



Photoionization in Eu-doped barium fluorohalide crystals

E. Radzhabov^{a,*}, T. Kurobori^b

^a*Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Siberian Branch Favorskii street 1a, PO Box 4019, 664033 Irkutsk, Russia*

^b*Department of Materials Science and Engineering, Kanazawa University, Kakuma-machi, Kanazawa-shi 920-1192, Japan*

Received 20 August 2000; received in revised form 26 March 2001; accepted 30 March 2001

Abstract

The absorption, excitation, photostimulation spectra and thermoluminescence creation spectra of pure BaFX (X = Br, Cl) and BaFX:Eu²⁺ single crystals were studied in the vacuum ultraviolet region 5–10 eV at temperatures 6–300 K. The creation of a V_k -related thermoluminescence peak was observed when the BaFX:Eu²⁺ crystal was illuminated with vacuum ultraviolet (VUV) photons with energy above 6 eV. Band-to-band transitions begin above 8–9 eV. Low temperature photostimulation spectra for Eu²⁺ luminescence created by 6–7 eV photons showed new bands in the infrared region, the intensities of which were directly proportional to the Eu²⁺ concentration. However, the same infrared photostimulation bands for exciton luminescence were observed also in undoped crystals after X-ray irradiation. The results show that trapped electrons and self-trapped holes were created by VUV photons in BaFX:Eu²⁺ crystals. It was concluded that Eu²⁺ ions assist in creation of free electrons and holes by photons with energy 2–3 eV lower than those of band-to-band transitions. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The best-known storage phosphor BaFBr-0.1% Eu is widely used in medical radiography (Takahashi and Konda, 1984). Upon X-ray irradiation, trapped electron and trapped hole defects are formed which allow a readout process of the stored X-ray information (Spaeth et al., 1993). It is not known clearly how the energy is transferred to the activator Eu²⁺ which emits at 3.2 eV. The photostimulation processes leading to the recovery of the stored image are of significant interest, but the mechanism of creation of blue (3.2 eV) Eu²⁺ luminescence by red light is not fully known. One of the main unsolved questions in the investigations of BaFBr:Eu²⁺ photostimulated phosphor is: can Eu²⁺ change its valence during X-ray irradiation or not?

Generally, two types of electron-transfer transitions may exist. Charge-transfer transitions involve an electron from

the valence band of the host being transferred to the impurity ion. Due to these transitions, self-trapped holes are created and the impurity becomes less positively charged. Photoionization transitions involve the transfer of electrons from the impurity to the host conduction band. The free electron may be trapped by another defect and leave the impurity ion more positively charged. Due to the large band gap of BaFX crystals the transition from Eu²⁺ state to conduction band and from valence band to Eu²⁺ has to be observed in the vacuum ultraviolet region. Therefore, we study the Eu²⁺ luminescence and photoionization processes induced by the absorption of vacuum ultraviolet photons.

Defects created in BaFX crystals were characterized using thermostimulated luminescence and photostimulated luminescence. The thermostimulated peaks below room temperature in rare-earth doped alkaline-earth fluorides belong to delocalization of trapped holes and radiative recombination with trapped electrons (Merz and Pershan, 1967; Hayes, 1974). Additionally, photostimulated luminescence characterizes the energy of photoionization of trapped electrons. Using both methods we investigate the creation of trapped holes and trapped electrons by absorption of VUV photons.

* Corresponding author. Tel.: +7-395-2-311462; fax: +7-395-2-464050.

E-mail address: eradzh@igc.irk.ru (E. Radzhabov).

2. Experimental details

Single crystals were grown in a helium fluorinated atmosphere to eliminate oxygen (Radzhabov and Otroshok, 1995). The samples of approximately $8 \times 8 \times (0.2-0.5)$ mm³ dimensions and of good optical quality were cleaved on a plane perpendicular to the *c*-axis. BaFBr and BaFCl crystals were doped by 0.01–0.2 wt% of EuF₃. No trivalent Eu³⁺ luminescence in the 1.5–2.5 eV region of the spectrum was found in our crystals. Crystals containing oxygen impurities alone and oxygen impurities together with Eu²⁺ were also investigated.

The concentration of defects, having their own absorption band, may be defined using Smakula-type relation:

$$C = A(K_{\max}H) = BK_{\max}(\text{cm}^{-1}), \quad (1)$$

where K_{\max} is the maximal absorption coefficient, H , is the width of absorption band at half-maximum in eV and A and B are constants.

