

Creation of Stable Defects by VUV Radiation, Electrons and Swift Ions in LiF Crystals at 8 or 300 K¹

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Abstract – Peculiarities of electron-hole (e-h) processes and the creation processes of Frenkel defects and their associations have been investigated using VUV and thermoactivation spectroscopy methods in LiF and LiF:Mg,Ti crystals irradiated by electrons, photons (9–32 eV), α particles, x-rays, uranium and gold swift ions. The excitation spectra for F_2 (1.9 eV) and F_3^+ (2.4 eV) centre emissions have been measured at 12 K in LiF uranium-ion-irradiated at 300 K. The efficiency of these emissions sharply increases at 27–31 eV, when one exciting photon forms two electronic excitations. Optical formation of anion excitons or e-h pairs causes the creation of F and H centres in pure LiF crystals. The diffusion of I and H centres is accompanied by the TSL peaks at ~30 and ~60 K, respectively. The decay of a cation exciton (62 eV) in LiF at 8 K causes the formation of an F'-H- V_K defect triplet. The creation efficiency of F_2 centres in LiF and LiF:Mg,Ti is especially high in the tracks of α particles and swift ions). The prospects of the dosimetry of heavy particles by using the photostimulated emission of F_2 centres and TSL at 580–720 K are discussed.

1. Introduction

For a long time, wide-gap LiF crystals have been used as optical and tissue-equivalent dosimetric materials. In LiF, the energy gap is $E_g = 14.2$ eV and the creation energy of anion and cation excitons equals 13.1 and 62 eV, respectively (see [1,2] and references therein). However, the low-temperature electron-hole processes and the processes of anion or cation exciton decay into elementary radiation defects are studied insufficiently. We have performed a complex study of these processes using the methods of VUV and thermoactivation spectroscopy at 6–750 K [1,3,4]. Low-temperature decay of anion excitons with the formation of Frenkel pairs (F-H pairs) has been thoroughly studied and compared with that in earlier investigated NaCl, KCl and KBr crystals [5].

Single LiF crystals were preliminarily irradiated by an electron beam (1.5–30 keV), α particles (5 MeV), x-rays (20–50 keV) or swift ^{238}U (2.25 GeV) and ^{198}Au (2.1 GeV) ions (using linear accelerator

UNILAC of the GSI, Darmstadt). Integral (1.7–4.0 eV) thermally stimulated luminescence (TSL) at 300–775 K was measured at the heating of the irradiated samples with a constant rate of $\beta = 2.86$ K s⁻¹, using a System 310 TLD reader. Low-temperature TSL (6–300 K) for a certain emission selected through a monochromator was measured with $\beta = 10$ K min⁻¹. The aim of the study is to elucidate the interrelation between electron-hole (e-h), excitonic and interstitial-vacancy (i-v) processes in LiF and LiF:Mg,Ti.

2. Decay of anion and cation excitons into pairs and triplets of structural defects

Figure 1 presents the TSL curves measured for a LiF crystal irradiated by electrons at 6 K. The analysis of the data obtained by several experimental methods allowed to conclude that the TSL peak at 27–30 K is connected with the annealing of I centres (fluorine interstitial ions), while the peak at 50–60 K is caused by the hopping migration of H centres. At 50–60 K a mobile H recombines with a two-electron F' centre and a released conduction electron subsequently participates in the radiative recombination with a localized hole. A similar process occurs at 100–115 K, when an H interstitial gets free from an impurity trap (e.g. a Na⁺ ion). The obtained TSL data as well as the additional direct measurements of temperature dependence of the radiation-induced absorption spectra and literature data on EPR and ENDOR of H and H_A centres [6] confirm the decay of an anion self-trapped exciton (STE) into an F-H pair in the LiF crystal. According to Figs. 1b and 1c, H and H_A interstitials are created at the direct optical formation of anion excitons by 13.8 eV photons or at the recombination of electrons with self-trapped holes (V_K centres), $h\nu_{\text{exc}} = 17$ eV. The efficiency of F-H pair creation by VUV radiation at 4–8 K is low. In many alkali halides the dihalide H interstitials are oriented along close-packed <110> anion rows and a low-temperature crowdion mechanism of interdefect separation inside F-H pairs provides defect stabilization (see [5,7] and references therein). However, such crowdion mechanism is impossible in LiF and NaCl because H center is orientated along <111> and a considerable spatial separation of F and H centres, formed at the STE decay,

