelength of the involved physical phenomenon. For example, for thermal radiation, the typical thermal wavelength depends on temperature, and it is around $10 \mu\text{m}$ at room temperature [53]. Thus, distances way smaller or larger than the characteristic thermal wavelength give rise to the two regimes, respectively.

In the photonics field, it is well known that one strategy to manipulate the features of light involves building up photonic nanostructures, where the artificial introduction of periodic patterns with subwavelength separation enables the modification of material dispersion relations and the excitation of propagating or localized surface waves, such as Surface Plasmon-Polaritons (SPPs) in metals and Surface Phonon-Polaritons (SPhPs) in polar dielectrics, leading to a strong increase of the density of states and thus field localization and enhancement close to the material surface [54]. A more detailed description of these excitations is discussed in Appendix B and D, and in Appendix C the equations describing surface waves are retrieved.

Figure 1.5 gives an overview of the possible polaritonic excitations, i.e., quasi-particles resulting from strong coupling between electromagnetic waves and excitations in matter that carry electric or magnetic dipoles, including surface plasmon-polaritons (SPP) (c), surface phonon polaritons (SPhP) (d), and surface exciton-polaritons (SEP) (e). Each excitation has its own electric field line distributions, as it is visible in the case of a material slab. The constraint to excite these bounded modes, confined within the material surface, is that the real part of the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ turns negative, happening up to the plasma frequency in metals and between transverse and longitudinal optical phonon frequencies in polar dielectrics. The confinement of these polariton modes is illustrated in Figure 1.5 (a), where the electric field modulus $|E|$ for an SPP versus z , i.e., the direction perpendicular to the material surface, shows the evanescent nature of the excitation at the metal/dielectric interface, which is exponentially damped as the distance from the interface increases in both materials. In the case where the metallic film is

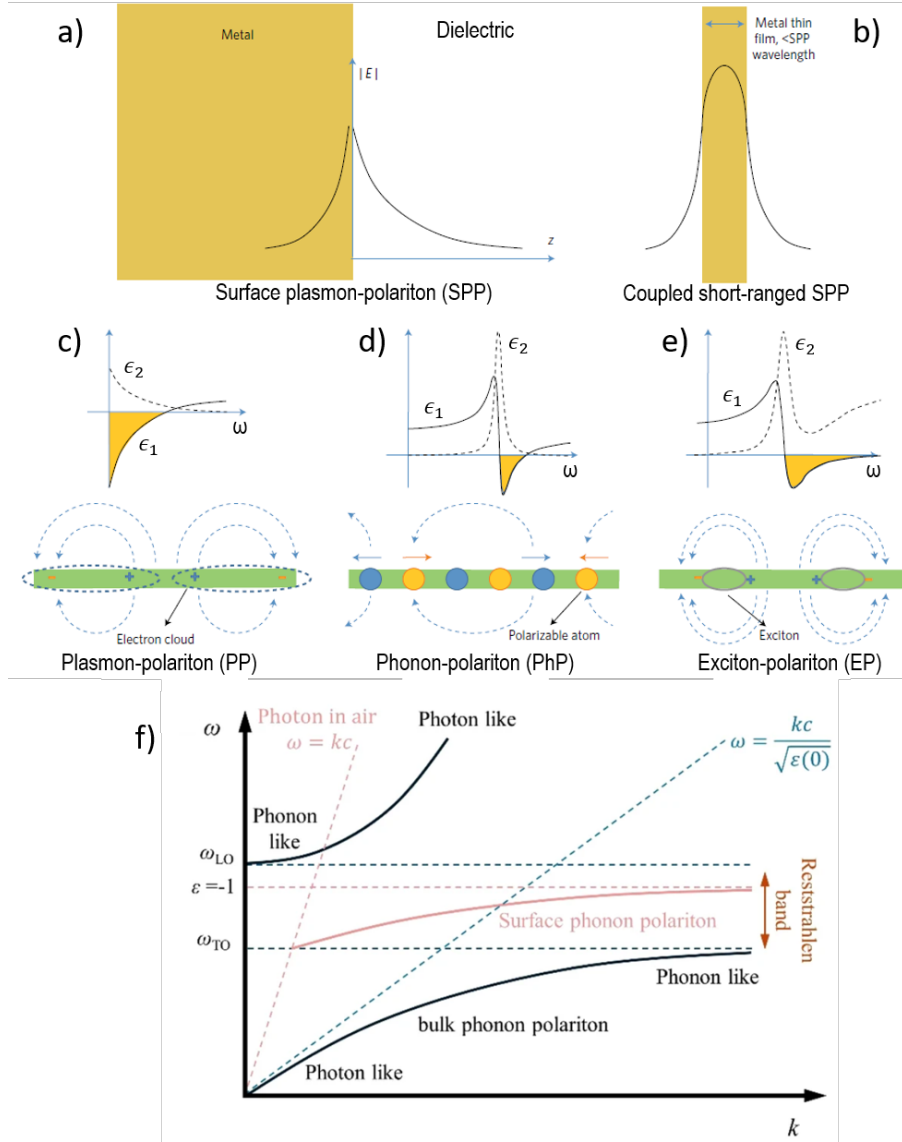


Figure 1.5. Examples of surface polariton excitations, i.e., quasi-particles resulting from strong coupling between electromagnetic waves and excitations in matter that carry electric or magnetic dipoles, including surface plasmon-polaritons (SPP) (c), surface phonon polaritons (SPhP) (d), and surface exciton-polaritons (SEP) (e) [55]. These different quasi-particles exhibit their own electric field line distributions, as depicted for the case of a 2D material slab. The requirement for getting these bounded evanescent modes is that the real part of the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ turns negative, happening up to the plasma frequency in metals, and between transverse and longitudinal optical phonon frequencies in polar dielectrics. Panel (a) depicts the modulus of the electric field $|E|$ versus z , i.e., the direction perpendicular to the material surface, for an SPP, showing the evanescent nature of the excitation at the metal/dielectric interface, which is exponentially damped as the distance from the interface increases in both materials. Panel (b), instead, depicts the modulus of the electric field $|E|$ concentrated in the metal film as illustrated for the case where the metal film thickness is smaller than its skin depth. This mode is more strongly confined and propagates a smaller distance than the isolated SPP. Images obtained from Ref. [56] and [57]. Panel (f) reports the dispersion relation of PhPs, confined between transverse and longitudinal optical phonon frequencies, within the so-called Reststrahlen band.

thinner than the typical SPP wavelength, as shown in Figure 1.5 (b), the electric field modulus $|E|$ is strongly concentrated within the slab.

Figure 1.5 (f) shows the dispersion relation for phonon polaritons [57]. In the bulk of polar materials, PhPs can exist below the transverse optical (ω_{TO}) phonon frequency and above the longitudinal optical (ω_{LO}) phonon frequency, as shown by the two curved black lines in the dispersion. Within the field of nanophotonics, polaritons on these two dispersion lines are often referred to as ‘bulk’ PhPs due to their extension into the volume of the polaritonic medium. Yet, between the ω_{TO} and ω_{LO} phonon frequencies, the real part of the complex dielectric function of polar materials becomes negative (as shown in panel (d)), and they exhibit high reflectivity to infrared photons within this regime. As a result, propagation of infrared photons in this frequency range (named Reststrahlen band) in the bulk of polar materials is prohibited. However, within the Reststrahlen band, the formation of sub-diffractive PhPs can be realized at the surface of polar materials or their interfaces with dielectric materials, which are called surface phonon polaritons (SPhPs). These SPhPs are highly confined to the surface or interface with their electric field intensity attenuating strongly, following an exponential decay along the normal direction of the surface/interface, as expected for evanescent waves. It is important to note that because of the evanescent nature of these SPhP modes, they can offer dramatic compressions of the wavelength and, consequently, an increase in the polariton wavevector, meaning that the excitation of the confined modes requires overcoming a significant momentum mismatch with free-space light, as visible in the plot, where, given the same frequency, the photon dispersion relation in air always has a smaller wavevector than SPhPs.

To sum up, the exceptional confinement of these surface evanescent waves is high in the near-field regime but strongly suppressed in the far-field case. Additionally, their excitation with free-space light is not possible due to the momentum mismatch. Metamaterials, metasurfaces, and photonic crystals find their place within this context, since here, thanks to the artificial pattern, additional momentum is furnished to the incident photons, overcoming the wavevector mismatch, and in this way this enhanced contribution can be coupled to free-space modes and also be detected in the far field due to the modes’ diffraction through the artificial nanostructures [58, 59, 60, 61, 62].

Similarly, the temporal and spatial coherence of thermal radiation can be tailored by introducing periodic artificial details responsible for the excitation of thermal surface modes, which in turn modify the bandwidth and the directional properties of the emitted thermal spectrum [63, 64, 65]. In fact, the excited modes can couple to free-space radiation and generate sharply localized resonant peaks in the far-field spectrum, modifying the amplitude, the spectral bandwidth, and direction of the emitted radiation. It is important to stress that this approach is *passive* because no external perturbation pumps additional energy into the system, so the energy is only redistributed differently in the body, amplifying the emissivity in certain frequency ranges and suppressing it in others, with no possibility of overcoming the blackbody limit. One of the simplest examples of nanostructures enabling the modification of the main properties of emissivity is a grating, obtained by patterning a polar material [52, 66, 67, 68]. SiC, a polar dielectric material with a high melting point of around 3000 K, is the ideal candidate for this purpose [21]. As already mentioned, within a special and restricted frequency range, named Reststrahlen band, extending from the transverse to the longitudinal optical phonon frequencies, the material’s response to an external electric field is strongly enhanced due to its polarity, and its dielectric function changes sign, allowing the excitation of polariton modes at

the SiC-air interface under specific conditions. In fact, the "momentum-matching condition" should be satisfied to manage this process, which can be obtained by adding momentum through an artificial spatial periodicity introduced by the pattern. In this way, the following additional momentum will be given [50]:

$$k_0 \sin \theta = k_{\parallel} + mG \quad (1.9)$$

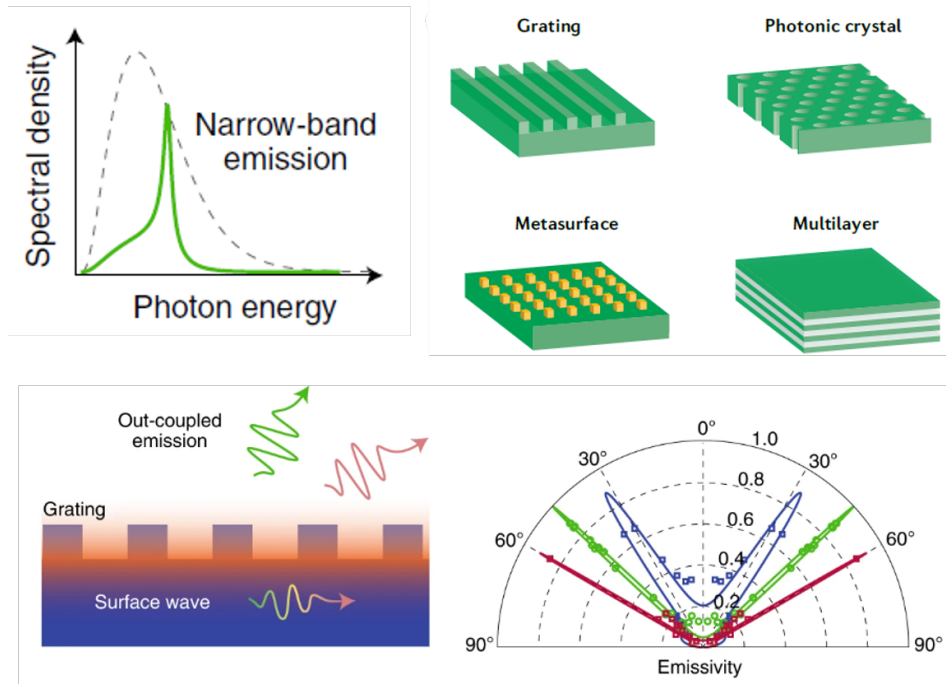


Figure 1.6. Examples of photonic nanostructures employed to modify the properties of thermal radiation, such as gratings, photonic crystals, metasurfaces, and multilayers. One of the effects produced by these structures is the spectrum shrink in terms of energy, generating narrow-band thermal emission, as shown in the upper panel. Both the bandwidth and the direction of emission can be tailored by using a grating, where, under emittance angles satisfying the momentum-matching condition, coupling is enabled between a thermally generated surface wave and free-space propagating modes. In this way, the angular distribution of thermal emission is significantly modified, as shown in the bottom panel, where the emissivity at three different wavelengths of the same grating is displayed, demonstrating the structure's selectivity in emitting toward specific directions. Obtained from Ref. [6].

where $k_0 = 2\pi/\lambda$ is the free-space wavenumber, θ is the emission angle for thermal nanostructures, $k_{\parallel}$ is the wavevector of the thermally excited surface mode, m is an integer number associated with the diffraction order, and $G = 2\pi/a$ is the grating reciprocal vector, with a the grating period. Under these constraints, the enhanced near-field contribution associated with the thermally excited surface modes can be coupled to far-field plane waves propagating in free space, detectable in the far-field regime, as shown in Figure 1.6. Under emittance angles satisfying the momentum-matching condition, the angular distribution of thermal emission can be tailored, as shown in the bottom panel of the same figure, where the emissivity at three different wavelengths (in blue, green, and red) of the same grating is shown, demonstrating the selectivity of the structure in emitting toward specific directions [6].

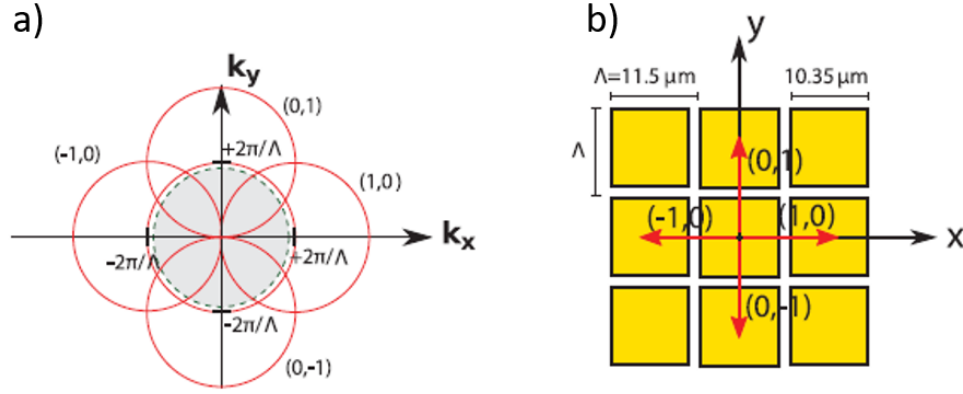


Figure 1.7. (a) Isofrequency projection of the SPhP dispersion relation on the surface of a 2D grating. (b) Sketch depicting the grating under investigation, with period $\Lambda_x = \Lambda_y = \Lambda = 11.5 \mu m$. The arrows represent the wavevectors of SPhPs which are coupled with the wave propagating perpendicularly to the surface. Obtained from Ref. [52].

Figure 1.7 shows how the introduction of an artificial 2D grating modifies the dispersion relation of a 6H SiC sample, allowing the coupling between evanescent SPhPs and free-space propagating modes. More in detail, Figure 1.7 (b) depicts the grating under investigation in Ref. [52], with period $\Lambda_x = \Lambda_y = \Lambda = 11.5 \mu m$. The isofrequency projection of the SPhP dispersion relation is no longer the one reported in Figure 1.4, but is modified. In fact, a lattice of additional circles of radius $|k_{SPhP}|$, centered on $2\pi m/\Lambda_x \mathbf{e}_x + 2\pi n/\Lambda_y \mathbf{e}_y$, where m and n are integers, and $\mathbf{e}_x$ and $\mathbf{e}_y$ are unit vectors along the x and y directions, is added. It is now possible that a part of these circles lies inside the cross-section of the light cone at this frequency (gray area in the figure). Considering only this condition on the wavevectors, i.e., the momentum-matching condition, the coupling between surface waves and outgoing waves takes place along arcs of circles in the light cone.

This nanophotonic approach to modify thermal emission relies on the strong connection between absorptivity and emissivity, expressed in Kirchhoff's radiation law, for which [69]:

$$\alpha(\omega, \mathbf{n}, \mathbf{p}) = \varepsilon(\omega, \mathbf{n}, \mathbf{p}^*) = \frac{I(\omega, \mathbf{n}, \mathbf{p}^*, T)}{I_{BB}(\omega, T)} \leq 1 \quad (1.10)$$

where $\alpha(\omega, \mathbf{n}, \mathbf{p})$ is the absorptivity, i.e., the ratio between the incident and absorbed electromagnetic power per unit of area at a given frequency ω , direction $\mathbf{n}$, and state of polarization $\mathbf{p}$, and $\varepsilon(\omega, \mathbf{n}, \mathbf{p}^*)$ is the emissivity, i.e., the ratio between the electromagnetic power $I(\omega, \mathbf{n}, \mathbf{p}^*, T)$ emitted from a material at a given frequency ω , direction $\mathbf{n}$, and state of polarization $\mathbf{p}$, and the one of a blackbody $I_{BB}(\omega, T)$ at the same temperature. The asterisk indicates the complex conjugate polarization and is required for time-reversal symmetry. According to this law, absorptivity and emissivity are equal, so the modification of one quantity implies the change of the other, and they are constrained to a maximum value. Therefore, engineering the material dispersion to modify the emission of thermal radiation is equivalent to manipulating the optical properties of a given material.

To sum up, the introduction of artificial geometrical details in a body at finite temperature T , having dimensions and distances comparable to or smaller than the

typical thermal wavelength, can lead to enhanced thermal emission. The origin of this phenomenon can be ascribed to interference effects due to multiple wave reflections in the gap between nearby objects and to the presence of evanescent modes at the material surface. The latter leads to a strong increase in the local density of states (LDOS), which strongly depends on the geometrical details of the body, and which can exceed the density of states associated with the thermal photons in the far-field. More in detail, within the fluctuational electrodynamics framework, LDOS can be expressed as [70]:

$$LDOS = \frac{\omega}{\pi c^2} \text{Im}[Tr(G^E(r, r', \omega) + G^M(r, r', \omega))] \quad (1.11)$$

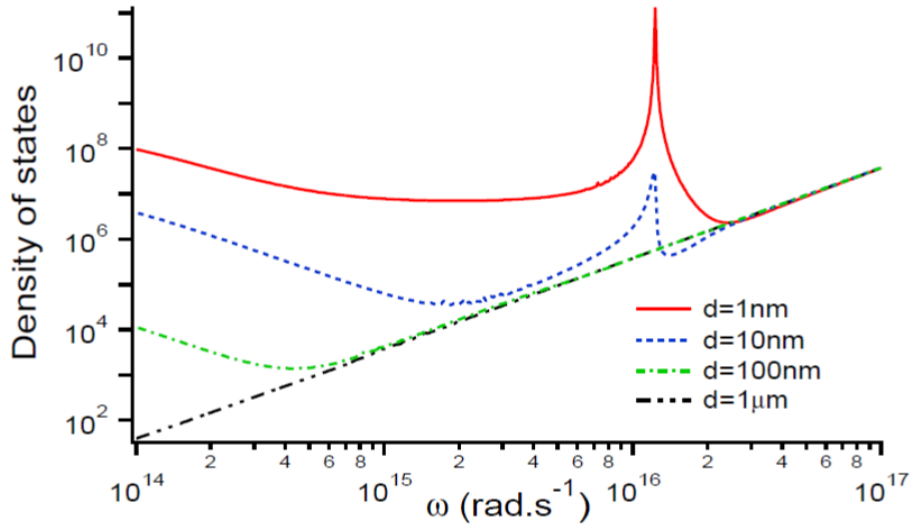


Figure 1.8. LDOS versus frequency above a semi-infinite plane of Aluminum at different distances d from the surface, ranging from 1 nm to 1 μ m. Obtained from [71].

where E and M refer to the electric and magnetic contributions to the dyadic Green's functions G , which describe the response of the medium to general perturbations. In the simplest case of a planar thermal emitter, the quasistatic approximation can be adopted, so that, in the limit of $k \rightarrow \infty$, i.e., in the limit of modes with large wavevector, the LDOS near the material surface is [71]:

$$LDOS(d, \omega) = \frac{1}{16\pi\omega d^3} \frac{\text{Im}[\epsilon(\omega)]}{|1 + \epsilon(\omega)|^2} \quad (1.12)$$

This expression clearly highlights the strong dependence of LDOS on the distance d from the emitter. Then, it stresses the dependence on the response function of the medium, embedded inside the dielectric function $\epsilon(\omega)$, showing that in the case of lossless media, for which $\epsilon(\omega) = 0$, LDOS and thus thermal emission vanish, highlighting the connection between dissipation and thermal emission. At last, it demonstrates the strong role of surface modes in the enhancement of thermal emission, since LDOS has a sharp peak when $\epsilon(\omega) = -1$, a condition satisfied for the frequencies at which surface polaritonic modes can be excited [72]. Figure 1.8 shows the LDOS versus frequency above a semi-infinite plane of Aluminum at different distances d from the surface, ranging from 1 nm to 1 μ m. It can be observed that

the LDOS peaks around $10^{16} \text{ rad} \cdot \text{s}^{-1}$ at distances $d = 1 \text{ nm}$ and 10 nm , increasing its value as d decreases. As predicted by Equation 1.12, increasing the distance by one order of magnitude ($d = 100 \text{ nm}$) totally cancels out the peak. The enhanced difference between the far and near-field regimes of thermal emission is shown in Figure 1.9 a) and b), where the radiative heat transfer between two

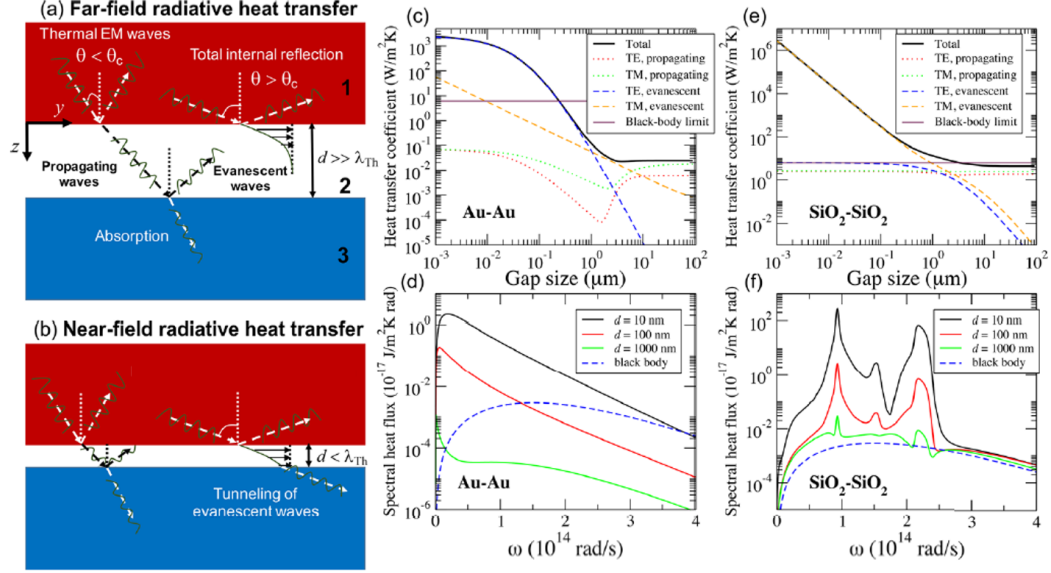


Figure 1.9. Far-field radiative heat transfer between two infinite parallel planar thermal emitters (media 1 and 3) separated by a vacuum gap (medium 2). In this case, the gap size, d , is much larger than the thermal wavelength, λ_{th} , and the two plates can exchange heat only via propagating waves. The evanescent waves generated in the vacuum gap by total internal reflection (when $\theta > \theta_c$) are not able to reach the second plate and do not contribute to the heat transfer in this regime. (b) When the gap size is smaller than λ_{th} , tunneling of evanescent waves is possible and gives rise to a significant contribution to the radiative heat transfer, and in this way, the Planckian limit can be greatly overcome in this near-field regime. (c) Heat transfer coefficient at room temperature (300 K) as a function of the gap size for two infinite parallel planar thermal emitters made of gold. The different lines correspond to the total contribution (black solid line) and the contributions of propagating and evanescent waves for transverse electric (TE) and transverse magnetic (TM) polarizations. The horizontal line shows the result for two blackbodies. (d) Spectral heat flux as a function of the radiation frequency corresponding to (c). The solid lines correspond to three different values of the gap size in the near-field regime, while the blue dashed line is the result for two blackbodies. (e, f) Same as in (c, d) for SiO_2 . Obtained from Ref. [2].

infinite parallel planar thermal emitters, represented by media 1 and 3, separated by a vacuum gap, which is medium 2, in the far-field a) and near-field b) regimes, is depicted [2]. In the first case, the gap size, d , is much larger than the thermal wavelength, λ_{th} , and the two plates can exchange heat only via propagating waves. The evanescent waves generated in the vacuum gap by total internal reflection (when $\theta > \theta_c$) are exponentially damped before reaching the second plate, and do not contribute to heat transfer in this regime. When the gap size is smaller than λ_{th} , as is the case in b), tunneling of evanescent waves between the two emitters is possible and gives rise to a significant additional contribution to the radiative heat transfer, and in this way, the Planckian limit can be greatly overcome in this near-field regime. Figure 1.9 c) and e) show the heat transfer coefficient calculated within the

fluctuational electrodynamics framework versus the gap size, expressed in μm , for two identical plates made of a metal (Au) and a dielectric (SiO_2), respectively. In both cases, the total contribution (black continuous line) is calculated, together with the individual transverse electric (TE) and transverse magnetic (TM) propagating and evanescent contributions. A comparison with the blackbody limit (brown continuous line) is also given.

For both materials, the Planck limit can be overcome for gap values up to $\sim 1 \mu\text{m}$, reaching the exceptional increase of five orders of magnitude in the case of SiO_2 for $d=1 \text{ nm}$. These images demonstrate that metals and dielectrics behave differently in terms of near-field heat transfer; for metals, the heat transfer coefficient is dominated by TE evanescent waves generated from total internal reflection waves that are evanescent in the vacuum gap but propagate inside the gold plates, whereas for dielectrics, the major contribution comes from TM evanescent waves, associated with SPhPs, resulting from the strong coupling of radiation and the optical phonon modes sustained by this polar material. This difference is even more pronounced in the spectral heat flux versus frequency, depicted in Figure 1.9 d) and f) for Au and SiO_2 , respectively, for different gap size values. Again, the blackbody limit, represented by the blue dashed lines, can be overcome. Furthermore, no specific spectral features are present in the case of Au, while two strong peaks are visible at the frequencies of the optical modes in the case of SiO_2 , demonstrating their strong role in heat transfer.

In Chapter 3 of this work, the emission of thermal radiation will be investigated from a fundamental point of view through the development of an experimental setup that allows the study of the emissivity properties of various materials as a function of frequency and temperature, assessing the change of the basic features of this mechanism. Different materials will be considered, such as standard SiC and micro-structured three-dimensional graphene sheets, which are found to be promising candidates as green infrared radiation sources. Thermal emission engineering is later considered in SiC, where an artificial fractal patterning of pillars will be investigated, demonstrating the alteration of the fundamental thermal emission properties due to the excitation of phonon-polariton modes.

1.2 Thermoelectric Materials

Thermoelectric materials have been attracting increasing interest because they are capable of direct energy conversion between heat and electricity, finding their place within the development of environmentally friendly solutions in the energy field [73]. In fact, these materials could be competitive with fluid-based systems employed in cooling, heating, and electrical power generation, such as air conditioners, refrigerators, heat pumps, and turbine engines. Being solid-state systems, thermoelectric materials exhibit several advantages compared to systems that must compress and expand working fluids: they have no moving parts, they are silent, reliable, and scalable, making them ideal for small, distributed power generation. Additionally, no environmentally harmful fluids are needed in the working process, as is the case with standard conditioners that use the R-134A refrigerant, a hydrofluorocarbon responsible for global warming. In fact, the "working fluid" of thermoelectrics is composed of moving electrical charges [74]. In this Section, the mechanism of thermoelectricity is explained, going through the calculations that allow for retrieving electrical and thermal transport properties for metals and semiconductors, such as the electrical conductivity σ , thermal conductivity k , and Seebeck coefficient S , all participating in the description of the conversion efficiency of thermoelectric materials. The

strategies to improve thermoelectricity are also described, with a strong accent on the best candidates for the enhancement of this process, i.e., topological insulator compounds.

The fundamental physical process behind the thermoelectric effect was discovered thanks to the complementary efforts of J. Peltier, T. J. Seebeck, and W. Thomson. Briefly, this effect arises because charge carriers in metals and semiconductors can move, carrying both charge and heat.

In 1834, Peltier observed that if a current is applied across a junction of dissimilar electrically conductive materials, either heating or cooling can occur at the junction. When the current is reversed, the opposite effect happens [75]. In the case of n-type materials, the moving charges are electrons, while in the case of p-type materials, holes move. Figure 1.10 A depicts how this effect can be employed to produce the cooling/heating of a material. If a voltage difference is applied in the right direction across a p-n junction, electrons and holes will flow away from the junction in the n-type and p-type material, respectively. The recombination process of charges releases energy and heats the junction (bottom part), whereas on the other side, cooling is produced to form electron/hole pairs.

In 1821, Seebeck noticed that the needle of a magnet is deflected in the presence of dissimilar metals that are connected (electrically in series and thermally in parallel) and exposed to a temperature gradient. Figure 1.10 B depicts how this effect can be exploited to generate power. A temperature gradient is produced in the junction by heating the upper part and cooling the lower part, so that electron/hole pairs are produced at the hot end and absorb heat in the process. On the cold side, the pair recombine and reject heat. Macroscopically, a voltage difference ΔV , named the Seebeck voltage, is generated between the hot and cold ends, and the ratio between this voltage and the applied temperature difference ΔT is named the Seebeck coefficient, described as:

$$S = -\Delta V / \Delta T \quad (1.13)$$

In order for this process to be efficient, it is necessary to find materials that are good electric conductors; otherwise, electron scattering generates heat on both sides of the barrier and throughout the materials. Additionally, the materials must be poor thermal conductors; otherwise, the temperature difference that must be maintained between the hot and cold sides will produce significant heat backflow. Similarly, the Seebeck effect should be maximized. Figure 1.10 c) shows a thermoelectric module made up of a large number of junctions placed in series to increase the operating voltage and spread heat flow. Specifically, the device is made up of many thermoelectric couples consisting of n-type and p-type thermoelectric elements wired electrically in series and thermally in parallel. When current flows within the module, one side is cooled and the other is heated up, depending on the direction of the current flow.

The conversion efficiency of a thermoelectric material is described by the dimensionless figure of merit, ZT , defined as:

$$ZT = \frac{S^2 \sigma}{(k_{el} + k_{lattice})} T = \frac{PF}{k_{tot}} T \quad (1.14)$$

where S is the Seebeck coefficient, and σ is the electrical conductivity, gathered in the power factor $PF = S^2 \sigma$, $k_{tot} = k_{el} + k_{lattice}$ is the total thermal conductivity of the system, including an electronic and a lattice contribution, and T is the temperature. From this formula, it looks clear that the efficiency is determined by the competition

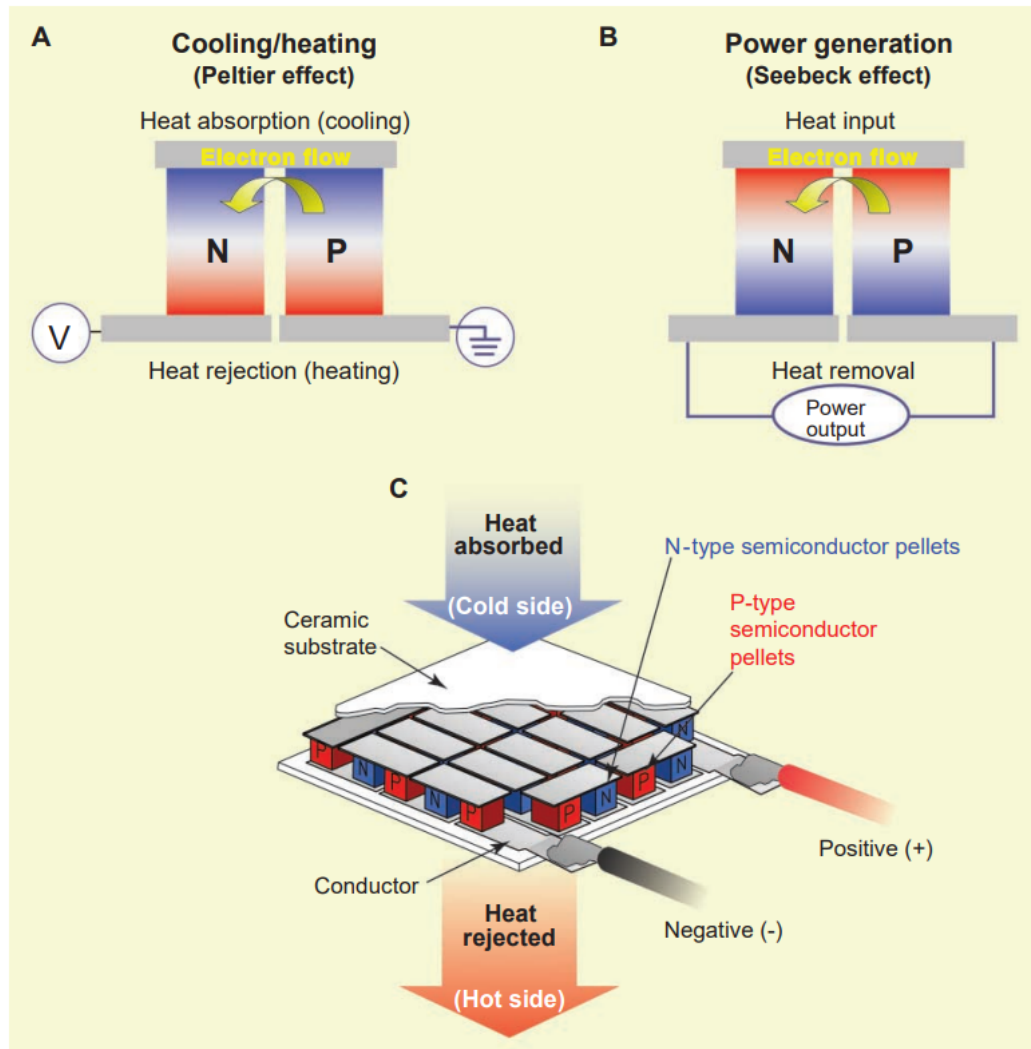


Figure 1.10. a) Example showing the cooling/heating process via the Peltier effect. When a current runs across a thermoelectric junction, it can heat or cool through the Peltier effect, depending on the direction of the current flow. b) Example showing how power can be generated exploiting the Seebeck effect. In this case, when heat flows across the junction due to the induced thermal gradient, electrical current is generated through the Seebeck effect. c) A thermoelectric module made up of a large number of junctions placed in series to increase the operating voltage and spread heat flow. The direction of charge flow on both cooling and power generation is shown. Image obtained from Ref. [75].

between electronic transport (PF) and thermal transport in the material. To achieve excellent thermoelectric performance, ZT should be high; thus, the power factor should dominate over the thermal contribution. A ZT value around 1 is already considered a good result, but it is still too inefficient to make these materials economically competitive. It is estimated that ZT in the range of 1.5 to 2 would enable significant waste-heat harvesting and power-generation applications, and that at these values, cooling and temperature control of microprocessors, communication circuitry, electro-optical systems, and other electronic components become attractive. Therefore, research into enhancing the thermoelectric efficiency of these materials is of great interest from both environmental and technological perspectives. Nevertheless, the increase of the ZT figure of merit is challenging due to the interdependency of S , σ , and k , which are conflictingly correlated and cannot be tuned independently.

1.2.1 Transport Properties in Metals and Semiconductors

Transport effects in semiconductors/metals can be described by using the kinetic transport theory [76]. Let's consider a system out of its equilibrium condition, described by the Fermi distribution function $f(E)$, relaxing back to the equilibrium condition, described by $f_0(E)$, according to the Boltzmann equation under the relaxation time approximation (RTA):

$$\frac{df(E)}{dt} = -\frac{f(E) - f_0(E)}{\tau_n} \quad (1.15)$$

where the relaxation time τ_n (now n refers to n -type carriers, so electrons) can be written, as an approximation, like $\tau_n = \tau_0 E^r$, being τ_0 and r constants for a given scattering process (e.g. $r = -1/2$ for scattering of the charge carriers by acoustic-mode lattice vibrations, $r = 3/2$ for scattering by ionized impurities). Therefore, if we suppose that the disturbance to the distribution is small, and for simplicity we consider transport only along the x direction, the collision integral is written as:

$$\frac{f(E) - f_0(E)}{\tau_n} = v_x \frac{df_0(E)}{dt} \left(\frac{dE_F}{dx} + \frac{(E - E_F)}{T} \frac{dT}{dx} \right) \quad (1.16)$$

where v_x is the velocity of the carriers along the x direction, E_F is the Fermi energy, and T is the temperature. By calculating the electric current density i and the heat flux density j , the transport parameters such as the electrical conductivity σ , the electronic contribution of thermal conductivity k_{el} , and the Seebeck coefficient S can be obtained:

$$\sigma = \frac{1}{\rho} = \frac{i}{E} \Big|_{\frac{dT}{dx}=0} = -\frac{2e^2}{3m^*} \int_0^\infty g(E) \tau_e(E, T) \frac{df_0(E)}{dE} dE \quad (1.17)$$

$$k_{el} = \frac{j}{-\frac{dT}{dx}} \Big|_{i=0} = \frac{2}{3m^* T} \left\{ \frac{\left[\int_0^\infty g(E) \tau_e(E, T) E^2 \frac{df_0(E)}{dE} dE \right]^2}{\int_0^\infty g(E) \tau_e(E, T) \frac{df_0(E)}{dE} dE} \right. \\ \left. - \int_0^\infty g(E) \tau_e(E, T) E^3 \frac{df_0(E)}{dE} dE \right\} \quad (1.18)$$

$$S = \frac{E}{T} \Big|_{i=0} = \pm \frac{1}{eT} \left[E_F - \frac{\int_0^\infty g(E) \tau_e(E, T) E^2 \frac{df_0(E)}{dE} dE}{\int_0^\infty g(E) \tau_e(E, T) \frac{df_0(E)}{dE} dE} \right] \quad (1.19)$$

where e is the electron charge, m^* the density-of-states effective mass, τ_e the relaxation time for charge carriers, and $g(E)$ the total density-of-states (DOS). The Fermi window factor $(-df_0(E)/dE)$ is a bell-shaped function centered at $E = E_F$, and has a width of $\sim k_B T$, being responsible for the fact that at finite temperature, only electrons near the Fermi surface contribute to the conduction process. The $\pm$ sign in Equation 1.19 refers to holes and electrons, respectively.

Concerning the Seebeck coefficient, it is possible to obtain two different expressions for metals and semiconductors.

- **Metals** ($E_F \gg k_B T$)

$$S = \mp \frac{\pi^2}{3} \frac{k_B}{e} \frac{(r + 3/2)}{\eta} \quad (1.20)$$

- **Semiconductors**

$$S = \mp \frac{k_B}{e} (\eta - (r + 5/2)) \quad (1.21)$$

where $\eta = \frac{E_F}{k_B T}$ is the reduced Fermi energy.

The substantial difference in the Seebeck coefficient for these two classes of materials lies in the fact that $S_{metal} \sim 1/\eta$ and $S_{semiconductors} \sim \eta$. Since the Fermi energy values for metals are large, up to tens of eV, the Seebeck coefficient can only be in the order of a few microvolts per degree. For typical extrinsic semiconductors, instead, η may be much greater than unity, and thus S may be several hundreds of microvolts per degree. Additionally, in semiconductors, the Seebeck coefficient is made up of two terms, a potential component and a kinetic component.

In the case of metals or degenerate semiconductors, under the approximation of parabolic bands and energy-independent scattering, the Seebeck coefficient expression 1.20 becomes [77]:

$$S = \mp \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad (1.22)$$

where k_B is the Boltzmann constant, e is the electron charge, h the Planck constant, m^* the effective mass of the carrier, T the temperature, and n the carrier concentration. From this equation, it is clear that S is increased with large m^* and small n . Nevertheless, as previously mentioned, the parameters involved in the ZT figure of merit are conflictingly correlated, as highlighted in the case of the electrical conductivity σ , for which the following relation holds:

$$\sigma = ne\mu \quad (1.23)$$

where μ is the carrier mobility. Therefore, to have a large σ , the carrier density n should be high, conflicting with the requirement of a small n to increase S . Additionally, another conflict is given by the fact that $S \sim m^*$ but $\sigma \sim 1/m^*$. In fact, heavy carriers move with slower velocities and, therefore, small mobilities, reducing the electrical conductivity.

It appears clear that a balance must be found among all these intercorrelated parameters. Figure 1.11 shows the ZT figure of merit *vs* the carrier concentration n , expressed in cm^{-3} , obtained by modeling data for Bi_2Te_3 . Optimization occurs for carrier concentration values between 10^{19} and 10^{20} carriers per cm^3 , as highlighted by the yellow band, corresponding to heavily doped semiconductors. The Seebeck coefficient S (between 0 and $500 \mu\text{V K}^{-1}$), electrical conductivity σ (between 0 and

$5000 \Omega^{-1} \text{ cm}^{-1}$), thermal conductivity k (between 0 and $10 \text{ W m}^{-1} \text{ K}^{-1}$), and power factor $PF = S^2\sigma$, are also plotted. Maximizing thermoelectric efficiency requires a compromise, as highlighted by the fact that the maximum of ZT doesn't correspond with the maximum of the power factor $S^2\sigma$.

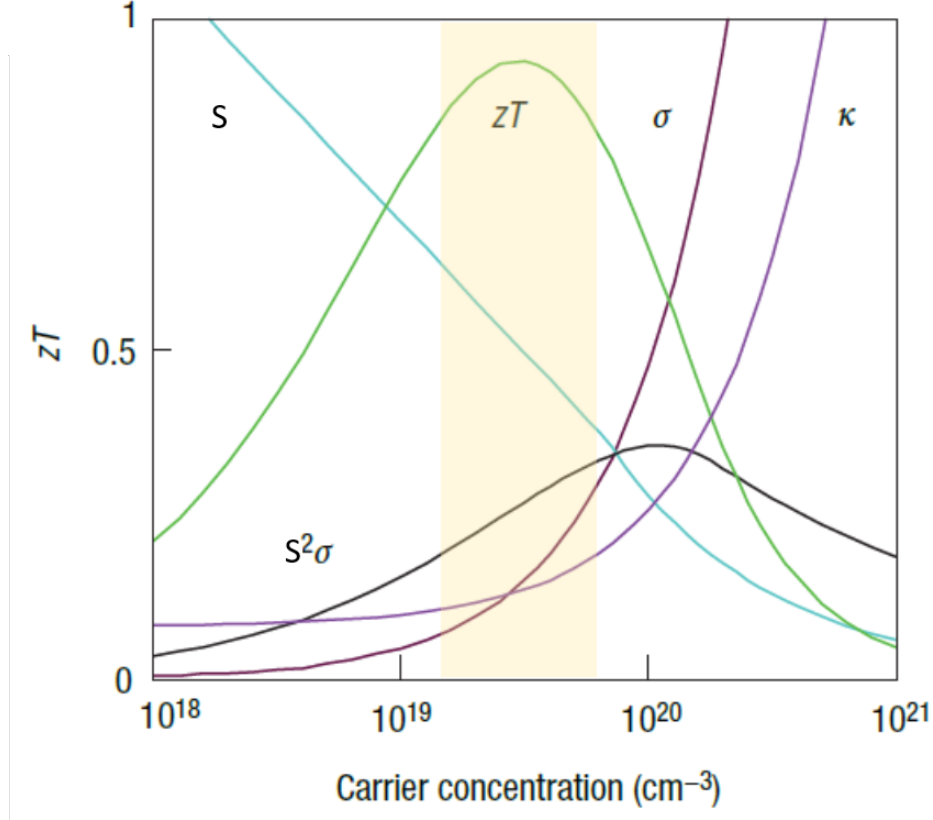


Figure 1.11. ZT figure of merit vs carrier concentration n , obtained from Ref. [74]. The Seebeck coefficient S (between 0 and $500 \mu\text{V K}^{-1}$), electrical conductivity σ (between 0 and $5000 \Omega^{-1} \text{ cm}^{-1}$), thermal conductivity k (between 0 and $10 \text{ W m}^{-1} \text{ K}^{-1}$), and power factor $PF = S^2\sigma$, are also plotted.

Semiconducting systems are typically bipolar, that is, systems where there are two types of carriers. This aspect affects the transport properties. In fact, the total current density i in the presence of both an electric field and a temperature gradient for the n or p carriers is:

$$i_{n,p} = \sigma_{n,p} \left(\frac{dV}{dx} - S_{n,p} \frac{dT}{dx} \right) \quad (1.24)$$

Consequently, it can be shown that [76]:

$$\sigma = \frac{i}{\frac{dV}{dx} \Big|_{\frac{dT}{dx}=0}} = \frac{\sigma_n \frac{dV}{dx} + \sigma_p \frac{dV}{dx}}{\frac{dV}{dx}} = \sigma_n + \sigma_p \quad (1.25)$$

$$k_{el} = k_n + k_p + \frac{\sigma_n \sigma_p}{\sigma_n + \sigma_p} (S_n - S_p)^2 T \quad (1.26)$$

$$S = \left. \frac{\frac{dV}{dx}}{\frac{dT}{dx}} \right|_{i=0} = \frac{\sigma_n S_n + \sigma_p S_p}{\sigma_n + \sigma_p} \quad (1.27)$$

Therefore, it can be deduced that:

- the electrical conductivity is the sum of the conductivities of the separate carriers;
- the total electronic thermal conductivity is not just the sum of the thermal conductivities of the separate carriers, but there is an additional term associated with the bipolar flow, which can be much larger than either k_n or k_p ;
- the Seebeck coefficient is the weighted average of the Seebeck coefficients of the two types of carriers, with electrical conductivities as weights. Since S_n and S_p have opposite signs, the total S is reduced. In fact, mixed n-type and p-type conduction will lead to both charge carriers moving to the cold end, canceling out the induced Seebeck voltages.

For most semiconductors, at least two distinct regions can be observed in Seebeck data covering a sufficiently broad temperature range. In the first of these regions, extrinsic charge carriers excited from impurity states are dominant, and the magnitude of the Seebeck coefficient, $|S|$, rises with temperature as the Fermi level moves away from the edge of the appropriate band. As the temperature is increased further, the second region is reached. Here, electron-hole pairs are excited across the energy gap, and $|S|$ falls due to the opposing effects of the two types of carriers. Between these two regions, $|S|$ must reach a maximum value, given by $S_{max} = E_g/2eT$, where E_g is the material energy gap. Figure 1.12 shows the Seebeck coefficient behavior *vs* temperature for three $\text{Bi}_{0.64}\text{Sb}_{1.36}\text{Te}_3$ films grown with different thicknesses via Molecular Beam Epitaxy (MBE) [78]. The increasing trend versus temperature is detectable in the three films, while the turnover is present only for the thickest film (200 nm, blue triangles) around 150 K due to the excitation of the impurity level. This aspect is absent in the 6 nm (black squares) and 15 nm (red circles) case since the reduced film thickness reduces the number of intrinsic defects and shifts the S maximum toward higher temperatures.

At this point, the question: "Where should the Fermi level be located in bipolar systems to maximize the thermoelectric efficiency?" naturally arises. Let's write again the expression for the Seebeck coefficient S of Equation 1.27. Indeed, we can write the electrical conductivities σ_n and σ_p for n and p-type carriers as:

$$\sigma_n = ne\mu_n \quad \sigma_p = pe\mu_p \quad (1.28)$$

The charge carrier densities can be written as:

$$n = 2 \left(\frac{2\pi m_n^* k_B T}{h^2} \right)^{3/2} e^{\eta_n}, \quad p = 2 \left(\frac{2\pi m_p^* k_B T}{h^2} \right)^{3/2} e^{\eta_p} \quad (1.29)$$

where m_n^* and m_p^* are the effective masses for electrons and holes, respectively, and $\eta_n = \frac{E_F - E_C}{k_B T}$ and $\eta_p = \frac{E_V - E_F}{k_B T}$, with E_F , E_C , and E_V the Fermi level, conduction band minimum, and valence band maximum energies. Therefore, S turns into:

$$S = \frac{\sigma_n S_n + \sigma_p S_p}{\sigma_n + \sigma_p} = \frac{k_B [(\eta_p - (r + 5/2)) - \sigma_n/\sigma_p(\eta_n - (r + 5/2))]}{e \left(\frac{\sigma_n}{\sigma_p} + 1 \right)} \quad (1.30)$$

with the factor $\frac{\sigma_n}{\sigma_p}$ expressed as:

$$\frac{\sigma_n}{\sigma_p} = \left(\frac{m_n^*}{m_p^*} \right)^{3/2} \frac{\mu_n}{\mu_p} e^{\eta_n - \eta_p} = C e^{\eta_n - \eta_p} \quad (1.31)$$

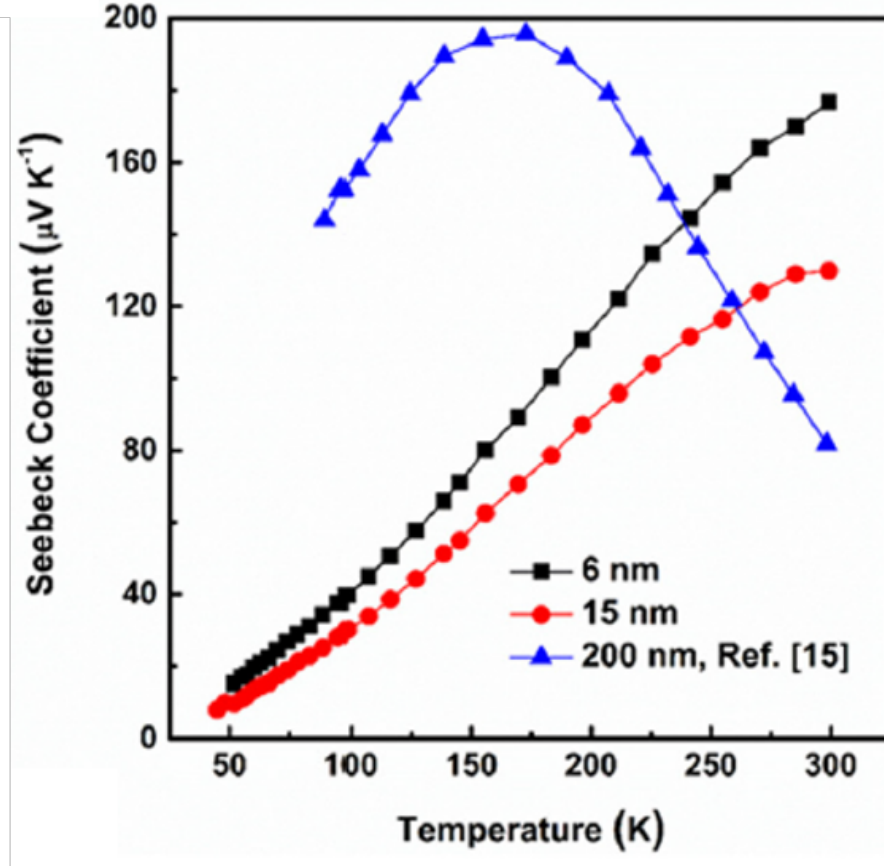


Figure 1.12. Seebeck coefficient *vs* temperature in the range between 50 K and 300 K for $\text{Bi}_{0.64}\text{Sb}_{1.36}\text{Te}_3$ films grown via Molecular Beam Epitaxy (MBE) [78]. Data are shown for 6 nm (black squares) and 15 nm (red circles) thick films, together with the data of a reference 200 nm film reported in Ref. [79].

From this Equation, we understand that the Fermi level position is essential in determining the Seebeck coefficient value for bipolar systems. Three possible situations can occur:

- the Fermi level is located in the middle of the gap, therefore $m_n^* = m_p^*$, $n = p$, $\mu_n = \mu_p$, which implies that $C = 1$, and $\eta_n = \eta_p$, which implies that $\sigma_n/\sigma_p = 1 \rightarrow S = 0$;
- the Fermi level approaches the edge of the conduction or valence band, making S small;
- the Fermi level is moved by a few $k_B T$ from the middle of the gap, making the ratio of the electron to hole concentration becomes very large or very small, so that the Seebeck coefficient is dominated by the contribution from one carrier or the other. The maximum S is found around $E_g/2K_B T$.

Additionally, a lot of research has been conducted to find the optimal band gap E_g value of a thermoelectric semiconductor to maximize its conversion efficiency. This topic was first investigated theoretically by Chasmar and Stratton for indirect gap semiconductors [80]. The best gap was found to be of $6k_B T$. Later, Mahan did a similar study and found $E_g \sim 10k_B T$ to be a more realistic value for indirect gap materials [81]. Sofo and Mahan extended the calculations to include direct gap materials and found that the optimum gap is always greater than $6k_B T$, but can be much larger depending on the dominant electron scattering mechanism [82]. Nolas et al. [83] used a single parabolic band model and optimized the position of the chemical potential for the single band model. They then added the bipolar contribution to the thermoelectric transport and calculated the modified ZT . It was concluded that the band gap should be larger than $8k_B T$ to suppress the minority carrier contributions to the thermoelectric transport.

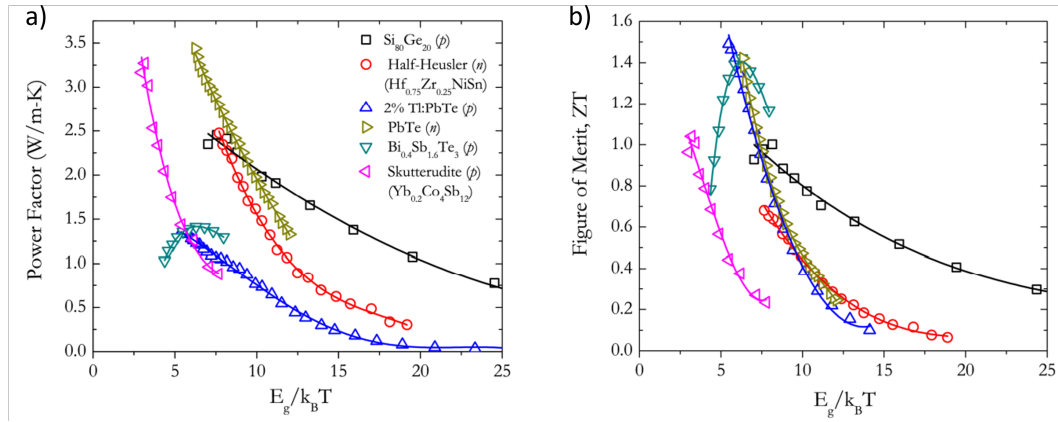


Figure 1.13. a) Thermoelectric power factor PF and b) figure-of-merit ZT for some of the best thermoelectric materials reported in the literature as a function of the band gap E_g . p-type $\text{Si}_{80}\text{Ge}_{20}$ [84], p-type $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ [85], p-type PbTe [86], n-type PbTe [87], n-type half Heuslers [88], and n-type skutterudites [89] are reported. An increasing value of E_g compared to $k_B T$ decreases the values of both quantities. Images obtained from Ref. [73].

Figure 1.13 a) and b) show the power factor PF and the figure-of-merit ZT as a function of $E_g/k_B T$ for some of the best thermoelectric materials found in the literature. More in detail, p-type $\text{Si}_{80}\text{Ge}_{20}$, p-type $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$, p-type PbTe, n-type PbTe, n-type half Heuslers, and n-type skutterudites are reported. The general trend for these semiconducting materials consists of a decrease in both PF and ZT values as E_g increases compared to $k_B T$. For p-type $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ an inversion point is also detectable around $E_g \sim 6k_B T$.

1.2.2 Strategies to improve ZT

As already mentioned, improving the conversion efficiency of thermoelectric materials constitutes a hard challenge due to the interdependency of S , σ , and k . In this Subsection, a brief overview of the most common strategies used to reach this goal is given.

Today, research is focusing on the use of chalcogenide materials ¹ as a starting

¹Chalcogenides are chemical compounds consisting of at least one chalcogen anion and at least one more electropositive element. The elements belonging to group 16 in the periodic table, such as

point in this field because they exhibit a peak value of the figure of merit ZT around room temperature [90, 91, 92]. Figure 1.14 (a) shows the value ZT for some efficient thermoelectric materials of n type, such as Bi_2Te_3 , PbTe , SiGe , as a function of temperature. Bi_2Te_3 exhibits a maximum value ZT of 1 at $\sim 50^\circ\text{C}$, which explains why it is the most widely used thermoelectric within this temperature range. Figure 1.14 (b) reports the figure of merit for some efficient p-type thermoelectric materials, such as Sb_2Te_3 , PbTe , $\text{CeFe}_4\text{Sb}_{12}$. Again, the chalcogenoid Sb_2Te_3 peaks around room temperature. By adjusting the carrier concentration, ZT can be optimized to peak at different temperatures, enabling the making of applications in the cooling/power generation field.

