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Temperature behavior of optical absorption bands in colored *LiF* crystals

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ABSTRACT

We measured the optical absorption spectra of thermally treated, gamma irradiated *LiF* crystals, as a function of temperature in the range 16–300 K. The temperature dependence of intensity, peak position and bandwidth of *F* and *M* absorption bands were obtained.

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Introduction

Among alkali halide crystals, lithium fluoride, *LiF*, has received great attention due to the peculiar optical properties of radiation-induced point defects, known as color centers [1]. They find applications in optically pumped tunable solid-state lasers [2,3], miniaturized optical devices [3,4], dosimeters and novel radiation-imaging detectors [5,6], mainly exploiting the light emission properties of aggregated electronic defects at room temperature (*RT*). *LiF* possesses the largest band gap, greater than 14 eV, of any solid in natural form. Its high optical transparency is particularly suitable for the investigation of lattice defect spectral features by optical spectroscopy, which has been studied extensively since 1960s [7]. Its theoretical description has been recently revisited [8], as prototype of simple localized defect. Irradiation of *LiF* crystals by several types of ionizing radiations induces the stable formation of primary *F* centers and aggregate electronic defects (F_2, F_3^+, etc.) [4]. According to the literature, at *RT*, the primary *F* absorption peak is at 248 nm [9], while the position of the *M* band, peaked around 450 nm, is dependent on the ratio between the volume concentrations of F_2 and F_3^+ aggregate color centers, consisting of two electrons bound to two and three adjacent anion vacancies, respectively [7]. With respect to other alkali halides, a peculiarity of radiation effects in *LiF* is the stable formation of high densities of F_3^+ centers, together with the *F* and F_2 defects [10].

Due to the strong electron–phonon coupling to the lattice, the absorption bands are homogeneously broadened [1]. Lowering the temperature, the peak positions shift toward lower energies and their full widths at half maximum (*FWHM*s) are reduced [11]; the intensities increase in order to keep constant the total area of each absorption band associated to a specific point defect, according to the physical meaning stated by the Smakula expression [1]. The values of spectral features of the *F* absorption band are found in the literature at a few low temperatures [1,9] and minor differences are found, although the band is isolated. Due to the full overlapping of the F_2 and F_3^+ absorption bands, the situation is more complex for these two kinds of point defects. Different values of peak positions and *FWHM*s are found in the literature. Suitable values were found in [12] at *RT* and 80 K, by a careful comparison of optical absorption spectra of several gamma irradiated polished *LiF* crystals. A systematic investigation into low temperature absorption spectra of radiation induced color centers in *LiF* is needed.

Experiment

The absorption spectra in the ultraviolet (*UV*), visible (*Vis*), and near infrared (*NIR*) regions were measured by a setup from Avantes BV (The Netherlands) [13]. The *UV–Vis–NIR* source was a combined
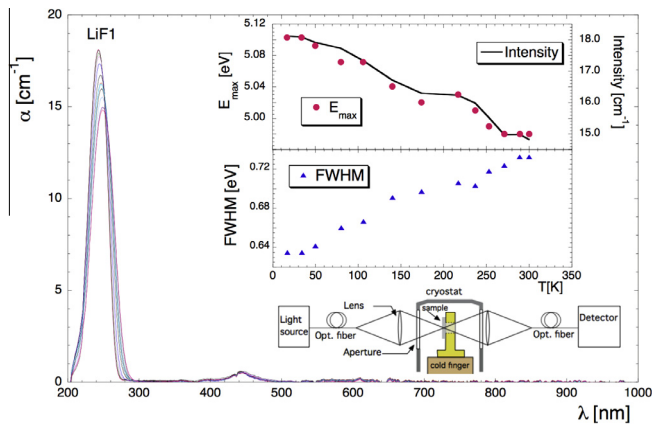
Fig. 1. Temperature dependence of optical absorption coefficient of the colored *LiF1* crystal. In the insets the peak position, FWHM and peak intensity of the *F* band as function of temperature are shown. A sketch of the experimental set-up is also shown.
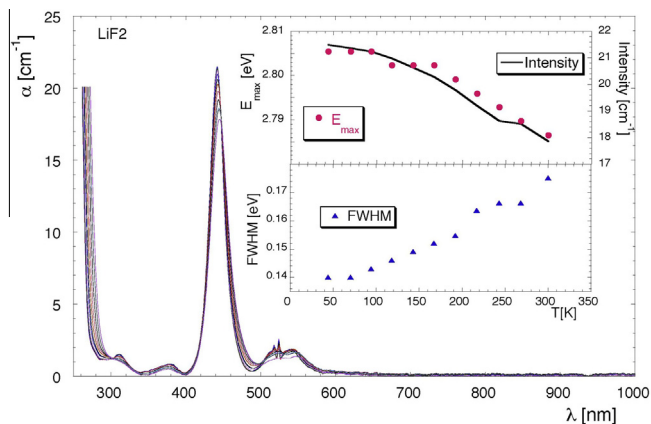

