

# Exciton interaction with impurity in barium fluoride crystals

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## Abstract

Optical absorption excitation and emission of alkaline-earth fluoride crystals doped with impurities, which did not introduce a new absorption band up to 8 eV, were investigated. Comparison of emission of BaF<sub>2</sub>–LaF<sub>3</sub>, BaF<sub>2</sub>–KF and doubly doped BaF<sub>2</sub>–LaF<sub>3</sub>, KF shows that interstitial fluorines are not the main exciton suppressors as thought before. The two stages of exciton suppression on the plot of exciton intensity against impurity concentration were observed. The first stage has the interaction length near 130 Å, while the interaction lengths of second stage are 10–30 Å, depending on impurity.

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## 1. Introduction

Exciton interaction with impurities plays an important role in the suppression of unwanted exciton slow components of scintillation pulse in barium fluoride crystals. It was found that many impurities (rare-earth ions [1–5], Mg, Sr [6], Cd [7]) can suppress the exciton emission. However, the details of the interaction and the reason for suppression remain unclear.

When trivalent rare-earth ions are introduced into BaF<sub>2</sub> lattices, the Re<sup>3+</sup> ion replaces Ba<sup>2+</sup> host ion. In the absence of oxygen the charge compensator is interstitial fluorine F<sup>–</sup> ion, situated in first or second interstitial position near to Re<sup>3+</sup>. In several papers, the interaction of excitons with interstitial fluorines is the main reason for exciton luminescence suppression [8,9]. Indeed the primary created self trapped holes can be effectively trapped by fluorine interstitials, which prevent the creation of self-trapped excitons [9].

When an alkali metal (Na, K, Rb, Cs) is introduced into fluorite lattices the alkali ion replace the host cation and introduce the anion vacancy as charge compensator. When the

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rare-earth ions and alkali ions are introduced together in equal molar concentration, they become charge compensators to each other. No interstitial fluorines were observed in this case [10]. Using this idea we prepare the  $\text{BaF}_2$  crystal doped with  $\text{LaF}_3$  and  $\text{KF}$  and investigate the exciton luminescence suppression of such doubly doped crystals.

In this paper, we measure the absorption and luminescence spectra of  $\text{BaF}_2$  crystals doped with  $\text{LaF}_3$ ,  $\text{KF}$  and  $\text{CaF}_2$ ,  $\text{BaF}_2$ ,  $\text{SrF}_2$  crystals doped by  $\text{YF}_3$  and  $\text{CdF}_2$  to investigate the influence of impurities on the exciton luminescence.

## 2. Experimental

We prepare the  $\text{BaF}_2$  crystal doped with impurities which did not introduce new absorption bands up to 8 eV. The impurities were— $\text{LaF}_3$ ,  $\text{YF}_3$ ,  $\text{CdF}_2$ , and  $\text{KF}$ . Crystals were grown in vacuum in graphite crucible. The  $\text{CdF}_2$  or  $\text{PbF}_2$  were used as oxygen scavengers. The  $\text{LaF}_3$  and  $\text{YF}_3$  were introduced in the usual manner, as they have low vapour pressure in the  $\text{BaF}_2$  melt. The  $\text{KF}$  and  $\text{CdF}_2$  have large vapour pressure; therefore we use the closed crucible to prevent the evaporation of impurities during crystal growth. The concentration of impurities varied from 0.001 to several weight percent. Concentration of impurities was measured by atomic emission analysis, which was done by Irina Vasil'eva in our institute.

To measure radiation defects the crystals were irradiated by Pd X-ray tube, operating at 40 kV, 40 mA for 10–30 min (Fig. 1).

## 3. Results

### 3.1. Role of interstitial fluorines

$\text{BaF}_2$  crystal containing La impurity becomes red after X-ray irradiation at room temperature. Coloration is mainly due to presence of charge compensating interstitial fluorides. The crystals containing alkaline metal impurity become blue after X-ray irradiation. The coloration is due to F-

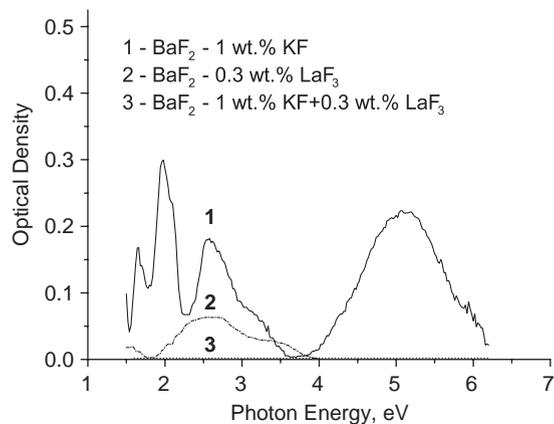


Fig. 1. Absorption spectra of crystal  $\text{BaF}_2\text{-KF}$ ,  $\text{BaF}_2\text{-LaF}_3$  and  $\text{BaF}_2\text{-KF,LaF}_3$  X-ray irradiated at room temperature.

aggregate centres created by charge compensating fluorine vacancies. Crystals containing  $\text{LaF}_3$  and  $\text{KF}$  were coloured according to impurity with greater concentration.  $\text{BaF}_2$  crystal with equal molar concentration of  $\text{LaF}_3$  and  $\text{KF}$  was not coloured after X-ray irradiation.

