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Study of optical and dosimetric properties of doped fluoride crystals

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Abstract

Optical properties and radiation effects of various fluoride crystals and their possible application to solid state dosimetry were studied. In particular optical absorption, PL, OSL, TL and OSTL of LiKYF₅ and LiKYF₅:Pr³⁺ crystals were measured and compared to those of pure and Eu³⁺-doped LiF. After X- or β -irradiation of LiKYF₅:Pr³⁺ a strong TL was recorded. In samples irradiated at RT also an OSTL could be stimulated at LNT; the stimulation maximum for the OSTL was at 442 nm. The traps responsible for the TL were stable to about 600 K. In LiF:Eu³⁺ the TL could also be excited by VUV radiation. The VUV excited TL had excitation maxima near 125 and 190 nm. An OSTL emission was recorded in pure irradiated LiF crystals; and had an excitation maximum at 190 nm, indicating that the TL in the doped samples and the OSTL in the pure crystals are due to the same trapping states. Prolonged illumination into the F-band caused in LiF a decrease of the M-luminescence and an increase of the R⁺-emission, which is apparently due to an M to R conversion. The dose dependence of the TL in LiKYF₅:Pr³⁺ was found to be linear for β doses to above 2 kGy. The TL sensitivity of the powdered LiF:Eu³⁺ samples was an order of magnitude greater than that of pure LiF crystals, but by an order of magnitude lower than that of the known efficient LiF:Mg Ti (TLD-100) phosphor. The sensitivity of LiKYF₅:Pr³⁺ crystals were of the order of the TLD-100 phosphor. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Optical properties of LiF crystals have been studied for several decades from both the point of view of basic as well as applied research [1]. LiF is one of the broadest band-gap alkali halides and is transparent in a wide spectral range from about

7 μ m to 110 nm and therefore has widely been used as optical material. Various research groups have also studied point defects in LiF and different models have been proposed for the mechanism of formation of F-aggregate centers e.g., [2]. Most of the previous studies on irradiation effects and the formation of point defects, concentrated on the effects of higher energy radiation, such as γ , β and X-rays. In some works also the formation of color centers by ion implantation was investigated [3]. In relatively very few

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works also effects of VUV radiation were investigated [4,5]. Much interest has recently been given to the search of new materials, which can be used for radiation detectors and solid state dosimeters. Various doped LiF crystals, such as TLD 100 (LiF:Mg, Ti), have recently been used for radiation detectors and efficient dosimeters [6]. For a few decades, mainly thermoluminescence (TL) methods have been applied for solid state dosimetry. More recently also on methods of optically stimulated luminescence (OSL) and optically stimulated TL (OSTL) are used [7,8]. For OSTL measurements the samples are X- or β -irradiated at RT then cooled to LNT and illuminated with light of wavelength which cannot excite any TL. Since no TL is expected to appear during heating between LNT and RT, the luminescence recorded in this case below RT is attributed to a process of optically stimulated TL. In this process carriers that were trapped by the ionizing radiation at RT in deep traps are transferred by the illumination at LNT to shallower traps, which are not stable at RT. During heating from LNT to RT these carriers are thermally released and during radiative recombination they may emit the observed OSTL. In the context of dosimetry and dating, the OSTL is sometimes called phototransferred TL (PTTL). For the OSTL measurements the irradiated samples are sometimes first heated from the irradiation temperature at T_1 to a higher temperature T_2 then recooled to T_1 and illuminated at T_1 with light of wavelength which cannot excite any TL in unirradiated crystals. If glow peaks are recorded during a second heating cycle between T_1 and T_2 these are OSTL peaks, due to a process of phototransfer. The OSTL method has various advantages over the common TL-method such as: (1) A short exposure to light causes, only a relatively slight depletion of the carriers, trapped at deep traps by the original ionizing radiation. This fact enables the repeated exposure of the sample to the UV light without markedly influencing the sensitivity and without necessity for additional exposure to X- or β -radiation. (2) The OSTL measurements are carried out at relatively low temperatures, while in the common TL measurements the main peaks may appear at high tem-

peratures and the specimen has to be heated to these temperatures in order to release the carriers from these deep traps. In this case, the TL emission may also be overlapped by the black-body radiation. (3) Fading effects, which are typical of the low temperature TL peaks, may be avoided by application of the OSTL method since in this method relatively deep primary traps are used as a reservoir. This is of importance for applications where specimens are kept for long periods between the exposure to the ionizing radiation and readout. (4) OSTL can also be used in dosimeters for the near UV.

