ISSN 1063-7834, Physics of the Solid State, 2008, Vol. 50, No. 9, pp. 1667–1670. © Pleiades Publishing, Ltd., 2008.
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PROCEEDINGS OF THE XIII FEOFILOV SYMPOSIUM "SPECTROSCOPY OF CRYSTALS DOPED BY RARE-EARTH AND TRANSITION-METAL IONS"

(Irkutsk, July 9–13, 2007)

Thermo- and Photostimulated Luminescence in LiF : Mg,Ti Single Crystals Irradiated by Ions and VUV Light

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Abstract—A coordinated study of the relaxation of optical absorption induced by vacuum ultraviolet radiation, x-rays, and α-particles, as well as of photo- and thermostimulated luminescence (TSL) of LiF : Mg,Ti crystals (TLD-100) in the 295–750-K interval, has revealed that TSL regions characterized by activation energies E_a = 2.2–2.4 eV and anomalously high frequency factors $p_0 = 10^{21}$–10^{22} s^{-1} alternate with regions where E_a = 1.5 eV and $p_0 = 10^{12}$–10^{14} s^{-1}. The relative intensities of the TSL peaks produced by UV illumination (10–17 eV) differ strongly under the conditions of selective photon-induced generation of anion excitons, free electrons and holes, or near-impurity electronic excitations. The latter are responsible for the high efficiency of tunneling radiative (involving titanium centers) or nonradiative (involving hydroxyl ions) recombination. The analysis of TSL peaks of LiF : Mg,Ti and LiF took into account two-step processes, namely, thermal dissociation of three-fluorine F_3^- molecules and recombination of the products of their decay (V_K and V_F centers, H interstices).

PACS numbers: 61.72.jn, 78.60.Kn, 78.55.Fv
DOI: 10.1134/S106378340809014X

1. Ions of the transition metal titanium are used widely in a variety of crystal matrices (in particular, as emitters in laser materials). The titanium centers are studied by highly informative methods of polarization spectroscopy developed by Feofilov [1]. The wide-gap, tissue-equivalent lithium fluoride (E_g = 14.2 eV) doped by titanium ions has been employed for many years in personal γ-ray dosimetry [2–4]. Thermally stimulated luminescence (TSL) of irradiated LiF : Mg,Ti, which is measured under constant heating rate β = 1–3 K s^{-1}, is dominated by a maximum peaking at ~480 K, whose light sum S reproduces linearly the absorbed dose up to ~10 Gy. As the dose is increased still more, one observes a region of superlinear scaling $S(D)$ followed by saturation and even attenuation of the dosimetric peak.

The development of LiF : Mg (100 ppm), Ti (10 ppm) single crystals, which were grown at the Institute of Geochemistry (Irkutsk) and described briefly in monograph [3], stimulated investigation of complex electron–hole (e–h) processes in TLD-100 γ dosimeters, as well as an analysis of the potential of these materials in the dosimetry of fast neutrons or heavy ions, which were introduced as a tool for selective destruction of cancer cells.

The present report is a necessarily brief account of the experimental results bearing not only on the usually considered e–h processes but on the exciton and interstitial–vacancy (i–v) processes as well. The latter give rise to formation of pairs of Frenkel anion and more complex groups of defects in irradiation of both LiF : Mg,Ti and other alkali halide crystals [5–7]. The LiF : Mg,Ti single crystals grown in Irkutsk were irradiated by x-rays, α-particles and vacuum ultraviolet (VUV) light. In the latter case, irradiation produced selectively anion excitons (12.2–13.8 eV), free electrons and holes (15–17 eV) and some near-impurity and near-defect electronic excitations (10–12 eV). The interpretation of the pioneering results for LiF : Mg,Ti presented below is based on the data obtained in our coordinated study of the optical and thermal activation characteristics of pure LiF single crystals, which have been published recently [8–11].

