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RADIATION EFFECTS IN $KMgF_3$ CRYSTALS

N. KRISTIANPOLLER*, D. WEISS and R. CHEN

School of Physics & Astronomy, Raymond and Beverly Sacker Faculty of Exact Sciences, Tel-Aviv University, Tel-Aviv 69978, Israel

Effects of x, β and UV irradiation on Tb^{3+} and Eu^{2+} doped $KMgF_3$ crystals were studied. Thermoluminescence (TL) excited by VUV radiation was compared to that induced by x and β rays. TL excitation spectra showed maxima at 125, 140, 155 and 180 nm. The main TL peaks appeared after VUV irradiation at about the same temperatures and with the same thermal activation energies as after x or β irradiation, indicating that these peaks are due to the same trapping levels. In samples, which had previously been exposed to ionizing radiation, TL could also be excited with longer wavelengths that could not excite any TL in un-irradiated crystals; this is attributed to a process of phototransfer (PTTL). The x and UV excited luminescence was measured at LNT and RT and showed essentially the same main emission bands that appeared in the TL and PTTL peaks of these crystals. The dose dependence of the 730 K TL peak in of $KMgF_3$:Eu^{2+} was linear up to about 2000 Gy. The TL sensitivity of $KMgF_3$:Eu^{2+} was by an order of magnitude higher than that of $KMgF_3$:Tb^{3+}, which was by a factor of two greater than that of the known TLD-l00 phosphor.

Keywords: $KMgF_3$; Radiation Effects; Luminescence; Dosimetric properties

1. INTRODUCTION

Optical properties as well as radiation effects in perovskite type fluorides have been studied by various authors (*e.g.* 1, 2). These compounds can be described by the general formula: ABF_3, where $A = $ Li, Na, K etc; $B = $ Ca, Mg etc. The various crystals have different structures; some are hexagonal (*e.g.* $RbMgF_3$), others are orthorhombic (*e.g.* $NaMgF_3$) and some like $KMgF_3$ have a cubic structure. These fluorides are among the broadest band-gap halides and $KMgF_3$ crystals are transparent from the IR to about 110 nm. They are thermally stable to high temperature and have melting points above 1000°C. Some of these perovskite-fluorides are therefore frequently used as optical materials and some of the doped crystals also for applications in solid state lasers and dosimetry (*e.g.* 3). Most studies on irradiation effects in these crystals dealt with effects of fast electron or x and γ rays. Relatively few works dealt with effects of UV radiation [4, 5]. Color centers have also been investigated in these crystals and a radiation induced absorption band at 270 nm was attributed to an F center and absorption bands at 430 and 330 nm were ascribed to F_2 and V_K centers respectively [1].

* Corresponding author.

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In the present work effects of x, β and VUV radiation on pure and doped $KMgF_3$ crystals were studied. Optical absorption, x and UV-excited luminescence (XL and PL), optically stimulated luminescence (OSL), thermoluminescence (TL) and phototransferred TL (PTTL) were measured. Dosimetric properties and possible application of these materials as solid state dosimeters were also investigated.

2. EXPERIMENTAL TECHNIQUE

The x-irradiations were performed with a W-tube (40 kV, 15 mA) and the β-irradiations with a Sr^{90} source of a 1.5 Gy/min. dose-rate. The x and UV irradiations were carried out at various temperatures between 80 and 300 K. The TL measurements from RT up were carried out in a TL compartment flushed by N_2 gas; the heating rate above RT was 5 K/sec. For the low temperature TL and PTTL measurements the samples were kept in a liquid nitrogen vacuum cryostat and heated at a rate of 20 K/min. The OSL was stimulated at various temperatures between 80 and 400 K by monochromatic UV light. The far UV irradiations were carried out with a one-meter normal-incident VUV monochromator and an H_2 arc lamp. The optical absorption was measured with a Cary 17 spectrophotometer. The PL, OSL, TL and OSTL measurements were taken with Aminco-Bowman/2 luminescence-spectrometer.

3. RESULTS AND DISCUSSION

3.1. Optical Absorption

Absorption was measured in the spectral region from 1000 to about 120 nm. All samples showed an increase of absorption toward the VUV and in particular below 140 nm. The non-irradiated Tb^{3+} doped crystals showed weak absorption bands at 230 and 340 nm and the Eu^{2+} doped samples at 238 and near 270 and 500 nm. After x or β irradiation at RT or LNT, a band appeared in all crystals near 270 nm, which had previously been attributed to F-center absorption [1]. The 270 nm band decreased by heating to above 550 K and a 430 nm band increased; this is attributed to an F to F_2 conversion. After x-irradiation at LNT the V_K band appeared at 330 nm but became unstable by heating to above 200 K.

