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Optical properties of some fluoride compounds and their application to dosimetry

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ABSTRACT

Effects of β, X and VUV irradiation on the optical properties have been studied in various simple and complex fluoride crystals by using optical absorption, X- and UV-excited luminescence (XL and PL), thermoluminescence (TL) and photo-transferred TL (PTTL) techniques. In most tested crystals, the main TL peaks with the same thermal activation energies appear after VUV as well as after X or β irradiation, thus indicating that the same traps are induced by the different types of radiation. The TL excitation spectra generally show absorption maxima on the long wavelengths tail of the fundamental absorption. Within this study, various dosimetric properties, as well as the possible application of the crystals as sensitive radiation detectors and dosimeters for the VUV have also been investigated. The TL sensitivities of the various studied materials have been compared to that of the classic dosimeter TLD-100 (LiF:Mg,Ti). For example, the sensitivity of $SrF_2:Pr^{3+}$ has been found to be the highest among the examined crystals and at a dose of 90 Gy its response is higher by a factor of ∼3 than that of TLD-100. The sensitivity of $CsGd_2F_7:Pr^{3+}$ and $KYF_4:Pr^{3+}$ are slightly higher than that of TLD-100, whereas that of nanostructured CaF_2:ZnO crystals is about twice that of TLD-100, but the sensitivity of LiF:Eu is much lower. The $SrF_2:Pr^{3+}$ crystals also showed some important dosimetric properties.

1. Introduction

Irradiation effects in fluoride crystals have been studied for several decades (e.g. Hayes, 1974). 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 LiF:Mg,Ti (TLD-100) or CaF_2: Dy (TLD-200) are radiation detectors and efficient TL dosimeters mainly for higher energy radiation (e.g. Prokić and Bøtter-Jensen, 1993). There is, however, a permanent interest in searching for new materials, which can be used as efficient solid-state dosimeters. Most solid-state dosimeters are based on effects of thermoluminescence (TL) and more recently also on methods of optically stimulated luminescence (OSL) and photo-transferred TL (PTTL). For the application of a material as a dosimeter, the luminescence efficiency as well as other optical 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 repeat measurements are of special importance. In most studies on TL and other radiation induced effects, high-energy radiation fields such as γ, β or X-rays are ordinarily applied, while relatively few investigations dealt with effects of VUV radiation on dielectric materials (e.g. Kristianpoller and Israeli, 1970; Lushchik et al., 2002). Dosimetric properties of some materials for detecting VUV radiation have recently also been investigated in this laboratory (Kristianpoller et al., 2002). It should also be noted that the application of monochromatic VUV radiation enables the evaluation of the photon energy which is most efficient for the formation of defects and the excitation of TL

In the present work optical properties of various simple and complex fluoride crystals undoped and doped with optically active ions, namely CaF_2, SrF_2, BaF_2, $CsGd_2F_7$, KYF_4 and some AMF_3 (A = Li, Na, K, Rb and M = Ca, Sr, Ba, Mg) as well as CaF_2:ZnO, have been studied and the effects of X, β and VUV radiation on the crystals have been compared. Optical absorption, X- and UV-excited luminescence (XL and PL), thermoluminescence (TL), photo-transferred TL (PTTL) and optically stimulated luminescence (OSL) techniques have been used within this research. Special attention has been given to dosimetric properties and the possible application of these crystals as VUV dosimeters.

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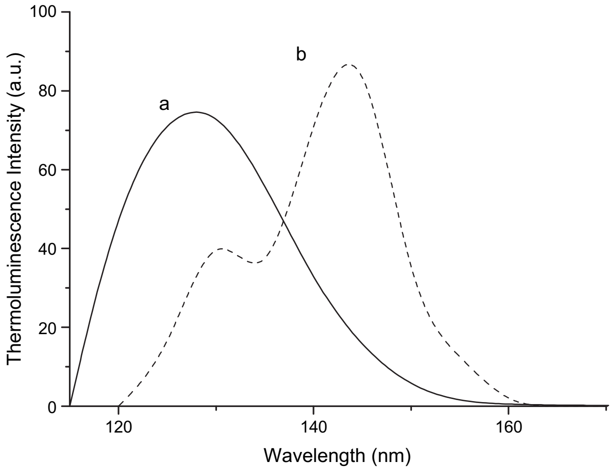

Fig. 1. TL excitation spectra in the VUV region for: a) $CaF_2:Pr^{3+}$ and b) $SrF_2:Pr^{3+}$ crystals.

