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Extrinsic Luminescence of $\text{BaF}_2 : R^{3+}$ Crystals
($R^{3+} = \text{La}^{3+}, \text{Y}^{3+}, \text{Yb}^{3+}$)

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Abstract—This paper reports on a study of cross-luminescence in barium fluoride crystals doped by a variety of impurities (K^+ , Cd^{2+} , Y^{3+} , Yb^{3+} , La^{3+}). It is shown that doping of the crystal with a trivalent impurity gives rise to the formation of an additional cross-luminescence band peaking at 7.5 eV, the intensity of this band increasing with increasing impurity concentration.

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1. INTRODUCTION

Barium fluoride crystals are at present the fastest of known inorganic scintillators (~ 0.8 ns) [1]. This specific feature of BaF_2 crystals originates from their having an energy gap between the valence-band and the upper core band, which is less than the gap of the crystal, thus making Auger effect impossible from energy considerations [2]. Therefore, these crystals allow core–valence-band transitions (cross–luminescence), which represent essentially radiative transitions of electrons from the valence band, which derives primarily from $2p$ states of F^- , into the upper core band of the crystal formed by the $5p$ states of Ba^{2+} . Cross luminescence has been by now observed in a number of wide-gap dielectrics in which the gap width E_g is larger than the width of the gap E_{vc} separating the valence- from the upper core band (i.e., $E_g > E_{vc}$) (Fig. 1).

Apart from the fast luminescence component, one observes in luminescence spectra of barium fluoride crystals, however, a slow component (~ 620 ns) as well, which derives from the emission of self-trapped anion excitons. This excitonic luminescence can be efficiently suppressed by inserting into the crystal matrix a rare-earth impurity [3]. Alkali halide fluorides can be easily doped with trivalent impurity, with the impurity ion substituting for the cation in the lattice, and the excess charge of the crystal being balanced by the fluorine ions occupying the empty cubes of the lattice (interstices). Activation of BaF_2 crystals with trivalent impurities gives rise to the appearance in the crystal gap of levels belonging to interstitial fluorine ions, whose formation can affect the cross–luminescence of barium fluoride. Therefore, when a new high-energy band peaking at

7.5 eV was found in the x-ray luminescence spectra of $\text{BaF}_2 : \text{La}^{3+}$ crystals [4], it was suggested that this luminescence derives from radiative transitions of electrons from the levels of interstitial fluorine ions into the upper core band of the crystal. (Fig. 1).

It is with elucidation of the nature of this luminescence that the present study deals with. This problem was approached by investigating thoroughly the effect of various impurities (K^+ , Cd^{2+} , Y^{3+} , Yb^{3+}) on the cross–luminescence of barium fluoride crystals.

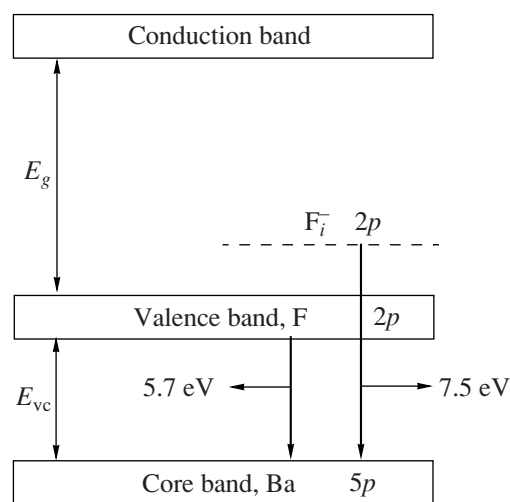


Fig. 1. Band diagram of the core–valence-band transitions in barium fluoride crystals.

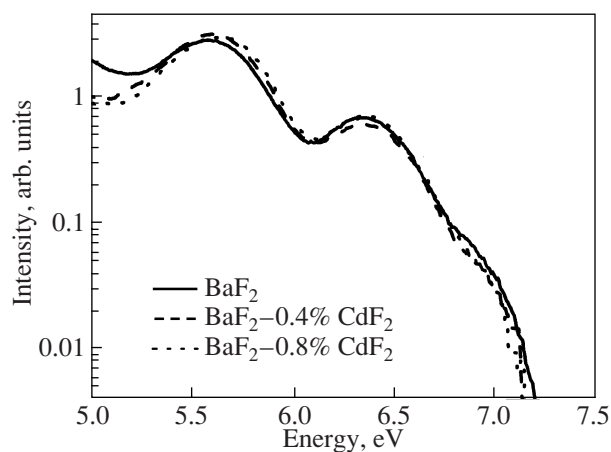


Fig. 2. X-ray luminescence spectrum of the BaF₂ : Cd²⁺ crystal. $T = 77$ K.