3.2. Luminescence

During x irradiation at LNT of a nominally pure $KMgF_3$ crystal broad and relatively weak emission bands were at about 220, 310, 460 and 510 nm. In the XL of Eu^{2+} doped crystals appeared a series of strong and sharp emission bands between 358 and 365 nm. In the Tb^{3+} doped crystals several sharp XL emission bands appeared; the main one at 383 nm and additional bands at about: 220, 260, 282, 315, 350, 415, 438, 458 and 470 nm. The 383 nm band was stronger than the XL of the pure samples but about one order of magnitude weaker than the emission bands in the Eu^{2+} doped samples. Curves a and b of Figure 1 show the XL emission spectra at RT of $KMgF_3$: Eu^{2+} and $KMgF_3$:Tb^{3+} respectively. The PL could be excited in the Eu^{2+} doped crystals by UV light up to about 270 nm and sharp emission bands appeared in these crystals at 358, 360, 362 and 365 nm. In the Tb^{3+} doped crystals only a very weak PL was recorded but in samples which had previously been exposed to x or β radiation and then illuminated with UV light, weak broad emission bands appeared during UV illumination at 290 and 355 nm and stronger sharp bands at 378 and 385 nm. This emission is attributed to a process of optical stimulation of trapped carriers (OSL)

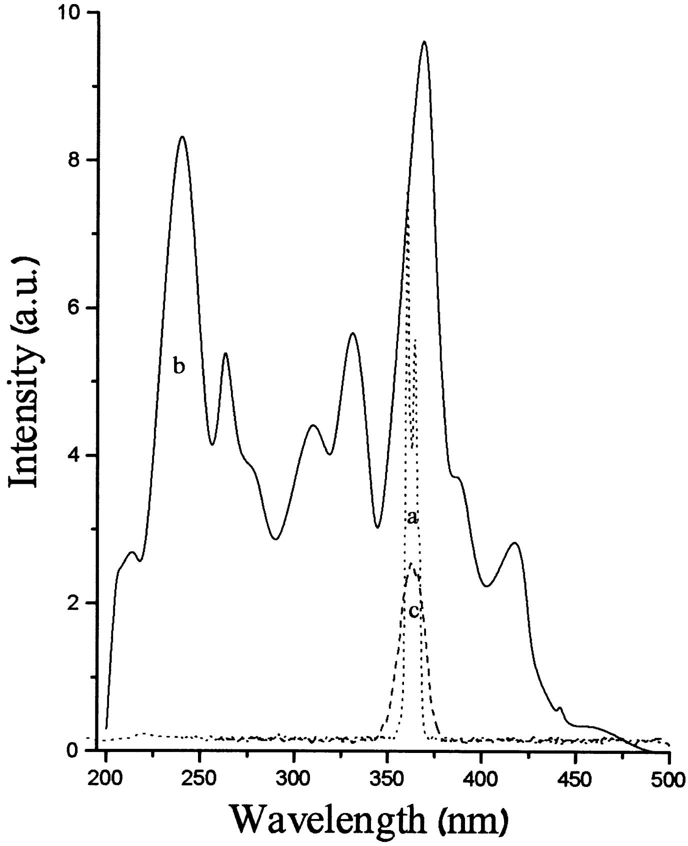

FIGURE 1 a) XL excited at RT in a $KMgF_3$: Eu^{2+} crystal, b) XL excited at RT in a $KMgE_3$:Tb^{3+} crystal (enlarged by factor of 10), c) Emission recorded at the 263 K PTTL peak of a $KMgF_3$:Eu^{2+}; the sample, was exposed to β radiation at RT and was subsequently illuminated with 340 nm light at LNT.

3.3. Thermoluminescence

After x or β-irradiation of Tb doped crystals at RT a main TL peak appeared at 470 K and additional peaks at 360, 410, 500 and 540 K. After irradiation at LNT the main TL peak was at 245 K and additional ones were at 142, 170, 183, 263, 397 and 440 K. After RT irradiation of Eu^{2+} doped samples TL peaks were recorded at 365, 475, 610, and 730 K and after LNT irradiation at 222, 262, 351, 450 and 475 K. TL could also be excited by monochromatic VUV radiation and even by 215 nm UV light. The main TL peaks appeared after VUV irradiation at the same temperatures as after x or β irradiation (Fig. 2). Excitation spectrum of the TL in the VUV region showed maxima near 180, 155 140 and 125 nm, the latter coincides with the long-wavelength tail of the fundamental absorption. This finding fits previous observations in various alkali halide crystals [6].