The OSL – as the OSTL – can be stimulated only in samples which have previously been exposed to ionizing radiation and subsequently illuminated with light of wavelengths which cannot directly excite luminescence in a non-irradiated crystal (the stimulation wavelength may even be longer than that of the OSL emission). This low energy light can, however, stimulate carriers, trapped by the ionizing radiation, which may then recombine with carriers of opposite sign, yielding the OSL emission. The OSL has some of the same advantages as the OSTL. And therefore, both methods have recently been applied to dosimetry and dating.

In the present work, the optical properties and effects of X, β and VUV irradiation were investigated in LiF:Eu³⁺ and in various composed fluorides and in particular of pure and Pr³⁺-doped LiKYF₅ crystals; the effects were compared to those induced in nominally pure LiF. Optical absorption, XL, PL and OSL as well as TL and OSTL were measured. The possible application of the various materials to solid state dosimetry was also investigated.

2. Experimental techniques

The pure and Pr³⁺-doped LiKYF₅ crystals were grown at the Institute of General and Inorganic Chemistry in Moscow. Optical properties and various applications of LiKYF₅ crystals doped with different impurities have recently been investigated [9]. The nominally pure single LiF crystals were from Harshaw. Pressed disks of LiF and

LiF:Eu³⁺ (0.1 mol%) were also used for the measurements.

The X-irradiations were performed with a W-tube (40 kV, 15 mA) and the β -irradiations with a Sr⁹⁰ 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 N₂ gas; the heating rate above RT was 5°C/s. 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°C/min. The OSL was stimulated at various temperatures between 80 and 400 K by monochromatic UV light in samples which had previously been exposed to X- or β -radiation. The far UV irradiations were carried out with a one-meter normal-incident VUV monochromator and a H₂ 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. Experimental results and discussion

3.1. Optical absorption

After the exposure to X- or β -irradiations of LiF at RT the well known F and F₂ (M) absorption bands appeared at 245 and 445 nm, respectively. An additional weak absorption band was recorded at 190 nm.

In unirradiated nominally pure as well as in Pr³⁺-doped LiKYF₅ crystals, weak absorption bands appeared at 215 and 295 nm. In the Pr³⁺-doped samples additional absorption bands were recorded at 442, 468, 480 and 600 nm; these bands are attributed to the Pr³⁺ transitions between the ³H₄ ground state and the ³P₂, ³P₁, ¹I₆, ³P₀, and ¹D₂ states, respectively. The 215 and 295 nm bands fit 4fⁿ to 4fⁿ⁻¹ 5d absorption transitions of Pr³⁺ and Ce³⁺ ions, respectively and may be due to casual traces of these ions, present even in the nominally pure samples. This is supported by the measured luminescence spectra.

