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Thermoluminescence of some Pr^{3+} doped fluoride crystals

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Abstract

Irradiation effects and dosimetric properties have been studied for CaF_2, KYF_4 and CsY_2F_7 crystals doped with Pr^{3+}. In particular, thermoluminescence (TL) excitation spectra have been measured in the 120–200 nm region and the $CaF_2:Pr^{3+}$ and $KYF_4:Pr^{3+}$ crystals show excitation maxima at 135 and 140 nm, respectively. Some of the main TL peaks appear after vacuum ultraviolet (VUV) irradiation at the same temperatures as after β irradiation, indicating that they are due to the same radiation-induced trapping levels. Optically stimulated luminescence (OSL) and phototransferred TL (PTTL) have also been recorded in pre-irradiated samples and stimulation spectra have been measured. The OSL emission spectra show some of the same bands as in the case of the XL and TL, indicating that they are due to the same luminescence centers. The TL sensitivity of $CaF_2:Pr^{3+}$ is ~5 times higher than that of TLD-100, and the TL sensitivity of $KYF_4:Pr^{3+}$ is slightly higher than that of TLD-100, whereas the sensitivity of $CsY_2F_7:Pr^{3+}$ is much lower. The main TL peaks of $KYF_4:Pr^{3+}$ and $CaF_2:Pr^{3+}$ appear above 480 K and, accordingly, only low TL fading is expected during storage at RT. The dose dependence of the main TL peaks is nearly linear in a dose range up to about 2000 Gy.

Keywords: Fluorides; Irradiation effects; VUV radiation; Thermoluminescence; Dosimetric properties

1. Introduction

Radiation effects and optical properties of fluoride crystals have been studied for a long time (e.g., Hayes, 1974; Tzalmona and Pershan, 1969). Some of these broadband crystals such as CaF_2 are transparent in a wide spectral range from vacuum ultraviolet (VUV) to the infrared (IR) region and are therefore widely used as optical materials. Some doped fluoride crystals like TLD-100 (LiF:Mg,Ti) are presently also used as radiation detectors and TL dosimeters. On the other hand, there is a permanent interest in the search of new materials, which can be used as efficient solid-state dosimeters. Most solid-state dosimeters are based on thermoluminescence (TL), and more recently also on methods of optically stimulated luminescence (OSL) and phototransferred TL (PTTL). For the application of a material as a dosimeter, the luminescence efficiency as well as other spectral and thermal properties have to be considered. In particular, the temperature of the main TL peaks, the wavelength of emission, the temperature of thermal annealing, reproducibility of the results and the possibility for re-use of the material for repeated measurements are of special importance. In most studies on TL and other radiation-induced effects, high-energy radiation fields such as β-, γ- or X-rays are ordinarily applied, while relatively few investigations dealt with effects of VUV radiation on dielectric materials (e.g., Sever et al., 1986; Lushchik et al., 2002; Radzhabov, 2001). The application of monochromatic VUV radiation also enables the evaluation of the photon energy, most efficient for the formation of defects and for the excitation of TL. In this context, the TL sensitivity of SrF_2 crystals doped with various rare earth ions has recently been investigated and the sensitivity of Pr^{3+} doped SrF_2 has been found to be the highest among these samples (Kristianpoller et al., 2004). In the present work, TL induced by β-, X and VUV radiation in some other Pr^{3+} doped fluorides has been studied. PTTL and OSL have also been measured in samples pre-irradiated with β- or X-rays. Special attention has been given to dosimetric properties and to the possible application of these crystals as dosimeters for the VUV.

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2. Experimental techniques

The Pr^{3+} doped CaF_2 crystals were grown at the Hebrew University and the undoped single crystals were from Harshaw. The KYF_4 and CsY_2F_7 crystals undoped and doped with Pr^{3+} were grown at the Institute of General and Inorganic Chemistry (Marcazzó et al., 2007). The X- and the β-ray irradiation were performed with a W-tube (40 kV, 15 mV) and a Sr^{90} source, respectively. The TL measurements from RT up to 750 K were carried out by using a heating rate of 5° C/s in a TL compartment flushed by N_2 gas. For the low temperature TL and PTTL measurements, the samples were kept in liquid nitrogen vacuum cryostat and were heated at a rate of 20° C/s. The UV irradiation was performed with a 1-m normal-incidence VUV monochromator and an H_2 arc lamp. This VUV monochromator was also used for the measurements of the optical absorption in the far-UV region. VUV photo-excitation measurements were performed with synchrotron radiation at the SUPERLUMI station (Zimmerer, 1991).