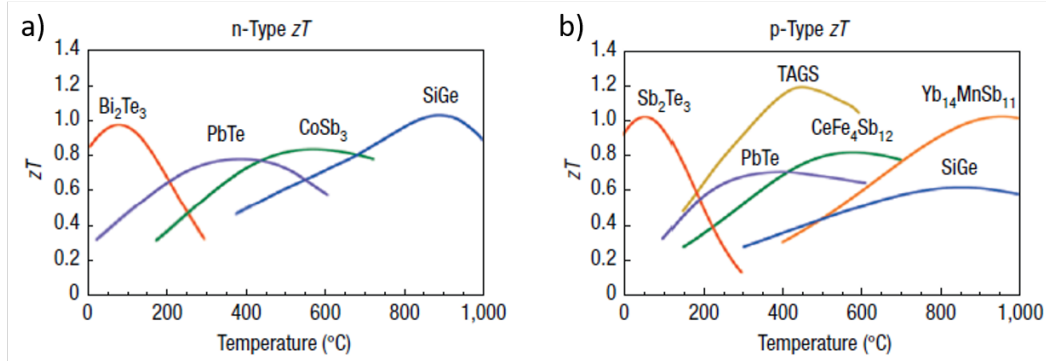


Figure 1.14. Figure of merit ZT for n-type (a) and p-type (b) materials as a function of temperature, up to 1000°C . Obtained from Ref. [74].

Over the past decade, a lot of research has been conducted on the possibility of decoupling electron and phonon transport, thus the power factor $S^2\sigma$ and the lattice thermal conductivity k_{lattice} . Recently, much of the research in bulk materials for thermoelectric applications has been based on the concept of the "phonon-glass electron-crystal" model (PGEC), developed by Slack [93]. This paradigm suggests that a good thermoelectric material should have the electronic properties of a crystalline material and the thermal properties of a glass, i.e., a lattice thermal conductivity as low as possible, which allows for the scattering of phonons without significantly compromising the electrical conductivity. This achievement is possible thanks to the strong difference that exists in the mean free paths of the involved carriers, electrons (or holes) on one side, and phonons on the other side. In fact, the mean free path of electrons is estimated to be around tens of nanometers, whereas typical phonon mean free paths at room temperature range around hundreds of nanometers [94]. This difference of at least one order of magnitude makes this strategy promising for enhancing the efficiency of these materials.

Several ideas were proposed to realize the increase of the conversion efficiency, including the decoupling between electrical conductivity and Seebeck coefficient. In fact, the density-of-states effective mass m^* and the mobility μ are strongly related [95]. It is possible to show that the power factor $S^2\sigma$ is an increasing function of $\mu(m^*/m_e)^{3/2}$ [96]. Mahn [97] showed that to increase the density-of-states effective mass without reducing the mobility too much, semiconductors with multivalleys and small inertial masses are desirable. In fact, the density-of-states effective mass can be written as $N_v^{2/3}(m_1m_2m_3)^{1/3}$, where N_v is the number of equivalent valleys (band degeneracy) and $m_{1,2,3}$ are the inertial masses in each direction. According to

S, Se, Te, Po, are named in this way.

theory, multivalley semiconductors with small inertial masses can have the largest $\mu(m^*/m_e)^{3/2}$. In this way, the power factor can be optimized. Additionally, for a fixed E_F , the multivalley band structure increases the total electronic density of states $g(E_F)$, resulting in a larger carrier density but the same Seebeck coefficient. For example, Bi_2Te_3 has 6 equivalent conduction valleys in the band structure, whereas PbTe has 4 [98].

The reduction in dimensionality of the system is a known strategy used to increase the Seebeck coefficient [99]. In fact, sharp features are present in the electronic density of states $g(E)$ when reducing the dimensionality from 3D bulk crystals to 2D quantum wells, 1D nanowires or nanotubes, and 0D quantum dots, which are favorable for increasing S . With the advent of the Molecular Beam Epitaxy (MBE) technique, this strategy was proven, and it was demonstrated that in n-type $\text{PbTe}/\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ quantum well superlattices, the Seebeck coefficient can be improved by a factor of 1.4 compared to the bulk PbTe counterpart [100, 101].

The idea of developing composite materials made up of more components to increase the power factor was first proposed by Bergman and Levy [102]. They developed an effective-medium theory to explain the thermoelectric properties of a two-component mixture, and discovered that the effective power factor $S^2\sigma$ can be larger than the power factors of the single components.

The possibility of adding dopants is an efficient strategy to increase the carrier density and increase the conductivity of the system. It was already pointed out that heavily doped semiconductors with charge carriers on the order of 10^{18} - 10^{20} cm^{-3} are optimum thermoelectrics. However, the added dopants act as scattering centers, hindering electron transport. Engineering the doping centers by modifying their shape, size, and chemical potential is an interesting route to suppress the deleterious effect of doping in these materials, creating the so-called "invisible dopants" [103].

The reduction of the lattice thermal conductivity is obtained by scattering phonons across various length scales. The introduction of atomic disorder through point defects such as interstitials, random vacancies, or the alloying procedure is an efficient strategy to scatter phonons within the unit cell. Alloying binary tellurides, including Bi_2Te_3 , Sb_2Te_3 , PbTe , and GeTe with other isoelectronic cations and anions affects phonon transport without hindering electron transport [104, 105]. Another route to reduce κ_{lattice} is the use of crystals possessing complex and large unit cells. Compared to Bi_2Te_3 , CsBi_4Te_6 has a lower lattice thermal conductivity because of the more complex structure due to the Cs layers and the Bi-Bi bonds absent in Bi_2Te_3 [106]. Another alternative way to do so is the scattering at the interfaces via the creation of nanostructured materials, such as thin-film superlattices or mixed composite structures. Thin films and nanowires belong to this category, together with polycrystalline materials with grains with specific dimensions that scatter phonons but not electrons [107, 108]. At last, the investigation of Phononic Crystals (PnC) constitutes another route to decrease thermal phonon transport [109, 110, 111, 112, 47]. The thermal conductivity of a crystal in a bulk material is reduced when the characteristic length of the system becomes comparable to or shorter than the phonon mean free path in the bulk material. In such a system, the thermal properties no longer follow the Fourier law [113] but instead are described by semiballistic phonon transport. In these artificial crystals, specifically designed periodic arrays of geometrical structures on the nanometric length scale affect phonon transport and reduce thermal conductivity [110]. However, this approach is challenging because thermal phonons are distributed over a broad range of frequencies [114, 115, 116], and thus there is a multiscale distribution of thermal phonon mean free paths. Therefore, a phonon scattering mechanism that covers the whole range

is required to efficiently reduce thermal conductivity.

1.2.3 Topological Insulators and Thermoelectricity

Many efficient thermoelectric materials belong to the class of topological insulators, since thermoelectric compounds and topological insulators share similar material features, such as heavy constituent elements, narrow band gaps, and high spin-orbit coupling [117, 118, 119].

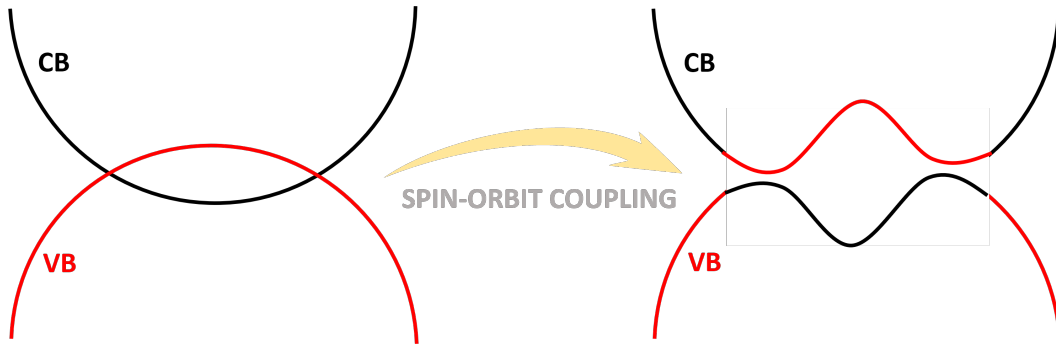


Figure 1.15. Schematics showing the "band inversion" mechanism for Bi_2Se_3 . On the left, the conduction band (CB), shown in black, is made of Bi-Bi p_z orbitals, and the valence band (VB), shown in red, of Se-Se p_z orbitals. However, the bands overlap, and the system has no band gap. When spin-orbit coupling is included (on the right), a gap opens at the crossing points, and now the conduction band has contributions from the band that made the valence band originally (red) and vice versa. This feature is very easy to recognize in the case of Bi_2Se_3 , but it may be harder in other materials.

All semiconductors with a nonzero band gap can be divided into two classes: trivial insulators and topological insulators. Continuous elastic deformations and other continuous perturbations cannot translate an insulator into another class of materials without closing the energy gap and passing through an intermediate conducting state [120]. In standard semiconductors, the top of the valence band is made up of the orbitals of more electronegative elements, while the orbitals of less electronegative elements form the bottom of the conduction band. In topological insulators, strong spin-orbit coupling (SOC) splits the energies of the band and inverts the normal ordering of the valence and conduction bands (band inversion), as shown in Figure 1.15 for the Bi_2Se_3 case. This feature leads to narrow band gaps, which prove to be efficient for room-temperature thermoelectrics. The main difference between trivial and topological insulators consists in the fact that the latter exhibit gapped bulk states and non-trivial gapless Dirac boundary states, originating from a linear dispersion relation, including edge states in the case of 2D topological insulators and surface states in the case of 3D topological insulators [121]. In the simplest case, the non-trivial states have a spectrum made up of two cones with a common vertex located in the gap between the projections of the bulk bands onto the surface band structure of the insulator, named the Dirac point. Due to such a linear dispersion, surface fermions behave as relativistic massless particles. The number of Dirac cones in the surface band structure has to be odd. Time-reversal symmetry of the Hamiltonian describing these systems protects these "metallic" surface states from perturbations that do not violate this symmetry. This property implies that backscattering by nonmagnetic impurities and crystal structure defects is forbidden, leaving phonon transport totally unaffected. In fact, it is easy to demonstrate that:

$$\langle -\mathbf{k}, \downarrow | U | \mathbf{k}, \uparrow \rangle = \langle \mathbf{k}, \uparrow | U^\dagger | -\mathbf{k}, \downarrow \rangle^* = \langle \mathbf{k}, \uparrow | T U | \mathbf{k}, \uparrow \rangle^* = \langle \mathbf{k}, \uparrow | T \rangle U | \mathbf{k}, \uparrow \rangle = \quad (1.32)$$

$$-(\langle \mathbf{k}, \uparrow | T^\dagger \rangle U | \mathbf{k}, \uparrow \rangle = -\langle -\mathbf{k}, \downarrow | U | \mathbf{k}, \uparrow \rangle \quad (1.33)$$

where $U(x)$ is the time-reversal invariant operator, which describes the potential of an impurity/defect, T is the antiunitary time-reversal operator such that $|-\mathbf{k}, \downarrow\rangle = T|\mathbf{k}, \uparrow\rangle$, and for particles with half-integer spin, $T^2 = -1$, therefore $T = -T^\dagger$ [122]. We deduce that the only way to satisfy this Equation is that the values of the matrix elements are zero, so the backscattering of an electron from state $|\mathbf{k}, \uparrow\rangle$ is forbidden. The strong SOC, responsible for the band inversion, is ensured by the presence of heavy elements like Bi, Sb, Te, Se, Pb in these compounds, which provide also a low lattice thermal conductivity $k_{lattice}$ [123]. In this way, electron and phonon transport properties can be decoupled, and the "phonon-glass electron-crystal" strategy can be pursued. The main properties of topological insulators that are responsible for high thermoelectric efficiency are summarized in Table 1.16.

TOPOLOGICAL INSULATORS	THERMOELECTRIC MATERIALS
Large SOC → heavy elements	Small lattice thermal conductivity $k_{lattice}$
Odd number of inverted bands between CB and VB	Small E_g
Conservation of Time-Reversal Symmetry → the interface state of a TI is robust against nonmagnetic impurities and surface disorder	Absence of electron backscattering

Figure 1.16. Table summarizing the main topological insulator properties which enable good thermoelectric efficiency.

Layered binary chalcogenides with the chemical formula M_2X_3 , with $M=\text{Sb/Bi}$, $X=\text{Te/Se}$, such as Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 , are 3D topological insulators. Strong SOC changes the order of two p_z orbitals, belonging to Bi and Se or Te, responsible for the formation of the valence band and conduction band, respectively, thus band inversion occurs at the Γ point [123]. These compounds crystallize in the rhomboedral phase (space group $R\bar{3}m$), made up of quintuple layers (QLs) of $X(1)\text{-}M\text{-}X(2)\text{-}M\text{-}X(1)$ stacked along the c -axis of the unit cell and separated by Van der Waals gaps, as shown in Figure 1.17 (a). These 3D topological insulators have a bulk band gap of 0.2 - 0.3 eV. Additionally, these materials are conducting because of the presence of anti-site point defects. The latter are the most dominant structural defects in these compounds, with formula A_B , which means that element A occupies the lattice site of element B. In Bi_2Te_3 , the n-type anti-site defects Te_{Bi} are dominant over the Bi_{Te} , therefore, transport is dominated by n-type carriers [124]. The Fermi level E_F is located within the conduction band. In Sb_2Te_3 , the dominance of Sb_{Te} defects determines a p-type conduction with the Fermi level located within the valence band [125]. At last, in Bi_2Se_3 , Se vacancies or Se substitutional defects on Bi sites (Se_{Bi} antisite defects) naturally make the material n-type, with the Fermi level located in the bulk conduction band [126].

Figure 1.17 (b), instead, depicts the electronic band structure of one of these chalcogenides, Bi_2Se_3 , measured via angle-resolved photoemission spectroscopy

(ARPES) along the K- Γ -K direction, where Γ is the center of the hexagonal surface Brillouin zone. Bulk conduction and valence bands are visible, together with surface state bands, with linear dispersion.

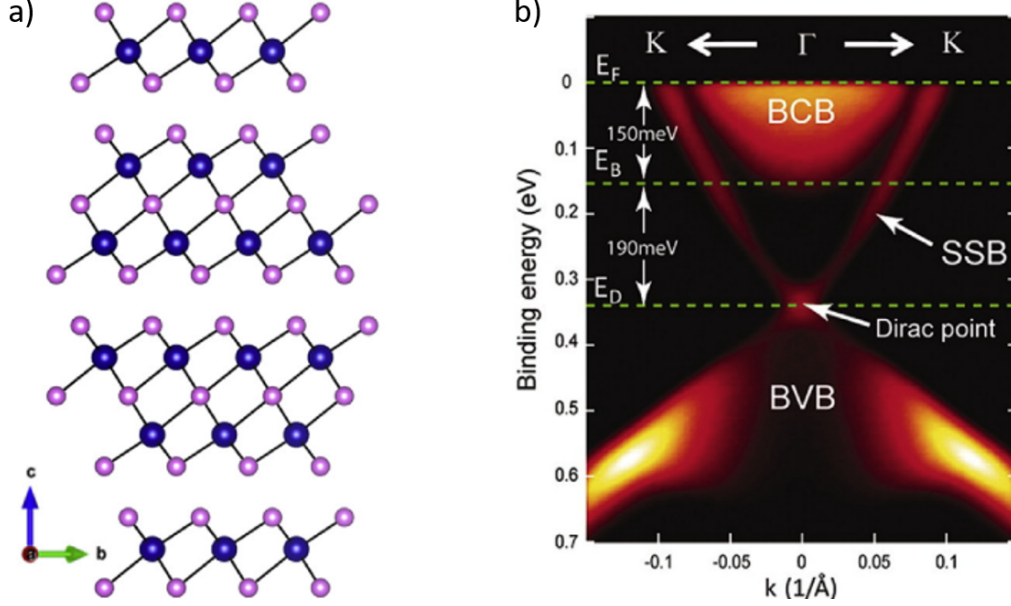


Figure 1.17. a) Crystal structure of M_2X_3 ($M=\text{Sb/Bi}$, $X=\text{Te/Se}$). Blue and magenta atoms represent M and X atoms, respectively [119]. Quintuple layers are alternated along the c -axis and separated by Van der Waals gaps. b) Electronic band structure of bulk Bi_2Se_3 measured by angle-resolved photoemission spectroscopy (ARPES). The Fermi energy E_F is located inside the bulk conduction band (BCB), 150 meV above the BCB minimum, in the Γ point. The Dirac point (E_D) associated with the surface state bands (SSB) is located 190 meV below the BCB minimum. Obtained from Ref. [127].

The Fermi energy E_F is located inside the bulk conduction band (BCB), 150 meV above the BCB minimum, at the Γ point. The Dirac point (E_D) associated with the surface state bands (SSB) is located 190 meV below the BCB minimum [127].

In real topological insulators, it is difficult to isolate the positive effects that the boundary states determine on transport properties from the bulk contribution. In fact, in real topological insulators, several non-topological states contribute to the electric current. To reduce the contribution of trivial states, the sample thickness is crucial: a thickness in the nanometer range ensures a large surface-to-bulk ratio, so that the contribution of topological boundary states to the electrical conductivity dominates over the bulk one. Additionally, the lattice thermal conductivity can be reduced due to phonon scattering with the material boundaries, which become comparable in size with the phonon mean free path. However, a too small thickness might open a gap in the Dirac fermion spectrum due to hybridization of the states on the upper and lower surfaces of the material [128, 129]. Dirac fermions acquire a mass, and the protection of electrons from backscattering is reduced, with an increase in resistance. The overall impact on the ZT figure of merit is shown in Figure 1.18 (a) and (b) for p-type and n-type Bi_2Te_3 films as a function of their thickness, expressed in QLs [130]. Two different values of the ratio $r_\tau = \tau_1/\tau_2$ are considered, 100 (a) and 1000 (b), where τ_1 and τ_2 are the relaxation times for carriers in boundary states in the bulk band gap and outside the gap, respectively. It is assumed that $\tau_1 \gg \tau_2$ because non-trivial states are protected from backscattering.

The non-monotonous trend comes from the competition between the surface and bulk contributions to the thermoelectric performance, coupled with the overall quantum size effects. The jump in the ZT value at ~ 3 QLs between the topologically trivial and non-trivial regimes originates from their different surface relaxation times, as discussed above. At sufficiently larger thicknesses, the contributions from the bulk states become more and more dominant, and the ZT values of such films approach those of bulk Bi_2Te_3 .

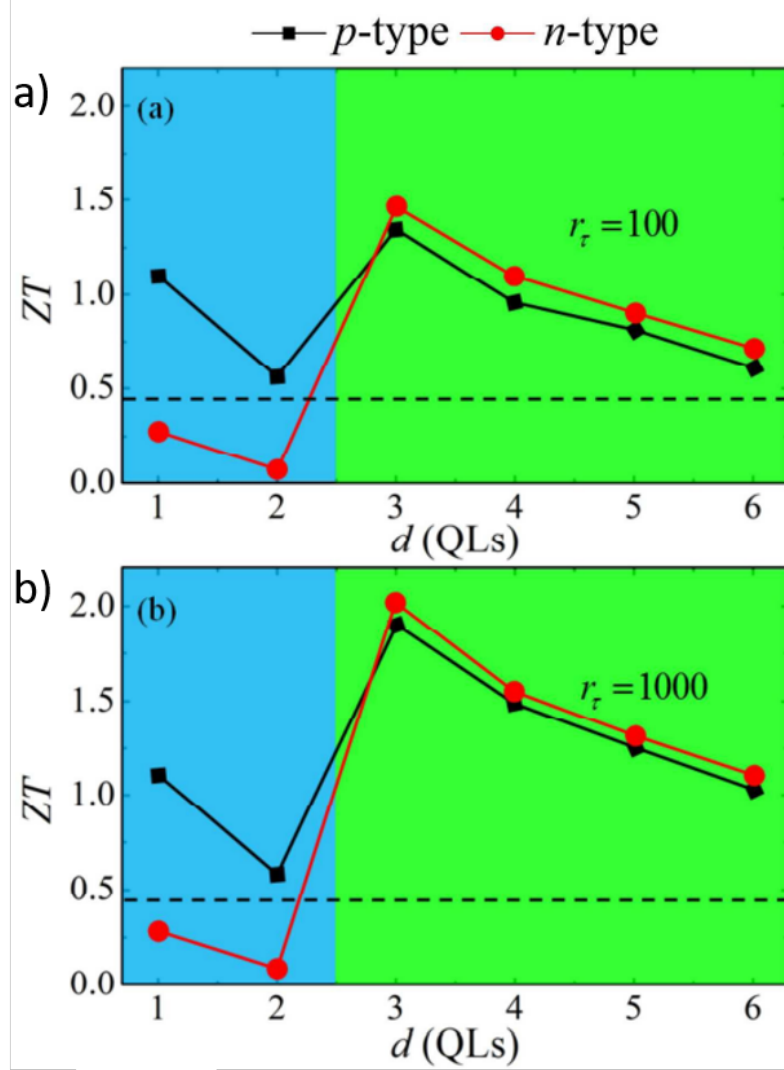


Figure 1.18. Calculated room-temperature ZT figure of merit for p-type and n-type Bi_2Te_3 films as a function of their thickness, expressed in QLs. Two different values of the ratio $r_\tau = \tau_1/\tau_2$ are considered, 100 (a) and 1000 (b). The blue and green regimes represent films with trivial and non-trivial surface states, respectively. The dashed line represents the ZT value for bulk Bi_2Te_3 . Image obtained from Ref. [130].

Concerning transport properties in topological insulators, two types of states, bulk and boundary, should be considered. These features can be described taking into account a multiple-channel model because these states have different band structures and exhibit different transport properties, being one topologically protected and the

other not. In particular, the total electrical conductivity σ and Seebeck coefficient S expressions become [131]:

$$\sigma = \sigma_b + \sigma_{bS} \quad (1.34)$$

$$S = \frac{\sigma_b S_b + \sigma_{bS} S_{bS}}{\sigma_b + \sigma_{bS}} \quad (1.35)$$

where the subscripts b and bS refer to bulk and boundary states, respectively. Again, the electrical conductivity is simply the sum of the electrical conductivities of the two available transport channels, whereas the total Seebeck coefficient is the weighted average of the Seebeck coefficients of the two types of channels, with electrical conductivities as weights.

In Chapter 3, thermoelectricity will be investigated in chalcogenide 3D topological insulator thin films grown by MBE at Professor Oh's lab, located at Rutgers University, New Jersey, USA, with a focus on their electrodynamic and the Seebeck coefficient behavior. Two material groups will be considered: the first class composed of Bi_2Te_3 , Sb_2Te_3 , and $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ alloys thin films, and the second made up of Bi_2Se_3 films grown with different thicknesses. In the first case, the Seebeck coefficient sign change is explored from room temperature up to 100 °C, starting from n-type Bi_2Te_3 and ending up with p-type Sb_2Te_3 , while moving across intermediate $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ alloys. In the second case, Bi_2Se_3 films with different thicknesses are investigated. The study of the electrodynamic properties in a wide spectral range, extending from THz to Visible, allows gaining insight into lattice vibration modes, free carrier contribution, and electronic transitions.

1.3 Phase-Change Materials

In this Section, an overview of phase-change materials (PCMs) is given, focusing mainly on their switching capability from an amorphous to a crystalline phase and vice versa, with the help of an external trigger. $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ van der Waals materials are later discussed.

1.3.1 Basic Functionality and Applications

Nowadays, a lot of research is focused on PCMs, which are semiconducting materials characterized by two allotrope phases, a crystalline and an amorphous one [132]. More in detail, these compounds exhibit reversible phase transitions from amorphous to crystalline phases and vice versa in the presence of an external trigger. The interest in these compounds has both technological and energy harvesting implications, considering that, on the one hand, they are used as the active material for non-volatile solid-state memories thanks to their faster switching speeds, but on the other hand, these materials require reduced switching energies with ultra-low energy consumption [133, 134, 135, 136].

The main advantage of PCMs compared to other materials that undergo phase transitions is the significant difference between the physical properties of the amorphous and crystalline states, such as electrical conductivity, optical reflectivity, mass density, or thermal conductivity. More specifically, the amorphous phase of PCMs is characterized by low reflectivity and high resistance. In contrast, the crystalline phase is characterized by high reflectivity and low resistance, since the atomic arrangement of the two phases is strongly different [137]. These differences and the

repeatability of the switching give these materials the ability to store information, distinguishing between logical states. Rewritable compact discs, digital versatile discs, and Blu-ray discs store information in thin films of PCMs, using the difference in reflectivity between the phases as the storage mechanism. The switch from the amorphous phase to the crystalline phase occurs if the material is heated above its crystallization temperature T_g for a long enough time (a process called the SET operation in the solid-state memory application, which writes "1") [138]. Switching from the crystalline phase to the amorphous phase is introduced by melting and quenching the material quickly enough so that it solidifies in the amorphous state (a process called the RESET operation in the solid-state memory application, which writes "0"). Figure 1.19 summarizes this process. In the reset phase, a short pulse of a focused, high-intensity laser beam locally heats the phase-change material above its melting temperature, as shown in panel (a). Rapid cooling of the alloy at speeds greater than 109 K s^{-1} quenches the liquid-like state into a disordered amorphous phase, as shown in panel (b). This amorphous state exhibits optical properties different from those of the surrounding crystalline state, making it straightforward to detect amorphous regions with a low-intensity laser beam. To erase the stored information, a laser pulse with intermediate power is used (panel (c)). The laser locally heats the phase-change film above the crystallization temperature. At temperatures above T_g the atoms become increasingly mobile and can revert to the energetically favourable crystalline state, erasing the recorded information.

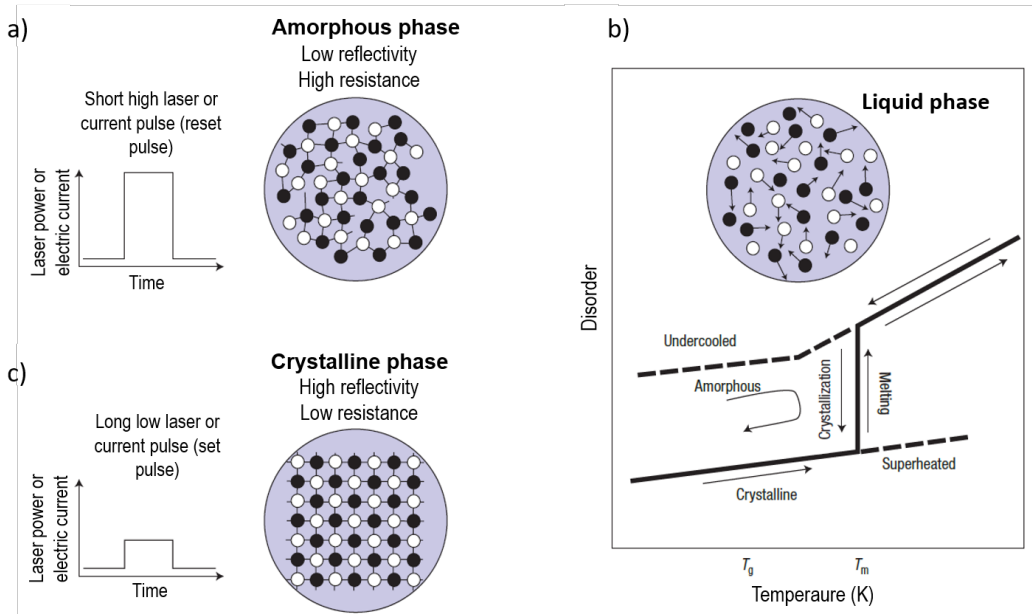


Figure 1.19. Sketch showing the optical data storage process. (a) A short pulse of a focused, high-intensity laser beam locally heats the phase-change material above its melting temperature. (b) Rapidly cooling the alloy at rates higher than 109 K s^{-1} quenches the liquid-like state into a disordered, amorphous phase. This amorphous state exhibits different optical properties from the surrounding crystalline state, making it straightforward to detect amorphous regions with a low-intensity laser beam. (c) To erase the stored information, a laser pulse with intermediate power is used. The laser locally heats the phase-change film above the crystallization temperature. At temperatures above T_g , the atoms become increasingly mobile and can revert to the energetically favourable crystalline state, erasing the recorded information. Image obtained from Ref. [132].

The fast atomic rearrangement required to crystallize again, taking from ten to one hundred seconds, explains why these compounds are promising candidates for realizing optical data storage.

Historically, chalcogenide materials exhibit good phase change properties. Ovshinsky was the first to talk about solid-state memory applications in 1960 [139]. He demonstrated that chalcogenide alloys of the $\text{Te}_{48}\text{As}_{30}\text{Si}_{12}\text{Ge}_{10}$ system can be switched repeatedly between a high-conductivity state and a low-conductivity state. He also proposed a large number of possible solid-state memory device configurations based on phase change switching. However, a main drawback hindering the application of this material in memory devices is that it is characterized by long crystallization times, in the microsecond range, and requires rather large switching currents in the hundred milliamperere range [140]. Feinleib et al. were the first to describe laser-induced phase change in a $\text{Te}_{81}\text{Ge}_{15}\text{Sb}_2\text{S}_2$ alloy [141]. This is the basis of phase change optical storage, in which the difference in optical reflectivity between the amorphous phase and crystalline phase of PCMs is utilized to store the information. A laser is applied to write and read the data. However, also in this case, the crystallization time is still in the microsecond range, too slow for an efficient technological impact. In 1987, Yamada et al. discovered fast-switching materials on the pseudobinary line between GeTe and Sb_2Te_3 [142]. Figure 1.20 depicts the ternary phase diagram of different phase-change alloys starting from Ge, Te, and Sb, and their use in different optical storage devices, such as Blu-ray discs, phase-change rewritable discs, and phase-change dual discs.

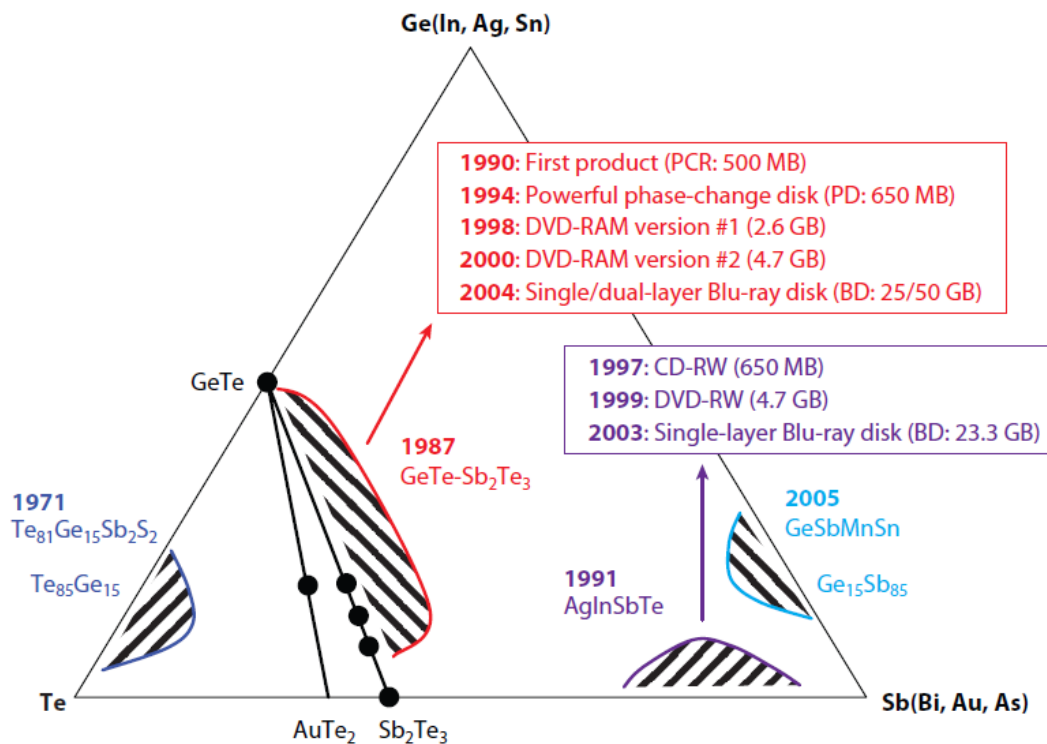


Figure 1.20. Ternary phase diagram depicting different phase change alloys, their year of discovery as a phase change alloy, and their use in different optical storage products, such as Blu-ray disc (BD); phase change rewritable disc (PCR); phase change dual disc (PD). Obtained from Ref. [138].

1.3.2 $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ van der Waals Materials

The most promising materials for the purposes mentioned above are the alloys along the GeTe-Sb₂Te₃ pseudo-binary line. More in detail, it has been demonstrated that the generation of superlattices, i.e., periodic structures composed of alternated GeTe and Sb₂Te₃ layers according to the formula $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ (GST), results in improved performance in terms of reduced switching energies with ultra-low energy consumption, enhanced write-erase cycle lifetimes, and faster switching speeds. The most studied GST materials include GeSb₄Te₇, GeSb₂Te₄, and Ge₂Sb₂Te₅ [143].

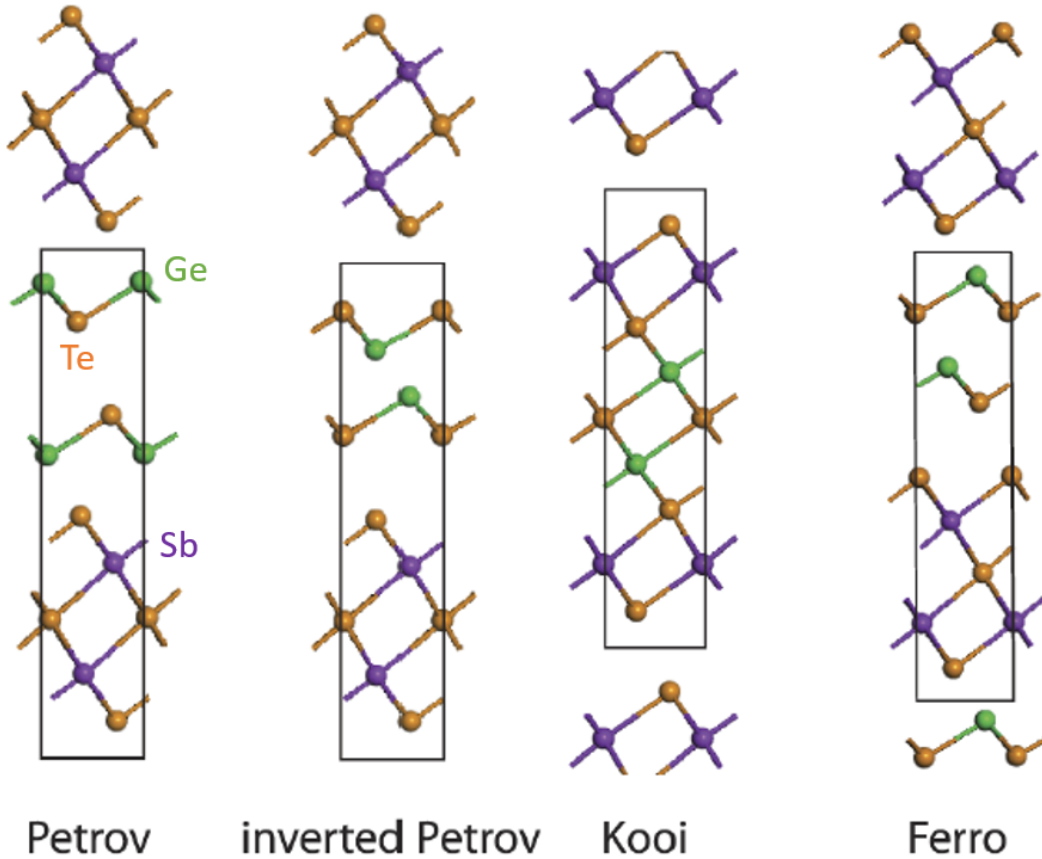


Figure 1.21. Possible stacking sequences for GeTe/Sb₂Te₃ superlattices: Petrov (P), inverted Petrov (iP), Kooi (K), and Ferro (F). Ge atoms are shown in green, Sb atoms in purple, and Te atoms in orange. Image obtained from Ref. [147].

Several theoretical predictions about the stacking order of the two compounds were made. In fact, GeTe is a 3D material with a rhombohedral structure [144, 145, 146] that can alternatively be viewed as a distorted rock-salt structure, characterized by three shorter and three longer bonds. Because of the pronounced difference between the shorter and longer bonds (2.83 vs 3.15 Å) and the accompanying bonding energy hierarchy, it can be considered as a quasi-2D structure made of GeTe buckled bilayers (BLs). As a consequence, GeTe usually cleaves along the [111] planes. Its quasi-2D nature suggested the possibility of growing heterostructures together with other 2D materials.

Within this class, Sb₂Te₃ is a promising candidate. In fact, it is a van der Waals material composed of quintuple layers, displaced along the c-axis, in the order Te-Sb-

Te-Sb-Te. However, the van der Waals surfaces of each quintuple layer are passive and prefer not to be bonded with the dangling bonds of GeTe [148]. Theoretically, four possible stacking sequences for GeTe/Sb₂Te₃ superlattices were proposed, reported in Figure 1.21: the Petrov (P) [$\cdots$ Te-Ge-Te-Sb-Te-Sb-Te-Ge-Te $\cdots$] phase, the Kooi (K) [$\cdots$ Te-Sb-Te-Ge-Te-Ge-Te-Sb-Te $\cdots$] phase (following the commonly used references to the different proposed structures for the bulk trigonal phases), the inverted Petrov (iP) [Ge-Te $\cdots$ Te-Sb-Te-Sb-Te $\cdots$ Te-Ge] phase, where the sequence of Ge and Te planes is inverted, and the ferro(electric) (F) phase [Te-Sb-Te-Sb-Te $\cdots$ Te-Ge-Te-Ge], where the ferroelectric structure of bulk GeTe was preserved [147].

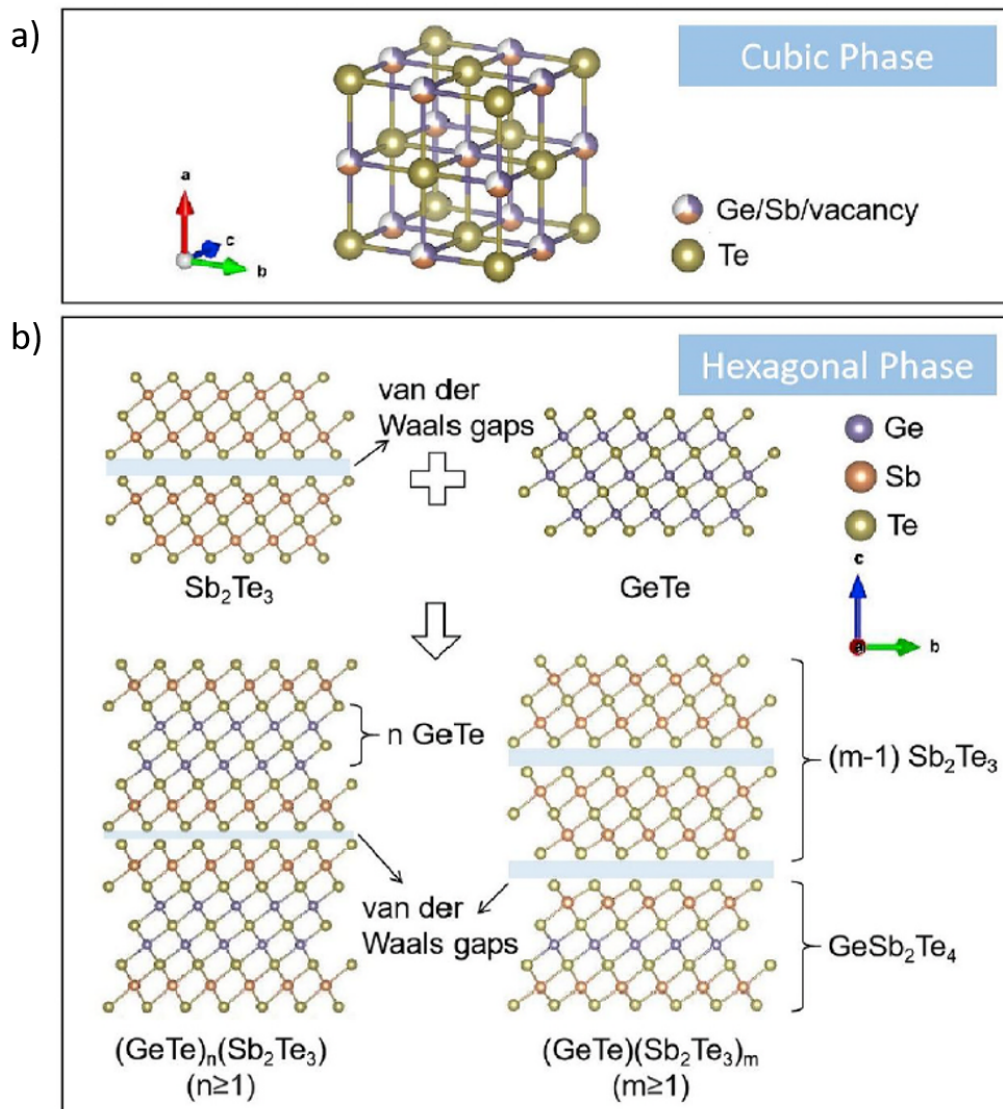


Figure 1.22. Crystal structure of metastable cubic GST (a), and stable hexagonal GST (b). Sb₂Te₃ and GeTe crystal structures are also shown in the case of the hexagonal phase GST. Obtained from Ref. [143].

In these notations, the ‘-’ sign denotes covalent bonds, whereas the ‘ $\cdots$ ’ sign corresponds to weaker vdW interaction between chalcogen atoms. The Kooi phase

better satisfies the bonding nature of GeTe and Sb_2Te_3 materials, since it presents GeTe BLs intercalated within the Sb_2Te_3 block, where the bonding is 3D, while the other models do not properly match the GeTe and Sb_2Te_3 bonding types. It was demonstrated that at 0 K the Kooi phase is the most stable. However, at elevated temperatures (above 180 °C), the iP- and F phases are energetically more favorable.

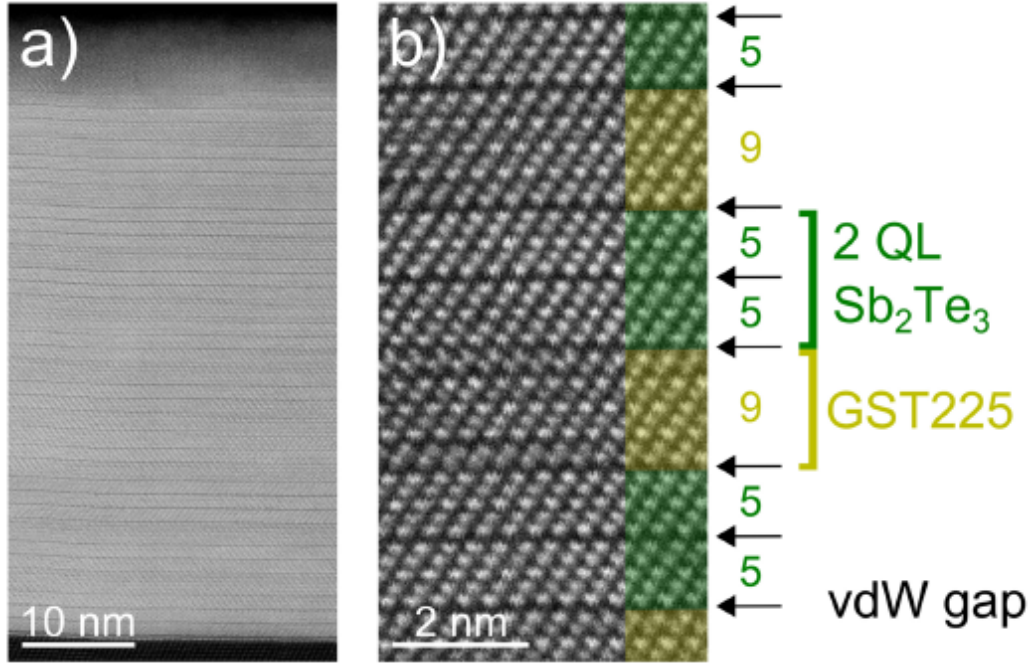


Figure 1.23. High-angle annular dark-field imaging scanning transmission electron microscopy (HAADF-STEM) cross-section images of a $10\times[\text{Sb}_2\text{Te}_3(2\text{ nm})/\text{GST}225(1.7\text{ nm})]/\text{Sb}_2\text{Te}_3(2\text{ nm})$ superlattice film grown via MBE on top of high-resistivity $\text{Si}(111)-\sqrt{3}\times\sqrt{3}\text{R}30^\circ\text{-Sb}$ passivated surfaces. The left image is an overview of the whole structure, whereas the right image is a high-resolution image, where 2 QLs of Sb_2Te_3 , each composed of five layers, are alternated with GST225 blocks, including nine layers. The dark horizontal lines identify van der Waals gaps. Image obtained from Ref. [150].

Experimentally, it was observed that room-temperature sputtering usually leads to amorphous GST films, therefore, annealing is necessary to obtain crystallization. Upon annealing, the most common phases for $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ with $n/m \leq 6$ are the metastable cubic and the hexagonal, as shown in Figure 1.22. The amorphous-to-cubic transition occurs at $\sim 420\text{ K}$, and the cubic-to-hexagonal at $\sim 600\text{ K}$. Once the hexagonal phase forms, it remains stable during steady heating and cooling. Panel (a) depicts the metastable cubic GST phase, exhibiting the NaCl rocksalt crystal structure, with Te occupying the anion sublattice and Ge/Sb/vacancies randomly occupying the cation sublattice. The transition from cubic phase to hexagonal phase can be viewed as the two-dimensional ordering of the cation vacancies with relaxation, which results in the formation of van der Waals gaps, as shown in panel (b). Thermodynamically stable hexagonal GST inherits the layered tetradymite structure of Sb_2Te_3 . Sb_2Te_3 slabs are enlarged by GeTe insertions in different ways depending on the ratio of n/m . $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)$ ($n \geq 1$) consists of identical Sb_2Te_3 slabs with n GeTe insertions, which are stacked along the c axis through van der Waals gaps. Each slab contains $(2n+5)$ layers due to every two layers introduced by one GeTe insertion. For $(\text{GeTe})(\text{Sb}_2\text{Te}_3)_m$ ($m \geq 1$), attributed to the limitation

of the GeTe-poor condition, GeTe can only be inserted into one of every m Sb_2Te_3 slabs. In summary, $(\text{GeTe})(\text{Sb}_2\text{Te}_3)_m$ consists of 5-layer Sb_2Te_3 slabs and 7-layer GeSb_2Te_4 slabs, with a ratio of $(m-1):1$ [148].

Therefore, it seems clear that the constituent materials in GST unintentionally intermix at the interfaces, forming alternating layers of Sb_2Te_3 and natural $\text{Ge}_x\text{Sb}_2\text{Te}_{3+x}$ blocks with 7-to 15-atomic layers randomly distributed along the growth direction [149]. This process is thermodynamically driven and is hard to control.

Experimentally, Cecchi et al. [150] managed to improve the structural quality of $\text{Sb}_2\text{Te}_3/\text{Ge}_x\text{Sb}_2\text{Te}_{3+x}$ van der Waals superlattices grown via MBE, where the GST is intentionally fabricated. In this way, they found a better structural quality compared to previously fabricated materials and improved the superlattice vertical ordering and interface sharpness. Figure 1.23 reports high-angle annular dark-field imaging scanning transmission electron microscopy (HAADF-STEM) cross-section images of a $10\times[\text{Sb}_2\text{Te}_3(2\text{ nm})/\text{GST225}(1.7\text{ nm})]/\text{Sb}_2\text{Te}_3(2\text{ nm})$ superlattice, where 2 QLs ($\sim 2\text{ nm}$) of Sb_2Te_3 are alternated with a $\sim 1.7\text{ nm}$ $\text{Ge}_2\text{Sb}_2\text{Te}_5$ block. The left image is obtained over a wider area, whereas the right image is a high-resolution image, showing the alternation between the two Sb_2Te_3 QLs, each composed of five layers, and the GST225 blocks, made up of nine layers. The black horizontal lines identify the van der Waals gaps.

In Chapter 3, the electrodynamic investigation of several GST layered alloy structures will be given, including $\text{Ge}_3\text{Sb}_2\text{Te}_6$ (GST326), $\text{Ge}_4\text{Sb}_2\text{Te}_7$ (GST427), $\text{Ge}_5\text{Sb}_2\text{Te}_8$ (GST528), and $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$ (GST10213) samples, together with a reference GeTe. A comparison with DFT calculations will also be provided.

Chapter 2

Experimental Setup and Data Analysis Procedure

In this Chapter, experimental setups and data analysis procedures used during this work are described. Different techniques were employed to accomplish the goals of this project, including standard material characterization via spectroscopic measurements in a broad spectral range, extending from Terahertz to Visible, material engineering via Electron Beam Litography, thermal emission investigation via measurements performed in the Infrared spectral range through a developed experimental setup, electromagnetic simulations performed to predict the optical response of engineered materials, the Molecular Beam Epitaxy technique, which was used to grow thin films, and Seebeck coefficient and resistivity measurements to study their transport and thermoelectric properties.

In the first part, the home-built experimental setup used to measure thermal emission intensity spectra from micro-structured materials, such as 3D graphene network structures and artificial SiC fractal metamaterials, is described, together with the finite element method used to perform electromagnetic simulations via the software COMSOL Multiphysics, used to predict the electromagnetic properties of the fractal systems.

Later, standard far-field spectroscopic interferometric techniques in the frequency domain, including Fourier Transform Infrared Spectroscopy (FTIR), are described. This technique was the core of this project and was used to characterize all of the materials presented in this work. Then, near-field spectroscopic techniques, such as scattering-type scanning near-field optical microscopy (s-SNOM) and Fourier transform infrared nanospectroscopy (nano-FTIR), are presented. These techniques were used to investigate the small spatial details (from 11.5 μm down to 430 nm) of SiC fractal metamaterials since they allow overcoming the diffraction-limited resolution of conventional FTIR spectroscopy.

A brief description of the Molecular Beam Epitaxy (MBE) technique, used to deposit thin-film topological insulators on sapphire, such as Bi_2Se_3 , Bi_2Te_3 , Sb_2Te_3 , and $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ alloys, is given. The "recipes" required to grow these materials are described, together with the Reflection High-Energy Electron Diffraction (RHEED) technique used to check their quality in situ. At last, the instruments to measure their Seebeck coefficient and resistivity are presented.

In the final part of the Chapter, models for data analysis are discussed, including the Drude-Lorentz model for extracting microscopic optical response functions and the analysis of blackbody-like intensity spectra obtained from thermal emission measurements.

2.1 Thermal Emission Measurements

Thermal emission measurements of 3D graphene samples, SiC, and SiC fractal metamaterials were performed under the same experimental conditions.

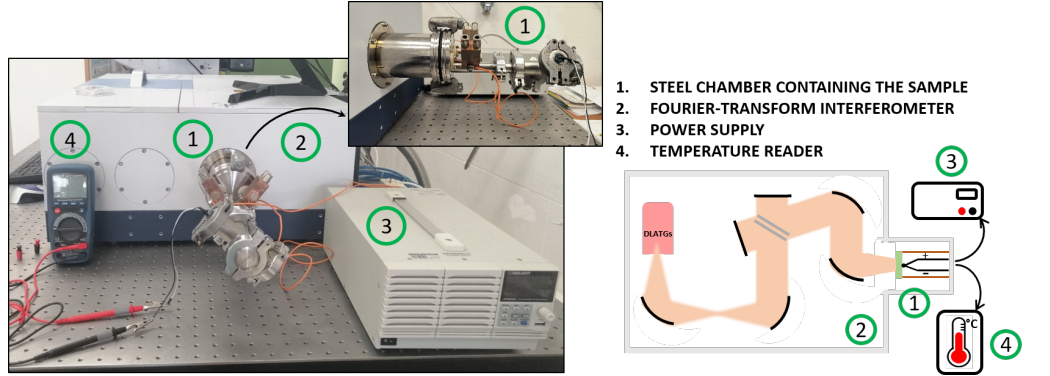


Figure 2.1. Experimental setup employed to acquire thermal radiation spectra of the investigated samples. The samples are clamped between two copper supports and suspended inside a steel cylindrical chamber (1), which is connected to one of the external ports of the Bruker Vertex 70V Fourier-transform interferometer (2). Copper wires connect the power supply (Siglent SPS5043X) (3) and the copper supports, allowing the heating of the sample. The temperature is monitored through a thermocouple (K type), placed in thermal contact with the sample surface, and a temperature reader (Holex 4733209917) (4) is employed to read it. Panel (b) shows a schematic view of the internal path of the Fourier-Transform interferometer. The thermal radiation emitted from the sample (green bar connected to the brown copper supports and to the thermocouple) is collected via a parabolic mirror, collimated, sent to the interferometer, and detected through a wide-range DLATGS detector.

A Bruker Vertex 70v Fourier-Transform interferometer (see Section 2.3.2 for further details), equipped with a Silicon beam splitter (the two gray oblique bars in the sketch on the right) and a wide-range DLATGS detector, was employed to acquire the black-body-like intensity spectra as a function of frequency, covering the IR spectral range from 30 cm^{-1} until 8000 cm^{-1} . Measurements were carried out under vacuum conditions. Fig. 2.1 shows a photo of the experimental setup and a sketch of the optical path of the emitted thermal radiation inside the interferometer. The samples under study, depicted in green, were clamped between two copper supports, shown in brown, and suspended inside a steel cylindrical chamber mounted in the focal plane of the Vertex 70v emission port. The chamber was then vacuum-sealed. Copper wires were used to connect a voltage generator (Siglent SPS5043X) and the copper supports, enabling the heating of the sample via the Joule effect. A K-type thermocouple was placed in thermal contact with the sample surface to obtain its equilibrium temperature. Temperatures ranging from $100 \text{ }^{\circ}\text{C}$ up to $650 \text{ }^{\circ}\text{C}$ were selected. The investigated sample and the reference were measured under the same experimental conditions. Each spectrum was averaged out 128 times, with a resolution of 4 cm^{-1} .

2.2 Electromagnetic Simulations

In order to predict the optical behavior of devices such as metamaterials, electromagnetic simulations are needed [151]. Indeed, the equations describing the physics

of complex metamaterials cannot be solved with analytical methods. An approximation to these equations can be constructed by using a discretization method, the *finite element method* (FEM) [152], in such a way that the obtained solution is an approximation of the real one. The degree of approximation depends on several parameters that will be briefly discussed here.

In this work, electromagnetic simulations were performed to predict the optical behavior of SiC fractal metamaterials; several attempts to optimize the lattice parameter and pillar dimensions were made before the fabrication process, since these parameters are important in determining the resonance modulation and position within the electromagnetic spectrum. For this purpose, the commercially available software COMSOL Multiphysics was used within the "Electromagnetic Waves, Frequency Domain" interface, in the Radio frequency module [153].

2.2.1 Finite Element Method in Frequency Domain Wave Electromagnetic Problems

Spectroscopic simulations in COMSOL can be done both in the time domain and in the frequency domain. In this work, the electromagnetic equations were solved in the frequency domain since the computational time is smaller. COMSOL discretizes the simulation space into modeling volumes, called elements, in which the electromagnetic field is achieved by means of the finite element method. Then all the single-element solutions are summed up with proper boundary conditions between one domain and the other. By combining Maxwell's equations in the presence of matter, and by assuming a sinusoidally varying field in time, at a known angular frequency $\omega = 2\pi f$, the governing frequency-domain form of Maxwell's equation in 3D is (see, for example, [154]):

$$\nabla \times (\tilde{\mu}_r^{-1} \nabla \times \mathbf{E}) - \frac{\omega^2}{c^2} \left(\tilde{\epsilon}_r - \frac{i\tilde{\sigma}}{\omega\epsilon_0} \right) \mathbf{E} = 0 \quad (2.1)$$

c , ϵ_0 , $\mathbf{E}$ being the speed of light in vacuum, the vacuum dielectric function, and the electric field. Additionally, $\tilde{\mu}_r$, $\tilde{\epsilon}_r$, and $\tilde{\sigma}$ are the complex relative permeability, relative dielectric function, and optical conductivity. These material properties can be inserted in the software as input quantities.

The above equation is solved for the electric field $\mathbf{E} = \mathbf{E}(x, y, z)$ in the "Electromagnetic Waves, Frequency Domain" interface available in the Radio Frequency module [153]. $\mathbf{E}$ is a vector with components E_x , E_y , E_z . All other quantities, such as magnetic fields, currents, and power flow can be derived from the electric field solution.

The finite element method can be summed up in four steps:

1. **Model Set-Up:** defining the equations to solve, creating the model geometry, defining the material properties, and setting up boundary conditions.
2. **Meshing:** discretizing the model space using finite elements.
3. **Solving:** solving a set of linear equations that describe the electric fields.
4. **Postprocessing:** extracting useful information from the computed electric fields.

A systematic description of these steps is beyond the scope of this thesis. In the following, a brief explanation of the postprocessing part is given to understand what kind of optical quantities can be simulated via COMSOL Multiphysics.

