Impurity Luminescence in $BaF_2:Y^{3+}$ and $BaF_2:Yb^{3+}$ Crystals

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Abstract—This paper presents both investigations of high-energy luminescence with maximum at 7.5 eV in $BaF_2:Y^{3+}$ and $BaF_2:Yb^{3+}$ crystals and theoretical calculations of cross-luminescence spectrum in crystals of barium fluoride with interstitial ions of fluorine. The dependencies of the 7.5 eV emission intensity as function of different impurities mol. concentration are presented. The intensity of this emission increases with concentration of rare-earth impurity, but in the case of doping by Yb^{3+} and Y^{3+} this intensity is less than that in the case of La^{3+} doping. This feature (as well as the nonlinear dependence) can be due to the creation of clusters, i.e., aggregation of impurity ions and F^- – interstitials. The intensity of the 7.5 eV luminescence in $BaF_2:Y^{3+}$ crystal after annealing at 1000 K increased by three times but it remained less than in the case of La^{3+} doping.

Theoretical calculations of the core hole electronic and spatial structure and cross-luminescence spectrum were performed in the $[Ba_6F_{12}]$ cluster. This cluster contains interstitial ion of fluorine, which is surrounded by six ions of Ba^{2+}. In the case of using Hartree-Fock method the calculated luminescence spectrum of BaF_2 crystal with interstitial fluorine shows cross-luminescence band with main maximum at 5.2 eV and high-energy band at 11.7 eV. In the case of using TD DFT method the energies of both cross-luminescence transitions and of transition between interstitial ion and core levels are in satisfactory agreement with experimental data, being all overestimated by approximately the average value of 0.8 eV.

Index Terms—Clustering method, impurity, luminescence.

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

I. INTRODUCTION

THE DEVELOPMENT of high-energy physics demands new scintillation materials, which must satisfy the requirements of short emission time, high quantum yield and radiation stability. After the discovery by Laval *et al.*. [1] of fast luminescence band in barium fluoride with main maximum at 5.7 eV and with short decay time ($\sim 0.8\,\mathrm{nsec}$), high intensity and temperature stability, this crystal attracted attention as a new inorganic scintillator. This fast luminescence is called core-valence or cross-luminescence and it is related to radiative transition between valence (F, *2p*) and core (Ba, *5p*) bands of the crystal. At present the cross-luminescence has been found in a great number of wide-gap materials, which are characterized by the band gap energy E_g greater than the gap E_{vc} between the valence and outermost core band (i.e., $E_g > E_{vc}$), so that Auger electron emission is energetically impossible (Fig. 1) [2].

However, fast cross-luminescence band in BaF_2 overlaps with intensive band of slow luminescence ($\sim 620\,\mathrm{nsec}$) due to self trapped excitons. This undesirable slow luminescence of barium fluoride in region of 4 eV can be reduced by doping with rare-earth elements [3], but the physics of this phenomenon is not yet completely clear.

Nevertheless, one of the important effects of the Re^{3+} impurity introduction is the appearance of levels in the band gap formed by *2p* states of fluorine interstitial ions (F_i^-), which enter the crystal as compensators of excess charge of trivalent impurities. When the concentration of impurity is increased to a few mol. percent this interstitial ion levels create a subband in the band gap of the crystal. Appearance of an interstitial fluorine subband can influence the mechanism of cross-luminescence. In x-rays excited luminescence spectrum of BaF_2 crystals doped with La^{3+} a new high-energy emission was observed [4], with intensity of this emission increasing with concentration of impurity. Authors of [4] supposed that this ultraviolet luminescence is due to radiative transitions from interstitial fluorine subband to outermost core band (Ba, *5p*) (Fig. 1).

The first theoretical calculation of the cross-luminescence had been performed by Andriessen *et al.* [5] with molecular cluster approach using $[BaF_8]^{5-}$ cluster. These calculations were reexamine by T. Ikeda and H. Kobayashi [6] using lager cluster $[Ba_{19}F_{32}]^{+6}$. The predicted spectra of both works agreed well with experimental, but transition energies were calculated only from one-electron states spectrum. It is well known that using one-electron energies for calculation of optical transition can lead to not only quantitatively, but also qualitatively wrong results. Also the results of [5], [6] were obtained without taking into account the lattice relaxation in the presence of core hole. Therefore these results have to be refined, since the data of ultraviolet photoelectron spectroscopy clearly indicate that the core hole induces lattice distortion around itself [7].

In the present work we have studied high-energy luminescence in BaF_2 crystals with rare-earth impurities (Y^{3+} and Yb^{3+}) both experimentally and theoretically by means of *ab initio* calculations.

