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Introducing alkali impurities into BaFBr:Eu²⁺ crystals and their effect on photo-stimulated luminescence

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Abstract

In alkali doped BaFBr:Eu²⁺ a considerable increase of photostimulated luminescence (PSL) intensity is observed. Upon Na doping the intensity of the PSL is increased by a factor of 15 in contrast to undoped samples. Moreover, the PSL peak shifted on 0.08 eV in the red region of spectrum upon Na doping. The potassium and rubidium doping results in the same effects, but with less efficiency. We prepared undoped BaFBr:Eu²⁺ crystals and those doped with varied concentrations of NaF, KF, RbF. The concentrations of alkali, which we doped before growth, were in the region of 0.1–5%. Atomic-Emission Analysis shows that the real alkali concentrations in the crystals are 0.0002–0.0025%. However, even such a small alkali doping concentration in BaFBr:Eu²⁺ influences effectively the PSL process. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

BaFBr crystals activated with europium is an important storage phosphor in which X-ray produced images are stable for long periods in the dark at room temperature.

We gained of effective improvements of PSL in this material by alkali doping (Na⁺, K⁺, Rb⁺). Appreciably rise of intensity and red shift of PSL excitation spectra are observed in BaFBr:Eu²⁺ with such doping [1,2]. However, the real concentration of alkali in our samples is by a several order of magnitude smaller than we doped before

growing. It is followed from the data of Atomic-Emission Analysis (AEA).

In this article we are considering the influence of a alkali impurities on the PSL and introduction of this impurities into BaFBr:Eu²⁺ crystals.

2. Experimental procedures

BaFBr crystals were grown with the Shteber method in a graphite crucible in helium–fluorine atmosphere in order to reduce oxygen contamination. Stoichiometric mixtures of BaBr₂ and BaF₂ were used. All samples were doped with 0.1 mol% of Eu²⁺.

The concentrations of alkali added before growth were in region 0.1–5%. We used direct

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AEA to determination of alkali concentration in the crystals. The equipment using is: the diffraction spectrograph DFS-458, the multichannel spectral recorder MAES-10. The source of spectra excitation was the alternating-current arc; the technique of complete evaporation of 10 mg of a sample from a carbon electrode; a spectrum was recorded in three various exposures. The calibration samples with concentration of Na and K from 0.00015% up to 1% had been prepared by sequential dilution of a crystal BaFBr:Eu²⁺, that was grown without alkali impurities.

The concentration of Na and K was determined by addition method. They are 0.002% and 0.01% accordingly, and hence were used as value of blank test. The calibration and the determination of concentrations were carried out using the ordinary least square (OLS) for each analytical line and the multivariate OLS (P2V2) using two analytical lines of determined element and Ba line (it's basis element) as internal standard.

3. Results and discussion

The results of AEA shows (see Table 1) that the real concentrations of alkali in the crystals are 0.0002–0.01%, i.e. most of the doping shoot out at growing. Moreover, potassium better enters into the crystal than sodium, possibly because of more likeness of the ionic size of replaced Ba-ion. We did not made the analysis of the rubidium doped samples. But rubidium concentration is alike to potassium concentration in the crystals, as ensuing from their absorption and excitation spectra.

Table 1
Content of alkali impurities in BaFBr:Eu²⁺ crystals by the results of AEA

| Sample name | K (%) | Na (%) |
|-----------------------|--------|---------|
| BaFBr:0.1% Eu:0.1% K | <0.005 | <0.0004 |
| BaFBr:0.1% Eu:2% K | 0.007 | ≤0.0004 |
| BaFBr:0.1% Eu:4% K | 0.01 | <0.0004 |
| BaFBr:0.1% Eu | 0.001 | 0.0002 |
| BaFBr:0.1% Eu:0.1% Na | 0.005 | ≤0.0004 |
| BaFBr:0.1% Eu:1.5% Na | <0.005 | 0.0007 |
| BaFBr:0.1% Eu:5% Na | <0.005 | 0.0024 |

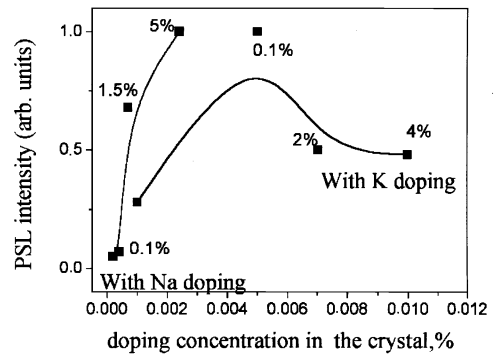


Fig. 1. Dependence of PSL intensity from alkali doping concentration in the BaFBr:Eu²⁺. The data that nearest to points are shows alkali concentration in the mixture before growing.

