



Luminescence of BaF₂–LaF₃

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Abstract

The luminescence properties of Ba_{1-x}La_xF_{2+x} single crystals have been investigated for La concentrations up to 5 mol%. The luminescence spectra of the crystals have been recorded during X-ray excitation. The intensity of the exciton emission in BaF₂-5% LaF₃ is reduced by a factor of 10, whereas the intensity of the cross-luminescence remains almost constant. Besides the main emission bands of the cross-luminescence at 6.3 and 5.6 eV, an additional weak emission band at about 7.2 eV has also been observed. We suggested that the newly observed emission arises from a radiation transition between the interstitial F_i⁻-ion and the outermost Ba²⁺ 5p core band. We found that with increasing La-doping, the edge of fundamental absorption of Ba_{1-x}La_xF_{2+x} crystals shifts to lower energies. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The BaF₂ crystal is known as the fastest scintillator. A fast ultraviolet emission under X-or particle irradiation is due to cross-luminescence transitions (Alexandrov et al., 1984; Rodnyi et al., 1991). In addition to the fast emission component with two maxima at 6.3 and 5.6 eV, there is a slow component of the luminescence at 4.0 eV, which is caused by self-trapped excitons (Ershov et al., 1982) (Fig. 1).

The suppression of the slow component is a crucial key to applying this crystal to high counting rate experiments. The slow component can be suppressed considerably by doping with La (Schotanus et al., 1989), Cd (Springis et al., 1995), or Mg, Sr (Hamada et al., 1994). Although the solid solutions Ba_{1-x}La_xF_{2+x} belongs to the most studied systems of this family, the effect of La-doping on its emission characteristics is still unclear and the crystal of the solid solution

looks promising to applying this crystal to high counting rate experiments. Therefore, we have performed a study of optical properties of the solid solutions Ba_{1-x}La_xF_{2+x}.

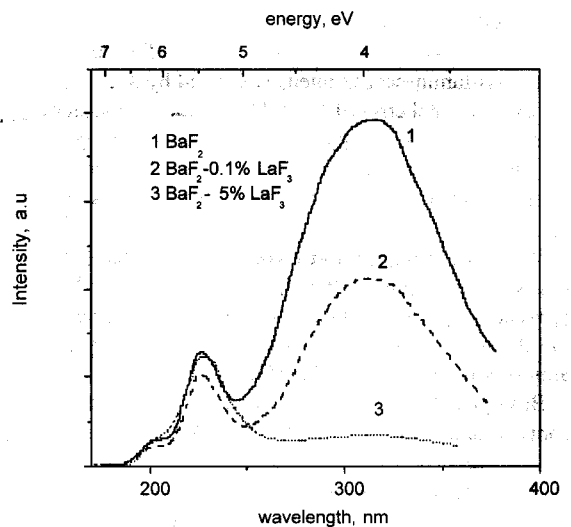


Fig. 1. X-ray excited luminescence spectra at room temperature of La-doped BaF₂ crystals.

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2. Experimental methods

The industrial technology for the production of pure BaF_2 for crystal (mean concentration of main metals and oxygen is in the order of a few ppm or still less) has been developed at the Angarsk Electrolysis Chemical Complex (AECC), from which we got the raw materials.

The $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ crystals were grown using the Stockbarger method in graphite crucibles and with 2% PbF_2 added as a scavenger for oxygen containing impurities. The concentrations of La in the crystals were determined by an emission spectroscopy. The perfect quality crystals of pure BaF_2 are created. The $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ crystals of enough quality for investigations are also created, but until now this quality is not enough for scintillator.

The absorption spectra in the vacuum ultraviolet region are obtained from home-made spectrophotometer. The emission spectra were measured using grating vacuum monochromator VM4 and FEU39A. The spectra were not corrected for the spectral response of the spectrometer, but the sensitivity in the region from 4 to 6.5 eV is not significantly varied. The high-energy threshold of sensitivity of FEU39A is close to 7.8 eV (160 nm). Decay of luminescence was measured by single photon counting technique using CAMAC time-to-digital converter. Samples $\varnothing 17 \text{ mm} \times 15 \text{ mm}$ were irradiated with ^{137}Cs γ -source or ^{90}Sr - ^{90}Y - β sources. Photomultipliers FEU 100 were used as start and stop ones.

