

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

Mechanism of exciton suppression in alkaline-earth fluorides doped with La, Y, Cd

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Abstract

The effect of doping by Cd^{2+} , Y^{3+} , La^{3+} ions on exciton emissions under illumination at 10.0 eV (into exciton band) and x-irradiation are studied. The excitation spectra in exciton and band-to-band regions of BaF_2 , SrF_2 , CaF_2 crystals doped with different closed shell ions - La^{3+} , Y^{3+} , Cd^{2+} are measured. The exciton luminescence of BaF_2 under excitation at band-to-band region or x-irradiation strongly suppressed by doping, while only slightly decrease under excitation at exciton band. The suppression mechanism is discussed.

1. Introduction

There is a practical need to diminish slow exciton luminescence of BaF_2 in the favorite of fast crossluminescence. Therefore many trivalent [1] divalent [2, 3] and monovalent [4] impurities have been investigated as exciton suppressors. To separate from known resonance energy transfer we will focus on those impurities which have no absorption and excitation bands within exciton emission region. Impurity La^{3+} , Y^{3+} , Cd^{2+} have filled outer shells and have no own absorption bands with energies below 12 eV. New strong absorption appears near exciton absorption edge in vacuum ultraviolet region [5]. Cadmium introduces impurity states lower the bottom of conduction band states, while La and Y accompanied interstitial fluorides, which have atomic p-states higher than top of valence band states. In all CaF_2 , SrF_2 , BaF_2 crystals these impurities considerably suppress the exciton emission [1-5], while fast crossluminescence of BaF_2 remains the same. These facts cannot be explained by interaction of excitons with impurities [6].

Other possible explanation is trapping of free charge carriers (electrons or holes), so the number of excitons created through electron-hole interaction is decreased with increasing of numbers of traps. The trapping of holes by charge compensating fluorine interstitials was proposed to lead exciton suppression in BaF_2 doped with LaF_3 impurity [7, 8]. However comparison of doubly doped $\text{BaF}_2\text{-LaF}_3\text{-KF}$ in equal molar concentration (in this case no fluorine interstitials in crystal) with $\text{BaF}_2\text{-LaF}_3$ are prove that

fluorine interstitials has a weak influence on exciton suppression [9].

Excitons in alkaline-earth fluorides are effectively created from separated free electron and hole as it

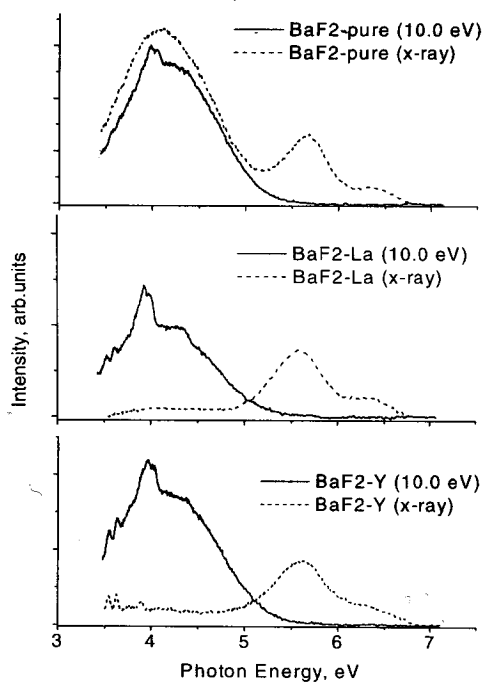


Fig. 1. Emission spectra of BaF_2 crystals under x-irradiation or illumination by 10.0 eV line of Kr discharge lamp at 295 K. The fine structure of emission near 3.5-4 eV is due to scattered light of lamp.

follows from excitation spectra of pure crystals. Therefore one could infer that there are two common ways to suppress excitons. At first impurity may decrease number of free electron and holes by

