Photoionization processes in barium fluorohalide crystals doped with Eu^{2+}

Photoionization processes in barium fluorohalide crystals doped with Eu²⁺

E Radzhabov[1,3] and T Kurobori[2]

[1] Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Favorskii Street 1a,
PO Box 4019, 664033 Irkutsk, Russia
[2] Department of Materials Science and Engineering, Kanazawa University, Kakuma-machi,
Kanazawa-shi 920-1192, Japan

E-mail: eradzh@igc.irk.ru (E Radzhabov) and laser@kenroku.kanazawa-u.ac.jp (T Kurobori)

Abstract
The absorption, excitation and photostimulation spectra and thermolumines-
cence creation spectra of pure BaFX (X = Br, Cl) and BaFX:Eu²⁺ single
crystals were studied in the vacuum–ultraviolet (VUV) region 5–10 eV at tem-
peratures of 6–300 K. Creation of a V_K thermoluminescence peak was ob-
served when the BaFX:Eu²⁺ crystal was illuminated with VUV photons with
energies above 6 eV while band-to-band transitions begin above 8–9 eV. Low-
temperature photostimulation spectra for Eu²⁺ luminescence created by 6–7 eV
photons show new bands in the infrared region, with intensities directly pro-
portional to the Eu²⁺ concentration. However, the same infrared photostimula-
tion bands for exciton luminescence were also observed for undoped crystals
after x-ray irradiation. Therefore, a trace concentration of the shallow elec-
tron traps is present in each undoped and Eu-doped BaFBr and BaFCl crystal.
The results show that self-trapped holes and electrons are trapped on different
non-europium centres, created by VUV photons in BaFX:Eu²⁺ crystals at low
temperature.

It was concluded that Eu²⁺ ions assist in the creation of free electrons
and self-trapped holes by photons with an energy 2–3 eV lower than those of
band-to-band transitions.

1. Introduction

The best-known storage phosphor BaFBr–0.1% Eu is widely used in medical radiography
[1]. Upon x-ray irradiation, defects are formed which allow a read-out of the stored x-ray
information. Electron- and hole-trap centres are involved in the image formation process [2].
It is not clearly known how the energy is transferred to the activator Eu²⁺ which emits at 3.2 eV.
The stimulation processes leading to the recovery of the stored image are of significant interest.

[3] www.igc.irk.ru/radzhabov/.

Three configurations of trapped electrons, trapped holes and Eu^{2+} centres were observed in x-ray-irradiated $BaFBr:Eu^{2+}$ [2,3]. However, the reason for the creation of such configurations is still unknown [4].

The band gap of BaFX crystals is very large (8–9 eV). Optical properties of $BaFBr:Eu^{2+}$ crystals have been investigated in several papers [5–7].

The aim of this paper is to study the photoionization processes leading to creation of electron and hole defects by vacuum–ultraviolet (VUV) photons in BaFCl and BaFBr crystals either undoped or doped with europium and/or oxygen. Defects created in BaFX crystals were characterized using thermostimulated luminescence and photostimulated luminescence. Usually, the most intense thermostimulated peaks below room temperature relate to delocalization of trapped holes and radiative recombination with trapped electrons. Photostimulated luminescence characterizes the energy of photoionization of trapped electrons. Using both of these sensitive methods we investigated the creation of trapped holes and trapped electrons by VUV photons.

We observed creation of a V_K peak of thermoluminescence after illumination of the $BaFBr:Eu^{2+}$, $BaFCl:Eu^{2+}$ crystals by VUV photons above 6 eV, far below the exciton or band-to-band region. We investigated low-temperature photostimulated luminescence for electron traps created along with V_K centres by VUV photons or x-rays in BaFX and in $BaFX:Eu^{2+}$. No additional low-temperature photostimulated bands specific to Eu impurity were observed for Eu^{2+}-doped BaFX crystals. Some preliminary results have been published elsewhere [8].

Generally, two types of electron-transfer transition 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. The other possibility involves the transfer of an electron 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.

We did not observed the creation of either Eu^{3+} or Eu^+ during VUV illumination, while other trapped electrons and self-trapped holes are created. The observed transitions can be considered as special types of charge-transfer transition, in which electrons transferred from the valence band to the Eu level are ejected after relaxation to the conduction band.

2. Experimental details

The single crystals were grown in a helium fluorinated atmosphere to eliminate the oxygen [9]. The samples, with dimensions $8 \times 8 \times (0.2–0.5)$ mm, of good optical quality, were cleaved along a plane perpendicular to the c-axis. BaFBr and BaFCl crystals were doped with 0.01–0.2 wt% of EuF_3. No trivalent Eu^{3+} red luminescence was found for our crystals. Crystals containing oxygen impurities alone and oxygen impurities together with Eu^{2+} were also investigated.