II. METHODOLOGY

The crystals of $BaF_2:Y^{3+}$ and $BaF_2:Yb^{3+}$ were grown from melt using Bridgman-Stockbarger method. High purity barium fluoride powder raw material (better than 99.99%) was used. A few percent of CdF_2 or PbF_2 were added as oxygen scavengers. These crystals have high optical quality and haven't indication oxygen contamination. Samples of these crystals of the dimension approximately $5 \times 5 \times 2$ mm were used. Excitation of X-rays induced luminescence at temperature 77 K was made from Pd tube operating at 30 kV and 30 mA. All luminescence spectra were normalized at main maximum of core-valence transitions (at 5.7 eV). The annealing of samples was done in vacuum tube at temperature 1000 K during 15 minutes.

The *ab initio* Hartree-Fock (HF) and density-functional theory (DFT) calculations of cross-luminescence have been performed in embedded-cluster approach implemented in the GUESS computer code [8]. In this approach a quantum-mechanical (QM) cluster with the defect and its nearest neighbors is surrounded by interface ions and by several hundreds of ions, which treated classically in the shell model. All quantum-mechanical, interface and classical ions are allowed to relax during the geometry optimization run. This region is surrounded by several thousands of fixed atoms, which are represented as point charges and provide accurate electrostatic potential inside classical and QM regions.

We used standard Huzinaga D95 basis set on fluorine ions and LANL2DZ basis and ECP (effective core potential) on barium ions. To avoid the distortion of ground and excited states with the presence of positive point charges in some vicinity of QM cluster they were replaced by LANL1 ECPs. Configuration interaction singles (CIS) and time-dependent DFT (TD DFT) methods were applied for calculation of transition energies. In DFT calculations a modified B3LYP functional has been used containing 40% of HF exchange and 60% of DFT exchange. The embedded-cluster calculation of cross-luminescence was performed using the $[Ba_6F_{12}]$ cluster with interstitial ion of
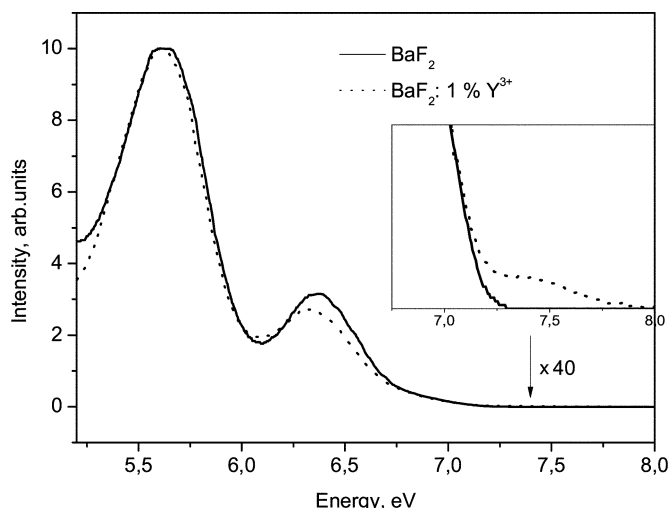

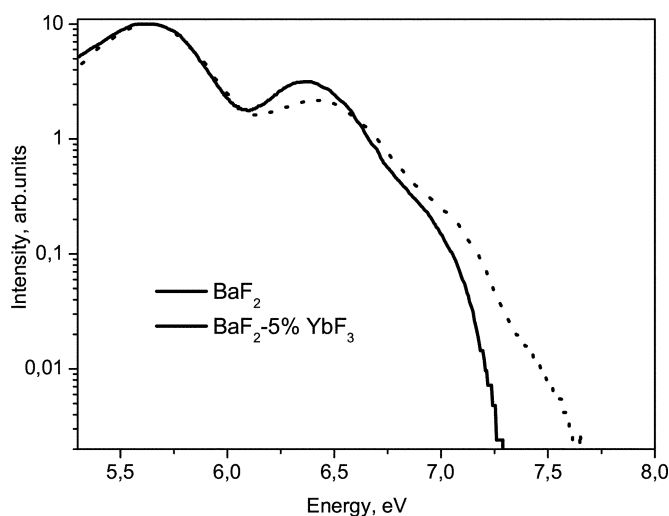Fig. 2. X-rays excited luminescence spectra of BaF_2 doped with 1% Y^{3+}.

