

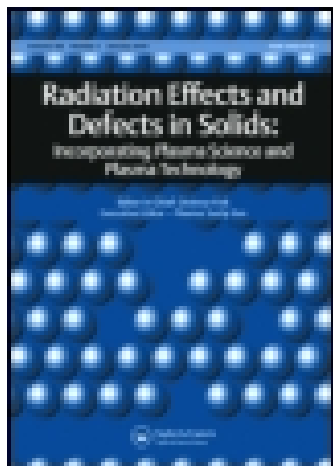
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LUMINESCENCE OF BaFCl:Eu²⁺ AND SrFCl:Eu²⁺

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The TL, XL, PTTL and OSL of BaFCl:Eu²⁺ and SrFCl:Eu²⁺ were studied. The PTTL stimulation spectra of BaFCl:Eu²⁺ had maxima at the Eu³⁺, Eu²⁺ absorption bands and at the long wavelength tail of F absorption. The PTTL appeared at the same temperatures and with the same thermal activation energies as the TL peaks, indicating that the same defects are responsible for the trapping states. The TL emission spectra of the BaFCl:Eu²⁺ crystals showed narrow bands at 315 and 365 nm and a broader band near 435 nm. The OSL and XL showed the same bands as well a 385 nm emission. The 365 nm band also appeared in SrFCl:Eu²⁺ and is attributed to the emission of Eu²⁺.

Keywords: BaFCl:Eu²⁺; SrFCl:Eu²⁺; Luminescence; Phototransferred TL;
Point defects

INTRODUCTION

Optical properties of alkaline-earth dihalides have previously been investigated by various authors (e.g. [1,2]). An important motivation for the study of the luminescence properties of these Eu²⁺ doped materials is due to the fact that they can be used as stable X-ray storage phosphors in radiography and crystallography. Some previous results have indicated that halide vacancies serve in these crystals as main electron

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traps and Eu^{2+} ions as hole traps. In the Eu doped crystals the 385 nm band and the sharp 363 nm line were ascribed to the emission of Eu^{2+} ion and the broader 389 nm band to a CTS (charge transfer state) transition of Eu^{3+} [3]. In the present work the thermoluminescence (TL), X-induced luminescence (XL), optically stimulated luminescence (OSL) and thermoluminescence (PTTL) of $\text{BaFCl}:\text{Eu}^{2+}$ and $\text{SrFCl}:\text{Eu}^{2+}$ were investigated. Emission and stimulation spectra, the temperature dependence of the main emission bands and thermal stability of the traps were studied.

EXPERIMENTAL RESULTS AND DISCUSSION

The single crystals of $\text{BaFCl}:\text{Eu}^{2+}$ and $\text{SrFCl}:\text{Eu}^{2+}$ were grown by a modified Bridgman method [4]. The X-irradiations were performed with a W-tube (40 kV, 15 mA) and the β -irradiations with a Sr^{90} source (~ 13 mCi). For the UV-illuminations a 150 W Xe lamp and a 0.25 m grating monochromator were used. The emission and excitation spectra were taken with Aminco-Bowman/2 luminescence-spectrometer.

After X-irradiation at LNT the main TL peak appeared at 170 K and weaker peaks at about 200, 220, 270, 320 K. After low dose X- or β -irradiation at RT the main peak was recorded at 320 K and additional peaks at about 350, 400, 440, 530 and 600 K. With increasing radiation dose, the 350 and 400 K peaks became dominant, indicating a different dose dependence of the various peaks. The PTTL was measured after X- or β -irradiation at RT, heating to about 600 K and subsequent monochromatic illumination at LNT. The main PTTL peaks appeared during reheating at the same temperatures and with the same thermal activation energies as the TL peaks, indicating that the same traps are responsible for the glow peaks. The excitation spectra of the total PTTL emission had a main maximum at 260 nm with a shoulder at 240 nm and a weaker maximum at 570 nm (Fig. 1, curve a). The latter maximum is located on the long wavelength tail of an F absorption band. The excitation near 240 and 260 nm coincides with the absorption bands of Eu^{3+} and Eu^{2+} respectively [1]. It is assumed that during the X-irradiation electron-hole pairs are generated; the electrons are trapped by anion vacancies and the holes by Eu^{2+} , forming F-centers and Eu^{3+} ions, while part of the F electrons may recombine radiatively with Eu^{3+} ,