The X-ray tube (W, 25 kV, 10 mA) was mounted apart from entrance slit of monochromator. Such type of measurement geometry allows to obtaining a minimal variation of emission intensity from sample to sample.

3. Results

Cross-luminescence of pure BaF_2 consists of two bands at 6.3 and 5.6 eV. The LaF_3 doping up to 5% does not affect cross-luminescence intensity excited by X-rays (within the experimental error of 10–20%). As the La concentration increases to about 5%, the intensity of the self-trapped exciton luminescence decreases by the factor of 10, whereas the intensity of the cross-luminescence remains almost constant (Fig. 1).

With increasing of LaF_3 concentration above 1% the emission spectrum of the fast component broadened to low-energy side and both bands become less resolved, while the decay time is not changed and the intensity remains almost constant up to 5% La (Fig. 1).

Besides the main emission bands at 6.3 and 5.6 eV, in some instances an additional weak emission band at about 7.0 eV has also been seen (Janson et al., 1987; Makhov et al., 1999). We found that in pure BaF_2 crystals the band is not observed, but in the crystals doped with LaF_3 the band at about 7.2 eV appears and its intensity grows with increasing La-doping at least up to 5% LaF_3 (Fig. 2). Fig. 2 shows the

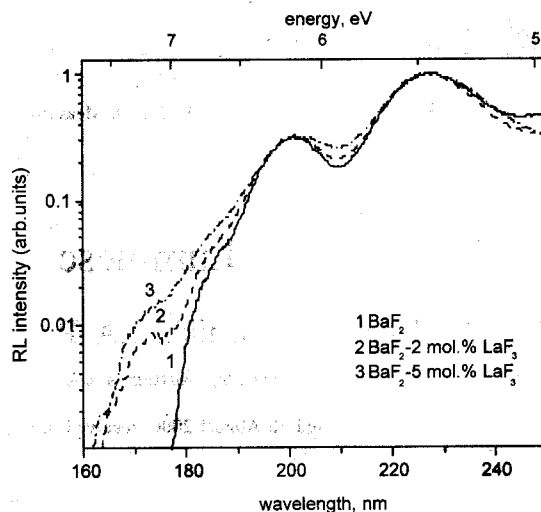


Fig. 2. X-ray excited luminescence spectra at 80 K of La-doped BaF_2 crystals.

change in the spectrum of luminescence, when the data are normalized to the peak intensity of cross-luminescence at 5.6 eV. It is validity as the intensities of this band are almost unaffected by the doping up to 5% LaF_3 (Fig. 1).

We assume that the appearance of the high-energy emission band in the crystals doped with La is associated with modification of a valence band. The defect structures of the disordered $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ crystals have been studied extensively (Cahill and Pohl, 1989); the dominant defect, at least for values of $x < 0.01$ in $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$, is an interstitial F_i^- neighbouring a La^{3+} that substitutes for a Ba^{2+} . Thermal activation barrier for diffusion of the interstitial ion is of order of 0.5 eV (Cahill and Pohl, 1989; Hayes, 1974).

At higher concentrations, complex defects composed of clusters of substitutional La^{3+} and interstitial F_i^- (fragments with tysonite structure of LaF_3) have been invoked to explain glass-like properties at low temperatures. It has been found that features characteristic for glasses and amorphous solids develop with increasing x . However, to a quite good approximation, the $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ crystals maintain the cubic fluorite structure up to large concentrations x of doping, approaching $x = 0.5$ (Cahill and Pohl, 1989).

We assume that the newly observed emission at about 7.2 eV arises from a radiation transition between the electron state of the interstitial F_i^- -ion, its electron state is located in the forbidden band at low concentration of lanthanum, and the outermost Ba^{2+} 5p core band (Fig. 3).