2.2.2 Postprocessing

Once the simulation has been performed, COMSOL allows for the extraction of useful information from the computed electromagnetic fields. For this work, the most interesting quantity is reflectance (R). Transmittance is not taken into account since the optical properties are simulated within the SiC Reststrahlen band, where transmittance is zero.

By default, the Radio Frequency module makes available the *Scattering parameters* (or S-parameters), typically used in the electromagnetic engineering field. S-parameters are complex-valued, frequency dependent quantities describing the behaviour of a linear electric N-port network upon the application of a steady state input [155]. They originate from transmission-line theory and are defined in terms of transmitted and reflected waves.

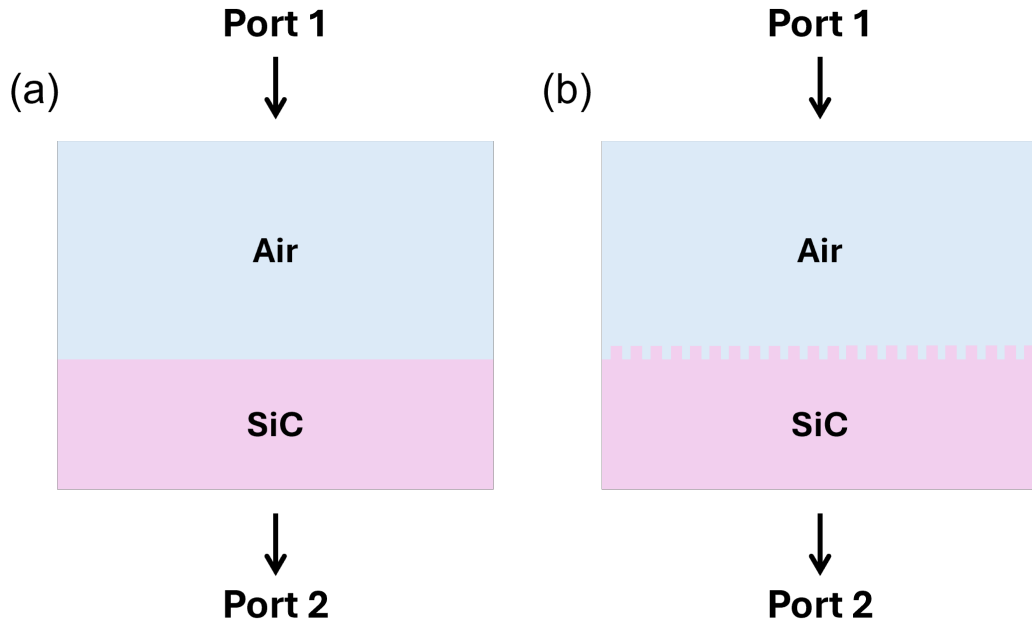


Figure 2.2. Schematics representing (a) SiC and (b) a first-order metamaterial unit cell cross section. The devices can be seen as two-port networks, with radiation entering port 1 and exiting through port 2.

Since our bare SiC sample and the corresponding SiC fractal metamaterials can be schematically represented as shown in Figure 2.2 (a) and (b), respectively, two-port networks are required. Through the *Scattering Matrix* (S-matrix) theory¹ the S-parameters for our metamaterials could be obtained [156]. In particular, S_{12} and S_{21} represent the transmission coefficients for waves incident on port 2 and transmitted to port 1 and vice versa. Referring to the configuration shown in Figure 2.2, at the end of our simulations, the S_{11} parameter was calculated to obtain the reflection coefficient.

These quantities can be related to the Fresnel's coefficients for reflection $\tilde{r}$ and transmission $\tilde{t}$ (see Section 2.7.1). At normal incidence, the following relations hold:

¹The Scattering Matrix relates the initial state and the final state of a physical system undergoing a scattering process.

$$\tilde{r} = S_{11} \quad (2.2)$$

$$\tilde{t} = \sqrt{\frac{n_1}{n_2}} S_{21} \quad (2.3)$$

where n_1 and n_2 are the refractive indexes of the two media at the interface. At last, to get the real quantities R and T , the square modulus of the Fresnel coefficients should be calculated:

$$R = |\tilde{r}|^2 = |S_{11}|^2 \quad (2.4)$$

$$T = |\tilde{t}|^2 = \left| \frac{n_1}{n_2} \right| |S_{21}|^2 \quad (2.5)$$

To resume, numerical simulations of the optical properties of the SiC fractal metamaterial arrays were performed through the software COMSOL Multiphysics via a finite-element method. The reflectance of the bare and patterned samples was simulated in the spectral range between 700 cm^{-1} and 1200 cm^{-1} , under an incident plane wave polarized along x , since the geometry is invariant upon 90° rotation. An infinite metamaterial array was simulated by drawing a single unit cell of period $a = 11.5 \text{ }\mu\text{m}$, adding pillars according to the Sierpinski carpet technique (see Chapter 3, Subsection 3.1.2 for further details), and applying periodic boundary conditions to it. More in detail, Floquet periodic conditions were used since they are suitable for frequency domain problems with a spatial periodicity of the geometry and solution [157]. Floquet conditions introduce a complex exponential term that accounts for the wave-like nature of the solution and the wave vector of the propagating wave. This allows for the efficient simulation of infinite, periodic systems by applying the conditions to a single unit cell and a fundamental wave vector, which simplifies the model and reduces computational cost [158]. These conditions are applied to parallel faces, and the wavenumber is user-defined. The phase shift between the fields on the parallel source and destination boundaries is defined as:

$$e^{-j\mathbf{k}_F \cdot (\mathbf{r}_{dst} - \mathbf{r}_{source})} \quad (2.6)$$

where $\mathbf{k}_F$ is the Floquet wave vector (the wave vector component tangential to the periodic port boundaries) and $\mathbf{r}_{dst}$ and $\mathbf{r}_{src}$ are the position vectors for the Floquet periodic condition destination and source boundaries, respectively.

The complex dielectric function and optical conductivity of the unpatterned sample, extrapolated from the RefFIT software (see Subsection 2.7.3), were used as input parameters. Maxwell's equations were solved inside all the elements, and electric field maps were extracted on the pillars' surface, i.e., in a condition close to the near-field regime, to understand the electromagnetic nature of the obtained PhP resonances.

2.3 Far-Field Spectroscopic Measurements

Spectroscopy is the investigation of matter through its interaction with a probe [154]. By analyzing the effects of the interaction on the probe, it is possible to gain information on the examined matter, the target. Several probe sources with different energies can be chosen, such as photons, neutrons, and electrons, and can provide information about a wide variety of properties of the sample. During this work, the selected probe source was electromagnetic radiation, ranging from Terahertz (40 cm^{-1}) to Visible (20000 cm^{-1}) frequencies. This broad frequency range could be explored thanks to the use of several spectroscopic techniques and devices.

2.3.1 Frequency Domain Spectroscopy

Investigation of the electrodynamic response as a function of frequency can be carried out straightforwardly by applying radiation and measuring macroscopic optical response functions: absorbance, reflectance, and transmittance. The further step consists of manipulating these data to extract the microscopic optical response functions, through which the material properties can be described: complex dielectric function $\tilde{\epsilon}$, refractive index $\tilde{n}$, and optical conductivity $\tilde{\sigma}$.

In the frequency domain, the electromagnetic source should have a low power, in such a way that the material response is linear in the applied electric field. The fulfillment of this condition ensures that the obtained properties can be attributed to the unperturbed system [159].

Generally, a spectrometer is exploited to perform the measurements, and its working principle can be based on two different techniques:

- *dispersive technique*, in which a diffraction grating is employed to select the required frequency. Combined with suitable detectors, the relative amount of radiation at each frequency is then recorded;
- *interferometric technique*, in which an interferometer is employed to record the intensity as a function of the path difference between the two arms of the device, and is later transformed into the spectrum through an appropriate mathematical procedure, the Fourier Transform.

In this work, considering the probed spectral range, extending from 40 cm^{-1} to 20000 cm^{-1} , only the interferometric technique was employed.

2.3.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) [160, 161, 162] is a powerful technique allowing the measurement of reflectance and transmittance. By regulating the optical path difference between the arms of an interferometer, a pattern of temporally and spatially varying light intensity, named *interferogram*, can be produced. By performing the Fourier transform of the interferogram, the spectrum is obtained. Among the available interferometers, the Michelson is the most widely used [163]. Its schematic is shown in Figure 2.3. Briefly, the electromagnetic radiation emitted by the source is split into two equal beams by a beamsplitter, since it reflects 50% of the radiation and transmits the other 50%. The two beams are sent to two different mirrors: a fixed mirror, at a distance L from the beamsplitter (1), and a movable mirror at a distance $L + \delta/2$ from the beamsplitter (2). The latter one can either be moved back and forth at a constant velocity (in a continuous scan interferometer) or

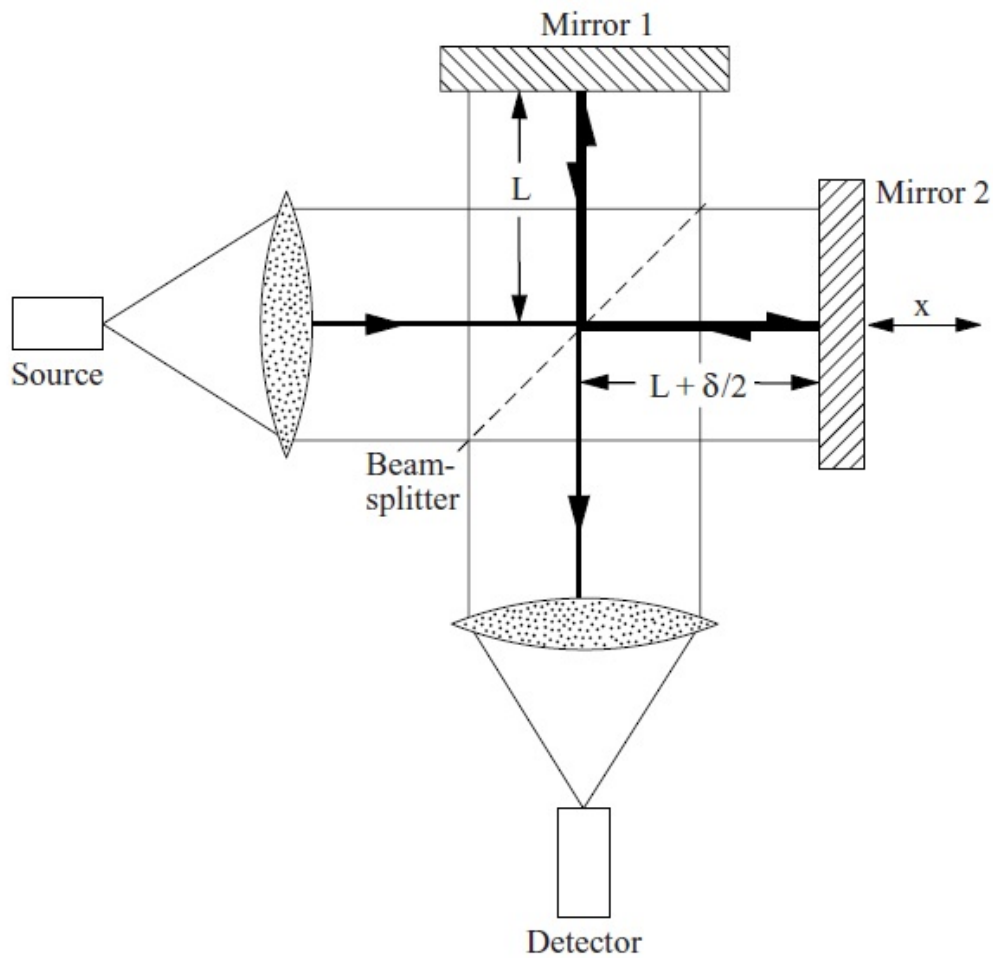


Figure 2.3. Basic outline of a Michelson interferometer displaying source, beam-splitter, mirror 1 (fixed), mirror 2 (movable), detector. The path difference between the two arms is δ . Image obtained from Ref. [154]

be held at equally spaced points for fixed short periods and stepped rapidly between these points (in a step-scan interferometer).

After being reflected by the two mirrors, the beams are again recombined through the beamsplitter and reach the detector. If the path difference between the two arms, δ , is smaller than $c\tau_0$, where τ_0 is the coherence time of the source, the recombination generates an interference pattern. When δ is equal to $n\lambda$, where n is an integer, constructive interference occurs; on the other hand, when δ is equal to $(2n + 1)\lambda/2$, destructive interference occurs. Hence, the instrument measures $I(\delta)$, that is, the intensity of the recombined beams as a function of optical path difference. The relation that links $I(\delta)$ and the spectrum $B(\nu)$ can be obtained by starting from the expression of the electric field at the beamsplitter [154]:

$$E(x, \nu)d\nu = E_0(\nu)e^{i(2\pi x\nu - \omega t)}d\nu \quad (2.7)$$

where $\nu = 1/\lambda = \omega/2\pi c$ is the wavenumber of the radiation. Since each of the two beams has undergone one reflection and one transmission at the beamsplitter, their amplitudes can be considered to be equal. Now we can write the reconstructed field, considering that one beam travels a distance $2L$ to the fixed mirror and the other $2L + \delta$:

$$E_R(\delta, \nu)d\nu = |\tilde{r}\tilde{t}|E_0(\nu)[e^{i(4\pi\nu L - \omega t)} + e^{i[2\pi\nu(2L + \delta) - \omega t]}]d\nu \quad (2.8)$$

where $\tilde{r}$ and $\tilde{t}$ are the complex reflection and transmission Fresnel coefficients of the beamsplitter (see Subsection 2.7.1). To get the intensity, the square modulus of the reconstructed electric field should be computed, so that:

$$I(\delta, \nu)d\nu \propto E_0^2(\nu)[1 + \cos(2\pi\nu\delta)]d\nu \quad (2.9)$$

By integrating the last equation, and by isolating just the modulated part (the

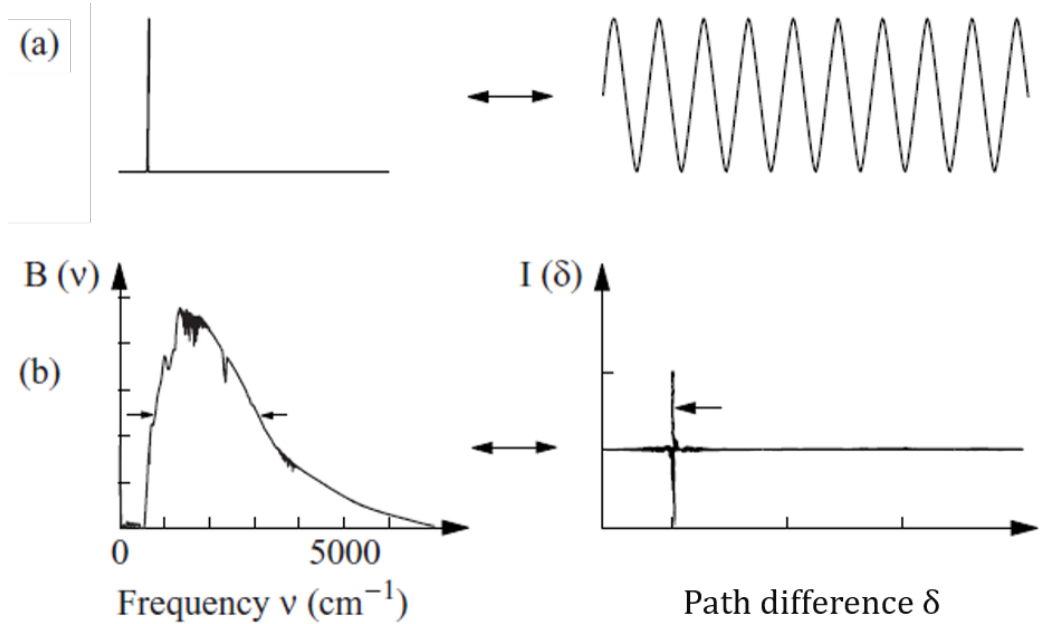


Figure 2.4. Spectrum $B(\nu)$ and its corresponding Fourier transform for (a) monochromatic light and (b) typical source in the mid-Infrared spectral range. Image obtained from Ref. [154].

cosine term), the interferogram expression can be retrieved:

$$\left[I(\delta) - \frac{I(0)}{2} \right] \propto \int_0^\infty E_0^2(\nu) \cos(2\pi\nu\delta) d\nu \quad (2.10)$$

where, for a broadband source, the intensity at infinite path difference $I(\infty)$ corresponds to the average intensity of the incoherent radiation, which is exactly half the intensity obtained at equal paths: $I(\infty) = I(0)/2$. At last, to obtain the power spectrum $B(\nu) \approx E_0^2(\nu)$, the inverse Fourier transform can be performed:

$$B(\nu) \propto \int_0^\infty \left[I(\delta) - \frac{I(0)}{2} \right] \cos(2\pi\nu\delta) d\delta \quad (2.11)$$

In Figure 2.4, two different examples of spectra and their relative interferograms are shown. The first corresponds to monochromatic light, exhibiting a Dirac-like delta spectrum and a sinusoidal interferogram, whereas the second corresponds to the spectrum of a typical source in the Infrared spectral range, containing more frequencies, whose interferogram exhibits some oscillations but has a more complex interference pattern due to the superposition of many different frequencies [164].

The integral in Equation 2.11 is infinite, but the interferogram is only measured over a finite mirror displacement $(\delta/2) \leq (\delta_{max}/2)$. As a consequence, a truncation effect arises, which in the specific case of a monochromatic source mainly results in a broadening of the spectral lineshape and additional oscillations. This effect can be mitigated by multiplying the interferogram by a function, named *apodizing function*. Truncating the interferogram also results in a limitation of the spectral resolution to $\Delta\nu = 1/\delta_{max}$. Moreover, it is important to stress that the spectrometer sampling is discrete and not continuous, so the Discrete Fourier Transform (DFT) is used to calculate the spectrum. A direct consequence of the discretization is a phenomenon known as *aliasing*, which consists of the replication of the original spectrum and its mirror image on the frequency and time axis [165]. For the Nyquist criterion, if any waveform that is a sinusoidal function of time or distance is sampled with a sampling frequency or wavenumber greater than or equal to twice the bandpass of the system, there is no loss of information [166]. If the Nyquist condition is not satisfied, the aliasing phenomenon arises, and the obtained power spectrum shows periodicity in the frequency and time domains.

The **Bruker-VERTEX 70v** spectrometer was used to collect transmittance and reflectance spectra on one side and thermal emission spectra on the other, in the Infrared spectral region, from 30 to 8000 cm^{-1} [167]. The instrument's working principle is based on the FTIR technique. The spectrometer is made up of five different compartments: the electronics, the detector, the interferometer, the sample, and the control compartments for the direction of the beam, as shown in the sketch of Figure 2.5.

Two sources are simultaneously installed inside the VERTEX 70v and can be exchanged: a medium-infrared (MIR) and a near-infrared (NIR-VIS) source, covering the mid-infrared and near-infrared-visible spectral ranges. The MIR source is a Globar, i.e., a sintered Silicon Carbide rod that is heated and emits mid-infrared light. Its behaviour corresponds approximately to that of a black body. The NIR-VIS source, instead, is a halogen lamp embedded inside a quartz protection. Concerning the optical path, after the light beam is generated, it goes through an aperture wheel, is reflected by a mirror, and then it enters the interferometer, which is a high-stability Michelson interferometer with rock-solid permanent alignment [168]. Compared to standard Michelson interferometers, this configuration allows eliminating mirror tilts and improves the stability of the system.

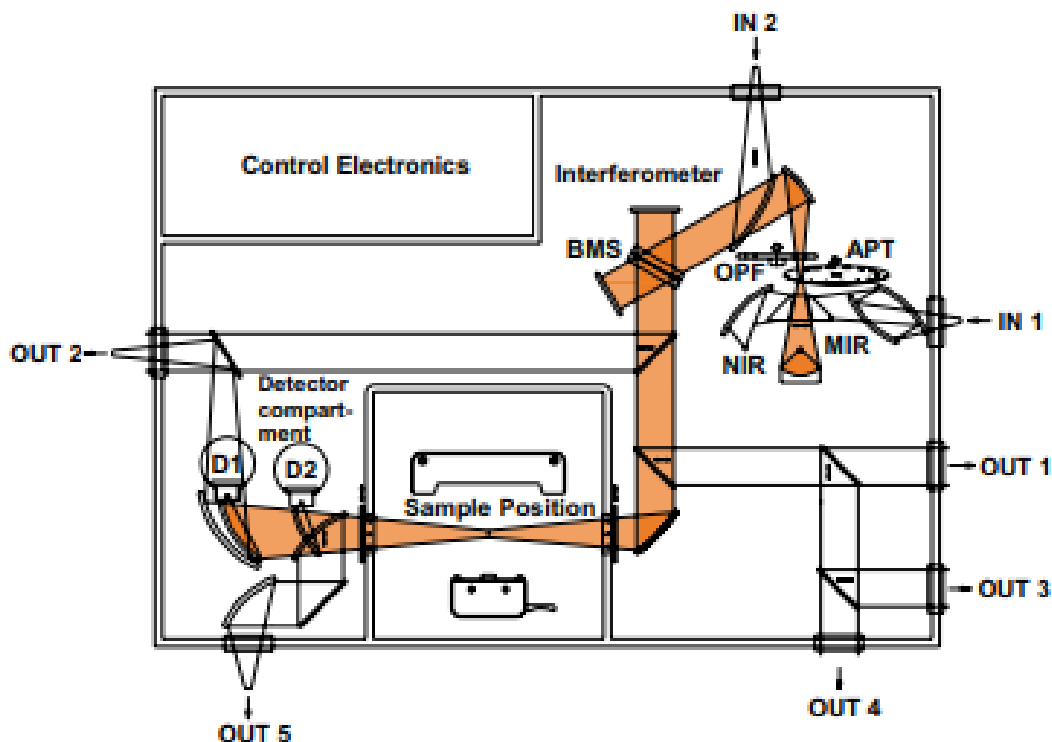


Figure 2.5. Internal structure and optical path of the Vertex 70v FTIR spectrometer [167].

The spectrometer is equipped with a HeNe laser that emits red light with a wavelength of 632.8 nm to control the position of the moving interferometer mirror (also called "scanner") and is used to determine the data sampling positions. After being reflected by another mirror, the light beam goes through the sample compartment and then reaches the detector. The standard one (D1 in Figure 2.5) is a pyroelectric DLaTGS detector which covers a spectral range from 30 to 8000 cm^{-1} . The spectrometer is equipped with a dry vacuum pump, which provides a vacuum level of less than 0.2 hPa (mbar), which helps to remove water vapor and carbon dioxide spectral features present in the Infrared spectral window.

The VERTEX 70v is coupled to a **Bruker-Hyperion-2000** microscope, which can work in the spectral region from far-infrared to Visible in both reflection and transmission modes. The system is equipped with a Cassegrain 15x objective, featuring an illumination angle of 30° and a numerical aperture (NA) of 0.4. For this thesis work, the microscope was used in reflection mode in the region between 400 and 20000 cm^{-1} . The lower frequency limit is constrained by a KBr window connecting the VERTEX 70 V and the microscope, which is not transparent below this frequency range. The microscope allows collecting the reflected/transmitted radiation up to a $270 \times 270\text{ }\mu\text{m}^2$ spatial area. Concerning the detectors, the microscope uses a Mercurium Cadmium Telluride (MCT) liquid nitrogen-cooled detector in the Infrared spectral range, and a Silicon detector for the Visible. The optical beam path of the microscope is shown in Figure 2.6. Two visible lamps, whose light shines from the bottom or the top in the transmittance or reflectance modes, respectively, are used to focus the sample deposited on the sample stage, between properly aligned condenser and objective.

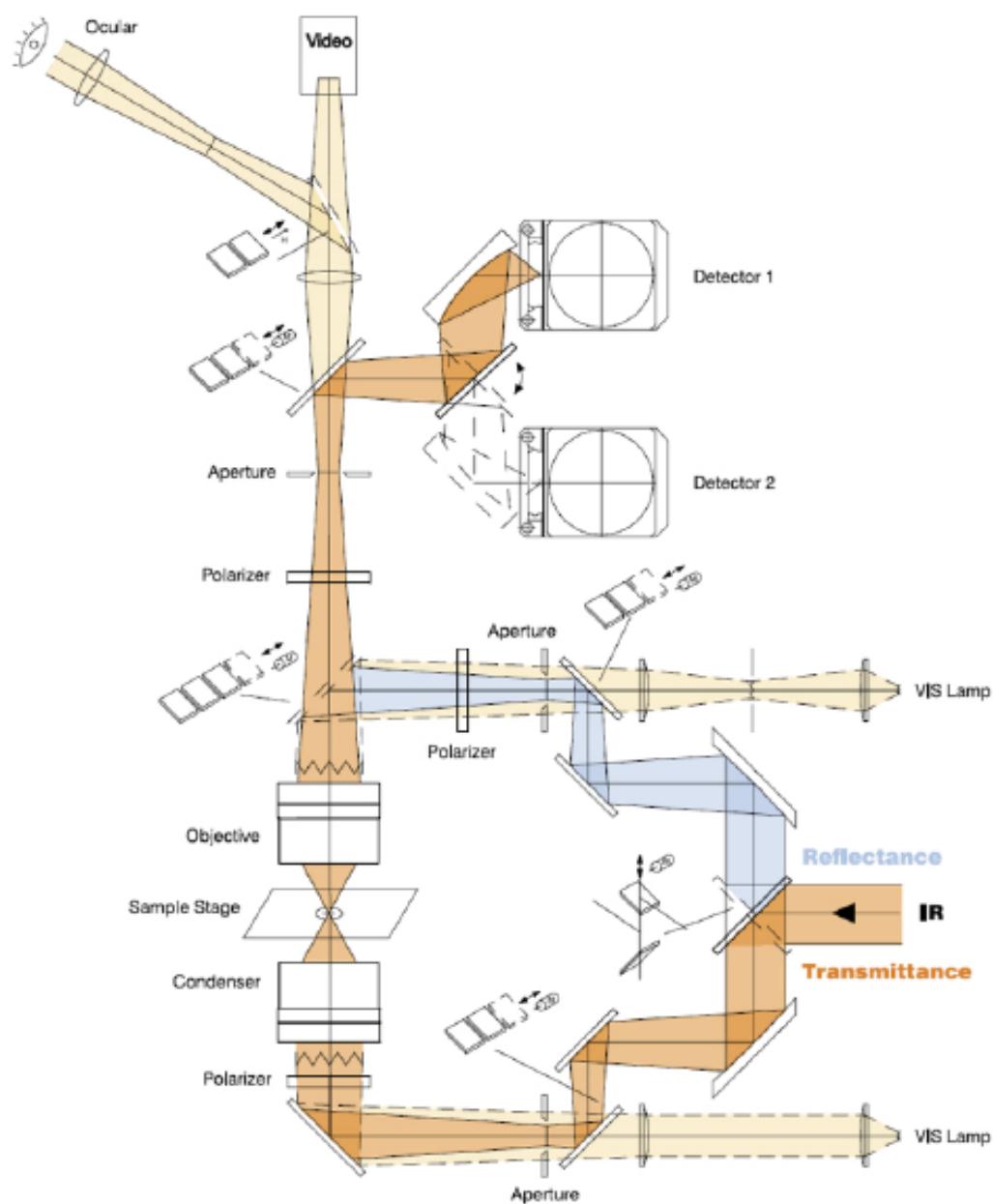


Figure 2.6. Optical beam-path of Hyperion microscope. The instrument was used for reflection measurements from 350 to 8000 cm^{-1} .

Then, the visible light coming from light bulbs is switched off, and the Infrared-Visible light coming from MIR and NIR sources in the VERTEX 70 V is used to perform the measurements. The microscope is equipped with special slits that allow for the collection of the reflected/transmitted intensity coming from a spatial area smaller than $270 \times 270 \mu\text{m}^2$. This equipment was used to acquire measurements for the SiC fractal metamaterials, enabling the collection of the reflected radiation coming from only the bare or patterned areas, respectively.

2.4 Near-Field Spectroscopic Measurements

Considering the spatial dimension of SiC fractal metamaterials, reaching scales down to 430 nm, near-field spectroscopic measurements were acquired to overcome the diffraction-limited resolution of conventional FTIR spectroscopy and capture the optical behavior of evanescent waves [169]. Two different instruments based on near-field techniques were used: scattering-type scanning near-field optical microscopy (s-SNOM) [170] and Fourier transform infrared nanospectroscopy (nano-FTIR) [171], from Neaspec GmbH, Germany. The first allowed the acquisition of infrared images with nanoscale (down to 20 nm) spatial resolution by recording the monochromatic infrared light scattered at a scanning probe metallic tip, whereas the second allowed the acquisition of infrared spectra with the same spatial resolution by illuminating the tip with broadband infrared radiation.

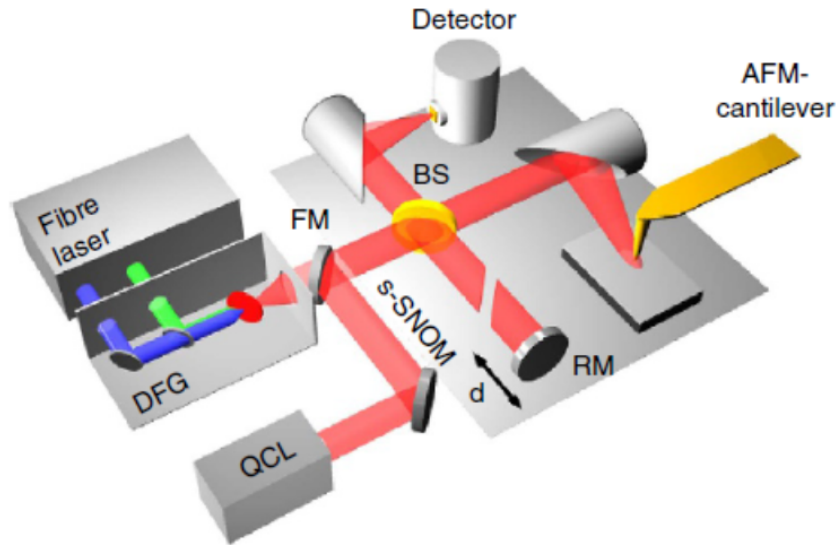


Figure 2.7. s-SNOM and nano-FTIR setups employing a tunable quantum cascade laser (QCL) or a mid-infrared continuum source, composed of a fiber laser and a difference frequency generator (DFG), for illuminating the atomic force microscopy (AFM) gold-coated tip, respectively. The different illuminations can be selected through a flip mirror (FM). The radiation backscattered from the tip is analysed with a Michelson interferometer, which includes a ZnSe uncoated beam splitter (BS), a movable reference mirror (RM), and a Mercury Cadmium Telluride (MCT) detector, operated either in a pseudoheterodyne mode, for s-SNOM, or as a Fourier transform spectrometer, for nano-FTIR spectroscopy. Obtained from Ref. [172].

The key to the wavelength-independent resolution of this technique is the optical field enhancement at the apex of the sharp, laser-illuminated tip scanning the sample

surface. The enhanced field is confined to the tip apex on the scale of its curvature radius, around 20 nm. The tip polarizes the sample, which in turn acts back on the tip, leading to a near-field interaction specific to the sample material. Depending on the sample, different amounts of elastic and inelastic light scattering may result from this interaction. The scattering cross section is thereby much larger for the elastic than for the inelastic scattering. A drawback of this technique consists of a large elastic scattering background originating from the tip shaft and sample, which contains no useful information or artifacts in s-SNOM images. Special background suppression methods are therefore required to extract the scattering contribution arising from the pure near-field interaction between the tip and sample. In this case, a pseudoheterodyne technique is employed, where the reference wave of the s-SNOM signal is modulated by a sinusoidal phase modulation [173]. This solution offers the advantage of requiring only one beam splitter and a mirror in a Michelson interferometer configuration, as shown in Figure 2.7, which oscillates at frequencies mM , with M an integer, belonging to the kilohertz spectral range. If the reference modulation frequency M is lower than the tip vibration frequency Ω , each of the scattered signal harmonics with frequencies $n\Omega$, $n > 0$, splits into sidebands with frequencies $n\Omega + mM$, the latter terms not containing the background signal (see Figure 2.8).

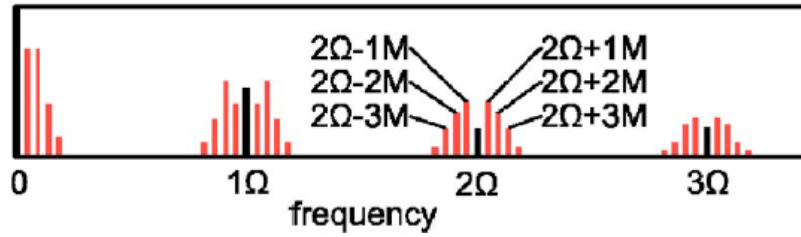


Figure 2.8. Sketch depicting the scattered signal spectrum at various harmonics of the tip vibration frequency Ω , together with sidebands at $n\Omega + mM$ surrounding each $n\Omega$. Image obtained from Ref. [173].

2.4.1 Scattering-type scanning near-field optical microscopy (s-SNOM)

The s-SNOM is based on an Atomic Force Microscopy (AFM) in which a Pt-Iridium coated Silicon tip (PPP-NCSTAu, Nanosensors) oscillates vertically at the mechanical resonance frequency $\Omega \sim 250$ kHz of the cantilever, with an amplitude of ~ 40 nm. As shown in Figure 2.7, the tip is illuminated by radiation from a tunable quantum cascade laser (QCL), which spans the $4.5 - 15 \mu\text{m}$ spectral range, at two individual frequencies, in (910 cm^{-1}) and out of (1200 cm^{-1}) resonance conditions for this work. An asymmetric Michelson interferometer is used to analyze the tip-scattered radiation, and the undesired far-field reflected background signal is removed thanks to a signal demodulation at a higher harmonic of the tip tapping frequency, $n\Omega$. In this way, both amplitude s_n and phase ϕ_n images of the near-field scattered field can be detected simultaneously. In this work, images were recorded under resonance and out-of-resonance conditions, with an integration time of 10 ms per pixel.

2.4.2 Fourier transform infrared nanospectroscopy (nano-FTIR)

For nano-FTIR, the tip is illuminated with a coherent mid-infrared broadband laser of approximately 100 μW total power. This beam is generated by a difference frequency generator (Lasnix, Germany), where two near-infrared, 100-fs pulse trains from a fibre-laser system (FemtoFiber pro IR and SCIR, Toptica Germany) are superimposed in a GaSe crystal, as shown in Figure 2.7. This mid-infrared source emits a continuous spectrum which can be tuned from 670 cm^{-1} to 2220 cm^{-1} . FTIR spectroscopy of the light scattered by the tip is performed by recording the demodulated detector signal I as a function of the reference mirror position d . Due to the asymmetry of the interferometer, for which the sample is located in one interferometer arm, the Fourier transformation of the interferogram $I(d)$ subsequently yields the near-field amplitude and phase spectra. In all presented nano-FTIR spectra, the demodulation order was $n = 2$. Interferograms of the samples were recorded with an acquisition time of 10 ms. Subsequent Fourier transformation of the averaged interferograms yields the complex-valued near-field spectra demodulated at a given order n , $E_{n,\text{sample}}(\omega) = s_{n,\text{sample}}(\omega)e^{i\phi_{n,\text{sample}}(\omega)}$ [172], where $s_n(\omega)$ and $\phi_n(\omega)$ are the local amplitude and phase spectra at a given order n , respectively. These spectra were normalized to the references obtained from a Silicon sample, $E_{n,\text{ref}}(\omega) = s_{n,\text{ref}}(\omega)e^{i\phi_{n,\text{ref}}(\omega)}$. Therefore, the normalized amplitude and phase spectra at a given order n can be obtained from the following equation [172]:

$$\frac{E_{n,\text{sample}}(\omega)}{E_{n,\text{ref}}(\omega)} = \frac{s_{n,\text{sample}}(\omega)}{s_{n,\text{ref}}(\omega)} e^{i(\phi_{n,\text{sample}}(\omega) - \phi_{n,\text{ref}}(\omega))} \quad (2.12)$$

and the near-field scattered intensity is obtained from:

$$I = \left| \frac{E_{n,\text{sample}}(\omega)}{E_{n,\text{ref}}(\omega)} \right|^2 = \left(\frac{s_{n,\text{sample}}(\omega)}{s_{n,\text{ref}}(\omega)} \right)^2 \quad (2.13)$$

2.5 Molecular Beam Epitaxy (MBE)

To deposit thin 2D topological insulator films on top of a 10 x 10 x 0.5 mm^{-3} Sapphire ($\text{Al}_2\text{O}_3(0001)$) substrate, the Molecular Beam Epitaxy (MBE) technique was used in Professor Seongshik Oh's laboratory, at Rutgers University, New Jersey, USA. Molecular beam epitaxy is a physical vapor deposition technique in which single-element thermal sources can be evaporated individually or simultaneously onto a substrate with a specific crystal orientation, allowing the arrangement of a new crystal on top of it [174, 175]. Since the topological insulators grown in this work naturally grow on axis (along c axis), terminating with a hexagonal surface, Sapphire is cut in such a way that it terminates along the (0001) surface, which is hexagonal, too. This thermal evaporation process is highly controllable, gentle, and reproducible, allowing for the control of ratios and rates of each element by simply adjusting the cell temperature to obtain the correct stoichiometry [176]. A clean and fresh substrate is necessary to succeed; thus, an ultra-high vacuum (UHV), with a pressure of around 10^{-10} Torr, is required to prevent substrate contamination from particles in atmospheric pressure and film contamination, as well as to reduce atom-to-atom scattering, enabling line-of-sight evaporation. Indeed, all kinds of adsorbed particles, from the strongly chemisorbed to the weakly physisorbed, form an adlayer on the topmost atomic layers of the substrate. This contamination adlayer, whose chemical composition and geometrical structure are not well defined,

hinders the controlled adsorption of single and pure selected species. To achieve such a level of vacuum, different pumps are employed, such as scroll, turbomolecular, and cryogenic pumps.

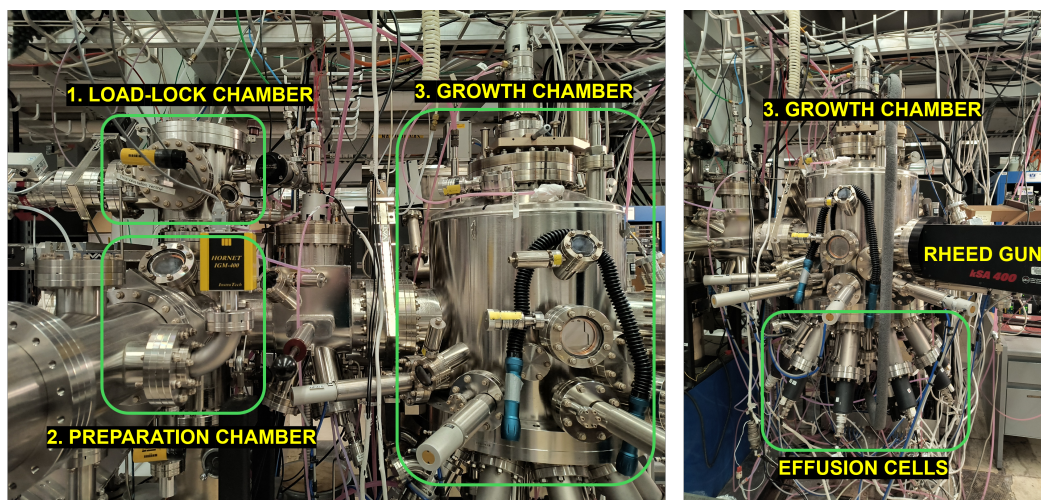


Figure 2.9. Molecular Beam Epitaxy system used at Rutgers University, New Jersey, USA. The system is composed of three chambers: load-lock (1), which is vented to atmospheric pressure to remove and load the substrates, preparation chamber (2), which is a middle chamber where substrates are transferred, and growth chamber (3), where the film deposition is performed in UHV conditions. The image on the right better shows the growth chamber, where the substrate is flipped upside down and the pure evaporated elements, such as Bi, Se, Te, and Sb, are evaporated from the effusion cells. The Reflection High-Energy Electron Diffraction (RHEED) gun is also shown.

Figure 2.9 shows the MBE machine used at Rutgers University [177]. The entire MBE system consists of three individual vacuum chambers to maintain UHV conditions in the last and main chamber, namely, the growth chamber: the load-lock (1), preparation (2), and growth (3) chambers. The load-lock chamber is where the substrates are loaded and removed from the MBE system, and is the only chamber that is regularly opened to the atmosphere. It is pumped by a turbo that is supported by an oil-free scroll or diaphragm pump, allowing the chamber pressures to range from atmospheric pressure (10^3 Torr) to 10^{-6} Torr. Vertically, below the load-lock chamber, there is the preparation chamber, where the substrate holders, loaded into a cassette, are staged for transfer into the growth chamber. Both the preparation and growth chambers are pumped by cryogenic pumps, having base pressures of $\sim 10^{-9}$ Torr and $\sim 10^{-10}$ Torr, respectively; the higher pressure of the preparation chamber is due to its exposure to the lower vacuum of the load-lock during transfer. Molybdenum metal plates are employed as substrate holders thanks to their resistance to high temperatures. Elements with a 99.999 % purity, commercially available, are loaded into the effusion cells and located in the lower part of the growth chamber, as shown in the left image of Figure 2.9, pointing towards the direction where the substrate holder will be placed, with the substrate flipped upside down. The cell temperature is set depending on the vapor pressure of the specific element: the higher the vapor pressure, the lower the temperature necessary to have a sufficient element flux, and thus, a significant deposition onto the substrate. For example, the cell temperatures for Bi, Se, Te, and Sb used for this work are 547 °C, 170 °C, 292 °C, and 342 °C, respectively.

2.5.1 Film Recipes

Different temperatures were selected for the substrate and sources, such as Bi, Se, Te, Sb, and different growth rates, too. All the films, including Bi_2Se_3 , Bi_2Te_3 , Sb_2Te_3 , and $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ alloys, were grown in excess of the anion, being Se and Te, respectively. Before mounting the sample in the growth chamber, the substrate was exposed to an ex situ UV ozone cleaning step to burn off the majority of the organic compounds that may be present on its surface. To further remove any possible contaminants from the substrate surface, Sapphire was heated in the growth chamber to 750 °C for 20 minutes, adding oxygen at 350 °C under a pressure of 5×10^{-7} Torr.

10, 20, 30, 50, 100 quintuple layers (QL, where 1 QL $\sim$ 1 nm) thick Bi_2Se_3 films were deposited, to study how the different thicknesses allow the interplay between surface and bulk transport channels. A two-temperature step scheme, already developed at Professor Oh's laboratory, was employed, and was developed in the following steps:

- growth of the first 3 Bi_2Se_3 QLs at 140 °C, setting the source temperatures of Bi and Se at 547 °C and 170 °C, respectively, ensuring the correct flux, and, thus, the correct film stoichiometry;
- growth of the remaining QLs after a slow annealing process at 300 °C, which helped further crystallization of the film;
- deposition of a 20-nm Se capping on top of the films during the cooling process, at 45 °C, to prevent film oxidation.

During the whole process, the Se shutter was left open to grow the films in excess of Se, which easily evaporates.

Bi_2Te_3 , Sb_2Te_3 , and $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ films were instead deposited on sapphire with a thickness of 20 QL. This kind of study aims at moving the Fermi level position from the conduction (Bi_2Te_3) to the valence (Sb_2Te_3) band, changing the Seebeck coefficient value and sign, and affecting the whole thermoelectric figure of merit. For these materials, the growth procedure can be summarized as follows:

- during the annealing of the substrate under oxygen pressure, growth of one unit cell of Cr_2O_3 at 720 °C on top of the substrate to help the sticking of Te on the substrate surface;
- growth of 20 QLs of the film at 260 °C, with source temperatures of 547 °C (Bi), 292 °C (Te), and 342 °C (Sb), respectively.

Three $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ alloys were grown with 20 %, 25 %, and 30 % Bi content to explore the behavior of the Seebeck coefficient for bipolar systems, i.e., systems having both electron and hole carrier types. Also these films were grown in excess of Te. The crystalline quality of all the films was monitored in situ via Reflection High Energy Electron Diffraction (RHEED), described in the next Subsection.

Knowing the lattice parameter of Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 a priori, and measuring the element flux, i.e., the number of atoms deposited per unit of time and area for each element, it is possible to calculate the deposition rate for 1 QL of the corresponding compound. Since the lattice parameters are $a_{\text{Bi}_2\text{Se}_3}=4.14$ Å, $a_{\text{Bi}_2\text{Te}_3}=4.39$ Å, and $a_{\text{Sb}_2\text{Te}_3}=4.26$ Å, it was found to be around 70 s/QL, 60 s/QL, and 128 s/QL for Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 , respectively.

2.5.2 Reflection High-Energy Electron Diffraction (RHEED)

The crystal structure and quality of thin 2D topological insulator films were examined in situ and in real-time using the Reflection High-Energy Electron Diffraction (RHEED) technique [178, 179, 180]. In this setup, the electron beam is sent to the sample surface in grazing angle conditions, around 1° , and the beam energy is set equal to 10 keV. After the beam diffracts off the sample, it is elastically scattered towards a phosphorus screen, giving rise to Bragg spots (3D case) or streaks (2D case), and imaged by a CCD camera. The surface sensitivity of this technique is due to the universal electron mean free path behavior as a function of energy [181]. Indeed, this path is nearly material-independent and has its minimum of $\sim 6 \text{ \AA}$ at $\sim 50 \text{ eV}$, as shown in Figure 2.10 (a). Considering an incident angle of 1° , the electron beam kinetic energy in the direction perpendicular to the sample surface is around $E \sim E_0 \cdot \sin^2(\theta) \sim 10 \text{ keV} \cdot \sin^2(1^\circ) \sim 100 \text{ eV}$, which corresponds to a short mean free path, around $10 \text{ \AA}$, while the electron beam kinetic energy in the direction parallel to the sample surface is around $E \sim E_0 \cdot \cos^2(\theta) \sim 10 \text{ keV} \cdot \cos^2(89^\circ) \sim 10 \text{ keV}$, which corresponds to a mean free path larger than $100 \text{ \AA}$.

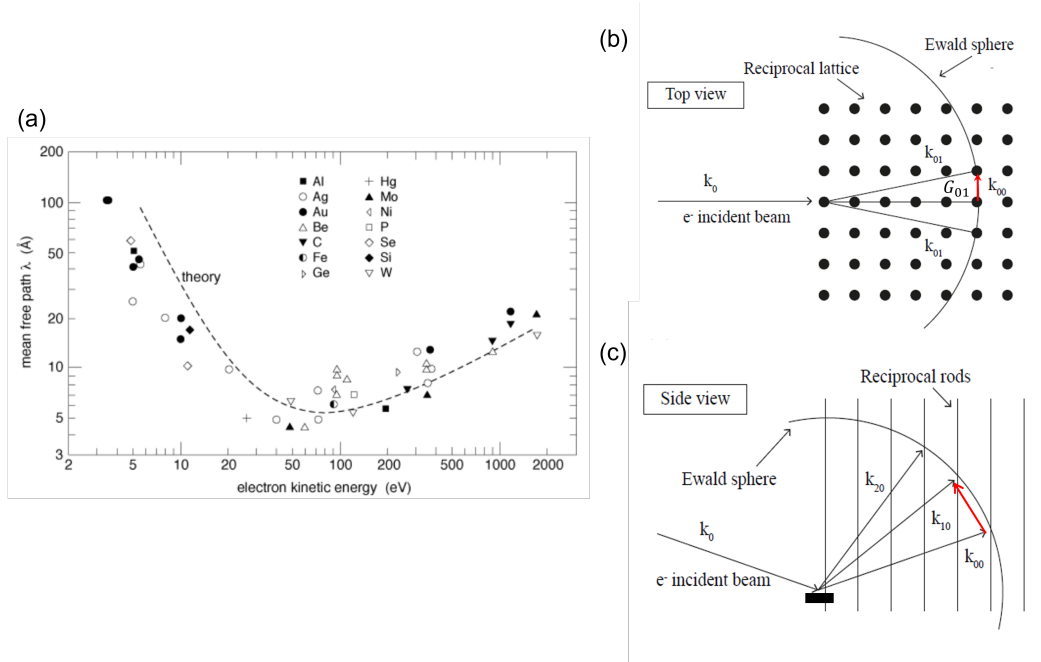


Figure 2.10. (a) Mean free path of electrons in solids as a function of their energy. The behavior is almost material independent, and the minimum mean free path of $\sim 6 \text{ \AA}$ is obtained at 50 eV . (b) Example of a top view of a 2D reciprocal lattice space, together with the Ewald sphere crossing it. A streak is observed when the difference between the incident electron beam momentum k_0 and the scattered electron beam momentum k_{0i} equals integer multiples of a reciprocal lattice vector G_i . (c) Side view of the 2D reciprocal lattice space in 3D, with the incident electron beam hitting the sample surface. The Ewald sphere with the corresponding reciprocal rods, or streaks, is also represented. Obtained from Ref. [180] and [182].

In the case of elastic scattering, i.e., of both energy and momentum conservation, the condition for the occurrence of an elastic Bragg peak is given by [180]:

$$K_{\parallel} = k_{0i,\parallel} - k_{0,\parallel} = G_{\parallel} \quad (2.14)$$

where $K_{\parallel}$ is the momentum of the scattered electron beam parallel to the sample surface, $k_{0,\parallel}$ the one of the incoming electron beam, $k_{0i,\parallel}$ the one of the diffracted electron beam, and $G_{\parallel}$ is the parallel component of a reciprocal lattice vector. The condition for $K_{\perp}$ is neglected. According to Equation 2.14, along most directions, the amplitudes of the scattered electrons add incoherently and do not contribute to the formation of the diffraction pattern. However, along certain crystal directions, the difference in the path lengths traveled by the electrons is an integer multiple of reciprocal lattice vectors and, therefore, the amplitudes add coherently. The same concept can be represented through the intersection of the reciprocal lattice with the Ewald sphere, as shown in Figure 2.10 (b) and (c). If the incoming wave vector is graphically terminated on a lattice position, and a circle is traced out around this point, with radius given by k_0 , a diffraction peak will appear where this circle intercepts a lattice point. This is true because for elastic collisions the magnitude of the momentum is conserved ($|k_0|=|K|$) and, therefore, the outgoing wave vector $|K|$ will also lie on the Ewald circle. For the case of a 3D crystal lattice, transformation to k-space yields another 3D lattice, whose lattice points are localized in 3D, and diffracted spots are observed in RHEED images. For the case of a 2D lattice whose real-space points are localized in 3D, instead, the k-space analog is a 2D lattice whose points are localized in 2D, but delocalized in the third dimension. A 2D lattice that is localized in the z direction can be approximated by a delta-function $\delta(z)$; transitioning to k-space involves a Fourier transformation, which, for a 2D lattice, yields $F[A\delta(z)] \rightarrow A$, a constant [177]. In this approximation, a real-space 2D lattice in k-space should be thought of as a series of rods, called reciprocal rods, or streaks, whose axes are along the z -direction, as shown in Figure 2.10 (c). Rotating the sample along the azimuthal angle ϕ , and noting the angular separation between repeating patterns, the rotational symmetry of the crystal's surface structure can be deduced; the most common symmetries are the cubic symmetry (4-fold, 90° between repetitions) and hexagonal symmetry (6-fold, 60° between repetitions). For the topological insulators grown in this work, two sets of different RHEED spacings appear every 30° when rotating the film. The relative ratio of the two spacings is $\sqrt{3}$, as expected for hexagonal structures.

2.6 Seebeck Coefficient and Resistivity Measurements

Both Seebeck coefficient and resistivity of thin film topological insulators deposited on Sapphire were measured using the LINSEIS LSR-1 instrument (Linseis Messgeräte GmbH, Germany) from 25°C to 100°C , under a static 0.1 bar N_2 pressure. Sample temperature and temperature gradient are controlled by a PT2000 heater embedded in the sample holder.

The Van der Pauw measurement technique [183] was employed to determine the specific electrical resistance (or electrical conductivity) of the sample, getting rid of interference influences such as contact or wire resistance. For the Van der Pauw measurement, the sample must be connected to four electrodes directly at the edge (see Figures 2.11 (a) and (b)). In the first step of the routing, a current is made to flow at two contacts on one edge of the sample (AB), and the voltage is measured at the other two contacts on the opposite edge (DC), and the same procedure is repeated by switching the current and voltage roles. In the linear regime condition, an average resistance $R_{horizontal} = \frac{R_{AB,DC} + R_{DC,AB}}{2}$ can be determined using Ohm's law. In the second step, the contacts are switched cyclically, and the measurement is repeated, retrieving an average resistance $R_{vertical} = \frac{R_{AC,DB} + R_{DB,AC}}{2}$ [184]. The sheet resistance of the sample can then be easily calculated by substituting the two

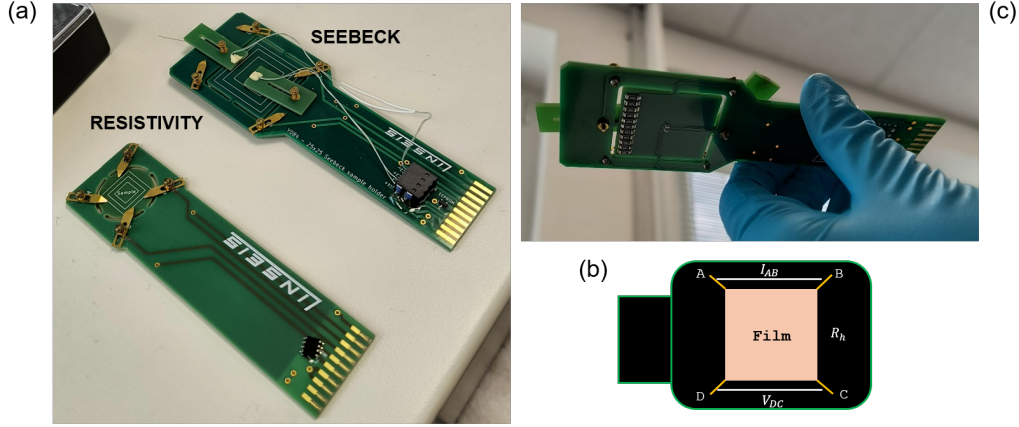


Figure 2.11. (a) Boards for measuring resistivity and Seebeck coefficient of topological insulator thin films, respectively. In the resistivity case, the sample is clamped by four contacts; in the Seebeck coefficient case, the sample surface is put in contact with two thermocouples. (b) Sketch showing the four contacts A, B, C, D of the Van der Pauw method. In this case, a current I_{AB} flows between A and B contacts, and a voltage V_{DC} is generated between D and C contacts, generating the horizontal contribution $R_{horizontal} = V_{DC}/I_{AB}$. (c) Seebeck coefficient board seen from below. Additional heaters are placed on the left side, beneath one of the two thermocouples, to generate the temperature gradient ΔT between the two opposite sides of the film, at a given temperature T.

measured resistances (horizontal and vertical) into the Van der Pauw formula [183]:

$$e^{-R_{vertical} \cdot \pi d / \rho} + e^{-R_{horizontal} \cdot \pi d / \rho} = 1 \quad (2.15)$$

where d is the film thickness and ρ the sample resistivity, and $R_S = \rho/d$ is the sheet resistance. The same procedure can be iterated, heating the sample at different temperatures.

Concerning the Seebeck coefficient measurements, two thermocouples located at two opposite ends of the sample are placed in thermal contact with the film surface, as shown in Figure 2.11 (a). Additional heaters are placed beneath the board where the sample is mounted (Figure 2.11 (c)), only on one edge, to create a temperature gradient ΔT (on the order of 3 K) between the positions of the two thermocouples, and induce a voltage gradient ΔV between the same two spots on the sample. The Seebeck coefficient value $S = -\Delta V / \Delta T$ at a given temperature T can be determined from the slope of the ΔV - ΔT curve measured while spanning ΔT [185]. Figure 2.12 shows an example of the ΔV - ΔT plot for a 20 nm Bi_2Te_3 film measured at 100 °C. From the slope, the absolute Seebeck coefficient value is estimated to be $S = -135.4 \mu V \cdot K$.