2. Experimental techniques

The Pr^{3+} doped CaF_2 crystals were grown at the Hebrew University and the nominally pure single crystals were from Harshaw. Some of the complex fluoride crystals were synthesized under hydrothermal conditions at the Kurnakov Institute of General and Inorganic Chemistry (Marcazzó et al., 2007). The CaF_2:ZnO single crystals in which ZnO was imbedded as nanoparticles, were fabricated by a zinc ion implantation ~160 keV, 1×10^{17} ions/cm^2 into a CaF_2 (111) single-crystal followed by thermal annealing up to 700 °C (Liu et al., 2003). The X- and the β-ray irradiations were performed with a W-tube (40 kV, 15 mA) and a ^{90}Sr source, respectively. The TL measurements from room temperature (RT) up to 750 K were carried out by using a heating rate of 5 K/s in a TL compartment flushed by N_2 gas. For the low temperature TL and PTTL measurements, the samples were heated in liquid nitrogen vacuum cryostat from liquid nitrogen temperature (LNT) to RT at a rate of 20 K/min. The irradiations and absorption measurements in the VUV were performed with a one-meter VUV monochromator and an H_2 arc lamp.

3. Results and discussion

3.1. Thermoluminescence and optical absorption

In all the investigated crystals, TL can be excited by X as well as by β-rays. In most cases, TL is also excited by monochromatic VUV radiation in the 120–200 nm region. In some of the crystals, TL excitation spectra have been measured in the VUV region, and have been compared with the optical absorption in this region by taking into account that the TL excitation maxima in various pure alkali-halide crystals are located on the long wavelength tail, of the first exciton absorption band (Kristianpoller and Israeli, 1970). In particular the first exciton absorption peaks are known to be at 11.18, 10.6 and 10.0 eV for CaF_2, SrF_2 and BaF_2 respectively (Hayes, 1974). Main TL excitation maxima for $CaF_2:Pr^{+3}$ and $SrF_2:Pr^{+3}$ have been recorded at somewhat longer wavelengths near 135 and 145 nm, corresponding to photon energies of about 9.18 and 8.55 eV respectively (Fig. 1). This may be due to the fact that 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. TL induced by monochromatic VUV radiation has also been compared to TL induced by X or β radiation in the various crystals. In Table 1, the temperatures of the main TL peaks, induced in some of the crystals by VUV and by X or β radiation as well as the evaluated thermal activation energies are summarized. The results show that in various crystals main TL peaks appeared at the same temperatures and with the same thermal activation energies after VUV as after X or β irradiation. These results indicate that the same traps are induced by the different types of radiation.

Table 1
Temperatures (T) and thermal activation energies (E) of TL peaks, induced in various fluorides by X or β and UV radiation.

Crystal	T (K) X or β	E (eV) X or β	T (K) UV	E (eV) UV
$NaMgF_3$	290	0.51	292	0.54
$KMgF_3$:Eu	298	0.53	298	0.53
$RbMgF_3$	165	0.34	160	0.34
$RbMgF_3$	236	0.58	238	0.55

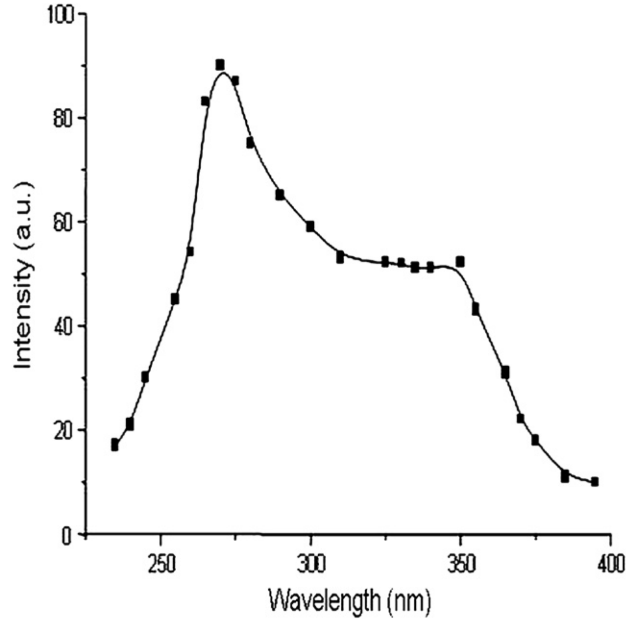

Fig. 2. PTTL excitation spectrum of a $KMgF_3 \cdot Eu^{+2}$ crystal.

