



Anomalous europium luminescence in LaF₃



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HIGHLIGHTS

- Optical spectra and dielectric relaxation were measured for Eu²⁺ in LaF₃.
- Bulk conductivity is directly proportional to absorption coefficient of Eu²⁺ bands.
- Dielectric relaxation peak of LaF₃–EuF₃ is attributed to ipoles Eu²⁺-anion vacancy.
- Broadband Eu emission at 600 is attributed to so-called anomalous luminescence.

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ABSTRACT

Optical spectra (absorption, emission, excitation, decay) and dielectric relaxation were measured for divalent europium and partially for ytterbium in lanthanum fluoride crystals. Optical absorption of LaF₃–Eu²⁺ contains not only asymmetric weakly structured band at 245 nm but also less intense bands at 330, 380 nm. Broadband Eu²⁺ emission at 600 nm appeared below 80 K with decay time 2.2 μs at 7.5 K. Emission at 600 nm is attributed to so-called anomalous luminescence. Bulk conductivity is directly proportional to absorption coefficient of Eu²⁺ bands. Dielectric relaxation peak of LaF₃–EuF₃ is attributed to rotation of dipoles Eu²⁺-anion vacancy. The long-wavelength absorption at 300–400 nm region are assigned to transitions from 4f⁷Eu²⁺ ground state to states of neighbouring fluorine vacancy.

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1. Introduction

Europium Eu²⁺ ions are known as very efficient luminescence centres in dense scintillating hosts. Europium is introduced into halide crystal in divalent or trivalent states. A number of investigations are devoted to trivalent lanthanides in LaF₃ crystals (Carnall et al., 1989; Heaps et al., 1976). At the same time authors noted the tendency of EuF₃ to reduce to EuF₂ at the temperatures required for LaF₃ crystal growth and the strong broadband, associated with Eu²⁺ in the visible and ultraviolet range, is due to 4f–4f5d transitions (Carnall et al., 1978).

Absorption bands of Eu²⁺ were observed at 280 nm in LaCl₃ (Gruen et al., 1956) and at 245 nm in LaF₃ (Heaps et al., 1976). Eu²⁺

luminescence was found in LaCl₃ crystal at 420 nm (Kim and Moos, 1967; Lehmann, 1975). Both absorption and emission are obviously due to transitions between ground 4f⁷ and excited 4f⁶5d¹Eu²⁺ states. No data on luminescence of Eu²⁺ in LaF₃ were found in literature.

Besides the normal 5d–4f luminescence in most materials, the Eu²⁺, Yb²⁺ in certain crystals show “anomalous” broadband luminescence with large Stokes shift (see review (Dorenbos, 2003; Grinberg and Mahlik, 2008)). For such crystals the excited 5d level falls into conduction band. Luminescence occurred after transitions from conduction band states, which have less energy than the 5d level, to 4f level of lanthanide impurity ion (Moine et al., 1989; Dorenbos, 2003).

Divalent europium ion has charge less than the charge of host lanthanum ion, therefore, the additional positive charge is needed for each divalent ion for the electrical neutrality of the LaF₃ crystal. In the absence of oxygen the charge compensation of divalent ion

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Ca^{2+} , Sr^{2+} or Ba^{2+} in LaF_3 is accomplished by fluorine vacancy (Roos et al., 1985a; Igel et al., 1982). Parallel growth of ac (alternating current) conductivity and absorption in the visible region was observed in $\text{LaF}_3\text{--Sm}^{2+}$. Conductivity was attributed to Sm^{2+} -fluorine vacancy reorientation (Radzhabov and Kozlovsky, 2015). The dipoles in solids were thoroughly investigated by dielectric relaxation (Jonscher, 1999; Schönhals and Kremer, 2003).

Conductivity of LaF_3 could be measured at mono-frequency. However, the bulk conductivity determined in this way appears to be mostly too small (Roos et al., 1985b). In previous paper we investigated the conductivity of $\text{LaF}_3\text{--Sm}^{2+}$ at frequency 1 kHz (Radzhabov and Kozlovsky, 2015). While the relation between conductivity of samples with different Sm^{2+} concentrations remains the same, the values of measured conductivity were several times less. Therefore, in this paper we measure true bulk LaF_3 conductivity from frequency dispersion (Schoonman et al., 1980).

The main topic of the present paper is to study the optical and dielectric properties of divalent Eu and Yb in LaF_3 .

2. Experimental

Crystals were grown in vacuum in a graphite crucible by the Stockbarger method (Radzhabov et al., 2012). The graphite crucible contained three cylindrical cavities 10 mm in diameter and 80 mm long, which allowed growing three crystals of $\varnothing 10 \times 50$ mm dimensions with different impurity concentrations at the same time. A few percent of CdF_2 were added into raw materials for purification from oxygen impurity during growth. Impurity LnF_3 (Ln – lanthanide) was added into LaF_3 powder in concentration of 0.01, 0.1 and 0.3 mol.%. In $\text{LaF}_3\text{--YbF}_3$ crystals the Ces absorption band at 245 nm and bands at lesser wavelengths were found, which not influenced on Yb^{2+} bands identification. The samples for measurements with sizes of $\varnothing 10 \text{ mm} \times 2 \text{ mm}$ were sawed from the grown rods and were polished.

Absorption spectra in the range 190–3000 nm were taken with spectrophotometer Perkin–Elmer Lambda-950, emission spectra were measured using grating monochromator MDR2 (LOMO). Emission, excitation spectra were measured with photomodule Hamamatsu H6780-04 (185–850 nm). No emission spectrum correction needs to be performed as the sensitivity only weakly changed in the region of Eu emission (400–700 nm). X-irradiation was performed using Pd-tube, operated at 40 kV and 20 mA.