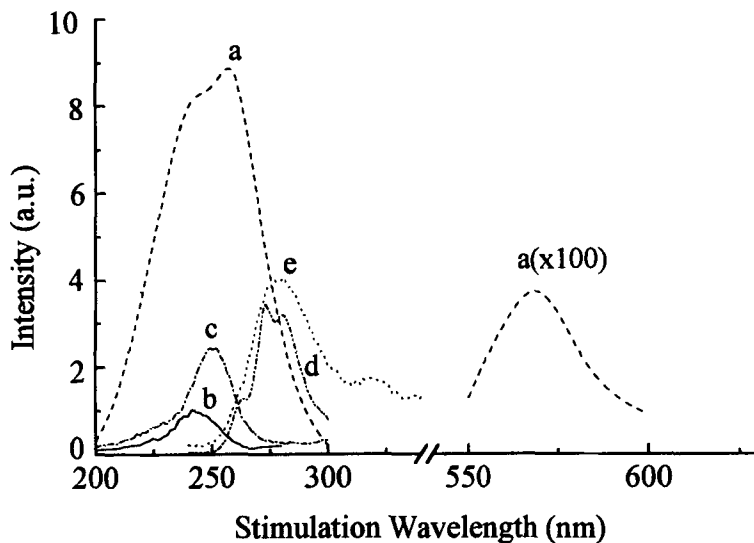


FIGURE 1 BaFCl:Eu²⁺, stimulation spectra: a – of 170 K PTTL peak and of OSL emission bands at: b – 315 nm, c – 365 nm, d – 430 nm, e – 385 nm (curves b–d were measured at LNT and curve e at RT).

forming Eu²⁺ ions and emit the observed XL bands. Heating to 1100 K caused the elimination of the effects induced by the X-irradiation and PTTL could not be excited in such samples. These findings indicate that the phototransfer is due to deep traps that are stable above 600 K, but become unstable at 1100 K. The emission spectrum of the main 170 K TL peak consisted of strong narrow bands at 315 and 365 nm as well as a band at 385 nm and weaker broad bands at about 280 and 435 nm. The spectra recorded at the other TL glow peaks showed also the strong 315 nm band and a broader band at about 385 nm (Fig. 2). The emission at the main PTTL peaks showed the same bands as well as a weak 520 nm band. The 365 nm band, which was relatively strong at the 170 K TL peak, did not appear in the PTTL peak at the same temperature. The other PTTL peaks consisted mainly of the strong narrow 315 nm band and a broad band at 385 nm, indicating that the same luminescence centers are responsible for these emissions. The XL emission at RT consisted also of the main narrow 315 nm band and of some broad bands at about 275, 385, 435 and 500 nm. At LNT, the narrow 365 nm band was dominant. The temperature dependence of the XL was

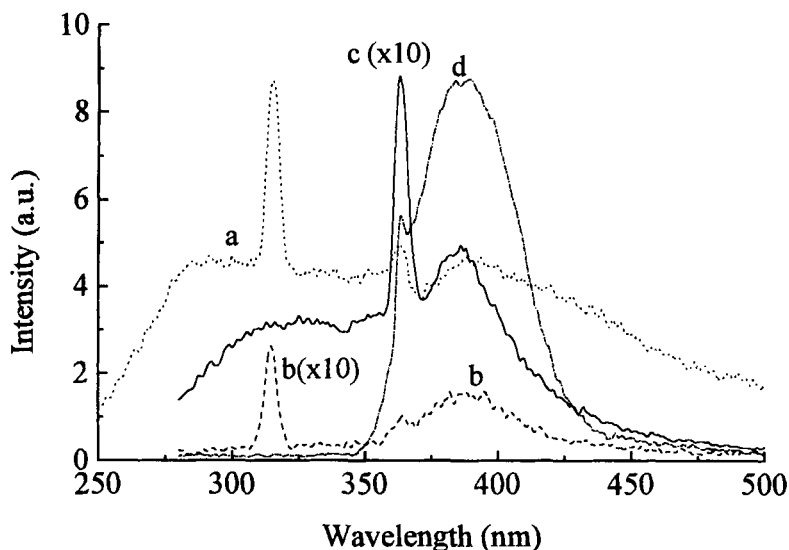


FIGURE 2 TL emission spectra recorded at: a - 170 K, b - 320 K glow peaks of BaFCl:Eu^{2+} and c - 160 K, d - 310 K glow peaks of SrFCl:Eu^{2+} .