3.2. XL, PL and OSL

During X-irradiation at RT of LiF:Eu³⁺ a main broad XL emission band appeared at about 420 nm and a weaker one near 355 nm. A broad STE emission band has previously been reported at 353 nm [10]. Narrow emission bands were recorded at 591 and 613 nm and are attributed to an impurity emission. At LNT the same emission bands appeared but the intensity of the 355 nm and the 420 nm maxima increased markedly, while no increase of the two longer wavelength bands was recorded. The XL of pure LiF crystals showed a broad emission band near 330 nm and the 420 nm appeared as a shoulder. The XL emission spectra of pure and Eu³⁺-doped samples at RT are given by curves a and b of Fig. 1. After X-irradiation a slow decaying after glow was recorded at LNT in the Eu³⁺-doped samples. Main broad phosphorescence bands appeared again near 350 and 420 nm; as well as a strong narrow maximum at 613 nm and weaker maxima at 591, 653 and 702 nm. No PL could be excited in pure pristine crystals. In the LiF:Eu³⁺ samples the PL emission showed the same 613 nm band and the other narrow impurity bands, which appeared in the XL (curve c of Fig. 1). The main excitation maximum was at 393 nm and additional maxima appeared at 468 and 535 nm. No F-luminescence could be excited in the pure or in the doped LiF. This non-occurrence of an F-luminescence in LiF crystals fits the predictions of the theoretical Dexter–Klick–Russel

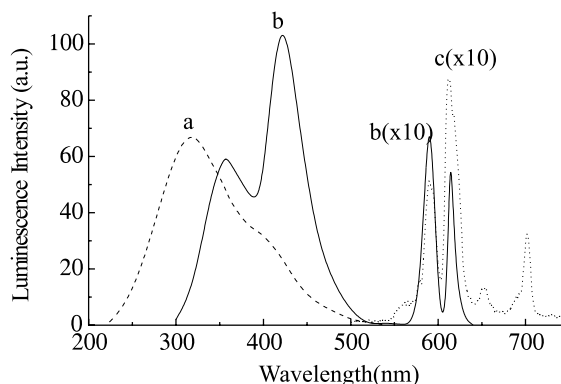


Fig. 1. Emission spectra recorded at RT: (a) XL of LiF; (b) XL of LiF:Eu³⁺ and (c) PL of LiF:Eu³⁺ excited by 393 nm.

model [11]. Illumination into the F-center of the Eu-doped samples resulted, however, in the emission of the narrow impurity bands, and mainly the 613 nm band. This is apparently due to the capture of the excited F-electron by a nearby impurity ion, followed by a radiative decay. A strong OSL emission was recorded at about 640 nm in LiF crystals which had previously been exposed to ionizing radiation and subsequently illuminated into the F_2 (M) center absorption near 445 nm and is attributed to an F_2 -luminescence. A weak 525 nm band appeared by optical stimulation at about the same wavelength and its intensity increased markedly after additional prolonged β -irradiation. This 525 nm band has previously been ascribed to an $F_3^+(R^+)$ emission [2]; the present results indicate that during the RT irradiations also F-aggregate centers were formed.

In pure LiKYF₅ crystals a main PL emission band was recorded at 385 nm and an additional broad, apparently composed, band at 340 nm. All these PL bands had an excitation maximum at 215 nm, but the 340 nm emission could also be excited by 295 nm light. In the LiKYF₅:Pr³⁺ crystals additional narrow emission bands appeared at 230, 479 and 605 nm. The 215 nm light, which excited in the nominally pure crystals mainly the 340 nm band, excited in the Pr³⁺ samples mainly two different bands at 230 and 270 nm (Fig. 2). The 479 nm emission had an additional excitation maximum at 442 nm and the 605 nm emission could also be excited with 442, 468 and 480 nm. Most of these emission bands appeared also in the XL. A comparison of the excitation wavelengths of these PL emissions with the above-mentioned absorption bands indicates that these bands are impurity related.

The 479 and 605 nm emission bands can be attributed to $^3P_0-^3H_4$ and to $^3P_0-^3H_6$ transitions; and the 230 nm and 270 nm emissions to $4f5d-4f^2$ transitions in Pr³⁺. The 340 nm emission may be due to a d-f transition of Ce³⁺.