The concentration of defects of an absorption band may be defined using the following relation:

$$C = AK_{max}H = BK_{max} \text{ (cm}^{-1}) \tag{1}$$

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

For the Eu^{2+} band in the ultraviolet region (at 4.5 eV for BaFX) the constant B_{Eu} is equal to 8–11 cm ppm for alkali halide crystals [10] and 5.6 cm ppm for alkaline-earth fluoride crystals [11]. We used the value $B_{Eu} = 10$ cm ppm or 10^{-3} cm mol%. Usually the concentration calculated using the absorption coefficient agreed within 30% with the

concentration of dopant. However, sometimes the difference was larger. Therefore, we used the calculated concentration for Eu-doping characterization.

The concentration of oxygen in BaFX crystals can be estimated using the photochemical dissociation of one oxygen–vacancy centre into one F centre and one O^- centre [9, 13]. The concentration of F centres can be calculated from the F-band absorption coefficient, using the oscillator strength for F centres in BaFBr [12] and $A_F = 1.04 \times 10^{16}$ cm^{-2} eV^{-1} [13]. Two types of oxygen–vacancy centre were found in BaFBr and BaFCl crystals by optical investigations [9] and EPR investigations [14]. A centre of the first type consists of an oxygen-occupied F site accompanied by an X-site vacancy (X = Br or Cl), while in a centre of the second type the oxygen occupies the X site also [9]. From absorption spectra we concluded that our crystals of BaFX:Eu^{2+}, O^{2-} contain oxygen centres of the second type. We estimate the concentration of oxygen in BaFX:O^{2-} crystals by measuring the decrease in the oxygen bands and increase in the F band during room temperature photodissociation of oxygen centres by 5–6.5 eV ultraviolet light from a deuterium discharge lamp. The following constants were obtained for the second absorption bands of oxygen defects at 5.23 eV (halfwidth $H = 0.37$ eV) in BaFBr and 5.60 eV ($H = 0.40$ eV) in BaFCl: $A_{O^{2-}}/A_F = 2.2$ and 1.7 for BaFCl and BaFBr respectively. Using the known halfwidths, we obtain $B_{O^{2-}} = 2.3 \times 10^{16}$ cm^{-2} = 1.6×10^{-4} cm mol% for BaFCl and $B_{O^{2-}} = 1.8 \times 10^{16}$ cm^{-2} = 1.3×10^{-4} cm mol% for BaFBr crystals at room temperature.

A more highly sensitive but less quantitative method, based on measuring luminescence spectra under ultraviolet illumination, yields yellow-green oxygen bands [9] well separated from the blue Eu^{2+} emission. No oxygen absorption bands or photoluminescence bands were found for Eu-doped BaFBr crystals.

The spectra in the 4–10 eV region were measured with a vacuum monochromator, VMR2. For thermoluminescence studies the crystal was illuminated with light from VMF25 (a 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 of 11 K min^{-1}. The creation spectra of thermoluminescence peaks were corrected for the spectral response of the monochromator and emission spectrum of the discharge lamp.

During the studies of the photostimulated luminescence, the crystals were irradiated by a W-anode x-ray tube with the following parameters: 30 kV, 1 mA, 1 min through a 1 mm Al filter. The experimental set-up includes three grating monochromators: one was used for VUV illumination, while the other two monochromators were used for photostimulation measurements and luminescence measurements. The photostimulation spectra were corrected for the spectral distribution of the halogen W lamp with a known filament temperature, as well as for different spectral widths of the grating monochromator slit. Corrections for the spectral response of the gratings were not made, but we use the central region of sensitivity for each grating, so the correction for spectral response may not be very significant.

