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Luminescence of $LiKYF_5 : Pr^{3+}$ crystals

N. Kristianpoller[a,*], A. Shmilevich[a], D. Weiss[a], R. Chen[a], N. Khaidukov[b]

[a] *School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, Tel-Aviv 69978, Israel*

[b] *Institute of General and Inorganic Chemistry, 117907 Moscow, Russia*

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Abstract

X-luminescence (XL), photoluminescence (PL), optically stimulated luminescence (OSL), thermoluminescence (TL), phototransferred thermoluminescence (PTTL) as well as optical absorption have been studied in pure and Pr^{3+} doped $LiKYF_5$ crystals. Dependencies of the luminescence efficiency on the Pr^{3+} concentration and on the radiation dose have been measured and possible applications of the novel TL phosphor based on $LiKYF_5 : Pr^{3+}$ for solid state dosimetry have been investigated. There are main emission bands at 340 and 385 nm in the XL and the PL spectra of pure crystals and both these PL emission bands have an excitation maximum at 215 nm. Additional narrow emission bands at 230, 270, 479, 530 and 605 nm are observed from the $LiKYF_5 : Pr^{3+}$ crystals. In the doped crystals, the 215 nm light mainly excites the 230 and the 270 nm emission, and there are additional excitation maxima at 442, 459, 468 and 480 nm. During heating of X- or β-irradiated crystals, TL peaks have been recorded and thermal activation energies have been evaluated by various methods. TL from the $LiKYF_5 : Pr^{3+}$ crystals shows emission bands at 229, 262, 340, 486, 527, 610, 640 and 705 nm whereas there are only a main 340 nm band and weaker bands at 486 and 450 nm on the TL spectra of the pure crystals. Samples exposed to prolonged X- or β -irradiation at RT and then illuminated with the 295 or 442 nm light at LNT show strong PTTL during heating from LNT to RT. The dose dependence of the TL intensities in $LiKYF_5 : Pr^{3+}$ has been found to be linear for radiation doses up to 2 kGy.

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1. Introduction

Much interest has recently been devoted to the search for new materials, which can be used for radiation detectors and solid state dosimeters. For a few decades, mainly thermoluminescence (TL) methods have been applied for solid state dosimetry. However, more recently, methods of phototransferred TL (PTTL) (Alexander and McKeever, 1998) and optically stimulated luminescence (OSL) (e.g. Kristianpoller and Oster, 1995) have been developed for applications in dosimetry and dating. These techniques have some advantages over the common TL method. In this context, it will be noted that variously doped fluoride crystals, for example TLD-100 (LiF : Mg, Ti), are frequently used for radiation detectors and efficient dosimeters (Prokic and Botter-Jensen, 1993). Optical properties and possible applications of $LiKYF_5$ crystals doped with different rare earth ions have recently been investigated (Balda et al., 1999). In the present work, the effects of X, β and UV irradiations on pure and Pr^{3+} doped $LiKYF_5$ crystals have been studied. XL, PL, TL, PTTL and OSL as well as optical absorption have been investigated. Thermal activation energies of the main TL peaks have been evaluated by various methods. Dependencies of the luminescence efficiency on

* Corresponding author. Tel.: +972-3-640-8684; fax: +972-3-642-9306.
E-mail address: nahum@post.tau.ac.il (N. Kristianpoller).

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the Pr^{3+} concentration and on the radiation dose have also been found, and possible applications of this novel material in solid state dosimetry have been discovered.

