

SCINT 2005

Proceedings of the 8th International Conference on
Inorganic Scintillators and their Use in Scientific and Industrial Applications

The Manuscript of the Proceedings was received by the publisher: **February 2006**.
National Academy of Sciences of Ukraine,
NTC "Institute for Single Crystals",
Institute for Scintillation Materials (ISMA)
Ukraine — Kharkov — 2006

ISBN 9666-02-3884-3

The investigation of high-energy luminescence in BaF₂

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Abstract

High-energy luminescence band, which is due to radiative transition between the electron state of interstitial ions and outermost core band of BaF₂, was investigated in crystals of barium fluoride doped with divalent and trivalent impurities. The theoretical calculations of cross-luminescence have been made in pure crystals of BaF₂.

1. Introduction

The pure crystal of barium fluoride is one of the fastest inorganic scintillators with decay time about 0.8 ns due to radiative transitions between valence band (F⁻ 2p) and outermost core band (Ba²⁺ 5p) of the crystal. This process is known as core-valence transition or cross-luminescence. However, this luminescence overlaps intensive band of slow luminescence (~ 620 nsec), which is due to self trapped excitons.

This undesirable slow luminescence of barium fluoride in region of 310 nm can be reduced by doping with rare-earth elements (La³⁺, Lu³⁺) [1]. It is known that in the crystals Ba_{1-x}La_xF_{2+x} interstitial ions of fluorine are formed as compensators of excess charge of trivalent La³⁺. These interstitial ions form level inside band gap of crystal. It was assumed that this formation causes appearance of high-energy luminescence band with a maximum 7.5 eV, which has been observed in luminescence spectrum of BaF₂ doped with La in addition to self trapped exciton

luminescence (4 eV) and cross-luminescence (5.7, 6.3, 7.1 eV), i.e. this emission is due to radiative transitions between the electron state of interstitial ions and outermost core band of barium fluoride crystals (Fig. 1) [2].

In this work we present results of high-energy luminescence band investigation of barium fluoride doped with Y³⁺ and Cd²⁺ impurities as well as theoretical calculations of cross-luminescence.

2. Experimental technique and methodology

The crystals of BaF₂ were grown from melt using Bridgman-Stockbarger method. These crystals have high optical quality and don't have indication of oxygen contamination. Excitation of X-rays luminescence at 77 K was made from Pd tube operating at 30 kV and 10 mA.

The calculation of cross-luminescence has been made at HF level by embedded cluster approach in pure crystal of BaF₂. Configuration Interaction Singles (CIS) method was used for calculations of transition energies. These methods don't allow to calculate the electron transition from valence band to outermost core band. Therefore we simulate hole on different valence band states and after that we calculate the transition between core band and valence band state, where the hole was simulated.

3. Results and discussion

X-rays excited luminescence spectra of BaF₂ doped both with Y³⁺ and Cd²⁺ consist of the band of self-trapped exciton luminescence (~ 4 eV), and

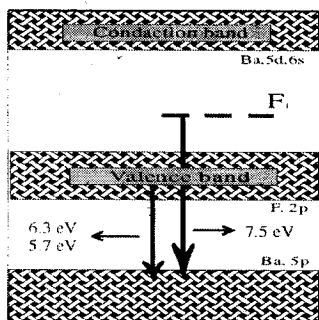


Fig. 1. Scheme of cross-luminescence transitions in crystals of barium fluoride.

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cross-luminescence bands (5.7eV, 6.3eV, 7.1eV) (Fig. 2 and Fig. 3). But in the case of doping with Y^{3+} -impurity the band at 7.5 eV is also observed. The intensity of this luminescence band is less than that in

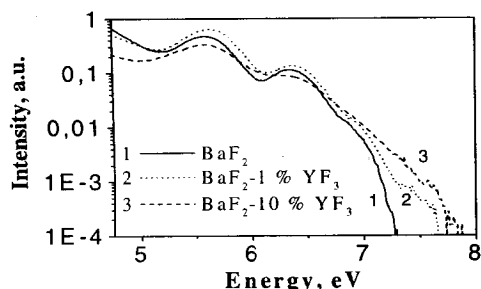


Fig. 2. X-rays excited luminescence spectra at 77 K Y-doped BaF_2 crystals.

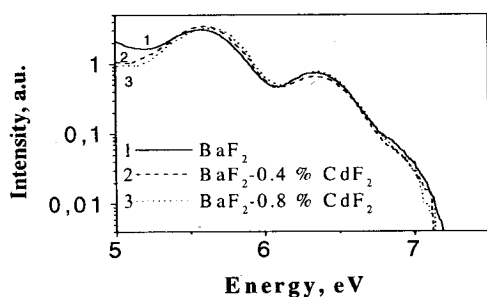


Fig. 3. X-rays excited luminescence spectra at 77 K Cd-doped BaF_2 crystals.

the case of doping with La^{3+} [2]. On the one hand this feature can be due to creation of clusters, i.e. due to aggregations of impurity ions and F^- interstitial ions [3]. The size of impurity ions influences on the formation of the clusters, therefore the ions of Y^{3+} -impurity aggregates more easily than ions of La^{3+} -impurity, because of the Y^{3+} ions ionization radius is bigger than that of La^{3+} ions. But on the other hand core hole is strongly localized state, and electron transition from 8 neighboring fluorine ions cause cross-luminescence. Therefore the core hole can't feel influence of impurity aggregates. Further investigations are needed to clarify the origin of this feature.