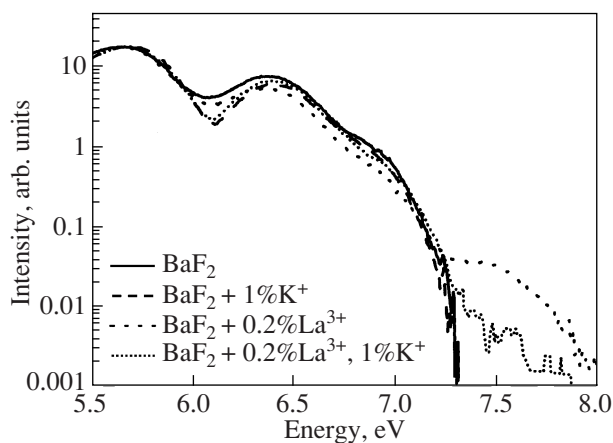


Fig. 3. X-ray luminescence spectrum of the BaF₂ crystals doped by La²⁺ and K⁺. $T = 77$ K.

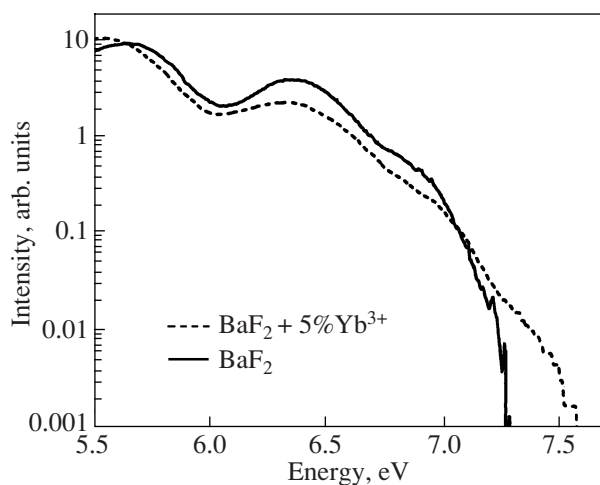


Fig. 4. X-ray luminescence spectrum of the BaF₂ : Yb³⁺ crystal. $T = 77$ K.

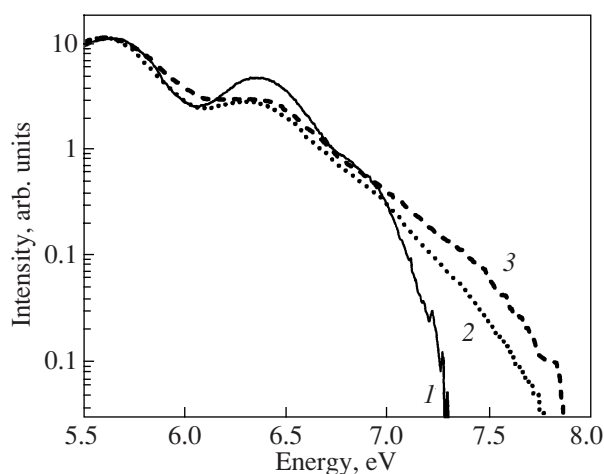


Fig. 5. X-ray luminescence spectrum of (1) the starting BaF₂ crystal and (2, 3) BaF₂ crystals doped by 4% Y³⁺ (2) before and (3) after annealing at $T = 1000$ K.

2. EXPERIMENTAL TECHNIQUE

Raw materials for growing single crystals of barium fluoride with a low content of base metals (particularly of ions of trivalent metals) and oxygen was obtained from the Angarsk chemistry and electrolysis plant. Barium fluoride crystals were melt-grown by the Bridgman–Stockbarger method in a graphite crucible, with about 2% PbF₂ or CdF₂ added to the charge to prevent formation of oxygen impurities. The x-ray luminescence was excited with a BKhV-12 x-ray tube with a palladium anode, which operated at 10 mA, 30 kV. The spectra were recorded with a VM-4 vacuum monochromator, and the luminescence was detected with a FÉU-39 A PM tube.

3. EXPERIMENTAL RESULTS

Figures 2–5 display x-ray luminescence spectra of BaF₂ crystals doped with various activators (La³⁺, Y³⁺, Yb³⁺, Cd²⁺, K⁺), which were measured at 77 K. The spectra of BaF₂ doped by divalent Cd²⁺ and univalent K⁺ ions reveal only the well-known cross-luminescence bands (5.7, 6.3, 7.1 eV) (Figs. 2, 3). The cadmium impurity concentration in the crystals under study did not exceed 0.8%, but this concentration is high enough to make sure that BaF₂ : Cd²⁺ crystals do not produce the 7.5-eV luminescence, because the lowest lanthanum concentration at which one succeeded in detecting this luminescence under x-ray excitation was 0.1% [4].