A TL excitation spectrum of $KMgF_3$ Eu^{2+} in the VUV region is given in Figure 3. The thermal activation energies of the TL were evaluated by using the "initial rise" and the "symmetry method" [7]. The activation energies were found to be the same for the x, and VUV induced TL. For example: values of 0.51 and 0.49 eV were obtained at the 263 K peak for the x and VUV excited TL respectively. The finding that the main TL peaks appeared in the VUV excited TL at about the same temperatures and with the same thermal activation energies as in the x or β irradiated samples indicates that these peaks are due to the

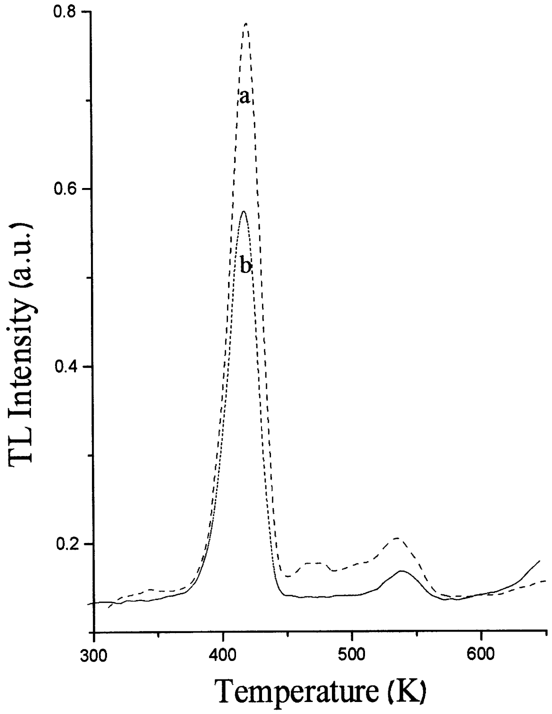

FIGURE 2 a) Thermoluminescence glow curve of KMgF3:Tb^{3+} crystal induced at RT by: β-radiation, b) UV light of 190 nm (Enlarged by factor of 10).

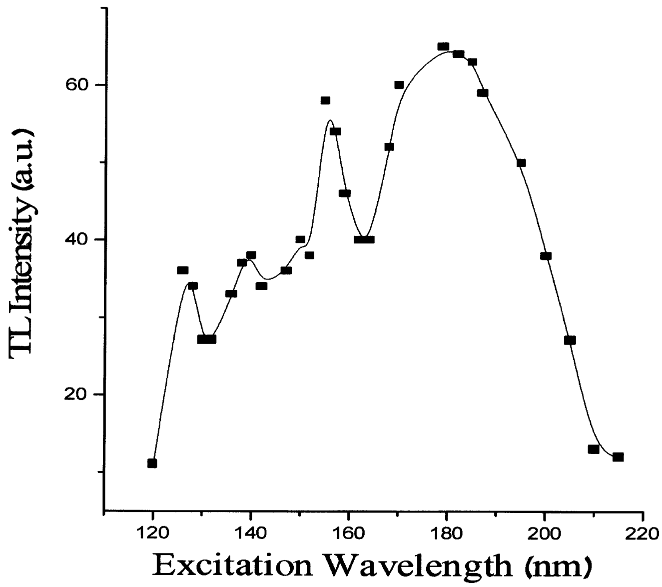

FIGURE 3 TL Excitation Spectrum of $KMgF_3$:Eu^{2+} in the VUV region 120–200 nm

same trapping levels and that the mentioned VUV wavelengths had the same effect as the x or β irradiations. The TL emission spectra showed the same main bands that appeared in the XL and PL of the two crystals.

UV irradiation with wavelengths above 280 nm could not excite any TL in non-irradiated crystals. In samples which had previously been exposed to ionizing radiation, TL could also be excited by illumination with longer wavelengths. This TL emission is attributed to a process of phototransfer, where carriers, trapped by the ionizing radiation, are transferred from deep to shallower traps. Phototransferred TL (PTTL) can be obtained when during subsequent heating these carriers are thermally released and recombine radiatively with carriers of opposite sign. After β-irradiation at RT of $KMgF_3$: Eu^{2+} crystals and subsequent UV illumination at LNT with 340 nm light a notable PTTL emission appeared during heating from LNT to RT. Main PTTL peaks were at 222 K and 263 K and had a main emission band at ~360 nm. In Figure 1, the PTTL emission spectrum recorded at the 263 K peak is compared to the XL emission spectrum of the same $KMgF_3$:Eu^{2+} sample. Essentially the same emission was also recorded at other PTTL peaks.