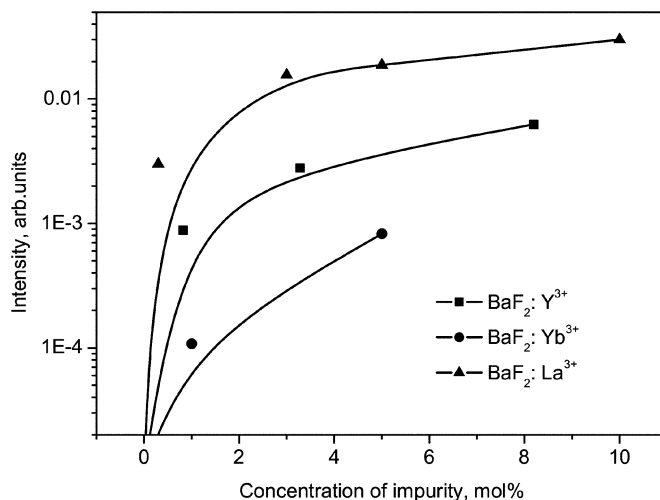Fig. 3. X-rays excited luminescence spectra of BaF_2 doped with 5% Yb^{3+}.

Fig. 4. The dependencies of the 7.5 eV luminescence band intensity as function of different impurities mol. concentration.

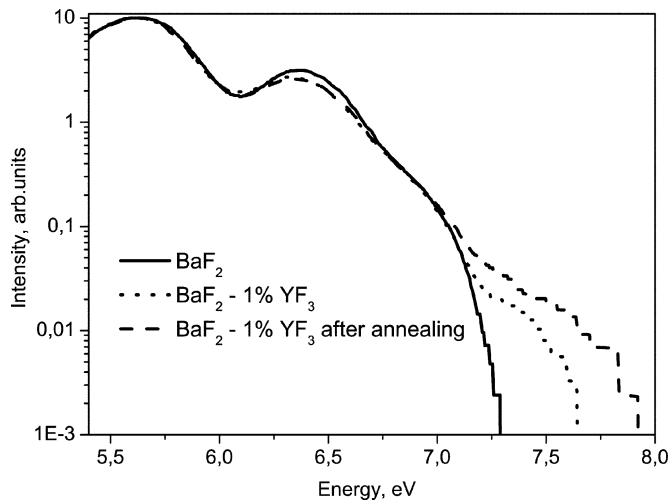fluorine (Fig. 6). Classical region of radius 13 Å included 700 ions.

Fig. 5. X-rays excited luminescence spectra of BaF_2 doped with 1% Y^{3+} before and after annealing at 1000 K.
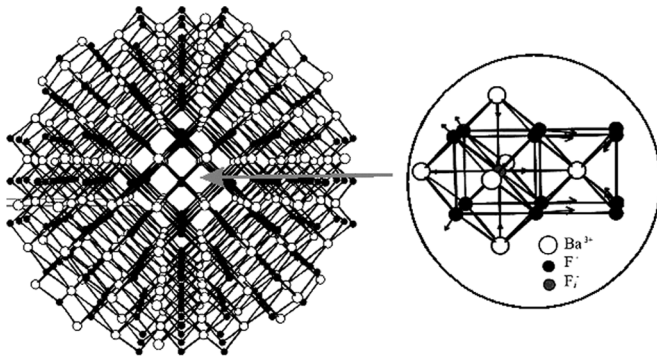

Fig. 6. Illustration of the embedded-cluster model used in the cross-luminescence calculation. The quantum cluster is shown enlarged.

III. RESULTS AND DISCUSSION

A. Experimental Results

Fig. 2 presents the X-rays excited luminescence spectra of BaF_2 doped with 1%Y^{3+} measured at 77 K. There are several bands: self-trapped exciton luminescence ($\sim 4\,eV$), cross-luminescence bands (5.7 eV, 6.3 eV, 7.1 eV) and high-energy emission with maximum at 7.5 eV. This emission was also observed at X-rays excited luminescence spectra of BaF_2 doped with different concentration of Yb^{3+} impurity (Fig. 3).

According to the Fig. 4 the intensity of 7.5 eV emission increases with concentration of rare-earth impurity, but in the case of doping by Yb^{3+} and Y^{3+} this intensity is less than that in the case of La^{3+} doping. In the case of Yb^{3+}-dopping the 7.5 eV emission band overlaps with carge-transfer absorbtion band with maximum at 8.1 eV, therefore we observed slight intensity of hight-energy luminescence in BaF_2:Yb^{3+} crystals. In case of Y^{3+}-dopping This feature (as well as the nonlinear dependence) can be due to the creation of clusters, i.e., aggregation of impurity ions and F^- – interstitials [9]. The size of impurity ions influences the formation of the clusters, therefore the Y^{3+} ions aggregate more easily than La^{3+} ions, because of greater ionic radius of the former. Authors of [9] show that dissolution

of impurity aggregates occurs at 800 K. Fig. 5 presents the X-ray excited luminescence spectra of BaF_2 doped with 4% Y^{3+} at 77 K before (2) and after (3) annealing at 1000 K. The intensity of the 7.5 eV emission increased by three times but it remained less than in the case of La^{3+} doping. In spite of this we can conclude that low intensity of the 7.5 eV luminescence in the case of Y^{3+} doping is mostly due to aggregation of defects and impurities.

