

Optical absorption of BaF₂ crystals with different prehistory when irradiated by high-energy electrons

E P Chinkov, S A Stepanov, V F Shtan'ko and T S Ivanova

Department of Lasers and Lighting Engineering, Institute of High Technology Physics, National Research Tomsk Polytechnic University, 30 Lenin Avenue, Tomsk 634050, Russia

E-mail: stepanovsa@tpu.ru

Abstract. The spectra of stable optical absorption of BaF₂ crystals containing uncontrollable impurities after irradiation with 3 MeV electrons are studied at room temperature. The dependence of the efficiency of stable color accumulation in the region of emerging cross-luminescence on the absorption coefficients measured near the fundamental absorption edge in unirradiated crystals of various prehistory is traced.

1. Introduction

Alkaline-earth metal fluorides are transparent over a wide spectral range, and they are used as an optical constructional material to transmit powerful UV and VUV radiation fluxes. BaF₂ crystals are of special relevance among them since cross-luminescence transitions at 195 and 220 nm and a decay time of less than 1 ns has been revealed and interpreted for the first time for these crystals [1]. This type of luminescence is also called as core-valence luminescence or Auger-free luminescence. BaF₂ crystals are currently the most widely used material for solid state scintillation detectors of x-ray, gamma radiation and other high energy particles.

The presence of intense inertial (600 ns) luminescence component at 300 nm due to the formed self-trapped excitons (STE) [2] restricts application of BaF₂ crystals as fast scintillators. Different methods are used to suppress the STE luminescence.

On the one hand, the studies were conducted to change the intensity relationship for the fast and slow luminescence components in pure BaF₂ crystals in favor of the fast component. For example, in [3], a special filter unit was used to reduce the intensity of the slow luminescence component. In [4], a gamma detector was developed based on the BaF₂ scintillator heated to 220 °C since the intensity and the decay time of the slow component are strongly dependent on temperature, whereas those of the fast component are not [5].

On the other hand, it was found that doping of BaF₂ crystals with some types of impurities results in suppression of the luminescence intensity of the slow component at 300 nm [6, 7]. Despite a large number of papers devoted to this problem, the effect of various impurities on the luminescent properties of BaF₂ crystals is still not clear. The problems are encountered when choosing the type and concentration of the dopant, and the technique for crystal growing.

The short-lived and unstable STE absorption occurs immediately after exposure of BaF₂ crystals to ionizing radiation [2, 8]. Pulsed spectroscopy with space-time resolution [9] was used to show that the efficiency of STE formation, and hence, the intensity of the slow luminescence component is



determined to a large extent by the coordinates of the irradiated sample in the growth region with small and large-scale distortion of the crystal lattice periodic potential.

As the total dose increases, the long-lived or residual absorption is accumulated. There are a number of papers describing the effects of radiation damage in scintillators [10, 11]. Earlier studies of the BaF₂ crystal radiation resistance show conflicting results. The residual absorption is highly sensitive to the crystal quality. Doping with impurities (especially heterovalent dopants) increases the radiation sensitivity of crystals of a fluorite structure [12]. Most of the differences from sample to sample are considered to be associated with different amounts of uncontrollable impurities.

Compared to pure BaF₂ crystal, the presence of uncontrollable impurities is to be followed by change in the transmission cutoff in the VUV spectral region. However, so far no attempts have been made to relate the changes in BaF₂ crystal transmission to their radiation sensitivity.

The aim of the research is to study the impact of changes in optical transmittance near the fundamental absorption edge in BaF₂ crystals of various prehistory on their radiation resistance.

2. Experimental methods

The objects of study were BaF₂ crystals grown by the Bridgeman-Stockbarger technique in fluorinating atmosphere in Crystallography Institute of the Russian Academy of Science (Moscow) and in State Optical Institute (St. Petersburg).

The BaF₂ crystals of different lots used in this research, designated by numbers in table 1, were not intentionally doped. The grown samples were of a cylindrical shape. To eliminate the impact of microsegregation of 6 pieces from the central part, 2 plates were cleaved out from each of the pieces. One parallel cleavage was analyzed to estimate the impurity content, and the second one was used to measure the optical transmittance in the VUV spectral region and radiation-induced optical absorption.

Table 1. Impurity contents in samples.