3.4. Dose Dependence and Radiation Sensitivity

Some dosimetric properties were also studied and the possible application of these materials as solid state dosimeters was investigated. The $KMgF_3$ crystals are stable to temperatures

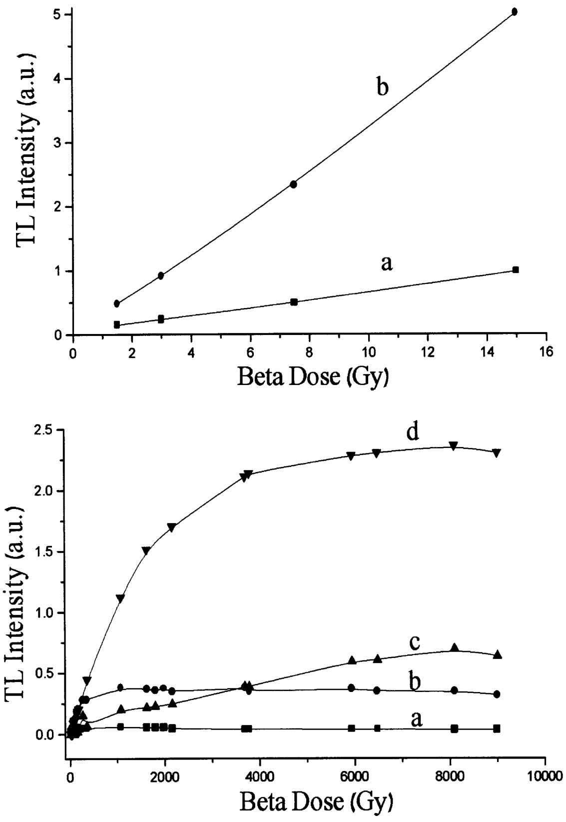

FIGURE 4 Dependence of the TL intensity of $KMgF_3$:Eu^{2+} on the β dose: I) for low doses (0–16 Gy); II) for doses 0–10000 Gy, recorded at about: a) 370 K, b) 480 K, c) 610 K and d) 730 K.

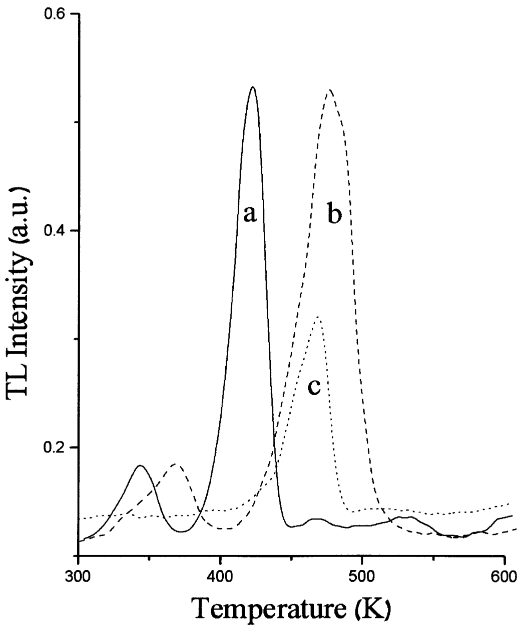

FIGURE 5 Comparison of TL sensitivity of: a) $KMgF_3:Tb^{3+}$, b) $KMgF_3:Eu^{2+}$ (reduced By 1/10), c) LiF:Mg, Ti (TLD-100). The TL was recorded after exposure of each sample to a β dose of 1.5–Gy at RT.

above 1300 K, but effects of previous irradiation are annealed at ~800 K and no PTTL could be excited after the heating to 800 K. The main TL peaks above RT are in a temperature region, which is quite convenient for TL dosimeters and also in a spectral region where the common photomultipliers are sensitive.

The dependence of the TL intensity on the radiation dose of the various samples was measured. The dose dependence of the 730 K peak in $KMgF_3:Eu^{2+}$ was found to be linear to about 2000 Gy and reached saturation for higher doses. The dose dependence of the lower temperature TL peaks was linear to about 15 Gy only. The dose dependence of the main TL peak in $KMgF_3:Tb^{3+}$ was linear up to ~900 Gy (Fig. 4).

The TL sensitivity of these crystals was also measured and compared to that of other known TLD materials (Fig. 5). The sensitivity of $KMgF_3$: Eu^{2+} was found to be by an order of magnitude higher than that of $KMgF_3:Tb^{3+}$ and the latter was by a factor or two larger than that of the known LiF: Mg, Ti (TLD-100) phosphor.

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