3.3. TL and OSTL

During heating of the irradiated samples, the TL was measured and thermal activation energies were evaluated at the main glow peaks by the

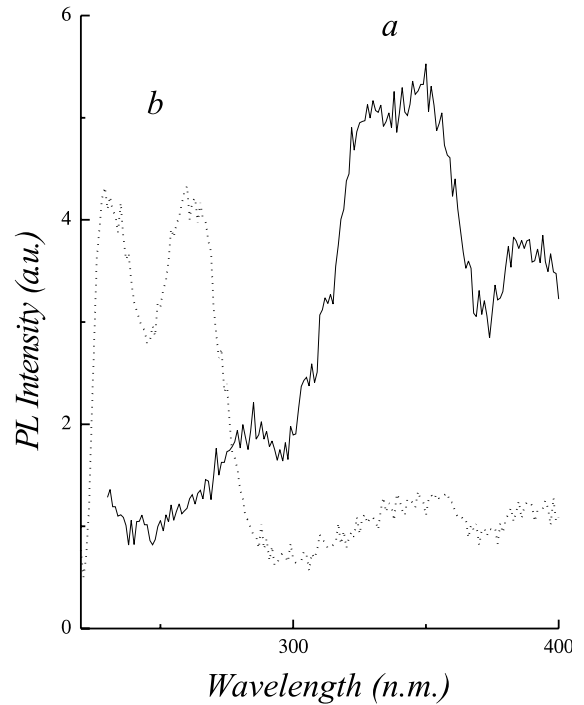


Fig. 2. PL spectra excited at RT by 215 nm light in (a) pure and (b) Pr³⁺-doped LiKYF₅ crystals.

initial-rise as well as by the symmetry method [12]. After RT irradiation the main glow peaks appeared in the Eu³⁺-doped LiF samples at 370, 430 and 480 K and in the pure crystals at 440 and 480 K (Fig. 3). After X- or β -irradiation at LNT the main glow peak appeared in the Eu-doped samples

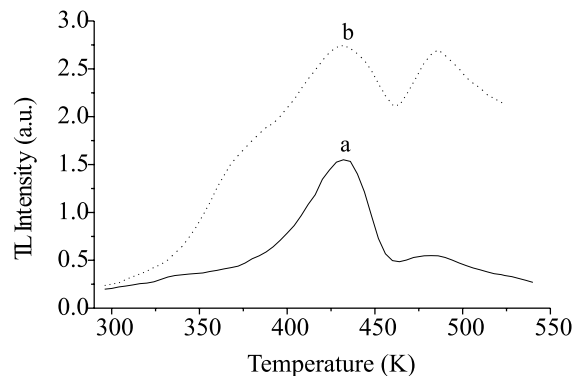


Fig. 3. TL glow curves of: (a) LiF and (b) LiF:Eu³⁺, recorded after β irradiation at RT.

at a somewhat lower temperature than in the pure ones (160 K compared to 175 K) and was much stronger. The glow peaks had, however, identical shapes and the same thermal activation energy of ~ 0.15 eV. These results indicate that the carriers are thermally released in both samples from the same traps but decay radiatively at different centers and with a higher recombination probability of the doped samples. This is also supported by the measured TL emission spectra.

Spectral decomposition of the TL emitted at the various glow peaks showed some of the same bands, which were recorded in the XL and OSL. The main 160 K peak of the Eu^{3+} -doped samples showed broad emission bands near 345 and 520 nm as well as the narrow 591, 613, 653 and 702 nm bands. The narrow bands decreased above 200 K while a 420 nm band appeared at the 265 K peak and became dominant at the TL peaks above RT. The 175 K peak in the pure crystals showed emission bands at: 345, 420 and 650 nm; the main emission of the 285 K peak was at 315 nm.

The TL excited by monochromatic VUV radiation was also investigated. TL excitation spectra of $\text{LiF}:\text{Eu}^{3+}$ were measured in the 110–250 nm region and showed maxima at the long wavelength tail of the fundamental absorption near 125 nm and at 190 nm. This wavelength coincides with a weak peak recorded in the VUV absorption spectrum.