2. Figure 1 presents the induced absorption spectra for a 0.5-mm-thick LiF : Mg,Ti crystal plate colored uniformly throughout its thickness by irradiation with x-rays (55 eV, 20 mA, 4 h, Al filter) at 295 K. The spectra were measured at T_0 = 295 K in the 1.8–6.5-eV interval with a JASCO V-550 spectrophotometer (base-

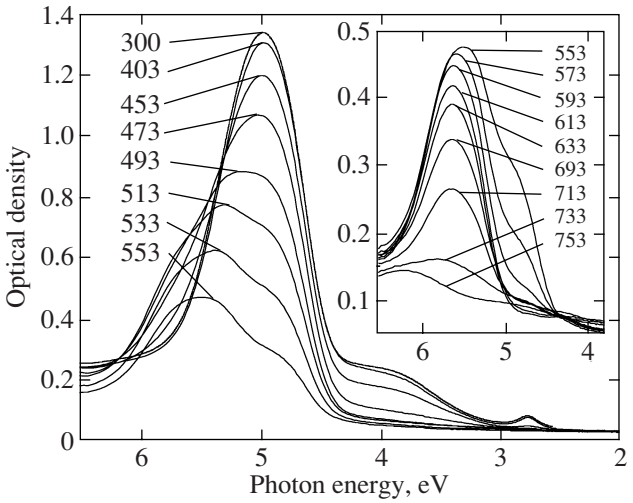

Fig. 1. Spectra of induced optical absorption in LiF : Mg,Ti irradiated by x-rays at 295 K. The spectra were measured at 295 K following intermediate annealing of the irradiated crystal to temperatures specified in the figure (in kelvins).

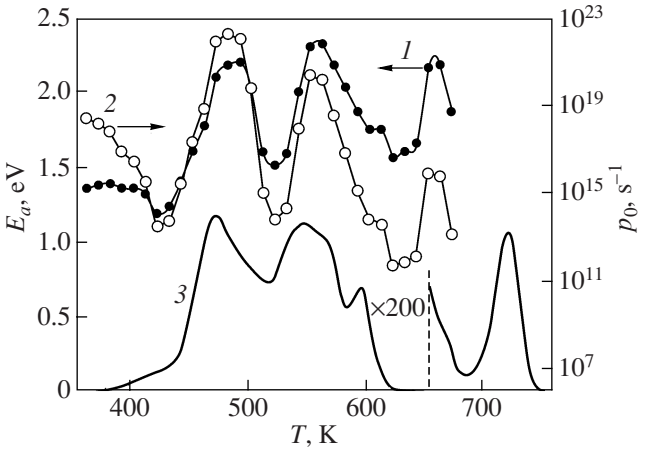

Fig. 2. (*1*) Activation energies E_a and (*2*) frequency factors p_0 for the TSL regions, which were measured under stepped heating (see text) of the LiF : Mg,Ti crystal preliminarily irradiated by x-rays. (*3*) TSL curve measured in the entire temperature interval covered. Heating rate $\beta = 2.86$ K s^{-1}.

line oscillation level $OD \le 0.001$). Following irradiation at T_0, the crystal was heated in SYSTEM 310 TLD Reader with a constant rate $\beta = 2.86$ K s^{-1} up to T_i and cooled rapidly (by keeping it for a few seconds in a nitrogen environment) to T_0, after which the absorption spectrum was again measured. After this, the crystal was heated up to $T_{i+1} = T_i + \Delta T$ etc. The intermediate heating temperature was varied from 343 to 753 K.

An analysis of induced absorption spectra measured under such ramped heating to 753 K revealed a number of distinct absorption bands, namely, an F center band peaking at 4.97 eV with a halfwidth $\delta = 0.79$ eV; a narrow F_2 center band with the maximum at 2.8 eV and $\delta = 0.2$ eV; a band peaking at ~5.62 eV and with $\delta = 0.78$ eV; a 6.2-eV band corresponding to absorption by complex titanium complexes [3, 12], as well as a band peaking at 4.1 eV which derives from electrons captured by Mg^{2+} ions. The F_2 centers are completely annealed by 473 K, while annealing of nearly all F centers requires heating up to 553 K. At this temperature, the band at ~5.62 eV, which is completely annealed by 753 K, reaches maximum intensity. We assign the ~5.62-eV band to a two-electron magnesium center with an anion and a cation vacancies. These centers are created under irradiation as a result of exciton decay near the magnesium center, or in complex F center transformations occurring in subsequent heatings and coolings.