2. Materials and experimental methods

A series of single crystals of $LiKY_{1-x}$ Pr_xF_5 was obtained by a hydrothermal technique at a temperature of about 750 K and pressures of 100–150 MPa. Crystals up to 1 cm^3 in size were synthesized by a direct temperature-gradient method as a result of the reaction of aqueous solutions of KF (20–25 mol%) and LiF whose mole ratio KF/LiF changed from 4.8 to 5.2 with appropriate mixtures of yttrium and praseodymium oxides (99.99% purity) (Balda et al., 1999). All the X- and the β-irradiations of the samples were performed with a W-tube (40 kV, 15 mA) and a Sr^{90} source of a 1.5 Gy/min. dose-rate, respectively. For monochromatic UV illuminations, a 150 W high pressure Xe lamp and a grating monochromator were used. The irradiations were carried out at RT or at LNT. 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. whereas above RT the heating rate was normally 5 K/s. The PL, OSL, TL and OSTL measurements were taken with an Aminco-Bowman/2 luminescence-spectrometer and further experimental details are given elsewhere (Kristianpoller et al., 1998)

3. Experimental results and discussion

3.1. Luminescence

Luminescence emitted from both pure and Pr^{3+} doped $LiKYF_5$ crystals during X-irradiation (XL) have been measured at RT and LNT. In the pure samples, the main emission bands are at 385 and 486 nm and some broad emission is observed at near 340 nm. This broad band is apparently composed of 336 and 346 nm components. In the $LiKYF_5 : Pr^{3+}$ samples, there are additional narrow bands at 230, 270, 479, 530 and 605 nm, which are attributed to the characteristic emission from d–f and f–f transitions of the Pr^{3+} ions. The XL emission recorded during X-irradiation of a $LiKYF_5 : Pr^{3+}$ crystal at RT is shown in Fig. 1. Some of these XL bands also appear in the photoluminescence (PL) emission. The excitation spectra of the PL bands have been measured and the emissions of the pure $LiKYF_5$ samples show a main excitation maximum at 215 nm. Besides, the 295 nm light can also excite the 340 nm emission in the pure crystals whereas the 215 nm light mainly excite the 230 and 270 nm emission bands in the Pr^{+3} doped $LiKYF_5$ crystals. There are excitation maxima for the Pr^{3+} emissions at 442, 459, 468 and 480 nm; an excitation spectrum of the 605 nm emission band is shown in Fig. 2.

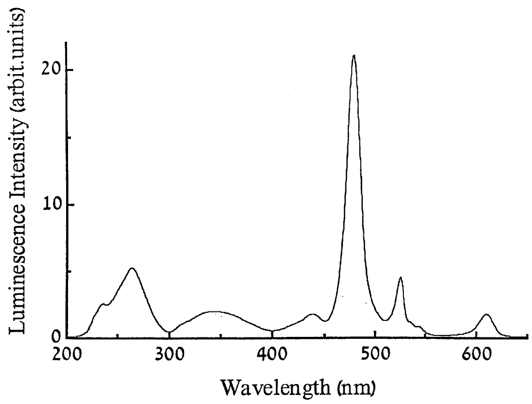

Fig. 1. XL emission spectrum of $LiKYF_5 : Pr^{3+}$ at RT.

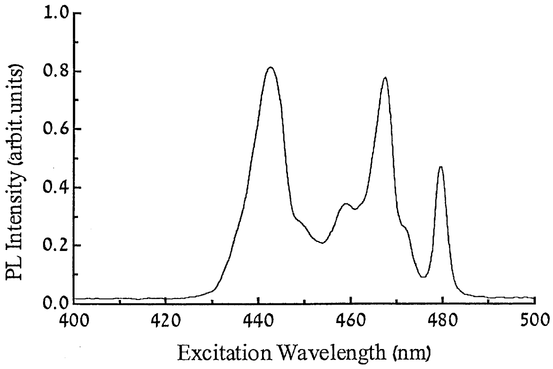

Fig. 2. Excitation spectrum of the 605 nm PL emission band of $LiKYF_5 : Pr^{3+}$ at LNT.