Fig. 2. Temperature dependence of optical absorption coefficient of the *LiF2* crystal. In the insets the peak position, *FWHM* and peak intensity of the F_2 (*M*) band as function of temperature are shown. *F*-band is not shown because it gives saturation in the spectrometer absorption range.

deuterium–halogen AvaLight-DH-S-BAL light source. This was connected by an 800 μm-diameter optical fiber to a CaF_2 lens, used to illuminate the sample. Radiation transmitted through the sample was collected by a second CaF_2 lens and focused to a 600 μm diameter optical fiber connected to an AvaSpec-2048 × 14-USB2 spectrometer equipped with a 2048 × 14 CCD detector. This setup allowed 2.4 nm spectral resolution (see inset of Fig. 1 for a schematic representation of the optical line). *UV–Vis–NIR* absorption spectra were subtracted of the scattering background.

The samples were mounted on a sample holder in mechanical contact with the cold finger of a *He*-gas close-cycle optical cryostat Leybold RDK10-320. The temperature of the sample could be slowly varied from *RT* down to about 16 K and was measured by two calibrated sensor placed close to the sample.

Measurements of optical absorbance were performed on two polished, nominally pure, *LiF* crystals colored by gamma irradiation from a ^{60}Co source at *RT* in air with a dose rate of 0.7 kC/kg h (6.7 Gy/s). One of the samples (hereinafter *LiF1*) was irradiated with 4.2 x 10^3 Gy nominal dose while the other (hereinafter *LiF2*) was irradiated at a higher dose of 6.8 x 10^4 Gy. Sample *LiF2* was also annealed at 200 °C for 20 min in air and then quickly cooled to *RT*, in order to selectively decrease the concentration of F_3^+

defects at the advantage of F_2 centers [12]. The thicknesses of the crystals are 0.198 cm for *LiF1* and 0.127 cm for *LiF2*.

Results and discussion

In Fig. 1 the experimental absorption coefficients of sample *LiF1* in the temperature range 16–300 K are shown. An intense *F* absorption band centered at 249 nm (4.98 eV) at *RT* is clearly observed together with a less intense *M* absorption band peaked at ~440 nm.

In the insets the temperature behavior of the *F* band main parameters, i.e. peak position, full-width-half-maximum (*FWHM*) and peak intensity, is also shown. Minor differences in the peak positions measured at the lowest temperatures are found with respect to those reported in the literature [1,9], and its evolution as a function of temperature can be fully investigated. It is to be noticed the presence of a plateau for all parameters placed in the 150–220 K range. A possible explanation is a crossover between two different coupling regimes of the electronic level of the *F* centers with the lattice dynamics, for instance a cross-over between localized and delocalized lattice vibrations.

In Fig. 2 the experimental absorption spectrum of sample *LiF2* is shown. *LiF2* crystal presents a saturated *F*-band and a much more pronounced *M* band with respect *LiF1*, which is mainly due to F_2 defects [12]; the F_2 band parameters follow a similar qualitative behavior. The presence of other absorption bands, clearly ascribed to more complex defects [14], is also measured. Lowering the temperature, the peculiar narrow spectral features of $F_4(N_1)$ zero-phonon lines at around 520 nm are identified [15].

A more complete analysis and discussion of these absorption spectra and the obtained results is underway together with the comparison with gamma colored *LiF* crystals mainly containing F_3^+ defects.

Acknowledgments

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