Figure 2 presents the TSL curve (the luminescence was isolated with a filter in the 1.7–3.7-eV interval) for LiF : Mg,Ti measured throughout the heating interval of 300–753 K (with the background generated by heater radiation subtracted at temperatures $T > 600$ K). The initial parts of the exponential growth of the TSL intensity measured at intermediate heatings up to T_i were used to calculate by standard techniques the activation energies E_a and frequency factors p_0, which are also shown in Fig. 2. For LiF : Mg,Ti, the parts of the spectra containing large E_a (2.2–2.4 eV) and anomalously high frequency factors p_0 (10^{21}–10^{22} s^{-1}) alternate with sections featuring considerably smaller E_a and "normal" frequency factors (10^{12}–10^{14} s^{-1}) which do not exceed the limiting frequencies of ion vibrations in the LiF crystal. A suggestion was ventured [13] that the parts with large E_a and p_0 are related with unusual two-step processes giving rise to TSL peaks, more specifically, thermal dissociation of the three-fluorine F_3^- molecules produced in the irradiation and recombination of the products of their decay with F centers or impurity centers. The F_3^- molecules could break up in two H centers, namely, an H center and a self-trapped hole (V_K center) or an H center and a hole localized near a cation vacancy, the so-called V_F center ($v_c h$).

Purposeful insertion into the LiF matrix of an Ti^{4+} impurity [2] in the presence of Mg^{2+} ions in the crystal brings about an increase of the dosimetric TSL peak in intensity. The structurally complex titanium centers described in [3, 12], which are responsible for the formation of the 3.1-eV luminescence, are involved in TSL when heated to ~570 K [3].Processes likely to occur in the region of the dosimetric peak at 480 K in an irradiated LiF : Mg,Ti crystal were considered in [14, 15]. In this complex model, an association of three $Mg^{2+}v_c^-$ dipoles is located close to a complex titanium center containing, in addition to Ti^{4+} (or Ti^{3+} after electron capture), O^{2-} and OH^- ions The anomalously large p_0 of the dosimetric TSL peak is related by the authors with the tunneling process of radiative recombination.

3. The radiation processes occurring when crystals are irradiated by particles and protons of high energies exceeding by far the band gap are extremely complex. The situation can be simplified considerably by studying the TSL in a LiF : Mg,Ti crystal irradiated selectively by photons of a variety of energies (from 11.0 to 16.7 eV). Figure 3 plots TSL curves for a LiF : Mg,Ti crystal preirradiated by equal quantum doses of 10^{14} cm^{-2} of photons of different energies at 295 K (except for the 16.7 eV photons). The dosimetric peak at 480 K, just as the low-temperature peaks at 380 and 425 K, are produced with the maximum efficiency by photons of energies 11.50–11.75 eV, outside the region of fundamental absorption of LiF. In this spectral region, electronic excitation of near-impurity centers and defects takes place. The high-temperature peaks at 525, 570, and 600 K exhibit efficient excitation after irradiation in the 12.2–12.4-eV region, i.e., in the region of the Urbach tail of exciton absorption, where the exciton becomes self-trapped immediately after the creation. Part of photons with an energy of 12.6 ± 0.15 eV create mobile free excitons as well. In the photocreation of free electrons and holes, part of the electrons recombine with self-trapped holes (V_K centers) to form self-trapped excitons, which, in their turn, break up with formation of Frenkel defects. Another part of electrons and holes become localized at the impurity centers. Significantly, two or three ramped heatings up to 653 K alternating with fast coolings give rise to a redistribution of impurity defects over the crystal lattice, which affects the TSL peak intensity ratios (particularly of the 380-K peak). This results in a difference between TSL curves obtained for "fresh" crystals and those studied more than once (see, for instance, curves *6* and *7* in Fig. 3).