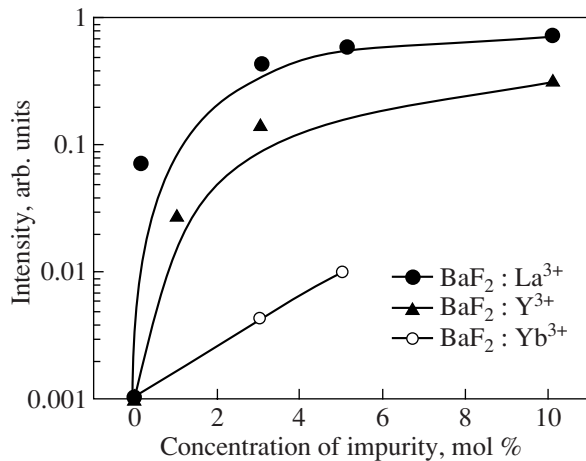


Fig. 6. Dependences of the 7.5-eV band intensity on the impurity concentration.

The x-ray luminescence spectra of barium fluoride crystals doped with Yb³⁺ ions exhibit, besides the well-known cross-luminescence bands, a high-energy band peaking at 7.5 eV as well (Fig. 4). The same luminescence is observed also in Y³⁺-activated crystals (Fig. 5), its intensity growing with increasing impurity concentration (Fig. 6).

Figure 5 presents a luminescence spectrum of BaF₂ : 4% Y³⁺ before (2) and after annealing at 1000 K followed by quenching (curve 3). The annealing was run in vacuum for 15 min. The intensity of the 7.5-eV luminescence grew threefold, but still remained weaker than that in the case of activation of the BaF₂ crystal with La³⁺ ions.

The x-ray luminescence spectra of BaF₂ crystals, doped either by the trivalent La³⁺ ions or by univalent K⁺, display reduction of the 7.5-eV luminescence in intensity compared with the BaF₂ : La³⁺ crystal (Fig. 3).

4. DISCUSSION OF THE RESULTS

Figure 1 presents the band diagram of the BaF₂ : R³⁺ crystal. The diagram specifies the transitions involving cross-luminescence (with the main peak at 5.7 eV) and those from the levels of fluorine interstices into the upper core band of the crystal. As follows from quantum-chemical calculations, the level of the fluorine interstitial ions lies in the gap of the crystal, 2 eV away from the valence band formed by the 2p F⁻ states [5]. It was also established that the La³⁺ 5p level lies 4 eV below the upper core band of the crystal (5p Ba²⁺) [5, 6] and is not involved in BaF₂ luminescence.

The luminescence band peaking at 7.5 eV was first observed in the emission spectra of pure barium fluoride crystals excited by 6-keV electrons [7], and, later, under excitation by 35-eV photons [8]. It was suggested [8] that this luminescence derives from electron transi-

tions from the valence band to the 5p_{1/2} state of Ba²⁺ produced in the spin-orbit splitting of the upper core band (5p Ba²⁺), while the main luminescence maximum (5.7 eV) is produced in the 5p_{1/2} Ba²⁺ → 2p F⁻ transitions. As shown by recent experimental data [9], the width of the gap separating the subbands of the Ba²⁺ 5p states is 2 eV. Within the frame of this hypothesis, the intensity of this luminescence should remain constant for different impurity concentrations; we observe, however, an increase in the intensity of the high-energy luminescence with increasing concentration of a trivalent impurity (see Fig. 5). These data permit a suggestion that the luminescence band peaking at 7.5 eV is related with extrinsic luminescence and connected primarily with the fluorine interstices. We come to the same conclusion by observing that the 7.5-eV band intensity decreases when the BaF₂ : La³⁺ crystal is doped with K⁺, i.e., when the number of interstitial fluorine ions decreases (Fig. 2).

It is well known that activation of alkaline-earth fluoride crystals with rare-earth impurities produce either simple cubic or tetragonal centers if the rare-earth and the interstitial fluorine ions occupy neighbor (*NN* dipole) or second-neighbor (*NNN*-dipole) interstices. At impurity concentrations above 0.1%, defect aggregates consisting of *NN* and *NNN* dipoles start to form [10]. It is defect clusterization that may account for the observation that the intensity of the high-energy band in BaF₂ : La³⁺ is substantially higher than that in barium fluoride crystals doped by Y³⁺ and Yb³⁺ (Fig. 5). It was shown [11] that annealing of a BaF₂ : Y³⁺ crystal brings about an increase in the concentration of *NNN* dipoles at temperatures above 850 K, which may be caused by cluster breakdown and, hence, with an increasing number of free dipoles. Indeed, after annealing of the BaF₂ : 4% Y³⁺ crystal at 1000 K the intensity of the 7.5-eV luminescence increased threefold, which may be considered as supportive evidence for the low intensity of the high-energy luminescence being related with defect clusterization.

Thus, we have studied cross-luminescence in barium fluoride doped by a range of impurities. It has been shown that the high-energy luminescence peaking at 7.5 eV is observed only in BaF₂ crystals activated by trivalent impurities. The low intensity of this luminescence observed with the Y³⁺ and Yb³⁺ dopants (compared with activation with La³⁺) is accounted for by aggregation of the impurity and interstitial fluorine ions. We come thus to the conclusion that the 7.5-eV luminescence is extrinsic and is associated with electron transitions from the levels of interstitial fluorine ions into the upper core band of the crystal.

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