3. Results

3.1. Thermostimulated luminescence creation

The excitation spectra for Eu^{2+} emission in BaFBr show bands at 4.4, 4.6 and 5.7 eV, which are known as 4f–5d bands, and 6.7 eV (figure 1). The dips at 7.6 and 8.1 eV (see figure 1) coincide well with the exciton peaks at 7.64 and 8.15 eV observed in absorption spectra of BaFBr thin film [15]. The excitation spectrum for Eu^{2+} luminescence in the exciton region 7–8 eV coincides with those for exciton 4.2 and 5.15 eV bands, observed for pure crystals and lightly Eu doped crystals (see figure 1). The exciton luminescence was suppressed in crystals heavily doped with Eu^{2+} (0.1 mol% and more).
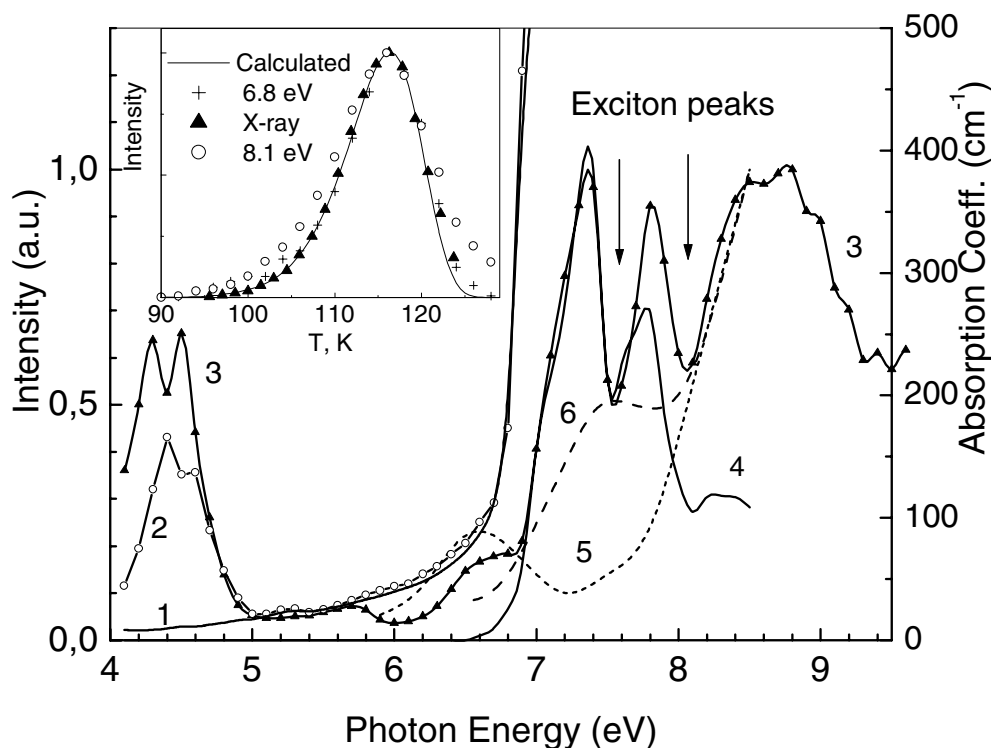
Figure 1. Absorption spectra of undoped BaFBr (1) and BaFBr:0.093 mol% Eu^{2+} (2) at 295 K; excitation spectra of 3.2 eV Eu^{2+} luminescence (3) and 4.3 eV exciton luminescence (4) for BaFBr:0.008 mol% Eu crystal at 78 K (arrows show the positions of exciton absorption bands [15]); and creation spectra of 116 K (5) and 166 K (6) thermostimulated luminescence peaks. The inset shows 3.2 eV thermostimulated luminescence curves for BaFBr:0.008 mol% Eu^{2+} after VUV excitation and x-ray irradiation at 78 K. The calculated curve is fitted with the parameters $E = 0.28$ eV and $\nu = 1.3 \times 10^{11}$ s^{-1}.

The creation of thermoluminescence peaks at 116 K and 166 K was observed after excitation by photons with energies above 6 eV (see figure 1). In the 6–6.8 eV region of the photon energies, only a sharp 116 K peak was observed with a halfwidth of 11 K. After illumination with higher-energy photons, the 116 K peak became broader with a halfwidth of 16 K, and a 166 K peak appeared. Creation spectra for both thermostimulated luminescence peaks show an increase above 7.8 eV (see figure 1). This growth is undoubtedly related to band-to-band transitions and creation of free electrons and holes. The creation spectrum of the 116 K peak shows a maximum at 6.6 eV, while that for the 166 K peak shows a maximum at 7.5 eV. For highly Eu-doped BaFBr crystals a second thermoluminescence peak was observed at 220 K.