For the Eu²⁺ band in the ultraviolet region (at 4.5 eV in BaFX) the constant B_{Eu} is equal to 8–11 cm ppm in alkali halide crystals (Hernandez et al., 1980) and 5.6 cm ppm in alkaline-earth fluoride crystals (Arkhangel'skaya et al., 1967). We used the value $B_{\text{Eu}} = 10$ cm ppm or 10^3 cm mol%. Usually the concentration calculated using absorption coefficient agrees within 30% with the concentration of the dopant. However, sometimes the difference was larger. Therefore, we use the calculated concentration for Eu-doping characterization.

The concentration of oxygen in the BaFX crystals was estimated using the photochemical dissociation of one oxygen-vacancy center into one F center and one O⁻ center (Fisher and Gummer, 1965; Radzhabov and Otroshok, 1995). The concentration of F centers was calculated from the F-band absorption coefficient, using an oscillator strength for F centers in BaFBr (Kurobori et al., 1999) and $A_{\text{F}} = 1.04 \times 10^{16} \text{ cm}^{-2} \text{ eV}^{-1}$ (Fisher and Gummer, 1965). We obtain $B_{\text{O}^-} = 2.3 \times 10^{16} \text{ cm}^{-2} = 1.6 \times 10^4 \text{ cm mol\%}$ for BaFCl and $B_{\text{O}^-} = 1.8 \times 10^{16} \text{ cm}^{-2} = 1.3 \times 10^4 \text{ cm mol\%}$ for BaFBr crystals at room temperature.

The spectra in 4–10 eV region were measured with a vacuum monochromator VMR2. For thermoluminescence studies the crystal was illuminated by light from a VMF25, 25 W hydrogen discharge lamp, dispersed by a VMR2 monochromator for a few minutes at 78 K. Then the crystal was warmed at a heating rate 11 K/min. The creation spectra of thermoluminescence peaks were corrected for the spectral response of monochromator and emission spectrum of discharge lamp.

During studies of photostimulated luminescence, crystals were irradiated by a W-anode X-ray tube with parameters: 30 kV, 1 mA, 1 min through 1 mm Al filter. Experimental setup includes three grating monochromators: one for VUV illumination, while the other two monochromators were used for photostimulation and luminescence measurements, respectively. The photostimulation spectra were corrected for

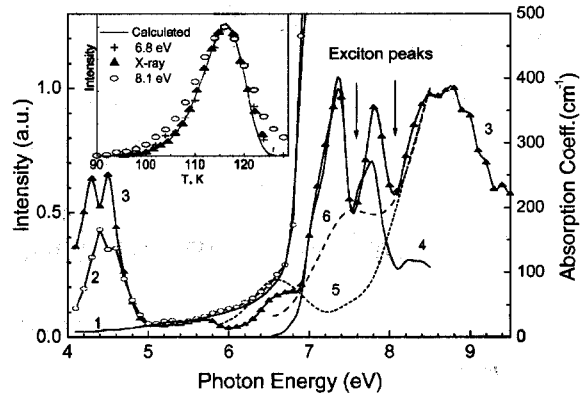


Fig. 1. Absorption spectra of undoped BaFBr (1) and BaFBr:0.093 mol% Eu²⁺ (2) at 295 K. Excitation spectra of 3.2 eV Eu²⁺ luminescence (3) and 4.3 eV exciton luminescence (4) in BaFBr:0.008 mol% Eu crystal at 78 K. Arrows show the position of the exciton absorption bands. Creation spectra of 116 K (5) and 166 K (6) thermoluminescence peaks. The inset shows 3.2 eV thermostimulated luminescence curves of BaFBr:0.008 mol% Eu²⁺ after vacuum ultraviolet excitation and X-ray irradiation at 78 K.

the spectral distribution of halogen W-lamp with known filament temperature as well as for the spectral width of grating monochromator slit. The corrections for spectral response of the gratings were not made, but we used the central region of the sensitivity for each grating, so the correction for spectral response has to be not so significant.

3. Results

3.1. Thermostimulated luminescence creation

The creation of thermoluminescence peaks at 116 and 166 K was observed after excitation by photons with energies above 6 eV (Fig. 1). At 6–8 eV region of photon energies only a 116 K peak was observed. The creation spectra for both thermostimulated luminescence peaks show an increase above 7.8 eV (see Fig. 1). This growth is undoubtedly related to a band-to-band transition and the creation of free electrons and holes.