At higher concentrations, complex defects composed of clusters of substitutional La and interstitial F_i^- -ions are formed and a fluorine 2p valence band broadened through the interstitial F_i^- -ions. At low La-doping this case is similar to the impurity cross-luminescence. Itoh and et al. (Itoh et al., 1997) shows that the linewidth of cross-luminescence does not depend sensitively on whether the upper filled band

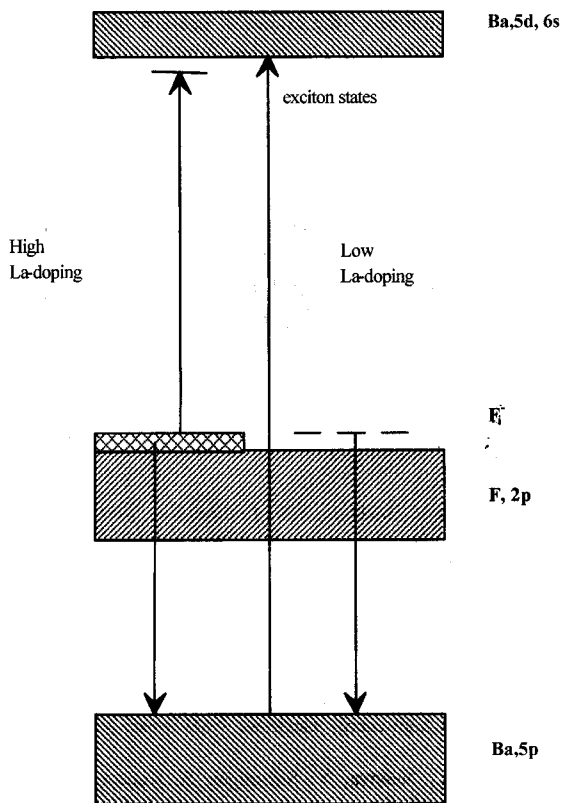


Fig. 3. Schematic energy diagram illustrating the emission at about 7.2 eV.

is derived from the valence state or the isolated impurity state.

In LaF_3 the valence band is sufficiently wider than that in BaF_2 due to existence of two different fluorine sites with different Madelung potentials. On the basis of the discussion, one would expect that the width of the forbidden band decreases with increasing of the concentration of lanthanum. We found that with increasing La-doping, the edge of fundamental absorption of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ crystals shifts to lower energies (Fig. 4). Each point on curve 1 in Fig. 4 is obtained from the spectra of absorption of the different crystals at the constant absorption coefficient, which equal 15 cm^{-1} . For comparison, in the $\text{BaF}_2\text{--MgF}_2$ crystal the forbidden band is larger than that of the BaF_2 crystal (Hamada, 1994). From Fig. 4 one can see that both curves (shift of the edge of fundamental absorption and the intensity of the emission at about 7.2 eV) tend to saturation with increasing of the concentration of lanthanum.

The intensity and the decay time of the slow luminescence constantly decrease with increasing of the LaF_3 concentration. This suggests that the activation energy for dissociation of self-trapped excitons decreases (as in this work (Schotanus et al., 1989)). It is similar to thermal quenching of the exciton luminescence in the "pure" BaF_2

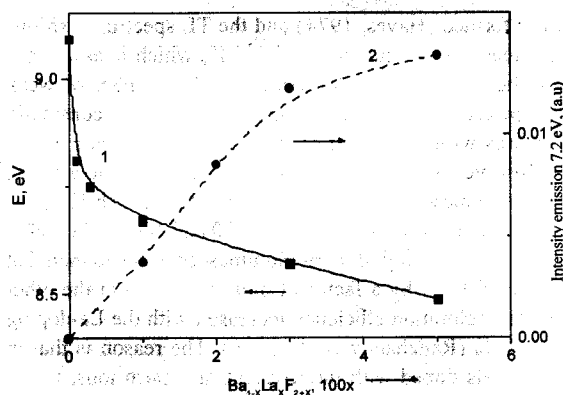


Fig. 4. Shift of the edge of fundamental absorption (1) and the intensity of the emission at 7.2 eV (2) of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ crystals vs. La-doping.