3.2. PTTL and OSL

In most of the crystals previously exposed to ionizing radiation at RT and subsequently illuminated at LNT with certain long wavelengths that cannot excite any TL in non-irradiated crystals, TL

Table 2
Comparison of TL intensities measured at main TL peaks of various fluorides after irradiation with a constant 90 Gy β-dose.

CaF_2:Pr	26
CaF_2:ZnO	20
$CsGd_2F_7$:Pr	10.5
$LiKYF_5$:Pr	14
KYF_4:Pr	10.6
LiF:Eu	5
SrF_2:Tb	3.5
SrF_2:Pr	32
TLD-100	10

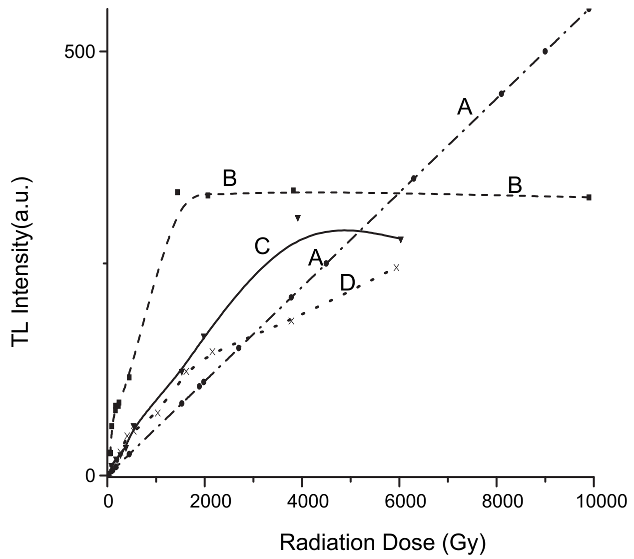

Fig. 3. Dependencies of the TL intensity on the β-dose for: (A) SrF_2:Pr, (B) CaF_2:ZnO, (C) KYF_4:Pr, (D) CaF_2:Pr, all samples after irradiation at RT with a constant β-dose of 90 Gy. The data were normalized for unit mass in all materials.

peaks are observed during heating from LNT to RT. This is attributed to a process of photo-transfer (PTTL), where trapped carriers induced by the ionizing radiation are transferred by the low energy light from deep to shallower traps. PTTL is observed when during subsequent heating; the trapped carriers are thermally released and recombine radiatively. In Fig. 2, the excitation spectrum of PTTL for $KMgF_3$ is given and it can be seen that for this sample, wavelengths of about 270 and 350 nm are most efficient for the excitation of the PTTL. In some of pre-irradiated crystals, optically stimulated luminescence (OSL) can also be excited by wavelengths that do not excite any photo-luminescence in non-irradiated samples. Both the OSL and PTTL methods have some advantage over the TL technique and are therefore applied to dosimetry.

3.3. Dosimetric properties

Some dosimetric properties have also been investigated in the various crystals (see: Table 2). Comparison of results shows that the Pr^{+3} doped SrF_2 crystals have the highest TL sensitivity among the tested crystals. The $SrF_2:Pr^{+3}$ crystals exhibit also some other important dosimetric properties. In particular, a linear dose dependence has been found up to high radiation doses of ~27000 Gy. In Fig. 3, the dependencies of the TL intensities on the β-dose of various examined crystals are given for comparison on a scale up to 10,000 Gy. The main emission bands of this crystal are also in a spectral range where most of commercial photomultiplier tubes have their maximum sensitivity. As for thermal stability, one of the main TL peaks is at about 300 K above RT and considerable thermal fading is not expected at RT.

4. Summary

Some common properties have been found in the different types of crystals.

- In most tested crystals, the same main TL peaks with the same thermal activation energies appear after both VUV and X or β irradiation, indicating that the same traps are induced by the different types of radiation.
- The TL excitation spectra show maxima in the VUV range at energies below the long wavelength tail of the fundamental absorption in various crystals.
- The TL emission spectra show some of the same emission bands for both XL and OSL from the same crystal, indicating that these emissions are due to the same luminescence centres.
- Some of the examined crystals also show a high TL sensitivity under VUV excitation.
- The Pr^{+3} doped SrF_2 crystals show the highest TL sensitivity among the tested crystals, and exhibit also some other important dosimetric properties.

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