The results for BaFCl:Eu^{2+} are similar to those for BaFBr:Eu^{2+} (figure 2). The dips in the excitation spectrum at 8.7 eV coincide with exciton peaks at 8.6 and 8.7 eV observed in absorption spectra of BaFCl thin films [15]. Thermoluminescence peaks at 154 K and 204 K were created due to excitation with 6–9 eV photons. For more heavily doped BaFCl:Eu the first peak shifts to lower temperatures. Two excitation bands and thermoluminescence creation bands near 6.8 eV and 7.7 eV were observed (see figure 2). This result applies apart from for BaFBr:Eu, where only one band at 6.7 eV was observed. Like for BaFBr:Eu, the
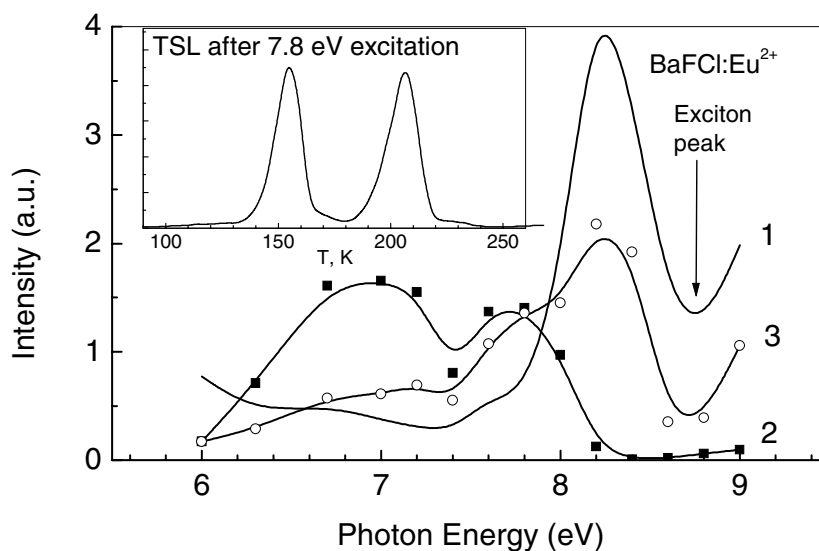
Figure 2. The excitation spectrum of BaFCl:0.16 mol% Eu^{2+} at 78 K (1) (the arrow shows the position of the exciton absorption band [15]); and the creation spectra of the thermoluminescence peaks at 154 K (2) and 204 K (3). Inset: 3.4 eV thermostimulated luminescence of BaFCl–Eu^{2+} created by 7.8 eV photon excitation at 78 K.

low-temperature thermoluminescence peak for BaFCl:Eu^{2+} is mostly created at lower photon energies, while the high-temperature thermoluminescence peak is more effectively created in the exciton region and band-to-band region of photon energies.

3.2. Photostimulated luminescence

3.2.1. BaFBr, BaFBr:Eu^{2+} and BaFBr:Eu^{2+}, O^{2-}. The photostimulation spectrum of Eu^{2+} luminescence of BaFBr: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 upon 6.5 eV excitation at 78 K (see figure 3). Much more intense 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. The emission spectrum during photostimulation consists of just the Eu^{2+} 3.2 eV band after 6.5 eV excitation. Additionally to Eu^{2+} luminescence, we observed also weak exciton-photostimulated 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 luminescence signals can be fully bleached from any part of the photostimulation spectrum.

The luminescence intensity stimulated at 1.4 eV is directly proportional to the Eu^{2+} concentration after 6.6 eV VUV excitation. Apart from this, the intensity was lower by nearly a factor of 3 for highly Eu^{2+}-doped crystals after x-ray irradiation at 78 K (see figure 3).

The photostimulated spectrum of undoped BaFBr crystals is very similar to those of BaFBr:Eu (figure 3). The photostimulated defects in undoped BaFBr can be created only by x-ray irradiation. 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 converted into another spectrum (see figure 3) without any measurable thermostimulated luminescence. Back-cooling to 17 K preserves the new photostimulated spectrum.
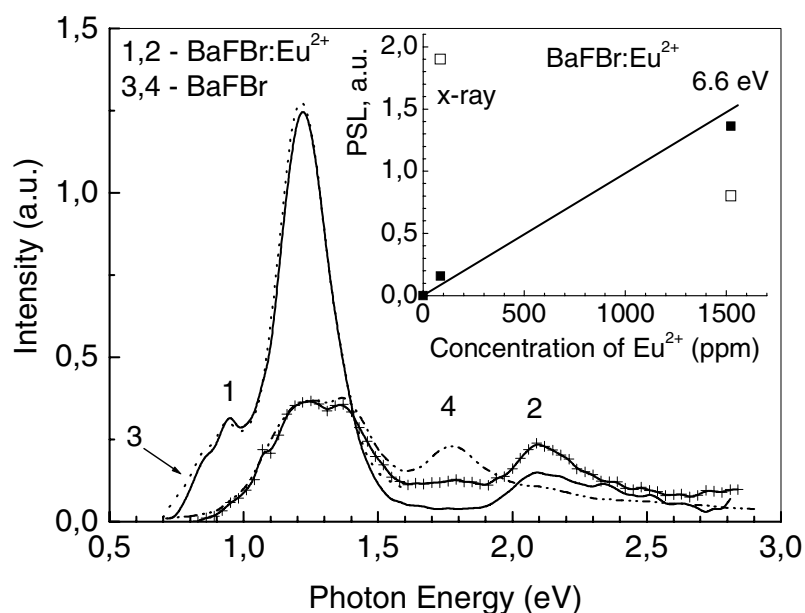
Figure 3. Photostimulation spectra of Eu^{2+} luminescence for BaFBr:0.093 mol% Eu^{2+} (1), (2) and undoped BaFBr (3), (4). Defects were created in BaFBr:Eu by 6.6 eV illumination and in undoped BaFBr by x-ray irradiation. Curves (1), (2) were measured at 17 K; curves (3), (4) were measured at 78 K. The curves for BaFBr:Eu were measured for Eu^{2+} luminescence; the curves for BaFBr were measured at maxima of exciton emission 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.