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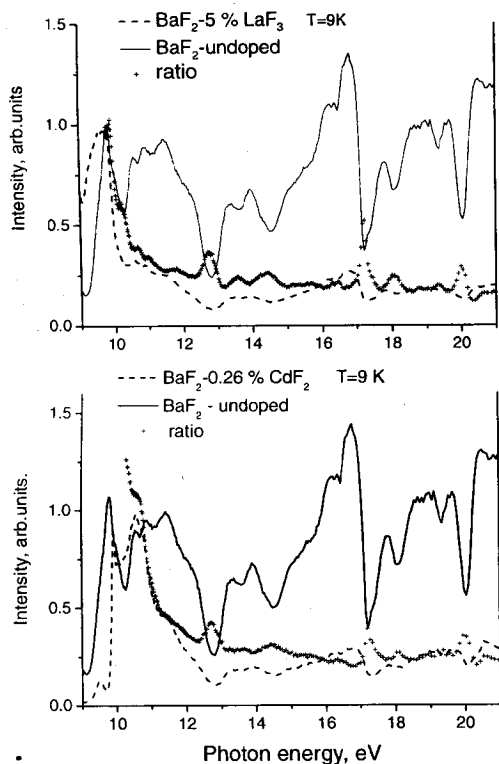


Fig.2. Excitation spectra of exciton emission at 4.3 eV in pure and doped BaF₂ at 9 K. Ratio of intensities of BaF₂ doped with CdF₂ or LaF₃ to those of undoped BaF₂ shown by cross.

sequential trapping at impurity. At second excitons may be suppressed due to interaction of created excitons with impurity. Therefore one needs to separate process of interaction of excitons with impurities from those of electron-hole interaction with impurities before creation of exciton. One of possible ways is the comparison of suppression of excitons directly created by photons from exciton absorption band region with suppression of excitons created through free electrons and holes by VUV photons or x-ray.

In this paper we investigate excitation spectra in exciton and band-to-band regions of BaF₂, SrF₂, CaF₂ crystals doped different closed shell ions - La³⁺, Y³⁺, Cd²⁺.

2. Experimental

All alkaline-earth fluorides were grown in our laboratory. Crystals were grown in vacuum in graphite crucible. Concentration of impurities was measured by atomic absorption method. Concentration of impurities varied up to 0.5% for Cd, 5% for La and Y.

For comparison of exciton intensity in samples with different concentration of impurities we prepare samples with same 8x10x2 mm³ dimensions sawed from bulk and one-side polished.

We measure emission spectra of different samples with excitation of Kr resonance discharge lamp, having most intensive line at 10.0 eV (123.6 nm). This line is suitable for illumination into first exciton peaks of CaF₂, SrF₂ and BaF₂ crystals. We measure the emission spectra of samples using the x-irradiation and using 10.0 eV line of discharge lamp on the same measurement geometry. The current of x-ray tube and current of discharge lamp were kept on the same level during all measurements. This method is most informative in the case of BaF₂. The crossluminescence peaks at 5.7 eV of BaF₂ under x-irradiation not depends on La, Cd, Y impurity concentration and peak intensity can be used as reference one. Our measurement setup has almost linear sensitivity in the range 7-3.8 eV.

In addition, excitation measurements were carried out using a low temperature luminescence set-up SUPERLUMI designed for vacuum ultraviolet spectral region, located in HASYLAB at DESY (Hamburg, Germany) [13].

3. Results

3.1. Measurements with resonance lamp

In all studied (Y, La or Cd) doped crystals the intensity of exciton emission 10-30% less than those in undoped crystals (for BaF₂ see Fig.1). However, the exciton intensity under x-ray irradiation considerably decreased with increasing of impurity concentration (see also [4]). Similar results were obtained for CaF₂-Y, CaF₂-Cd, SrF₂-Cd crystals.

3.2. Excitation spectra

The excitation spectra of BaF₂-LaF₃ (Fig.2) show two main features. First is the broadening exciton band at 9.8 eV and appearing new excitation band near 9.0 eV. The position of new band shifts from 9.18 eV in BaF₂-0.1%LaF₃ to 8.87 eV in BaF₂-5% LaF₃. This new excitation band was assigned to transitions from interstitial fluorines [9]. The shift of position of excitation band to lower energies with increasing of La concentration possibly related with creation of interstitial fluorine sub-band.

The excitation spectra of BaF₂-Cd crystals are shifted to higher energies (see Fig.2). The shift was ascribed to be from strong Cd absorption band [5].