¹ The work was supported by Estonian Science Foundation (grant 6652) and the European Community – Research Infrastructure Action under the FP6 "Structuring the European Research Area" Programme (through the Integrated Infrastructure Initiative "Integrating Activity on Synchrotron and Free Electron Laser Science").

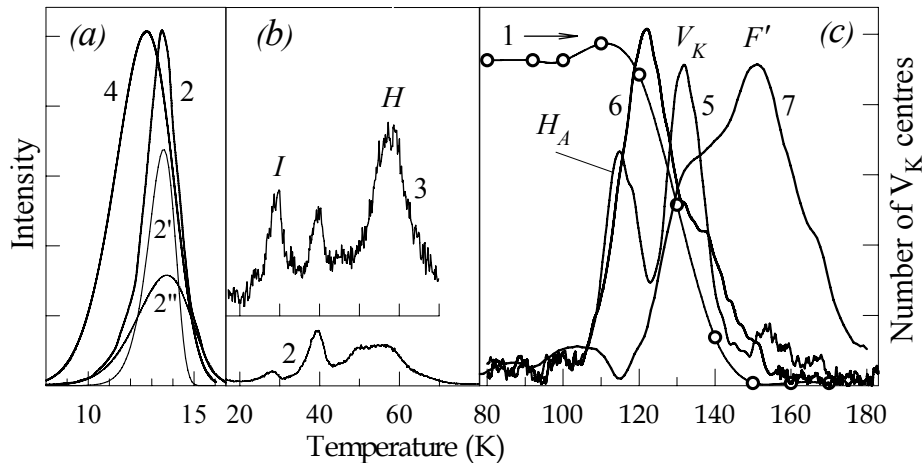


Fig. 1. The annealing of the EPR signal of V_K centres (1). The TSL measured for 3.4 eV (2, 2', 2''), 4.6 (3), 5.4 eV emissions (4) or an integral signal (5-7) at the heating ($\beta = 10$ K/min) of LiF (Korth) irradiated by 13.8 eV (5), 17 (6) and 62 eV photons (7), 30 keV electrons (2, 2', 2'', 3, 4) or x-rays (1) at 6-8 K

is impeded. The efficient displacement of an H centre from an F centre becomes possible at $T > 50$ K due to a hopping diffusion of H centres. At $T > 60$ K the mobile H centres interact with V_K centres resulting in the formation of trihalide X_3^- molecules (an absorption band at 11 eV) stable in LiF up to ~ 500 K [4,8]. Several TSL peaks were detected in a LiF crystal irradiated at 8 K by 62 eV photons selectively creating cation excitons (see Fig. 1c): the 115 K peak is connected with the decay of H_A centres, TSL at 130-140 K is accompanied by the annealing of the EPR signal of V_K centres, the thermal ionisation of F' centres takes place at 155-160 K.

Of particular interest is the origin of the intense 13 K TSL peak in irradiated LiF crystals (see [1,3,4]). The peak intensity is especially high after the irradiation of LiF by x-rays (30-50 keV) or 1.5-30 keV electrons, while the 13 K TSL peak cannot be induced after selective photoexcitation forming anion excitons (12.5-14 eV) or separated electrons and holes ($h\nu_{\text{exc}} > E_g$). In our opinion, the creation of a group of spatially correlated electronic excitations by a VUV exciting photon is needed for the appearance of the 13 K peak. This TSL peak can be formed after the irradiation of LiF at 8 K by 62 eV photons that selectively create cation excitons [3]. The 13 K peak can be suppressed by additional stimulation of the irradiated sample at 8 K by the photons that cause the ionization of F' centres. Such F' -illumination simultaneously leads to the appearance of a rapidly dumping out with time photostimulated luminescence at 5.7, 3.4 or 2.9 eV. Fig. 1a shows the TSL curves measured for 5.4 and 3.4 eV emissions connected with the direct or stepwise tunnel recombination of either of two electrons from an F' center with a V_K centre. The ~ 13 K