No measurable TL could be excited by VUV irradiation in pure pristine LiF crystals, but a strong OSTL was recorded in pure samples which had previously been X- or β -irradiated at RT and subsequently UV illuminated at LNT, as well as in samples, irradiated at RT, heated to about 550 K then recooled and UV illuminated at RT. Main OSTL peaks appeared at 125, 310 and 425 K. The OSTL of the pure LiF crystals had also an excitation maximum at 190 nm. The fact that the OSTL and the TL have the same excitation maxima indicates that they are due to the same trapping states. Some different emission bands were, however, recorded at low temperatures TL in $\text{LiF}:\text{Eu}^{3+}$ and in nominally pure LiF, indicating that the emissions at the same peaks are due to different luminescence centers. The present measurements have also shown that the OSTL has no

excitation maximum at the F-absorption band neither in the pure nor in the Eu-doped LiF, while illumination into the F-absorption band is known to be most efficient for the excitation of OSTL in other alkali halides. This finding resembles the above mentioned non-appearance of an F-luminescence in the OSL of LiF, which was explained by the values of the configurational parameters in the Franck–Condon diagram of LiF [11]. These parameter values probably also exclude the possibility of the transfer of an excited F-electron from a deep to a shallower trap in LiF; such a phototransfer is known to be a precondition for an OSTL emission.

In irradiated $\text{LiKYF}_5:\text{Pr}^{3+}$ a main TL peak was recorded at 450 K and weaker peaks near 360, 470 and 520 K. The emission of the 450 K peak was at 229 nm; additional TL emissions were recorded at 262, 350, 468, 527, 610 and 705 nm. The results show that the main TL peaks are in a convenient temperature region for TL dosimetry and that the main emission are in a spectral region where the commonly used PM tubes are sensitive. No TL was recorded in crystals after sole UV irradiation. Samples which were exposed to a prolonged β -irradiation at RT and subsequently illuminated with monochromatic light at LNT showed a significant emission during heating from LNT to RT which is apparently due to a OSTL emission. The optimal excitation wavelengths for OSTL stimulation were at 295 and 442 nm. Main OSTL peaks appeared at about 185, 220 and 260 K, and showed a main emission band at 486 nm and additional bands at 535, 609 and 645 nm. TL and OSTL emission spectra of pure and doped LiKYF_5 are shown in Fig. 4.

Effects of optical and thermal treatment on the various materials were also investigated in this study. In Fig. 5, these effects of prolonged RT illumination into the F-center on the intensities of the 640 and 525 nm emissions in pure LiF are shown. It can be seen that prolonged illumination into the F-band caused in LiF a decrease of the $\text{F}_2(\text{M})$ -luminescence and an increase of the $\text{F}_3^+(\text{R}^+)$ -emission, which is apparently due to an M to R conversion. It is known that anion vacancies in LiF have a higher diffusion coefficient than neutral F-centers and our present results support a previous

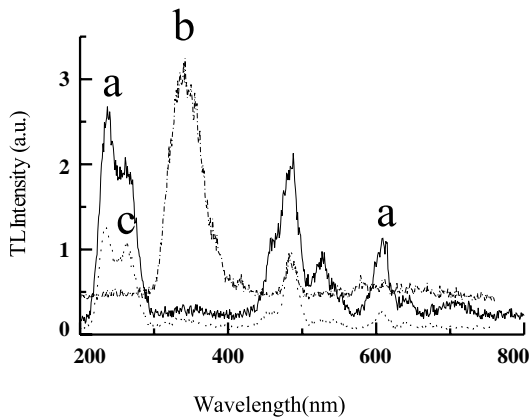


Fig. 4. TL and OSTL emission spectra recorded at 280 K: (a) TL of $\text{LiKYF}_5:\text{Pr}^{3+}$, (b) TL of LiKYF_5 and (c) OSTL of $\text{LiKYF}_5:\text{Pr}^{3+}$ (stimulated with 295 nm light).