In doped BaF₂ crystals we observe the strong relative decrease of excitation intensity above 10 eV against the excitation intensity in undoped crystal (see Fig.2).

No such strong decrease was found in Cd-doped CaF₂ and SrF₂ crystals at 9K. We assume that effective luminescence of Cd-centres, which was found only in CaF₂ and SrF₂ at low temperature [11], affect the excitation spectra at band-to-band region.

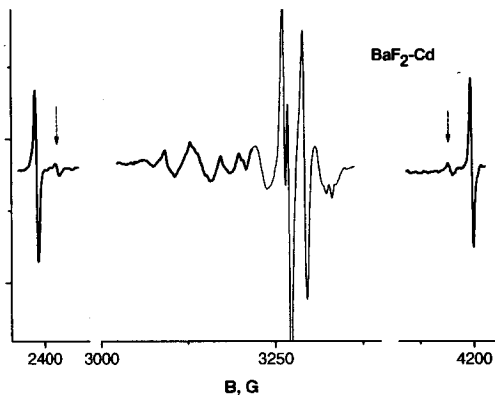


Fig.3 EPR spectrum of $\text{BaF}_2\text{-}0.35\% \text{CdF}_2$ crystal x-irradiated at 77 K and subsequent thermal annealing at 150 K, $B \parallel \langle 100 \rangle$. The arrows indicate the additional lines

Future room temperature measurements are planned to clarify this assumption.

3.3. EPR measurements

The exposure of $\text{BaF}_2\text{:CdF}_2$ crystals at 77 K to x-ray radiation results in the trapping of holes as F_2^- , V_k centers, and electron as Cd^+ [15]. There are two type of the self-trapped holes just after x-irradiation at 77 K: pure V_k and perturbed V_k -centers (hereafter V_{k1} centers). We propose that the perturbation is due to the influence by nearby Cd^+ by Coulomb interaction such as for V_F center. If concentration of cadmium in the crystal is of order 0.35 %, x-irradiation produced at about 50 % pure and 50 % perturbed V_k centers.

It seems reasonable that upon warming the crystal above 110 K (the temperature range of thermal activation of "pure" V_k -centers) the holes move to the Cd^+ ions because of Coulomb interaction, but the efficient recombination between them with or without emission do not occurs. The thermal annealing above 110 K the crystals containing 0.35 % Cd which are previously x-ray irradiated at 77 K, leads to the destruction less than 10 % of total concentration of V_k -type and Cd^+ centers. The destruction is accompanied with a weak thermoluminescence (as compared with pure BaF_2) at about 110 K [15].

The thermal annealing at about 110 K leads to the destruction of "pure" V_k and perturbed V_k centers, V_{k1} , and to the formation a new type of V_k -center (hereafter V_{k2} centers). EPR signal of the V-type centers (V_{k1} and V_{k2}) is somewhat similar to "pure" V_k -centers in pure BaF_2 , but after the thermal annealing additional lines arise in spectrum of V_{k2} centers which are due to splitting of edge lines of V_k center (Fig. 3). The splitting is due to the magnetic interaction of electron V_k center with another paramagnetic electron. Taking into account Coulomb interaction between V_k and Cd^+ centers, it seems reasonable that the other partner in the magnetic interaction is Cd^+ ion and the interaction occurs

between nearby $[\text{Cd}^+\text{-V}_k]$ pairs. Therefore, as result of the thermal activation of this self-trapped hole, the "excitonic molecule" (see as example [16]), which is bound states of electron of Cd^+ ion and hole of V_k -center is formed in $\text{BaF}_2\text{-Cd}$. The "excitonic molecule" disappears at about 260 K without thermoluminescence [15].

4. Discussion

The main result followed from excitation spectra is that the suppression of exciton emission is not more than 10-30% when excited into exciton band, however the suppression becomes five and more times when excited into band-to-band region or excited by x, γ -rays. This result observed for all studied impurities La, Y, Cd doped into alkaline-earth fluorides CaF_2 , SrF_2 or BaF_2 . Based on these results we may conclude that impurity do not suppress the exciton emission, the impurity decrease the number of free electrons and holes which able to create excitons.

