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Editorial

Sol–Gel Method Applied to Crystalline Materials

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Sol–gel chemistry is a versatile synthesis used to produce modern materials at near-room temperature. Glasses, ceramics, composites, and new hybrid materials that are not easy to obtain using other methods have been, instead, obtained in the last three decades and nowadays are widely used. Changing the chemical composition, many parameters of the sol-gel process can be adapted to control the properties and the microstructure of the obtained materials. Sol-gel technology is a multidisciplinary science which allows the expansion of materials for many applications. In this Special Issue, special attention is paid to the properties of materials obtained by using sol–gel methods and to their potential applications in environmental science and materials science as in catalysis, optics, electronics, energy, biosensors, medicine, and so on. This issue collects four contributions, starting with the paper of A.I.M. Greer et co-workers [1] that studied TiO_2 in the anatase polymorph synthesized by sol–gel method as an effective self-cleaning agent under subaquatic conditions. It is known that TiO_2 in the anatase polymorph is a semi-conductor with a band gap energy of 3.2 eV, able to degrade pollutants in air. Positive charges have an oxidizing action on any organic matter (dirt) on the surface, and negative charges combine with atmospheric oxygen to create oxygen radicals that react with oxidized dirt to produce a release of CO_2 and H_2O and ultimately a cleaning of TiO_2 surface. Due to the increasing range of subaquatic system monitoring devices based on optics properties, A.I.M. Greer et co-workers have also tested TiO_2 self-cleaning capacity under water by using crude oil from North Sea Troll B. Dopants of higher (Mn), lower (Gd), and equal (Si) oxidation states were all tested as well as the effects of both the increase in the anatase particle size and the surface roughness. They established that the undoped TiO_2 has the best performances and that the larger the particle size, the lower the roughness and the lower the performances. Finally, they demonstrate that sol–gel-derived TiO_2 in the anatase polymorph is an effective self-cleaning coating under subaquatic conditions. In addition, biological contamination may also be cleansed from the surface using the titania coating, making it suitable for a range of subaquatic applications, where oil or biofilms are known contaminants. In a different context, A. Alsaad and co-workers [2] studied the properties of TiO_2 nanoparticles prepared by using the sol–gel method. They report the synthesis of hybrid thin films based on poly(methylmethacrylate) (PMMA) and poly(vinylalcohol) (PVA), doped with different concentrations of titanium dioxide nanoparticles (TiO_2 NPs), which obtained a hybrid polymeric nanocomposite thin films. This kind of polymeric nanocomposite thin films has received great attention, owing to their unusual physical, chemical, and optical properties. Indeed, high refractive index polymers are good candidates for advanced display devices, micro lens components, organic light emitting diode devices, and lithography. Synergy between metal nanoparticles and polymers exalts the optical properties and modifies the mechanical behavior of the polymer composite. The advancement of polymeric composite

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thin films is basically determined by the selection of ionic fillers and optimum filler loads. In this scenario, A. Alsaad and co-workers studied the transmittance, reflectance, absorption coefficient, optical constants, and optical dielectric functions of hybrid polymeric thin films. Increasing TiO_2-NPs contents in PMMA-PVA polymeric thin films lead to the increase in refractive index values, while the optical band gap energy (4.101 eV) slightly decreases as (TiO_2-NPs) doping levels introduced in (PMMA-PVA) polymeric thin films are increased. The obtained high refractive indices of these thin films indicate that they could be key candidates for strong optical confinement applications and can enhance the optical intensities of nonlinear interactions in optical components of modern devices. The high transmittance, wide bandgap energy, and high refractive index indicate that these films could be employed in the fabrication of a wide range of optoelectronic devices. As far as the sensors field is concerned, D. Triyono and co-workers [3] studied the effect of Zr as a doping agent into $LaFeO_3$. The interest in $LaFeO_3$ among perovskite inorganic materials significantly increased due to their applicability as chemical sensors and electrode materials, etc. Doping the La-site with divalent metals and/or Fe-site with transition metals has been reported to increase the structural and thermal stability, magnetic, and electrical properties as compared with the parent compound.

Many papers on $LaFeO_3$ perovskite doping by substitution of La-site with divalent metals and/or Fe-site with transition metals have been produced, but research investigations on the effect of Zr cations on the Fe-site of $LaFeO_3$ are still lacking information. The question of the effect of Zr, as tetravalent cations occupying the Fe-site of $LaFeO_3$ on the structural parameters and electrical transport mechanism, has not been deeply studied yet. In this context, the authors studied and characterized $LaFe_{(1-x)}Zr_xO_3$ by XRD, Raman scattering analysis, SEM, and impedance spectroscopy method. The $LaFe_{(1-x)}Zr_xO_3$ (x = 0.01, 0.05) ceramics were prepared by sol–gel and annealing methods. Their analysis revealed that the crystal structure tends to preserve its ideal orthorhombic structure, following the increase in driving force of the Fe/ZrO6 octahedral tilting. The frequency-dependent dielectric parameters at each temperature decreased with increasing Zr content, while the temperature dependence with dielectric relaxation increased with increasing Zr content. Zr substitution, until 5% molar concentration, still preserves the single phase of orthorhombic perovskite structure with Pbnm symmetry, followed by the increase in lattice constant with increasing Zr content. Analyses revealed a decrease in lattice disorder and crystal distortion with Zr content which is consistent with the decreased calculated tolerance factor. However, the average crystallite and grain size decrease with Zr content indicating the reduced degree of crystallinity. Finally, the dielectric parameters decrease with increasing Zr content and the activation energy calculated in the relaxation and dc conduction mechanism is found increase with increasing Zr content. The last paper deals with bioactive material synthesized by sol–gel method. T.H. Dang and and co-workers [4] produced a bioactive glass with the composition of $70SiO_2$-30CaO (mol.%) by using, in particular, a modified sol–gel process in hot water without acid catalysts. The original bioactive glass was first discovered in 1970 by Larry L. Hench. The bioactivity of this glass is expressed by the formation of a new layer of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) on its surface when immersed in a physiological solution or implanted in the human body (SBF). Many bioactive glasses have then been synthesized and used as artificial biomaterials for bone substitutes. In the past fifty years, melting and sol–gel have been the two main methods used for the synthesis of bioactive glasses. However, melting bioactive glasses require synthesis processes at high temperatures, where volatile compounds, such as P_2O_5, can be evaporated, resulting in a difference in glassy compositions. Furthermore, the obtained glasses usually have dense structures and low specific surface area values, which produce low bioactivities of synthetic glasses. The sol–gel method overcomes the drawbacks of the melting technique because glasses are synthesized at lower temperatures. Sol-gel bioactive glasses normally have mesoporous structures with larger specific surface area values, leading to higher bioactivity. However, most sol–gel bioactive glasses are prepared using strong inorganic acids as catalysts, which have negative effects on health and the environment

in view of green chemistry. In this context, the breakthrough is to obtain a glass as a totally amorphous material with a mesoporous structure without using acid catalysts. The in vitro experiments confirmed the bioactivity of glass by formation of apatite after one day. In vitro assay in cellular medium confirmed good biocompatibility of synthetic glass. Therefore, the bioactive glass synthesized by an environmentally friendly method in this study can find potential application as artificial bone substitutes.

In summary, this Special Issue highlights the importance of the sol–gel method applied to crystalline materials which are useful in a wide range of applications, reaching a big breakthrough in many fields of science. We would like to thank all authors who have contributed their brilliant papers to this Special Issue, and we also wish to thank the Editorial Office of Crystals for the fast and professional handling of the manuscripts during the whole submission process.

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