3.2. Optical absorption

Optical absorption and TL and PTTL have been investigated in order to find effects of prolonged irradiation for the crystals. The absorption spectra of the $LiKYF_5 : Pr^{3+}$ crystals have been measured before and after β- or X-irradiation and compared to those of nominally pure samples. There are weak absorption bands at 215 and 295 nm in both the nominally pure and the Pr^{3+} doped $LiKYF_5$ crystals. In the Pr^{3+} doped samples, absorption bands are also observed at 442, 468, 480 and 600 nm and these bands can be attributed to the Pr^{+3} transitions between the 3H4 ground state and the 3P2; 1I6, 3P1; 3P0 and 1D2 states, respectively. The exposure to prolonged X- and β-irradiation induces an additional absorption band at about 350 nm in both the pure and the Pr^{3+} doped $LiKYF_5$ crystals.

3.3. Thermoluminescence

During heating of the irradiated pure and Pr^{3+} doped $LiKYF_5$ crystals a notable TL emission is observed. There

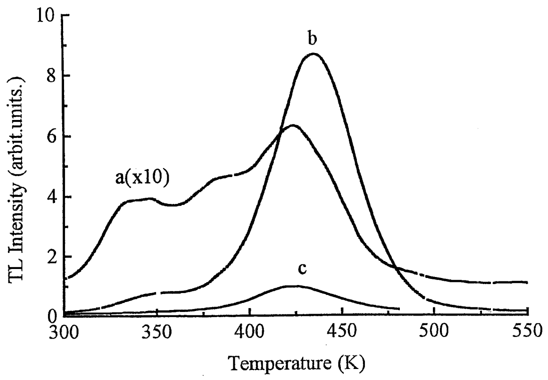

Fig. 3. TL recorded after the 2 min β-irradiation at RT in (a) an undoped $LiKYF_5$ crystal; (b) a 5 at.% Pr^{+3} doped $LiKYF_5$ crystal and (c) a 10 at.% Pr^{3+} doped $LiKYF_5$ crystal.

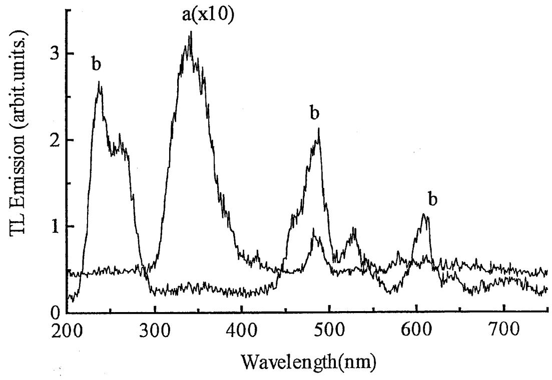

Fig. 4. Emission spectra recorded at TL peak near 450 K in (a) an undoped $LiKYF_5$ crystal and (b) a Pr^{3+} doped $LiKYF_5$ crystal; both after β-irradiation at RT.

are main TL peaks at about 360, 450, 470 and 520 K in X- or β-irradiated crystals. The exact peak temperatures have been found to depend slightly on the Pr^{3+} concentration as well as on the radiation dose. However, the TL sensitivity of the $LiKYF_5$ crystals strongly depends on the Pr^{3+} concentration and the TL sensitivity of the Pr^{3+} doped $LiKYF_5$ samples is much higher than that of the undoped crystals. The sensitivity of the $LiKYF_5$ crystals doped with Pr^{3+} in the range from 3 to 5 at.% is higher than that of the other crystals for the $LiKY_{1-x}Pr_xF_5$ series and of the order of the well known LiF : Mg, Ti (TLD-100) phosphor. The TL from some crystals of the $LiKY_{1-x}Pr_xF_5$ series β-irradiated at RT is shown in Fig. 3.