Crystals, containing only  $\text{KF}$  impurity or only  $\text{LaF}_3$  impurity, suppress exciton emission in similar manner.  $\text{BaF}_2$  crystals containing near 0.3 mol.% La and 0.3 mol.% K shows slightly less decrease of exciton intensity than the crystals doped with 0.3 mol.%  $\text{LaF}_3$  only. This means that interstitial fluorides have moderate influence on  $\text{BaF}_2$  exciton emission suppression. Therefore, the interstitial fluorides are not the main reason of exciton luminescence suppression (Fig. 2).

### 3.2. Interaction with impurities

Generally there are two ways of interaction. The primary radiation defects are free electrons and holes. The excitons are a result of electron-hole recombinations. Therefore the total number of excitons can be reduced due to electrons/holes trapping, preventing the excitons creation. To distinguish these, we measured the luminescence suppression of exciton, created by X-ray irradiation and created by VUV illumination into exciton band. In the case of VUV excitation the number of initially created excitons is the same for all

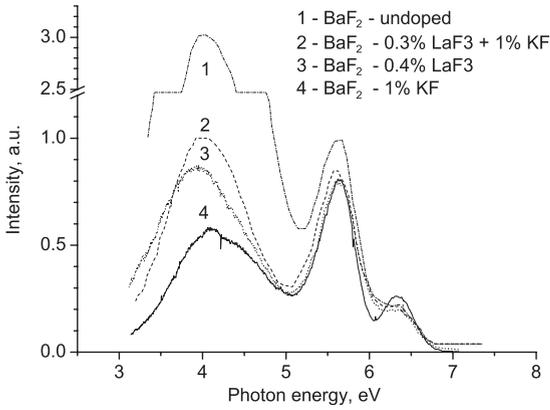


Fig. 2. Emission spectra of doped BaF<sub>2</sub> crystals under X-ray irradiation.

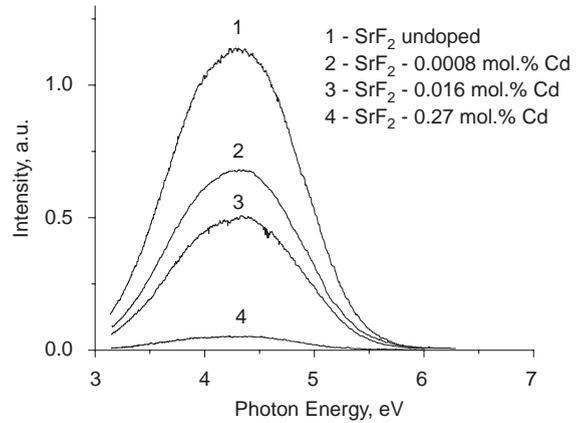
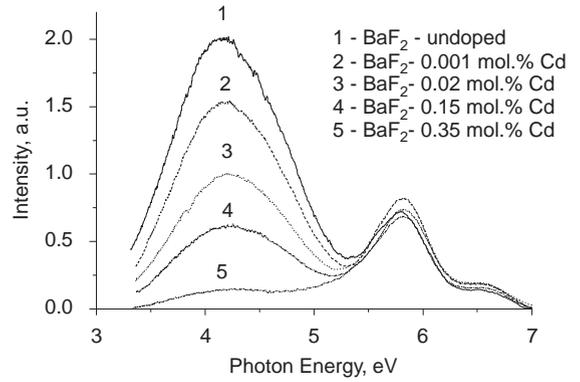


Fig. 3. Emission spectra of cadmium doped BaF<sub>2</sub> and SrF<sub>2</sub> crystals under X-ray irradiation at room temperature.

crystals. The suppression in both cases was similar for La impurity. However, for Cd impurity the exciton created by VUV is much less suppressed than excitons created by X-rays.

For all dopants we observe the continuous decrease in the intensity of exciton emission with increase in impurity concentration. We also observed this tendency in Cd-doped SrF<sub>2</sub> (Fig. 3) and CaF<sub>2</sub>.

The total exciton intensity against the La, Y, Cd impurity concentration shows two stages. In the first stage the intensity falls near two times when the concentration of impurity reach 0.1%. During the second stages the exciton intensity falls 10–50 times when concentration reaches a few weight percent. The second stage shows the exponential decrease of exciton emission with increase in concentration of impurities (Fig. 4). The exponential parameter varied from 0.6 to 3 mol% in row Cd, Y, La.