The photostimulation spectra and thermoluminescence curve of BaFBr: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 large for x-ray-irradiated samples.

F(Br) bands become prominent in the low-temperature photostimulation spectrum of BaFBr:Eu^{2+}, O^{2-} upon VUV illumination. The infrared (IR) photostimulation spectrum becomes smooth. The IR photostimulated bands disappear upon heating up to 150 K. Two thermoluminescence peaks at 116 K and 140 K were observed.

X-ray irradiations lead to a similar photostimulated luminescence spectrum, while the F(Br) bands become relatively large. The thermoluminescence peaks were observed at slightly higher temperatures (figure 4).

Therefore the additional presence of F centres apparent in photostimulated spectra in comparison to those of oxygen-free BaFBr:Eu is caused by the presence of oxygen.

3.2.2. BaFCl, BaFCl:Eu^{2+} and BaFCl:Eu^{2+}, O^{2-}. The photostimulation spectrum for Eu^{2+} luminescence of BaFCl:Eu after x-ray irradiation at room temperature shows the F(Cl) band at 2.2 eV. The F(Cl) band is more than three times weaker for a 78 K x-ray-irradiated crystal. Additionally, new bands appeared in the 1–2 eV region (figure 5). The Eu^{2+} and 3.35 eV exciton emissions were observed at 78 K upon stimulation by red light. A high-energy exciton luminescence band at 5.45 eV appeared at 6 K.

A part of the red excitation band decreased near 150 K (see figure 5). At the same time the intensity of the F(Cl) band for weakly Eu-doped samples sharply increased. For heavily Eu-doped BaFCl samples the first decreasing step was observed around 130 K and
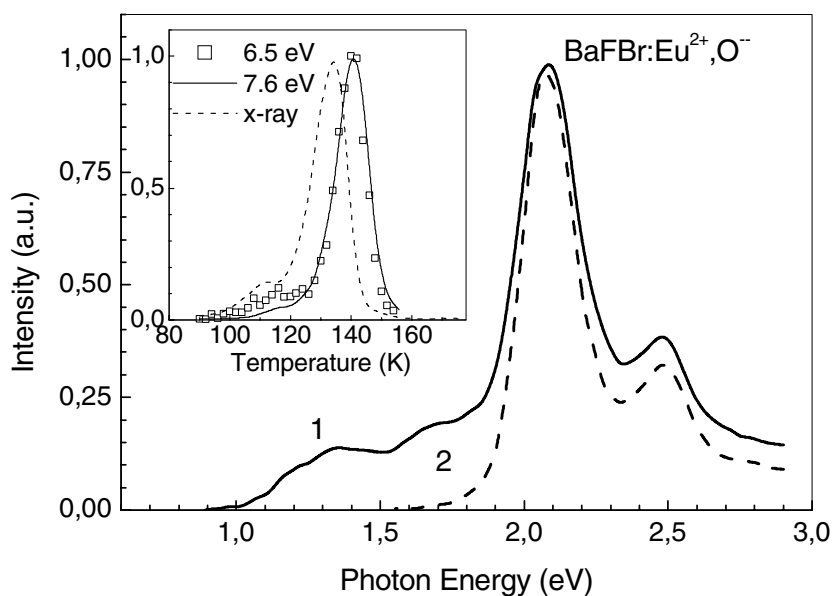
Figure 4. Photostimulation spectra of Eu^{2+} luminescence for oxygen-containing BaFBr:0.22 mol% Eu^{2+} and 0.008 mol% O^{2-} crystal at 78 K. The sample was x-ray irradiated at 78 K (1) and heated up to 150 K (2). The inset shows the 3.2 eV thermostimulated luminescence after 6.5 eV, 7.7 eV excitation and after x-ray irradiation.
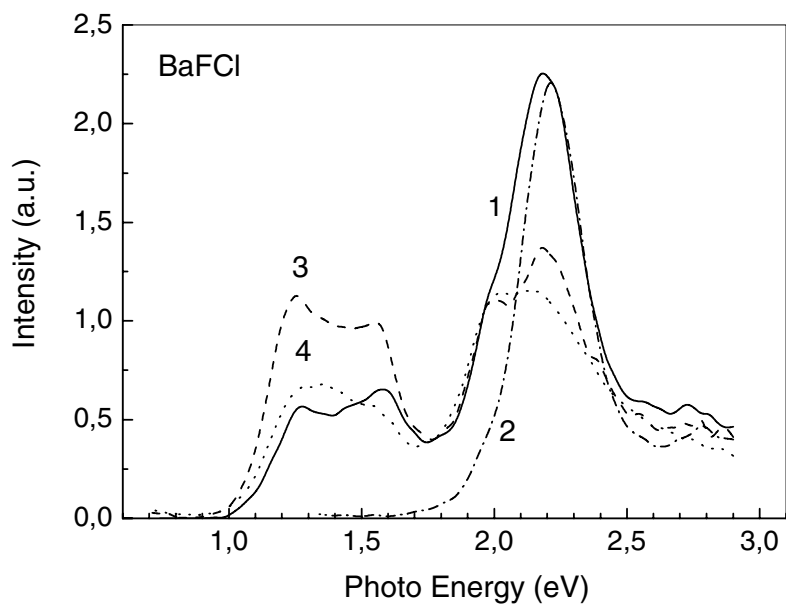

