Electronic and ionic processes in LiF:Mg,Ti and LiF single crystals

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Abstract

Thermally stimulated luminescence (TSL, 5–750 K) and the annealing of induced optical absorption have been investigated in LiF:Mg,Ti and pure LiF single crystals irradiated at 5–295 K by electrons, X-rays, α particles, uranium swift ions and especially VUV radiation selectively forming anion excitons, electron–hole pairs and excitations localized near impurity centres. It is shown that besides electron–hole processes, the interstitial-vacancy (ionic) ones should be taken into account. The irradiation of LiF and LiF:Mg,Ti at high fluxes and fluences leads to the appearance of the TSL peaks at 570–630 K by a two-step process: thermal dissociation of two types of F_3^- trihalide molecules and sequent recombination of the products of this dissociation with intrinsic and impurity electron colour centres. The origin of some TSL peaks at 5–750 K is discussed.
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1. Introduction

For about 50 years the wide-gap ($E_g = 14.2$ eV) lithium fluoride crystal has been successfully used as a material for personal dosimetry of γ- and X-rays as well as of thermal neutrons. In particular, thermally stimulated luminescence (TSL) and sometimes photostimulated luminescence of LiF crystals doped with magnesium, titanium and hydroxyl ions are used for dosimetric purposes. The complicated function processes in LiF:Mg,Ti have been considered up to now on the basis of electron–hole (e–h) processes and ionic processes connected with the motion and recharging of pre-irradiation defects. Recently, a demand arose for LiF-based dosimeters operating at the irradiation by protons or swift ions (see, e.g., Bos and d'Errico, 2006; Bilski, 2002; Horowitz et al., 2003).

The goal of the present study is to underline that, similar to other alkali halides (see, e.g., Lushchik et al., 2000), the irradiation of LiF by photons, electrons and high-energy ions causes the formation, besides separated electrons and holes, of anion excitons (formation energy of 12.2–14 eV at 300 K), the non-radiative decay of which leads to the creation of anion Frenkel defect pairs and of the groups of spatially correlated radiation defects. Special attention is paid to the high-temperature stabilization of radiation-induced anion interstitials (H centres).

The possible mechanisms of e–h processes in LiF:Mg,Ti are thoroughly studied (see reviews by Stoebe and Watanabe, 1975; Nepomnyachikh et al., 1984; McKeever et al., 1995). Recently, considerable advances have been made in the understanding of the e–h processes by taking into account the tunnel radiative recombination involving Mg and Ti impurity complexes (Horowitz et al., 2003; Oster et al., 2007 and references therein). Some aspects of the coexistence of e–h, excitonic and interstitial–vacancy processes in LiF and LiF:Mg,Ti have been pointed out as well (Lushchik et al., 2006; Nakonechnyi et al., 2006).

This paper focuses on new experimental results obtained in nominally pure LiF single crystals as well as in LiF:Mg,Ti single crystals grown in Irkutsk, Russia (100 ppm of Mg^{2+} and 10 ppm of Ti^{4+}). Particular attention has been paid to the investigation of thermally stimulated processes at 300–750 K by means of luminescent and absorption versions of

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thermoactivation spectroscopy. TSL was measured at the heating of irradiated crystals with a constant rate of $\beta = 2.86 \, \text{K s}^{-1}$ (300–750 K, System 310 TLD Reader with flowing nitrogen) or $\beta = 0.17 \, \text{K s}^{-1}$ (6–420 K). Crystals were irradiated by α particles (5.1 MeV), X-rays (55 keV), U ions (2.44 GeV, linear accelerator UNILAC of the GSI, Darmstadt), an electron beam (5–20 keV) or photons of 4–17 eV at 5–295 K.