Element (10 ⁻⁴ mol%)	No.1	No.2	No.3	No.4	No.5	No.6
O	1	0,5	0,7	0,7	1	0,9
Pb	3	3	3	4	7	10

Crystals No. 1 have been used previously [8, 9] in the study of the short-lived absorption. It is known that hygroscopicity of BaF₂ crystals is low. To prevent entry of oxygen into the crystals the so called scavenger is added to remove oxygen from the melt. For BaF₂ crystals, the scavenger is typically PbF₂ [10]. When changing the technology of growing, lead and oxygen impurities remain in BaF₂ crystals, which reduces the transmission in the VUV spectral region. The results of the preliminary oxygen impurity proton-activation analysis, as well as the lead impurity spectroscopic analysis of BaF₂ crystals are shown in table 1. The data of the spectroscopic analysis indicate the presence of other impurities (Ca, Sr, Fe, Al, Mg, Mo, Zn, W), the concentration of which varies from sample to sample within the range (10⁻⁵–10⁻⁴) mol%.

The transmission spectra of the unirradiated BaF₂ crystal in the VUV spectral region were measured at room temperature with the spectrophotometer of BMP-2 type in State Optical Institute (St. Petersburg) by V.M. Reyterov.

All samples were irradiated with the dose ~10⁵ Gy at room temperature. The radiation source was a continuous electron beam accelerator. The accelerated electron energy was equal to 3 MeV. The sample thickness was within 2 mm to ensure uniform in-depth coloring. The absorption spectra of the irradiated BaF₂ crystals were measured at room temperature with the spectrophotometer of SF-256 type in the spectral range from 6.2 to 1.55 eV.

3. Results

Figure 1 shows the spectra of the induced optical absorption for BaF₂ crystals subjected to irradiation, which contained uncontrollable impurities. The spectra were measured at room temperature within 1

hour after the end of irradiation. The analysis of the data presented in figure 1 reveals the following patterns.

In irradiated BaF₂ crystals, the induced absorption is of complex spectral distribution in the range from 6.2 to 1.55 eV.

In all the irradiated crystals, the induced optical absorption is found to grow in the spectral region of the detected cross-luminescence at 5.64 eV. The greatest increase in absorption at 5.64 eV occurs in sample No. 4.

In the spectral position, the observed bands do not fit the absorption bands F (2.03 eV) and F₂ centers (1.71 eV) in the BaF₂ crystal reported in [13].

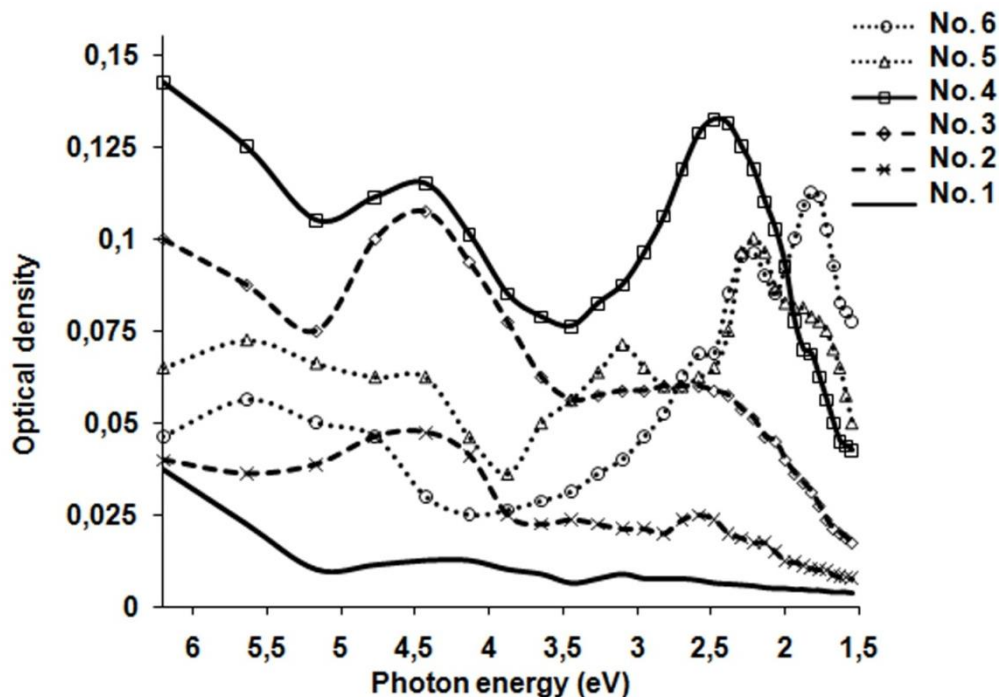


Figure 1. Optical absorption spectra of BaF₂ crystals of various prehistory at irradiation to the same dose.