3. Results and discussion

After X or β-irradiation at RT, strong TL peaks appear at about 495, 645 and 695 K in $CaF_2:Pr^{3+}$, at 485 K in $KYF_4:Pr^{3+}$ and at 423 K in $CsY_2F_7:Pr^{3+}$ (Fig. 1). TL is also induced by monochromatic VUV radiation and the results show that some of the main TL peaks appear after VUV radiation at the same temperatures as after X or β irradiation, indicating that the same traps are responsible for the TL induced by the different excitations. Optical absorption, TL excitation and photo-excitation spectra were measured in the deep UV/VUV region and, in particular, the spectra of $KYF_4:Pr^{3+}$ are given in Fig. 2. The photo-excitation spectrum with the threshold at ~ 220 nm corresponds to interconfigurational 4f–5d transitions in Pr^{3+}. The $CaF_2:Pr^{3+}$ and $KYF_4:Pr^{3+}$ crystals have TL excitation maxima at 135 and 140 nm, respectively, although the band gap exceeds 11.4 eV for these hosts (Makhov and Khaidukov, 1991). Apparently, the Pr^{3+} ion can be photo-ionized through 5d excitation by taking into account that higher energy components of the 5d Pr^{3+} state seem to overlap the conduction band (Dorenbos, 2003). Accordingly, the traps can be filled by electrons after photo-ionization of Pr^{3+} ions by photons with energy lower than the band-gap value, which will lead in turn to the appearance of TL with ion-specific emission spectrum (Grimm et al., 2007). The threshold in the TL excitation spectrum should correspond to photo-ionization edge for Pr^{3+} 5d electrons. This threshold is not well pronounced in experimental spectra but could be located near 160 nm (7.8 eV). This value well corresponds to the energy distance between the ground 4f level of Pr^{3+} and conduction band in the energy level diagram for Pr^{3+} in CaF_2 (Dorenbos, 2003). On the other hand, the maximum in the TL excitation spectrum is situated about 1.2–1.4 eV above the photo-ionization edge. In Fig. 3 emission spectra of the $KYF_4:Pr^{3+}$ crystal measured under different conditions are shown. At Pr^{3+} 4f–5d photo-excitation the crystal emits broadband Pr^{3+} 5d–4f luminescence with two maxima in the UV region at 235 and 255 nm and decay time of 26 ns. In

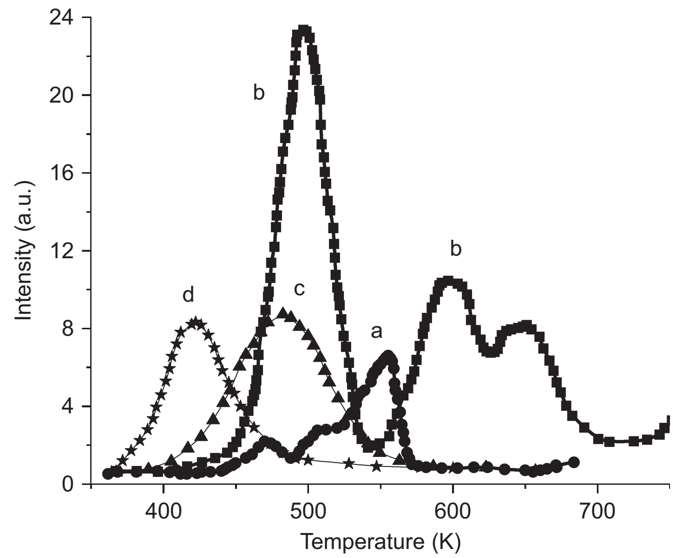

Fig. 1. TL glow curves of (a) TLD-100, (b) $CaF_2:Pr^{3+}$, (c) $KYF_4:Pr^{3+}$ and (d) $CsY_2F_7:Pr^{3+}$ (×200). All the crystals were irradiated to a 100 Gy β dose at RT.

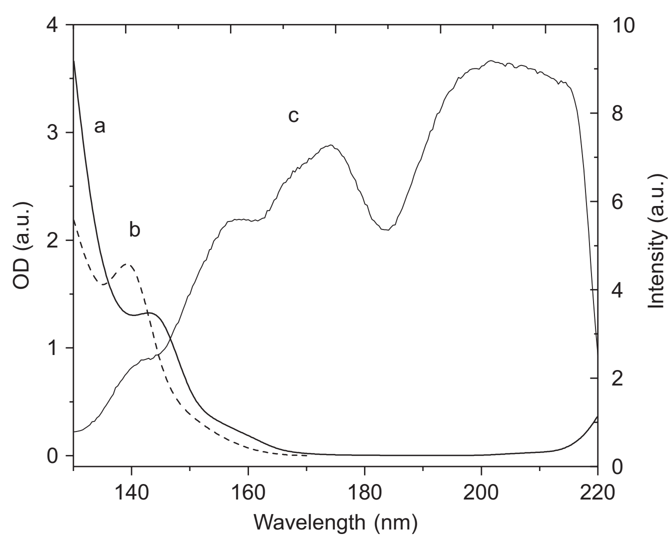

Fig. 2. (a) Absorption for undoped KYF_4; (b) TL excitation and (c) photo-excitation ($\lambda_{em} = 255$ nm) spectra in the VUV region for $KYF_4:Pr^3$.