For the first time the 7.5 eV emission was observed in luminescence spectrum of pure BaF_2 at 8 K during excitation by 6 keV electrons [10] and later in the emission spectrum of this crystal exited by photons with energies above 35 eV [11]. According to the authors opinion [11] 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, since the spin–orbit splitting of $5pBa^{2+}$ band is about 2 eV. However this suggestion implies that the intensity of the 7.5 eV luminescence band should not depend on concentration of impurity. But the intensity of 7.5 eV luminescence band increases with concentration of rare-earth impurity (Fig. 3), therefore we can conclude that this band is connected with impurity doping (namely with fluorine interstitial ions).

B. Theoretical Calculation

1) Simulation of Core Hole as Point Charge: As a first step we calculated the equilibrium geometry of the cluster [Ba_6F_{12}] which contains core hole. The core hole is a highly excited state, which is impossible to simulate using HF or DFT method. In order to optimize its geometry the following approach has been used. It was assumed that core hole is strongly localized on the barium ion and 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 the barium ion and then allowed the cluster and lattice to relax. The maximum displacement of nearest fluorine ions was 0.289 Å (i.e., 9.5% of fluorine-fluorine lattice separation) in the direction to the barium ion with core hole (Fig. 6). The displacements of interstitial fluorine ion and central barium ion with additional charge were 0.223 Å (7%) and 0.083Å (2.6%), respectively. The relaxation energy was 3.73 eV.

The cross-luminescence spectrum calculated with CIS method is presented on Fig. 7(a). After lattice relaxation 24 states of nearest fluorines were splitted from valence band, and for these states the optical transitions into core hole 5p Ba state were calculated. For the calculation of the energies and intensities of core-valence transitions the following approach has been used. Since the core hole on Ba *5p* level is highly excited state it's impossible to converge the electronic density of such state in SCF procedure. Therefore the densities corresponding to the hole on 24 different states splitted from valence band were obtained first with SCF calculations, and after that the transitions of these holes to Ba 5p core level were calculated with CIS.

The calculated spectrum demonstrates three peaks at 5.2, 6.1 and 7.1 eV and agrees well with experimental data. However the energies of electron transition from interstitial ion level is around 11.2 eV (it greater by 50% than experimental value). HF
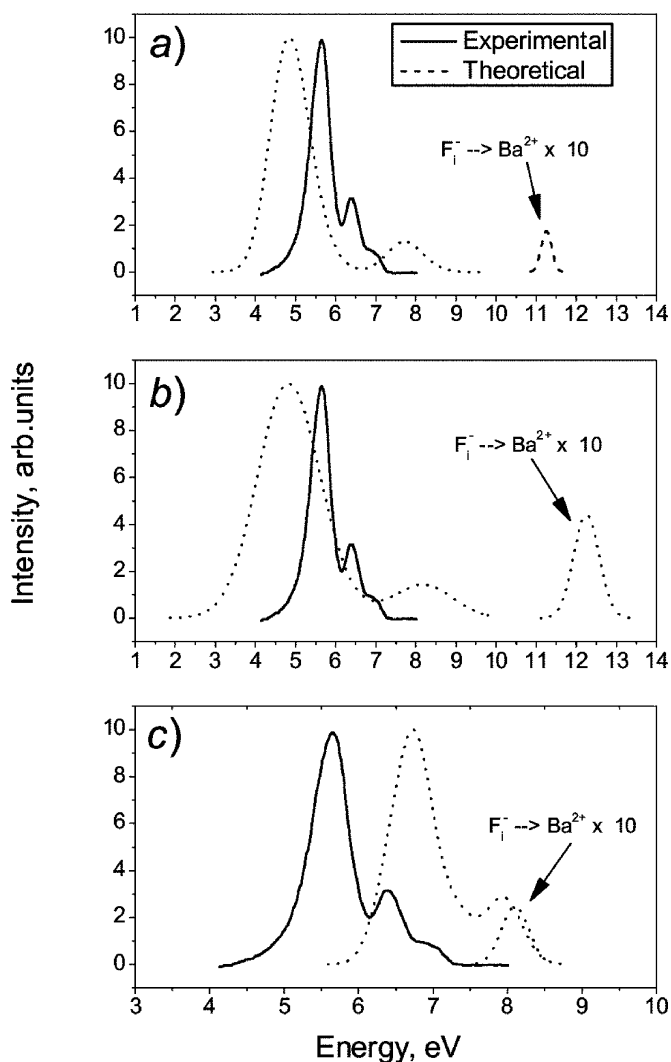
Fig. 7. Calculated cross-luminescence spectrum (solid line) in comparison with experimental data (dotted line): (a) optimized geometry of core hole as additional point charge, CIS method; (b) optimized geometry of core hole as excited state, CIS method; (c) Optimized geometry of core hole as excited state, TD DFT method. The intensities of transitions from interstitial level to core band is scaled by the factor of 10.