TSL peak has a complex structure. A low-temperature component is efficiently detected for 5.4 eV emission caused by the direct tunnel recombination of an electron from an F' centre with a V_K . The STE emission (3.4 eV) arises due to the tunneling of an electron from an F or F' centre to a V_K via an excited triplet exciton state. Fig. 1a shows two components of the ~ 13 K peak measured for 3.4 ± 0.1 eV emission (curves 2' and 2'').

The analysis of the above-mentioned results allowed us to conclude that the cation exciton in LiF decays into an anion exciton (~ 13 eV), while the rest of the energy (~ 49 eV), after intermediate processes, is expended on the creation of up to three e-h pairs. A short-wavelength analogue of the Raman effect, when excitons act as phonons at the scattering of x-rays, was theoretically considered by Agranovich and Ginzburg back in 1961 [9]. The decay of a cation exciton in LiF at 8 K causes the formation of an F-H pair spatially separated by several interion distances from a V_K centre and a conduction electron. This group of electronic excitations transforms mainly into a triplet of spatially correlated defects - F' -H- V_K .

3. Peculiarities of e-h and i-v processes in the crystals irradiated by x-rays or swift ions

According to a comprehensive study of LiF crystals irradiated at 300 K by various light and heavy swift ions ([8] and references therein), the number ratio of F_2 and single F centres in these samples is significantly higher than that in γ -irradiated LiF. We have confirmed this fact by comparing the spectra of optical absorption induced at 300 K by x-rays, α particles or ^{238}U ions in nominally pure LiF (Korth Kristalle, Germany) and LiF:Mg,Ti crystals (dosimetric material prepared in Irkutsk [10]). High density of the energy

transfer from a uranium ion to an electronic subsystem ($dE/dx > 20$ keV/nm) undoubtedly facilitates the creation of F-H pairs and other defects spatially close to each other. Thus, under the conditions of high mobility of anion vacancies at 300 K, F_2 , F_3 and more complex aggregate centres are formed. Already in 1982 the first creation spectrum of F_2 centres by synchrotron radiation of 9–20 eV was measured at 295 K using a highly sensitive luminescent method [11]. It was shown that a hopping diffusion of an anion vacancy toward an F centre causes the formation of an F_2^+ centre and its subsequent transformation into an F_2 by the trapping of a conduction electron. We have continued the investigation of these processes in LiF.

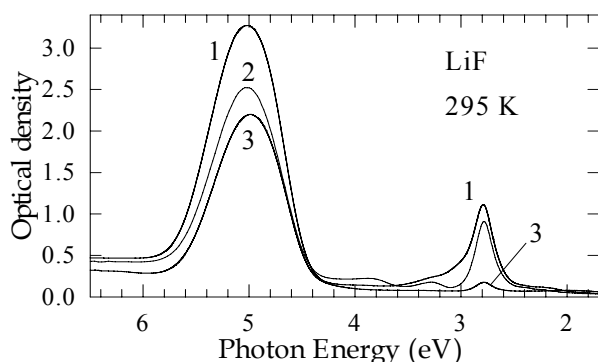


Fig. 2. The absorption spectra for highly pure LiF crystals irradiated by ^{238}U ions (1), α particles (2) or x-rays (3) at 300 K

Figure 2 presents the absorption spectra for LiF irradiated by ^{238}U ions (2.5 GeV, 2×10^{11} U/cm 2 , penetration depth of 90 μm), α particles (5 MeV, 20 μm) or x-rays (a 1-mm thick sample was uniformly coloured) at 300 K. The absorption band peaked at 2.8 eV and the emission band at 1.85 eV correspond to F_2 centres [12]. At low values of optical density, $\kappa d < 0.2$ the excitation spectrum of the 1.85 eV emission coincides with the 2.8 eV band of induced absorption. Although the absorption bands of F_2 and F_3^+ centres overlap, the emission of F_3^+ lies at 2.4 eV [12].