Figure 5. Photostimulation spectra of BaFCl:0.16 mol% Eu^{2+}, 0.0007 mol% O^{2-} (curves 1, 2), BaFCl:0.12 mol% Eu^{2+} (curve 3) and undoped BaFCl with oxygen contamination of a few ppm (curve 4) at 78 K. The Eu-doped samples were illuminated by 7–7.7 eV photons at 78 K (1, 3) and heated up to 240 K (2). The undoped BaFCl sample was x-ray irradiated at 78 K. The luminescence was monitored at 3.4 eV for the Eu^{2+}-doped sample and at the 3.3 eV exciton band for the undoped sample.

the second decreasing step in the 180–230 K region (see figure 5). The red photostimulation band completely disappears upon heating the crystal above the temperature 220 K of the main thermoluminescence peak.

4. Discussion

4.1. Thermostimulated luminescence peaks

The largest glow peak at 116 K for x-ray-irradiated BaFBr crystals (see figure 1) was assigned to recombination of moving self-trapped holes (V_K centres) with trapped electrons [16]. The V_K centres in BaFBr and BaFCl can diffuse above about 120 K [17, 18]. It seems that the thermostimulated luminescence peak at 120–140 K for BaFCl and the decrease in intensity of the red photostimulated bands can be related to recombination of self-trapped holes with trapped electrons. The shape of the peak of the thermoluminescence at 116 K for BaFBr was the same after x-ray irradiation and 6.8 eV excitation (see figure 1). Therefore it is reasonable to assume that the V_K centres as well as trapped electrons are created by 6–7 eV excitation of BaFBr:Eu^{2+} and BaFCl:Eu^{2+} at 78 K.

Upon excitation of BaFBr–Eu^{2+} crystal into the exciton region 7–8 eV, the 116 K thermoluminescence peak becomes wider (see figure 3) and a new peak, at 166 K, of the thermostimulated luminescence was observed. It seems that a V_K centre was created rather far from the trapped electron. In this case, some proportion of the self-trapped holes can be trapped by some defects during heating. Possibly the 7–8 eV photons create more energetic holes, which move a large distance from Eu before self-trapping.

The V_K TSL peak can be fully diminished by photostimulation into IR bands in weakly doped BaFBr:Eu. Also, no photostimulated IR bands remain after warming to a temperature above the V_K 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 valency during VUV illumination.

4.2. Infrared photostimulation bands

Infrared photostimulated centres are created in parallel with F centres in BaFCl and BaFBr crystals containing oxygen impurity. These centres can be photobleached leaving the F centres unchanged. Similarly to that of F centres, the photobleaching of the IR centres leads to decreases in the V_K thermoluminescence peak. Therefore the low-temperature infrared photostimulated bands observed in all BaFX crystals are shallow electron traps.

The low-temperature photostimulated spectra of undoped and Eu-doped crystals are very similar (see figure 3). The presence of Eu^{2+} ions does not influence IR electron traps. For heavily x-ray-irradiated crystals at 78 K we cannot measure any absorption in the 1.5–6 eV region. Therefore the concentration of V_K centres with allowed transitions near 4 eV, as well as electron traps, is less than 10^{16} cm^{-3}. The photostimulation spectra of BaFBr and BaFCl crystals show similarities (see figures 3 and 5), which indicate a similarity of the natures of the defects in the two crystals. At this moment the nature of these defects in not so important. The presence of some shallow electron traps which can be filled by x-ray irradiation or VUV illumination of crystal BaFX doped with Eu and/or oxygen is very important.

The IR-photostimulable defects can be created by x-ray irradiation in all crystals or by VUV illumination in Eu-doped crystals. The same types of trapped electron and trapped hole are created in BaFBr and BaFCl crystals doped with Eu by x-ray irradiation as well as by VUV illumination. The possibilities of tunnel filling the electron traps during VUV illuminations are diminished by the very low concentration of traps. We conclude that VUV illumination of

BaFX:Eu leads to the creation of electrons in the conduction band. Therefore the Eu^{2+} are not recharged during VUV illumination, but the presence of Eu^{2+} ions stimulates the creation of electrons and holes by 6–8 eV VUV photons.