2. Thermoactivation spectroscopy of LiF:Mg,Ti at 5–750 K

Similarly to other alkali halides, there are three decay channels of self-trapped excitons in LiF: radiative decay with light emission and nonradiative channels with heat release or with the formation of stable Frenkel pairs. In contrast to KCl, KBr and RbCl, the efficiency of defect creation (the third channel) in LiF (as well as in NaF and NaCl) significantly decreases by changing the irradiation temperature from 295 to 5 K. In a close-packed LiF crystal, an anion exciton decays into an F centre and an interstitial fluorine—an H centre oriented along $\langle 1\,1\,1 \rangle$ directions (Chu and Mieher, 1969) and not along $\langle 1\,1\,0 \rangle$ anion rows as in the majority of alkali halides. Such orientation of an H centre impedes a crowdion motion of interstitials at 5 K and, consequently, the formation of stable Frenkel pairs with spatially separated defects.

Fig. 1 presents the TSL measured at 6–400 K for 3 eV emission (selected through a double monochromator), used for dosimetric purposes, after irradiation of LiF:Mg,Ti by 5 keV electrons at 5.2 K. The TSL peak at 132 K corresponds to the hopping diffusion of self-trapped holes (V_K centres) and their sequent recombination with the electrons trapped by complex impurity centres during irradiation. The 235 K peak is tentatively related to the hopping diffusion of the holes localized near cation vacancies (V_F centres, v_ch, Känzig, 1960). The annealing of the optical absorption of V_K centres at 3.6 eV takes place at 120–140 K, while the annealing of the absorption band at 6.2 eV occurs at 230–250 K (see Fig. 1), i.e., close to the annealing region of the EPR signal of V_F centres in pure LiF crystals. The TSL peak at ~ 250 K dominates in an electron-irradiated pure LiF crystal, where V_F centres overcome a sufficiently large distance before recombination (Nakonechnyi et al., 2006). Weak TSL peaks at 27 and 58 K correspond to the hopping diffusion of I centres (interstitial fluorine ions) and H centres, respectively (see Fig. 1). Similarly to NaCl (Lushchik and Frorip, 1990), the efficiency of I centre creation by electrons or X-rays at 5 K in LiF is extremely low. The phosphorescence was detected in our LiF:Mg,Ti sample after the 5–10 keV electron irradiation at 5.2 K had been stopped. According to the inset in Fig. 1, this emission with distinctive features of tunnel luminescence has the maximum at 3 eV both at 5 or 290 K, after an additional heating of the sample.

The irradiation of LiF by X-rays or electrons at 295 K leads to the creation of F–H pairs of Frenkel defects via the decay of electronic excitations. Single stable F centres are easily detected by a direct absorption method, while highly mobile H centres (their hopping diffusion takes place at $T > 58$ K) undergo pair interaction with other H centres (formation of H–H pairs) or V_K and V_F centres forming trifluorine F_3^- molecules
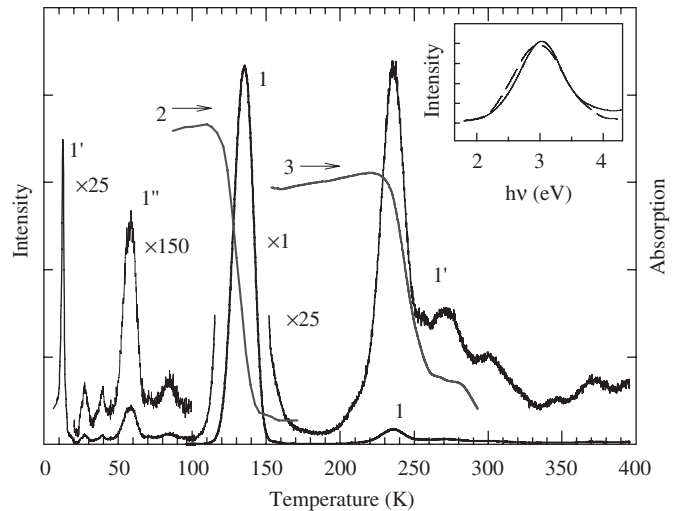

Fig. 1. TSL curve measured for 3 eV emission in a LiF:Mg,Ti crystal irradiated by 5 keV electrons at 5.2 K (curves 1, 1′ and 1″, $\beta = 10 \, \text{K min}^{-1}$). The annealing of the optical absorption at 3.6 eV (curve 2) and 6.2 eV (3) in LiF irradiated by X-rays at 80 K. Inset shows the spectra of phosphorescence measured at 5.2 K (solid line) or 290 K (dashed line) in LiF:Mg,Ti electron irradiated at 5.2 K.