For the first time the 7.5 eV luminescence band was observed in luminescence spectrum of pure BaF_2 at 8 K under excitation of 6 keV electrons [4] and later in emission spectrum of this crystal excited by photons with energies above 35 eV [5]. According to authors opinion [5] the radiative transitions of electrons from valence band to $5p_{1/2}Ba^{2+}$ core level can cause the 7.5 eV band of luminescence, while the main maximum of cross-luminescence is due to radiative transitions of electrons to $5p_{3/2}Ba^{2+}$ core level, due to spin-orbit splitting of $5pBa^{2+}$ band is about 2 eV. According to this theory the intensity of the 7.5 eV luminescence band must be constant with different concentration of impurity. But the intensity of 7.5 eV luminescence band increases with

concentration of Y impurity (Fig. 2) and La impurity [2]. Furthermore, luminescence band 7.5 eV is not observed in X-rays excited luminescence spectra of BaF_2 doped with Cd^{2+} (Fig.3). Although the maximum concentration of CdF_2 is about 1%, this is enough to assume that the band 7.5 eV is not created with Cd^{2+} -doping, since for doping with La^{3+} this band becomes observable at concentration level of 0.1%[2]. These results are expected if this luminescence band is due to electron transitions from the state of interstitial F^- ions in BaF_2 crystals, which are created only by trivalent impurities. Thus intensity of this luminescence band will decline with decreasing of the number of interstitial ions. This decreasing can be achieved by doping with one-valent ions of K^+ . Figure 4 shows X-rays excited luminescence spectra of BaF_2 doped with La^{3+} and K^+ . In this figure suppression of luminescence band 7.5 eV is observed with K^+ -doping BaF_2-LaF_3 crystals. This experimental data confirm the assumption that the high-energy band is due to transitions from electron state of interstitial ions to outermost core band of crystal.

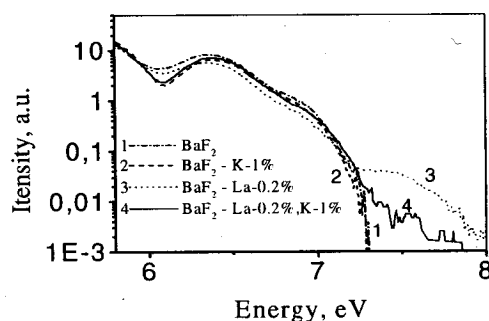


Fig. 4. X-rays excited luminescence spectra at 77 K La and K-doped BaF_2 crystals.

Theoretical calculations of the core hole electronic and spatial structure and cross-luminescence spectrum were performed in the cluster containing 5 Ba^{+2} and 8 F^- ions. The cluster was embedded in deformable and polarizable crystal lattice, which was described classically with pair potentials and shell model. Calculations were performed by GUESS computer code [6].

First, we calculated the equilibrium geometry of cluster, which contains core hole. The core hole is a highly excited state, which is impossible to simulate using HF method. In order to optimize its geometry the following approach has been used. Since core hole is strongly localized on the barium ion, the nearest surrounding fluorine ions feel it mainly as additional positive charge positioned on cation, which becomes Ba^{3+} . Thus we placed additional +1 charge on central barium ion and then allowed the cluster and lattice to relax. The displacement of nearest fluorine ions was 0.268Å in the direction to the barium ion with core hole.

Using this optimized geometry we have performed CIS calculation of optical transitions of hole between core state of barium ion and perturbed valence states of the nearest fluorines. The number of such states is 24, but only 12 transitions are symmetry enabled. These 12 valence states correspond to A_{1g} , E_g , T_{1g} and T_{2g} irreducible representations of O_h group. The calculated spectrum demonstrates three peaks at 5.6, 6.5 and 7.1 eV and conforms well with experimental data (Fig.5). Calculations were performed by Gaussian computer code [7].

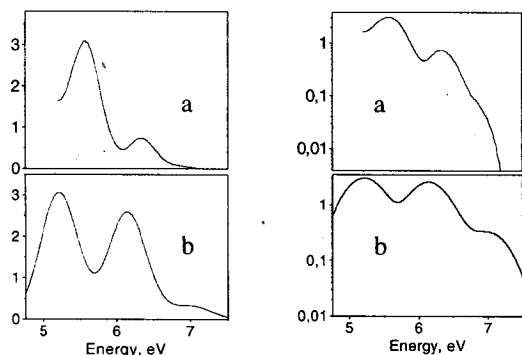


Fig. 5. Calculated (a) and experimental (b) spectra of BaF_2 in linear and logarithmic scale.

4. Conclusions

According to the data obtained the 7.5 eV emission is due to radiative transitions between the electron state of interstitial ions and outermost core band of BaF_2 crystal.

The spectrum of cross-luminescence calculated for localized core hole agrees qualitatively with experimental cross-luminescence spectrum. Different bands in the calculated spectrum originate from transitions between the core hole ($5p$ of Ba^{2+} ion) and several states of different symmetry splitted from valence band ($2p$ states of neighboring fluorine ions).

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