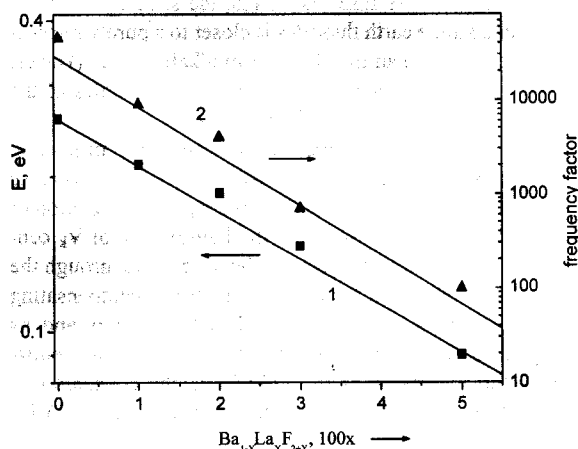


Fig. 5. Temperature dependence of the activation energy (1) and frequency factor (2) of exciton luminescence vs. concentration of lanthanum.

crystal. In addition, temperature dependence measurements of the exciton emission have been performed. As the temperature decreases to 77 K, the exciton emission is partially restored. We found from the thermal quenching of the self-trapped exciton luminescence that the activation energy for thermal quenching of the self-trapped excitons decreases with increasing La-doping from 0.26 eV for the "pure" BaF_2 crystals to 0.09 eV for the crystals doped with 5% lanthanum (Fig. 5).

It is conceivable that the mechanism of the slow component suppression by La^{3+} -doping is also related to the modification of the valence band by the formation of the interstitial anion sub-band (Fig. 3).

For this purpose, in addition, preliminary thermoluminescence measurements in the temperature range from 77 to 300 K have been performed. When the undoped barium fluorides are X-irradiated at 77 the V_k center is predominant hole

center formed (Hayes, 1974) and the TL spectrum exhibits the intense glow peak at about 110 K, which is associated with the destruction of V_k centers, and a number of weak glow peaks. The intensity of the main glow peak constantly decreases with increasing of the LaF_3 concentration and is not observed at the concentration above 1% whatever. The thermoluminescence spectrum of BaF_2 doped with 5% LaF_3 exhibits weak glow peaks at about 130 and 180 K, therewith the integral intensity of thermoluminescence is less than that for “pure” BaF_2 by a factor of more than 10. On the other hand the coloration efficiency increased with the La-doping up to 20% (Radzhabov et al., 1998). The reason is that in the crystals doped with the trivalent rare-earth ions, in addition to the V_k centers, H-centers and its complexes are formed which are not produced in observable concentration in the undoped crystals (Hayes, 1974). When the crystals are heated to induced migration of V_k centers a fraction of the moving holes are retrapped at F_i^- sites produced additional H centers. As ESR shows that the structure of the H center in alkaline earth fluorides is closer to a purely interstitial neutral atom than the H center in alkali halides (Hayes, 1974). By this is meant that the electrons and holes of the H-centers do not interact with each other.

We assume that the suppression of the exciton emission in the crystals doped with LaF_3 is associated with the decrease of thermal stability of V_k centers, that is, the dissociation of self-trapped exciton arises from the hole release of V_k centers. In these crystals the holes of the V_k centers through the potential barrier could be retrapped at charge-compensating interstitial fluorine ions (F_i^-) produced H centers and its complexes, which are not involved in the exciton emission. With increasing of the La-doping, the concentration of charge-compensating interstitial fluorine ions (F_i^-) increases and the energy of the potential barrier for retrapping hole from V_k center decreases.

4. Conclusion

- The crystal of the solid solution $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ with the optimal concentration of lanthanum at about 5% looks promising to applying these crystals to high counting rate experiments. The main difficulty in the application of such system as scintillator is preparation of the perfect quality crystals.
- The introduction of trivalent impurities into BaF_2 leads to formation of the charge compensated interstitial F_i^- -ions. The electron states of these excess anions are located in the forbidden band, resulting in the spread of the valence band. We suggested that the modification of the valence band by the formation of the interstitial anion sub-band in the crystal of solid solution $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ leads to
 - the shift of edge of fundamental absorption to lower energies
 - the appearance of the emission band at about 7.2 eV, which arises from a radiation transition between the electron state of the interstitial F_i^- -ion and the outermost Ba^{2+} 5p core band
 - the suppression of the self-trapped exciton emission, which is due to the radiation recombination of electrons with self-trapped holes (V_k+e recombination), by the decrease of thermal stability of V_k centers. In these crystals the holes of the V_k centers through the potential barrier could be retrapped at charge-compensating interstitial fluorine ions (F_i^-) produced H centers and its complexes, which are not involved in the self-trapped exciton emission.

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