stable up to 500–600 K. The spectra of the induced optical absorption have been measured in the region of 1.5–6.5 eV for a LiF:Mg,Ti crystal X-irradiated at 295 K (the sample was uniformly coloured in thickness of $d = 0.5$ mm). The irradiated LiF:Mg,Ti was heated with $\beta = 2.86 \, \text{K s}^{-1}$ to the temperature T_1, rapidly (~ 10 s) cooled down to $T_0 = 295$ K and the absorption spectrum was measured at T_0. Thereafter, the sample was preheated up to $T_2 > T_1$, cooled down and the absorption spectrum was registered once more at T_0. In such a manner, 33 spectra of optical absorption were measured for the irradiated sample, while the preheating temperature was changed from 350 to 750 K.

Fig. 2 presents the dependence of the absorption constant (measured at several photon energies $h\nu_{\text{exc}}$) on the preheating temperature, $A(T_{\text{pr}})$ of LiF:Mg,Ti irradiated by X-rays at 295 K. The $A(T_{\text{pr}})$ curves were constructed for three $h\nu_{\text{exc}}$ within the F band (maximum at 4.97 eV, bandwidth of 0.79 eV). The curves for $h\nu_{\text{exc}} = 4.97$ eV and 4.6 eV practically coincide with each other, while at $h\nu_{\text{exc}} = 5.34$ eV (high-energy wing) there is an overlapping between the F band and the band (maximum at 5.62 eV, bandwidth 0.78 eV—see inset in Fig. 3) related to complex magnesium centres (this two-electron centre is named further as 5.62-eV centre). The intensity of the 5.62-eV band (measured at 5.7 eV) increases with the rise of T_{pr} from 420 to 500 K and then decreases in several stages. In the region of the 485 K dosimetric peak, the optical absorption at $h\nu_{\text{exc}} = 4.1$ eV decreases, while at $h\nu_{\text{exc}} = 5.7$ eV, increases. The decrease in the optical absorption of F and 5.62-eV centres in the region of 600 K is accompanied by a narrow TSL peak (see Fig. 2, X-ray dose of ~ 200 kGy). High-temperature TSL was registered for the integral signal of 1.7–3.7 eV, and the thermal background emission from the heater was subtracted for the temperatures above 600 K. The inset in Fig. 3 shows the
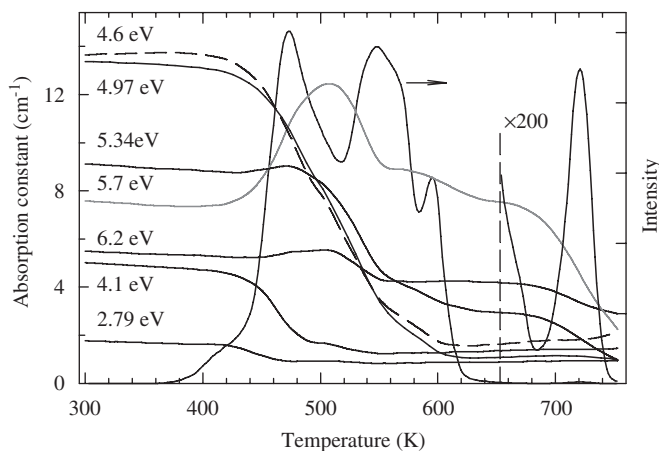
Fig. 2. Integral TSL curve ($\beta = 2.86\,\mathrm{K\,s^{-1}}$) and the annealing of optical absorption measured at several photon energies (see text for details) in a LiF:Mg,TI crystal (thickness of 0.5 mm) irradiated by X-rays at 295 K (dose of $\sim 200\,\mathrm{kGy}$). The values of absorption constants measured at 4.97 and 5.34 eV are reduced by a factor of 2.
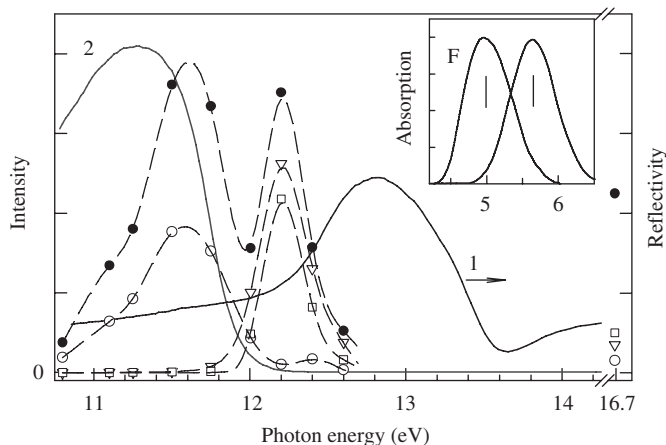