Figure 3 shows the excitation spectra of 1.85 eV (F_2) and 2.45 eV emissions (F_3^+) measured using synchrotron radiation at 12 K for a LiF crystal previously irradiated by ^{238}U ions (kinetic energy of 2.25 GeV at fluence of 2×10^{11} ion/cm 2). The emission of both colour centres is efficiently excited at $h\nu_{\text{exc}} > E_g = 14.2$ eV, when an exciting photon forms a single e-h pair. The emission efficiency η_L is low at 21–24.5 eV because of high values of absorption constants. The value of η_L at $h\nu_{\text{exc}} = 20$ –31.5 eV increases more than three times for F_2 and doubles for F_3^+ centre emission. The additional preheating of ion-irradiated LiF to 573 K with $\beta = 2.86$ K s $^{-1}$ decreases the values of η_L for 1.9 and 2.45 eV emissions at 13–31 eV by a factor of 3 or 1.2, respectively. Such preheating causes the thermal annealing of a significant number of F_2 centres.

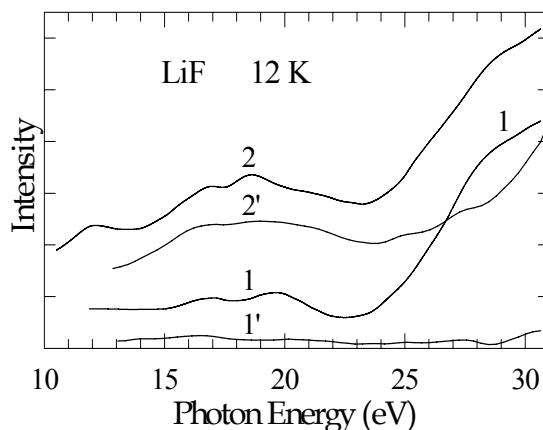


Fig. 3. The excitation spectra of 1.85 eV (1, 1') and 2.45 eV emissions (2, 2') measured at 12 K for a LiF crystal (Korth) irradiated by ^{238}U ions at 300 K (1,2) and additionally preheated to 573 K (1', 2')

According to experimental data and theoretical calculations the width of a valence band in LiF is close to 4 eV [3]. So, the energy of hot valence holes is insufficient for the creation of secondary anion excitons or e-h pairs. Therefore, threshold energy of the multiplication of electronic excitations in LiF exceeds the minimum value of $E_g + E_e = 14 + 13 = 27$ eV (E_e is the formation energy of anion excitons), but does not exceed 31 eV. Right at $h\nu_{\text{exc}} = 28$ –32 eV one can expect the creation of a primary e-h pair and a secondary anion exciton by one exciting photon, i.e. favourable conditions for the formation of F_2 centres. A similar high efficiency of F_2 centre creation was detected after the sequential irradiation of LiF by photons forming anion excitons and e-h pairs [11].

Figure 4 presents the integral TSL measured for a LiF:Mg,Ti crystal irradiated by α particles at 300 K or by electrons at 6 K. Both types of irradiation cause the appearance of the intense TSL at 480–510 K, which is widely used for γ - and x-dosimetry, while several TSL peaks at 580–720 K could be detected in α -irradiated LiF:Mg,Ti. In LiF:Mg,Ti samples x-irradiated at 300 K or 5-keV electron-irradiated at 6 K, the intensity of the TSL peaks at 600–720 K is by several orders of magnitude lower. On the other hand, the 600–720 K TSL peaks can be easily detected in a pure LiF crystal irradiated by U and Au ions or even α particles at 300 K and preheated to 573 K (see Fig. 4). The sample heating from 320 to 520 K causes the annealing of the majority of F_2 centres – see the curve of pulse annealing of the 2.75 eV-photon-stimulated emission of F_2 centres (1.9 eV) in Fig. 4. The stimulation spectra of F_2 centre emission are shown in the inset.