The results for BaFCl:Eu²⁺ are similar to those for BaFBr:Eu²⁺ (Fig. 2). The dips on excitation spectrum at 8.7 coincide with exciton peaks at 8.6 and 8.7 eV observed in absorption spectra of BaFCl thin film (Nicklaus, 1979). Thermoluminescence peaks at 154 and 204 K were created due to excitation with 6–9 eV photons. In more highly doped BaFCl:Eu, the first peak shifts to lower temperatures with increased doping. Two excitation bands and thermoluminescence creation bands near 6.8 and 7.7 eV were observed (see Fig. 2). Similar to BaFBr:Eu the low temperature thermoluminescence peak in BaFCl:Eu²⁺ is mostly created at lower photon energies, while the high

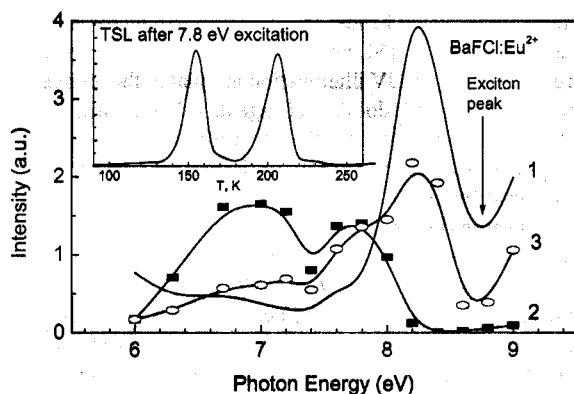


Fig. 2. Excitation spectrum of Eu^{2+} luminescence of $\text{BaFCl}:0.16 \text{ mol}\% \text{Eu}^{2+}$ at 78 K (1). The arrow shows the position of exciton absorption band. Creation spectra of thermoluminescence peaks 154 K (2) and 204 K (3). Inset—3.4 eV thermostimulated luminescence of $\text{BaFCl}-\text{Eu}^{2+}$ created by 8 eV photon excitation at 78 K.

temperature thermoluminescence peak is more effectively created in the exciton region and the band-to-band region of photon energies.

3.2. Photostimulated luminescence

The photostimulation spectrum of Eu^{2+} luminescence of $\text{BaFBr}:\text{Eu}^{2+}$ illuminated by 6.5 eV photons at room temperature shows the known weak F(Br) bands at 2.15 and 2.4 eV. The photostimulation spectrum drastically changed after 6.5 eV excitation at 78 K (see Fig. 3). Much more intensive bands appeared at 1.4 and 1.8 eV. Similar photostimulation spectra were observed after 6.5, 7.7 and 8.2 eV excitation at 78 K. Emission spectrum during photostimulation consists of only Eu^{2+} 3.2 eV band after 6.5 eV excitation. In addition, to Eu^{2+} luminescence, we also observed weak exciton luminescence after 7.7 eV excitation. The photostimulated luminescence as well as thermostimulated luminescence created by VUV excitation proportionally decreased during red photobleaching or pulse annealing. Both luminescences can be fully bleached from any part of photostimulation spectrum. Therefore, all bands that are seen in the photostimulation spectrum (see Fig. 3) belong to excitation of one type of defects.

The luminescence intensity stimulated at 1.4 eV is directly proportional to the Eu^{2+} concentration after 6.6 eV excitation. The intensity was near 3 times lower in highly Eu^{2+} doped crystals after X-ray irradiation at 78 K (see Fig. 3).

Photostimulated defects in undoped BaFBr can be created only by X-ray irradiation. The photostimulated spectrum of undoped BaFBr crystals is very similar to that of $\text{BaFBr}:\text{Eu}$ (Fig. 3). When crystals were irradiated below 20 K, a new large photostimulated band at 1.23 eV was created. Above 25–30 K this spectrum is irreversibly con-