Fig. 3. Reflection spectrum (curve 1) and the excitation spectrum of 3 eV emission (2) measured for a LiF:Mg,Ti crystal using synchrotron radiation at 295 K. The creation spectra of the TSL peaks at 380 K (○○), 485 K (●●), 525 K (▽▽) and 570 K (□□) measured for LiF:Mg,Ti after isodose VUV irradiation at 295 K (see text for details). Inset shows the normalized absorption bands of F and 5.62-eV centres at 295 K (see text).

normalized absorption bands of F and 5.62-eV centres registered as a decrease in the induced optical absorption caused by an intermediate preheating $583 \to 613\,\mathrm{K}$ and $673 \to 693\,\mathrm{K}$, respectively.

The activation energies E_a and frequency factors S were determined in a multi-stage heating regime (similar to the annealing of optical absorption) using the initial sections of TSL (intensity increases exponentially), measured after every preheating. E_a equals 2.2 and 2.3 eV for the regions about 480 and 540 K, respectively, while the values of frequency factor are abnormally high (10^{20} and 10^{21} $\mathrm{s^{-1}}$). Similar values of S were reported by many authors (see, e.g., Bilski, 2002). In our opinion, abnormally high values of S tentatively represent a two-step recombination process causing the appearance of TSL. In LiF:Mg,Ti, the main annealing stage of F absorption

occurs below 600 K (see Fig. 2), i.e., in the same temperature region as the annealing of a broad and, probably, nonelementary band at 10.4–11.2 eV, which was revealed in X-irradiated LiF crystals (Davidson et al., 2002; Vasil'chenko et al., 2005) and tentatively ascribed, by analogy with other alkali halides, to trihalide $\mathrm{F_3^-}$ molecules occupying either two anion and one cation lattice sites $(\mathrm{F_3^-})_\mathrm{aca}$ or two anion sites—less stable configuration $(\mathrm{F_3^-})_\mathrm{aa}$. Such trihalide molecules are formed at a pair interaction of highly mobile H centres (formed at the decay of self-trapped excitons or at e–h recombination) with V_F and V_K centres. The thermal annealing of $\mathrm{F_3^-}$ occurs due to their thermal dissociation ($E_a \approx 2, 2{-}2.3\,\mathrm{eV}$) and sequent recombination of an H, V_K or V_F centre with an electron from two-electron impurity centre. The second electron recombines with a titanium luminescence centre or other competitive centre. The highest-temperature TSL peak in LiF:Mg,Ti is registered at 720 K, i.e., in the region of a complete annealing of F centres.