According to the experience obtained during the prolonged use (about 50 years) of LiF:Mg,Ti crystals and ceramics for personal γ -dosimetry, there is approximately linear dependence of a TSL (480 K peak) light sum S_{TSL} on relatively low irradiation dose (see,

e.g. [10]). At higher doses, $D \geq D_{\text{crit}}$ the dependence becomes superlinear and then reaches a saturation stage. The analysis of our experimental data has shown a sharp rise in the efficiency of e-h recombination with the creation of Frenkel defects in the region of nonlinear dependence $S_{\text{TSL}} = f(D)$ (see also [1]). The essential part of the energy absorbed by a crystal is expended on the creation of the defects stable at room temperature. However, only some of these defects remain stable in LiF at 450 K and the photo-stimulated emission of these defects does not undergo thermal quenching. These requirements are fulfilled for F_2 centres, which likely could be used for dosimetric purposes.

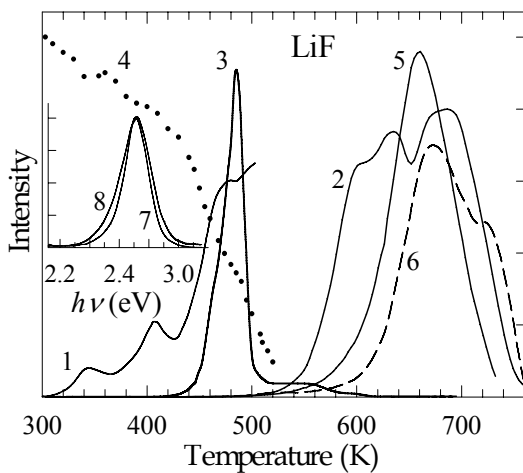


Fig. 4. The integral TSL measured at 300-510 K (1) and 500-750K (2) for a LiF:Mg,Ti crystal irradiated by 5-MeV α particles (1,2) at 300 K or by 5-keV electrons at 6 K (3). The pulse annealing of the 2.75-eV photon-stimulated emission of F_2 centres (1.9 eV) in α -irradiated LiF:Mg,Ti (4). The integral TSL measured for a LiF crystal (Korth) irradiated by ^{238}U (fluence of 2×10^{11} ion/cm 2 , curve 5) or ^{198}Au ions (6×10^{11} ion/cm 2 – 6) at 300 K and preheated to 573 K. The inset shows the normalized stimulation spectra of F_2 centre emission measured at 300 K for α -irradiated LiF:Mg,Ti (7,8) The irradiation dose for curve 8 is forty times higher than for curve 7. $\beta = 2.86$ K s $^{-1}$ (1,3,4) or $\beta = 10$ K min $^{-1}$ (2,5,6)

It should be noted that the efficiency of F_2 centre creation by x-rays decreases at $T < 230$ K, while the creation efficiency of F_2 remains high under irradiation of LiF (and NaCl) by swift ^{238}U , ^{198}Au etc. ions even at low temperatures (no freezing of defect production). It may be caused by high local heating in the ion tracks, where the density of electronic excitations is very high [13].

The processes discussed above may be useful for the development of radiation physics of solids (under conditions of high excitation density) as well as for the elaboration of personal dosimeters of fast neutrons (see [10,14–16]) required for fission and especially fusion reactors. In our opinion, photostimulated emission of F_2 centres and high-temperature TSL (580–720 K) in LiF are promising factors for the detection of fast neutrons.

Acknowledgements

We would like to thank Prof. Cheslav Lushchik for valuable and stimulating discussions.

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