#### 4. Discussion

Experimental results show that nearly half of all created excitons decay with concentration parameter less than 0.001 mol.% (see Fig. 1). The mean distance between impurity ions is larger than 50 lattice constants, therefore, the mean distance between exciton and impurity is larger than 25

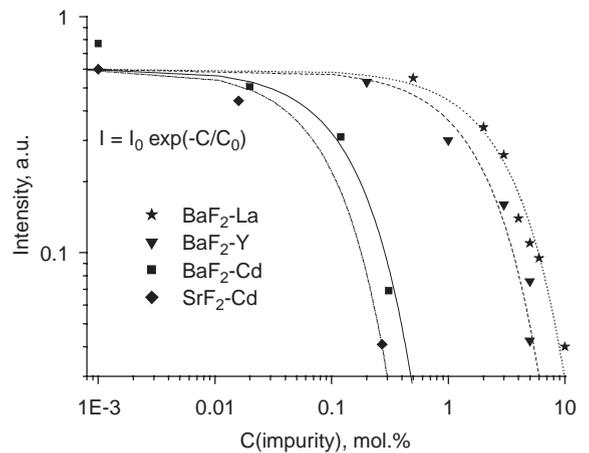


Fig. 4. Intensity of exciton emission of doped BaF<sub>2</sub>, SrF<sub>2</sub> crystals at room temperature against the impurity molar concentration.

Table 1  
Exciton luminescence quenching parameters for the investigated crystals

Crystals	$C_0$ , mol%	$R_0$ , Å	$R_{\text{interaction}}$ , Å
BaF <sub>2</sub> –LaF <sub>3</sub>	3.3	19	9.5
BaF <sub>2</sub> –YF <sub>3</sub>	2	22	11
BaF <sub>2</sub> –CdF <sub>2</sub>	0.16	52	26
SrF <sub>2</sub> –CdF <sub>2</sub>	0.1	57	28.5

$C_0$ —the concentration of impurity at which the exciton luminescence decrease  $e$  times.  $R_0$ —the mean distance between two impurity ions in lattice with impurity concentration  $C_0$ .  $R_{\text{interaction}}$ —is equal  $R_0/2$ .

lattice constant (or near 130 Å). Remaining excitons decay with concentration parameter 0.1–3 mol.%. The mean distance between exciton and impurity in this case is 3–6 lattice constant (or near 10–30 Å) (Table 1).

The suppression of exciton luminescence in BaF<sub>2</sub>–LaF<sub>3</sub> was numerically fitted using two models, based on transfer of exciton energy to quenching centers by multipole–multipole interaction (resonance transfer) or by exchange interaction [3]. However, both interactions take place when excitation or absorption spectrum of quenching centers (acceptors) overlap with emission spectrum of excitons (donor). However all studied impurity did not introduce any measured absorption up to 8 eV while the exciton emission is observed in the region of 3–5 eV.

It is reasonable to assume that the first stage of exciton suppression is related with diffusion of self-trapped excitons. The diffusion length of self-trapped excitons in CaF<sub>2</sub> at room temperature was estimated as 37 Å [11]. The diffusion length of excitons in BaF<sub>2</sub> can be estimated using known data on diffusion self-trapped holes. Beaumont et al. [12] have found that the 90° jump frequency of the self-trapped hole in BaF, is  $\nu = 3.2 \times 10^{12} \exp(-0.30 \text{ eV}/kT)$ . The self-trapped hole diffusion constant can be calculated from this using the approximate relation  $D_h = 1/3\lambda\nu$ , where  $D_h$  is hole diffusion constant and  $\lambda = 2.2$  is the distance the hole moves per jump. The result at 294 K is  $D_h = 3.6 \times 10^{-9} \text{ cm}^2/\text{s}$  [3]. Using  $L = (D\tau)^{1/2}$  we obtain the 12 Å as the estimation of self-trapped

exciton diffusion length in BaF<sub>2</sub> at room temperature. Both estimations show that the diffusion of self-trapped excitons cannot explain the long-range energy transfer of about 130 Å at the first stage. Possibly the interaction of impurity with unrelaxed excitons (or unrelaxed electrons and holes) lead to large interaction length.

The interaction radius of second stage increases in the row La–Y in BaF<sub>2</sub>, and BaF<sub>2</sub>–SrF<sub>2</sub> in Cd doped crystals (see Fig. 3). The interaction radii for Y and La impurities are closed to estimation of exciton diffusion length, but the radii are more then twice larger the diffusion length for Cd impurity. Taking into account the difference in X-ray and VUV excitation we conclude that the diffusion mechanism of exciton suppression dominated in the case of La and possibly Y impurities. Another mechanism such as electron trapping is favorable in the case of Cd impurity.

## 5. Conclusion

The interstitial fluorine is not the main exciton suppressor.

The exciton luminescence follows a simple exponential decrease with increasing impurity concentration. Two stages were observed. Interaction radii as large as 100 Å on the first stage and 10–30 Å at the second stage were estimated.

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