2.7 Models for Data Analysis

2.7.1 Optical Response Functions

In this thesis, *transmittance* and *reflectance* measurements at normal incidence were performed as a function of photon energy. These two quantities are defined as [154]:

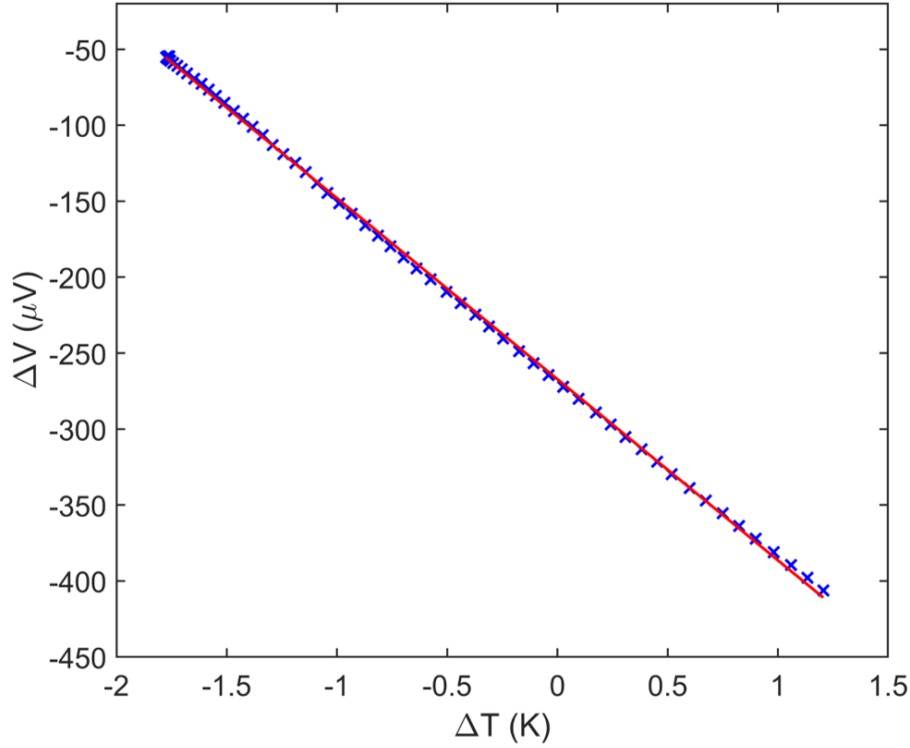


Figure 2.12. ΔV - ΔT curve measured at 100 °C for a 20 nm Bi_2Te_3 film.

$$T(\omega) = \frac{I_T(\omega)}{I_0(\omega)}, \quad R(\omega) = \frac{I_R(\omega)}{I_0(\omega)} \quad (2.16)$$

where I_0 represents the intensity incident on the sample, whereas I_T and I_R represent the transmitted and reflected intensities from the sample. The purpose of this section is to show how these macroscopic quantities are related to the microscopic optical response functions that describe the material properties. In the following, a list of these functions is reported:

- $\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$: *dielectric function*
- $\tilde{n}(\omega) = n(\omega) + ik(\omega)$: *refractive index*
- $\tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$: *optical conductivity*

These frequency-dependent quantities are complex because they account for both propagation and attenuation effects, which can be induced by an electromagnetic wave while travelling through matter. More specifically, n , ϵ_1 and σ_2 describe dispersive effects whereas k , ϵ_2 and σ_1 describe dissipative effects. Since the functions in Equation 2.16 are real, it is necessary to calculate a couple of complex parameters connected to T and R , the Fresnel's coefficients for transmission and reflection. They contain information about the phase and the amplitude of the reflected and transmitted electric field and are defined as [154]:

$$\tilde{t} = \frac{\mathbf{E}_T}{\mathbf{E}_0} = |\tilde{t}|e^{i\phi_t}, \quad \tilde{r} = \frac{\mathbf{E}_R}{\mathbf{E}_0} = |\tilde{r}|e^{i\phi_r} \quad (2.17)$$

where the phases ϕ_t and ϕ_r represent the difference between the phases of the transmitted/reflected and the incident waves.²

In this context, radiation-matter interaction is treated within a semiclassical approach, i.e., treating radiation in a classical picture and matter in a quantum picture, and the Coulomb Gauge ($\nabla \cdot \mathbf{A} = 0$) is adopted. The optical parameters can be derived through Maxwell's equations in presence of an infinite medium³ and in absence of external charges and currents ($\rho_{ext} = \mathbf{J}_{ext} = 0$) [154][186]:

$$\nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = 0 \quad (2.18)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (2.19)$$

$$\nabla \times \mathbf{H} - \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} = \frac{4\pi}{c} \mathbf{J} \quad (2.20)$$

$$\nabla \cdot \mathbf{D} = 4\pi \rho_{ext} \quad (2.21)$$

where $\mathbf{E}$ and $\mathbf{B}$ are the electric and the induction magnetic fields, respectively. The latter one is connected to the magnetic field $\mathbf{H}$ via the relation $\mathbf{B} = \tilde{\mu} \mathbf{H} = \mathbf{H} + 4\pi \mathbf{M}$, where $\mathbf{M}$ and $\tilde{\mu}$ are the magnetization and the magnetic permeability. In presence of non-magnetic matter, they can be set equal to zero and one, respectively. Within the framework of linear response theory⁴, $\mathbf{J} = \tilde{\sigma} \mathbf{E}$ is the current arising from the motion of electrons in presence of an electric field, $\mathbf{D} = \tilde{\epsilon} \mathbf{E} = \mathbf{E} + 4\pi \mathbf{P}$ is the electric field displacement and $\mathbf{P} = \tilde{\alpha} \mathbf{E}$ is the polarization. The dielectric function $\tilde{\epsilon}$ and the polarizability $\tilde{\alpha}$ are connected through the relation $\tilde{\epsilon} = 1 + 4\pi \tilde{\alpha}$.

By assuming a sinusoidal spatial and time variation for the electric field:

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)} \quad (2.22)$$

and by combining Maxwell's equations, the wave equation for the electric field is obtained:

$$\nabla^2 \mathbf{E} - \frac{\tilde{\epsilon} \tilde{\mu}}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} - \frac{4\pi \tilde{\mu} \tilde{\sigma}}{c^2} \frac{\partial \mathbf{E}}{\partial t} = 0 \quad (2.23)$$

Substituting Equation 2.22 into Equation 2.23, the dispersion relation between the complex wavevector $\mathbf{q}$, parallel to the propagation direction, and ω is retrieved:

$$\tilde{q} = \frac{\omega}{c} \left[\tilde{\epsilon} \tilde{\mu} + i \frac{4\pi \tilde{\mu} \tilde{\sigma}}{\omega} \right]^{1/2} \hat{n} \quad (2.24)$$

where $\hat{n}$ is the versor along the $\mathbf{q}$ direction. The complex refractive index appears in the following relation:

$$\tilde{q} = \frac{\omega}{c} \tilde{n} = \frac{\omega}{c} (n + ik) = \frac{\omega}{c} \left[\tilde{\epsilon} \tilde{\mu} + i \frac{4\pi \tilde{\mu} \tilde{\sigma}}{\omega} \right]^{1/2} \quad (2.25)$$

where n is the refractive index and k is the extinction coefficient.

The microscopic optical response functions are interrelated among themselves, as it is noticeable from the following relations:

$$n^2 - k^2 = \epsilon_1 = 1 - \frac{4\pi \sigma_2}{\omega} \quad (2.26)$$

²Equations 2.16 and 2.17 are related because $I \propto |E|^2$. At normal incidence and at the interface between two media with ϵ_1 and ϵ_2 , $T = \sqrt{\frac{\epsilon_2}{\epsilon_1}} |\tilde{t}|^2$, $R = |\tilde{r}|^2$.

³In this way, finite size and surface effects are not considered.

⁴In linear response theory, the perturbation is weak enough to consider the response of the system linear in the external perturbation.

$$2nk = \frac{4\pi\sigma_1}{\omega} = \epsilon_2 \quad (2.27)$$

Combining the last two equations, the final expression for the complex dielectric function is retrieved:

$$\tilde{\epsilon}(\omega) = 1 + i \frac{4\pi\tilde{\sigma}(\omega)}{\omega} \quad (2.28)$$

As previously mentioned, Fresnel's coefficients are used to link the microscopic optical response functions to T and R . Considering an interface between two media, the first one characterized by $\tilde{n}_1$ and the second one by $\tilde{n}_2$, each with semi-infinite thickness, and in the normal incidence configuration:

$$\tilde{t}_{12} = \frac{2\tilde{n}_2}{\tilde{n}_1 + \tilde{n}_2} \quad (2.29)$$

$$\tilde{r}_{12} = \frac{\tilde{n}_1 - \tilde{n}_2}{\tilde{n}_1 + \tilde{n}_2} \quad (2.30)$$

In real situations, samples have a finite thickness, which causes multiple reflections to occur inside the sample itself.⁵ These internal reflections give rise to interference effects, which can manifest themselves as oscillations in the transmitted/reflected intensities. The total transmission and reflection coefficients can still be calculated for multilayer systems. In this work, the samples are schematized as one-layer (350 μm thick SiC sample), two-layer (20 nm thick Bi_2Te_3 , Sb_2Te_3 , and $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ alloys deposited on top of 500 μm Al_2O_3 substrate, and ~ 30 nm GST layered alloys deposited on top of 500 μm Si substrate), and three-layer systems (10 - 100 nm Bi_2Se_3 films deposited on top 500 μm Al_2O_3 substrate, together with a 20 nm Se capping), as shown in Figure 2.13.

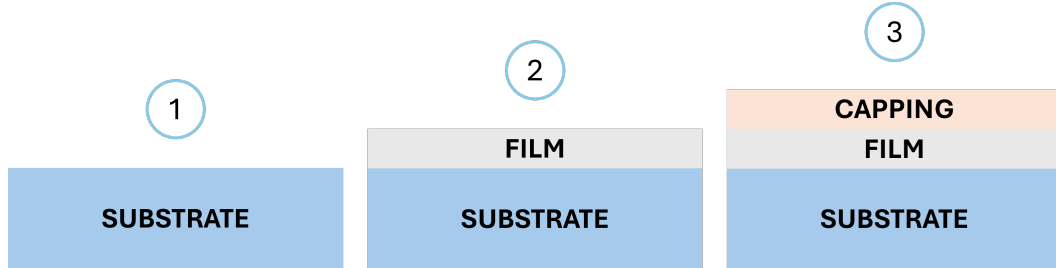


Figure 2.13. Schematics of the different layers used in this work: one-layer system, indicated with number 1, for the 350 μm thick SiC sample, two-layer system, indicated with number 2, for the 20 nm thick Bi_2Te_3 , Sb_2Te_3 , and $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ alloys deposited on top of 500 μm Al_2O_3 substrate, and for the ~ 30 nm GST layered alloys deposited on top of 500 μm Si substrate, and three-layer system, for the 10 - 100 nm Bi_2Se_3 films deposited on top of the 500 μm Al_2O_3 substrate, together with a 20 nm Se capping.

In the one-layer system case, a material of finite thickness d , with refractive index n and extinction coefficient k , situated between two media, labelled as 1 and 3, has [154]:

$$\tilde{t}_{123} = \frac{\tilde{t}_{12}\tilde{t}_{23}e^{2i\delta}}{1 + \tilde{r}_{12}\tilde{r}_{23}e^{2i\delta}} \quad (2.31)$$

⁵The electromagnetic radiation that is transmitted through the first interface does not entirely pass through the second interface because part of it is reflected from the back of the material. This portion hits the surface, where again part of it is transmitted, while the remaining radiation is reflected again and stays inside the material, giving rise to infinite multiple reflections with decreasing intensity.

$$\tilde{r}_{123} = \frac{\tilde{r}_{12} + \tilde{r}_{23}e^{2i\delta}}{1 + \tilde{r}_{12}\tilde{r}_{23}e^{2i\delta}} \quad (2.32)$$

where $\delta = \beta + i\alpha d/2$, with α the power absorption coefficient and β the ratio between the sample thickness and the wavelength inside the medium. From Equations 2.31 and 2.32, the expressions for transmittance and reflectance can be obtained:

$$T = \frac{[T_F^2 + 4R_F \sin^2(\phi_r)]e^{-\alpha d}}{(1 - R_F e^{-\alpha d})^2 + 4R_F e^{-\alpha d} \sin^2(\beta + \phi_r)} \quad (2.33)$$

$$R = R_F \frac{(1 - e^{-\alpha d})^2 + 4e^{-\alpha d} \sin^2(\beta)}{(1 - R_F e^{-\alpha d})^2 + 4R_F e^{-\alpha d} \sin^2(\beta + \phi_r)} \quad (2.34)$$

where ϕ_r is the phase change upon reflection, while T_F and R_F are the transmittance and reflectance for a single slab face, expressed as:

$$T_F = \frac{4n}{|n + ik + 1|^2} \quad (2.35)$$

$$R_F = \left| \frac{n + ik - 1}{n + ik + 1} \right|^2 \quad (2.36)$$

The second term in the denominator of Equations 2.33 and 2.34 describes the interference.

In the two-layer system case, instead:

$$\tilde{t}_{1234} = \frac{\tilde{t}_{12}\tilde{t}_{23}\tilde{t}_{34}e^{i(\delta_2+\delta_3)}}{1 + \tilde{r}_{12}\tilde{r}_{23}e^{2i\delta_2} + \tilde{r}_{23}\tilde{r}_{34}e^{2i\delta_3} + \tilde{r}_{12}\tilde{r}_{34}e^{2i(\delta_2+\delta_3)}} \quad (2.37)$$

$$\tilde{r}_{1234} = \frac{\tilde{r}_{12} + \tilde{r}_{23}e^{2i\delta_2} + \tilde{t}_{34}e^{2i(\delta_2+\delta_3)} + \tilde{r}_{12}\tilde{r}_{23}\tilde{r}_{34}e^{2i\delta_3}}{1 + \tilde{r}_{12}\tilde{r}_{23}e^{2i\delta_2} + \tilde{r}_{23}\tilde{r}_{34}e^{2i\delta_3} + \tilde{r}_{12}\tilde{r}_{34}e^{2i(\delta_2+\delta_3)}} \quad (2.38)$$

where $\tilde{t}_{pq}$ and $\tilde{r}_{pq}$ are the transmission and reflection coefficients at the boundaries between media p and media q ($q, p=1,2,3,4$) and $\delta_p = \beta_p + i\alpha_p d_p/2$. Analogously, the expressions for transmittance and reflectance can also be retrieved in the two-layer system case, but they start to be very long and difficult to manage. In some cases, some simplifications can be applied in order to have an expression that is easier to handle. For example, when the slab thickness d is much larger than the coherent length of light, the optical interference among multiple reflections is averaged out, and incoherent summations of the multi-reflected intensities can be considered. In this case [187]:

$$T = \frac{T_F^2 e^{-\alpha d}}{1 - R_F^2 e^{-2\alpha d}} \quad (2.39)$$

$$R = R_F + \frac{R_F T_F^2 e^{-2\alpha d}}{1 - R_F^2 e^{-2\alpha d}} \quad (2.40)$$

The same equations can be iterated for a given number of layers.

Microscopic optical response functions for a one-layer system could be obtained by inverting the previous complicated transmittance and reflectance equations. However, it is quite common that the substrate's transmittance exhibits a null value within a region of the entire probed spectral range; thus, the equations make no sense anymore in that spectral window. To overcome this drawback and to manage

multi-layer systems, the RefFIT software (see Section 2.7.3) was used to model the reflectance of the investigated systems using Drude and Drude-Lorentz models, as described later in Sections 2.7.2. The microscopic optical response functions were directly extrapolated from the software, considering Kramers-Kronig constraints. This software allows for modeling one layer at a time if the reflectance of each layer composing the system is measured, such as the substrate alone, then the substrate plus capping, and the substrate plus film plus capping. Air was also taken into account.

2.7.2 The Drude-Lorentz Model

In order to explain the physics that lies behind the microscopic optical response functions, the Drude-Lorentz models can be exploited. Although based on a classical description, they agree with the major features of the electrodynamics of solids.

The *Lorentz model* describes the optical properties of an insulator in which the valence electrons are bound to the nuclei by an elastic potential [186]. In the presence of a local external electric field of the form $\mathbf{E}(t) = \mathbf{E}_0 e^{-i\omega t}$, the equation of motion for a single valence electron is:

$$m \frac{d^2 \mathbf{r}}{dt^2} + m\gamma \frac{d\mathbf{r}}{dt} + m\omega_0^2 \mathbf{r} = -e\mathbf{E} \quad (2.41)$$

where m is the electron mass, $\mathbf{r}(t)$ the electron position, $\omega_0 = \sqrt{K/m}$, with K the restoring constant and $\gamma = 1/\tau$ a damping factor. Equation 2.41 is the one of a classical harmonic oscillator in the presence of a driving force and a viscous contribution, proportional to the electron speed. Assuming for the electron position the same oscillating behaviour of the electric field, $\mathbf{r}(t) = \mathbf{r}_0 e^{-i\omega t}$, it is found:

$$\mathbf{r}_0 = -\frac{e}{m} \frac{\mathbf{E}_0}{(\omega_0^2 - \omega^2) - i\omega\gamma} \quad (2.42)$$

The induced microscopic electric dipole for a small displacement is defined as:

$$\mathbf{d} = -e\mathbf{r}_0 \quad (2.43)$$

whereas the macroscopic polarization is obtained summing over all the n atoms per unit volume:

$$\mathbf{P} = n\mathbf{d} = \frac{ne^2}{m} \frac{\mathbf{E}_0}{(\omega_0^2 - \omega^2) - i\omega\gamma} = \tilde{\alpha}(\omega)\mathbf{E}_0 \quad (2.44)$$

At this point, the expression for the complex dielectric function can be derived, reminding that it is related to the polarizability in the following way:

$$\tilde{\epsilon}(\omega) = 1 + 4\pi\tilde{\alpha}(\omega) = 1 + \frac{4\pi ne^2}{m} \frac{1}{(\omega_0^2 - \omega^2) - i\omega\gamma} = 1 + \frac{S_{el}^2}{(\omega_0^2 - \omega^2) - i\omega\gamma} \quad (2.45)$$

The quantity $S_{el} = (4\pi ne^2/m)^{1/2}$ describes the oscillator strength. Once $\tilde{\epsilon}(\omega)$ is known, the optical conductivity can be expressed using Equation 2.28 as follows:

$$\tilde{\sigma}(\omega) = \frac{ne^2}{m} \frac{\omega}{i[(\omega_0^2 - \omega^2) - i\omega\gamma]} \quad (2.46)$$

These quantities are calculated assuming that each atom contributes one electron to the absorption process, but in some cases more electrons can contribute, so the

dielectric function becomes the sum of an arbitrary number of oscillators N , each of which has its own ω_{0i} . As already pointed out before, although the Lorentz model describes the behaviour of a bound charge system in a classical framework, it is in agreement with the major features of the electrodynamics of solids. In fact, from a quantum mechanical point of view, it is suitable for describing both radiation absorption due to interband transitions and the contribution to the dielectric function due to IR-active optical phonons. The latter phenomenon is taken into account by introducing the ionic oscillator strength $S_{ph} = (4\pi n(Ze)^2/m^*)^{1/2}$, where m^* is the ion reduced mass, Ze the ionic charge, n the density per unit volume, ω_0 the normal mode frequency and $\tau = 1/\gamma$ the normal mode lifetime.

On the other hand, the *Drude model* describes metals as a classical gas of free electrons which undergo a diffusive motion [154]. It can be obtained by setting to zero the oscillator frequency ω_0 of the previous model; therefore, the equation of motion for a free carrier becomes:

$$m \frac{d^2 \mathbf{r}(t)}{dt^2} + m\gamma \frac{d\mathbf{r}(t)}{dt} = -e\mathbf{E}(t) \quad (2.47)$$

where m is the electron mass, $\mathbf{r}(t)$ the electron position and $\gamma = 1/\tau$ the scattering rate. In fact, according to this model, electrons are subject to scattering processes due to other electrons, impurities, ions. Following a similar procedure, the dielectric function is obtained:

$$\tilde{\epsilon}(\omega) = 1 - \frac{4\pi ne^2}{m} \frac{1}{\omega^2 + i\omega\gamma} = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \quad (2.48)$$

According to the Drude model, all the microscopic optical response functions are fully characterized by two parameters: the plasma frequency ω_p and the scattering rate γ . In conventional metals typical values of the plasma frequency are of the order of $10^{15} - 10^{16}$ Hz, therefore in the visible range, whereas typical values of τ at room temperature are around 10^{-14} s.

The total dielectric function incorporates different contributions, associated to the motion of free and bound charge carriers and to the motion of ions:

$$\tilde{\epsilon}(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} + \sum_{i=1}^N \frac{S_{el,i}^2}{(\omega_{0i}^2 - \omega^2) - i\omega\gamma_i} + \sum_{j=1}^N \frac{S_{ph,j}^2}{(\omega_{0j}^2 - \omega^2) - i\omega\gamma_j} \quad (2.49)$$

The effect of other contributions at higher frequencies is included in ϵ_∞ , also called "high-frequency dielectric function". It comes from the limit $\epsilon_1(\omega \rightarrow \infty) \rightarrow 1$, which satisfies the physical requirement that at very high frequencies the optical properties of matter are those of vacuum, so $\epsilon_1(\omega \rightarrow \infty) \rightarrow 1$ and $\epsilon_2(\omega \rightarrow \infty) \rightarrow 0$.

2.7.3 The RefFIT Software

As already mentioned at the end of the Subsection 2.7.1, the RefFIT software was used to extract the microscopic optical response functions of the investigated samples starting from macroscopic reflectance data. This software was developed by Alexey Kuzmenko (University of Geneva) to get the complex dielectric function $\tilde{\epsilon}$ of the studied material [188]. In fact, the linear macroscopic optical characteristics are completely determined by $\tilde{\epsilon}$, from which $\tilde{\sigma}$ and $\tilde{n}$ can be subsequently obtained. In order to accomplish this goal, the optical spectra are fitted using a model of the dielectric function with a set of adjustable parameters within the Drude-Lorentz

model, such as ω_0 , ω_p , γ . RefFIT firstly allows for varying these parameters to reproduce as much as possible the experimental spectra, and then to perform a fit.

The fitting procedure consists of a "least-square" technique, i.e., of a minimization of the chi-square (χ^2) with respect to the adjustable parameters. To define the χ^2 functional, we need a set of N experimental data points (x_i, y_i, σ_i) , where x_i is the frequency, y_i the data value of transmittance or reflectance and σ_i the data error bar, a model which calculates the data value y as a function of x , and a set of internal parameters $(p_1, p_2, \dots, p_M)$: $y = f(x, p_1, \dots, p_M)$. The χ^2 functional is defined as:

$$\chi^2 = \sum_{i=1}^N \left(\frac{y_i - f(x_i, p_1, \dots, p_M)}{\sigma_i} \right)^2 = \chi^2(p_1, \dots, p_M) \quad (2.50)$$

Assuming that all measured values y_i are normally distributed with standard deviations σ_i , the best match between the experimental and the calculated points would correspond to the minimal value of χ^2 . In general, in optical modeling $f(x, p_1, \dots, p_M)$ is a non-linear function of parameters, so the minimization of the χ^2 is performed through the Levenberg-Marquardt algorithm [189]. The explanation of the algorithm is outside the scope of this work; for further information, see, for example, Ref. [189].

As already mentioned before, RefFIT aims at getting the dielectric function $\tilde{\epsilon}$, which should satisfy some physical requirements:

- $\epsilon_1(\omega) = \epsilon_1(-\omega)$ and $\epsilon_2(\omega) = -\epsilon_2(-\omega)$, therefore, it is sufficient to model $\tilde{\epsilon}(\omega)$ for $\omega \geq 0$ only;
- $\epsilon_2(\omega > 0) \geq 0$, which means that light intensity cannot increase in the direction of propagation;
- at very high frequencies, the optical properties of matter match those of vacuum, so $\epsilon_1(\omega \rightarrow \infty) \rightarrow 1$ and $\epsilon_2(\omega \rightarrow \infty) \rightarrow 0$;
- Due to causality, $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are coupled through the Kramers-Kronig relations, and therefore only one of the two functions is independent.

2.7.4 Blackbody-like Spectra Analysis

The blackbody-like intensity spectra, acquired using the experimental setup described in Section 2.1, were fitted with Planck's law to assess whether the experimental temperatures measured with the thermocouple agree with the theoretical values. For real bodies, the spectral radiance expression, i.e., the energy emitted per unit of time, wavenumber, solid angle, and area, turns into [8, 9]:

$$I(\theta, \phi, \tilde{\nu}, T) = \varepsilon(\theta, \phi, \tilde{\nu}, T) \cdot 2 \cdot 10^8 h c^2 \tilde{\nu}^3 \frac{1}{e^{\left(\frac{100hc\tilde{\nu}}{k_B T}\right)} - 1} \quad (2.51)$$

where $\varepsilon(\theta, \phi, \tilde{\nu}, T)$ is the emissivity, h is the Planck constant, c is the speed of light, $\tilde{\nu}$ is the wavenumber, k_B is the Boltzmann constant, T is the absolute temperature, and $2 \cdot 10^8$ is a numerical factor needed to obtain the correct units, i.e. $W \cdot m^{-2} \cdot sr^{-1} \cdot (cm^{-1})^{-1}$ [1, 2]. $\varepsilon(\theta, \phi, \tilde{\nu}, T)$ is defined as the ratio between the spectral radiance of the real body and that of an ideal black body at the same temperature. Its values range between 0 and 1, setting an upper limit for the emission of thermal radiation ($\varepsilon(\theta, \phi, \tilde{\nu}, T)=1$ corresponds to the maximum spectral radiance, that is, the one of a black body), and its wavenumber dependence highlights that real bodies exhibit spectral selectivity.

In this work, each spectrum was normalized over its emissivity area and fitted using the following equation:

$$I(\tilde{\nu}, T) = C \cdot 2 \cdot 10^8 hc^2 \tilde{\nu}^3 \frac{1}{e^{\left(\frac{100hc\tilde{\nu}}{k_B T}\right) - 1}} \quad (2.52)$$

where C is a constant taking into account the sample area and the fraction of the solid angle accepting the emitted thermal radiation, which depends on the acceptance angle of the parabolic mirror placed after the steel cylindrical chamber, as shown in Figure 2.1. C takes into account $\varepsilon(\theta, \phi, \tilde{\nu}, T)$ as well, which is assumed to be angle- and wavenumber-independent. Additionally, the spectrum of the investigated material at a given temperature was compared with a reference measured at the same temperature in the same experimental conditions. In the case of 3D graphene sheets, SiC and black soot were used, whereas in the case of SiC fractal metamaterials, bare SiC was used. In this way, an emissivity-like quantity could be calculated.

Chapter 3

Experimental Results and Discussion

This Chapter gathers all the experimental results and discussions obtained in this project.

At first, thermal emission properties of two different groups of micro-structured materials are discussed: self-standing 3D graphene samples, grown via Chemical Vapor Deposition, exhibiting a 3D structure where pores in the 60 - 150 μm spatial scale randomly alternate with material branches, and SiC fractal metamaterials, in which artificially patterned pillars are displaced on top of a bulk 350 μm thick 4H-SiC with fractal arrangement, up to the third order, with spatial scales varying from 11.5 μm to 430 nm. In the latter case, the optical properties of the bare and patterned samples are also discussed to help give a better interpretation of the data. Later, the analysis of thin 2D topological insulator films is presented. These materials, including Bi_2Se_3 , Bi_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$, and Sb_2Te_3 , were grown via Molecular Beam Epitaxy at Rutgers University, New Jersey, USA. Their optical properties are discussed in a wide spectral range, extending from 40 cm^{-1} to 20000 cm^{-1} , thus from THz up to part of the Visible spectral range, to capture both the phononic and the electrodynamic response of these samples. Seebeck coefficient and resistivity measurements are shown as a function of temperature for the class of samples including Bi_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$, and Sb_2Te_3 , and a rough estimation of the ZT figure of merit is given, to assess their good thermoelectric behavior.

Finally, the optical properties of Ge-Sb-Te layered alloys are discussed and compared with DFT calculations performed at Bicocca University in Milan, focusing on the spectral range where electronic transitions occur.

3.1 Thermal Emission from Micro-Structured Materials

In this Section, the results concerning the thermal emission intensity spectra of micro-structured materials, such as 3D graphene structures with pores in the 60-150 μm range, and SiC fractal metamaterials, with pillars in the 11.5-0.430 μm spatial dimension, are presented. Results are shown in the Infrared spectral range, from 30 cm^{-1} to 8000 cm^{-1} , and at different temperatures, up to 650 $^\circ\text{C}$. The idea behind this Section is to retrieve an emissivity-like quantity for these materials and investigate how it behaves as a function of frequency and temperature. A brief anticipation of the results is illustrated in the graphical abstract in Figure 3.1.

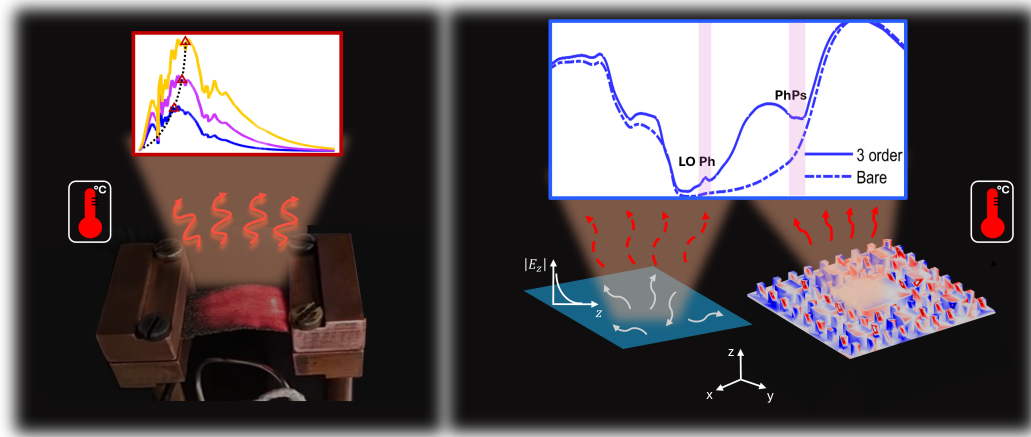


Figure 3.1. Sketch resuming the thermal emission properties of the two sample types investigated in this Section: 3D graphene networks on one side, and SiC fractal metamaterials on the other side. In the first case, the capability of emitting thermal radiation spectra that closely resemble blackbody emission, along with the robust mechanical flexibility of the composing material, is highlighted. In the second case, the difference between bare and patterned SiC (third-order fractal) samples is emphasized, highlighting the release of otherwise evanescent thermal energy due to the diffraction of phonon polaritons through the pillars.

3.1.1 3D Graphene Thermal Emission

Sample Preparation and Characterization

Three 3D graphene structures, designated as S1, S2, and S3, with varying densities and pore sizes, were investigated. The latter were prepared through a porous Ni-based chemical vapor deposition (CVD) growing technique, as reported in the work of Ito et al. [32, 33, 34, 35, 36, 37]. Porous Ni (Celmet, Sumitomo Electric Industries, Ltd.) was loaded into a quartz tube (external diameter 26 mm x internal diameter 22 mm x 250 mm length) as an inner tube which was further inserted into the center of a larger quartz tube (external diameter 30 mm x internal diameter 27 mm x 1000 mm length) in the open-box-type furnace. Ni was annealed at 1000 °C for 10 min to clean the Ni surface under a mixed atmosphere of H₂ (100 sccm) and Ar (200 sccm). Subsequently, graphene/chemically doped graphene was grown at 800 °C for 10 min under a mixed atmosphere of H₂ (100 sccm), Ar (200 sccm), benzene (0.1 mbar, 99.8 %, anhydrous, Sigma-Aldrich) and/or pyridine (0.2 mbar, 99.8 %, anhydrous, Sigma-Aldrich) as precursors. The furnace was quickly opened, and the inner and outer quartz tubes were cooled with a fan down to room temperature. The Ni substrates were dissolved in a 1.0 M HCl solution for four days and then etched at 50 °C in a 1.5 M HCl solution for 1 day. The resulting graphenes in the solution were repeatedly washed with pure water five times and kept in the water for 2 days. Then, they were transferred into 2-propanol for 1 week to dry them with a supercritical CO₂ (scCO₂) fluid drying method [190, 191]. To prevent the collapse and damage of the fragile 3D curved structures, caused by the capillary force of water during the drying process, the graphene samples were immersed in 2-propanol and dried using the scCO₂ fluid drying method, to substitute 2-propanol with scCO₂ fluid without the capillary force taking place. The samples were first transferred to a glass bottle (volume: 5 mL) filled with 2-propanol (400 μL), which was then placed in an 80 mL pressure-resistant container (TAIATSU techno Corp). After

removing the air inside the container through gaseous CO₂ purging, the pressure of the container was gradually increased to 15 MPa by introducing liquid CO₂ (5 MPa, 4 °C, density of 0.964 g/mL) at a flow rate of 20 mL/min (19 g/min) using a high-pressure plunger pump (NIHON SEIMITSU KAGAKU Co. Ltd, NP-KX-540). The scCO₂ fluid drying process was carried out at 70 °C, with a constant CO₂ flow rate of 5 mL/min (4.8 g/min), by forming a homogeneous phase of 2-propanol and scCO₂ to minimize the capillary force. The pressure was maintained at 15 MPa during the scCO₂ drying procedure for at least 5 h. Once completely dried, the temperature of the system was set at 40 °C, and it was gradually depressurized over 43 h, from 15 MPa down to atmospheric pressure, by gradually venting CO₂ from the system.

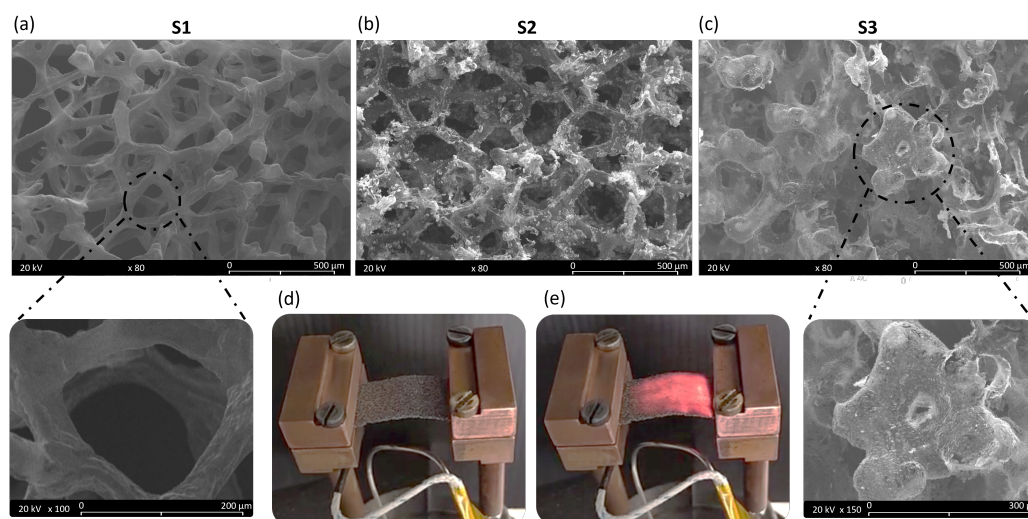


Figure 3.2. SEM x80 magnified images of S1 (a), S2 (b), and S3 (c) samples. Images (a) and (c) are accompanied by a further magnified image (x100 and x150, respectively) of the same sample, to better highlight the structure of these materials. Panels (d) and (e) show sample S1 clamped between two copper supports at room temperature (d) and when heated up via the Joule effect (e). In both images, the high mechanical flexibility of the sample is demonstrated, showing that it can withstand mechanical stress at high temperatures, too.

Figure 3.2 reports SEM images of the 3D graphene samples S1, S2, and S3, revealing their 3D porous nature. More in detail, panels (a), (b), and (c) are associated with x80 magnified pictures of S1, S2, and S3, showing how branches and pores alternate in a bicontinuous three-dimensional graphene network, exhibiting randomly oriented polygons. These three samples were selected to emphasize their different structural nature. Despite sharing the same chemical composition, their different growth procedures are responsible for larger (a,b) and smaller (b) pores, respectively. According to the scale bar in each image, the average pore sizes are estimated to be around 150 μm for S1 and S2, and 60 μm for S3. Each image is associated with a zoom (x100 and x150 magnification factors for S1 and S3 samples, respectively) around a specific polygon, showing the pore size difference between the two 3D structures. This variation is attributed to the density difference between the samples (see Table 3.6). The other two panels (d,e) show the setup built for clamping and heating the samples through two copper supports at different temperatures, mounted in the focal plane of the emission port of the Vertex 70v Bruker interferometer, as better described in Figure 2.1 in Chapter 2. Panel (d)

shows sample S1 at room temperature, while panel (e) shows it when heated via the Joule effect. The different sample colors, gray at room temperature and red when heated, stress this fact. In both images, the high mechanical flexibility of this material is further highlighted. Indeed, the clamping procedure induces a given curvature in the sample, which can withstand this mechanical stress without any damage at high temperatures, too. This feature underlines the easier handling of 3D graphene compared to its standard 2D counterpart, overcoming the rigidity and cracking under the same experimental conditions of widely spread IR radiation sources such as SiC. The bendable nature of this porous material is also suitable for many flexible applications in curved devices [192].

Additional SEM images of the three samples with magnification factors ranging from x40 to x150 are reported in Appendix E, together with their Raman spectra and images demonstrating the degree of flexibility of the investigated 3D graphene networks.

Thermal Radiation Spectra

Figure 3.3 shows the thermally emitted spectra at six different temperatures, ranging from 240 °C (blue curve) to 500 °C (yellow curve), for the S1 (a), S2 (b), S3 (c), and SiC (d) samples in the IR spectral range.

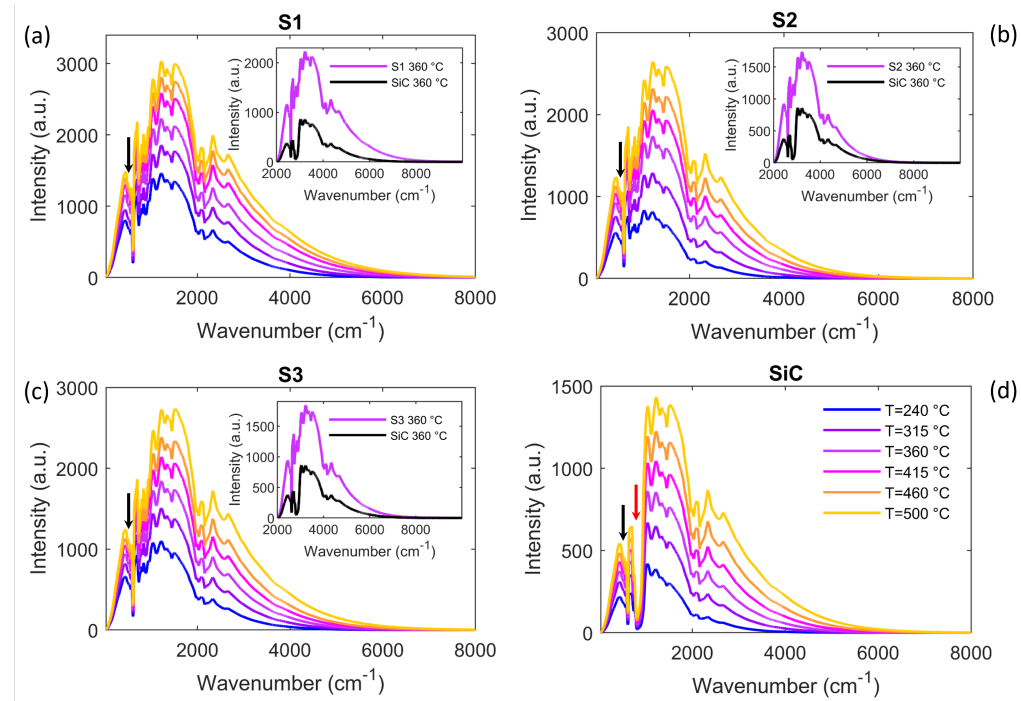


Figure 3.3. Thermal radiation spectra of S1 (a), S2 (b), S3 (c), and SiC (d) in the Infrared spectral range, from 30 cm^{-1} to 8000 cm^{-1} , at six different temperatures, ranging from 240 °C (blue curve) up to 500 °C (yellow curve). All the spectra are normalized over the emitting area of the corresponding sample. Each 3D graphene sample panel contains an inset where its thermal radiation spectrum at 360 °C (purple curve) is compared with the SiC spectrum (black curve) at the same temperature. Black arrows highlight the dip located at 610 cm^{-1} , associated with a Si-Si lattice vibration of the Silicon beam splitter, whereas the red arrow (d) highlights the SiC Reststrahlen band, extending from 797 cm^{-1} until 970 cm^{-1} .

All spectra were normalized to their emitting area to allow a proper comparison among emission intensities. The spectra are broadband and show the typical Wien's displacement trend [193], with a shift of the bell-shaped curves towards higher frequencies, and an overall increase of their amplitude. For the S1, S2, and S3 3D graphene samples, one can notice the absence of specific spectral features, i.e., dips associated with phonon excitations, obtaining spectral homogeneity, as expected from Planck's law [193]. Figure 3.4 provides a clearer representation of this result. The black dashed curve depicts the best fit obtained using Equation 2.52 in Chapter 2. A good agreement between the shape of theoretical and experimental curves is observed, together with a good match regarding the position of the maximum and the behaviour of the tails of the bell-shaped function. Although scaled, the fitting curve maximum is always larger than the experimental one due to several absorptions of the internal optics of the interferometer. The overall $\Delta T/T$, where $\Delta T = |T_{fit} - T_{exp}|$ is the difference between the fitting and the experimental temperatures, is within 4 %.

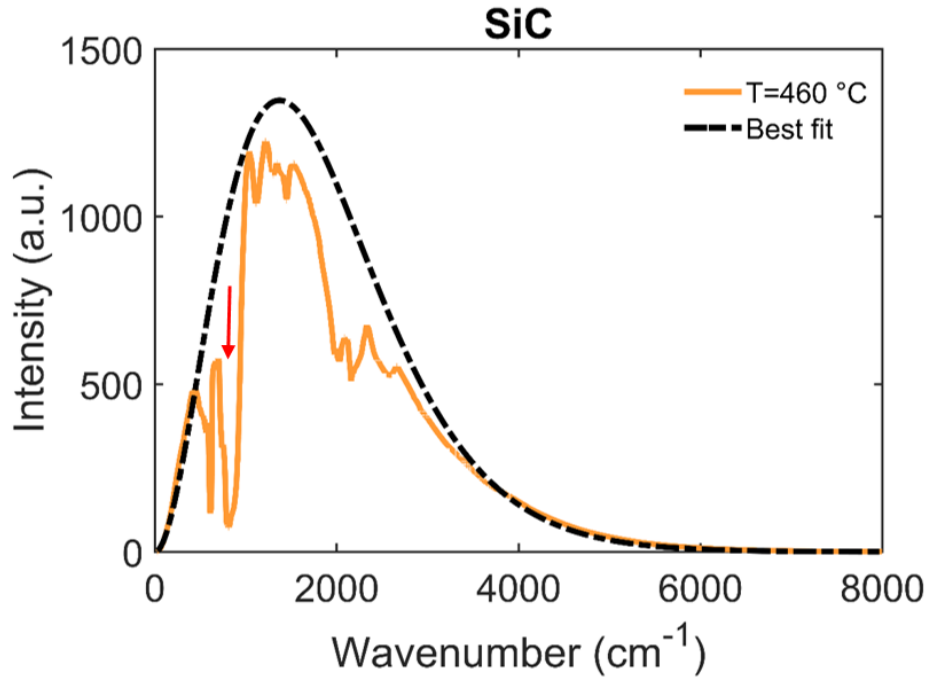


Figure 3.4. Experimental thermal radiation spectrum of SiC (orange curve) in the Infrared spectral range, from 30 cm^{-1} to 8000 cm^{-1} , at 460 °C. The spectrum is normalized over the emissivity area of the corresponding sample. The red arrow highlights the SiC Reststrahlen band, extending from 797 cm^{-1} to 970 cm^{-1} . The black dashed curve represents the best fit obtained by using the spectral radiance formula of Equation 2.52 in Chapter 2.

Coming back to Figure 3.3, it can be observed that the dip located at 610 cm^{-1} (black arrow) corresponds to a Si-Si lattice vibration (a combination of a transverse optic "TO" and a transverse acoustic "TA" mode) of the silicon beam splitter in the Vertex 70v interferometer [194, 195] used in this experiment, and the other dips are associated with absorptions from the internal optics of the interferometer. Thus, no phonon modes are ascribable to 3D graphene. On the other hand, SiC spectra exhibit a strong and wide dip extending from around 800 cm^{-1} to 970 cm^{-1} (red arrow in Figure 3.3 (d)), which identifies the SiC Reststrahlen band, where the

emitted thermal radiation is evanescent and not captured in the far-field regime. The S1 sample (the one with the lowest density, see below) shows higher intensity spectra compared to S2 and S3, which are similar to each other. All 3D graphene samples emit more intensely than the reference SiC sample at each temperature. This trend is further illustrated in the insets of panels (a), (b), and (c), where the spectrum (normalized to the sample surface) of each graphene sample (purple curve) is compared with that of SiC (black curve) at 360 °C.

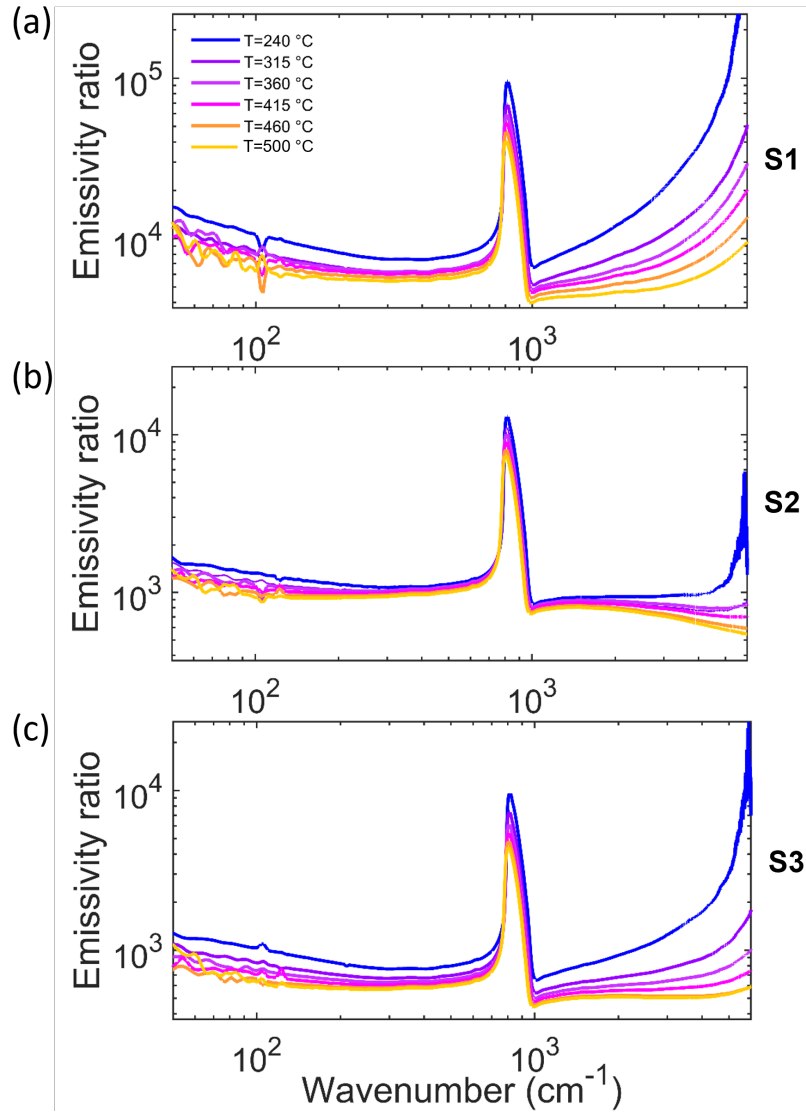


Figure 3.5. Emissivity ratio of S1 (a), S2 (b), and S3 (c) over SiC in the Infrared spectral range, from 30 cm^{-1} to 8000 cm^{-1} , at six different temperatures, ranging from $240 \text{ }^{\circ}\text{C}$ (blue curve) up to $500 \text{ }^{\circ}\text{C}$ (yellow curve). For a given temperature, each spectrum was normalized over its emitting area and density.

To further demonstrate that 3D graphene networks are exceptional thermal emitters, we calculated the ratio between the thermally emitted IR spectrum of 3D graphene (shown in Figure 3.3 (a), (b), (c)) and that of crystalline SiC (Figure 3.3 (d)), which is commonly regarded as the benchmark thermal emitter.

To account for differences in sample density, each spectrum in the ratio is further normalized to the density of the corresponding sample. The densities were estimated from the measured mass and volume of each sample and are reported in Table 3.6 in g/mm^3 , together with uncertainties obtained from error propagation on masses and volumes.

SAMPLE	S1	S2	S3	SiC
DENSITY (10^{-3} g/mm^3)	$(10 \pm 5) \cdot 10^{-4}$	$(77 \pm 5) \cdot 10^{-4}$	$(130 \pm 8) \cdot 10^{-4}$	3.3 ± 0.5

Figure 3.6. S1, S2, S3, and SiC densities, expressed in 10^{-3} g/mm^3 units, together with their uncertainties.

The densities of S1, S2, and S3 correspond to 0.03%, 0.23%, and 0.40% of the SiC density, respectively. The resulting curves, representing the “emissivity ratio,” are reported in Figure 3.5 for each sample. The emissivity ratio (see Figure 3.5) exhibits a moderately flat behavior between approximately 50 cm^{-1} and 800 cm^{-1} , where a peak associated with the SiC phonon absorption is observed, followed by a progressive increase at higher wavenumbers. This increase reduces as the temperature rises, evidencing the broadening of the thermally emitted radiation spectrum with temperature. The “emissivity ratio” shows an interesting behavior *vs.* the 3D graphene density. For the S1 sample, which has the lowest density $(10 \pm 5) \times 10^{-7} \text{ g/mm}^3$, the emissivity ratio reaches the order of 10^4 , decreasing to approximately $2 \cdot 10^3$ for S2, and to nearly 10^3 for S3. This decrease is consistent with the corresponding increase in density from S1 to S3.

Unlike SiC, which possesses a well-ordered crystal structure, the random alternation of voids and branches at the microscopic scale for the graphene network samples appears to strongly influence the overall thermal emission performance. The complex interplay of 3D graphene with light was already investigated in our previous paper [27], where branch surface roughness, in the order of hundreds of nanometers, was found to strongly scatter radiation in the IR spectral range. It has already been shown that microstructuring is an effective strategy for improving the emissivity of materials. For example, Ref. [196] reports that microstructured Silicon exhibits an emissivity of around 0.9 at 100°C , higher than the value of 0.4 measured for bare Silicon in the $2.5 \mu\text{m} - 25 \mu\text{m}$ spectral range. Likewise, Ref. [197] shows that Si/SiO₂ nanostructured thin films experience high near-infrared (NIR) emissivity at 200°C and 350°C . The introduction of pores also results in improved emissivity. To understand how pore structures influence emission intensity, the optical properties of 3D graphene networks must be considered. As shown in our previous work [27], 3D graphene networks exhibit low transmittance and reflectance, resulting in high absorption, and, consequently, strong thermal emission in agreement with Kirchhoff’s radiation law. From the microscopic point of view, pores act as cavity-like features that trap (absorb) and subsequently release (emit) heat through multiple internal reflections within the network. For instance, in Ref. [198], theoretical calculations demonstrate that increasing the porosity within a fibrous material strongly improves the emissivity performance. Having a closer look at the micro and nanoscale, in Ref. [49], local IR spectroscopic measurements with high spatial resolution were performed via s-SNOM (scattering-type scanning near-field optical microscopy) on nanoporous graphene films with a nature similar to our samples (see Figure 2b in the paper), revealing that density, that is, the dimension

of the pores, affects heat irradiation. In fact, strong IR radiation is localized in the vicinity of larger pores (lower density), in contrast to weaker radiation observed around smaller pores (higher density). Consequently, this IR radiation localization is translated into heat radiation. This independent spectroscopic result indicates that nanoporous graphene with larger pores, and thus with lower density, tends to radiate heat more efficiently, in very good agreement with our experimental findings. Indeed, sample S1 exhibits the highest emissivity ratio among all the investigated samples.

Comparison with Black Soot Reference

For comparison, additional measurements were performed using a black soot sample as a reference, which is a well-known thermal emitter.

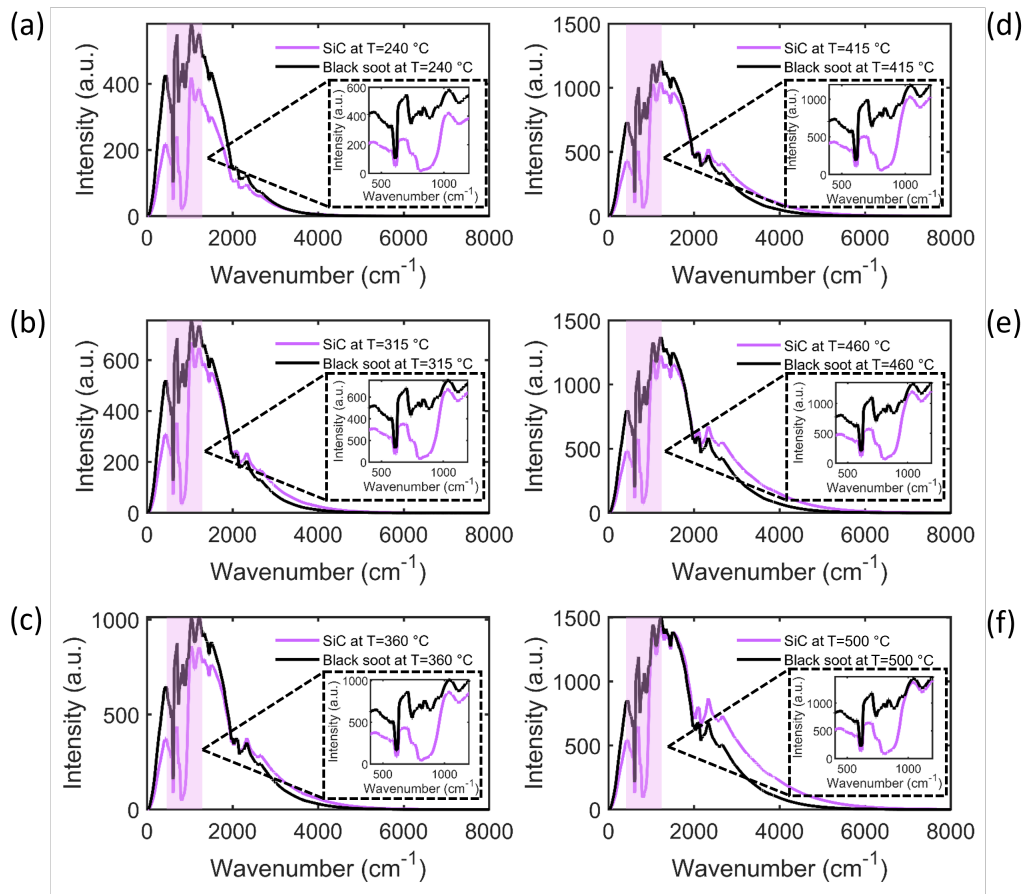


Figure 3.7. Thermal radiation spectra of SiC (pink curves) and SiC covered with black soot (black curves) in the Infrared spectral range, from 30 cm^{-1} to 8000 cm^{-1} , at six different temperatures, ranging from $240 \text{ }^{\circ}\text{C}$ (panel (a)) up to $500 \text{ }^{\circ}\text{C}$ (panel (f)). All the spectra are normalized over the emissivity area of the corresponding sample. Each panel contains an inset with a zoom in the 400 cm^{-1} - 1200 cm^{-1} spectral window, showing that the dip associated with the SiC Reststrahlen band (797 cm^{-1} - 970 cm^{-1}) is strongly suppressed.

Additionally, black soot was used as a strategy to suppress the contribution coming from the SiC Reststrahlen band (797 cm^{-1} - 970 cm^{-1}), which determines a strong

peak in the emissivity ratio (see Figure 3.5). Therefore, black soot was deposited on top of the SiC sample and used as a reference instead of SiC. Indeed, black soot is regarded as a perfect reference thanks to its high and homogeneous spectral emissivity [3, 4]. Black soot was obtained by firing the same SiC substrate surface with a lighter for around 1 minute until the surface turned into a uniformly black surface. Figure 3.7 shows a comparison between SiC (pink curves) and SiC covered with black soot (black curves) thermal radiation spectra in the Infrared spectral range, from 30 cm^{-1} until 8000 cm^{-1} , at six different temperatures, ranging from $240\text{ }^{\circ}\text{C}$ (panel (a)) up to $505\text{ }^{\circ}\text{C}$ (panel (f)). All the spectra are normalized over the emissivity area of the corresponding sample. Each panel contains an inset that is a zoom in the 400 cm^{-1} - 1200 cm^{-1} spectral window, to show that the dip associated with the SiC Reststrahlen band is strongly suppressed at all the temperatures. All the black soot spectra exhibit no spectral selectivity. By increasing the temperature, the high-frequency tails approach a zero intensity at smaller wavenumbers compared to SiC, determining a steep increase in the emissivity ratio (see Figure 3.8).

Figure 3.8 shows the emissivity ratio between S1 (a), S2 (b), S3 (c), and SiC covered with black soot in the Infrared spectral range, from 30 cm^{-1} to 8000 cm^{-1} , at six different temperatures, ranging from $240\text{ }^{\circ}\text{C}$ (blue curve) up to $500\text{ }^{\circ}\text{C}$ (yellow curve). For a given temperature, each spectrum was normalized over its emissivity area and density. For black soot, a density of $1.860 \pm 0.150 \times 10^{-3}\text{ g/mm}^3$ was used, as reported in [199]. Each curve is the ratio between the normalized 3D graphene spectrum (over its emissivity area and density) and the normalized SiC covered with black soot spectrum (over its emissivity area and density) at the same temperature. The peak related to the SiC Reststrahlen band is strongly suppressed, as can be noticed in the insets of each panel, which are a zoom in the 400 cm^{-1} - 1200 cm^{-1} spectral window. For each temperature, the emissivity ratio is moderately flat until 1000 cm^{-1} , and has a strong increase for larger wavenumbers. In the emissivity ratio with respect to SiC (see Figure 3.5), instead, this increase is visible only for the smallest temperature ($240\text{ }^{\circ}\text{C}$). For both cases, this kind of behaviour is ascribable to the small intensity value of the high-frequency tails, which makes the ratio large. Compared to SiC, black soot spectra tails in the high-frequency region have lower intensity.

