



Single crystal growth of BaFBr:Eu storage phosphor with alkali impurities

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Abstract

BaFBr:Eu²⁺ is a commercial storage phosphor which is widely used in medical X-ray diagnostics, replacing conventional photographic film. The BaFBr crystals were grown by the Shteber method in a graphite crucible in helium–fluorine atmosphere in order to reduce oxygen contamination. The stoichiometric mixtures of BaBr₂ and BaF₂ were used. All samples were doped with 0.1 mol% of Eu²⁺, the concentrations of alkali in the crystals are 0.0002–0.01%.

The X-ray storage phosphor BaFBr:Eu²⁺ doped with alkali impurities (Na⁺, K⁺, Rb⁺) gives a photostimulated spectrum shifted to the lower photon energies. The photostimulation luminescence (PSL) intensity considerably increases compared to BaFBr:Eu²⁺ upon room-temperature X-ray irradiation. This redshift of the photostimulation spectrum is caused by formation of F_A-centers in the Br⁻ sublattice as electron traps.

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1. Introduction

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

readout, the phosphor is optically stimulated, frequently with a laser (633 nm), leading to a Eu²⁺ activator emission at 390 nm. Currently it is widely applied for production of the imaging plates for radiography. Medical imaging plates are used in X-ray diagnostics, replacing conventional photographic film. This results in a greatly reduced X-ray dose for patients. Commercial systems are available for general and protein crystallography, for auto-radiography. New

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applications have been suggested in the field of data storage, electron microscopy, detection of soft X-rays, and dosimetry [1].

However, until now the mechanisms of the storage and readout processes have not been completely understood, preventing improvements in the efficiency of the phosphor material and providing a challenging fundamental problem of defect interactions. Usually, the imaging plates are applied for scientific research. In imaging plates flexible plastic support plate is coated with fine BaFBr:Eu grains mixed uniformly with a binder [2]. The characteristics obtained for these imaging plates are not informative enough on the luminescence centers and their role in radiation mechanisms of creation, transformation and photostimulated luminescence. For such kind of research single crystals are more acceptable, for they allow the comprehensive methods of absorption spectroscopy to be used. For this purpose, the BaFBr single crystals have been synthesized.

We reported about an improvement in luminescence properties of BaFBr:Eu²⁺ with alkali doping in previous works [3,4]. The present article is devoted to growth technique of BaFBr:Eu²⁺ single crystals by Shteber method in details.

2. Experimental technique and results

BaFBr, like PbFCl, has the matlockite structure, a tetragonal symmetry with layers perpendicular to the *c*-axis. The crystal has the tetragonal space group P4/nmm. The melting point is at about 1010 °C [2]. Usually the BaFBr crystals are grown with Stockbarger method. However, we decided to grow BaFBr crystals with the Shteber method considering high growth rate, low melting temperature and the fact that BaFBr crystal cracks at temperature leaps. The Shteber method implies soft regime of growing.

The phase diagram of BaFBr shows two eutectic points: one at 15 mol% BaF₂ (with a corresponding melting point of 840 °C) and another at 73 mol% BaF₂ (a melting point of 940 °C) [5].

The BaFBr crystals are synthesized using the universal growth unit OKB-8093. The heater with the thermal screens and crucible were made of

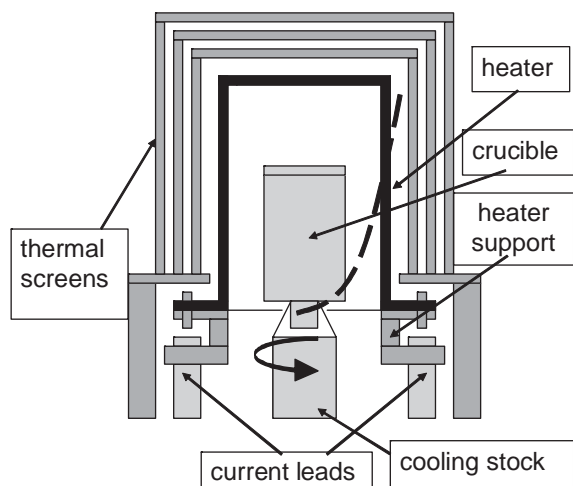


Fig. 1. The scheme and calibration of the graphite heater system.

graphite because of its thermal properties and because the graphite do not get wet by the barium fluoridebromine melt (Fig. 1). This gives a possibility to extract crystals from the crucible freely after growing.