Efficient photostimulation of Eu^{2+} luminescence below 1.5 eV was observed in BaFBr:Eu x-ray irradiated at 20 K [16]. However, the 1.4 eV limit of the experimental set-up prevented measurement of the complete spectrum. It was suggested that the photostimulated band below 1.5 eV corresponds to some trapped electron centres [16].

4.3. The nature of Eu^{2+}-related transitions in the VUV region

Combining the results discussed in previous sections, we may conclude that under 6–7 eV VUV illumination of BaFX:Eu^{2+}, free electrons and self-trapped holes are created. We speculate that the creation of electrons and holes in the vicinity of Eu^{2+} is the primary process after absorption of 6–7 eV photons in BaFX:Eu^{2+} crystals. The electrons become trapped on available traps (IR centres or F centres), while the self-trapped holes remain in the vicinity of the Eu^{2+}. When the energy of photons increases to 7–8 eV, created holes have an additional energy and move far from the Eu^{2+}. In this case we observe photostimulated 4.3 eV exciton emission in BaFBr:Eu.

The peak at 6.6 eV was observed earlier in the excitation spectrum, the photostimulation formation spectrum and even in the absorption spectrum of highly doped BaFBr:Eu crystals [7] also containing oxygen. The intensity of the 6.6 eV band in the photostimulation formation spectra grows linearly with increasing Eu^{2+} concentration [7]. The intensity of the photoconductivity in this region is independent of the existence of the Eu^{2+} ion. It seems that photoconductivity due to Eu^{2+} photoionization is masked by that due to the oxygen impurity photoionization. The authors tentatively assumed that 6.6 eV photons photoionize the Eu^{2+} electron to the conduction band [7]. Additionally to creation of trapped electron centres, we observed the creation of self-trapped holes. Therefore the conclusion of [7] is incorrect.

Creation of self-trapped holes by ultraviolet photons is known for CsI doped with Pb or Tl impurity [20–22]. Band-to-band transitions in pure CsI crystals were observed above 6.4 eV. Impurity ions with trapped electrons, an EPR spectrum of V_K centres [20] and V_K-centre thermoluminescence peaks [21] were observed. It was concluded that the excitation of CsI:Tl by the photons of 4.4–5.6 eV energy leads to creation of trapped electrons and non-relaxed holes. The higher the excitation energy of the photons, the larger the trapped-electron–V_K-centre separations [21].

The photoionization of Ce^{3+} in CaF_2 has been investigated for CaF_2:Ce^{3+} and CaF_2:Ce^{3+}, Na^+ [23, 24]. Excitation of the singly doped crystals with 308 nm laser light at room temperature produces colour centres by a two-photon process similar to those obtained with x-rays or γ-rays. The low-temperature thermoluminescence curves, created by VUV illumination or x-ray irradiation, are similar for Ce^{3+}-doped CaF_2, SrF_2 and BaF_2 [25].

All of the above-cited papers show that in alkali halide crystals and in alkaline-earth fluoride crystals containing different impurities (Tl^+, Pb^{2+}, Ce^{3+}), during illumination with ultraviolet photons with energy lower than the energy of band-to-band transitions, trapped-electron and trapped-hole defects are created. In several papers it was assumed that impurity levels in the band gap were filled by electrons by a charge-transfer mechanism [20, 23–25]. However, in the case of BaFX:Eu^{2+} we have shown that impurities assist in the creation of trapped electrons and holes.

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 calculated distortion of the lattices around the impurity in CsI:Tl and NaI:Tl shows an increase of the anion–cation distance d by not more than a few tenths per cent [26]. The ion Tl^+ is 18% smaller than Cs^+, but 39% larger than Na^+. The main part of the energy needed to transfer an electron from the anion to the cation is the Madelung energy $E_M = \text{constant}/d$. Therefore we obtain a few tenths of an eV as a typical value for the decrease of the energy of band-to-band transitions in the vicinity of Eu^{2+} in BaFBr and BaFCl. The observed value is at least ten times larger. 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 [27]. 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^{2+} levels in the process of 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 [28]. The energy distance in unrelaxed states is near 1–2 eV; during relaxation the distance is reduced to 0.1 eV. The effect is associated with the increase of the radii of F centres after excitation into the 2p level. We suppose that in the case of BaFX:Eu^{2+} the effect has to be more prominent, because the Eu^+ ions become significantly larger than the Eu^{2+} ones. However, more experimental investigations are needed.