The thermal activation energies have been evaluated by using the “initial rise” and “different heating rate” method, that is, the Booth formula (Chen and McKeever, 1997). The activation energies of the main TL peaks at near 360 and 440 K are 0.35 and 0.80 eV, respectively, for both the pure and the doped samples. The results indicate that these TL peaks are due to the same trapping states in the pure and the Pr^{3+} doped samples. However, the TL emission spectra of the doped crystals markedly differ from those of the undoped crystals. Spectral decomposition of TL from the $LiKYF_5 : Pr^{3+}$ crystals shows main emission bands at 229, 262, 340, 486, 527, 610 and 705 nm whereas only the 340 and 486 nm bands can be observed in TL from the undoped crystals. TL emission spectra are shown in Fig. 4. No TL has been observed in the crystals exposed to sole UV illumination. On the other hand, the samples exposed to prolonged β- or X-irradiation at RT and subsequently illuminated with monochromatic light at LNT show strong glow peaks at 185, 220 and 260 K during heating. Obviously these peaks are due to phototransferred thermoluminescence and the optimal wavelengths for the PTTL stimulation are 295 and 442 nm. The main PTTL emission is at 486 nm and additional bands are at 535, 609 and 645 nm in the Pr^{3+} doped $LiKYF_5$ crystals. The dependence of TL on the beta dose has also been investigated and has been found to be linear for doses of above 2 kGy (Fig. 5). The effects of previous X- or β-irradiations are thermally bleached by heating to about 500°C, and the samples can be used in new measuring cycles repeatedly.

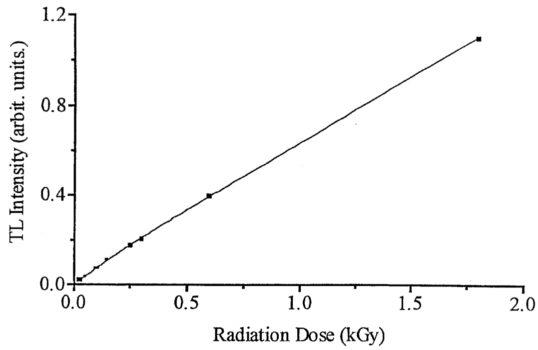

Fig. 5. Dependence of the TL intensity of $LiKYF_5 : Pr^{3+}$ on the β dose.

4. Summary

The luminescence properties of the $LiKYF_5 : Pr^{3+}$ crystals show that these compositions may be promising materials for applications in solid state dosimetry. In particular, the TL sensitivity of the Pr^{3+} doped $LiKYF_5$ crystals is relatively high and comparable to that of the TLD-100 phosphor. On the other hand, the dose dependence is linear over a wide range of radiation doses and the wavelengths of the main TL emission bands are in a spectral region where the common photomultipliers are sensitive. Besides, the main TL peaks are more than 90°C above room temperature and, accordingly, thermal fading is not expected to occur during storage at RT. Also, the temperature of 500°C, required for thermal bleaching of previous irradiation effects, is not very high, and this may be of importance when repeated use of the same sample is required.

Acknowledgements

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References

Alexander, C.S., McKeever, S.W.S., 1998. Phototransferred thermoluminescence. J. Phys. D 31, 2908–2920.

Balda, R., Fernandez, J., Saez de Ocariz, I., Voda, M., Garcia, A.J., Khaidukov, N., 1999. Laser spectroscopy of Pr^{3+} ions in $LiKY_{1-x}Pr_xF5$ single crystals. Phys. Rev. B 59, 9972–9980.

Chen, R., McKeever, S.W.S., 1997. Theory of Thermoluminescence and Related Phenomena, World Scientific Publ. Co., Singapore, pp. 101–113, 122.

Kristianpoller, N., Oster, L., 1995. Optically-stimulated luminescence in anion-defective carbon doped $-Al_2O_3$ crystals. Radiat. Eff. Def. Solids 134, 311–313.

Kristianpoller, N., Rehavi, R., Shmilevich, A., Weiss, D., Chen, R., 1998. Radiation effects in pure and doped Al_2O_3 crystals. Nucl. Instr. and Meth. B 141, 343–346.

Prokic, L., Botter-Jensen, 1993. Comparison of main thermoluminescent properties of some TL dosimeters. Radiat. Prot. Dosim. 47, 195–199.