Similar results were observed in $\text{BaF}_2\text{-}1\% \text{DyF}_3$ crystals [12]. In this crystal, following band-to-band transitions, exciton emission drastically decreases whereas Dy^{3+} emission shows up. Authors concluded that energy transfer arises from relaxing free carriers before electron-hole recombination [12].

From measurements of exciton intensities and exciton decay times of BaF_2 doped up to 6 weight % LaF_3 it was concluded that the number of self-trapped excitons formed decreased in doped crystals [10].

Therefore one may assume that free electron (or free hole) can trap by impurity ion, then the moving free hole (or electron) may localized in vicinity of excess charged impurity ion and recombine unradiatively. It is known that Cd^{2+} ion can trap the electron in all CaF_2 , SrF_2 , BaF_2 crystals and Cd^+ ion is stable at room temperature [3-5]. Therefore it is probably that at first free electron is trapped by Cd^{2+} ion and then the trapped electron recombines with nearest hole (free of self-trapped).

Generally, the processes of transfer of ionizing radiation absorbed energy to quenching centres and to luminescence centres are very similar. The results of basic experiments such as radioluminescence, VUV spectroscopy, time profiles and thermoluminescence on RE-activated scintillator materials can be consistently explained assuming that the dominant mechanism of scintillation light production is due to radiative recombination of charge carriers at luminescent RE ions [14].

Figure 4 shows an energy-level scheme for the ground states of Cd^+ , F-center (for comparison), and V_k center in BaF_2 . From previous works it was determined that the ground state of Cd^+ lies about 4.1 eV [4] and that of F-center places at 2.3 eV below the conduction band in BaF_2 . Since the energy of the transition ${}^2\Sigma_u \rightarrow {}^2\Sigma_g$ of V_k -center is about 3.4 eV

[8], the ground state of the center lies a minimum of 3.4 eV above the valence band.

Since the energy gap in BaF₂ is 10.6 eV, in the case of pure BaF₂ crystal, the difference between the energies of the F and V_k, namely, 4.9 eV is more than energy of the self-trapped exciton emission, namely, 4.1 eV and the recombination between them is accompanied with emission of self-trapped exciton upon warming the crystal.

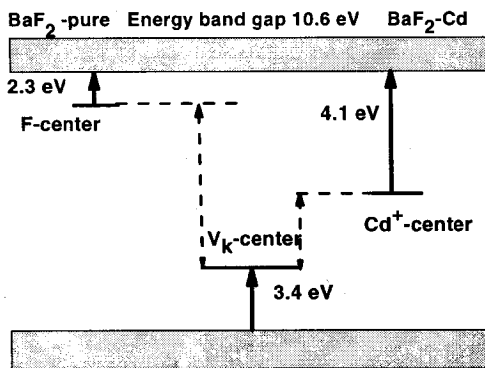
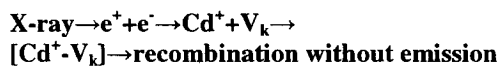


Fig. 4 Energy-level scheme for the ground states of Cd⁺, F-center, and V_k center in BaF₂.

In the case of Cd-doped crystal, Cd⁺ center is the deep electron trap (as compared with F center) and the difference between the energies of the Cd⁺ and F₂, namely, 3.1 eV is less than energy of the exciton emission and self-trapped exciton can not be created by interaction hole of V_k-center with electron of Cd⁺ center. The recombination between electron and hole of these centers is not observed up to 250 K and "excitonic molecule", which is bound states of electron of Cd⁺ ion and hole of V_k-center, is formed [Cd⁺-V_k].

Therefore we proposed a new electronic system composed of electron of Cd⁺ ion and hole of V_k center separated by a barrier which is high enough to prevent tunneling and recombination.

Process of the suppression of the self-trapped exciton emission under x-ray or thermal excitation (thermoluminescence) can be described as:



5. Conclusions

The impurity ions Y²⁺, Cd²⁺ and La³⁺ strongly suppress exciton emission under x-irradiation or illumination at band-to-band region in BaF₂ crystals. However the impurities only slightly decrease the exciton emission under illumination at exciton bands. Evidently the suppression is due to sequential trapping of charge carriers (free electron and holes) by impurity and following unradiative recombination at quenching impurity sites.

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