the 110 K TL peak the spectrum also contains this broadband luminescence but most of the energy is emitted in characteristic narrow lines, which are due to Pr^{3+} 4f–4f transitions from the $^3P_0$ level. Only the latter kind of emission is observed in the phosphorescence spectrum. In samples previously exposed to β or X radiation, TL is also excited by near UV and visible light, which cannot excite any TL in non pre-irradiated samples. This effect is apparently due to a PTTL process. In Fig. 4, PTTL of $CaF_2:Pr^{3+}$ recorded after β irradiation at RT and subsequent 390 nm illumination at LNT, as well as the PTTL emission spectrum, are given. In X- or β-irradiated samples, OSL bands are also stimulated by wavelengths longer than those of the OSL emission. The OSL emission spectra show some of

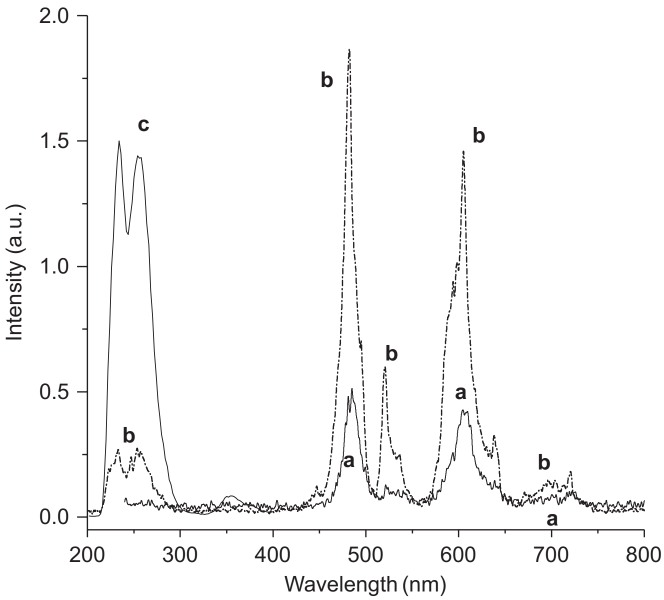

Fig. 3. (a) Phosphorescence emission after X irradiation at LNT, (b) TL emission at the 110 K peak and (c) emission under Pr^{3+} 4f–5d photo-excitation (175 nm) at RT (c) for $KYF_4 : Pr^{3+}$.

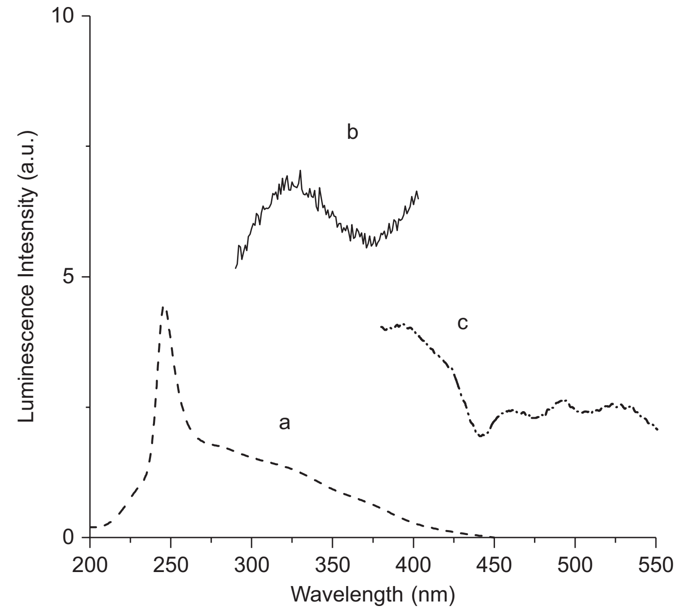

Fig. 5. (a) XL; (b) OSL after β irradiation and subsequent 395 nm stimulation and (c) excitation spectrum of the 320 nm OSL emission for $CsY_2F_7 : Pr^{3+}$ at RT.