A silver paint (kontaktol "Kettler") was employed as electrode contact material. Diameter of paint electrodes was around 5 mm and sample thickness was around 2 mm. Conductivity measurements were done at room temperature using the impedance (RLC) meter E7-20 (MNIP) in frequency range of 25 Hz–1 MHz. The unit for conductance is S (siemens) which is equal to ohm^{-1} .

3. Results

3.1. Optical spectra

Eu^{3+} ions are easily recognized in LaF_3 (Carnall et al., 1989) and in many other materials by sharp red emission lines due to f–f transitions. No red luminescence due to Eu^{3+} was found in all our $\text{LaF}_3\text{--Eu}$ crystals at 7.5–300 K while intensive ultraviolet absorption was observed. Therefore europium is introduced in divalent form into our LaF_3 crystals. High melting temperature of LaF_3 and reducing conditions due to graphite crucible result in introducing the divalent samarium (Radzhabov and Kozlovsky, 2015) and europium into LaF_3 during crystal growth. In the case of $\text{LaF}_3\text{--SmF}_3$ we obtained the crystal with trivalent Sm and several crystals with different proportions of divalent and trivalent Sm (Radzhabov and Kozlovsky, 2015). Other rare-earth elements are observed in LaF_3 in

trivalent form.

Absorption spectrum of $\text{LaF}_3\text{--}0.01 \text{ mol.}\% \text{ EuF}_3$ contains intensive asymmetric band at 245 nm with unresolved structure and weaker long wavelength bands at 330, 380 nm (Fig. 1). With increasing of EuF_3 doping the ultraviolet absorption becomes larger and at concentration near one percent of EuF_3 the crystal LaF_3 becomes yellow, due to absorption tail above 400 nm (see Fig. 1). The shape of absorption spectra does not depend on concentration of europium up to 0.3 mol.%. At higher concentration the absorption near 245 nm becomes too large. Therefore the long-wavelength bands at 300–400 nm region belong to Eu^{2+} also. Absorption band at 245 nm was ascribed to Eu^{2+} ions (Heaps et al., 1976). The authors have measured absorption spectrum up to 300 nm, which prevents observation of the Eu^{2+} bands at 330, 380 nm.

Red luminescence band at 600 nm was observed in $\text{LaF}_3\text{--Eu}$ at low temperature. Excitation spectrum (see Fig. 1) generally correlates with 245 nm absorption band. However, the red luminescence not observed with excitation into the Eu^{2+} long wavelength bands (see Fig. 1).

With increasing temperature the intensity of luminescence sharply decreases above 40 K (Fig. 2). The decay time of red luminescence was 2.2 μs at 7.5 K. The decay time was sharply decreased above 50 K together with the luminescence intensity (see Fig. 2).

Next most probable divalent lanthanide in LaF_3 is ytterbium. The Yb^{2+} long-wavelength bands were observed around 360, 310 nm in alkaline-earth fluoride crystals (Moine et al., 1989). The Yb^{3+} in LaF_3 shows infrared absorption near 970 nm (Rast et al., 1967). The Yb^{3+} infrared bands grown with increasing of YbF_3 concentration in $\text{LaF}_3\text{--YbF}_3$. No Yb^{2+} ultraviolet bands observed in $\text{LaF}_3\text{--YbF}_3$. After x-ray irradiation of $\text{LaF}_3\text{--YbF}_3$ at room temperature the absorption bands at 270, 300 and 376 nm appear (Fig. 3). Additionally, a very intensive absorption band at 200 nm, belonging to stable at room temperature F_3^- hole defects (Radzhabov, 2016), appear. Evidently the bands at 270, 300 and 376 nm belong to the Yb^{2+} in LaF_3 .

No luminescence in the range 400–1200 nm, excited in the region of Yb^{2+} bands, found in x-irradiated $\text{LaF}_3\text{--}0.3\% \text{ YbF}_3$ at temperatures down to 7.5 K.

3.2. Dielectric relaxation

Fig. 4 presents examples of admittance plots in the complex-

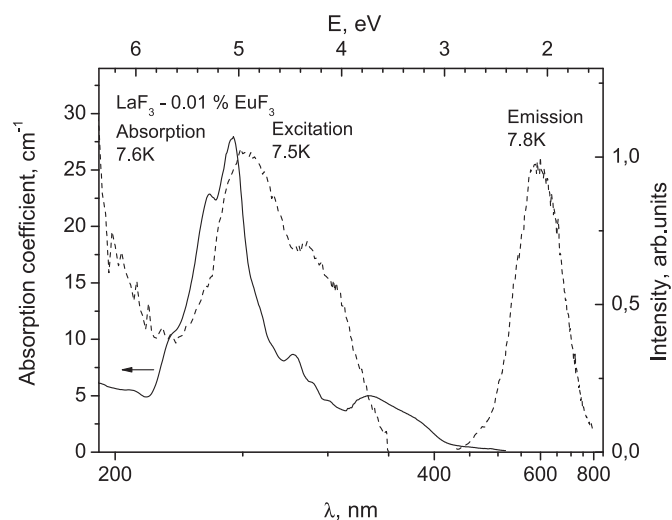


Fig. 1. Absorption spectrum (full curve), excitation and emission (dashed curves) of $\text{LaF}_3\text{--}0.01 \text{ mol.}\% \text{ EuF}_3$ at shown temperatures. Excitation was measured for emission at 580 nm, the emission was measured for excitation at 270 nm.

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