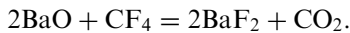
The heater with the thermal screens and the crucible are annealed at 1500 °C in a vacuum for 5–6 h before crystal growing. Then initial chemical BaBr₂·2H₂O is loaded into the crucible and is fired at 500 °C in a vacuum during 10 h or more. Thereafter the barium bromine melts at helium atmosphere. Weighing and adding of the wantage BaBr₂ were accomplished after cooling in order that compound should provide the reaction:



The vacuum drying is repeated again after fluoride is added but the time of the residual water removing is reduced to 3–4 h. After those operations the growth camera is filled with helium to 1.1 atm. and temperature raises to the melting point in the bottom crucible. The mixture melted and remained for about 1–2 h for the melt homogenization. Then, the temperature of the melt slowly decreased. The crystal-melt front rose up at 5 mm/h. When the melt was hardened, the speed of temperature decrease rose to 1 °C/min. This prevented crystals from cracking.

The crucible with flat bottom was used for growing BaFBr crystals. In this case, the layers of the crystals were parallelly oriented to the crucible bottom.

The fluoroplastic was introduced into the zone at a temperature above 400 °C. It is conducive for the formation of CF₄ and the reaction is described as



The procedure of fluorination reduced the oxygen contamination of the crystals.

This technique enabled us to establish growth conditions allowing to produce comparably big BaFBr single crystal samples with controlled doping of alkali. Chemicals NaF:2H₂O, KF:2H₂O and RbF:2H₂O were used for BaFBr doping. Weight corrections were applied for 2H₂O presence before growing. The alkali was doped in the crucible with the sintered BaFBr. All samples were doped with 0.1 mol% of Eu²⁺. The vacuum drying was carried on during 5 h and the crystal grew as described above.

The concentrations of alkali, which we doped before growth, were about 0.1–5%. The atomic-emission analysis shows that real concentrations of alkali in the crystals is from 0.0002 to 0.0025%, i.e. most of the doping took place at the time of growing. However, such small alkali-doping concentration in the BaFBr:Eu²⁺ crystals has effective influence on the PSL process [3].

In the alkali-doped BaFBr:Eu²⁺ considerable increase of PSL intensity was observed. Upon Na doping the intensity of the PSL is increased by a factor of 12, in contrast to undoped samples. At one time the PSL peak shifted on 0.08 eV in the red region of spectrum upon Na doping. The potassium and rubidium doping result in the same effects, but with little less efficiency [4].

The electron excites to the conduction band, leaving the holes in the valence band on X-ray irradiation of this material. The free electrons are trapped both by the fluorine or bromine anion

vacancies making F(F⁻) and F(Br⁻) centers. The redshift of PSL spectra can be interpreted assuming the additional generation of F_A(Br⁻)-centers during X-ray irradiation of alkali-doped storage phosphor. The optical absorption of these centers is shifted to the lower energy in contrast to the regular F(Br⁻)-centers [4]. Possibly the increase of photostimulated luminescence is due to the presence of charge compensating bromine vacancies that lead to the creation of more F-centers.

3. Conclusion

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 in the crystals are 0.0002–0.01%. The X-ray storage phosphor BaFBr:Eu²⁺ doped with alkali impurities (Na⁺, K⁺, Rb⁺) gives a photostimulated spectrum shifted to the lower photon energies. The photostimulation luminescence intensity considerably increases compared to BaFBr:Eu²⁺ upon room-temperature X-ray irradiation. This red shift of the photostimulation spectrum is caused by formation of F_A-centers on the Br⁻ sublattice as electron traps. These centers contribute greatly to the luminescence properties of the material.

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