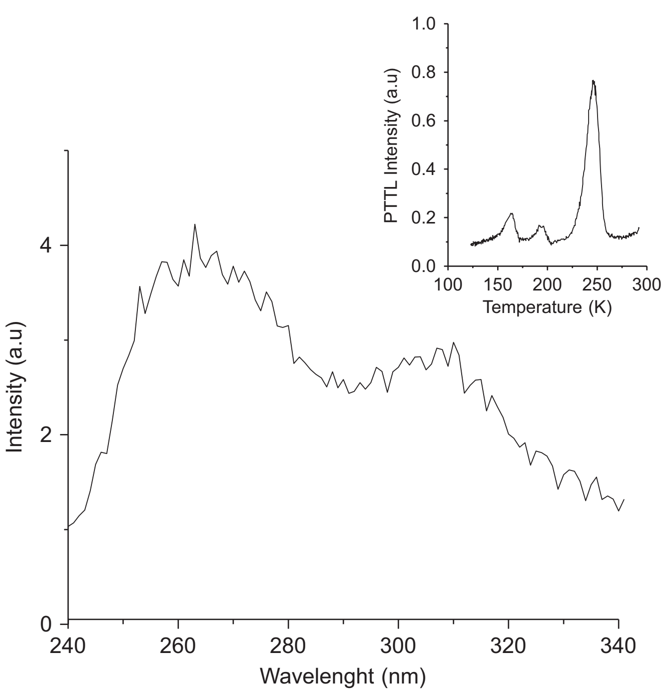

Fig. 4. Emission spectrum at the 240 K PTTL peak for $CaF_2 : Pr^{3+}$. The PTTL recorded after β irradiation at RT and subsequent 390 nm illumination at LNT is given in the inset.

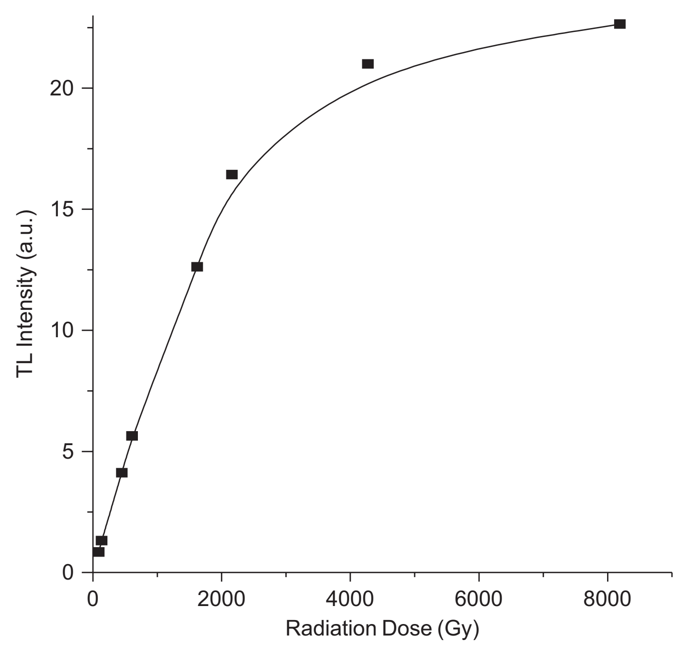

Fig. 6. Dependence of the TL intensity on the β dose for $KYF_4 : Pr^{3+}$.

the same bands as XL and TL, indicating that they are due to the same centers. In Fig. 5, the OSL and X-ray luminescence (XL) emission spectra as well as the stimulation spectrum of the 320 nm OSL band of a $CsY_2F_7 : Pr^{3+}$ crystal are given. In $CaF_2 : Pr^{3+}$, OSL shows strong emission bands near 265 and 310 nm with stimulation maxima at 395 and 465 nm. Under 280 nm stimulation at LNT the $KYF_4 : Pr^{3+}$ crystals show some weak OSL emission bands at 315, 375 544 and 570 nm. OSL and PTTL are annealed by heating to $\sim 500\,°C$.

4. Summary of dosimetric properties

The TL intensity of the examined fluorides after exposure to equal β doses of 100 Gy as compared to that of the standard TLD phosphor; the TL emitted at the main peak of $CaF_2 : Pr^{3+}$

was found to be about 5 times higher than that emitted at the main peak of TLD-100 and that emitted at the main TL peak of $KYF_4 : Pr^{3+}$ was slightly higher than that of TLD-100, whereas the $CsY_2F_7 : Pr^{3+}$ sensitivity was much lower. The $CaF_2 : Pr^{3+}$ and $KYF_4 : Pr^{3+}$ crystals also exhibit other important dosimetric properties. The main TL peaks of these crystals are above 200 °C and a very small thermal fading of TL is expected during storage at RT. The main emission bands are in a spectral range where most of commercial photomultiplier tubes have their maximum sensitivity. The dose dependence of the main TL peaks is nearly linear in a dose range up to about 2000 Gy (Fig. 6). Some of these crystals show a high TL sensitivity also under VUV excitation.

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