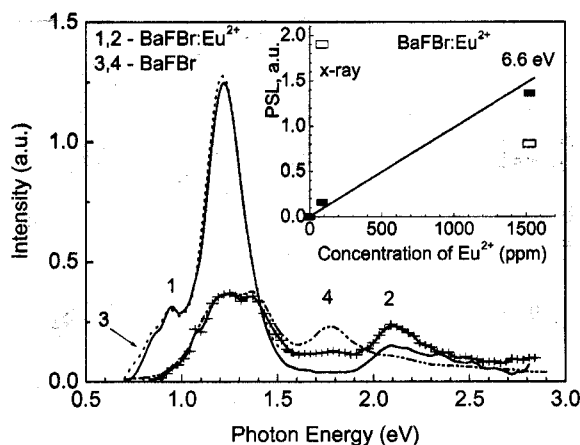


Fig. 3. Photostimulation spectra of Eu^{2+} luminescence for $\text{BaFBr}:0.093 \text{ mol}\% \text{Eu}^{2+}$ (1,2) and undoped BaFBr (3,4). Defects were created in $\text{BaFBr}:\text{Eu}$ by 6.6 eV illumination and in undoped BaFBr —by X-ray irradiation. Curves 1 and 3 were measured at 17 K; curves 2, 4 were measured at 78 K. Curves for $\text{BaFBr}:\text{Eu}$ were measured at 3.2 eV maximum for Eu^{2+} luminescence, curves for BaFBr were measured at the maxima of the exciton emissions at 4.3 eV (78 K) or 5.1 eV (17 K). The inset shows the intensity of the 3.2 eV luminescence stimulated by 1.4 eV photons at 78 K against the concentration of Eu in BaFBr . Samples were illuminated by 6.6 eV photons or irradiated by X-ray at 78 K.

verted to another spectrum (see Fig. 3). The photostimulation spectra and thermoluminescence curve of $\text{BaFBr}:\text{Eu}^{2+}$ after X-ray irradiation are very similar to those after VUV-excitation, while the F(Br)-bands at 2.1 and 2.45 eV become relatively larger in X-ray irradiated samples.

The F(Br) band becomes prominent in low-temperature photostimulation spectrum of $\text{BaFBr}:\text{Eu}^{2+}, \text{O}$ after VUV illumination. The IR photostimulation spectrum becomes smooth. The IR photostimulated bands disappear after heating up to 150 K. Two thermoluminescence peaks at 116 and 140 K were observed. It seems that the presence of oxygen leads to additional F centers in comparison to oxygen-free $\text{BaFBr}:\text{Eu}$.

The photostimulation spectrum for Eu^{2+} luminescence of $\text{BaFCl}:\text{Eu}$ after X-irradiation at room temperature shows the F(Cl) band at 2.2 eV. The F(Cl) band is more than three times lower in a crystal X-irradiated at 78 K. Additionally, new bands appear in 1–2 eV region (Fig. 4). The Eu^{2+} and 3.35 eV exciton emissions were observed at 78 K when stimulated by 1–2 eV light. High-energy exciton luminescence band at 5.45 eV appeared at 6 K.

Part of the red excitation band decreased near 150 K (see Fig. 4). At the same time the intensity of the F(Cl) band in weakly Eu-doped samples increased sharply. In heavily Eu-doped BaFCl samples the first decreasing step was observed around 130 K with a second decreasing step in the 180–230 K region (see Fig. 4). The red photostimulation band completely disappears after heating the crystal above the temperature 220 K of main thermoluminescence peak.

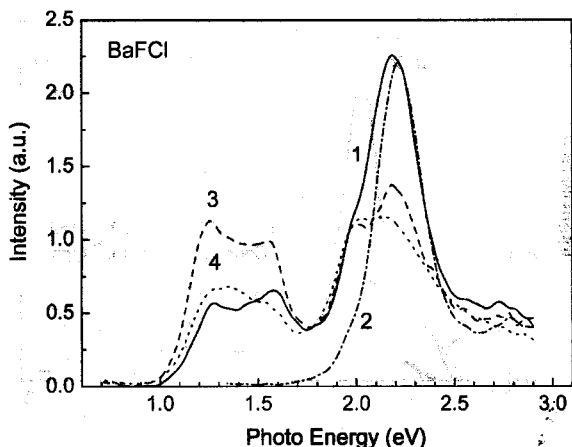


Fig. 4. Photostimulation spectra of BaFCl: 0.12 mol% Eu^{2+} (curve 3) and BaFCl: 0.16 mol% Eu^{2+} :0.0007 mol% O (curves 1, 2) and undoped BaFCl with oxygen contamination few ppm (curve 4) at 78 K. The Eu-doped samples were illuminated by 7–7.7 eV photons at 78 K (1, 3), heated up to 240 K and measured at 78 K (2). The undoped BaFCl sample was X-ray irradiated (30 kV, 6 mA, 3 min) at 78 K. The luminescence was monitored at 3.4 eV for the Eu^{2+} -doped sample and at 3.3 eV exciton band for the undoped sample.