Of particular interest is the intensity ratio of the TSL generated after equal-dose irradiation at 80 or 295 K. X-ray irradiation at 80 K gives rise to formation in the crystal of both free electrons and holes and of excitons, with the holes becoming self-trapped as V_K centers, which at low temperatures are immobile and not involved in the recombination luminescence of the impurity centers. If the crystal, however, is irradiated at 295 K, the V_K centers are mobile and become trapped at the impurity luminescent centers. This is why the TSL intensity of the dosimetric peak of the crystal irradiated by x-rays at 80 K is approximately one half that obtained after irradiation at room temperature. On the other hand, the intensity of the 480-K TSL peak measured under equal-dose illumination of the crystal by 11.5-eV photons, which produce localized near-impurity excitations, at 80 K is only 20% lower than that at 295 K. This observation matches with the hypothesis [14, 15] of the recombinations responsible for the dosimetric peak being of the tunneling nature.

4. Particular attention was paid to thermal stability of the F_2 ($v_a^+ e v_a^+ e$) centers whose characteristics were studied in considerable detail in [16, 17]. Figure 4 presents curves of a pulsed annealing of the F_2-center

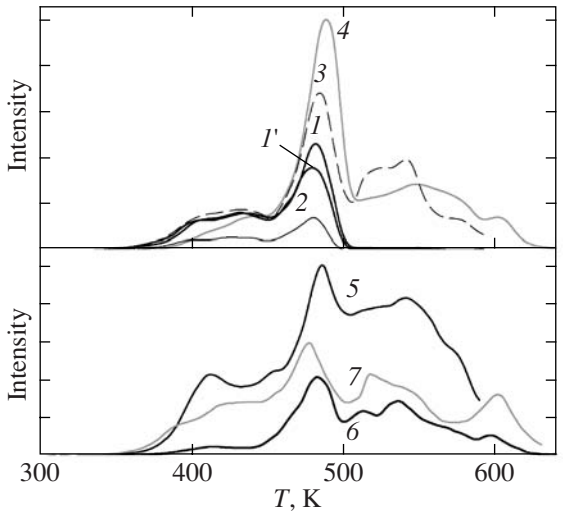

Fig. 3. TSL curves of the LiF : Mg,Ti crystal irradiated by photons with energies of (eV) (*1*) 11.5, (*2*) 11.1, (*3*) 12.0, (*4*) 16.7, (*5*) 12.4, and (*6*, *7*) 12.6 eV at 295 K and by photons with an energy of (*1*') 11.5 eV at 80 K. Heating rate β = 2.86 K s^{-1}.

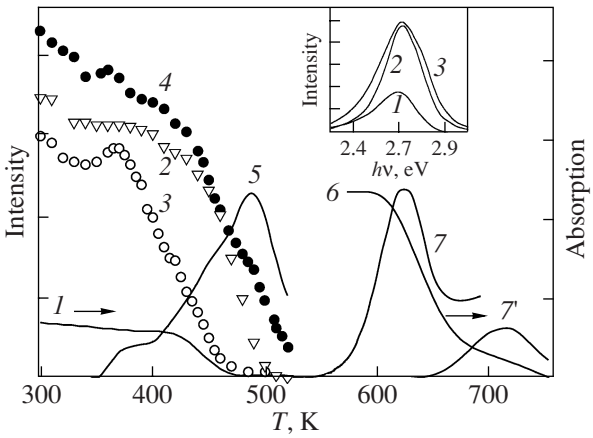

Fig. 4. (*1*, *6*) Annealing of the F_2-center optical absorption, as well as pulsed annealing of (*2–4*) PSL and (*5*, *7*, *7*') TSL in (*1–5*) LiF : Mg,Ti and (*6*, *7*, *7*') LiF crystals irradiated by (*1*, *2*, *6*, *7*, *7*') x-rays and α particles with doses of (*3*) 10^{11} and (*4*, *5*) 10^{12} cm^{-2}. Heating rate β = (*1*, *6*, *7*, *7*') 2.86 and (*2–5*) 0.17 K s^{-1}. The inset shows 1.85-eV luminescence excitation spectra of the LiF : Mg,Ti crystal preirradiated by (*1*) x-rays and α particles with doses of (*2*) 10^{11} and (*3*) 10^{12} cm^{-2}.