3. Defect creation by VUV radiation or ions

Fig. 3 shows the reflection spectrum and the excitation spectrum of 3 eV emission measured for a LiF:Mg,Ti crystal using synchrotron radiation at 295 K. Fig. 3 also presents the creation spectra of four TSL peaks measured for the same crystal irradiated by VUV radiation of gaseous discharge sources. After irradiation at 295 K along [0 0 1] direction by an equal quantum dose of photons at each of several energies (10^{14} photons $\mathrm{cm^{-2}}$, different irradiation time at a constant slit-width of a vacuum monochromator, optical slit of $\pm 0.15\,\mathrm{eV}$ at 12 eV, reference signal for dose normalization from a sodium salicylate), the sample was heated up with $\beta = 2.86\,\mathrm{K\,s^{-1}}$ and the lightsum of a TSL peak was taken as a measure of the centres created by VUV radiation and responsible for this peak. A dosimetric peak at 485 K is efficiently excited in a wide spectral region outside a fundamental absorption of LiF, the maximum of creation efficiency is at 11.5–11.6 eV. After irradiation by 12.1–12.7 eV photons forming anion excitons, the 485 K peak is not a dominant one, while the peak is efficiently created by 16.7 eV photons which form separated electrons and holes (e–h pairs). According to Vasil'chenko et al. (2005), a similar behaviour is typical of the TSL peak at $\sim 130\,\mathrm{K}$ connected with a hopping diffusion of self-trapped holes (V_K centres) in an LiF crystals with the traces of Mg and Ti impurities. The TSL peak at $\sim 570\,\mathrm{K}$ has been also detected in LiF and LiF:Mg,Ti crystals irradiated at 295 K. This peak is created exclusively by the photons from the region of fundamental absorption (see Fig. 3). The creation efficiency of the 570 K peak is especially high in the region of Urbach tail of exciton absorption, where photons of 12.2–12.4 eV (penetration depth of dozens of nm, absorption constant of $\sim 3 \times 10^4\,\mathrm{cm^{-1}}$) directly form already self-trapped excitons. Direct formation of anion excitons by 12.6 eV photons or e–h pairs by 16.7 eV photons leads to the appearance of the 570 K peak as well as a narrow TSL peak at $\sim 600\,\mathrm{K}$ (see also Fig. 4a). On the other hand, the TSL peaks at 570 and 600 K do not practically arise after the irradiation by 11.5 eV photons, which efficiently excite the main emission (3 eV) of LiF:Mg,Ti. The 380 K
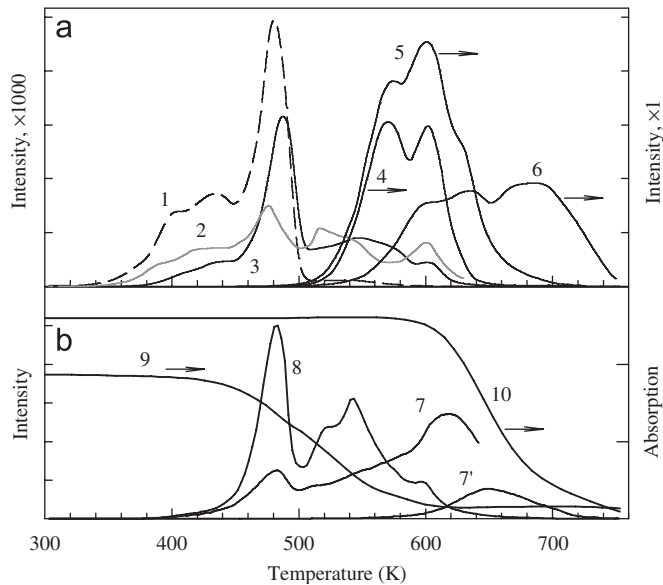
Fig. 4. TSL curves measured in LiF:Mg,Ti irradiated by photons of 11.5 eV (curve 1), 12.6 eV (2) and 16.7 eV (3), or α particles (5.1 MeV) at fluence of $10^{10}\alpha\,cm^{-2}$ (curve 4), $3 \times 10^{11}\,\alpha\,cm^{-2}$ (5) or $10^{12}\alpha\,cm^{-2}$ (6) at 295 K. TSL curves measured for a top (7 and 7′, intermediate preheating to 643 K) and a deep layer (8) of LiF:Mg,Ti irradiated by 2.44 GeV ^{238}U ions at 295 K. The annealing of F absorption (at 4.97 eV) in LiF:Mg,Ti (curve 9) and LiF (10) irradiated by X-rays at 295 K. $\beta = 2.86\,K\,s^{-1}$.

peak is excited only by the photons outside the region of the fundamental absorption.