4. Discussion

Unknown electron traps cause the low-temperature infrared photostimulated bands. The low-temperature photostimulated spectra of undoped and Eu doped crystals are very similar (see. Fig. 3). The presence of Eu^{2+} ions does not influence these electron traps. The photostimulation spectra show similarity in BaFBr and BaFCl crystals (see Figs. 3 and 4), which points to a similar nature for the defects in both crystals. The infrared photostimulable defects can be created by X-ray irradiation in all crystals or by 6–8 eV illumination in Eu-doped crystals. The same types of trapped electrons and trapped holes are created in BaFBr, BaFCl crystals doped with Eu as by X-ray irradiation as well as by VUV illuminations. The possibility of filling the electron traps by tunnelling during VUV illuminations is low due to the very low concentration of traps. We conclude, therefore, that VUV illumination of BaFX:Eu leads to the creation the electrons in conduction band.

The largest glow peak at 116 K in X-irradiated BaFBr crystals (see Fig. 1) was assigned to recombination of mobile self-trapped holes (V_k centers) with trapped electrons (Ohnishi et al., 1999). The V_k centers in BaFBr can diffuse above about 120 K (Hangleiter et al., 1990). The shape of the thermoluminescence peak at 116 K was the same after X-irradiation and 6.8 eV excitation (see Fig. 1). Therefore, it is very reasonable that V_k centers as well as trapped electrons are created by 6–7 eV excitation of BaFBr: Eu^{2+} and BaFCl: Eu^{2+} at 78 K.

The V_k TSL peak can be fully diminished by photostimulation into the infrared bands in BaFBr: Eu. Also, no photo-

stimulated infrared bands remain after warming to temperatures above the V_k TSL peak. Therefore, the number of electrons created by VUV illumination is equal to the number of holes, and the Eu^{2+} does not change its valence during VUV illumination. We conclude that the creation of free electrons and holes in the vicinity of Eu^{2+} is the very process occurring after absorption of 6–7 eV photons in BaFX: Eu^{2+} crystals. The electrons become trapped at unknown defects, while the hole becomes self-trapped in the vicinity of Eu^{2+} . When the energy of the photons increases to 7–8 eV, the created holes have an additional energy and become self-trapped far from Eu^{2+} . In this case we observe photostimulated exciton emission in BaFBr: Eu. In the presence of oxygen, some parts of the created electrons and holes are trapped by oxygen defects and, therefore, will survive after warming to room temperature.

The peak at 6.6 eV was observed earlier in the excitation spectrum, the PSL formation spectrum and even in the absorption spectrum of highly doped BaFBr:Eu crystals containing also oxygen (Iwabuchi et al., 1994).

Creation of defects after irradiation with ultraviolet photons having energies lower than the band gap energy was observed in several crystals doped with Eu (Knitel et al., 1998), Pb or Tl impurity (Babin et al., 1998; Chernov et al., 1998).

What is the reason for the considerable decrease in energy of the optical creation of electron–hole pairs by impurities? We can see at least two possible reasons for this phenomenon in BaFX: Eu^{2+} . The first one is lattice distortion. The ionic radius of Eu^{2+} is nearly 20% less than the radius of the host Ba^{2+} . The main part of the energy needed to transfer an electron from the anion to the cation is the Madelung energy $E_M = \text{constant}/d$. In fact, the lattice relaxation around Eu^{2+} in BaFBr measured by means of ENDOR is very small. It was concluded that the ^{19}F neighbours are possibly relaxed towards Eu^{2+} by at most about 1% of the usual distance (Assmann et al., 1999). Therefore the lattice distortion cannot adequately explain the decrease in the electron–hole creation energy in the vicinity of Eu^{2+} .

The second reason may be connected with a temporal participation of Eu level in the process of the creation of an electron–hole pair. The electron transfers from the valence band to the Eu level. Any Eu^+ ions become unstable after a short relaxation, ejecting an electron to the conduction band. The effect of decreasing the energy distance between levels in the band gap and the bottom of the conductivity band is known for F centres in alkali halides (Luty, 1968).

In conclusion, self-trapped holes as well as trapped electrons are created in BaFBr: Eu^{2+} and BaFCl: Eu^{2+} by photons with energy above 6 eV at low temperatures. The self-trapped hole is localized in the vicinity of Eu^{2+} , while electrons are trapped by available shallow traps or by a bromine vacancy associated with the oxygen ion.