In this Subsection, the emissivity properties of three 3D graphene samples synthesized via a chemical vapor deposition technique were investigated in the Infrared spectral range and at six different temperatures, ranging between $240\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$. Measurements reveal that 3D graphenes exhibit broadband, spectrally homogeneous, and high-intensity thermal emissivity. Notably, the thermal emission spectra of the samples display exceptionally strong intensity without autoabsorption features, closely resembling the characteristic behavior of an ideal black body. Comparison with a reference thermal emitter, such as a highly crystalline SiC, was made. A normalization procedure taking into account both the emitting area and the density of all materials allowed us to observe, under the same experimental conditions, that the 3D graphene samples emit more than the reference, reaching emissivity to density ratios around 10^3 - 10^4 times more than the SiC one. Thus, the combination of elevated intensity, broadband, and homogeneous spectral emissivity with the intrinsic properties of 3D graphene, such as its mechanical flexibility, structural robustness, and excellent resistance to elevated temperature, indicates that this material is a highly promising candidate for the development of innovative broadband infrared radiation sources. These unique features not only distinguish 3D graphene from conventional emissive materials but also open new opportunities for its integration into advanced technologies, such as thermal imaging, optoelectronic

devices, energy harvesting, and next-generation sensing platforms.

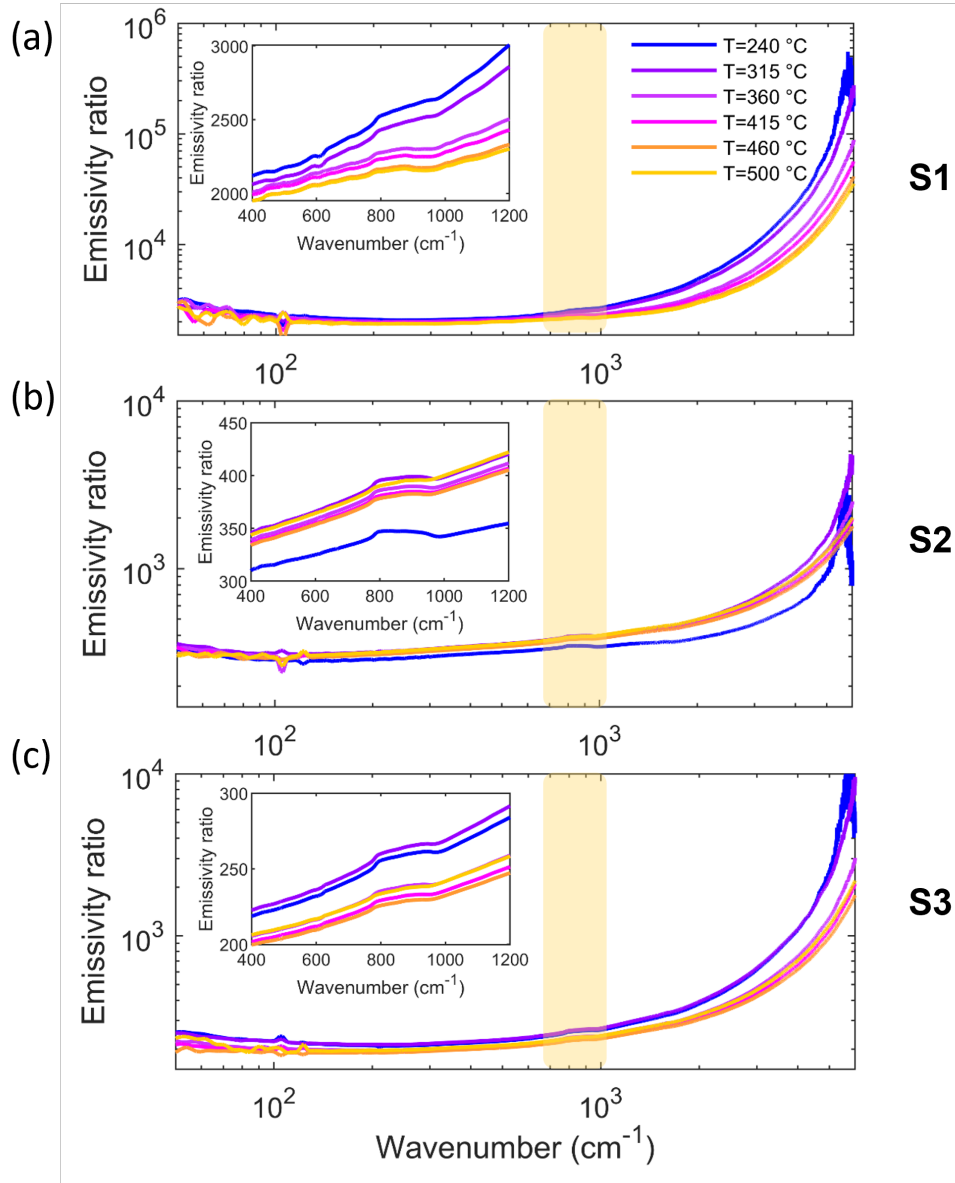


Figure 3.8. Emissivity ratio of S1 (a), S2 (b), and S3 (c) over SiC covered with black soot in the Infrared spectral range, from 30 cm^{-1} to 8000 cm^{-1} , at six different temperatures, ranging from $240 \text{ }^{\circ}\text{C}$ (blue curve) up to $500 \text{ }^{\circ}\text{C}$ (yellow curve). For a given temperature, each spectrum was normalized over its emissivity area and density. For black soot, a density value of $1.860 \pm 0.150 \times 10^{-3} \text{ g/mm}^3$ was used (see [199]). The yellow bars highlight the region where the suppressed peak is present. Each panel contains an inset depicting a zoom in the 400 cm^{-1} - 1200 cm^{-1} spectral window to better show the peak suppression in the emissivity ratio of each sample.

3.1.2 SiC Fractal Metamaterials

The second part of this Section deals with the investigation of both the optical and thermal emission properties of SiC phononic metamaterials based on the Sierpinski

carpet space-filling fractal. To our knowledge, this kind of patterning has been studied by De Nicola et al. in Ref. [200] for gold metamaterials, but not for polar dielectrics, which offer an interesting and physically rich alternative to collective plasmonic excitations.

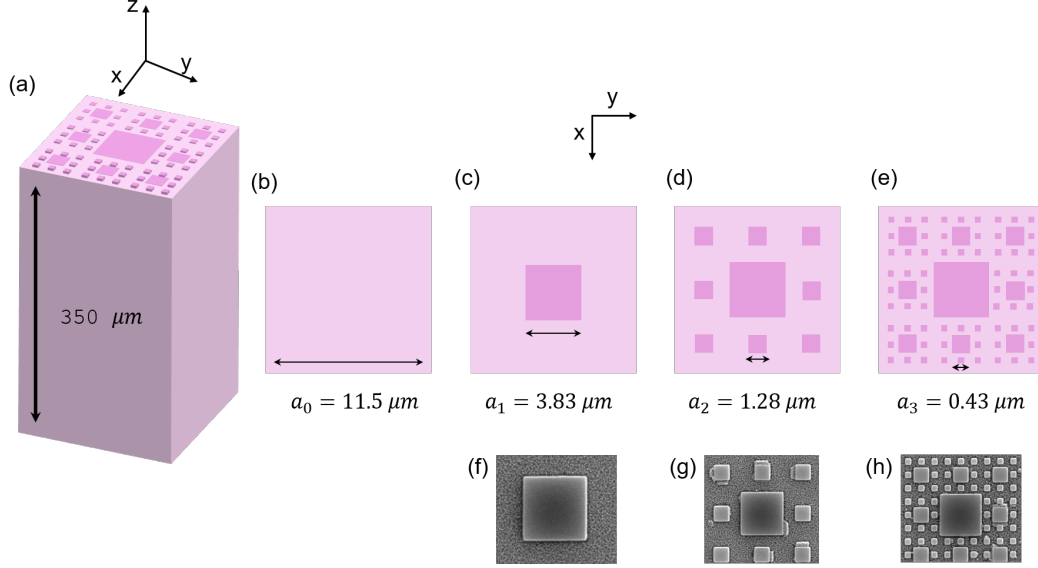


Figure 3.9. Sketch showing the SiC Sierpinski carpet patterned for this work. (a) 3D view of the third-order fractal carpet, with ~ 750 nm high pillars patterned on a $350 \mu\text{m}$ thick SiC sample. The top view of the fractal carpets is shown as well, depicting the square unit cell of size $a_0 = 11.5 \mu\text{m}$, i.e., the periodicity of the system (b), the first order carpet with size $a_1 = a_0/3 = 3.83 \mu\text{m}$ (c), the second order carpet with size $a_2 = a_0/9 = 1.28 \mu\text{m}$ (d), and the third order carpet with size $a_3 = a_0/27 = 0.43 \mu\text{m}$ (e). SEM images of single unit cells of first-order (f), second-order (g), and third-order (h) fractal metamaterials.

Three different orders of complexity were tested to assess how these properties are tailored by reducing the dimensionality of the system. More in detail, measurements were performed in the Infrared spectral range, from 30 cm^{-1} to 8000 cm^{-1} , for both purposes, since surface phonon polariton excitation is constrained within the SiC Reststrahlen band, covering the $\sim 800 \text{ cm}^{-1}$ - 1000 cm^{-1} spectral window. The same 4H $350 \mu\text{m}$ thick Nitrogen-doped SiC wafer, double-side polished, with a $0.01\text{-}0.03 \Omega \times \text{cm}$ resistivity (University Wafer, Inc), used in the previous Subsection, was employed.

Electron Beam Lithography and Dry Etching

Sierpinski carpets [201, 202] can be generated by a recursive geometrical algorithm, as shown in Figure 3.9. Starting from a square unit cell of size a_0 , the first order is obtained by dividing this cell into a 3×3 matrix and drawing a square of size $a_0/3$ in its center. The algorithm can be iterated for the other orders, each time dividing the previous squares in 3×3 matrices, and drawing a square of size $a_n = a_0/3^n$ in the center of the central square of each new matrix. In this work, the following parameters were chosen: $a_0 = 11.5 \mu\text{m}$, $a_1 = a_0/3 = 3.83 \mu\text{m}$, $a_2 = a_0/9 = 1.28 \mu\text{m}$, and $a_3 = a_0/27 = 0.43 \mu\text{m}$, respectively, generating pillars with a ~ 750 nm height, as reported in Figure 3.9 (a) - (e). The periodicity of the system, i.e., the

size of $a_0 = 11.5 \mu\text{m}$, was chosen to allow the excitation of phonon polaritons, as will be demonstrated later.

The same Figure reports SEM images of single unit cells obtained with a ZEISS Sigma 300 machine operating at an accelerating voltage of 20 kV, with a 10x magnification factor of first-order (f), second-order (g), and third-order (h) fractal metamaterials. The patterning of the artificial structures was performed by Dr. Andrea Notargiacomo and Dr. Marialilia Pea at the Institute of Photonics and Nanotechnologies (IFN) of the CNR in Rome. The patterning was achieved using electron beam lithography (EBL) and a lift-off process to obtain a hard mask for etching. The electron resist used for this work was 6% diluted PMMA 650 K, spin-coated at 3000 rpm and baked on a hotplate at 170°C for 5 minutes. The resulting PMMA film thickness is ~ 700 nm. The sample was then loaded into an EBL system (50 kV beam energy) and exposed to a current of 20 nA at an electron dose of 300 mC/cm². Development was made in a MIBK:IPA 1:1 solution for 60 seconds. A mild oxygen plasma treatment was used to clean the surfaces before metal deposition. The metal mask pattern was achieved using an electron beam evaporator to deposit 40 nm of Chromium. Rinse in acetone with sonication was used to produce the dissolution of PMMA and consequently the release of unwanted metal present on the polymer surface, so that the chromium film remains only in the windows created by the EBL process.

The SiC etching for the pillars was performed in a Reactive Ion Etching (RIE) system using the following procedure. The sample was introduced into the vacuum chamber of the RIE system and subjected to a mild oxygen plasma to clean the sample surfaces. An etching step was then performed with the process parameters reported in Table 3.10, leading to an etched thickness of $\sim 550 - 600$ nm as measured with AFM.

CHF_3 (sccm)	SF_6 (sccm)	O_2 (sccm)	Argon	RF power	Gas Pressure (mTorr)	Etching time
100	4.5	10	Valve set to have +20 mTorr of total pressure	100 W on a 20 cm diameter bottom plate corresponding to $\sim 0.3 \text{ W/cm}^2$	85	25 min

Figure 3.10. Reactive Ion Etching parameters for CHF_3 , SF_6 , and O_2 , expressed in Standard Cubic Centimeters per Minute (sccm), the Argon pressure, the Radio Frequency power, the gas pressure, and the etching time.

Optical Properties - Far-Field Data

Far-field normal incidence reflectance measurements (see Chapter 2, Subsection 2.3.2) were performed on a bare SiC sample in the Infrared spectral range, from 400 cm^{-1} to 6000 cm^{-1} , and with a 4 cm^{-1} resolution, to gain information about the behavior of the dielectric function of this material. In fact, the spectral range in which the real part of the dielectric function $\epsilon_1(\omega)$ changes sign allows the excitation of phonon polaritons (see Chapter 1, Appendix B). The electric field was polarized in the plane perpendicular to the c-axis. Figure 3.11 (a) depicts the experimental SiC reflectance (black continuous line) between 400 cm^{-1} and 6000 cm^{-1} . The red dashed line represents the corresponding fit obtained using the RefFIT software, described in Chapter 2, Subsection 2.7.3, considering a slab of finite thickness interfacing with air. Drude-Lorentz contributions were added to reproduce the experimental curve. More in detail, the reflectance curve was fitted using one main oscillator at $\omega_T = 797 \text{ cm}^{-1}$, with linewidth $\gamma = 2 \text{ cm}^{-1}$, corresponding to a transverse optical E_1 mode, and a weak

contribution at $\omega_T=914 \text{ cm}^{-1}$, with linewidth $\gamma=24 \text{ cm}^{-1}$ [22, 23, 24]. Considering the polarization of the incoming electric field and the hexagonal symmetry of the SiC crystal, only modes vibrating in the plane perpendicular to the c-axis can be excited. The high-frequency dielectric function ϵ_∞ was set equal to 6.66 [22, 23, 24]. Additionally, a Drude contribution was added to take into account the Nitrogen doping of the SiC sample, responsible for the reflectance deformation between 800 cm^{-1} and 1000 cm^{-1} , as visible in the inset of Figure 3.11 (a). In this spectral range, SiC exhibits a special behavior typical of some polar materials, having a reflectance value of around $\sim 98 \%$. This special spectral window, named the Reststrahlen band [203], is where electromagnetic radiation cannot propagate within the material medium and exhibits a total external reflectance behavior, sustaining the excitation of evanescent waves. Outside this range, reflectance drops and assumes a nearly constant value of $\sim 20 \%$ up to 6000 cm^{-1} . No further modulations ascribable to electronic transitions are present since SiC is an insulator, and the latter are expected around $\sim 3 \text{ eV}$ [204, 205, 206]. Transmittance is not shown since it is null within the whole explored spectral range due to several factors, such as the Drude contribution, the presence of the Reststrahlen band, and the large thickness of this sample.

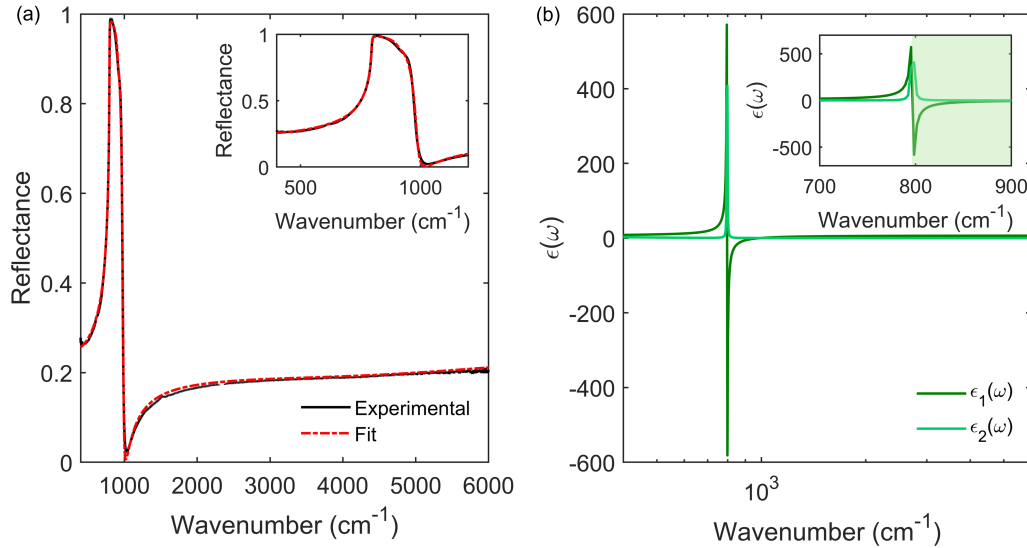


Figure 3.11. (a) Experimental SiC reflectance (black continuous line) and corresponding fit (red dashed line), between 400 cm^{-1} and 6000 cm^{-1} . The same quantity is zoomed in on the inset in the $400 - 1200 \text{ cm}^{-1}$ spectral range. (b) Dielectric function $\epsilon(\omega)$ between 400 cm^{-1} and 6000 cm^{-1} . More in detail, the dark green line corresponds to the real part of the dielectric function $\epsilon_1(\omega)$, while the light green line corresponds to the imaginary part of the dielectric function $\epsilon_2(\omega)$. The inset is a zoom between 700 cm^{-1} and 900 cm^{-1} to show better the region where ϵ_1 turns negative, highlighted by the green band.

From the fitting procedure, the real and imaginary parts of the microscopic optical response functions were extracted. A strong focus was put on the dielectric function, whose expression is [154]:

$$\epsilon(\omega) = \epsilon_\infty \frac{(\omega_L^2 - \omega^2 - i\gamma\omega)}{(\omega_T^2 - \omega^2 - i\gamma\omega)} \quad (3.1)$$

where ω_T and ω_L are the transverse and longitudinal optical phonon frequencies, γ is the damping factor, and ϵ_∞ is the high-frequency dielectric function. Figure

3.11 (b) depicts the real and imaginary parts of the dielectric function $\epsilon(\omega)$, ϵ_1 and ϵ_2 , in dark green and light green, respectively, between 400 cm^{-1} and 6000 cm^{-1} . As expected, ϵ_2 is nearly zero everywhere and peaks at 797 cm^{-1} , the E_1 mode frequency, with a large value of ~ 500 , as shown in the inset of Figure 3.11 (b). On the other hand, the dispersive part ϵ_1 has a maximum value of ~ 600 around 796 cm^{-1} and then a strong drop at 798 cm^{-1} , where it turns negative and remains so until 970 cm^{-1} , as highlighted by the green band in the inset. As already pointed out, this sign change enables the excitation of surface evanescent waves.

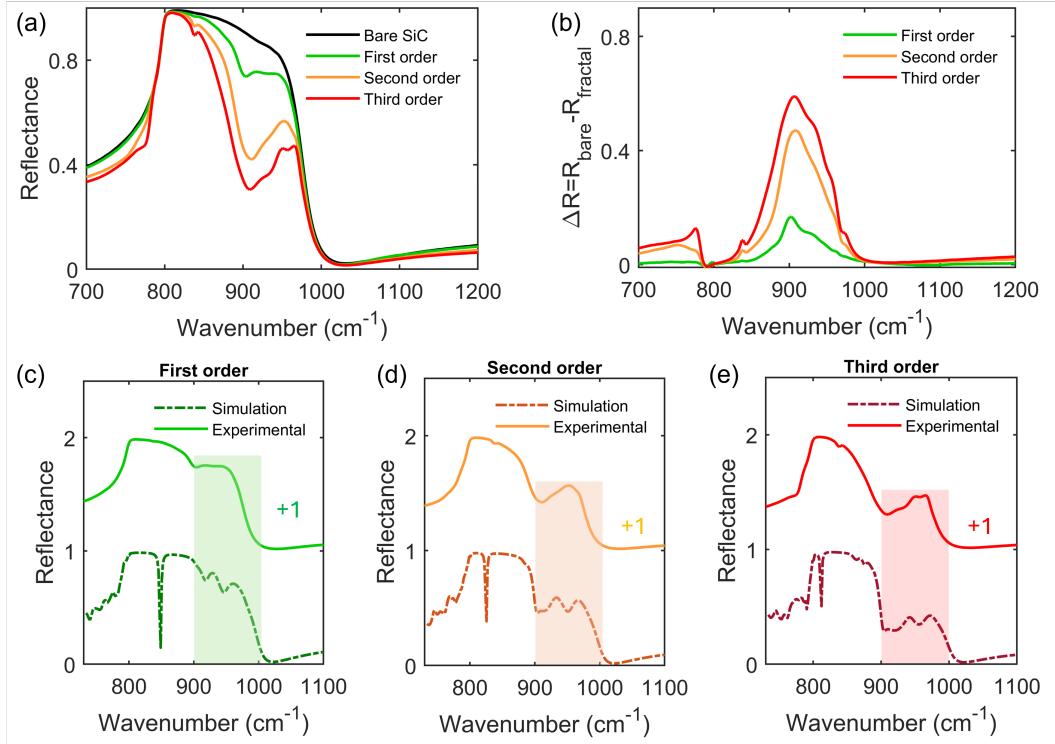


Figure 3.12. (a) Normal incidence reflectance for the bare SiC, first, second, and third order fractal metamaterials, in black, green, orange, and red, respectively, zoomed in between 700 cm^{-1} and 1200 cm^{-1} . (b) Differential reflectance $\Delta R = R_{\text{bare}} - R_{\text{fractal}}$ with respect to the bare SiC sample for the first, second, and third order fractal metamaterials, in green, orange, and red. (c), (d), and (e) Comparison between simulation (dashed) and experimental (continuous) curves for the first, second, and third order fractal, in dark and light green, dark and light orange, and dark and light red, respectively. For better clarity, the experimental curves were shifted along the y-axis. The coloured panels highlight the resonant spectral range.

At this point, the concept of metamaterials was developed. As already anticipated, the periodicity value a_0 was chosen to be $11.5 \mu\text{m}$ to allow excitation and thus modulation of far-field reflectance. Figure 3.12 (a) reports normal incidence reflectance measurements for the bare SiC sample, the first, second, and third order fractal metamaterials, in black, green, orange, and red, respectively, zoomed in the region of interest, between 700 cm^{-1} and 1200 cm^{-1} . A reflectance depression, together with strong modulations, is visible within the Reststrahlen band for the three orders, becoming more pronounced as the order is increased. More in detail, a reflectance drop is present at $\sim 900 \text{ cm}^{-1}$ for the three orders, and resonances are mainly localized in the spectral window extending from 900 cm^{-1} up to 980 cm^{-1} .

The first-order fractal carpet (green curve) has a fairly broad and flat resonance, located in the frequency window from 900 cm^{-1} to 950 cm^{-1} . A closer look reveals the presence of two weak modulations at 914 cm^{-1} and 935 cm^{-1} .

The second-order fractal carpet (orange curve) has a quite strong peak at 945 cm^{-1} , together with weak modulations at 928 cm^{-1} and 966 cm^{-1} , and another modulation at smaller frequencies, at 755 cm^{-1} . At last, the third-order fractal carpet (red curve) exhibits the largest number of resonances, being at 760 cm^{-1} , 928 cm^{-1} , 948 cm^{-1} , and 960 cm^{-1} . Compared to first and second-order fractal carpets, these resonances are well-defined and more easily recognizable. Additionally, the three orders share the presence of a small dip at 838 cm^{-1} , becoming more pronounced with increasing order, attributed to a longitudinal optical (LO) phonon, normally not infrared active and not visible in the bare SiC case, as already observed in the case of SiC cylindrical and rectangular pillars in Refs. [207, 208, 209]. More in detail, this is a weak zone-folded phonon with reduced wave vector $x=1$, thus a high-wavevector state, accessible near the Γ point due to Bragg scattering induced by the periodicity of the crystal lattice [210, 211]. To better enhance the difference between the bare SiC sample and the fractal metamaterials, the differential reflectance, named $\Delta R = R_{bare} - R_{fractal}$, was calculated and depicted in Figure 3.12 (b) between 700 cm^{-1} and 1200 cm^{-1} , in green, orange, and red, for the first, second, and third order fractal cases, respectively. As expected, this quantity peaks at $\sim 900\text{ cm}^{-1}$ for the three samples, becoming more intense as the order increases. Then, each metamaterial exhibits its own resonances, visible as weak modulations. A small peak associated with the longitudinal optical phonon mode at 838 cm^{-1} is present, too.

Before proceeding with the EBL patterning, electromagnetic simulations were carried out via the software COMSOL Multiphysics (see Chapter 2, Section 2.2) to determine the expected spectral position of the resonances, assuming a periodicity of a_0 . The results are shown in Figure 3.12 (c), (d), and (e), where the simulated reflectances (dashed curves) are compared with the experimental curves of the first, second, and third order fractal metamaterials, in dark and light green, dark and light orange, and dark and light red, respectively. All the experimental curves were shifted along the y -axis to better compare the data. Overall, there is a good match. As might be expected, the simulations have better-defined and narrower resonances compared to the experimental curves. Indeed, perfectly shaped pillars were considered in the case of simulations, whereas some imperfections and irregularities are present in the samples, as can be observed in Figure 3.9 (f), (g), and (h). In the first-order case, the simulation (dark green dashed curve) shows two well-defined dips, which appear to merge into one in the experimental case, since the two modulations are weak and broad. The same happens for the second-order case. Finally, the third sample has the best match, as three resonances are detectable in both the simulation and the experimental curves. The dip associated with the zone-folded longitudinal optical phonon is also present in the simulations, but, unlike in the experimental case, it redshifts with increasing order and changes its strength, increasing with decreasing order. This feature was already observed in Ref. [208], where this mode strengthens as the localized SPhP resonances spectrally approach and cross through it, resulting in Fano-like interference during the crossing. On the other hand, this shift was not observed in Ref. [209] for square arrays of cylindrical pillars. Overall, Figure 3.12 demonstrates that the effect of the fractal geometry on SiC is a progressive suppression of the reflectance with increasing fractal order within a frequency window of $\Delta\omega=100\text{ cm}^{-1}$; no multiband resonances are detected, as in the work of De Nicola et al. [200], but for each order, a broad reflectance depression is detected.

The reflectances of the fractal metamaterials in Figure 3.12 (a) were fitted

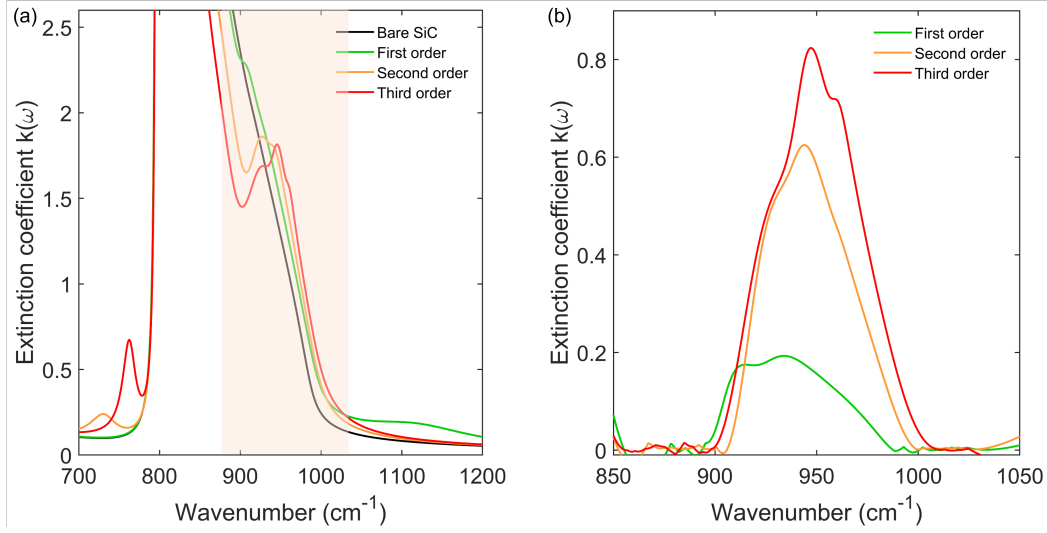


Figure 3.13. (a) Extinction coefficient $k(\omega)$ between 700 cm^{-1} and 1200 cm^{-1} for the bare SiC sample, first, second, and third order fractal metamaterials, in black, green, orange, and red. To appreciate the $k(\omega)$ variation in the resonant spectral range, an orange band was placed in the $850 - 1050 \text{ cm}^{-1}$ spectral window. (b) Extinction coefficient $k(\omega)$ with a baseline correction between 850 cm^{-1} and 1050 cm^{-1} for the first, second, and third order fractal samples, in green, orange, and red.

via a Drude-Lorentz model with RefFIT, and the extinction coefficient $k(\omega)$, i.e., the imaginary part of the refractive index, was extracted and compared with the unpatterned SiC sample. The fitted curves are available in Appendix F. Figure 3.13 (a) reports the extinction coefficient $k(\omega)$ between 700 cm^{-1} and 1200 cm^{-1} for the bare SiC sample, first, second, and third order fractal metamaterials, in black, green, orange, and red. A zoom along the y axis allowed for a better distinction of the modulations. As expected, in all the cases k peaks at 797 cm^{-1} , the frequency of the E_1 mode, reducing its intensity with increasing fractal order, and decreases smoothly to zero at higher frequencies due to the presence of the other mode at 914 cm^{-1} ; additional peaks are present in the patterned samples, at 760 cm^{-1} and 838 cm^{-1} , and several modulations are detectable between 850 cm^{-1} and 1050 cm^{-1} , as highlighted by the orange band in panel (a), associated with surface phonon polariton resonances. A baseline correction was applied to the metamaterial extinction coefficients within this spectral range, following the behavior of bare SiC (black curve), where modulations are absent, to remove the large background contribution from the SiC phonons and isolate the surface phonon polariton resonances, as shown in Figure 3.13 (b). Here, the different peaks are better distinguishable. The two weak reflectance modulations in the first-order fractal metamaterial (green curve in Figure 3.12) (a) are translated here into two peaks at 914 cm^{-1} and 935 cm^{-1} . Concerning the second-order sample (orange curve), there is a stronger peak at 945 cm^{-1} , surrounded by two weaker bands at 928 cm^{-1} and 966 cm^{-1} . Finally, the third-order fractal carpet, in red, exhibits three well-defined peaks at 928 cm^{-1} , 948 cm^{-1} , and 960 cm^{-1} , all of which exceed the intensity of the previous orders.

To understand the nature of the resonances, electric field distribution maps were calculated using COMSOL Multiphysics. Within the simulation, the electric field was polarized along the x direction due to the system's invariance upon a 90°

rotation, whereas during measurements, it was polarized in the xy plane.

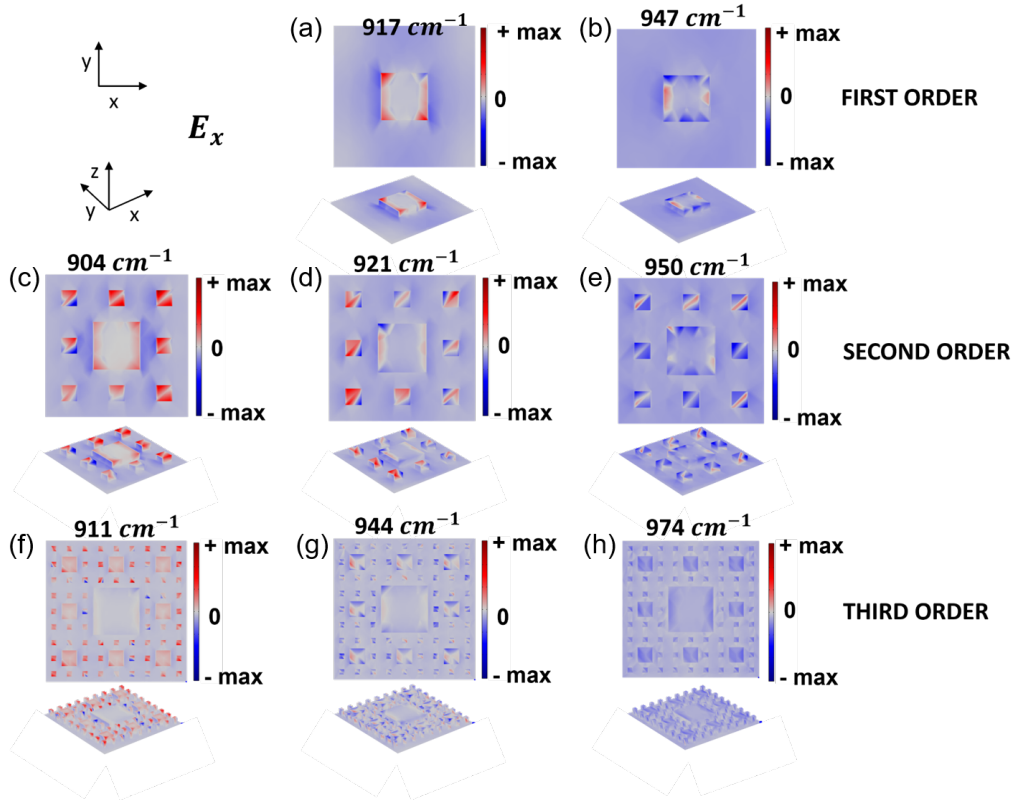


Figure 3.14. Calculated E_x distribution maps within a unit cell for the resonances calculated and reported in Figure 3.12 of first-order, second-order, and third-order fractal metamaterials. For each resonance, both the top view in the xy plane and a 3D view are shown. For a given order, the E_x values were normalized with respect to the maximum and minimum values for that order. In the first-order case, the maps are reported for the resonances at 917 cm^{-1} (a) and 947 cm^{-1} (b), for the second order for the resonances at 904 cm^{-1} (c), 921 cm^{-1} (d), and 950 cm^{-1} (e), and for the third order for the resonances at 911 cm^{-1} (f), 944 cm^{-1} (g), and 974 cm^{-1} (h).

For this reason, Figure 3.14 shows maps for the x component of the electric field E_x of the first-, second-, and third-order fractal metamaterials. A single unit cell is shown. The resonances are the same as those reported in Figure 3.12 (c), (d), and (e). In all cases, the minima of the reflectance modulations were considered. For the first-order, the maps are reported for resonances at 917 cm^{-1} (a) and 947 cm^{-1} (b), for the second order at 904 cm^{-1} (c), 921 cm^{-1} (d), and 950 cm^{-1} (e), and for the third order at 911 cm^{-1} (f), 944 cm^{-1} (g), and 974 cm^{-1} (h). In all cases, the largest contributions to E_x come from the edges or faces of the pillars, as well as some from the area of the substrate close to the pillars; the rest of the substrate makes a nearly null contribution. It is immediately understood that the resonances have different natures because the dipole distributions change with frequency within the same fractal order. In fact, the top face of the pillar has a monopole and a transverse dipolar nature for resonances (a) and (b), respectively; in resonance (a), the top area of the pillar has a positive electric field distribution close to the edges without any nodes, and it is null inside the square; (b), instead, depicts a higher-order localized excitation with sign change and with two nodes along the pillar edges. Additionally,

in the monopole case (a), the field is localized along the edges in the y direction (E_x is nearly in the x direction), while in (b), there is also a negative contribution along x . The same reasoning also holds for the lateral faces of the pillars.

Resonances (c), (d), and (e) have more complex electric field distributions compared to the first-order case. In resonance (c), the first-order square has the same monopole distribution as in resonance (a). The second-order squares, instead, report monopoles positively charged with a node along the diagonal of the top face of the pillars. The lateral faces are mainly negatively charged. The substrate gives a larger contribution to the electric field in the inter-pillar spacings along the x direction. The first-order pillar in resonance (d) has a dipole distribution similar to that in resonance (b), and dipoles on the top faces of the second-order pillars. Resonance (e) has a major negative E_x on all the pillars, with some positive electric field contributions along the diagonal of the top face of the second-order squares.

At last, in the third-order fractal sample, the E_x distributions are even more complex and strikingly different from the previous cases. The largest square in (f) has $E_x \sim 0$ along the edges of the pillar and a weak negative contribution inside the top face. In contrast, all other pillars have a positive charge distribution. In resonance (g), the largest square has a dipolar distribution similar to that of resonances (b) and (d), whereas the medium pillars again have a dipolar distribution (which differs from that of resonance (d)), and the smallest pillars have negative monopoles with nodes along the diagonal of the top face of the pillars. At last, the E_x map for resonance (h) differs from all others because all the pillars have a negative contribution.

In summary, increasing the fractal order generates complex electromagnetic interactions among the pillars. As a result, except for a similar trend in the E_x distribution on the largest pillar, it is understood that the resonance of a given fractal order is not the simple sum of the electromagnetic contributions of the single subunits it is composed of.

Calculated E_z distribution maps, reported in Figure 3.15, give a more powerful and richer explanation of the nature of the resonances; in fact, localized surface phonon polaritons are transverse modes, meaning that their electric field contribution along z contains richer physics. At first sight, the striking difference in comparison with the E_x distribution maps lies in the dipole formations on top of the substrate. As a general rule, these dipoles form around each pillar, with negative and positive E_z components alternated when moving from one pillar to the next neighbor. Resonances (g) and (h) are exceptions since here only one main dipole splits the unit cell along x . Looking at resonance (a), a well-defined dipole depicts the top face of the pillar, with a net node cutting the face into two equal parts. This time, the corners are also polarized with strong + and - contributions, which affect the substrate polarization, and the lateral faces follow the dipolar distribution as in the substrate.

Resonance (b) has a similar dipolar distribution on the top face of the pillar, and an alternated disposition of the + and - components on the faces along y compared to (a). Dealing with second-order samples, it is observed that the largest square has a strong dipole formation on the top face of the pillar in the case of resonance (c), resembling that of (a), and weaker and less defined distributions in (d) and (e). In (c), monopolar distributions are detected on the top faces of the smallest squares, negatively charged on the first column, and positively charged on the third column. The two pillars in the central column show instead dipoles. For (d) and (e), dipole distributions are instead detected. At last, for the third-order sample, the first resonance (f) again has a weak dipole on top of the largest square, whereas in (g) and (h) there are weak contributions on the pillar corners. All medium squares exhibit dipoles with + and - components alternated between one pillar and the next

neighbor, and with different spatial distributions of E_z . The top face of the smallest subunits is mainly composed of monopoles with the same sign as the substrate, as better understood from (g) and (h). Interestingly, the same field pattern is extended over different spatial scales, as observed for the second and third-order fractals, where most of the pillars exhibit dipolar resonances repeated for each pillar size. Therefore, the fractal patterning is responsible for introducing spatial self-similarity, which is the excitation of the same mode with the same electromagnetic field distribution across different spatial scales.

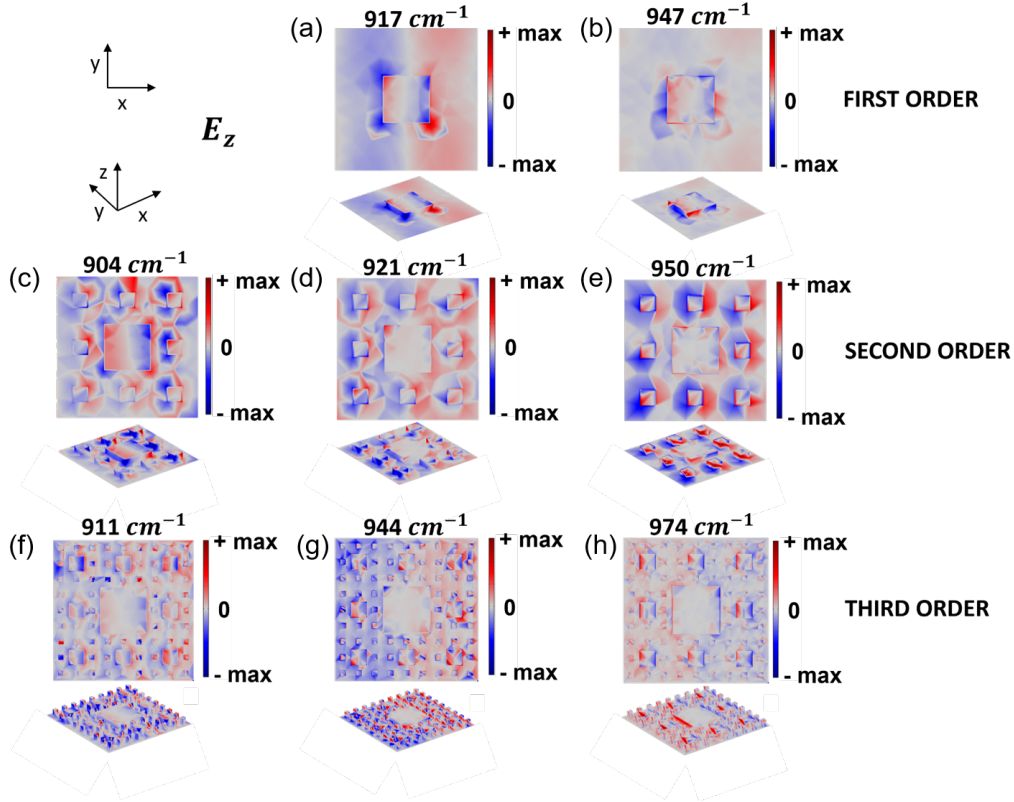


Figure 3.15. Calculated E_z distribution maps within a unit cell for the resonances calculated and reported in Figure 3.12 of first-order, second-order, and third-order fractal metamaterials. For each resonance, both the top view in the xy plane and a 3D view are shown. For a given order, the E_z values were normalized with respect to the maximum and minimum values for that order. In the first-order case, the maps are reported for the resonances at 917 cm^{-1} and 947 cm^{-1} , for the second order for the resonances at 904 cm^{-1} , 921 cm^{-1} , and 950 cm^{-1} , and for the third order for the resonances at 911 cm^{-1} , 944 cm^{-1} , and 974 cm^{-1} .

To resume, from the electric field distribution maps, it can be inferred that complex electromagnetic interactions occur among the various pillars. Moreover, the strong confinement of the modes near the nanostructures reveals the localized nature of the SPhPs, as expected from this type of geometry.

Optical Properties - Near-Field Data

Near-field measurements (see Chapter 2, Section 2.4) were performed on fractal metamaterials to gain information about the excited evanescent waves locally. Indeed,

in the far-field regime, only the diffraction of the excited localized surface modes is captured, with no particular information on the evanescent nature of the surface modes.

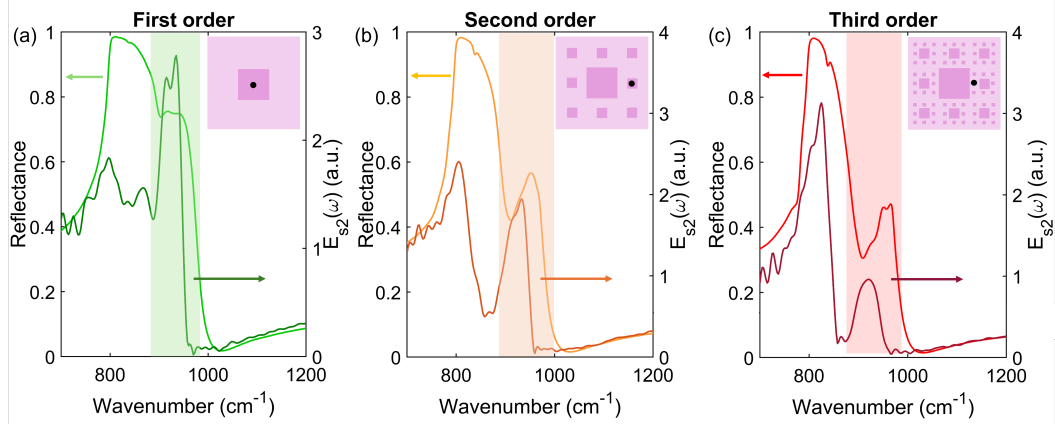


Figure 3.16. Comparison between far-field reflectance and near-field scattered signal between 700 cm⁻¹ and 1200 cm⁻¹. (a) Comparison between far-field reflectance (light green curve) and second-order near-field scattering spectrum $E_{s2}(\omega)$ (dark green curve) obtained from a point in the center of the pillar, as indicated by the black dot in the image, for the first-order fractal sample. (b) Comparison between far-field reflectance (light orange curve) and second-order near-field scattering spectrum $E_{s2}(\omega)$ (dark orange curve) obtained as a weighted average from a point in the center of the medium pillar, as indicated by the black dot in the image, and a point in the center of the first-order pillar, for the second-order fractal sample. (c) Comparison between far-field reflectance (light red curve) and second-order near-field scattering spectrum $E_{s2}(\omega)$ (dark red curve) obtained as a weighted average from a point in the center of the smallest pillar, as indicated by the black dot in the image, a point in the center of the medium pillar, and a point in the center of the first-order pillar, for the third-order fractal sample.

The scattered near-field spectra were acquired by nano-FTIR, as described in Chapter 2, Section 2.4, between 700 cm⁻¹ and 1200 cm⁻¹. More in detail, the normalized amplitude of second-order near-field scattering spectra $E_{s2}(\omega)$ was measured by placing the tip close to one of the first-order squares of the first-order fractal sample, on one of the medium squares of the second-order fractal sample, and on one of the smallest squares of the third-order fractal sample, as shown in Figure 3.16.

Panel (a) shows a comparison between the first-order far-field reflectance, in light green, and the second-order near-field scattering spectrum $E_{s2}(\omega)$, in dark green, obtained from a point in the center of the first-order pillar. Although the far-field signal is mediated over a 270 x 270 μm² spatial area, and the near-field one probes the scattered signal locally, there is a good match in terms of shape and resonance positions. In fact, the two main modulations detectable in the far-field signal at 914 cm⁻¹ and 935 cm⁻¹ are mapped into the two peaks at 915 cm⁻¹ and 935 cm⁻¹ in the near-field regime. The E_1 mode at 797 cm⁻¹ is visible, although less intense than the PhP resonances, and also the longitudinal phonon at 838 cm⁻¹. Compared to the far-field spectrum, there is an additional resonance at 867 cm⁻¹. Concerning the second-order fractal sample (panel (b)), the far-field reflectance, in light orange, is compared with the near-field signal, in dark orange. The latter was obtained by measuring with the tip on a first-order pillar and a medium pillar, and then considering a weighted average of the signals within one unit cell. Indeed, given the inter-pillar spacings in this sample, which are 7.67 μm and 1.28 μm in length, it is likely that the modes can couple at least with the nearest neighbors and interfere.

Thus, to compare far-field and near-field regimes, the signal was approximately averaged out, taking into account the one coming from a first-order pillar and the ones coming from eight medium pillars within one unit cell.

The shapes of the two signals also match in this case, but there are some frequency shifts and a redistribution of the intensities of the various modes. The E_1 mode shifts from 797 cm^{-1} to 807 cm^{-1} , increasing its intensity; the longitudinal phonon frequency remains at 838 cm^{-1} but appears as a flex, and the same is true for the additional peak at 867 cm^{-1} , which is strongly reduced in intensity. Three modulations are still detectable: a weak one at 890 cm^{-1} , and then two peaks at 917 cm^{-1} and 932 cm^{-1} , respectively. These peaks appear redshifted when compared to the far-field reflectance. Finally, panel (c) depicts a comparison between the far-field reflectance of the third-order fractal metamaterial, in red, and the corresponding near-field spectrum, in dark red. The latter was obtained by averaging the near-field signals coming from a first-order pillar, eight medium pillars, and 64 smallest pillars. The frequency shifts are even more pronounced in this last image, starting from the E_1 mode, which shifts to 825 cm^{-1} , gaining even more intensity. A weak mode is still visible at 867 cm^{-1} , and then a broad peak appears at 920 cm^{-1} , followed by a weak shoulder at 960 cm^{-1} . The interplay between modes is again responsible for frequency shifts in this sample, where the inter-pillar spacings vary from $7.67 \text{ }\mu\text{m}$ to $0.42 \text{ }\mu\text{m}$.

To sum up, Table 3.17 reports the SPhP resonance frequencies ω_{0i} , both in near-field and in far-field, for the first, second, and third order fractal metamaterials. As already described, in the first-order case, there is an optimum match between near-field and far-field data. Concerning the other two orders, fewer resonances, which are redshifted, are detectable in the near-field compared to the far-field.

	FIRST ORDER		SECOND ORDER		THIRD ORDER	
	Near-field	Far-field	Near-field	Far-field	Near-field	Far-field
$\omega_{01} (\text{cm}^{-1})$	915	914	917	928	920	928
$\omega_{02} (\text{cm}^{-1})$	935	935	932	945	/	948
$\omega_{03} (\text{cm}^{-1})$	/	/	/	966	960	960

Figure 3.17. Table reporting SPhP resonance frequencies ω_{0i} in cm^{-1} for the first, second, and third-order metamaterials, both in the near-field and far-field cases.

To demonstrate the local nature of these excitations and the interactions among the modes excited on different pillars, normalized nano-FTIR spectra were acquired in various positions along a line of $\sim 3.83 \text{ }\mu\text{m}$ in length, every $\sim 640 \text{ nm}$. Figure 3.18 shows second-order near-field scattering spectra $E_{s2}(\omega)$ acquired between 700 cm^{-1} and 1200 cm^{-1} . For each fractal order, six spectra (in cyan, lilac, blue, violet, fuchsia, pink), acquired in different positions along the x direction, are reported. In general, the modulations in the spectra undergo redshifts and intensity reduction. Panel (a) refers to the first-order sample, showing the evolution of the spectrum reported in Figure 3.16 (a) while moving inside and outside the pillar. As can be seen, the two resonances at 915 and 935 cm^{-1} exchange the relative difference between their intensities; the resonance at 935 cm^{-1} in the cyan spectrum is strongly reduced during the scan along x , until it disappears around the edge of the pillar (violet spectrum).

The resonance at 915 cm^{-1} is also reduced and redshifted during the scan, reaching a value of 905 cm^{-1} at the edge of the pillar. The E_1 mode at 797 cm^{-1} is also

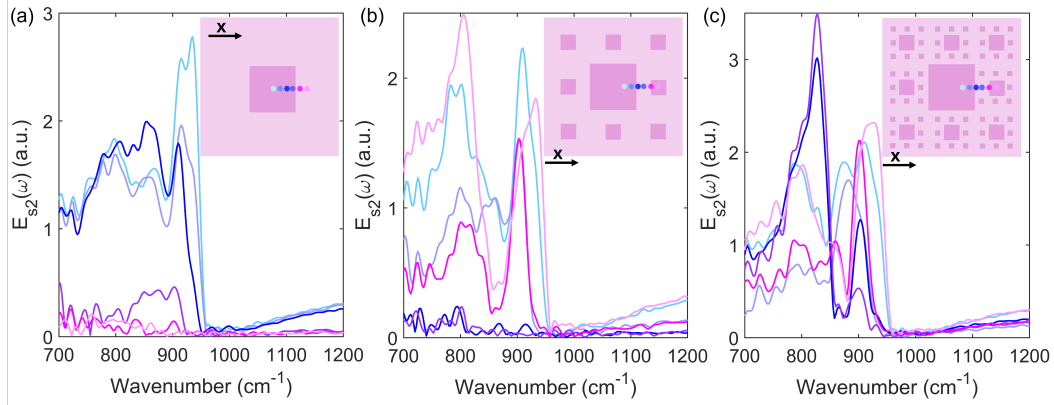


Figure 3.18. Normalized second-order near-field scattering spectra $E_{s2}(\omega)$ acquired between 700 cm^{-1} and 1200 cm^{-1} in different positions of a first-order (a), second-order (b), and third-order (c) fractal samples. The scan is performed along the x direction, acquiring a spectrum every $\sim 640 \text{ nm}$, for a total length of $3.83 \mu\text{m}$. (a) Second-order near-field scattering spectra $E_{s2}(\omega)$ acquired starting from the center of the pillar (cyan spectrum) and moving towards its edge (violet spectrum), and outside the structure (pink spectrum). (b) Second-order near-field scattering spectra $E_{s2}(\omega)$ acquired starting from a point close to the center of the largest pillar (cyan spectrum), and moving towards its edge and in the inter-pillar spacing, reaching the medium pillar (fuchsia and pink spectra). (c) Second-order near-field scattering spectra $E_{s2}(\omega)$ acquired starting from a point close to the center of the largest pillar (cyan spectrum), moving towards its edge and in the inter-pillar spacing, reaching the medium pillar (violet spectrum), and approaching the smallest pillar (fuchsia and pink spectra).

strongly reduced. The fuchsia and pink spectra are associated with the region outside the pillar. In fact, no modulations ascribable to the localized resonances are detectable. Panel (b) refers to the second-order sample. In this case, the scan is performed by starting from a larger pillar and moving toward a smaller one. The inter-pillar spacing is also crossed, as highlighted by the blue and violet spectra, where modulations are absent. This time, the cyan spectrum is obtained from a point closer to the edge of the larger pillar; therefore, the peak at 935 cm^{-1} is already highly reduced compared to the cyan spectrum of panel (a), and the other peak is already redshifted to 910 cm^{-1} . Moving toward the edge of the larger pillar again leads to a redshift of the main peak, which shifts from 910 cm^{-1} to 902 cm^{-1} , until the smaller pillar is reached. Here, the two peaks at 917 cm^{-1} and 932 cm^{-1} , also reported in Figure 3.16 (b), are detected. The strength of the E_1 mode also changes, becoming more intense when the smaller pillar is reached.

At last, panel (c) reports normalized nano-FTIR spectra for the third-order fractal sample. The scan is performed by moving across three pillars of different dimensions: large, small, and medium. The cyan spectrum was obtained from a point closer to the edge of the large pillar, explaining the peak position at 910 cm^{-1} . The violet spectrum corresponds to the position of the small pillar, recovering the spectrum reported in Figure 3.16 (c). However, the pink spectrum, obtained inside the medium pillar, differs from the pink spectrum reported in panel (b). As already pointed out previously, in the third-order fractal sample, additional smaller pillars surround the medium pillar at distances of $0.42 \mu\text{m}$. In this case, mode interactions due to the vicinity of other pillars cannot be neglected, affecting the shape of the recorded spectra.

Figure 3.19 (a-d) depicts images of third-order E_z fields both under resonant (a)

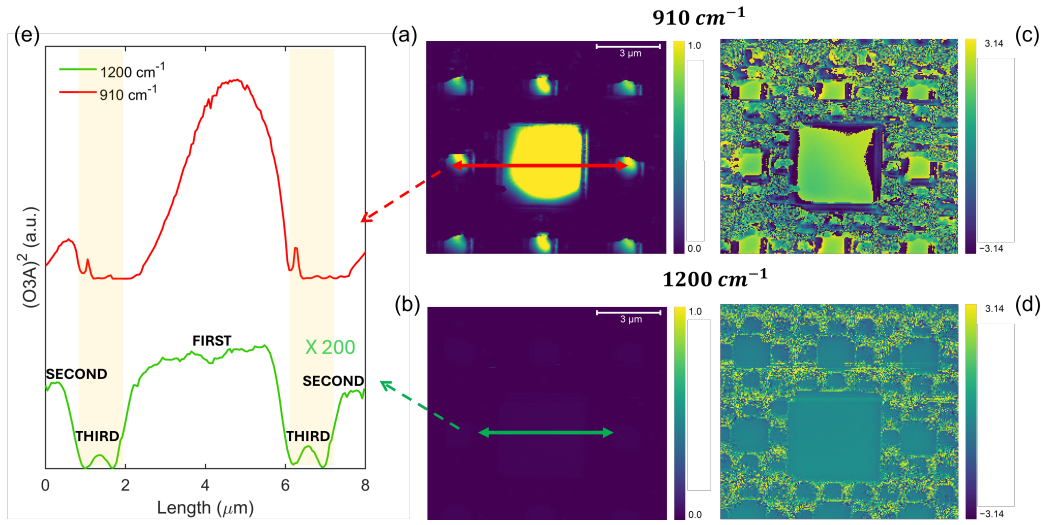


Figure 3.19. SNOM images of third-order E_z fields (E_{s3}), collected in resonant condition at 910 cm^{-1} (a and c), and outside resonance (b and d), at 1200 cm^{-1} , on a unit cell of the third-order fractal sample. More in detail, (a) and (b) are the square of the normalized scattered amplitude signals, E_{s3}^2 , whereas (c) and (d) are the raw phases. (e) E_{s3}^2 obtained along a straight line connecting two medium squares, two small squares, and a first-order square, extracted from the resonant case (red line), and the out-of-resonant case (green line).

and c) and out of resonant (b and d) conditions for a unit cell of the third-order fractal sample. For the first case, the frequency of the main far-field reflectance dip was selected at 910 cm^{-1} , whereas for the second case, a frequency was chosen well outside the Reststrahlen band, at 1200 cm^{-1} . Panels (a) and (b) are the squares of the normalized scattered amplitude signals, E_{s3}^2 , that is, the intensity of the scattered signals, proportional to reflectance, as described in Section 2.4.2, in Chapter 2. In the resonant case (a), strong reflection comes from the center of first- and second-order pillars (yellow areas), and only a weak contribution is associated with the third-order pillars, everything embedded inside a weak background intensity coming from the inter-pillar spacings (blue areas). In addition, a strong contrast is recorded between the center and the edges of these objects, where the signal is strongly suppressed. In the out-of-resonant case, in panel (b), the whole unit cell turns uniformly blue, indicating a weak reflected intensity everywhere. To better stress this difference, panel (e) depicts E_{s3}^2 obtained along a straight line connecting two medium pillars, two smaller pillars, and a first-order pillar, extracted from the resonant case (red line), and the out-of-resonant case (green line, multiplied by 200). A strong variation is present, since the resonant curve records a strong signal coming from the center of the largest pillar, and some signal from the medium pillars, with strong suppression close to the edges; the out-of-resonant curve, instead, mainly reproduces the morphology of the unit cell. In fact, the curve recovers the correct shape of the pillars, showing the presence of edges. Panels (c) and (d) refer to the raw phase of the scattered signal, in resonance and out-of-resonance, respectively. Again, a stronger contrast is visible in panel (c) compared to panel (d). In the resonant case, first-order and medium squares are more highlighted than the smaller ones, whereas in the non-resonant case, a uniform signal distribution is detectable from the whole unit cell. A comparison between panel (a) and simulations in Figures 3.14 and 3.15 reveals a difference in the localization of the modes in the pillar structures:

in the experimental case, the localization is not close to the edges but mainly in the central part of the top face of the pillars. This difference might be ascribed to a non-perfect scan of the tip on top of the sample surface and potential damage to the tip itself.