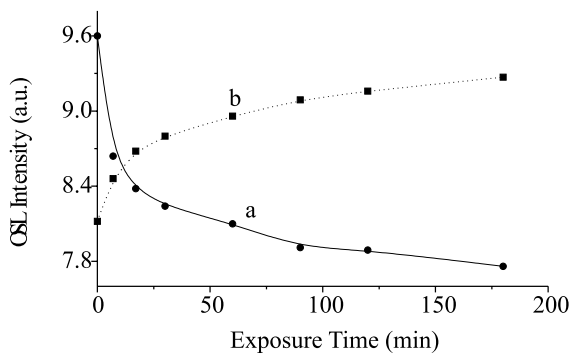


Fig. 5. Effects of prolonged 245 nm illumination at RT on: (a) the F_2 and (b) the F_3^+ emission bands of LiF.

suggestion that an F_3^+ center is produced by a diffusion of a $\text{F}^+(\alpha)$ -center to an F_2 complex [1]. Heating to about 700 K had a reversed effect and caused an increase of the F_2 emission band, while the F_3^+ (525 nm) and the F_3 (475 nm) bands sharply decreased. Both the neutral and ionized F_3 centers become obviously unstable at the same temperature.

In the LiKYF_5 crystals prolonged illumination with 295 nm caused at RT a strong increase of the 340 nm emission. Heating to about 600 K caused a disappearance of the 229 and 260 nm bands while

the other bands decreased by about 70%. After annealing to 400–500°C the effects of previous irradiations are thermally bleached and the $\text{LiKYF}_5:\text{Pr}^{3+}$ samples can be used again in a new measuring cycle.

The dose dependence was found to be linear for doses up to about ~ 20 h of β irradiation. (Dose rate of the source was ~ 1.5 Gy/min.)

A comparison of the TL sensitivity of the various investigated materials showed that the sensitivity of powdered $\text{LiF}:\text{Eu}^{3+}$ samples was by an order of magnitude greater than that of pure LiF crystals, but by an order of magnitude lower than that of the $\text{LiF}:\text{Mg}$, Ti (TLD-100) phosphor. The TL sensitivity of the $\text{LiKYF}_5:\text{Pr}^{3+}$ crystals were of the order of the TLD-100 phosphor. The results indicate that the $\text{LiKYF}_5:\text{Pr}^{3+}$ crystals have a high TL efficiency and other appropriate properties, required for a good TL dosimeter.

References

- [1] Y. Farge, M. Lambert, R. Smoluchowski, *Phys. Rev.* 159 (1967) 700.
- [2] J. Nahum, *Phys. Rev.* 158 (1967) 814.
- [3] A.T. Davidson, J.D. Comins, T.E. Derry, *Rad. Eff.* 90 (1985) 213.
- [4] Yu.M. Aleksandrov, Ch.B. Lushchik, V.N. Makhov, T.I. Syreishchikova, M.N. Yakimenko, *Sov. Phys. Solid State* 24 (1982) 968.
- [5] B.R. Sever, N. Kristianpoller, F.C. Brown, *Phys. Rev. B* 34 (1986) 1257.
- [6] M. Prokic, L. Botter-Jensen, *Rad. Prot. Dos.* 47 (1993) 195.
- [7] S.W.S. McKeever, M.S. Akselrod, L.E. Colyott, N. Ager-snap Larsen, J.C. Polf, V. Whitley, *Rad. Prot. Dosimetry* 84 (1999) 163.
- [8] L. Oster, D. Weiss, N. Kristianpoller, *J. Phys. D.* 27 (1994) 1732.
- [9] J.F.H. Nicholls, et al., *Opt. Commun.* 137 (1997) 281.
- [10] A. Wasiela, B. Block, *J. Phys.* 37 (1976) C7.
- [11] R.H. Bartram, A.M. Stoneham, *Solid State Commun.* 17 (1975) 1593.
- [12] R. Chen, S.W.S. McKeever, *Theory of Thermoluminescence and Related Phenomena*, World Scientific, Singapore, 1997, pp. 101, 113.