1.85-eV luminescence stimulated by photons of 2.75 eV. The inset to the figure plots F_2 center luminescence spectra excited by equal quantum doses of incident photons and measured at 295 K for a LiF : Mg,Ti crystal, which had been irradiated by α-particles or x-rays. The spectra excited by low irradiation doses, where the optical density in the region of the F_2 center absorption band is less than 0.5, largely reproduce the profile of the F_2 absorption band. For crystals irradiated

by large doses of α-particles or x-rays, the profile of the stimulated spectrum broadens slightly. Formation of the F_2 centers in the LiF crystal depends on the dose and intensity of the radiation. In our experiments, we have not been able to detect formation of the F_2 centers under VUV illumination of the crystal, even with the highly sensitive method of photostimulated luminescence (PSL). Figure 4 displays thermal bleaching curves of the narrow absorption bands of F_2 centers for the LiF : Mg,Ti and LiF crystals subjected to x-rays at 295 K. In the LiF : Mg,Ti crystal, nearly all the F_2 centers disappear already at 380–460 K (see also Fig. 1). In the high-purity LiF crystal containing not over 3 ppm of impurity ions, the F_2 centers become annealed only at 580–680 K. The concept developed in [13] suggests thermal dissociation in this temperature region of the three-halogen molecule $(F_3^-)_{aca}$ (oriented along the [100] direction and occupying two anion and one cation vacancies) with formation of a high-mobility H interstitial and a V_F center. The low-temperature annealing of F_2 centers at 420 K in LiF : Mg,Ti is probably the result of thermal dissociation of H–H pairs. Interaction of single H interstices with the F centers culminates in nonradiative recombination restoring the regular lattice. H interstices interacting with F_2 centers produce an F center, which becomes ionized at the expense of the energy liberated in recombination. The capture of the released electron by the magnesium center brings about growth of the number of two-electron centers with absorption of ~5.62 eV.

We heated LiF : Mg,Ti irradiated by α-particles to study the PSL, which was observed against the background of simultaneously emitted TSL in the red region of the spectrum (through a KS-13 filter), with peaks at 440 and 490 K. In this case, annealing of F_2 centers occurs in thermal dissociation of the $(F_3^-)_{aa}$ molecule which carries a positive effective charge with respect to the lattice. One observes mobile products of the decay, namely, an H interstices and a V_K center. For the α-particle irradiation doses used by us (10^{11} and 10^{12} cm^{-2}), the average distance between their tracks is 35 and 10 nm. For low doses, the electronic excitations created around the axis of a single track interact only weakly with those of the neighboring tracks. By contrast, for the α particle dose of 10^{13} cm^{-2}, the interaction among electronic excitations belonging to neighboring particles is high, and this affects noticeably both the TSL and the pattern of annealing of an F_2 flash. An increase of the excitation density in this region of irradiation doses produces a sizable effect on the interaction of H interstices both with one another and with the V_K and V_F centers, whose lifetimes are short at temperatures substantially in excess of the point at which their hopping diffusion becomes activated (130 and 250 K, respectively; see, for instance, [8]). At high irradiation doses one succeeds in detecting in LiF : Mg,Ti TSL peaks with maxima at 650 and 725 K. The 725-K peak (curve 7' in Fig. 4) stands out clearly following a preliminary heating at 693 K. At 700–750 K, intrinsic ionic conduction dominates already in LiF [2], and thermal fluctuations can probably create cation Frenkel defects.

ACKNOWLEDGMENTS

We are grateful to Ch.B. Lushchik, Academician of the Estonian Academy of Sciences, for stimulating interest in this work and fruitful discussions.

This study was supported by the Estonian Scientific Foundation (grant no. 6652).

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Translated by G. Skrebtsov