Thermal Emission Properties

Thermal radiation spectra were acquired in the Infrared spectral range, from 30 cm^{-1} to 8000 cm^{-1} , and from 27°C to 650°C , with the same setup used for 3D graphene samples, described in Chapter 2, Section 2.1. The same measurements were performed on both fractal metamaterials and a reference bare SiC sample to compare their emissivity properties. All the samples have the same areas.

As an example, Figure 3.20 (a) depicts thermal radiation spectra for the third-order fractal metamaterial, from 30 cm^{-1} to 8000 cm^{-1} , and from 27°C (blue curve) to 650°C (green curve). The spectra associated with the other patterned samples and the bare SiC are reported in Appendix F. As expected, all the spectra are broadband and show a clear temperature dependence, following Planck's law. Again, the dip located at 610 cm^{-1} (black arrow) is associated with a Si-Si lattice vibration (a combination of a TO and a TA mode) of the silicon beam splitter [194, 195], and the other dips are associated with absorptions from the internal optics of the interferometer.

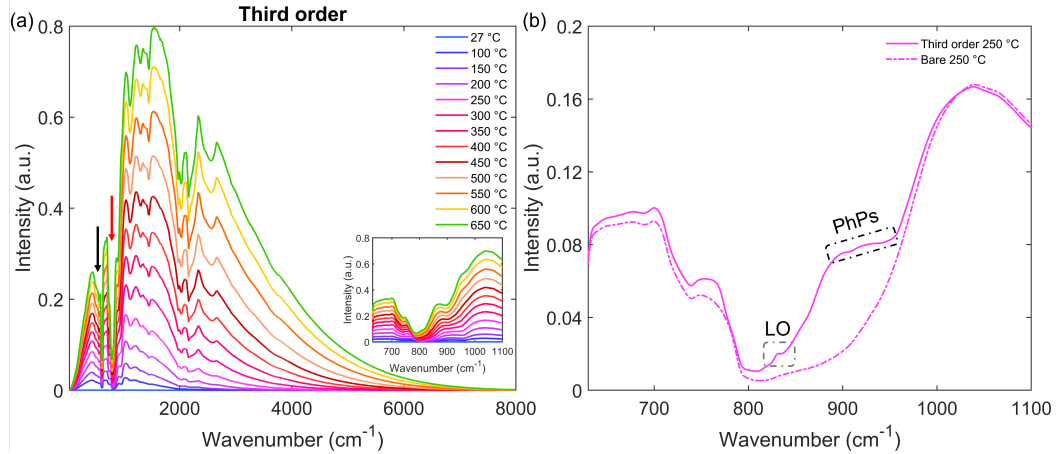


Figure 3.20. (a) Third-order fractal metamaterial thermal radiation spectra in the Infrared spectral range, from 30 cm^{-1} to 8000 cm^{-1} , at thirteen different temperatures, ranging from 27°C (blue curve) up to 650°C (green curve). The black arrow highlights the Si-Si lattice vibration (a combination of a TO and a TA mode) of the silicon beam splitter, whereas the red arrow highlights the SiC Reststrahlen band. The inset is a zoom of the region between 630 cm^{-1} and 1100 cm^{-1} . (b) Comparison between a bare SiC (fuchsia dashed line) and a third-order fractal emission spectrum (fuchsia line) at 250°C , between 630 cm^{-1} and 1100 cm^{-1} . The LO phonon and the PhP modes are highlighted.

The SiC Reststrahlen band, indicated by the red arrow, is present at all temperatures, as more clearly highlighted in the inset of the same Figure, which is a zoom of the region between 630 cm^{-1} and 1100 cm^{-1} . Compared to bare SiC, several modulations appear within this band and change with temperature. Figure 3.20 (b) shows a zoom between 630 cm^{-1} and 1100 cm^{-1} , comparing a bare SiC (fuchsia dashed line) and a third-order fractal emission spectrum (fuchsia line) at 250°C . The patterned curve shows some deviations compared to the unpatterned one.

The weak peak detectable at 838 cm^{-1} is mapped to the longitudinal optical phonon present in the optical measurements. Furthermore, the spectrum exhibits two dips at 910 cm^{-1} and 950 cm^{-1} , associated with phonon-polariton modes. For further comparison between thermal radiation spectra of bare and fractal metamaterial samples at the various temperatures, see Figures F.3, F.4, and F.5 in Appendix F.

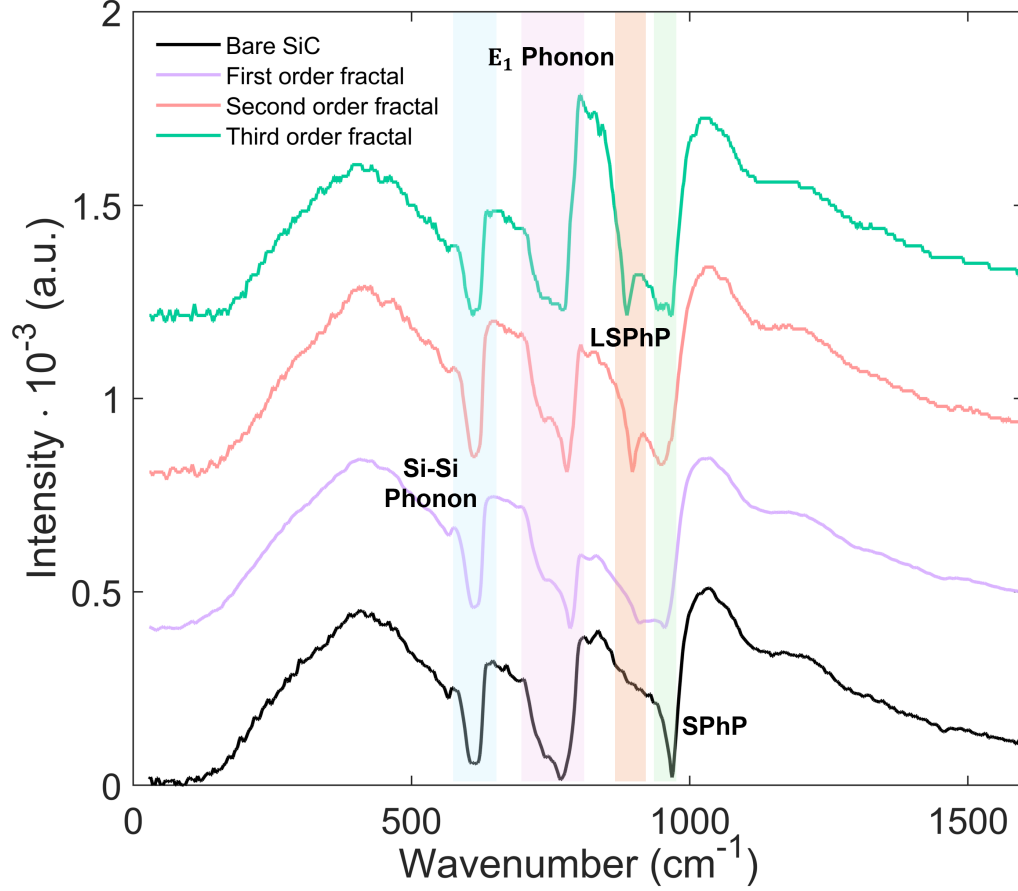


Figure 3.21. Room temperature thermal radiation spectra of bare SiC (black curve), first-order (lilac curve), second-order (red curve), and third-order (green curve) fractal samples, between 30 cm^{-1} and 1600 cm^{-1} . Several excitations are highlighted by colored areas: cyan for the Si-Si lattice vibration, at 610 cm^{-1} , pink for the E_1 phonon, at $\sim 770 \text{ cm}^{-1}$, orange for the localized surface phonon polaritons induced by the artificial patterning, at $\sim 900 \text{ cm}^{-1}$, and green for the surface phonon polariton, at $\sim 968 \text{ cm}^{-1}$.

Room temperature thermal radiation spectra are displayed in Figure 3.21 for bare SiC (black curve), first-order (lilac curve), second-order (red curve), and third-order fractal samples (green curve), zoomed in between 30 cm^{-1} and 1600 cm^{-1} . Spectra were displaced along the y axis to obtain a better comparison. All the curves contain the dip corresponding to the Si-Si lattice vibration, at 610 cm^{-1} , highlighted by the cyan band. Additionally, at 25°C , it is possible to distinguish two separate dips that merge with increasing temperature, as observed in Figures 3.20 and F.2: one at $\sim 770 \text{ cm}^{-1}$ (pink band), and one at $\sim 960 \text{ cm}^{-1}$ (green band). The first is associated with the E_1 transverse optical phonon, whereas the second is associated with surface phonon polaritons, detected as missing radiation in the far-field regime. Indeed, in bare SiC, this dip is located at 968 cm^{-1} , where $\epsilon_1(\omega) \sim -1$ (see Figure 3.11 (b)).

When this condition is satisfied, thermal radiation is dominated by the resonant excitation of surface phonon polaritons, as observed in the behavior of LDOS, whose expression for a planar thermal emitter is:

$$LDOS(d, \omega) = \frac{1}{16\pi\omega d^3} \frac{Im[\epsilon(\omega)]}{|1 + \epsilon(\omega)|^2} \quad (3.2)$$

as already reported in Equation 1.12 in Chapter 1. This expression has a strong increase when $\epsilon_1(\omega) \sim -1$. The same behavior is detected in the patterned samples, where an additional dip occurs at 910 cm^{-1} , 897 cm^{-1} , and 887 cm^{-1} for the first, second, and third-order fractals, respectively, highlighted by the orange band. This dip is associated with the excitation of localized surface phonon polaritons, induced by the geometry of the artificial patterning.

To understand how this spectral region is affected by temperature within the same fractal order, each curve was normalized over the spectrum at 650°C (green curve in Figures F.2 (a-c) and 3.20 (a)) of the same order, as shown in Figure 3.22 (a-d), between 700 cm^{-1} and 1000 cm^{-1} , for bare SiC (a), first order (b), second order (c) and third order (d) fractal metamaterials. As a general rule, for bare SiC and each order, the modulations redshift and change their strength with increasing temperature.

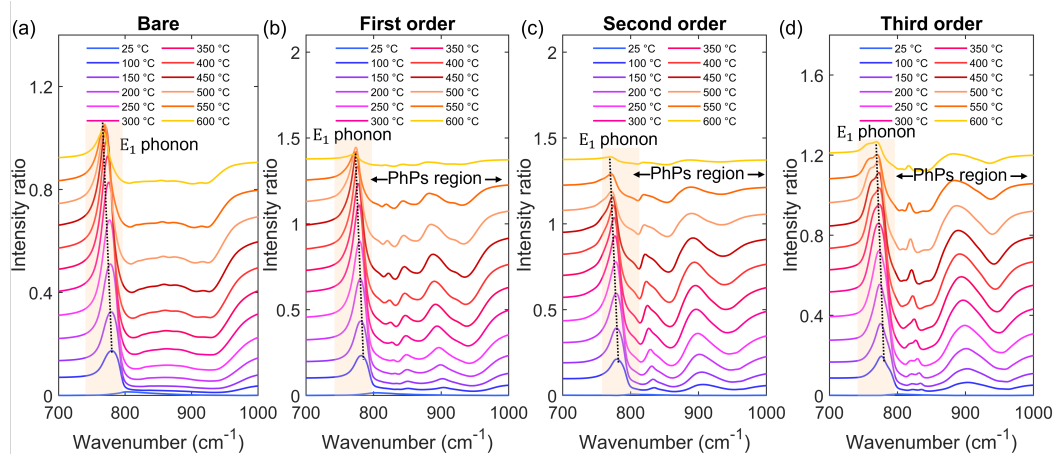


Figure 3.22. Thermal radiation spectra from 27°C (blue curve) to 600°C (yellow curve) normalized over the spectrum at 650°C for bare SiC (a), first-order (b), second-order (c), and third-order (d) fractal metamaterials. These intensity ratios are zoomed in between 700 cm^{-1} and 1000 cm^{-1} . The orange band highlights the IR active E_1 phonon mode, common to all panels, whereas the region between 800 cm^{-1} and 1000 cm^{-1} , corresponding to phonon-polariton excitations, is common to panels (b), (c), and (d).

The main peak at low frequency corresponds to the transverse phonon detectable in optical measurements at 797 cm^{-1} , and it is the only excitation visible in bare SiC ((a)). This phonon undergoes a redshift of 3.4% , moving from 797 cm^{-1} at 27°C to 770 cm^{-1} at 600°C for all samples. In panel (b), which corresponds to the first-order fractal sample, there are four peaks that redshift and change their strength with increasing temperature. The first modulation corresponds to the longitudinal optical phonon at 838 cm^{-1} ; the second modulation is at 852 cm^{-1} , and the third at 904 cm^{-1} . An additional modulation at 923 cm^{-1} appears starting from 250°C . Panel (c) is associated with the second-order sample. Here, the longitudinal optical phonon is again detected at 838 cm^{-1} and undergoes a redshift of 2.5% with increasing

temperature, reaching 817 cm^{-1} at 600°C . An additional shoulder appears at 846 cm^{-1} and redshifts up to 833 cm^{-1} at 600°C , undergoing a redshift of 1.5 %, and a strong modulation at 906 cm^{-1} redshifts to 883 cm^{-1} at the highest temperature, with a 2.5 % redshift. Panel (c) shows the normalized thermal radiation spectra for the third-order fractal. Here, more modulations occur: the first is embedded within the E_1 mode at 797 cm^{-1} , initially appearing as a high-frequency shoulder of this phonon mode, located at 790 cm^{-1} at room temperature, and progressively redshifts with increasing temperature, becoming a low-frequency shoulder of the E_1 mode. At the highest temperature, the modulation peaks at 758 cm^{-1} , with a total redshift of 4 %. In addition to the longitudinal optical phonon located at 838 cm^{-1} , other modulations occur at 823 cm^{-1} , 844 cm^{-1} , and 904 cm^{-1} .

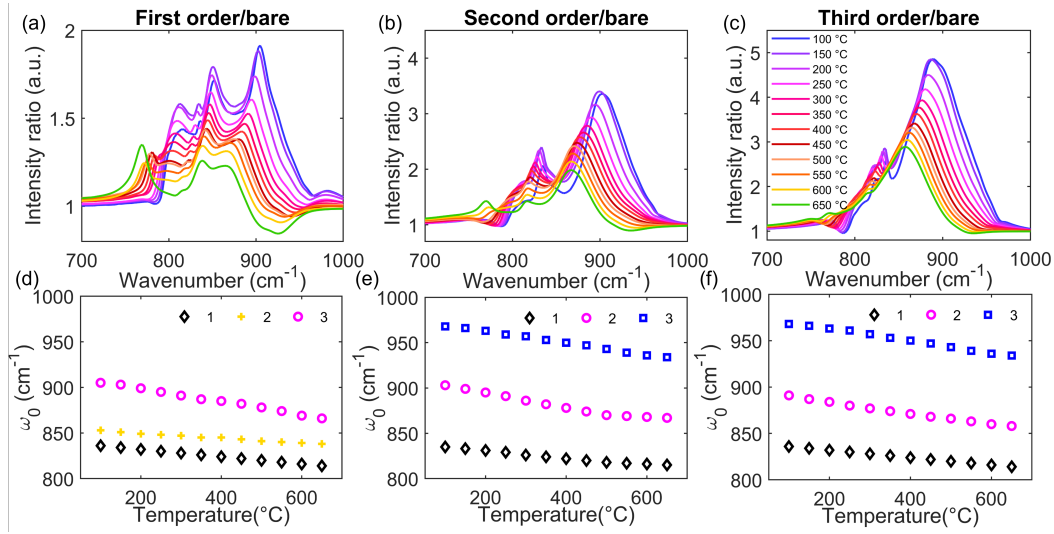


Figure 3.23. Intensity ratio between first-order (a), second-order (b), third-order (c) fractal carpet thermal radiation spectra and bare SiC at the same temperature, from 100°C (blue curve) to 650°C (green curve), between 700 cm^{-1} and 1000 cm^{-1} . Resonance frequency ω_0 , expressed in cm^{-1} , versus temperature, of the different modulations of first-order (d), second-order (e), and third-order (f) samples.

To better quantify and visualize the difference between patterned and bare SiC samples as a function of temperature, the intensity ratio between the spectra reported in Figures F.2 (b), (c), 3.20 (a), and F.2 (a) was performed. Figure 3.23 reports the intensity ratio between first-order (a), second-order (b), third-order (c) samples and the bare SiC spectra at the same temperature, in the spectral range extending from 700 cm^{-1} and 1000 cm^{-1} , and from 100°C (blue curve) to 650°C (green curve). Strong modulations appear for the three orders, following a common trend *vs* temperature: the intensity ratio decreases and the peaks redshift with increasing temperature. This behavior reflects the trend visualized in Figures F.3, F.4, and F.5, where the difference between thermal radiation spectra of bare and fractal metamaterial samples is less prominent as the temperature increases. For a given temperature, a comparison between ratios of different orders reveals that the modulation strength is larger as the fractal order increases. In panel (a), the modulation corresponding to the longitudinal optical phonon reduces its intensity ratio value of 31 % between 100°C and 650°C . The second resonance at 850 cm^{-1} reduces its value of 30 %, and the third at 905 cm^{-1} of 36 % between 100°C and 650°C . In panel (b), the longitudinal optical phonon reduces its intensity by 40

%, the second resonance at 900 cm^{-1} by 41 %, and the third at 970 cm^{-1} by 23 % within the same temperature window. At last, in panel (c), the longitudinal optical phonon reduces its intensity by 35 %, whereas the other two resonances by 40 % and 22 %, respectively.

Panels (d), (e), and (f) show the frequency ω_0 of the various resonances, obtained from the peaks of panels (a), (b), and (c) *vs* temperature for the first-order, second-order, and third-order fractals, respectively. All of them are redshifted with increasing temperature. The black diamonds are associated with the longitudinal optical phonon, which experiences a redshift of 2.5 % from 100°C to 650°C for the three orders. In panel (d), the other resonance (yellow crosses) undergoes a redshift of $\sim 4\%$, and the third resonance (fuchsia circles) of 2 %. In panel (e), the second resonance has a redshift of 4 %, and the third resonance of 3.5 %, and in panel (f) the second resonance has a redshift of 3.7 %, and the third of 3.5 %.

To conclude this Subsection, a proof of the validity of Kirchhoff's radiation law is given. Figure 3.24 compares the differential reflectance $\Delta R = R_{\text{bare}} - R_{\text{fractal}}$, reported in Figure 3.12 (b) at 25°C for fractal samples of the first order in green (a), the second order in orange (b), and the third order in red (c), with the intensity ratio at 100°C for the three orders (blue curves). In general, a good match is found for the three fractals, with some deviations that are more pronounced in the case of the first-order fractal carpet. The maxima of the differential reflectance and intensity ratio at $\sim 900 \text{ cm}^{-1}$ are superimposed in the case of panel (a), whereas a redshift of 5 cm^{-1} and 16 cm^{-1} of the maxima of the intensity ratio curves is found in panels (b) and (c), respectively. The longitudinal optical phonon undergoes a small redshift, from 838 cm^{-1} in the differential reflectance to 835 cm^{-1} in the intensity ratio.

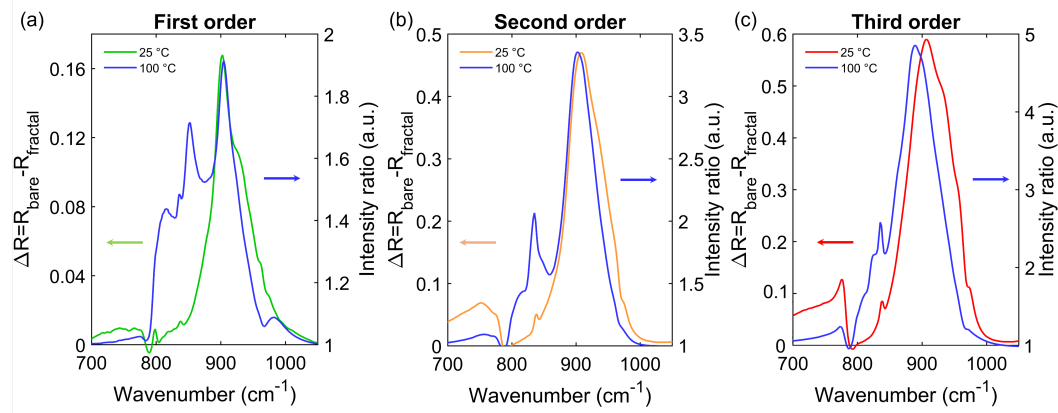


Figure 3.24. Comparison between differential reflectance $\Delta R = R_{\text{bare}} - R_{\text{fractal}}$ at 25°C for fractal samples of the first order in green (a), second order in orange (b), and third order in red (c), with the intensity ratio at 100°C for the three orders (blue curves).

These redshifts are in line with the fact that the intensity ratio data reported in this Figure were obtained at 100°C and not at 25°C like the differential reflectance data.

In this Subsection, the optical and thermal emission investigation of a SiC-based phononic fractal metamaterial was presented. Three fractal orders were fabricated to study the alteration of optical and thermal properties as the spatial scale decreases, assessing the formation and diffraction of localized surface phonon polaritons for the three cases. The modulation of these properties is constrained within the SiC Reststrahlen band. Far-field and near-field measurements were performed to

investigate the macroscopic and local nature of these surface excitations, finding a match between the two regimes. Electromagnetic simulations were performed via the COMSOL Multiphysics software to predict the resonance behavior and understand the nature of the excited modes. Strong electric field confinement was found near the nanostructures. Additionally, it was understood that the resonance of a given fractal order is not the simple sum of the electromagnetic contributions of the single subunits it is composed of due to the interactions among the excited modes. Indeed, non-trivial electric field distributions were found, meaning that complex electromagnetic interactions occur among the various pillars. Finally, thermal emission properties were probed over frequency and temperature and compared to those of bare SiC, finding that the emitted thermal spectrum of the patterned sample is modified in the far-field regime by the polariton modes, following a specific trend. The modulation increases when the complexity of the system increases, i.e., when the fractal order is increased, in agreement with the reflectance suppression observed in far-field measurements, as expected from Kirchhoff's law. For a given order, the effect is more pronounced at lower temperatures, while increasing temperature leads to a gradual broadening of the resonant features. To sum up, these results demonstrate that fractal patterning provides an effective strategy for tuning optical and thermal emission properties, enabling a geometry-controlled enhancement of the response within a broad spectral window of approximately $\Delta\omega = 100 \text{ cm}^{-1}$. This broadband reflectance suppression and thermal emission enhancement, distinct from the narrow resonances typically observed in conventional photonic structures, may be particularly attractive for the development of broadband infrared thermal sources. Unlike previous studies on plasmonic fractal metasurfaces [200], where spatial self-similarity was directly mapped onto spectral self-similarity, the present phononic system exhibits a more complex spectral response governed by collective polaritonic interactions.

3.2 Topological Insulator Thin Films

In this Section, the main results associated with the thin 2D topological insulators, such as Bi_2Se_3 , Bi_2Te_3 , Sb_2Te_3 , and $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ alloys, are shown.

As described in Section 2.9 in Chapter 2, these films were grown onto 500 μm thick $\text{Al}_2\text{O}_3(0001)$ substrates via Molecular Beam Epitaxy at Rutgers University, New Jersey, USA, in Professor Oh's laboratory. Figure 3.25 shows RHEED patterns for each of the basic compounds, obtained in situ. More in detail, panel (a) is associated with a 10 QL Bi_2Se_3 film at 300 $^\circ\text{C}$, panel (b) with a 20 QL Bi_2Te_3 film at 260 $^\circ\text{C}$, and panel (c) with a 20 QL Sb_2Te_3 film at 260 $^\circ\text{C}$. In all the images, vertical streaks are visible, indicating the 2D nature of the grown films, as explained in Subsection 2.5.2 of Chapter 2. In addition, some bright spots are also present. The latter indicates atomically flat morphology and high crystallinity of the films. To assess the symmetry of the obtained crystals, two images were obtained for each film upon its rotation along the azimuth direction. In fact, two sets of RHEED spacings appear every 30 $^\circ$ when rotating each film, and the relative ratio of the distance between two adjacent vertical streaks is $\sqrt{3}$, corresponding to the hexagonal symmetry, as expected for these materials [212]. Indeed, Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 crystallize in the same rhombohedral structure with space group $D5\ 3d\ (R\bar{3}m)$ and have five atoms in the primitive unit cell.

The crystal structure of Bi_2Se_3 is shown as an example in Figure 3.25(d), and consists of a layered structure where individual layers form a hexagonal lattice [213]. The important symmetry axes are a trigonal axis (three-fold rotation symmetry), defined

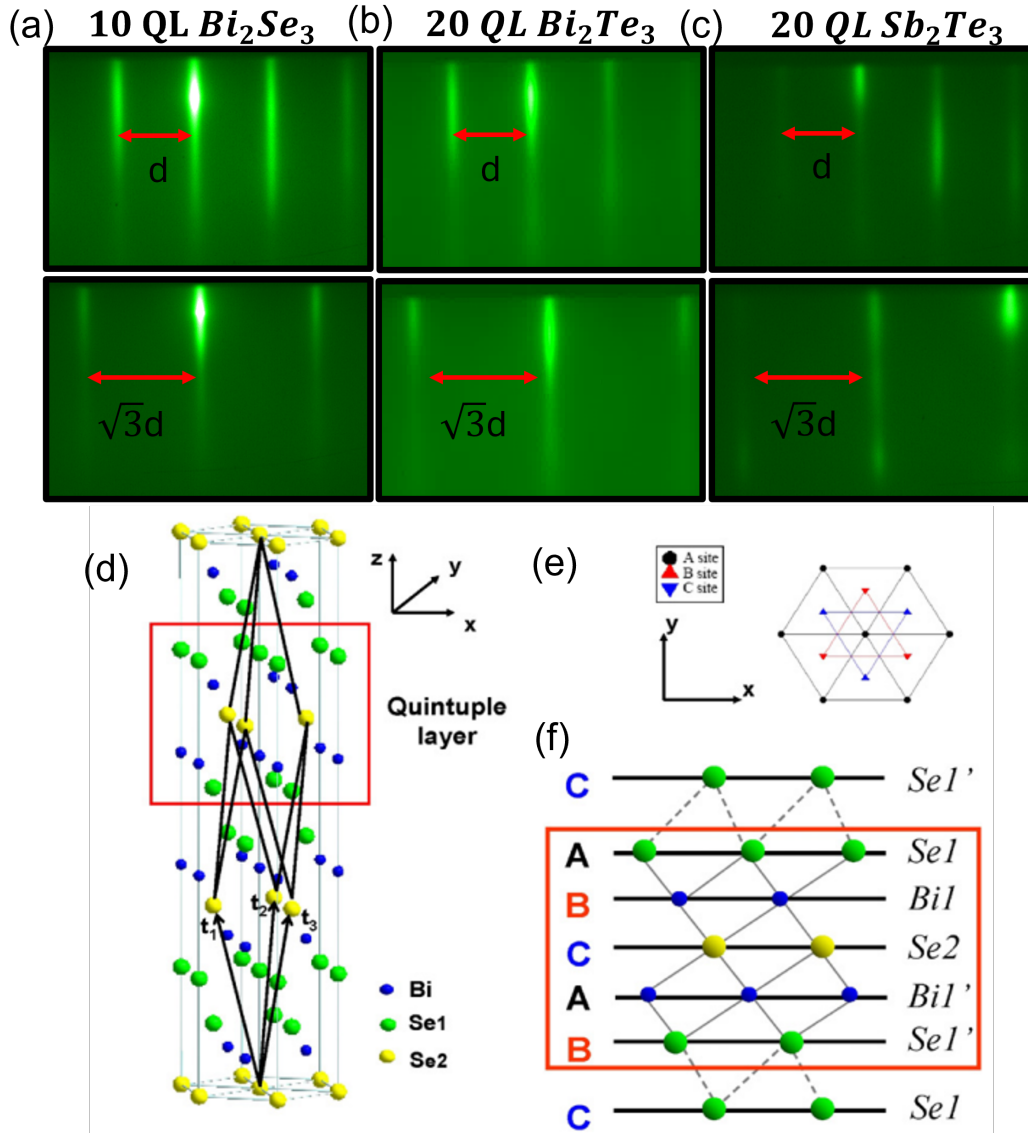


Figure 3.25. RHEED patterns of 10 QL Bi_2Se_3 at 300 °C (a), 20 QL Bi_2Te_3 at 260 °C (b), and 20 QL Sb_2Te_3 at 260 °C (c). Sharp streaks, indicating the 2D nature of the grown films, and bright specular spots are visible in all the images. Two sets of RHEED spacings appear every 30° when rotating each film. The relative ratio of the two spacings is $\sqrt{3}$, corresponding to the hexagonal symmetry, as expected for these materials. (d) Example of Bi_2Se_3 crystal structure with three primitive lattice vectors denoted as t_1 , t_2 , and t_3 . A quintuple layer with Se1–Bi1–Se2–Bi1'–Se1' is illustrated inside the red square. (e) Top view along the z-direction. The triangle lattice in one quintuple layer has three different positions, denoted as A, B, and C. (f) Side view of the quintuple layer structure. Along the z-direction, the stacking order of Se and Bi atomic layers is ...–C(Se')–A(Se1)–B(Bi1)–C(Se2)–A(Bi1')–B(Se1')–C(Se1)–.... The Se1 (Bi1) layer can be related to the Se1' (Bi1') layer by an inversion operation in which the Se2 atoms have the role of inversion centres. Obtained from Ref. [213].

as the z -axis, a binary axis (two-fold rotation symmetry), defined as the x -axis, and a bisectrix axis (in the reflection plane), defined as the y -axis. The material consists of five-atom layers stacked along the z direction, referred to as a quintuple layer (QL), with 1 QL $\sim$ 1 nm. Each QL consists of five atoms per unit cell with two equivalent Se atoms denoted by Se1 and Se1', two equivalent Bi atoms denoted by Bi1 and Bi1', and a third Se atom denoted by Se2 in Figure 3.25 (f). The coupling between two atomic layers within a QL is by strong chemical binding, while that between QLs is much weaker and is predominantly of the van der Waals type. The primitive lattice vectors t_1 , t_2 , and t_3 , and rhombohedral primitive unit cells are shown in Figure 3.25 (d). The Se2 site plays the role of an inversion center. Under inversion, Bi1 is mapped to Bi1' and Se1 is mapped to Se1'.

Appendix G reports ω - 2θ and azimuth X-ray diffraction (XRD) patterns of a 20 QL Bi_2Se_3 sample, together with a Scanning Tunneling Microscopy (STM) image of a 100 QL Bi_2Se_3 .

3.2.1 Optical Properties of Topological Insulators

The optical properties of thin 2D topological insulators were probed in a wide spectral range, ranging from 40 cm^{-1} to 20000 cm^{-1} , through the use of the Vertex 70V coupled with a Hyperion Microscope, as described in Subsection 2.3.2, Chapter 2. Normal incidence transmittance and reflectance measurements were performed, with the electric field polarized in the plane perpendicular to the c -axis.

Bi_2Te_3 , Sb_2Te_3 , and $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ Alloys

Initially, a class composed of five films is proposed, including Bi_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$, and Sb_2Te_3 . All share the same thickness, equal to $\sim 20 \text{ nm}$. The idea behind this class of materials is to show that the Fermi level position is changed from above to below the Dirac point while moving from Bi_2Te_3 to Sb_2Te_3 , increasing the Sb content through the alloys, and how this change affects the Seebeck coefficient and transport properties.

Figure 3.26 (a) depicts the transmittance of Bi_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$, and Sb_2Te_3 , in blue, red, orange, yellow, and light-blue, respectively, in the Infrared spectral range, from 40 cm^{-1} to 8000 cm^{-1} and with a 4 cm^{-1} resolution, together with a reference Al_2O_3 substrate (black curve). Due to the strong Al_2O_3 resonances, [214, 215], transmittance is zero in the 300 cm^{-1} - 1400 cm^{-1} spectral region, whereas it exhibits a nonzero behavior outside this band. More in detail, between 40 cm^{-1} and 80 cm^{-1} , phonon modes associated with Bi_2Te_3 and Sb_2Te_3 are visible, as highlighted in the inset of the same Figure. Since the electric field is polarized in the plane perpendicular to the c axis, only E_u modes are excited [216]. Bi_2Te_3 has two phonon modes, an E_u^1 mode at $\sim 52 \text{ cm}^{-1}$, and a weak E_u^2 mode at $\sim 95 \text{ cm}^{-1}$ [217]. Sb_2Te_3 , instead, has an active IR E_u mode at $\sim 62 \text{ cm}^{-1}$ [218]. Both modes at $\sim 52 \text{ cm}^{-1}$ and at $\sim 62 \text{ cm}^{-1}$ are detected in the three alloys, the intensity of the Bi_2Te_3 mode increasing with increasing Bi content, as highlighted by the two black arrows. Figure 3.26 (b) better stresses this concept, illustrating the corresponding absorbance of the FIR modes, zoomed in between 40 cm^{-1} and 85 cm^{-1} . The absorbance was calculated as $-\ln(T)$, where T is the transmittance. A baseline correction was then applied following the optical behavior of Sapphire, for which modulations are absent in this frequency range. A slight blueshift of the two modes is visible in all alloy compounds, since the first mode shifts to $\sim 53 \text{ cm}^{-1}$ and the second to $\sim 67 \text{ cm}^{-1}$. Additionally, the fitting curves

for each mode are shown, demonstrating that the alloy's curves are a convolution of the Bi_2Te_3 and Sb_2Te_3 modes.

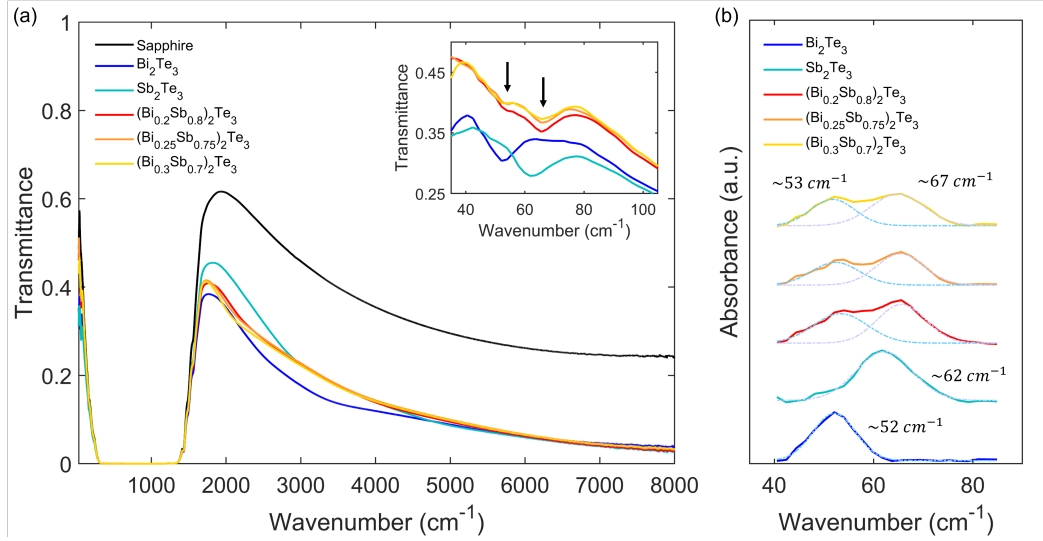


Figure 3.26. (a) Normal incidence Infrared transmittance, from 40 cm^{-1} to 8000 cm^{-1} , of Bi_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$, and Sb_2Te_3 , in blue, red, orange, yellow, and light-blue, respectively. The reference Sapphire substrate transmittance is shown in black. The inset depicts a zoom from 35 cm^{-1} to 100 cm^{-1} , to show the Infrared E_u active modes of these compounds, highlighted by two black arrows. (b) Absorbance of the phonon modes, zoomed between 40 cm^{-1} and 85 cm^{-1} . The Bi_2Te_3 E_u^1 mode at $\sim 52\text{ cm}^{-1}$ (blue curve) and the Sb_2Te_3 E_u mode at $\sim 62\text{ cm}^{-1}$ (light-blue) are also detected in the three alloys, as highlighted by the two fitting curves corresponding to the two modes; the mode at $\sim 52\text{ cm}^{-1}$ becomes increasingly intense with increasing Bi content.

Figure 3.27 reports normal incidence reflectance measurements of Bi_2Te_3 , Sb_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$, and the reference Al_2O_3 , in blue, light-blue, red, orange, yellow, and black, respectively. Figure 3.27 (a) is a zoom in the 40 cm^{-1} - 1000 cm^{-1} spectral range. Here, four distinct phonon modes that can be attributed to the Al_2O_3 substrate are recognizable, at 385 cm^{-1} , 442 cm^{-1} , 569 cm^{-1} , and 635 cm^{-1} , explaining the null transmittance in this spectral window [214, 215].

Again, only E_u modes can be excited in normal incidence conditions since sapphire has a rhombohedral crystal structure like Bi_2Te_3 and Sb_2Te_3 , and only modes vibrating perpendicular to the c axis can be probed. All films follow the reflectance behavior of the first three phonon modes. In contrast, deviations are visible in the low-frequency region and around the spectral region of the fourth phonon mode. Indeed, all these materials are semiconductors, presenting a free charge carrier contribution (Drude term), which explains the increasing trend in reflectance from 40 cm^{-1} to 300 cm^{-1} compared to the Sapphire substrate, which is an insulator. Additionally, electronic transitions associated with the thin film's electrodynamic response, absent in the sapphire substrate in the whole probed spectral range, are responsible for the reflectance reduction in the fourth phonon mode range. Indeed, Figure 3.27 (b) depicts the samples' reflectance up to 20000 cm^{-1} , highlighting the presence of a strong increase in the reflectance, together with modulations ascribable to interband electronic transitions between 1000 cm^{-1} and 20000 cm^{-1} . The Al_2O_3 substrate, instead, has a relatively flat reflectance in this spectral window, around

10 %; the optical gap of this material is indeed around 9 eV [219]. At first sight, the alloys reflectance curves better follow the Sb_2Te_3 spectral behavior, as expected considering the larger Sb content with respect to Bi.

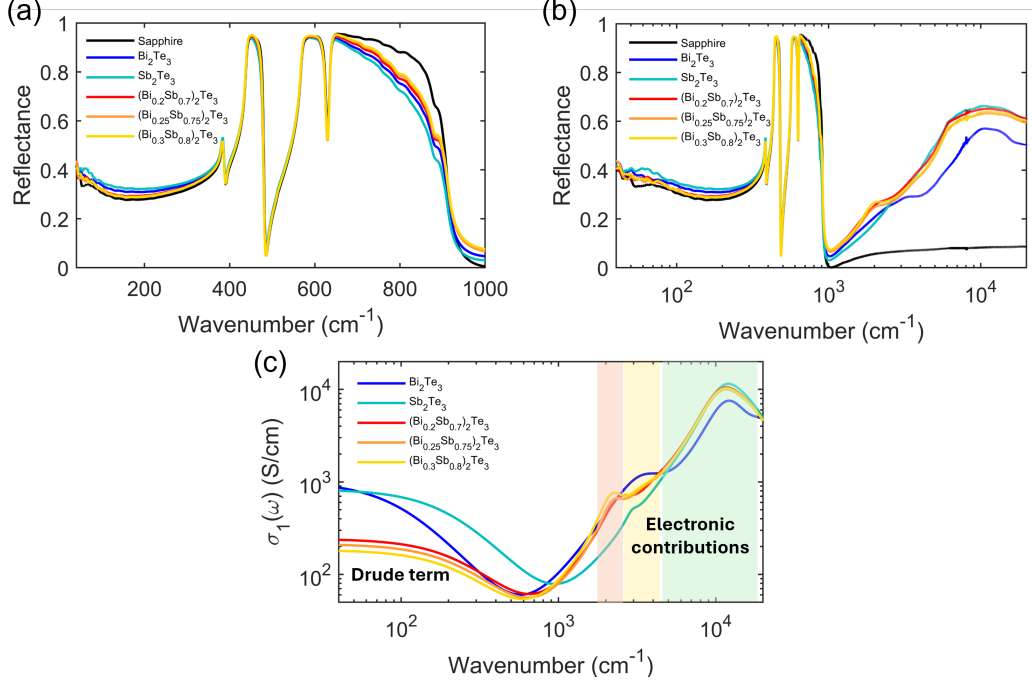


Figure 3.27. (a) Normal incidence reflectance measurements in the Infrared spectral range, from 40 cm^{-1} to 1000 cm^{-1} , of Bi_2Te_3 , Sb_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$, and the reference Al_2O_3 , in blue, light-blue, red, orange, yellow, and black, respectively. (b) Normal incidence reflectance measurements in a larger spectral range, from 40 cm^{-1} to 20000 cm^{-1} , probing also the electronic transitions. (c) Real part of the optical conductivity $\sigma_1(\omega)$, in S/cm, from 40 cm^{-1} to 20000 cm^{-1} . Free carrier contribution (Drude term) and electronic transitions regions are indicated, respectively. The main electronic oscillators are highlighted with orange, yellow, and green bands.

Reflectance was modeled through Drude and Drude-Lorentz contributions via the ReFFIT software (see Subsection 2.7.3 in Chapter 2), considering a three-layer system composed of air, substrate, and film. From this fitting procedure, real and imaginary parts of microscopic optical response functions were extracted. The corresponding fitting curves are shown in the Appendix G.0.2. Figure 3.27 (c) reports the real part of the optical conductivity $\sigma_1(\omega)$, expressed in S/cm, as a function of frequency. The Drude term is associated with the non-zero contribution of σ_1 from 40 cm^{-1} to $\sim 1000 \text{ cm}^{-1}$, as indicated in the Figure. This term appears to be larger for the pure compounds and smaller for the alloys. Then, the oscillators corresponding to electronic transitions appear as peaks. Figure G.4 in Appendix G.0.2 shows a table with the detailed values of the plasma frequency ω_p of the Drude term and the central frequency ω_0^i of the i -th electronic oscillator for all the samples. As in Figure 3.27 (a), the phonon contributions are too weak to appear in reflectance, and thus are also not visible in the optical conductivity.

Considering the semi-conducting nature of these films, $\sigma_1(\omega)$ starts to increase from $\sim 1000 \text{ cm}^{-1}$. Bi_2Te_3 reflectance was fitted by three Drude-Lorentz oscillators, at 3400 cm^{-1} , highlighted by the yellow band in Figure 3.27 (c), 12000 cm^{-1} , and a main contribution at 20000 cm^{-1} , contained within the green band. Sb_2Te_3

reflectance was instead fitted by an oscillator at 3000 cm^{-1} and another one at 4800 cm^{-1} , both within the yellow band, and then two main oscillators at 11630 cm^{-1} and at $\sim 16000 \text{ cm}^{-1}$ (green band). As already commented, the alloy's optical behavior is more similar to that of Sb_2Te_3 , as expected considering that they contain way more Sb than Bi. Therefore, the reflectances of the three alloys were fitted by two main Lorentz oscillators at 11200 cm^{-1} and 16000 cm^{-1} , within the green band. Two additional oscillators were placed at $\sim 2400 \text{ cm}^{-1}$ and $\sim 4000 \text{ cm}^{-1}$, both redshifting with increasing Bi content, as visible in Figure 3.27 (c) in the orange panel region.

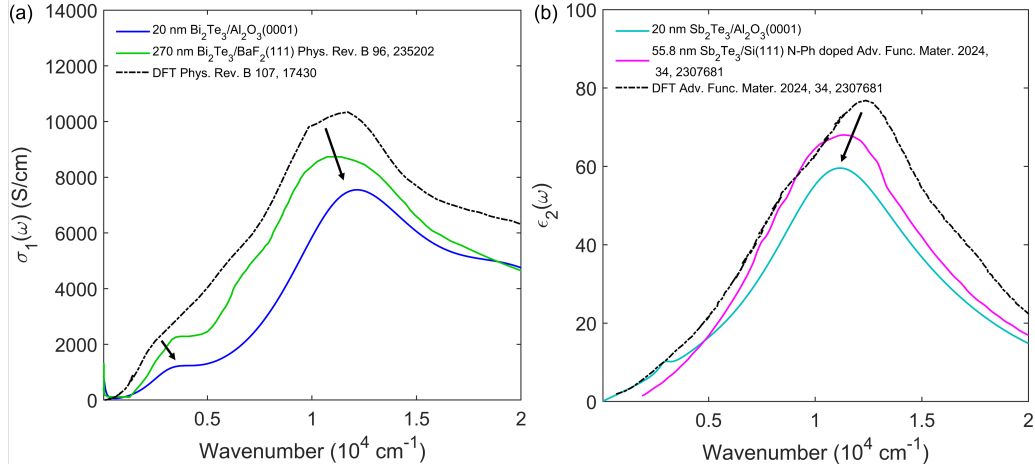


Figure 3.28. (a) Comparison of the real part of the optical conductivity $\sigma_1(\omega)$ between the as-grown 20 nm $\text{Bi}_2\text{Te}_3/\text{Al}_2\text{O}_3(0001)$ film (blue continuous curve), a 270 nm $\text{Bi}_2\text{Te}_3/\text{BaF}_2(111)$ MBE grown film (green continuous curve), from Ref. [220], and DFT calculations (black dashed curve), from Ref. [221], from 40 cm^{-1} to 20000 cm^{-1} . (b) Comparison of the imaginary part of the dielectric function $\epsilon_2(\omega)$ between the as-grown 20 nm $\text{Sb}_2\text{Te}_3/\text{Al}_2\text{O}_3(0001)$ film (light-blue curve), a 55.8 nm $\text{Sb}_2\text{Te}_3/\text{Si}(111)$ N-Ph doped MBE grown film (magenta curve), from Ref. [222], and DFT calculations (black dashed curve), from Ref. [222].

To lend robustness to these results, microscopic optical response functions were compared with other experimental data and density functional theory (DFT) ab initio calculations. Figure 3.28 (a) shows a comparison of the real part of the optical conductivity of our 20 nm Bi_2Te_3 film (blue curve), of a $\sim 270 \text{ nm}$ film grown via MBE on a 1 mm thick $\text{BaF}_2(111)$ substrate (green curve) from Ref. [220], and of theoretical DFT ab-initio calculations (black dashed curve) from Ref. [221], from 40 cm^{-1} to 20000 cm^{-1} . In these other two cases, $\sigma_1(\omega)$ peaks at $\sim 12000 \text{ cm}^{-1}$ instead of 11300 cm^{-1} , so there is a blueshift of the main peak in the film grown during this work, as highlighted by the black arrow. The peak at around 3400 cm^{-1} is visible in the case of the other film and less pronounced in the theoretical case, whereas the opposite trend holds for the peak at the highest frequency. The overall comparison shows a good match. The differences in the peak positions might be related to the different film thickness: the film grown in this work is indeed 20 nm thick, whereas the film grown in Ref. [220] is 270 nm thick, approaching more and more a bulk condition, as the one reported in the DFT case.

Figure 3.28 (b) reports instead a comparison of the imaginary part of the dielectric function $\epsilon_2(\omega)$ of our 20 nm Sb_2Te_3 film (light-blue curve), of a 55.8 nm film grown via MBE on a $\text{Si}(111)$ N-Ph doped substrate (magenta curve), from Ref. [222], and of theoretical DFT ab-initio calculations (black dashed curve) from the same

Ref., from 40 cm^{-1} to 20000 cm^{-1} . The Drude contribution was subtracted in both experimental cases. $\epsilon_2(\omega)$ peaks at 11600 cm^{-1} for both films, demonstrating an optimum agreement between the two samples. This time, the peak position is blueshifted in the bulk theoretical case, as highlighted by the black arrow; however, a good match is still present. According to Ref. [222], the optical transitions responsible for the maximum of the dielectric function are due to transitions from Te p-like states from all sites to the Sb p-like states.

Bi₂Se₃ thin films

The results for the second class of thin 2D topological insulators are now presented. In this case, five Bi₂Se₃ films with varying thickness are shown: 10 QL, 20 QL, 30 QL, 50 QL, and 100 QL. The purpose is to show how the surface state nature of the samples evolves with increasing thickness.

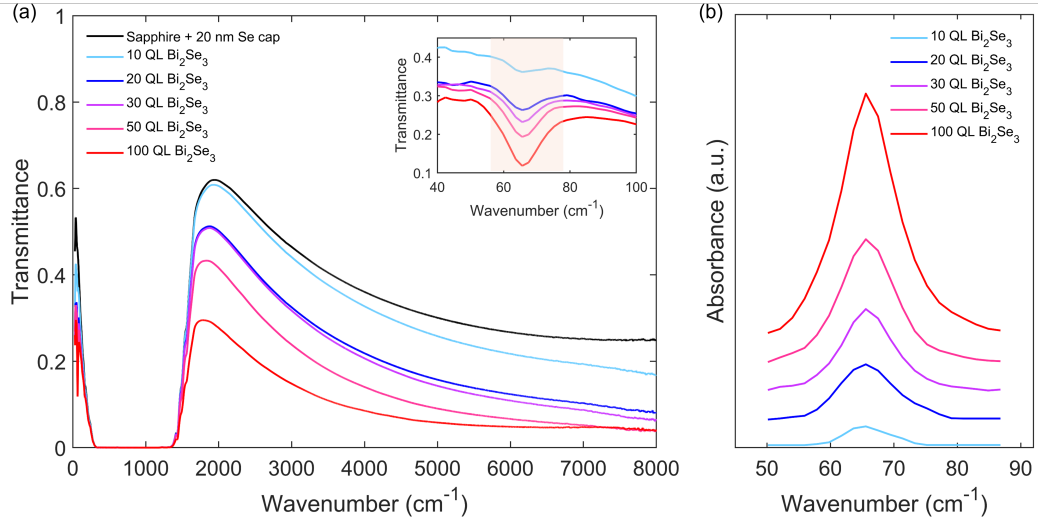


Figure 3.29. (a) Normal incidence Infrared transmittance, from 40 cm^{-1} to 8000 cm^{-1} , of 10 QL Bi₂Se₃, 20 QL Bi₂Se₃, 30 QL Bi₂Se₃, 50 QL Bi₂Se₃, and 100 QL Bi₂Se₃, in cyan, blue, rose pink, fuchsia, and red, respectively. The reference Sapphire substrate plus 20 nm Se capping transmittance is shown in black. The inset depicts a zoom from 40 cm^{-1} to 100 cm^{-1} , to show the Infrared E_u active mode of this material, highlighted by the shaded orange band. (b) Absorbance of the phonon mode, located at $\sim 65 \text{ cm}^{-1}$, zoomed between 45 cm^{-1} and 92 cm^{-1} . This mode becomes more and more intense with increasing film thickness.

Figure 3.29 (a) depicts again the transmittance of 10 QL Bi₂Se₃, 20 QL Bi₂Se₃, 30 QL Bi₂Se₃, 50 QL Bi₂Se₃, and 100 QL Bi₂Se₃, in cyan, blue, rose pink, fuchsia, and red, respectively, in the Infrared spectral range, from 40 cm^{-1} to 8000 cm^{-1} and with a 4 cm^{-1} resolution, together with a reference Al₂O₃ substrate with 20 nm Se capping (black curve). Due to the strong Al₂O₃ resonances, transmittance is zero in the 300 cm^{-1} - 1400 cm^{-1} spectral region, whereas it exhibits a non-zero behavior outside this band. More in detail, between 40 cm^{-1} and 80 cm^{-1} , one phonon mode associated with Bi₂Se₃ is visible, as highlighted in the inset of the same Figure. Again, considering the rhombohedral crystal structure of Bi₂Se₃, and that the electric field is polarized in the plane perpendicular to the c axis, only E_u modes can be excited, as is the case with the mode at $\sim 65 \text{ cm}^{-1}$ [223, 224]. This phonon exhibits increasing intensity with increasing film thickness, as illustrated in

Figure 3.29 (b), which shows the absorbance of the mode, zoomed in between 45 cm^{-1} and 92 cm^{-1} . Again, a baseline correction was applied following the optical behavior of Sapphire. The presence of the 20 nm Se capping layer doesn't modify the optical response of the substrate in this spectral range. Figure 3.30 reports the intensity, expressed in cm^{-1} , of the Bi_2Se_3 IR active E_u mode, obtained by calculating the area of the absorbance curves from Figure 3.29 (b), versus sample thickness, expressed in nm. As expected, the trend is linear; in fact, the number of ions involved in the absorption process increases with increasing thickness, and consequently, the area of the absorbance curve.

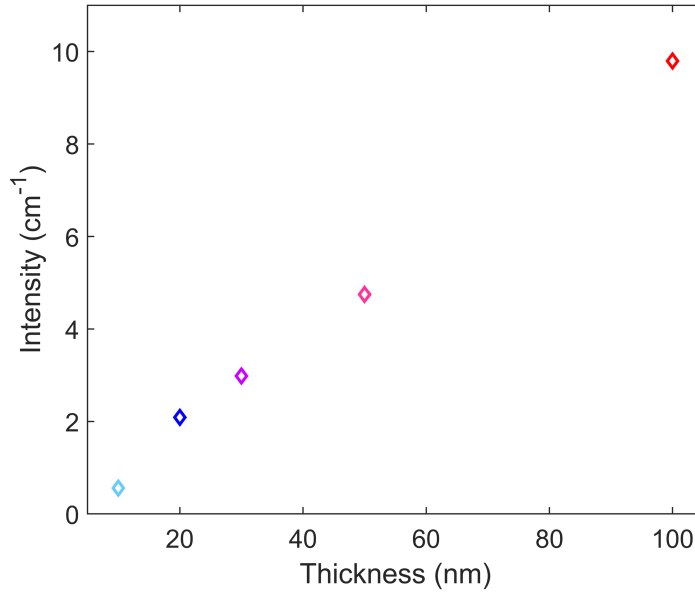


Figure 3.30. Intensity (in cm^{-1}) of the Bi_2Se_3 IR active E_u mode, calculated from Figure 3.29 (b), versus sample thickness, in nm. As expected, the trend is linear; in fact, the number of ions involved in the absorption process increases with increasing thickness, and consequently, also the integrated area of the absorbance curve.

Figure 3.31 (a) reports normal incidence reflectance measurements of 10 QL, 20 QL, 30 QL, 50 QL, 100 QL Bi_2Se_3 , and the reference Al_2O_3 with 20 nm Se capping, in cyan, blue, rose pink, fuchsia, red, and black, respectively, between 40 cm^{-1} and 8000 cm^{-1} . Also here, four distinct phonon modes ascribable to the Al_2O_3 substrate are recognizable, at 385 cm^{-1} , 442 cm^{-1} , 569 cm^{-1} , and 635 cm^{-1} , explaining the null transmittance in this spectral window [214, 215]. Again, only E_u modes can be excited in normal incidence conditions since Sapphire has a rhombohedral crystal structure like Bi_2Se_3 , and only modes vibrating perpendicular to the c axis can be probed. In this case, the additional phonon mode of Bi_2Se_3 is visible at $\sim 65 \text{ cm}^{-1}$. All the films follow the reflectance behavior of the first three phonon modes. In contrast, deviations are visible in the low-frequency region and around the spectral region of the fourth phonon mode. Indeed, this material is a semiconductor, presenting a free charge carrier contribution (Drude term), which explains the increasing trend in reflectance from 40 cm^{-1} to 300 cm^{-1} compared to the Sapphire substrate, which is an insulator. Additionally, electronic transitions associated with the thin film's electrodynamic response, absent in the Sapphire substrate in the whole probed spectral range, are responsible for the reflectance reduction in the fourth phonon

mode range. Indeed, the presence of a strong increase in the reflectance is due to interband electronic transitions between 1000 cm^{-1} and 20000 cm^{-1} .