Acknowledgements

One of the authors (E.R.) is grateful to Dr. K. Kan'no, Dr. K. Tanimura, Dr. K. Inabe for valuable detailed discussions during the visit to Japan under JSPS Fellowship program (S-99220).

References

- Arkhangel'skaya, V.A., Kiselyova, M.N., Shraiber, V.M., 1967. Molar absorption coefficients and oscillators forces of transitions to f-d configurations of Re^{2+} ions (in Russian) *Opt. Spectrosc.* 23, 509–511.
- Assmann, S., Schweizer, S., Spaeth, J.M., 1999. ENDOR investigation of the Eu^{2+} activator in the X-ray storage phosphor BaFBr. *Phys. Status Solidi B* 212, 325–334.
- Babin, V., Fabeni, P., Kalder, K., Nikl, M., Pazzi, G.P., Zazubovich, S., 1998. Photo- and thermally stimulated luminescence and defects in UV-irradiated CsI:Tl and CsI:Pb crystals. *Radiat. Meas.* 29, 333–335.
- Chernov, S.A., Trinkler, L., Popov, A.I., 1998. Photo- and thermo-stimulated luminescence of CsI-Tl crystal after UV light irradiation at 80K. *Radiat. Eff. Def. Solids* 143, 345–355.
- Fisher, F., Gummer, G., 1965. Quantenausbeute für den photochemischen Abbau von O^{2-} zentren in KCl. *Z. Phys.* 189, 97–112.
- Hangleiter, T., Koschnick, F., Spaeth, J., Nuttall, R.H.D., Eahus, R.S., 1990. Temperature dependence of the photostimulated luminescence of X-irradiated BaFBr:Eu²⁺. *J. Phys. Condens. Matter* 2, 6837–6846.
- Hayes, W. (Ed.), 1974. *Crystals with the Fluorite Structure*. Oxford University Press, Oxford.
- Hernandez, J., Cory, W.K., Rubio, J.O., 1980. Optical investigation of divalent europium in the alkali chlorides and bromides. *J. Chem. Phys.* 72, 198–205.
- Iwabuchi, Y., Mori, N., Takahashi, K., Matsuda, T., Shionoya, S., 1994. Mechanism of photostimulated luminescence process in BaFBr:Eu²⁺ phosphors. *Jpn. J. Appl. Phys.* 33 Part I, 178–185.
- Knitel, M.J., Dorenbos, P., Andriessen, J., VanEijk, C.W.E., Berezovskaya, I., Dotsenko, V., 1998. Trapping of charge carriers in $\text{Sr}_2\text{B}_5\text{O}_9\text{Br}:\text{Eu}^{2+}$ under irradiation with UV light. *Radiat. Meas.* 29, 327–331.
- Kurobori, T., Kozake, S., Hirose, Y., Ohmi, M., Haruna, M., Kimura, T., Inabe, K., Somaiah, K., 1999. Determination of the optical constants of the photostimulable BaFCl:Eu²⁺ and KCl:Eu²⁺ crystals. *Jpn. J. Appl. Phys. Part 1 Regular Papers Short Notes & Review Papers* 38, 901–904.
- Luty, F., 1968. In: Fowler, W. (Ed.), *Physics of Color Centers*, Academic Press, New York (Chapter 3).
- Merz, J.L., Pershan, P.S., 1967. Charge conversion of irradiated rare-earth ions in calcium fluoride. I. *Phys. Rev.* 162, 217–235.
- Nicklaus, E., 1979. Optical properties of some alkaline earth halides. *Phys. Status Solidi B* 53, 217–224.
- Ohnishi, A., Mori, N., Kanno, K., 1999. Thermal stability of photostimulated luminescence centers in BaFBr and BaFBr:Eu²⁺ single crystals. *Jpn. J. Appl. Phys.* 38 (1), 208–216.
- Radzhabov, E., Otroshok, V., 1995. Optical spectra of oxygen defects in BaFCl and BaFBr crystals. *J. Phys. Chem. Solids* 56, 1–7.
- Spaeth, J.M., Koschnick, F.K., Eachus, R.S., Mcdugle, W.G., Nuttall, R.H.D., 1993. Investigation of the storage phosphor BaFBr-Eu by multiple magnetic resonance techniques. *Nucl. Tracks Radiat. Meas.* 21, 73–79.
- Takahashi, K., Konda, K.J.M., 1984. Mechanism of photostimulated luminescence in BaFX:Eu²⁺ (X = Cl, Br) phosphors. *J. Lumin.* 31&32, 266–268.