A fraction of the Eu defects, as well as the V_K and $F(Br^-)$ centres, are produced at low temperature by x-ray irradiation, and have a spatial correlation [2, 29]. The mechanism is still unknown [4]. The question was whether a shift of Eu^{2+} or such a small lattice relaxation can be responsible for the spatial correlation of the electron- and hole-trap centres generated by x-rays [27]. The results of our investigations explain this phenomenon naturally, as the energy of electron–hole pair creation in the vicinity of Eu is substantially lower than in the perfect lattice.

5. Conclusions

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. Transitions observed in BaFBr:Eu and BaFCl:Eu can be considered as specific types of charge-transfer transition where electrons are transferred from the valence band to the Eu level, and ejected after relaxation to the conduction band.

Acknowledgments

References

[1] Takahashi K, Kohda K and Miyahara J 1984 *J. Lumin.* **31+32** 833
[2] Spaeth J-M, Eachus R S, Mcdugle W G and Nuttall R H D 1993 *Nucl. Tracks Radiat. Meas.* **21** 73
[3] Thoms M, von Seggern H and Winnacker A 1991 *Phys. Rev.* B **44** 9240

  [4] Spaeth J-M 2000 *Lumdetr2000: 4th Euroconf. on Luminescence Detectors and Transformers of Ionizing Radiation (14–17 August 2000, Riga, Latvia)* book of abstracts, p 4
  [5] Mikhaylin V V and Terekhin M A 1989 *Nucl. Instrum. Methods* **60** 2545
  [6] Ruter H H, von Seggern H, Reininger R and Saile V 1990 *Phys. Rev. Lett.* **65** 2438
  [7] Iwabuchi Y, Mori N, Takahashi K, Matsuda T and Shionoya S 1994 *Japan. J. Appl. Phys.* **33** 178
  [8] Radzhabov E A 1999 *Physics and Chemistry of Luminescent Materials (Electrochem. Soc. Proc. Ser. PV 98-24)* ed C W Strucjk, K C Mishra and B Di Bartolo (Pennington NJ: The Electrochemical Society) p 145
  [9] Radzhabov E and Otroshok V 1995 *J. Phys. Chem. Solids* **56** 1
  [10] Hernandez J A, Cory W K and Rubio J O 1980 *J. Chem. Phys.* **72** 198
  [11] Arkhangelskaya V A, Kiselyova M N and Shraiber V M 1967 *Opt. Spectrosk.* **23** 509
  [12] Kurobori T, Kozake S, Hirose Y, Ohmi M, Haruna M, Kimura T, Inabe K and Somaiah K 1999 *Japan. J. Appl. Phys.* **38** 901
  [13] Fisher F and Gummer G 1965 *Z. Phys.* **189** 97
  [14] Eachus R S, Nuttall R H D and Spaeth J-M 1995 *Phys. Rev. B* **52** 3941
  [15] Nicklaus E 1979 *Phys. Status Solidi* a **53** 217
  [16] Ohnishi A, Mori N and Kan'no K 1999 *Japan. J. Appl. Phys.* **38** 6782
  [17] Hangleiter T, Koschnick F K, Spaeth J-M, Nuttall R H D and Eachus R S 1990 *J. Phys.: Condens. Matter* **2** 6837
  [18] Yuste M, Taurel L and Rahmani M 1975 *Solid State Commun.* **17** 1435
  [19] Ohnishi A, Kimoto I, Kan'no K, Iwabuchi Y and Mori N 1997 *J. Lumin.* **72–74** 775
  [20] Zazubovich S *et al* 1997 *J. Phys.: Condens. Matter* **9** 7249
  [21] Babin V, Fabeni P, Kalder K, Nikl M, Pazzi G P and Zazubovich S 1998 *Radiat. Meas.* **29** 333
  [22] Chernov S, Trinkler L and Popov A I 1998 *Radiat. Eff. Defects Solids* **143** 345
  [23] Hollingsworth G J and McClure D S 1993 *Phys. Rev. B* **48** 13 280
  [24] Pogatshnik G J and Hamilton D S 1987 *Phys. Rev. B* **36** 8251
  [25] Radzhabov E A and Nepomnyashikh A I 2000 *Proc. SCINT99: 5th Int. Conf. on Inorganic Scintillators and Their Applications (Moscow)* p 357
  [26] Aguado A, Ayuela A, Lopez J M and Alonso J A 1998 *Phys. Rev. B* **58** 11 964
  [27] Assmann S, Schweizer S and Spaeth J-M 1999 *Phys. Status Solidi* b **216** 925
       Assmann S, Schweizer S and Spaeth J-M 1999 *Phys. Status Solidi* b **212** 325
  [28] Luty F 1968 *Physics of Color Centers* ed W B Fowler (New York: Academic) ch 3
  [29] Koschnick F K, Spaeth J-M and Eachus R S 1992 *J. Phys.: Condens. Matter* **4** 8919