The dosimetric peak at 485 K as well as the TSL peaks at 525, 570, 600 and 720 K are detected in LiF:Mg,Ti crystals irradiated at 295 K by an electron beam (5–20 keV), X-rays (55 keV) or α particles (see Fig. 4a). The number of e–h pairs formed by X-rays is significantly higher than that of anion excitons. However, the role of anion excitons, the formation of which is clearly detected in the spectrum of electron energy losses (Creuzburg, 1966), should not be underestimated. According to our experimental data, the intensity of the 485 K dosimetric TSL peak is practically the same at the irradiation of LiF:Mg,Ti by (11.5 ± 0.3) eV photons at 295 or 80 K. However, the intensity of this peak after X-irradiation at 295 K is at least twice as high as that after isodose X-irradiation at 80 K. An X-irradiation mainly causes the formation of separated electrons and holes, and only a part of the holes reaches spatially correlated magnesium and titanium complexes (see also Oster et al., 2007). Photons of 11–12 eV create electronic excitations localized near magnesium and/or titanium complexes providing radiative tunnel transitions with the maximum at ~ 3 eV at 295 and 80 K.

Fig. 4a presents the TSL curves measured for LiF:Mg,Ti irradiated at 295 K by α particles (5.1 MeV, range of 20 μm, flux of $\sim 2 \times 10^{6}\alpha\,cm^{-2}\,s^{-1}$) at three fluences. Intense TSL peaks at 570 and 600 K are detected for all fluences, while the peaks at 635 and 720 K arise after the sample irradiation at the highest fluence ($10^{12}\alpha\,cm^{-2}$), when there is already significant overlapping of the regions of electronic excitations created by single α particles (the average distance between

particle impacts of ~ 11 nm). Fig. 4b shows the TSL curves measured for a LiF:Mg,Ti crystal irradiated at 295 K by uranium ions (2.44 GeV, 10^{11} ions cm^{-2}). The thickness of the irradiated sample was $d = 1.1$ mm, ion penetration depth about 90 μm. The TSL was measured for a top layer with $d = 0.34$ mm and the remainder of a cleaved crystal (deep layer). Intense TSL peaks at 475 and 540 K are detected for the deep layer of the irradiated sample, while the intensity of the TSL at 450–550 K is reduced and high-temperature peaks at 620, 660 and 700 K are well pronounced for the top layer of LiF:Mg,Ti. A local heating in the tracks of swift ions is responsible for several peculiarities of radiation damage. The extremely high density of excitations formed at the irradiation of LiF and LiF:Mg,Ti by swift uranium ions (~ 25 keV nm^{-1}, average distance between ion impacts of ~ 35 nm, Schwartz et al., 2004) leads mainly to the appearance of the TSL peaks at 560–750 K related to intrinsic structural defects, while the intensity of the peaks connected with impurity centres is rather low.

According to Fig. 4b, the thermal annealing of the optical absorption of F centres differs drastically in LiF:Mg,Ti and high-dose X-irradiated pure LiF (< 3 ppm of impurities). In LiF, the annealing of F centres at 580–680 K is tentatively caused by a two-step process: thermal dissociation of $(F_3^-)_{aca}$ trihalide molecules into H and V_F centres, which sequently recombine with F and other centres. In LiF:Mg,Ti with numerous impurity centres, the interaction of V_K with H centres leads to the formation of $(F_3^-)_{aa}$ molecules, the dissociation of which at 450–580 K provides the recombination of V_K and H with F centres and the electrons localized at impurity centres. The highest-temperature TSL peak in LiF:Mg,Ti is registered at 720 K (see also Fig. 2). Stoebe and Watanabe (1975) detected intrinsic ionic conductivity in the same temperature range in highly pure LiF. In our opinion, thermal fluctuations at 700–750 K might cause the creation of cation Frenkel pairs. The study of the role of thermal fluctuations in the radiation creation of v_c and Li$^+$ interstitials or v_ch and Li^0 interstitials lies ahead.

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