The spectra of the induced absorption in samples No. 2, No. 3 and No. 4 contain bands in the region of ~4.3 eV, as well as a broad structureless band at 2.48 eV. Apparently, these bands are due to formation of metal colloidal nanoparticles [14] which are to be more stable defects than the aggregates of F centers. The spectra of the induced absorption in samples No. 5 and No. 6 contain absorption bands in the region of 2.25 eV and about 1.77 eV. An extremely large width of the absorption bands, and the shift of the maxima to longer wavelengths can be due to the distribution of the colloidal particle in size and/or due to nonspherical particle shape [15].

The concentration of impurities in BaF₂ crystals of various prehistory changes within a rather narrow range (table 1). Nevertheless, the data in figure 1 shows that the crystal colorability varies dramatically from sample to sample.

Oxygen, lead, yttrium, and sodium ions are commonly referred to uncontrollable or "biographical" impurities in crystals of a fluorite structure. The presence of these impurities leads, firstly, to the shift of the transmission cut-off of fluorite crystals to longer wavelengths, and secondly, to occurrence of selective absorption bands in the VUV spectral region [10, 11, 16-18].

At higher concentration of the doped, for example, oxygen impurity, the colorability of fluorite crystals is determined by the intensity of the selective absorption in the VUV spectral region of

unirradiated samples [10, 11]. At low concentration of the doped impurity this dependence cannot be typically traced.

The area under the absorption curve of an individual sample was assumed to be the crystal colorability efficiency.

Figure 2 shows the dependence of the colorability for BaF₂ crystals of various prehistory on the absorption coefficients, measured in unirradiated samples near the fundamental absorption edge at 150 nm, as well as in the region of the oxygen impurity selective absorption at 190 nm. These results indicate that the greater the absorption coefficients in the VUV spectral region in unirradiated crystals, the higher the colorability of BaF₂ crystals by high-energy electrons.

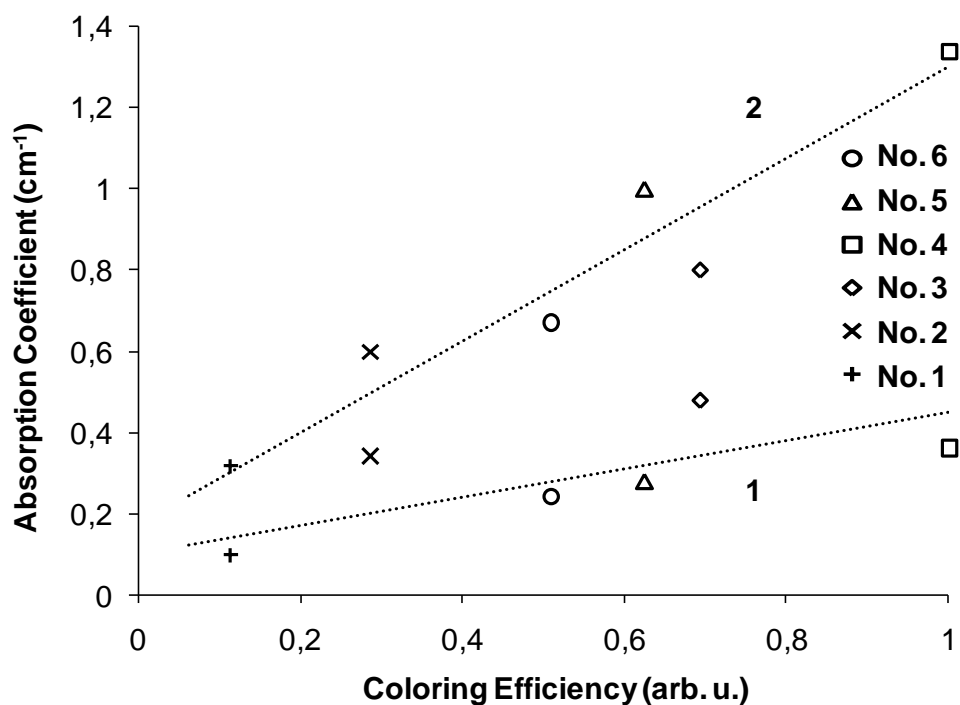


Figure 2. Influence of absorption coefficients of BaF₂ crystals in the fundamental absorption edge of unirradiated sample on coloring efficiency (curve 1 - 190 nm, curve 2 - 150 nm).