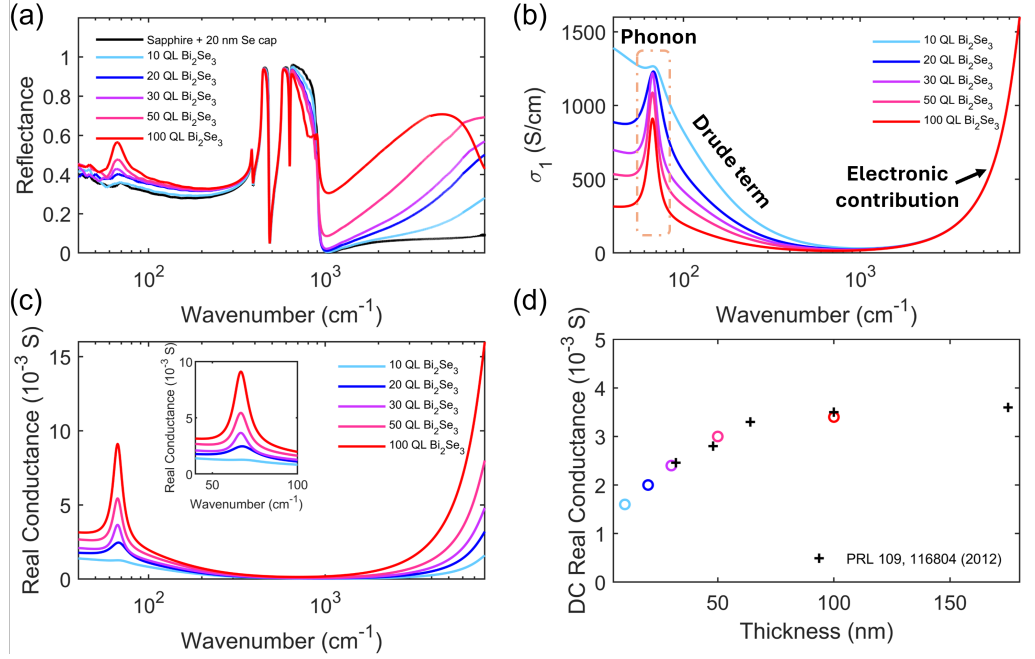


Figure 3.31. (a) Normal incidence reflectance measurements in the Infrared spectral range, from 40 cm^{-1} to 8000 cm^{-1} , of 10 QL Bi_2Se_3 , 20 QL Bi_2Se_3 , 30 QL Bi_2Se_3 , 50 QL Bi_2Se_3 , 100 QL Bi_2Se_3 , together with a reference Al_2O_3 plus 20 nm Se capping, in cyan, blue, rose pink, fuchsia, red, and black, respectively. (b) Real part of the optical conductivity $\sigma_1(\omega)$, in S/cm, from 40 cm^{-1} to 8000 cm^{-1} . Free carrier contribution (Drude term), phonon mode, and electronic contribution regions are indicated, respectively. (c) Real conductance, expressed in S, from 40 cm^{-1} to 8000 cm^{-1} . The inset is a zoom around the phonon mode, between 40 cm^{-1} and 100 cm^{-1} . (d) DC real conductance, obtained by extrapolating the $\sigma_1(\omega)$ at $\omega=0$ from the ReFFIT software, versus film thickness. Additional data obtained at room temperature from Ref. [212] for 32 QL, 48 QL, 64 QL, 100 QL, and 175 QL Bi_2Se_3 films are plotted with black crosses for comparison.

The modulation around 8000 cm^{-1} redshifts with increasing thickness. The Al_2O_3 substrate, together with its 20 nm Se capping, instead, has a relatively flat reflectance in this spectral window, around 10 %. At first sight, noticeable changes in reflectance are evident, which become more pronounced with increasing film thickness. The Bi_2Se_3 phonon mode reported in Figure 3.29 is also detected in reflectance curves, becoming better defined with increasing thickness.

Reflectance was modeled through Drude and Drude-Lorentz contributions via the ReFFIT software, considering a four-layer system composed of air, capping, substrate, and film. From this fitting procedure, real and imaginary parts of microscopic optical response functions were extracted. The corresponding fitting curves are shown in Figure G.5 in Appendix G. Figure 3.31 (b) reports the real part of the optical conductivity $\sigma_1(\omega)$ of the films as a function of frequency, in the same spectral range as panel (a). The Drude term is associated with the non-zero contribution of σ_1 from 40 cm^{-1} to $\sim 1000 \text{ cm}^{-1}$, as indicated in the Figure. This term decreases with increasing thickness. The modulation related to the E_u mode appears as a peak located at approximately 67 cm^{-1} , in agreement with the spectral position found in the transmittance curves. To better distinguish the role of bulk and surface states,

the real conductance, i.e., $\sigma_1(\omega) \cdot d$, where d is the film thickness, was calculated and plotted in Figure 3.31 (c), to get rid of the thickness dependence. The phonon mode and the electronic transitions are volume-dependent quantities since they change even upon this normalization. The inset in the same panel is a zoom on the phonon mode between 40 cm^{-1} and 100 cm^{-1} , reported to show the increasing strength of the excitation with increasing volume. A similar trend is found for the real conductance behavior from 3000 cm^{-1} on, where the increase due to electronic transitions changes with thickness. The Drude term varies following a specific trend that will be reported in panel (d). By extrapolating the $\sigma_1(\omega)$ at $\omega=0$ from the ReFFIT software, the DC real conductance was calculated and plotted (with open circles) in panel (d) *vs* the film thickness. Additional data (black crosses) from Ref. [212], corresponding to 32 QL, 48 QL, 64 QL, 100 QL, and 175 QL Bi_2Se_3 films, are reported for comparison.

This quantity has a slight increasing trend, more evident up to 30 QL (rose pink circle), and approaches a nearly constant value of $\sim 3.5 \times 10^{-3} \text{ S}$ for larger thicknesses, in agreement with the values from Ref. [212]. Indeed, the black cross at 175 QL still exhibits a similar value. These results suggest that the DC conductance in this thickness range is dominated by some surface transport channels, as expected for topological insulators.

In this Subsection, the optical properties of topological insulator thin films grown via MBE were investigated. Two groups of chalcogenide compounds were considered: Bi_2Te_3 , Sb_2Te_3 , and $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ alloys composed of 20 QLs on the one hand, and Bi_2Se_3 with thicknesses between 10 QLs and 100 QLs on the other hand. In the first case, the free-carrier contribution (Drude term), phonon modes, and electronic transitions were probed to assess the influence of Bi_2Te_3 and Sb_2Te_3 on the optical properties of the alloys. A good match was found between the experimental and DFT data for the pure compounds. In the case of Bi_2Se_3 , instead, it was assessed that, unlike phonons and electronic transitions, the Drude term is a thickness-independent quantity, revealing the presence of surface transport channels, as expected for topological insulators.

3.2.2 Seebeck Coefficient and Resistivity Measurements

Seebeck coefficient and resistivity were measured with the LINSEIS-LSR 1 instrument from 25°C to 100°C , under a static 0.1 bar N_2 pressure, as described in Section 2.6 in Chapter 2, for the first class of thin 2D topological insulators, such as Bi_2Te_3 , Sb_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, and $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$.

	$\sigma(\omega = 0) \text{ (S/cm)}$	$\sigma_{DC} \text{ (S/cm)}$
Bi_2Te_3	1083	1000
Sb_2Te_3	837	830
$(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$	246	240
$(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$	210	203
$(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$	184	180

Figure 3.32. Comparison between the σ value at $\omega=0$, extrapolated from the ReFFIT fitting procedure, from Figure 3.27, and the DC value obtained with the LINSEIS-LSR 1 instrument, both at room temperature, for Bi_2Te_3 , Sb_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, and $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$.

Figure 3.33 (a) reports the resistivity, expressed in $\Omega\cdot\text{m}$, measured versus temperature

from 25 °C up to 100 °C, for Bi_2Te_3 , Sb_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, and $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$, with blue, light-blue, red, orange, and yellow diamond symbols.

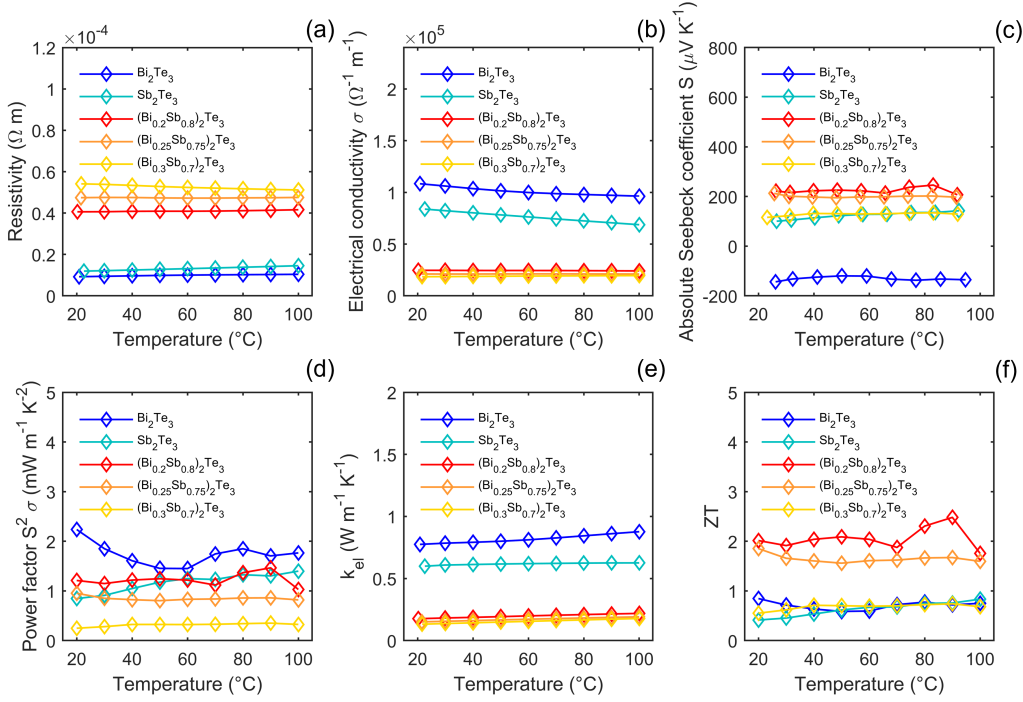


Figure 3.33. (a) Resistivity, expressed in $\Omega\cdot\text{m}$, measured versus temperature from 25 °C up to 100 °C (b) Electrical conductivity σ , expressed in $\Omega^{-1}\cdot\text{m}^{-1}$, measured versus temperature from 25 °C up to 100 °C (c) absolute Seebeck coefficient S , expressed in $\mu\text{V}\cdot\text{K}^{-1}$, measured versus temperature from 25 °C up to 100 °C (d) power factor $S^2\sigma$, expressed in $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$, measured versus temperature from 25 °C up to 100 °C (e) electronic thermal conductivity k_{el} , expressed in $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, measured versus temperature from 25 °C up to 100 °C (f) ZT adimensional figure of merit, measured versus temperature from 25 °C up to 100 °C. Blue diamond symbols refer to Bi_2Te_3 , light-blue to Sb_2Te_3 , red to $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, orange to $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, and yellow to $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$. Continuous lines are a guide for the eye.

Continuous lines are a guide for the eye. Sapphire properties are not reported because it is an insulator and, therefore, does not affect the properties of the deposited films. For a given temperature, the resistivity of the pure compounds, i.e., Bi_2Te_3 and Sb_2Te_3 , is always smaller than alloys, for which there is more disorder. In this restricted temperature range, the resistivities of Bi_2Te_3 and Sb_2Te_3 show a slight increase trend, while the alloys show a slight decrease trend. As expected, the opposite trend holds for the electrical conductivity (σ) behavior, reported in Figure 3.33 (b). For each temperature, the highest σ comes from Bi_2Te_3 , followed by Sb_2Te_3 ; then $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, and $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$ come. The DC value at room temperature for each compound was compared with the DC value of $\sigma(\omega)$ at $\omega=0$, extrapolated from the fitting procedure, and reported in Table 3.32. An optimum agreement is found.

Figure 3.33 (c) shows the absolute Seebeck coefficient S , in $\mu\text{V}\cdot\text{K}^{-1}$. Except for Bi_2Te_3 , all other materials exhibit a positive coefficient; all have values around $|\pm 200| \mu\text{V}\cdot\text{K}^{-1}$. The positive sign indicates that the Fermi level is located closer to the valence band, as expected for Sb_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, and

(Bi_{0.3}Sb_{0.7})₂Te₃, with p-type majority carriers, while the negative sign indicates that the Fermi level is closer to the conduction band, as is the case for Bi₂Te₃, with n-type majority carriers. The trend versus temperature appears to be linear because the measurements were performed in a limited temperature range, where the Seebeck coefficient is expected to be maximized for these materials. The highest Seebeck is reported for the alloys; more in detail, (Bi_{0.2}Sb_{0.8})₂Te₃ heads, followed by (Bi_{0.25}Sb_{0.75})₂Te₃, (Bi_{0.3}Sb_{0.7})₂Te₃, and then there is Sb₂Te₃. Therefore, it is demonstrated that moving the Fermi level from the edge of the conduction and valence bands improves the Seebeck coefficient.

To estimate the thermoelectric efficiency of these compounds, the dimensionless figure of merit ZT is estimated. The latter is given by:

$$ZT = \frac{S^2\sigma}{(k_{el} + k_{lattice})}T \quad (3.3)$$

where $S^2\sigma$ is named the power factor, k_{el} is the electronic thermal conductivity, $k_{lattice}$ is the thermal conductivity of the lattice, and T is the absolute temperature. The power factor $S^2\sigma$ was calculated and depicted in Figure 3.33 (d) as a function of temperature. Again, the trend versus the temperature is quite linear for all the films. Although the alloys exhibit the best Seebeck coefficient, they don't have the best power factors; the pure compounds dominate in this case. The contribution of the electronic thermal conductivity k_{el} can be retrieved by using the Wiedemann-Franz law [225]. In fact, as an approximation, $k_{el} = L \cdot \sigma \cdot T$, where σ is the electrical conductivity, T is the temperature, and $L = 2.44 \cdot 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ is the Lorenz number. The same trend as that of the optical conductivity σ is retrieved, as shown in Figure 3.33 (e). The lattice thermal conductivity $k_{lattice}$ is neglected; this approximation is valid considering that thermal phonons undergo several scattering events due to the small thickness of the investigated films (20 nm thick), and in the alloy case, additional scattering centers are introduced.

Figure 3.33 (f) shows the rough estimation of the adimensional figure of merit ZT using the measured power factor $S^2\sigma$ and the retrieved electronic thermal conductivity k_{el} . As can be seen, the trend versus temperature is again linear, with the highest ZT being ~ 2 for (Bi_{0.2}Sb_{0.8})₂Te₃. (Bi_{0.25}Sb_{0.75})₂Te₃ follows with $ZT \sim 1.8$, and then (Bi_{0.3}Sb_{0.7})₂Te₃, Bi₂Te₃, and Sb₂Te₃, with $ZT \sim 0.8$. This parameter is over-estimated because $k_{lattice}$ is not taken into account; if bulk systems were considered, the overall ZT would be drastically reduced. In Ref. [226], the room temperature $k_{lattice}$ for bulk Bi₂Te₃ is estimated to be $\sim 1.2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, in Ref. [227], the room temperature $k_{lattice}$ for bulk Sb₂Te₃ is estimated to be $\sim 1.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and in Ref. [228], the room temperature $k_{lattice}$ for bulk (Bi_{0.25}Sb_{0.75})₂Te₃ is estimated to be $\sim 0.6 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. All these values exceed k_{el} of the investigated thin films. If these values were added to the values of k_{el} obtained in this work at the same temperature ($0.77 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $0.60 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and $0.13 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), ZT would reduce to 0.33, 0.14, and 0.37, respectively. This result demonstrates the importance of the lattice thermal conductivity in establishing the thermoelectric properties of material systems, suggesting that the choice of thin films is a good strategy to reduce its value and improve the thermoelectric figure of merit. Moreover, this final result again shows how the Fermi level position influences the transport properties.

3.3 Optical Properties of (GeTe)_n(Sb₂Te₃)_m Alloys

Epitaxial (GeTe)_n(Sb₂Te₃)_m (GST) layered alloys were grown via Molecular Beam Epitaxy at the Paul-Drude-Institut für Festkörperelektronik (PDI) in Berlin,

Germany, in collaboration with Dr. Stefano Cecchi from Bicocca University, located in Milan. These samples include n GeTe bilayers and m Sb_2Te_3 quintuple layers. In this work, the optical properties of some GST layered alloys films were probed from 400 cm^{-1} to 20000 cm^{-1} through the use of the Vertex 70V coupled with a Hyperion microscope, and compared with Density Functional Theory (DFT) calculations performed by Dr. Omar Abou El Kheir and Prof. Marco Bernasconi, at Bicocca University, Milan. These materials might pave the way towards interesting thermoelectric applications; indeed, they are composed of Sb_2Te_3 and GeTe, which are already good thermoelectric materials around room and higher temperatures, respectively. Their narrow band gaps constitute another key point for achieving good conversion efficiency. Normal incidence reflectance measurements were performed with the electric field polarized in the plane perpendicular to the c -axis. To our knowledge, no other works have reported the optical properties of GST alloys within this spectral range, covering the region where electronic transitions occur.

	Thickness
<i>GeTe</i>	28 nm
<i>Ge₃Sb₂Te₆</i>	24 nm
<i>Ge₄Sb₂Te₇</i>	27 nm
<i>Ge₅Sb₂Te₈</i>	25 nm
<i>Ge₁₀Sb₂Te₁₃</i>	24 nm

Figure 3.34. Table reporting the sample thickness of the films under study.

All films were deposited on top of $500 \mu\text{m}$ thick high-resistivity Si(111) substrates and capped with $\sim 30 \text{ nm}$ $\text{ZnS}:\text{SiO}_2$ to prevent film oxidation. The films were fabricated by MBE on Si(111)- $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ -Sb passivated surfaces. The substrates were wet-cleaned before loading them into the MBE system. Annealing at 150°C in the load-lock chamber and subsequent annealing at 350°C in the transfer chamber ensured desorption of residual water from the surface before introducing the substrate into the growth chamber. For sample GST326, flux ratios of ~ 0.5 and ~ 1.8 were used for Ge/Sb and Te/Sb, respectively. For the GeTe-rich sample (GST528 and so on), the alloy composition was controlled by increasing the atomic flux of Ge. All other growth parameters were unchanged. For both experiments, the substrate temperature was approximately 230°C , and the deposition time was 90 min. The capping layer was removed immediately before measurements began by a sputtering technique. Subsection H.0.1 in Appendix H reports XRD and STEM images for GST225 and GST528 samples. Table 3.34 reports the sample composition and thickness of the analyzed films, including a series of $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ with n ranging from 3 to 10, $m = 1$, and thickness ranging from 24 nm up to 27 nm. A reference 28 nm thick GeTe film was also grown. Dealing with simulations, the optical conductivity along the x and y directions of optimized models at zero temperature was calculated from Kohn-Sham (KS) orbitals with proper integration of the Brillouin zone and using the hybrid functional HSE06 [229], which better reproduces the band gap. The real part of the optical conductivity $\sigma_1(\omega)$ was obtained from the relation $\sigma_1(\omega) = \omega \cdot \epsilon_0 \cdot \epsilon_2(\omega)$.

Figure 3.35 (a) shows normal incidence reflectance measurements from 400 cm^{-1} to 20000 cm^{-1} of GeTe, $\text{Ge}_3\text{Sb}_2\text{Te}_6$, $\text{Ge}_4\text{Sb}_2\text{Te}_7$, $\text{Ge}_5\text{Sb}_2\text{Te}_8$, $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$, and the

Si(111) substrate, in dark green, light green, brown, yellow, orange, and black, respectively. The thin films show a weak variation compared to the substrate, with a reflectance increase starting from 4000 cm^{-1} , associated with interband electronic transitions, and a weak free carrier term (Drude) at low frequencies.

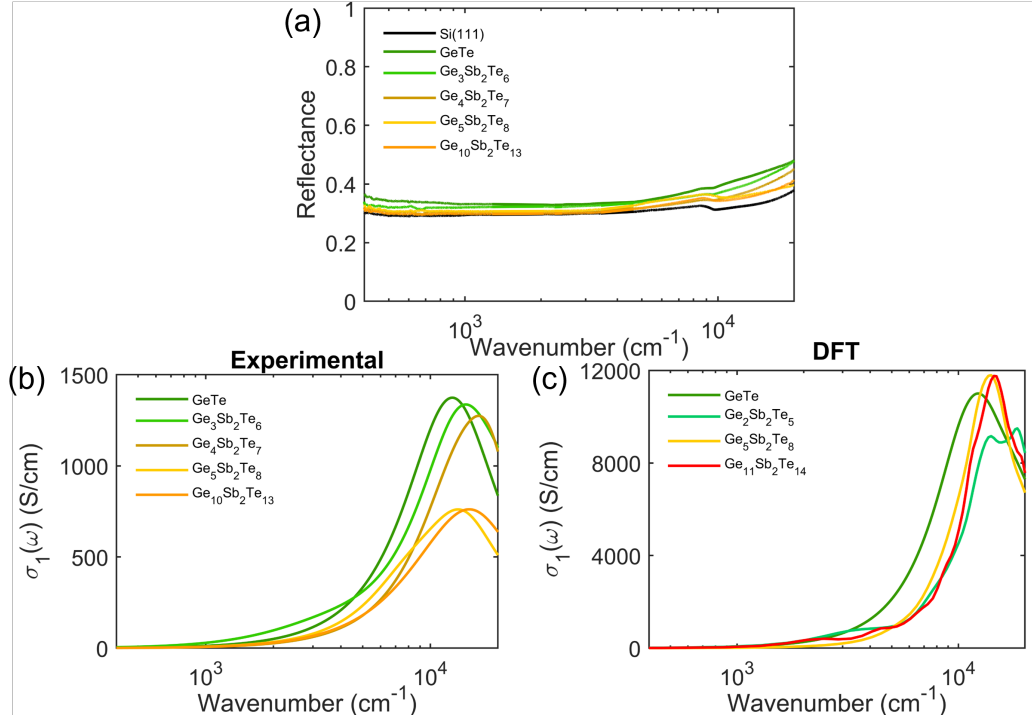


Figure 3.35. (a) Normal incidence reflectance measurements, from 400 cm^{-1} to 20000 cm^{-1} , of GeTe, $\text{Ge}_3\text{Sb}_2\text{Te}_6$, $\text{Ge}_4\text{Sb}_2\text{Te}_7$, $\text{Ge}_5\text{Sb}_2\text{Te}_8$, $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$, and the reference high-resistivity Si(111) substrate, in dark green, light green, brown, yellow, orange, and black, respectively. (b) Real part of the experimental optical conductivity $\sigma_1(\omega)$, in S/cm, from 400 cm^{-1} to 20000 cm^{-1} , of GeTe, $\text{Ge}_3\text{Sb}_2\text{Te}_6$, $\text{Ge}_4\text{Sb}_2\text{Te}_7$, $\text{Ge}_5\text{Sb}_2\text{Te}_8$, $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$. The Drude contribution was removed from the experimental data to have a better comparison with DFT data. (c) Real part of the calculated optical conductivity $\sigma_1(\omega)$, in S/cm, from 400 cm^{-1} to 20000 cm^{-1} , of GeTe, $\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\text{Ge}_5\text{Sb}_2\text{Te}_8$, and $\text{Ge}_{11}\text{Sb}_2\text{Te}_{14}$, in dark green, light green, yellow, and red, respectively.

By fitting the experimental curves via RefFIT software (see Figure H.2 in Appendix H), taking into account the bilayer composed of the substrate and the thin film, the microscopic optical conductivity $\sigma(\omega)$ was extracted and compared with DFT calculations. Figure 3.35 (b) shows the experimental optical conductivity $\sigma(\omega)$ of GeTe, $\text{Ge}_3\text{Sb}_2\text{Te}_6$, $\text{Ge}_4\text{Sb}_2\text{Te}_7$, $\text{Ge}_5\text{Sb}_2\text{Te}_8$, and $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$, from 400 cm^{-1} to 20000 cm^{-1} , whereas panel (c) shows DFT calculations for GeTe (dark green curve), $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (light green curve), $\text{Ge}_5\text{Sb}_2\text{Te}_8$ (yellow curve), and $\text{Ge}_{11}\text{Sb}_2\text{Te}_{14}$ (red curve). The Drude contribution was removed from the experimental data to have a better comparison with DFT data. All curves exhibit a main peak at $\sim 13000\text{ cm}^{-1}$. More in detail, the σ_1 maximum for GeTe is at 12630 cm^{-1} , whereas it is blueshifted for the alloys, at 14300 cm^{-1} for $\text{Ge}_3\text{Sb}_2\text{Te}_6$, 16600 cm^{-1} for $\text{Ge}_4\text{Sb}_2\text{Te}_7$, 13400 cm^{-1} for $\text{Ge}_5\text{Sb}_2\text{Te}_8$, and 14800 cm^{-1} for $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$. Additionally, with increasing GeTe content, the maximum value of the optical conductivity σ_1 is reduced, as observed for $\text{Ge}_5\text{Sb}_2\text{Te}_8$ and $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$.

Experimental and DFT data for the same samples exhibit electronic transitions with

	Experimental ω_0 (cm^{-1})	Calculated ω_0 (cm^{-1})
GeTe	12630	12400
$\text{Ge}_2\text{Sb}_2\text{Te}_5$	/	14100 + 18500
$\text{Ge}_3\text{Sb}_2\text{Te}_6$	14300	/
$\text{Ge}_4\text{Sb}_2\text{Te}_7$	16600	/
$\text{Ge}_5\text{Sb}_2\text{Te}_8$	13400	13700
$\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$	14800	/
$\text{Ge}_{11}\text{Sb}_2\text{Te}_{14}$	/	14870

Figure 3.36. Table reporting the central frequency ω_0 of the electronic transition in experimental and DFT data.

similar spectral positions, as highlighted in Table 3.36 for GeTe and $\text{Ge}_5\text{Sb}_2\text{Te}_8$, where a shift of approximately 2 % is found. In both experimental and calculated results, the central frequency ω_0 blueshifts while moving from GeTe to $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Ge}_3\text{Sb}_2\text{Te}_6$ compounds, redshifts, and finally blueshifts again for $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$ and $\text{Ge}_{11}\text{Sb}_2\text{Te}_{14}$. Considering that the intensity of the optical conductivity is volume-dependent, a difference between thin films (experiment) and bulk (DFT case) is expected. Additionally, it is likely that during the capping layer removal procedure, some part of the films was also removed, ending up with films thinner than those reported in Table 3.34.

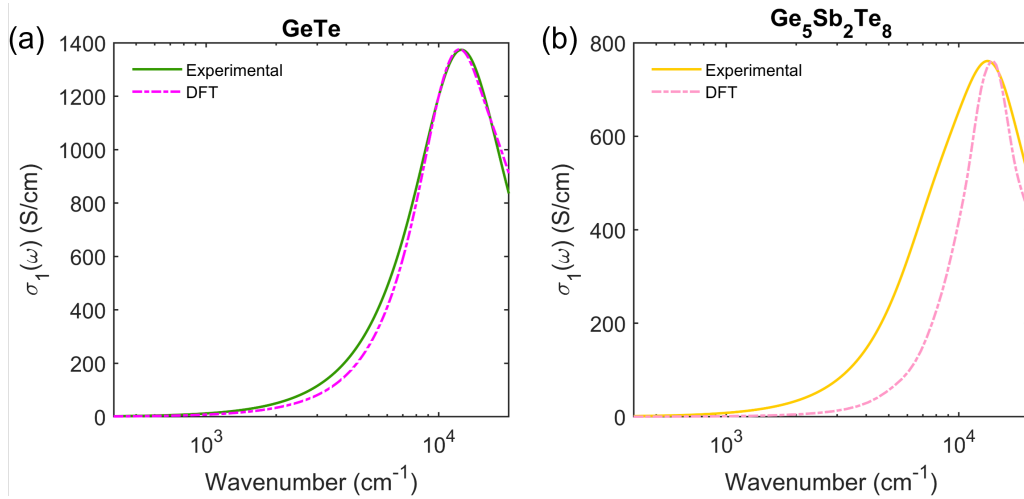


Figure 3.37. (a) Comparison between experimental (dark green continuous curve) and DFT (fuchsia dashed curve) $\sigma_1(\omega)$ of GeTe , and between experimental (yellow continuous curve) and DFT (pink dashed curve) $\sigma_1(\omega)$ of $\text{Ge}_5\text{Sb}_2\text{Te}_8$ (b), between 400 cm^{-1} and 20000 cm^{-1} . In both panels, the DFT data were normalized to the experimental curves.

Figure 3.37 shows the comparison between experimental (dark green continuous curve) and DFT (fuchsia dashed curve) $\sigma_1(\omega)$ of GeTe (a), and between experimental (yellow continuous curve) and DFT (pink dashed curve) $\sigma_1(\omega)$ of $\text{Ge}_5\text{Sb}_2\text{Te}_8$ (b), between 400 cm^{-1} and 20000 cm^{-1} . An optimum match is found between the GeTe data in terms of both the central frequency ω_0 of the electronic transition and the width of the curves. Concerning $\text{Ge}_5\text{Sb}_2\text{Te}_8$, beyond the shift of 2 % between the maxima, there is a difference in the width of the electronic transition, which is larger in the case of the experimental data. A similar situation was detected for the other GSTs. This result can be explained in terms of the intrinsic compositional

disorder present within GST compounds, i.e., the presence of lamellae with varying compositions, as well as vacancy layers and van der Waals gaps, which are absent in pure GeTe. The compositional disorder is expected to play a major role as the GeTe content is increased, resulting in a mixture of lamellae with GeTe content different from the expected one, as reported in Ref. [230]. This kind of disorder was also found to be responsible for noisy DC resistivity measurements in Ref. [231]. In DFT calculations, instead, ordered structures with Kooi stacking (see Subsection 1.3.2 in Chapter 1) were considered for all GST compositions, finding narrow linewidths for all the σ_1 curves. Thus, compositional disorder was not taken into account. Table 3.38 reports the experimental and calculated linewidths $\Delta\omega$ for GeTe, $\text{Ge}_3\text{Sb}_2\text{Te}_6$, $\text{Ge}_4\text{Sb}_2\text{Te}_7$, $\text{Ge}_5\text{Sb}_2\text{Te}_8$, and $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$ for the electronic transition reported in Table 3.36. As can be observed, in the experimental case, GST compounds exhibit wider linewidths compared to GeTe, which increase with the GeTe content, as expected for films containing a mixture of different lamellae.

	$\Delta\omega$ (cm^{-1})	
	Experimental	Calculated
<i>GeTe</i>	15200	16340
<i>Ge₂Sb₂Te₅</i>	/	14400
<i>Ge₃Sb₂Te₆</i>	18130	/
<i>Ge₄Sb₂Te₇</i>	16180	/
<i>Ge₅Sb₂Te₈</i>	16660	12000
<i>Ge₁₀Sb₂Te₁₃</i>	20750	/
<i>Ge₁₁Sb₂Te₁₄</i>	/	12400

Figure 3.38. Table reporting the linewidth $\Delta\omega$ of the electronic transition reported in Table 3.36 in experimental and DFT data.

In this Subsection, the optical properties of epitaxial $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ (GST) layered alloys were probed from 400 cm^{-1} to 20000 cm^{-1} . The real part of the optical conductivity $\sigma_1(\omega)$ was retrieved and compared with theoretical DFT calculations in the same spectral range, finding a good match in terms of the central frequency ω_0 of the electronic transition, and the same trend in the frequency shift of the peak while increasing the GeTe content. The experimental linewidths of the electronic transition broaden as the GeTe content increases because, during the growth procedure, lamellae with different GST compositions are incorporated, resulting in compositional disorder.

Conclusions

In this work, several experimental and computational techniques were gathered to find a solution to the demand for new energy sources and novel materials capable of energy generation/conversion. The aspect of thermal energy management was mainly addressed by considering heat transfer and energy conversion mechanisms in various materials, focusing on two main processes:

- The generation of energy through the emission of thermal radiation from micro-structured materials.
- The reversible electrical-to-thermal energy conversion in topological insulator thin films, together with the basic investigation of GST compounds, that might be efficient in performing this process.

Before investigating these processes, the far-field optical characterization of all the materials was provided to gain insight about phonon modes and the electrodynamic response of the systems. Then, a plethora of additional techniques were employed, including thin-film deposition techniques such as Molecular Beam Epitaxy, near-field and far-field spectroscopic and thermal emission measurements, Seebeck coefficient and resistivity measurements, and electromagnetic simulations.

Initially, the fundamentals of thermal radiation emission were investigated in micro-structured 3D graphene samples featuring pores in the 60-150 μm range. To pursue this goal, a new setup was employed to heat the samples at six different temperatures, ranging between 240 °C and 500 °C, and collect their thermal radiation spectra in the Infrared spectral range. Measurements revealed that 3D graphenes exhibit broadband, homogeneous, and high-intensity thermal emissivity, closely resembling the characteristic behavior of an ideal black body. A comparison with reference thermal emitters, such as highly crystalline SiC and black soot, was made. A normalization procedure taking into account both the emitting area and the density of all materials allowed us to observe, under the same experimental conditions, that our 3D graphene samples emit more than the reference, reaching emissivity to density ratios around 10^3 - 10^4 times more than the SiC one. Thus, the combination of elevated intensity, broadband, and homogeneous spectral emissivity with the intrinsic properties of 3D graphene, such as its mechanical flexibility, structural robustness, and excellent resistance to elevated temperature, indicates that this material is a highly promising candidate for the development of innovative broadband infrared radiation sources. These unique features not only distinguish 3D graphene from conventional emissive materials but also open new opportunities for its integration into advanced technologies such as thermal imaging, optoelectronic devices, energy harvesting, and next-generation sensing platforms.

Later on, the optical and thermal emission properties of a SiC-based phononic fractal metamaterial were studied. The fundamental nature of localized surface phonon polaritons was experienced through several techniques and facilities, including

far-field optical and thermal emission measurements, near-field measurements, and electromagnetic simulations. It was observed that the introduction of artificial pillars is responsible for modifying these properties within the SiC Reststrahlen band, where polar materials can sustain polaritonic modes. Three fractal orders, sustaining different resonances, were investigated. A deep study of the local nature of the resonances revealed that complex electromagnetic interactions occur among the modes excited in the pillars, which exhibit non-trivial electromagnetic distributions and strong electric field confinement close to the microstructures. At last, the thermal emission properties of micro-structured pillars were probed over frequency and temperature, between 100 °C and 650 °C, and compared to those of bare SiC. The results showed that the emitted thermal spectrum of the patterned sample is modified in the far-field regime by the polariton modes. More deeply, the larger the fractal order, the larger the modulation, and the larger the temperature, the wider the resonances.

The optical properties of two different groups of MBE-grown thin films topological insulators were investigated: ~ 20 nm Bi_2Te_3 , Sb_2Te_3 , and $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ alloys on the one hand, and Bi_2Se_3 films with thickness ranging between ~ 10 nm and ~ 100 nm on the other hand. Both transmittance and reflectance were measured to appreciate the phonon modes, the Drude term, and the electronic transition contributions. Concerning the first material group, transmittance measurements in the far-Infrared spectral range allowed the detection of E_u normal modes, assessing that the alloys contain the modes of both Bi_2Te_3 and Sb_2Te_3 pure compounds, in agreement with the literature. Reflectance was measured between 40 cm^{-1} and 20000 cm^{-1} , probing the Drude term and electronic transitions. Again, the alloys were found to have electronic contributions coming from both pure compounds. From the Seebeck coefficient sign, it was assessed that the majority carriers are holes for Sb_2Te_3 , and electrons for Bi_2Te_3 , and $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ alloys. Additionally, the largest Seebeck coefficient was found for the alloys, followed by the pure compounds, in agreement with the theory. A rough estimation of the figure of merit ZT was calculated, neglecting the lattice thermal conductivity. It turned out that these materials maximize their thermoelectric performance around room temperature, and that alloying is a good strategy to improve their conversion efficiency. Dealing with the second material group, some considerations about the optical properties *vs* thickness were made. Indeed, transmittance measurements in the far-Infrared revealed that the intensity of the Bi_2Se_3 active E_u mode increases with increasing thickness since more ions are involved in the process; additionally, reflectance measurements revealed the emergence of some surface transport channels: the real conductance, i.e., $\sigma_1(\omega) \cdot d$, shows that, unlike phonons and electronic transitions, the Drude term is a nearly thickness-independent quantity, revealing the presence of surface transport channels, as expected for topological insulators. The investigation of the Seebeck coefficient of these samples *vs* thickness could allow us to distinguish the different transport channels.

At last, the optical properties of epitaxial $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ (GST) layered alloys were probed from 400 cm^{-1} to 20000 cm^{-1} . The real part of the optical conductivity $\sigma_1(\omega)$ was retrieved and compared with theoretical DFT calculations in the same spectral range, finding a good match in terms of the central frequency ω_0 of the electronic transition and the same trend in the frequency shift of the peak while increasing the GeTe content. The experimental linewidths of the electronic transition broaden as the GeTe content increases because, during the growth procedure, lamellae with different GST compositions are incorporated, resulting in compositional disorder. Overall, a good match was found.

This work is a starting point for improving thermal energy management; several open questions arose, and new frontiers and future perspectives were opened during the development of this thesis project.

Engineering far-field thermal emission spectra through spatial structures involves modifying the emissivity or absorptivity of the system without altering the photon distribution, which serves as a fixed frequency window that sets an upper limit for radiative heat transfer. In this way, energy is only redistributed differently in the body, amplifying the emissivity in certain frequency ranges and suppressing it in others, with no possibility of overcoming the blackbody limit, as observed for fractal structures. Interestingly, it is possible to actively modulate the photon distribution by introducing an external perturbation (a laser, for example) that pumps additional energy into the system, overcoming the blackbody limit in the far-field regime.

As highlighted in the last Chapter, the lattice thermal conductivity has a fundamental role in boosting or quenching the performance of thermoelectric materials; a strong focus should be put on measuring this quantity, with specific attention on thin films. Among the various techniques, time-domain thermoreflectance (TDTR) is a promising non-contact technique to reach this objective. Different strategies might be used to decrease this quantity, including the introduction of obstacles to scatter phonons, i.e., the major heat carriers in solids. Alloying materials means adding new point defects, which lead to large phonon scattering. An alternative way consists of the introduction of an artificial patterning that affects the propagation of phonons but not of electrons, generating phononic band gaps in the material dispersion, which forbid phonon propagation at given frequencies. Other than increasing their scattering with the artificial geometrical details, destructive interference would take place in the band gap, lowering the lattice thermal conductivity and increasing the thermoelectric efficiency. Additionally, there is still a lot to know about the interplay between the surface and bulk transport channels.

At last, thermoelectric investigation of $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ might produce promising results since GeTe and Sb_2Te_3 are good thermoelectric materials, the first one performing better at high temperatures, and the second one around room temperature.

Appendix A

Macroscopic Quantum Electrodynamics and Thermal Emission

The purpose of this Appendix is to show that polaritonic modes can be treated within a quantum and a classical (see Appendix B, C, and D) picture, leading to the same results. In this specific case, the equivalence between the quantum and the fluctuational electrodynamics treatment of the emission of thermal radiation will be demonstrated.

Macroscopic Quantum Electrodynamics (QED) is a theoretical framework that quantizes the electromagnetic field in the presence of complex, absorbing, or dispersive environments, such as dielectric materials [232]. It combines quantum optics, electrodynamics, and *ab initio* methods to describe the quantum interactions between light and matter on a macroscopic scale, utilizing the dyadic Green's function [233] to represent the environment. In this formalism, instead of dealing with bare photons, quasiparticles, or electromagnetic field-matter coupled states, described by a continuum of harmonic oscillators with frequencies ω_f , are considered. These are called *polaritonic modes*, and are described through quantum operators of creation $\hat{\mathbf{f}}(\mathbf{r}, \omega_f; t)$ and annihilation $\hat{\mathbf{f}}^\dagger(\mathbf{r}, \omega_f; t)$, which, in the Heisenberg picture, must fulfill the following commutation relations:

$$[\hat{\mathbf{f}}(\mathbf{r}, \omega_f; t), \hat{\mathbf{f}}(\mathbf{r}', \omega'_f; t)] = 0 \quad (\text{A.1})$$

$$[\hat{\mathbf{f}}^\dagger(\mathbf{r}, \omega_f; t), \hat{\mathbf{f}}^\dagger(\mathbf{r}', \omega'_f; t)] = 0 \quad (\text{A.2})$$

$$[\hat{\mathbf{f}}(\mathbf{r}, \omega_f; t), \hat{\mathbf{f}}^\dagger(\mathbf{r}', \omega'_f; t)] = I \delta(\Delta \mathbf{r}) \delta(\Delta \omega_f) \quad (\text{A.3})$$

where I is the identity operator. Within this framework, the behavior of a quantum photonic system can be described through a total Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_{int}$, which is the sum of the polaritonic environment, where light and matter are coupled, and the interaction contribution due to a polarization field induced by an external electric field. The two contributions to the total Hamiltonian can be written as:

$$\hat{H}_0 = \int d^3 \mathbf{r} \int_0^\infty d\omega_f \hbar \omega_f \hat{\mathbf{f}}^\dagger(\mathbf{r}, \omega_f; t) \cdot \hat{\mathbf{f}}(\mathbf{r}, \omega_f; t) \quad (\text{A.4})$$

$$\hat{H}_{int} = - \int d^3\mathbf{r} \hat{P}(\mathbf{r}, t) \cdot \hat{E}(\mathbf{r}, t) \quad (\text{A.5})$$

where all the involved quantities described with a hat are quantum operators. For example, the polarization field operator is expressed as $\hat{P}(\mathbf{r}, t) = \int_0^t d\tau \Delta\chi(\mathbf{r}, t, \tau) \hat{E}(\mathbf{r}, \tau)$, where $\Delta\chi$ is the susceptibility. The electric field operator, instead, has two contributions, taking into account the creation and annihilation of polaritonic states $\hat{E}(\mathbf{r}, t) = \hat{E}^+(\mathbf{r}, t) + \hat{E}^-(\mathbf{r}, t)$, since, for example:

$$\hat{E}^+(\mathbf{r}, t) = \int_V d^3\mathbf{r}' \int_0^\infty d\omega_f G^E(\mathbf{r}, \mathbf{r}', \omega_f) \hat{f}(\mathbf{r}', \omega_f; t) \quad (\text{A.6})$$

and

$$G^E(\mathbf{r}, \mathbf{r}', \omega_f) = i \sqrt{\frac{\hbar}{\pi\epsilon_0}} \left(\frac{\omega_f}{c} \right)^2 \sqrt{\epsilon_2(\mathbf{r}', \omega_f)} G(\mathbf{r}, \mathbf{r}', \omega_f) \quad (\text{A.7})$$

is the response function of the medium, depending on the dyadic Green's function $G(\mathbf{r}, \mathbf{r}', \omega_f)$, which obeys the following equation:

$$\nabla_x \nabla_x G(\mathbf{r}, \mathbf{r}', \omega) - k^2 G(\mathbf{r}, \mathbf{r}', \omega) = I \delta(\mathbf{r} - \mathbf{r}') \quad (\text{A.8})$$

At this point, the thermal emission spectrum can be obtained from the electric field correlations, obtaining:

$$S(\mathbf{r}, \omega) = \langle [\hat{E}^+(\mathbf{r}, \omega)]^\dagger \cdot \hat{E}^+(\mathbf{r}, \omega) \rangle_{th} \quad (\text{A.9})$$

which is the same expression obtained in Subsection 1.1.2 except for the presence of operators instead of functions.

Appendix B

Surface Plasmon Polaritons

In this Appendix, Surface Plasmon Polariton excitations are discussed without any loss of generality. In fact, a similar treatment can also be applied to Surface Phonon Polaritons, with the caveat that in this case, the region of excitation is restricted to the Reststrahlen band.

Before approaching the study of surface plasmon polaritons and localized surface plasmons, we remind that *volume plasmons* are the fundamental excitation of the conduction electron gas. However, being longitudinal collective oscillations, they cannot couple to transverse electromagnetic waves, having thus the possibility to be excited only by fast electrons, which is something beyond the scope of this thesis.

Surface plasmon polaritons (SPPs) are electromagnetic excitations propagating at the interface between a dielectric and a conductor, evanescently confined in the perpendicular direction [234] [235]. These electromagnetic surface waves originate from the coupling between electromagnetic fields and oscillations of the electron plasma at the surface of a conductor, giving rise to composite particles called surface plasmon polaritons. Considering an interface between a metal, described by the dielectric function $\epsilon_1(\omega)$, and a dielectric, described by the dielectric function $\epsilon_2(\omega)$, the dispersion relation for SPPs propagating at the interface between the two media can be obtained:

$$\beta = k_{SPP} = k_0 \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \quad (\text{B.1})$$

where $\beta = k_x$ is the propagation constant along the propagation direction of SPPs, and $k_0 = \frac{\omega}{c}$ is the wave vector of the propagating wave in vacuum. For detailed calculations, see Appendix C. This expression is valid for both real and complex ϵ_1 , which means that it is valid for metals without and with a damping factor γ . Figure B.1 shows the dispersion relation for SPPs at the interface between a Drude metal with negligible damping ($\gamma \approx 0$) and air ($\epsilon_2 = 1$) and fused silica ($\epsilon_2 = 2.25$). In this plot, three regions can be identified considering the plasma frequency ω_p and the surface plasmon frequency ω_{sp} :

- the $\omega < \omega_{sp}$ region, in which bound evanescent modes (SPPs) are allowed;
- the $\omega_{sp} < \omega < \omega_p$ region, which represents a prohibiting region with purely imaginary β ;
- the $\omega > \omega_p$ region, where radiative modes are allowed, i.e., where radiation can propagate through the interface.

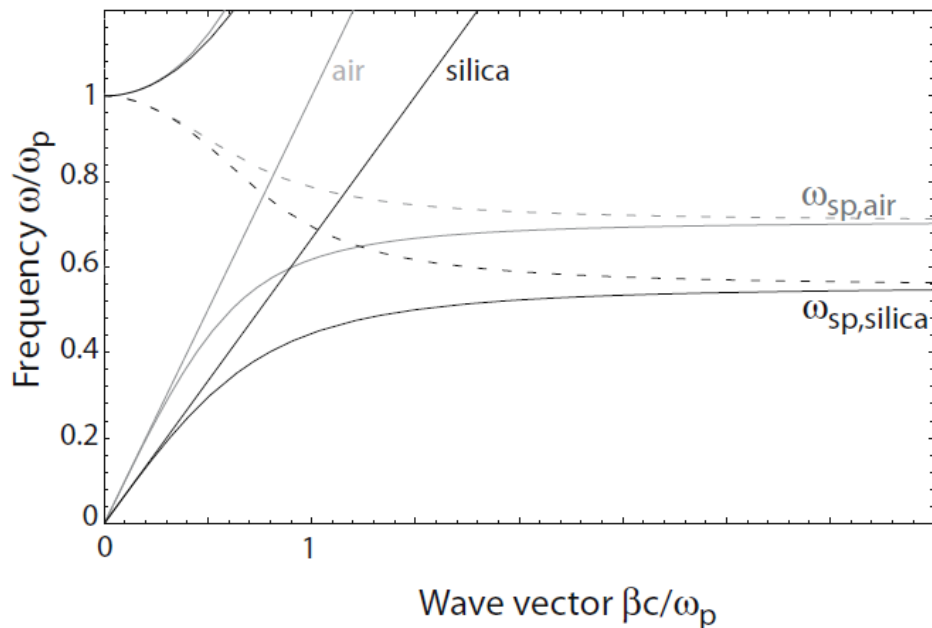


Figure B.1. Dispersion relation for SPPs at the interface between a Drude metal (see Section 2.7.2 in Chapter 2) with a negligible damping and air (gray curve) and silica (black curve). Real part of β corresponds to continuous curves, imaginary part to dotted curves. ω_p indicates the plasma frequency of the metal, whereas ω_{sp} the surface plasmon frequency. Image obtained from Ref. [50].

As shown in Figure B.1, the SPP dispersion curve lies to the right with respect to the dispersion light line, leading to an energy match but a momentum mismatch between light and SPP waves. This means that in order to excite SPPs with light, some extra momentum is needed¹. For small wave vectors, corresponding to mid-infrared or lower frequencies, β is close to k_0 of the light line, so surface waves extend over many wavelengths into the dielectric space. On the other hand, for large wave vectors, the frequency of the SPPs reaches the surface plasmon frequency $\omega_{sp} = \omega_p / \sqrt{1 + \epsilon_2}$, where ω_p is the metal plasma frequency. For negligible damping of the conduction electron oscillation, i.e., for $\text{Im}(\epsilon_1(\omega))=0$, $\beta \rightarrow \infty$ as $\omega \rightarrow \omega_{sp}$ and the group velocity goes to zero. The mode acquires an electrostatic nature and is called *surface plasmon*. In real metals, electron-electron and interband damping do exist; therefore, SPPs are damped within a length scale $L=1/2\text{Im}(\beta)$, typically between 10 and 100 μm . Damping implies that β reaches a finite wave vector when $\omega \rightarrow \omega_{sp}$.

As already pointed out, there is a wave vector mismatch between the SPP and the light dispersion lines, meaning that surface modes cannot be excited with incident light. One possible way to overcome this barrier consists of introducing a *periodic perturbation* along the metallic surface, with a sub-wavelength period with respect to the electromagnetic wave. The defects could be holes, slits, or more complex structures, separated by a period a , for simplicity assumed to be the same along the two in-plane directions. Consequently, a series of reflection planes for the electromagnetic waves is generated, leading to diffraction. Constructive diffraction occurs when the Bragg condition $n\lambda = 2a$ is satisfied, where n is an integer number, λ is the SPP wavelength, and a the period. The periodicity defines a Brillouin zone

¹In the excitation process both energy and momentum should be conserved.

in the reciprocal lattice along k_x , in the same way as for Bloch states in crystalline solids. Therefore, the reciprocal lattice provides the missing wave vector needed to excite SPPs through an electromagnetic wave. In the general case of a regular array with a different periodicity in the in-plane directions, the wave vector conservation can be written as [236, 237, 238]:

$$\mathbf{k}_{spp} = \mathbf{k}_x \pm i\mathbf{G}_x \pm j\mathbf{G}_y \quad (\text{B.2})$$

where $\mathbf{k}_x = \mathbf{k}_0 \sin\theta$ is the light wave vector component parallel to the interface along x , $|\mathbf{G}_x| = 2\pi/a_x$ and $|\mathbf{G}_y| = 2\pi/a_y$ are the reciprocal lattice vectors associated with the two in-plane periodicities of the perturbation, and i and j are integer numbers indicating the order of the scattering event that couples incident light and SPP. In the simplified case of a square array, $a_x = a_y = a$ and $|\mathbf{G}_x| = |\mathbf{G}_y| = 2\pi/a$.

Appendix C

Surface Plasmon Polariton Dispersion Relation

To get the dispersion relation of SPPs, it is necessary to start from the wave equation, obtained by combining Maxwell's equations in the absence of external charge and currents (for the derivation see, for example, [50]):

$$\nabla^2 \mathbf{E} - \frac{\epsilon}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = 0 \quad (\text{C.1})$$

Substitution of an electric field with a harmonic time dependence $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r})e^{-i\omega t}$ in Equation C.1 leads to the Helmholtz equation:

$$\nabla^2 \mathbf{E} + k_0^2 \epsilon \mathbf{E} = 0 \quad (\text{C.2})$$

where $k_0 = \frac{\omega}{c}$ is the wave vector of the propagating wave in vacuum. Figure C.1 shows an interface between a dielectric and a metal. The $z > 0$ region

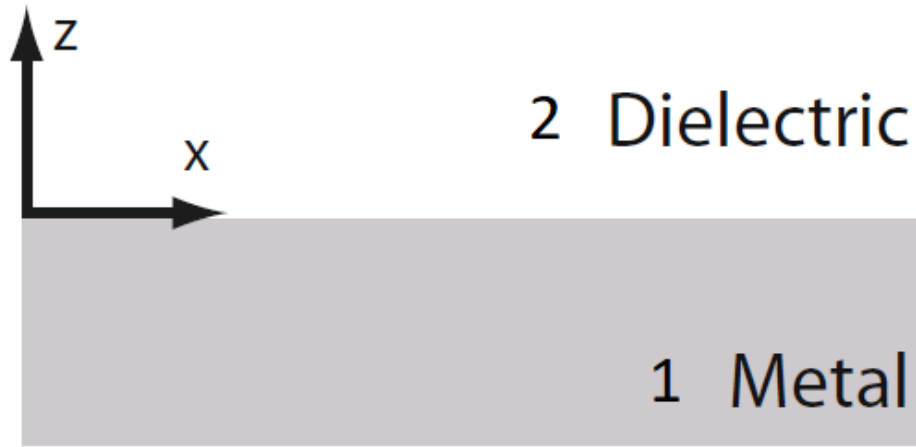


Figure C.1. Interface between a metal (1) and a dielectric (2) able to sustain surface plasmon polaritons. Image obtained from Ref. [50].

is described by a positive real dielectric function ϵ_2 , while the $z < 0$ region by the dielectric function $\epsilon_1(\omega)$. Let's assume that the waves propagate along the x -direction and show no spatial variation along the y -direction. Therefore, the propagating

waves can be written as $\mathbf{E}(x, y, z) = \mathbf{E}(z)e^{i\beta x}$, where $\beta = k_x$ is the propagation constant. Substituting this expression in Equation C.2 gives:

$$\frac{\partial^2 \mathbf{E}}{\partial z^2} + (k_0^2 \epsilon - \beta^2) \mathbf{E} = 0 \quad (\text{C.3})$$

Using Maxwell's equations (the two with the curl) and assuming homogeneity in the y-direction ($\frac{\partial}{\partial y} = 0$), the following set of coupled equations is obtained:

$$\frac{\partial E_y}{\partial z} = -i\omega\mu_0 H_x \quad (\text{C.4})$$

$$\frac{\partial E_x}{\partial z} - i\beta E_z = i\omega\mu_0 H_y \quad (\text{C.5})$$

$$i\beta E_y = i\omega\mu_0 H_z \quad (\text{C.6})$$

$$\frac{\partial H_y}{\partial z} = i\omega\epsilon_0 \epsilon E_x \quad (\text{C.7})$$

$$\frac{\partial H_x}{\partial z} - i\beta H_z = -i\omega\epsilon_0 \epsilon E_y \quad (\text{C.8})$$

$$i\beta H_y = -i\omega\epsilon_0 \epsilon E_z \quad (\text{C.9})$$

where μ_0 is the vacuum permeability. At this point, two sets of solutions with different polarization are allowed: transverse magnetic (TM) modes, for which the only nonzero components are E_x, E_z, H_y , and transverse electric modes (TE), for which only H_x, H_z, E_y are nonzero. It can be shown that SPPs only exist for TM polarization [50], then the treatment will be done just for TM modes. Using the only non zero components in the previous equations in both the $z > 0$ and $z < 0$ regions leads to:

$$H_y(z) = A_2 e^{i\beta x} e^{-k_2 z} \quad (\text{C.10})$$

$$E_x(z) = iA_2 \frac{1}{\omega\epsilon_0\epsilon_2} k_2 e^{i\beta x} e^{-k_2 z} \quad (\text{C.11})$$

$$E_z(z) = -A_1 \frac{\beta}{\omega\epsilon_0\epsilon_2} e^{i\beta x} e^{-k_2 z} \quad (\text{C.12})$$

$$H_y(z) = A_1 e^{i\beta x} e^{k_1 z} \quad (\text{C.13})$$

$$E_x(z) = iA_1 \frac{1}{\omega\epsilon_0\epsilon_1} k_1 e^{i\beta x} e^{k_1 z} \quad (\text{C.14})$$

$$E_z(z) = -A_1 \frac{\beta}{\omega\epsilon_0\epsilon_1} e^{i\beta x} e^{k_1 z} \quad (\text{C.15})$$

where $k_i = k_{z,i}$ ($i=1,2$) is the component of the wave vector perpendicular to the interface in the two media, and $\hat{z} = 1/|k_z|$ is the evanescent decay length, determining the wave confinement at the interface. Continuity of H_y and $\epsilon_i E_z$ at the interface requires that $A_1 = A_2$ and:

$$\frac{k_2}{k_1} = -\frac{\epsilon_2}{\epsilon_1} \quad (\text{C.16})$$

Since k_1, k_2 , and ϵ_2 are positive, continuity in the latter equation implies that $Re(\epsilon_1) < 0$, meaning that surface waves exist only at interfaces between media with real parts of their dielectric function of opposite signs. Metals have $Re(\epsilon_1) < 0$ for

$\omega < \omega_p$ (see Section 1.1.3), thus the two media should be a dielectric and a conductor. The continuity condition for H_y can be derived from the wave equation and requires that:

$$k_1^2 = \beta^2 - k_0^2 \epsilon_1 \quad (\text{C.17})$$

$$k_2^2 = \beta^2 - k_0^2 \epsilon_2 \quad (\text{C.18})$$

In the end, combining the latter two equations and C.16, the dispersion relation for SPPs propagating at the interface between the two media can be obtained:

$$\beta = k_{SPP} = k_0 \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \quad (\text{C.19})$$

where $\beta = k_x$ is the propagation constant along the propagation direction of SPPs and $k_0 = \frac{\omega}{c}$ is the wave vector of the propagating wave in vacuum.