TABLE I
COMPARATIVE ENERGY OF CROSS-LUMINESCENCE

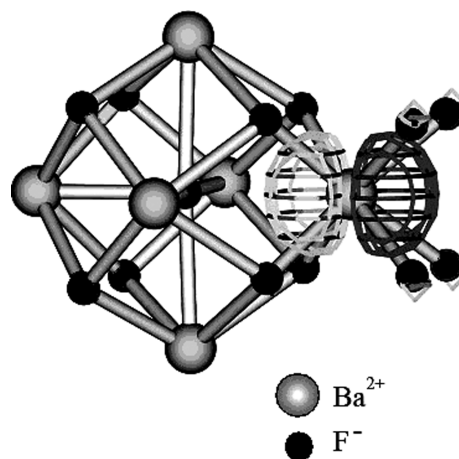| Calculation approach	Energy of cross-luminescence maxima, eV	Energy of electron transition from interstitial ion level to core band, eV
Optimized geometry of core hole as additional point charge (CIS)	5.2 6.1	11.2
Optimized geometry of core hole as excited state (CIS)	4.5 8.1	12.5
Optimized geometry of core hole as excited state (TD DFT)	6.7 7.9	8.1
Experiment	5.7 6.3	7.5

Fig. 8. Plot of exited state orbital for geometry optimization.

method usually gives overlocalized electronic states and over-estimated transition energies, therefore the calculated data can be approximately 1.5 times greater than experimental, but this feature is not observed for cross-luminescence transitions. Calculated energies are presented in the Table I together with experimental data.

2) Simulation of Core Hole as Excited State: The described above method of geometry optimization for core hole as positive point charge does not take into account that core hole le vel is formed mainly by *5p* states of Ba^{2+} and so it is necessary to take into account Jahn-Teller effect. Therefore the second step was to calculate the equilibrium geometry of the excited state.

We have selected in the CIS spectrum of excited state the one corresponding to the hole at Ba 5p orbital directed along 4-fold symmetry axis of the cluster and then optimized the geometry of this state (Fig. 8). The maximum displacements of nearest and interstitial fluorine ions were 0.232 Å (i.e., 7.3% of fluorine-fluorine lattice separation) and 0.308 Å (9.7%) respectively in the

direction to the barium ion with core hole. One can see that the displacements agree with that calculated from geometry where core hole simulated as additional charge. However the central barium ion with simulated core hole is shifted from its initial lattice site for value 0.202 Å (6.4%), which more then 2 time greater than that for described above method.

Fig. 7(b) presents the cross-luminescence spectrum calculated for the geometry optimized with described approach. The cross-luminescence spectrum is shifted in comparison with previous calculations in high-energy side by about 0.7 eV. The energy of electron transition from interstitial ion levels increased by 1 eV too. The results are presented in Table I.

Then using the same geometry of core hole we have repeated the calculation of core-valence transitions with TD DFT method (Fig. 7(c)). All results are collected in the Table I. One can see that energies of both cross-luminescence transitions and of transition between interstitial ion and core levels are in satisfactory agreement with experimental data, being all overestimated by approximately the average value of 0.8 eV.

IV. CONCLUSION

In this work we have studied cross-luminescence in BaF_2 doped with rare-earth impurities (Y^{3+} and Yb^{3+}). The

high-energy emission with maxima 7.5 eV was observed in these crystals. The lower intensity of this emission in comparison with doping by La^{3+} is due to aggregation of defects and impurities. The cross-luminescence spectrum and high-energy emission have been calculated using the HF and DFT methods in embedded-cluster approach. The theoretical cross-luminescence spectrum reproduces well the characteristic structures in the experimental 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). According to the data obtained we can suggest that high-energy 7.5 eV emission is due to radiative transitions from interstitial fluorine levels to outermost core band (Ba, *5p*).

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