It is well known that imperfection of the anion sublattice, mainly determines the radiation sensitivity of crystals of a fluorite structure. One of the techniques to control the number of excess anionic vacancies or interstitial fluoride ions is co-doping of crystals [17].

For example, doping of the CaF₂ crystal with yttrium or sodium leads to a long-wavelength shift of the transmission cutoff in the VUV spectral region and increase in the radiation sensitivity, as compared to those in an undoped crystal [16–18]. If the concentration ratio of these impurities is optimum, the transmission cutoff in the VUV spectral region of the crystal is comparable to that of a pure crystal, the radiation resistance of the co-doped crystal increases [17].

When oxygen enters the crystal through substituting fluorine ions, the compensation of an excess charge is followed by occurrence of anion vacancies [13]. We can assume that in BaF₂ crystals the compensation of the impurity oxygen (O²⁻) excess charge occurs in substituting the barium ions in the lattice by positively charged ions of other impurities (R³⁺). Ions of rare earth elements or transition metals can be regarded as these impurities. If the concentration ratio of these impurities is optimum, dipoles of (O²⁻ – R³⁺) type are formed. The anion vacancies are not formed and the radiation resistance of the co-doped BaF₂ crystal increases. In BaF₂ crystals of various prehistory not intentionally doped, the concentration ratio of the uncontrollable impurities compensating the electroneutrality breakdown

can be random. Therefore, the effect of the impurities on radiation resistance of the crystals is unpredictable.

4. Conclusion

The spectra of the stable absorption of BaF₂ crystals of various prehistory are measured after irradiation with high-energy electrons at room temperature.

It was found that in the spectral region of the detected cross-luminescence, the colorability efficiency of BaF₂ crystals of various prehistory can be determined by the absorption coefficient near the fundamental absorption edge of the unirradiated crystal.

The results can be the basis for a method to perform the in-process control of the radiation resistance of materials of a fluorite structure.

References

- [1] Aleksandrov Yu M, Makhov V N, Rodnyi P A, Syreishchikova T I and Yakimenko M N 1984 *Sov. Phys. Solid State* **26** 2865
- [2] Williams R T, Kabler M N, Hayes W and Stott J P H 1976 *Phys. Rev. B* **14** 725
- [3] Han H, Zhang Z, Weng X, Liu J, Guan X, Zhang K and Li G 2013 *Rev. Sci. Instrum* **84** 073503
- [4] Biasini M, Cassidy D B, Deng S H M, Tanaka H K M and Mills A P 2005 *Jr. Nucl. Inst. and Meth. A* **553** 550
- [5] Schotanus P, Van Eijk C W E, Hollander R W and Pijpelink J 1985 *Nucl. Inst. and Meth. A* **238** 564
- [6] Hamada M M 1994 *Nucl. Inst. and Meth. A* **340** 524
- [7] Dorenbos P, Visser R, Doll R, Anderssen J and Van Eijk C W E J 1992 *Phys.: Condens. Matter* **4** 5281
- [8] Shtan'ko V F and Chinkov E P 1998 *Phys. Sol. State.* **40** 1119
- [9] Shtan'ko V F and Chinkov E P 1998 *Phys. Sol. State.* **40** 1326
- [10] Woody C L 1991 *GEM TN-91-38*
- [11] Lecoq P, Annenkov A, Gektin A, Korzhik M, Pedrini C 2006 *Inorganic Scintillators for Detector Systems: Physical Principles and Crystal Engineering* (Berlin: Springer) p 251
- [12] Nikl M, Sato H, Mihokova E, Mabuchi T, Nawata T, Yoshikawa A, Pejchal J, Kawaguchi N, Ishizu S, Fukuda K, Suyama T 2009 *Proc. SPIE* **7361** 73610S
- [13] Hayes W 1974 *Crystals with the Fluorite Structure: Electronic, Vibrational, and Defect Properties* (Oxford: Clarendon Press) **13** 9780198512776
- [14] Alcalá R, Orera V M 1976 *Journal de Physique* **37** 520
- [15] Hughes A E, Jain S C 1979 *Advances in Physics* **28** 717
- [16] Arkhangel'skaya V A, Reiterov V M, Trofimova L M 1980 *J. of Applied Spectroscopy* **32** 67
- [17] Lisitsyna L A, Chinkov E P, Reiterov V M and Trofimova L M 1983 *J. of Applied Spectroscopy* **38** 673
- [18] Radzhabov E, Nepomnyashchikh A and Kirm M 2007 *Phys. stat. sol. A* **204** 670