Similar results can be obtained in the case of interfaces between polar dielectrics. In the latter case, Surface Phonon Polaritons (SPhPs) are excited, with a dispersion relation confined within the Reststrahlen band, as shown in Subsection 1.1.3. In fact, the spectral region where Equation C.16 is satisfied is where the dielectric function becomes negative, happening between transverse and longitudinal optical phonon frequencies.

Appendix D

Localized Surface Plasmons

Unlike SPPs, localized surface plasmons (LSPs) are non-propagating excitations of the conduction electrons of decoupled metallic nanostructures coupled to the electromagnetic field [5]. These modes arise naturally from the scattering problem of a sub-wavelength metallic nanoparticle in an oscillating electromagnetic field. The curved surface of the nanoparticle generates a sort of restoring force on the driven electrons, so that a *resonance* can arise, leading to field amplification both inside and in the near-field zone outside the nanostructure. The interesting aspect about plasmon resonances is that particle size and shape are responsible for their spectral position and width, allowing a direct control on the resonant behaviour. The main difference between SPPs and LSPs is that SPPs do have a given wavevector-dependent dispersion relation (as it happens in all localized excitations): to excite these modes, phase-matching techniques are needed. On the other hand, LSP excitation doesn't possess a specific value of the wave vector k , so direct excitation by light is allowed. As a consequence, LSP resonances can also be observed in single nanoparticles without the need for a periodic array.

LSPs can be approached by solving the problem of a homogeneous sphere with radius a and dielectric function $\tilde{\epsilon}(\omega)$ inside a uniform and static electric field $\mathbf{E} = E_0 \hat{\mathbf{z}}$, as shown in Figure D.1. The surrounding medium is isotropic, with dielectric function ϵ_m .

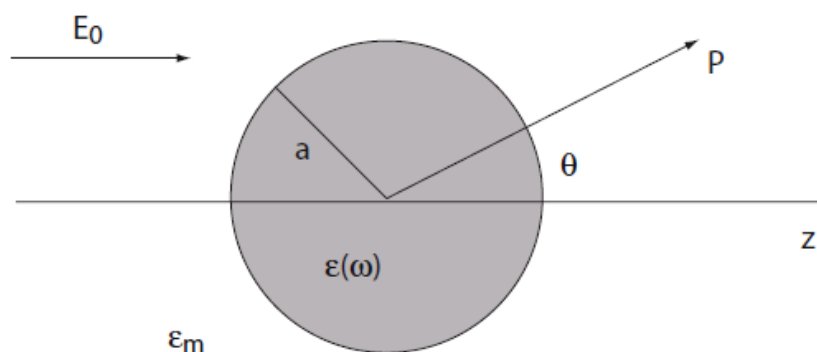


Figure D.1. Homogeneous sphere of radius a and dielectric function $\tilde{\epsilon}(\omega)$, surrounded by a non-absorbing medium with dielectric function ϵ_m . Image obtained from Ref. [50].

The quasi-static approximation can be applied, being $a \ll \lambda$. Solving the Laplace equation for the potential, $\nabla^2 \phi = 0$, it is possible to obtain the electric field $\mathbf{E} = -\nabla \phi$. After some calculations (for further details see [50]), the dipole moment $\mathbf{p} = \epsilon_0 \epsilon_m \alpha \mathbf{E}_0$

induced by the electric field inside the sphere is obtained. The expression for the polarizability α is:

$$\alpha = 4\pi a^3 \frac{\tilde{\epsilon} - \epsilon_m}{\tilde{\epsilon} + 2\epsilon_m} \quad (\text{D.1})$$

Considering a silver sphere described by a Drude $\tilde{\epsilon}(\omega)$, it can be seen that the polarizability has a resonant behaviour when the Fröhlich condition is satisfied:

$$\text{Re}(\tilde{\epsilon}(\omega)) = -2\epsilon_m \quad (\text{D.2})$$

as depicted in Figure D.2. This resonance is associated to the so-called *dipole surface plasmon*. The interesting aspect of these resonances is that they lead to a resonant

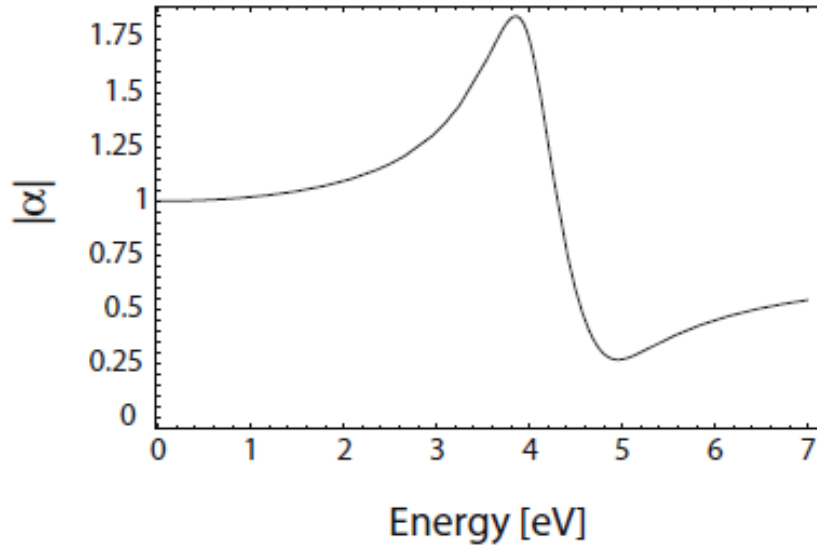


Figure D.2. Absolute value of the polarizability α of a sub-wavelength silver sphere. The resonance shows a finite magnitude because the dielectric function of silver has a non-vanishing imaginary part. Image obtained from Ref. [50].

enhancement of both the internal and external electric fields, as well as the scattering and absorption cross sections, which is extremely useful for applications [239].

A similar treatment can be applied to nanoparticles with other shapes and to other materials, such as polar dielectrics, leading to more complex expressions for α . However, there is a general relationship between the position of the resonance and the nanoparticle size: when the latter is increased, the resonance experiences a red shift. In fact, as the particle size increases, the distance between the charges on opposite sides of the particle increases, resulting in a smaller restoring force and, consequently, a lower resonance frequency.

Appendix E

3D Graphene Networks - Structural Characterization

Figure E.1 reports additional SEM images of samples S1, S2, and S3. For each sample, two magnification factors are reported: x40 and x150 for S1 and S2, and x50 and x80 for S3. More in detail, the lower magnification factors help provide a broader perspective on the samples at a larger spatial scale. With a wider view, it is possible to appreciate the pore-size distribution. It appears that the pores are distributed uniformly over space and do not aggregate in favoured spatial regions. Additionally, it is possible to appreciate the similarity between the structures of S1 and S2.

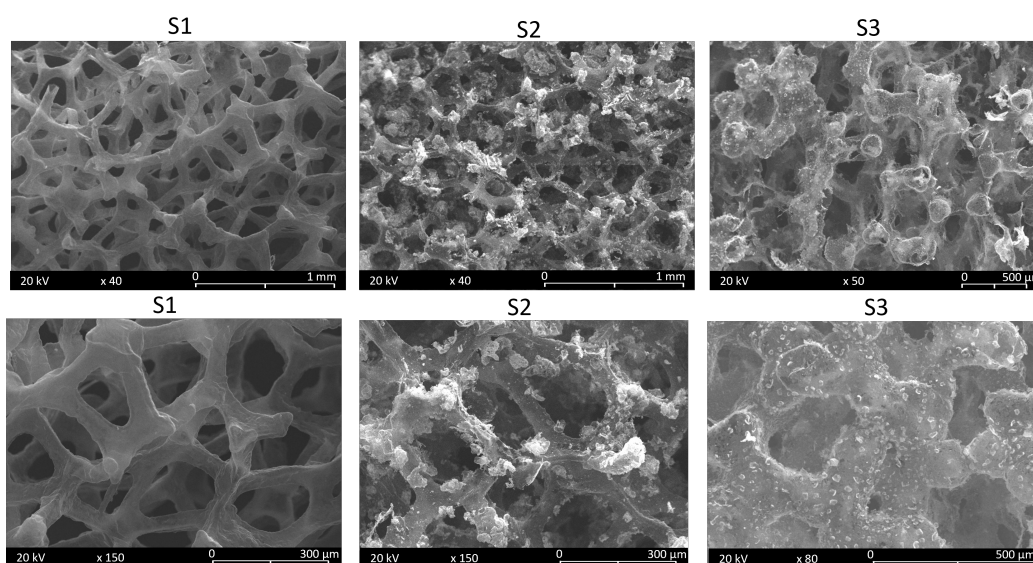


Figure E.1. SEM x40 and x150 magnified images of S1 and S2, and x50 and x80 of S3.

The experimental parameters for controlling the porosity of 3D graphene materials include the CVD temperature and CVD time, which are related to the crystal coarsening of the CVD metallic Ni template. Increasing the temperature and/or time results in larger ligament and pore sizes, but the porosity remains at 99 % due to the presence of hollow and tubular graphene structures. Detailed experimental data and discussions are provided in Ref. [240, 241, 242]. Additionally, the CVD

time affects the wall thickness: the longer the time, the larger the grown 3D branch thickness, which can range from monolayer to bilayer and multilayers.

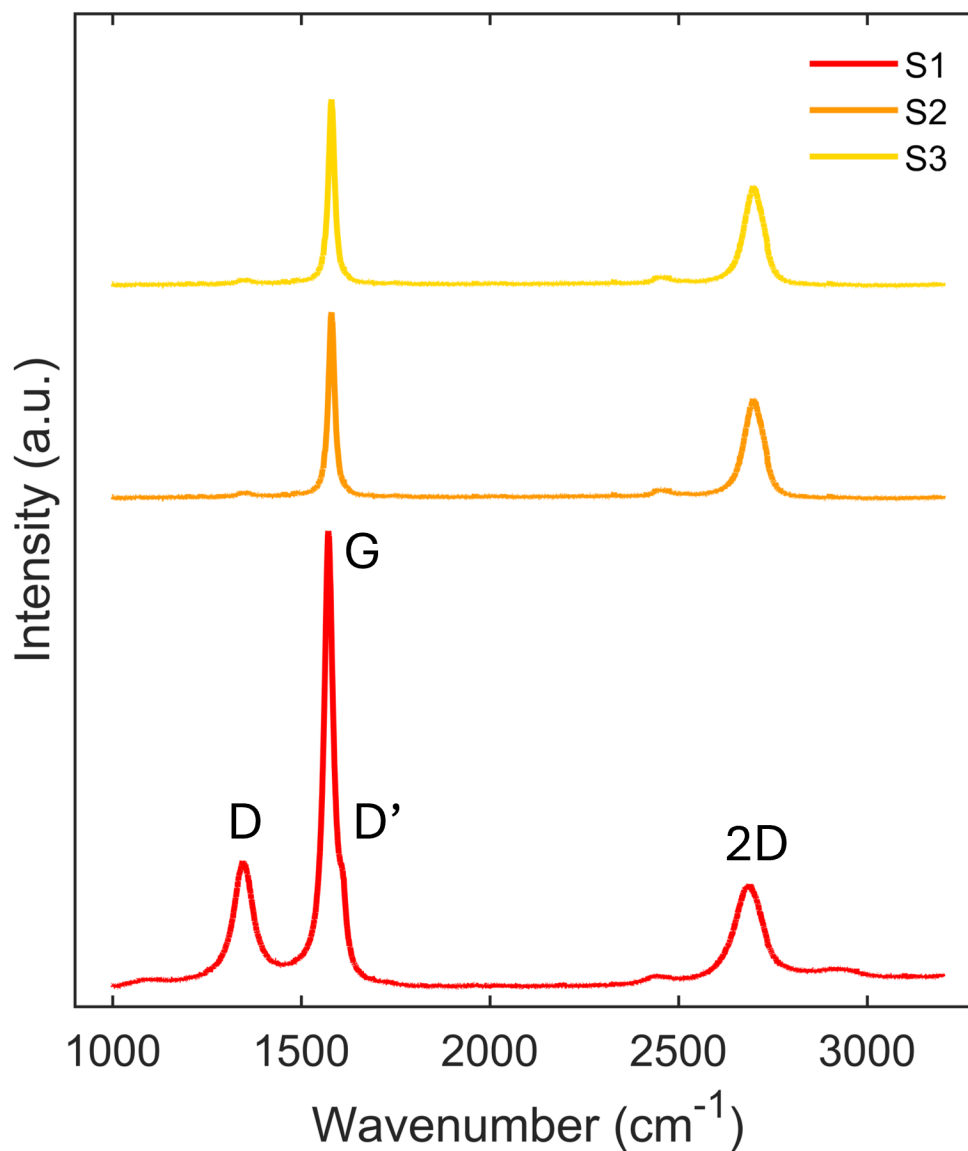


Figure E.2. Raman spectra of S1 (red curve), S2 (orange curve), and S3 (yellow curve) samples between 1000 cm^{-1} and 3200 cm^{-1} . The spectra were shifted along the y-axis for better clarity. D, G, D', and 2D bands are indicated.

Raman spectra were collected on S1, S2, and S3 samples between 1000 cm^{-1} and 3200 cm^{-1} employing a NRS-5100 Laser Raman Spectrometer by Jasco, by using a 20x objective and a green laser (532 nm). Figure E.2 depicts these spectra in red (S1), orange (S2), and yellow (S3), respectively. All samples present D, G, and 2D bands, located at approximately 1350 cm^{-1} , 1575 cm^{-1} , and 2695 cm^{-1} . S1 also exhibits a visible D' band at 1610 cm^{-1} . Based on this, it can be concluded that 3D graphenes are not amorphous. Considering D and G bands, associated with defects and in-plane vibration of sp^2 carbon atoms, respectively, it is observed that in S1, a

strong D band and a dominant and broad G band appear. This indicates a high defect density of the sample. Dealing with S3, a much weaker D band, a sharp G peak, and a barely visible D' band are observed, indicating a better quality of the sample. At last, S2 exhibits the best structural quality since the D band is almost suppressed and the G peak is very sharp.

Figure E.3 shows a significant amount of flexibility of the S1 sample (the same shown in Figure 3.2 (d)-(e) in Subsection 3.1.1). Starting from a flat position (a), the bending angle is increased in (b), reaching a high curvature in (c). Then, 3D graphene is folded back to its original position in Figure (d). These images show that these networks are bendable and can keep the desired amount of deformation, but are also capable of recovering the original configuration, in agreement with the claimed flexibility. At last, Figure E.3 (e) depicts the S1 sample folded via the use of tweezers, demonstrating that it can be bent in the desired configuration. All the images were acquired after performing the thermal emission measurements, demonstrating that the sample keeps its flexibility after withstanding high temperature conditions.

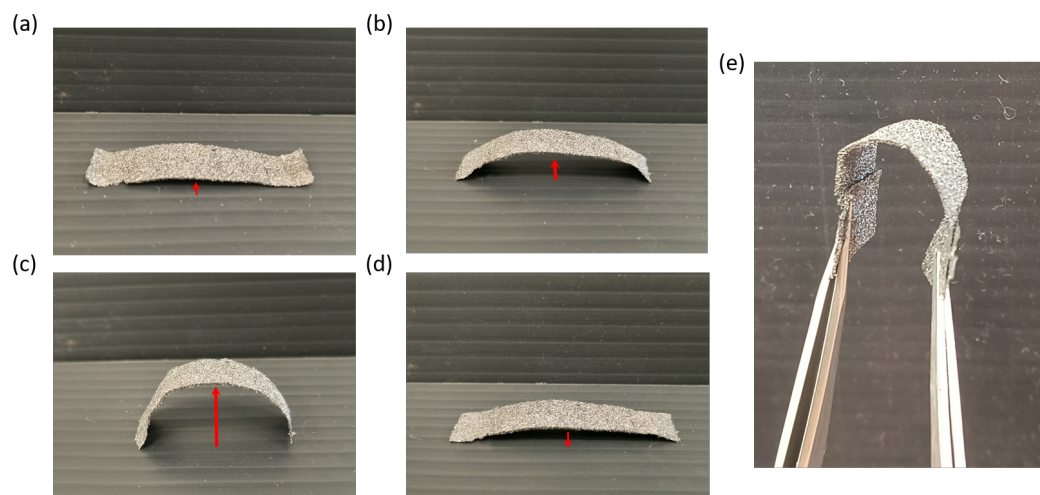


Figure E.3. S1 sample in different bending configurations, starting from a flat position in (a), and approaching curved positions in (b) and (c). Then, 3D graphene is folded back to its original position in panel (d). Figure (e) depicts the S1 sample folded via the use of tweezers, demonstrating that it can be bent in the desired configuration.

Appendix F

Fractal Metamaterials

Figure F.1 reports the comparison between experimental reflectance (continuous lines) and the corresponding fitting curves (black dashed lines) obtained via the RefFIT software in the 700 cm^{-1} - 1200 cm^{-1} spectral range. A good match is found for all the orders.

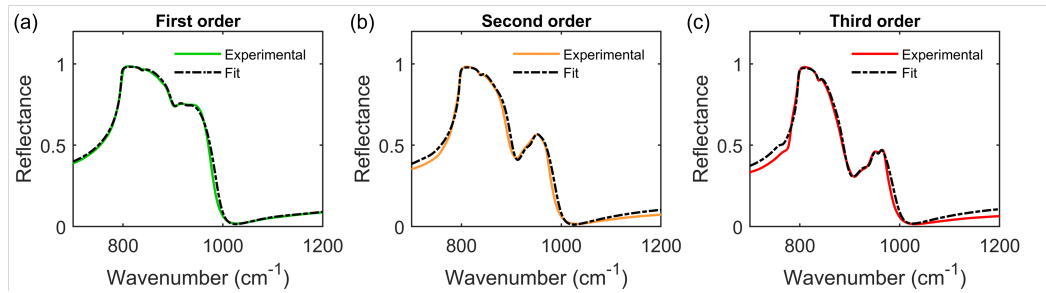


Figure F.1. Comparison between experimental (continuous lines) and fitting (black dashed lines) reflectance curves in the 700 cm^{-1} - 1200 cm^{-1} spectral range for the first order (a), second order (b), and third order (c) fractal metamaterials, in green, orange, and red, respectively.

Figure F.2 shows thermal radiation spectra for the bare (a), first-order (b), and second-order (c) fractal metamaterials, from 30 cm^{-1} to 8000 cm^{-1} , and from $27\text{ }^{\circ}\text{C}$ (blue curve) to $650\text{ }^{\circ}\text{C}$ (green curve). The black arrows highlight the Si-Si lattice vibration (a combination of a TO and a TA mode) of the silicon beam splitter, whereas the red arrows highlight the SiC Reststrahlen band. In each panel, the inset is a zoom between 630 cm^{-1} and 1100 cm^{-1} . The larger the fractal order, the more evident the modulations within the Reststrahlen band.

In the following, a comparison between thermal radiation spectra of bare (dashed lines) and first, second, and third-order fractal metamaterial samples (continuous lines), zoomed in the $630\text{--}1100\text{ cm}^{-1}$ spectral window, and for each of the investigated temperatures, ranging from $100\text{ }^{\circ}\text{C}$ (blue) to $650\text{ }^{\circ}\text{C}$ (green), is reported. In this way, the evolution of the resonances with temperature can be visualized better. As a general trend, common to all the fractal orders, the main difference between the bare and patterned samples lies between $\sim 800\text{ cm}^{-1}$ and 950 cm^{-1} ; outside this range, the spectra overlap. With the increase in the fractal order, the variation between the spectra of the patterned and bare samples becomes more prominent, and, for a given fractal order, with the increase in temperature, the spectra of the patterned and bare samples become more similar.

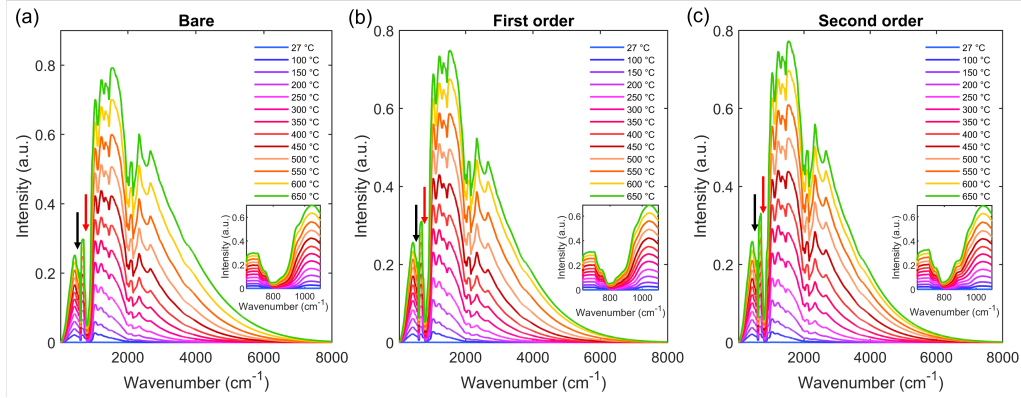


Figure F.2. Thermal radiation spectra for the bare (a), first-order (b), and second-order (c) fractal metamaterials, from 30 cm^{-1} to 8000 cm^{-1} , and from $27 \text{ }^{\circ}\text{C}$ (blue curve) to $650 \text{ }^{\circ}\text{C}$ (green curve). The black arrows highlight the Si-Si lattice vibration (a combination of a TO and a TA mode) of the silicon beam splitter, whereas the red arrows highlight the SiC Reststrahlen band. In each panel, the inset is a zoom between 630 cm^{-1} and 1100 cm^{-1} .

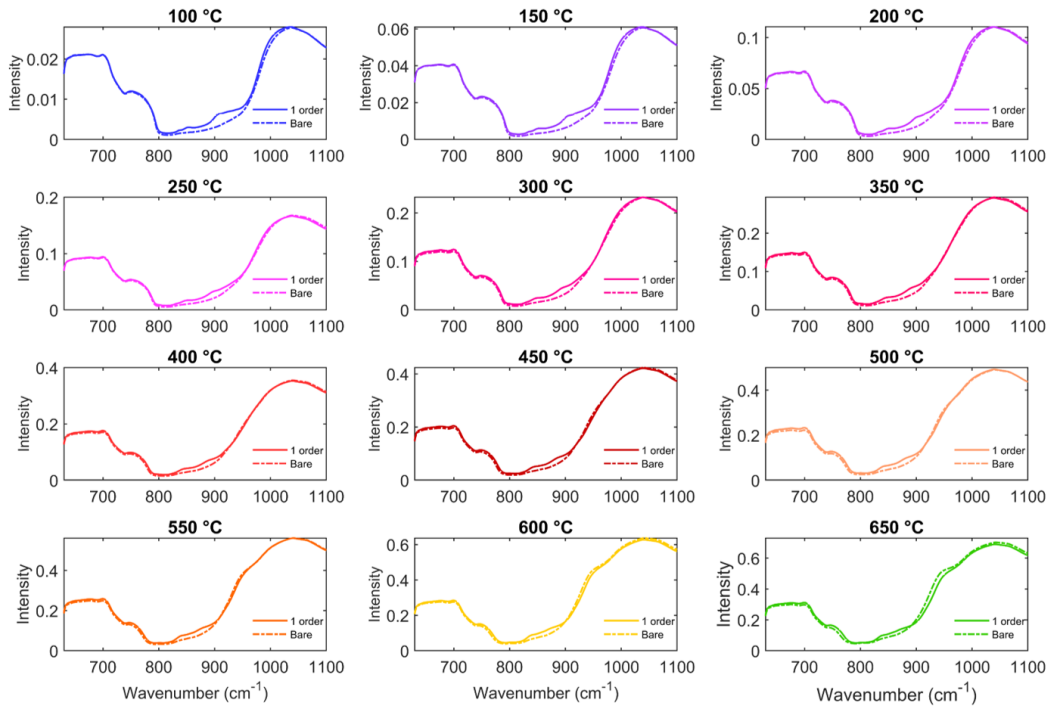


Figure F.3. Comparison between thermal radiation spectra of bare (dashed lines) and first-order fractal metamaterial sample (continuous lines), zoomed in the $630\text{--}1100 \text{ cm}^{-1}$ spectral window, and for each of the investigated temperatures, ranging from $100 \text{ }^{\circ}\text{C}$ (blue) to $650 \text{ }^{\circ}\text{C}$ (green).

Figure F.3 reports a zoom between 630 cm^{-1} and 1100 cm^{-1} of thermal radiation spectra of the bare (dashed lines) and first-order fractal metamaterial sample (continuous lines) for each of the investigated temperatures. As already anticipated, some small modulations are detectable compared to bare SiC, such as the small peak at 838 cm^{-1} and the one at $\sim 900\text{ cm}^{-1}$, which broaden, redshift, and reduce their intensity with increasing temperature, until they almost disappear at $650\text{ }^{\circ}\text{C}$.

Figure F.4 reports a zoom between 630 cm^{-1} and 1100 cm^{-1} of thermal radiation spectra of the bare (dashed lines) and second-order fractal metamaterial sample (continuous lines) for each of the investigated temperatures. The same trend is still true for this sample, even though stronger resonances are present. The small peak at 838 cm^{-1} is now more defined at lower temperatures and disappears already at $500\text{ }^{\circ}\text{C}$.

At last, Figure F.5 reports a zoom between 630 cm^{-1} and 1100 cm^{-1} of thermal radiation spectra of the bare (dashed lines) and third-order fractal metamaterial sample (continuous lines) for each of the investigated temperatures. In this case, the modulations are even stronger than in the previous sample. For this fractal order, it is possible to see the two small modulations at 948 cm^{-1} and 960 cm^{-1} , detected in the far-field reflectance (see Figure 3.12). These dips exhibit a redshift and broaden rapidly; from $250\text{ }^{\circ}\text{C}$ onwards, it is difficult to distinguish them. Additionally, the large peak at $\sim 900\text{ cm}^{-1}$ exhibits a similar trend, diminishing its intensity.

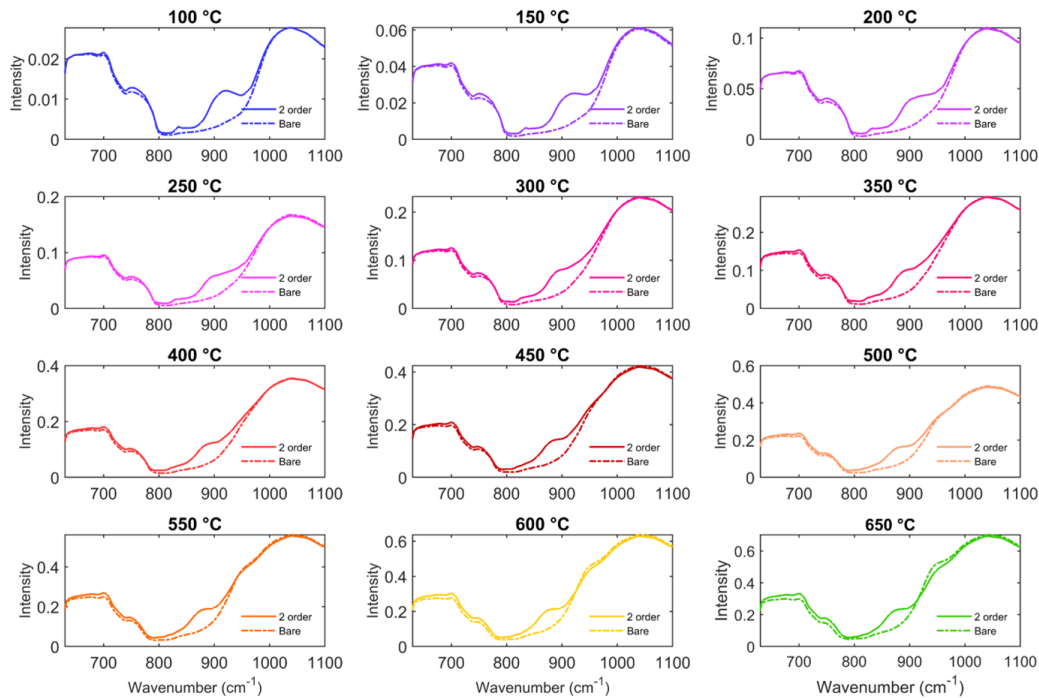


Figure F.4. Comparison between thermal radiation spectra of bare (dashed lines) and second-order fractal metamaterial sample (continuous lines), zoomed in the $630\text{-}1100\text{ cm}^{-1}$ spectral window, and for each of the investigated temperatures, ranging from $100\text{ }^{\circ}\text{C}$ (blue) to $650\text{ }^{\circ}\text{C}$ (green).

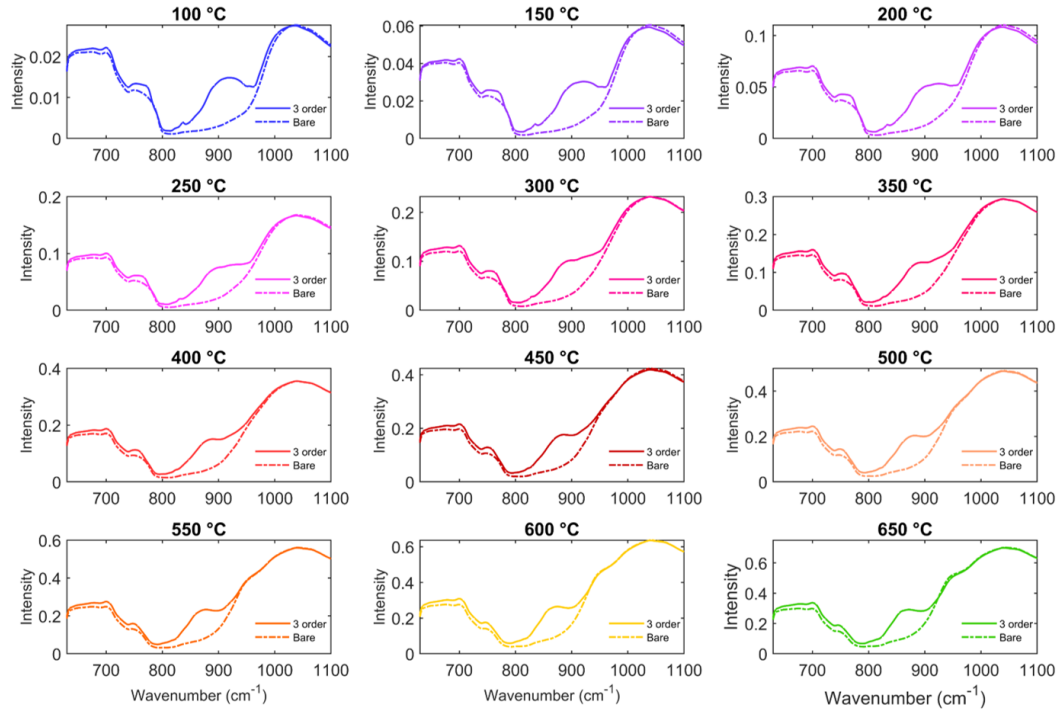


Figure F.5. Comparison between thermal radiation spectra of bare (dashed lines) and third-order fractal metamaterial sample (continuous lines), zoomed in the $630\text{--}1100\text{ cm}^{-1}$ spectral window, and for each of the investigated temperatures, ranging from $100\text{ }^{\circ}\text{C}$ (blue) to $650\text{ }^{\circ}\text{C}$ (green).

Appendix G

Topological Insulator Thin Films - Structural Characterization and Fitting Curves of Reflectance Measurements

G.0.1 Structural Characterization

As already stressed in Chapter 2, topological insulators were grown via Molecular Beam Epitaxy, a highly controllable and reproducible technique that allows for the control of ratios and rates of each element by simply adjusting the cell temperature to obtain the correct stoichiometry. In these materials, the bonding between different quintuple layers is a weak van der Waals type, commonly associated with layered structures. However, the bonding within the stack or the Bi-Te (Bi-Te, Sb-Te) bonding is stronger, enabling the film to grow QL-by-QL. Earlier methods to prepare these films, such as electrodeposition, solvo-thermolization, thermal evaporation, successive ionic layer adsorption and reaction, chemical bath deposition, etc, generally produce lower-quality polycrystalline films. Thus, MBE can challenge the difficulty in growing high-quality single-crystalline films. These materials present intrinsic structural defects, such as anti-site defects in Bi_2Te_3 and Sb_2Te_3 , and vacancies or substitutional defects in Bi_2Se_3 .

The topological insulators' growth developed by the group of Prof. Oh at Rutgers University is a highly efficient and consolidated technique with strong repeatability. The two-temperature growth scheme is a promising strategy for producing high-quality topological insulator films. Indeed, this scheme ensures an atomically sharp interface between film and substrate (Sapphire in this case), instead of disordered layers. Additionally, the order and cleanliness of the substrate are fundamental, since any surface contamination would result in crystal defects or second phases in the epitaxial layers. The ex situ UV (Ultra-Violet) ozone cleaning step, described in Subsection 2.5.1 in Chapter 2, is essential for this purpose. Highly reactive radical oxygen formed in the presence of UV light burns off the majority of organic compounds from the surface. Depending on the substrate, there might be dangling bonds to be saturated to avoid the reaction of the employed elements with the substrate. Once the cleaning step is accomplished, good-quality films can be obtained. However, exposure to the atmosphere at the end of the growth might affect the electronic properties of the films. N_2 is chemically inert (like a vacuum), but O_2 and water molecules are not. For example, for Bi_2Se_3 , N_2 and water provide n-type

carriers through Se out-diffusion or water in-diffusion, whereas O_2 is a p-type dopant (O fills vacant Se slots); therefore, the material will be n or p-type depending on which of these components dominates. Based on this, the deposition of a capping layer on top of the film is essential to preserve the Fermi level position and the correlated electronic properties.

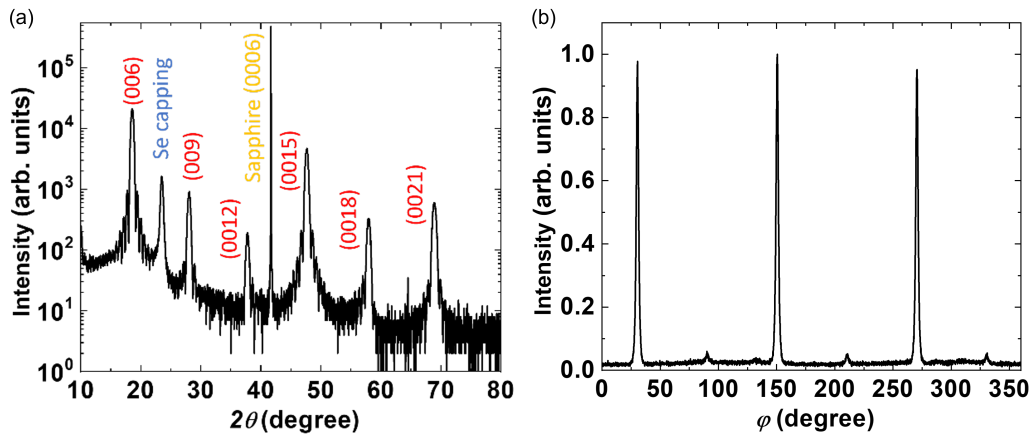


Figure G.1. ω - 2θ (a) and azimuth (b) X-ray diffraction (XRD) pattern for a 20 QL Bi_2Se_3 sample I grew at Rutgers University. In panel (a), the corresponding film peaks are indicated in red, whereas the Se capping and substrate peaks are indicated in blue and yellow, respectively.

As an example, Figure G.1 shows an ω - 2θ (a) and an azimuth (b) X-ray diffraction (XRD) pattern for a 20 QL Bi_2Se_3 sample I grew at Rutgers University. The group of Professor Oh is extremely expert in the growth of these materials, and developed a well-established and reproducible procedure; therefore, I deposited the thin films presented in this work following the “recipe” they found, described in Subsection 2.5.1 in Chapter 2, reproducing standard samples with the same electrical and structural properties. Panel (a) shows the ω - 2θ XRD pattern performed by Jane Chen and Matthew Brahlek at the Materials Science and Technology, Oak Ridge National Laboratory, in Tennessee (United States) on a 20 QL Bi_2Se_3 film. The narrow and intense peak located at $\sim 42^\circ$ corresponds to the 0006 Bragg reflection of the sapphire substrate, and the peak at 23° corresponds to the deposited Se capping layer. The other Bragg peaks at 18° , 28° , 38° , 48° , 58° , and 68° are instead associated with Bragg reflections of the as-deposited film, consistent with the c-axis oriented Bi_2Se_3 phase [243, 244]. The oscillations that surround the film’s peaks are an index of good alignment between the various lattice planes in the deposited film.

The morphology of chalcogenide films usually exhibits triangular pyramidal structures due to twin domains. The latter arise due to the use of a substrate with hexagonal symmetry and result from the two possible layer stacking sequences. Because of the weakly bonded van der Waals gap, these chalcogenides (mainly Bi_2Se_3 and Bi_2Te_3) are prone to twin formation. A twinned domain exhibits the inverted AcBaCB... stacking sequence with respect to the ordinary AbCaBC... and can be described as rotated by 60° around the $[0001]$ c axis of the crystal with respect to that of the ordinary domain. The boundary dividing ordinary and twinned domains, also known as a twin boundary, is the most common planar defect in these materials, and it can be parallel or inclined to the sample surface. The most common ones are perpendicular to the c-axis, i.e., along the growth direction, since the change of the stacking can easily occur in the van der Waals gap. These

defects might affect the electronic properties of topological insulators because the (0001) surface of these materials exhibits topological surface states. Therefore, a vertical propagation of these defects, reaching the sample surface, might importantly influence the performance of these samples. Additionally, twin boundaries act as additional scattering centers, hindering transport properties. Growth temperature plays a major role in the formation and distribution of this type of defect; thus, particular attention should be given to this aspect.

Panel (b) reports XRD azimuth scans for the same 20 QL Bi_2Se_3 sample of the (015) Bragg peak, which has a threefold symmetry according to the rhombohedral crystal structure. The figure shows this threefold symmetry, represented by the intense peaks equally spaced by 120° , located at $\phi \sim 30^\circ$, 150° , and 280° , and corresponding to ordinary domains. Only a small fraction of the total scattered intensity is found at azimuths of 90° , 210° , and 330° , associated with twin domains, indicating the high quality of the film I grew at Rutgers University.

Figure G.2 shows a Scanning Tunneling Microscopy (STM) image of a 100 QL Bi_2Se_3 film obtained from Ref. [244], demonstrating an atomically flat film with long terraces. Triangular terraces are formed, reflecting the threefold symmetry of the bulk Bi_2Se_3 along the hexagonal [001] direction, and each terrace step is ~ 1 nm, i.e., 1 QL along the c-axis, indicating that the growth occurs 1 QL-by-1 QL. Over this area, all triangles exhibit the same orientation, demonstrating once again the high quality of the films grown at Rutgers University.

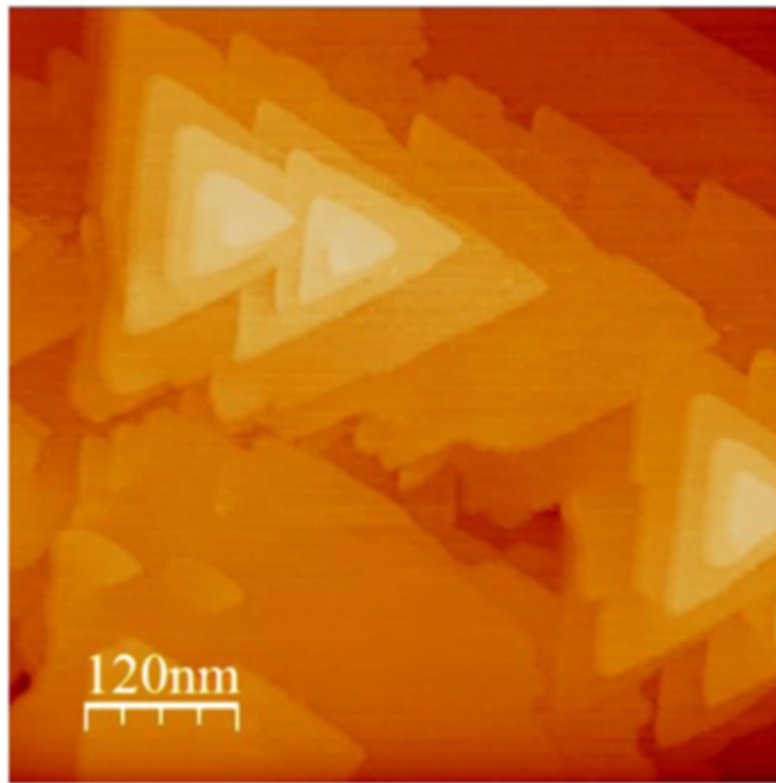


Figure G.2. Scanning Tunneling Microscopy (STM) image of a 100 QL Bi_2Se_3 film obtained from Ref. [244]. The white scale bar in the lower left corner corresponds to a length of 120 nm.

G.0.2 Bi_2Te_3 , Sb_2Te_3 , $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ Alloys films

Figure G.3 shows the fitting curves, depicted with dashed gray lines, obtained

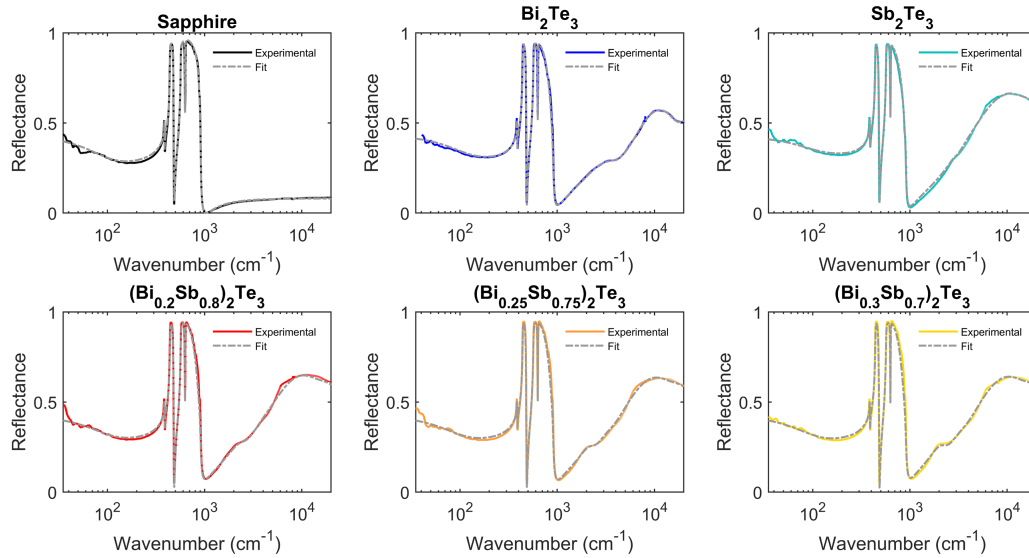


Figure G.3. Experimental reflectance (continuous line) and corresponding fitting curve (dashed gray line) for Sapphire, Bi_2Te_3 , Sb_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, and $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$, in black, blue, light-blue, red, orange, and yellow, respectively, from 40 cm^{-1} to 20000 cm^{-1} . The fitting curves were obtained via the RefFIT software using Drude-Lorentz oscillators.

by modeling the experimental reflectance of the Sapphire substrate, Bi_2Te_3 , Sb_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, and $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$, in black, blue, light-blue, red, orange, and yellow, respectively, from 40 cm^{-1} to 20000 cm^{-1} . The RefFIT software was employed to account for the layered structure of the samples, consisting of a substrate and a thin film, whose surface interfaces with air. Drude-Lorentz contributions were used for each compound.

	Drude term $\omega_p \text{ (cm}^{-1}\text{)}$	$\omega_0^1 \text{ (cm}^{-1}\text{)}$	$\omega_0^2 \text{ (cm}^{-1}\text{)}$	$\omega_0^3 \text{ (cm}^{-1}\text{)}$	$\omega_0^4 \text{ (cm}^{-1}\text{)}$
Bi_2Te_3	2480	/	3400	12000	20000
Sb_2Te_3	3270	3000	4800	11630	16000
$(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$	1950	2440	4420	11200	16000
$(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$	1830	2240	3500	11200	16000
$(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$	1700	2190	3500	11200	16000

Figure G.4. Table reporting the plasma frequency value ω_p , in cm^{-1} , of the free carrier contribution (Drude term) for Bi_2Te_3 , Sb_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, and $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$. The central frequency value ω_0^i of the i -th Lorentz oscillator corresponding to an electronic transition is reported as well.

Table G.4 reports both the plasma frequency value ω_p , expressed in cm^{-1} , of the free carrier contribution (Drude term), and the central frequency value ω_0^i of the first

three or four Lorentz oscillators corresponding to the electronic transitions of Bi_2Te_3 , Sb_2Te_3 , $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$, $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, and $(\text{Bi}_{0.3}\text{Sb}_{0.7})_2\text{Te}_3$. All the plasma frequencies lie in the mid-infrared spectral range; the ones of the pure compounds are larger than those of the alloys. Bi_2Te_3 reflectance was fitted by three Drude-Lorentz oscillators, a minor one at 3400 cm^{-1} , and two main at 12000 cm^{-1} and 20000 cm^{-1} . Sb_2Te_3 reflectance was instead fitted by an oscillator at 3000 cm^{-1} and another one at 4800 cm^{-1} , and then two main oscillators at 11630 cm^{-1} and at $\sim 16000\text{ cm}^{-1}$. The reflectances of the three alloys were fitted by two main Lorentz oscillators at 11200 cm^{-1} and 16000 cm^{-1} , and two additional oscillators were placed at $\sim 2400\text{ cm}^{-1}$ and $\sim 4000\text{ cm}^{-1}$. More in detail, ω_0^1 redshifts from 2440 cm^{-1} to 2190 cm^{-1} , whereas ω_0^2 shifts from 4420 cm^{-1} to 3500 cm^{-1} with increasing Bi content.

G.0.3 Bi_2Se_3 films

Figure G.5 shows the fitting curves, depicted with dashed gray lines, obtained by modeling the experimental reflectance of the Sapphire substrate + 20 nm Se cap, 10 QL Bi_2Se_3 , 20 QL Bi_2Se_3 , 30 QL Bi_2Se_3 , 50 QL Bi_2Se_3 , and 100 QL Bi_2Se_3 , in black, cyan, blue, rose pink, fuchsia, and red, respectively, from 40 cm^{-1} to 8000 cm^{-1} . The RefFIT software was employed to account for the layered structure of the samples, consisting of a substrate, a thin film, and a capping layer, whose surface interfaces with air. Drude-Lorentz contributions were used for each compound.

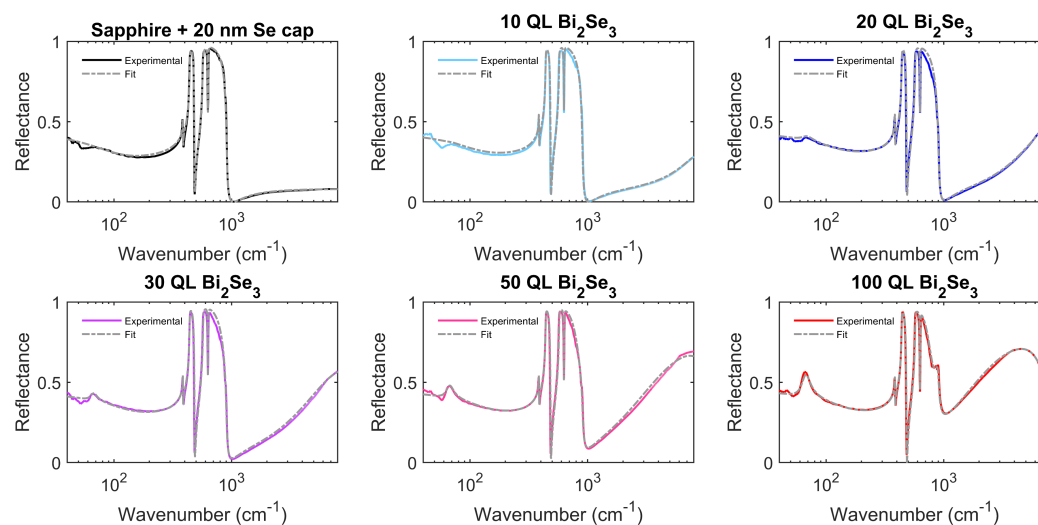


Figure G.5. Experimental reflectance (continuous line) and corresponding fitting curve (dashed gray line) for Sapphire + 20 nm Se cap, 10 QL Bi_2Se_3 , 20 QL Bi_2Se_3 , 30 QL Bi_2Se_3 , 50 QL Bi_2Se_3 , and 100 QL Bi_2Se_3 , in black, cyan, blue, rose pink, fuchsia, and red, respectively, from 40 cm^{-1} to 8000 cm^{-1} . The fitting curves were obtained via the RefFIT software using Drude-Lorentz oscillators.

Appendix H

GST Alloys - Structural Characterization and Fitting Curves of Reflectance Measurements

H.0.1 Structural Characterization

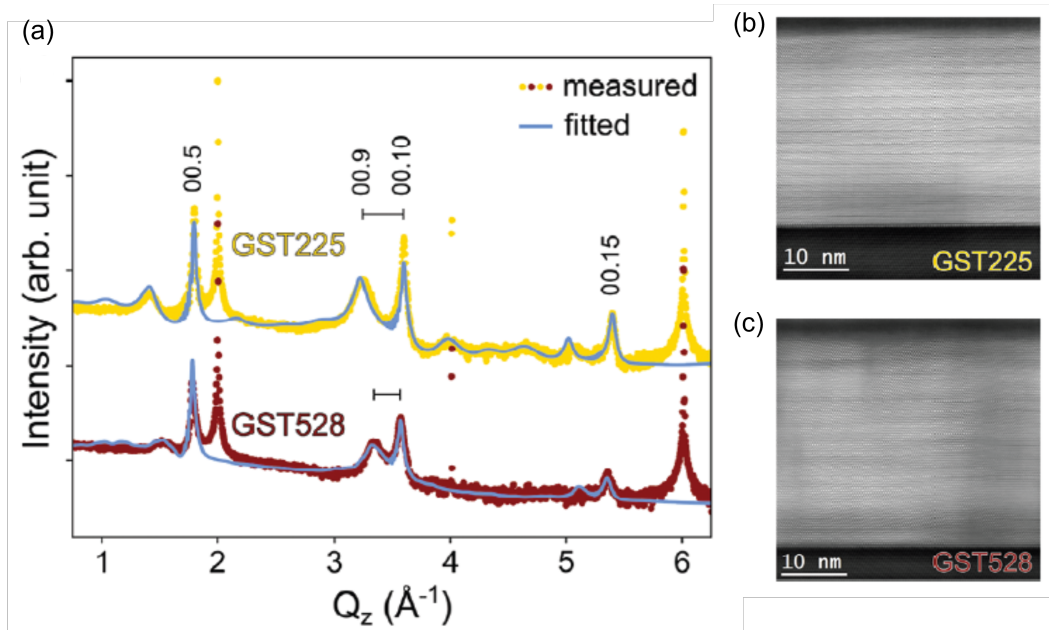


Figure H.1. (a) ω - 2θ XRD pattern for GST225 (yellow curve) and GST528 (red curve) samples grown by Dr. Stefano Cecchi. Instead of 2θ , $Q_z = 4\pi\sin\theta/\lambda$, i.e., the out-of-plane component of the scattering vector, is used. Film peaks are assigned. High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) cross-section images for GST225 (b) and GST528 (c). The scale bar on the bottom left corner corresponds to 10 nm.

The growth of phase-change materials is complex because these are ternary compounds that combine a 2D van der Waals material (Sb_2Te_3) and a 3D one (GeTe). In

this case, the cleaning of the Si(111) substrate is essential, along with its appropriate surface reconstruction, to prevent disordered layers at the film/substrate interface. GST films were deposited on top of a Si(111)-($\sqrt{3} \times \sqrt{3}$)R30°-Sb passivated surface. This kind of surface reconstruction was already found to improve the quality of GeTe films compared to the standard Si(111)-(7×7), almost suppressing in-plane twisted domains and twinned domains, resulting in a quasi-single-crystalline film, intended as a film with single out-of-plane and defined in-plane orientations, except for a small percentage of twinned areas [245]. This improvement positively affects transport properties.

Figure H.1 (a) shows an ω - 2θ XRD pattern for GST225 and GST528 samples grown by Dr. Stefano Cecchi. Instead of 2θ , $Q_z = 4\pi\sin\theta/\lambda$, i.e., the out-of-plane component of the scattering vector, is used. Both samples were deposited on top of a Si(111)-($\sqrt{3} \times \sqrt{3}$)R30°-Sb passivated surface. The sharp peaks at $\sim 2, 4$, and $6 \text{ \AA}^{-1}$ correspond to the 111, 222, and 333 Bragg reflections of the Si(111) substrate. With respect to GST225 (yellow curve), the effect of the increased Ge flux is here underlined. Both curves show the typical pattern of epitaxial GST: the more intense and sharper crystal main peaks are accompanied by broader vacancy layer (VL) peaks, resulting from the disordered, still layered, structure of GST. While the features attributed to GST are qualitatively similar, the Q_z separation between the GST main and VL peaks decreases (see black bars), corresponding to a larger atomic thickness of the average GST block in real space. Indeed, one GST225 block is made up of 9 lamellae, whereas one GST528 block consists of 15 lamellae.

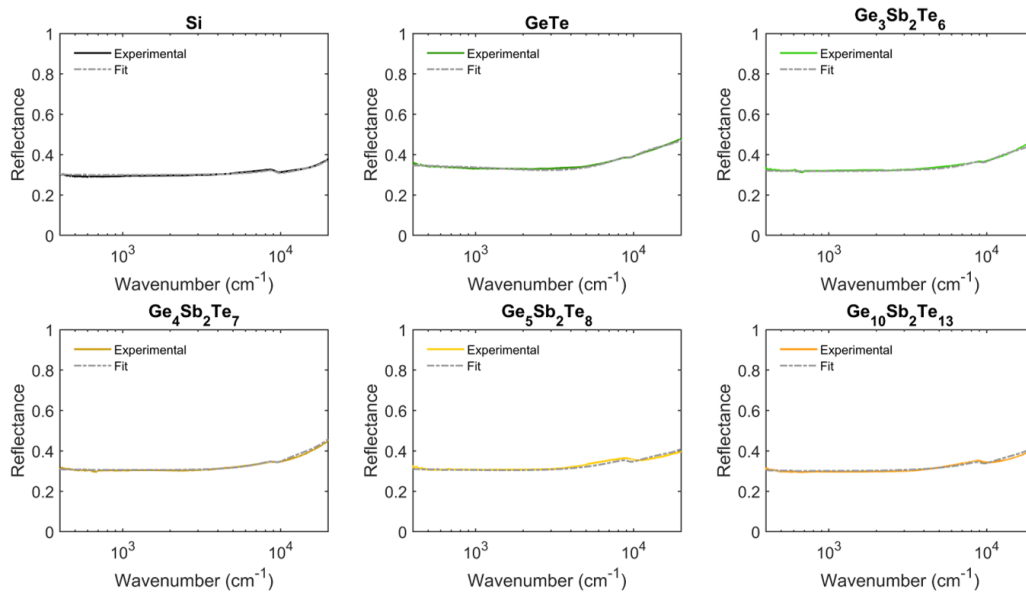


Figure H.2. Experimental reflectance (continuous line) and corresponding fitting curve (dashed gray line) for the reference high-resistivity Si(111) substrate, GeTe, $\text{Ge}_3\text{Sb}_2\text{Te}_6$, $\text{Ge}_4\text{Sb}_2\text{Te}_7$, $\text{Ge}_5\text{Sb}_2\text{Te}_8$, $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$, in black, dark green, light green, brown, yellow, and orange, respectively, from 400 cm^{-1} to 20000 cm^{-1} . The fitting curves were obtained via the ReFFIT software using Drude-Lorentz oscillators.

High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) cross-section images were obtained on the same two samples, and are shown in Figure H.1 (b)-(c). For both, the dark horizontal lines repeated along the vertical direction represent the absence of atoms, i.e., van der Waals gaps.

The separation between two subsequent gaps is smaller for GST225 and larger for GST528, as expected, considering the 9 and 15 lamellae making up a single GST block, respectively. Both images were obtained from Ref. [246].

H.0.2 Fitting Curves of Reflectance Measurements

Figure H.2 shows the fitting curves, depicted with dashed gray lines, obtained by modeling the experimental reflectance of the high-resistivity Si(111) substrate, GeTe, $\text{Ge}_3\text{Sb}_2\text{Te}_6$, $\text{Ge}_4\text{Sb}_2\text{Te}_7$, $\text{Ge}_5\text{Sb}_2\text{Te}_8$, $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$, in black, dark green, light green, brown, yellow, and orange, respectively, from 400 cm^{-1} to 20000 cm^{-1} . The RefFIT software was employed to account for the layered structure of the samples, consisting of a substrate and a thin film, whose surface interfaces with air. Drude-Lorentz contributions were used for each compound.

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