But even such a small alkali doping concentration in BaFBr:Eu²⁺ has an effective influence on the PSL process. In the alkali doped BaFBr:Eu²⁺ considerable increase of PSL intensity is observed. Upon Na doping the intensity of the PSL increased by a factor of 15 in contrast to undoped samples. Moreover, the PSL peak shifted on 0.08 eV in the red region of spectrum upon Na doping. The potassium and rubidium doping results in the same facts but with less efficacy [1,2]. In Fig. 1. the dependence of PSL intensity from alkali doping concentration in the BaFBr:Eu²⁺ is shown. The data that nearest to points gives alkali concentration in the mixture before growing. From this curve it is apparent that that the PSL intensity rises upon alkali concentration to about 0.004%, then decreases above 0.005%.

M. Thoms [3] calculated the photons number in the PSL process of BaFBr:Eu²⁺, which amounted to about 10¹⁴ photons/cm³ with an irradiating dose rate of 10 mGy/s. Number of the emitted photons is equal to number of the photostimulable centers. Thus their concentration is rated to 10⁻⁶ mol%. It is known that only F(Br⁻) centers (F centers based on bromine vacancies) act as occupied photostimulable electron traps at and below room temperature. However, an alkali concentration increase gives a stimulation energy decrease. Stimulation energy is the necessary energy for bleaching a photostimulable centers.

For the PSL stimulation, a low-intensity light at 633 nm has been used. The sum of PSL increased

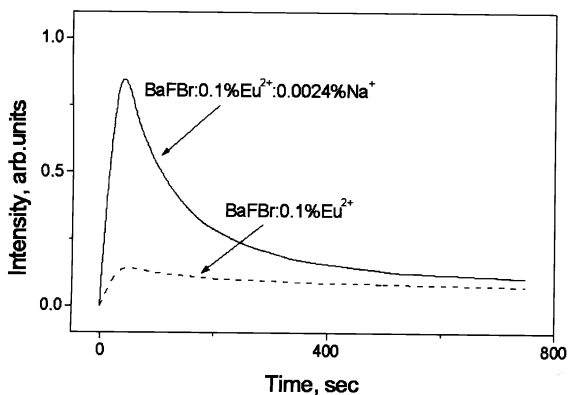


Fig. 2. Dependence of PSL intensity from blanching time in undoped BaFBr:Eu²⁺ (dashed line) and BaFBr:Eu²⁺ with 0.0024%Na⁺ (solid line).

threefold in the sodium doped BaFBrEu²⁺ compared to undoped crystals (Fig. 2). It follows that the number of photostimulable centers increases in case of alkali doping. This doping induces the creation of additional electron traps involved in PSL process at room temperature. The optical absorption band at 2.2 eV of those centers is broadened to lower energies by about 0.2 eV compared to the regular F(Br⁻) centers. This is in agreement with the red shift of the PSL spectra of BaFBr:Eu²⁺:Na⁺ [1,2]. It is due, perhaps, to the substitution of Ba²⁺ ions by a small percentage of alkali impurities, which results in the generation of charge compensating Br⁻ vacancies caused by alkali doping of BaFBr:Eu²⁺. The FA(Br⁻) centers are produced by X-irradiation at room temperature.

However in a recent work [4] the behavior of BaFBr:Eu²⁺:Na⁺ absorption spectra at liquid nitrogen temperature (LNT) was considered. The obtained results show that Na⁺ ion can not pin the F(Br⁻) center at room temperature (RT). Although FA(Br⁻) centers are stable at LNT, they can be thermally activated and move away from the Na⁺ ions at RT, transforming themselves into F(Br⁻) center. In this case the red shift of absorption and PSL excitation spectra with alkali doping of BaFBr:Eu²⁺ crystals is not clear. The solution of this question requires additional investigations.

4. Conclusion

Real concentrations of alkali in BaFBr:Eu²⁺ crystals is 0.0002–0.01%, i.e. most of the doping shoot out at growing. However, even such a small alkali doping concentration in BaFBr:Eu²⁺ has an effective influence on the PSL process.

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