measured during cooling from RT to LNT. The intensity of the 275 nm band increased continuously during cooling, while the 315 nm emission decreased by a factor of 1/2. An additional 365 nm band appeared at about 190 K, increased during further cooling and became dominant at LNT. The 385 nm emission decreased sharply below 135 K and disappeared at LNT, while the weak 435 and 500 nm bands increased during cooling between RT and 150 K. The finding that the strong 365 nm emission appeared in the XL at low temperatures only, may also explain the fact that this band does not appear in the 170 K PTTL peak, but dominates the TL peak at the same temperature. The luminescence center, which is responsible for this emission band is apparently unstable above this temperature and is therefore not formed during the X-irradiation at RT, which precedes the phototransfer. The OSL showed the same 315, 365, 385 and 430 nm emissions. These bands showed different temperature dependencies. The 315 nm emission bands, which was strong in the XL, was relatively weak and appeared in the OSL mainly at about 140 K. The 365 nm band appeared in the OSL as in the XL below 190 K, increased strongly during cooling and became dominant at LNT. The 385 nm emission was recorded at RT

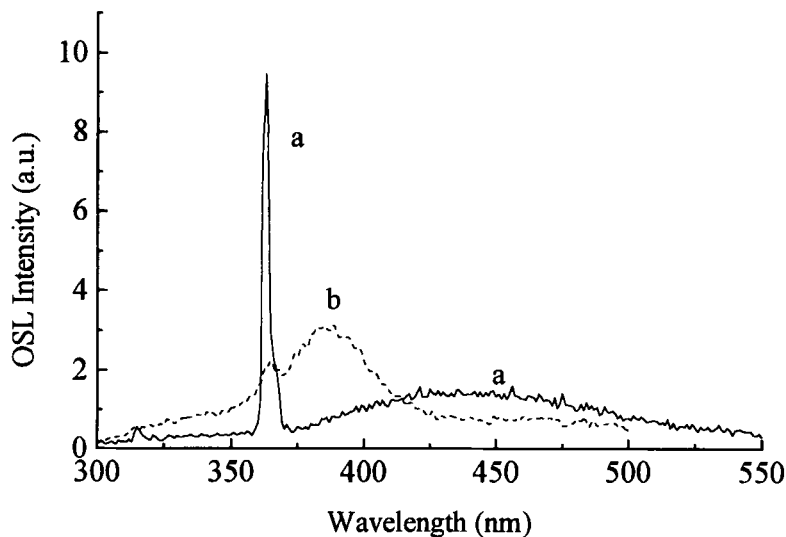


FIGURE 3 BaFCl:Eu²⁺, OSL emission spectra recorded after 10 min X-irradiation and stimulation with 260 nm light at: a - LNT, b - RT.

and disappeared near LNT. The 430 nm emission increased near LNT (Fig. 3). Stimulation spectra of OSL are given by curves b–d of Fig. 1. The 365 nm band had excitation maxima at 263, 275 and 285 nm and the 315, 385 nm and the band near 430 nm had excitation maxima at 242, 278 and near 250 nm respectively. For comparison SrFCl:Eu²⁺, crystals were investigated. The main TL peak appeared at 310 K and additional peaks at about 120, 160, 275, 340 and 370 K. After X-irradiation the phosphorescence at LNT as well as the TL peaks near LNT showed a main 365 nm band and weaker bands at 320 and 415 nm. The main 310 K TL peak contained a strong 385 nm band and a narrow 365 nm band, which also appeared in most of the other peaks. It may be noted that near LNT the 365 nm band was dominant; at higher temperatures the 385 nm emission became stronger. The main 160 and 310 K PTTL peaks showed 365, 385 and 415 nm emission bands. The latter band, which was weak in the TL, was the dominant at the 160 K PTTL peak. The PTTL stimulation spectra had a maximum near 230 nm. The XL showed at RT a 385 nm band. This emission became very weak during cooling to LNT while a strong narrow band appeared at 365 nm and a weaker one at 415 nm. The OSL showed the same 365,

385, 415 nm emission bands. The UV light of 340 nm was most efficient for the stimulation of these OSL emission bands. The temperature dependence of the OSL emission was similar to that of the XL emission. The 365 nm band, which appeared in both crystals at analogous conditions is attributed to the emission of Eu^{2+} ions. This is in agreement with previous reports, which attributed a 363 nm line, observed in the photo- and roentgen- luminescence of $\text{BaFCl}:\text{Eu}$, to the emission of an Eu^{2+} ion [3]. This is also supported by the fact that the here observed OSL excitation maximum at 263 nm fits the wavelength of the d–f transition into the first excited $4f^65d$ level of the Eu^{2+} .

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