COLOR CENTERS INDUCED IN LIF CRYSTALS BY LOW TEMPERATURE ELECTRON IRRADIATION

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Tayanch so'zlar: litiy ftorid (LiF), elektron nurlantirish, rang markazlari, Li nanokolloidlari.
Ключевые слова: фторид лития (LiF), электронное облучение, центры окраски, наноколлоиды Li.
Key words: lithium fluoride (LiF), electron irradiation, color centers, Li nanocolloids.

Introduction. Lithium fluoride (LiF) is a well-known luminescent and optical material. The refractive index of LiF n=1.39 is one of the lowest among dielectric materials, while energy band gap ∼14 eV, one of the largest. LiF possesses one of the highest UV transmissions among all materials, therefore it was the first material used in practice for ionizing radiation thermoluminescent dosimetry. The color centers and their luminescence effects in LiF have been studied and applied in practice for several decades [1-12,14-16]. Since that time several versions of LiF-based TL detectors were developed, differing in methods of synthesis, doping and properties. Two of them: LiF:Mg,Ti and LiF:Mg,Cu,P are probably the most widely used TL detectors in the world [2]. Yu.L. Gusev and co-authors [3] irradiated LiF crystals with electron accelerated to an energy of 3 MeV at a beam current density of 1 μA/cm^2 to create laser elements on F_2^+ and F_2- color centers. E.F.Martynovich and co-authors [4] investigated the red laser generation on F_2 centers in LiF crystals without an external resonator after irradiation with accelerated electrons, and it was noted that the advantage of such irradiation over gamma irradiation is not limited to the possibility of quickly reducing high concentrations of color centers (CC). Investigation of radiation defects induced by the irradiation of LiF crystals with 5-or 10-MeV Au ions (fluencies of 10^{11}–2×10^{14} ions/cm^2; flux varies by 2 orders of magnitude) at room temperature has been performed using the methods of optical absorption and high-temperature (400–750 K) thermoactivation spectroscopy. The creation efficiency of color centers (F, F_2, F_3,...) and colloids drastically depends on both the fluence and ion flux beam current. Besides impurity magnesiumcolloids with the absorption band peakedat 4.4–4.6 eV, the broad absorption band at 2.3–3.3 eV related to intrinsic Li colloids is reliably distinguished. The creation efficiency of Li colloids by 5-MeV Au ions was found to be lower than that by 10-MeV ions, which generate secondary electrons with higher energies sufficient for the creation of cation excitons (~62 eV). The cation exciton decays, in turn, with the formation of a group of spatially close F-centers. At a high ion flux, the next bombarding ions hit the same crystal region with a short time delay (10-100 s) and also form, after similar intermediate processes, the groups of F centers that participate in the formation of stable agglomerates of several F_3 or even more complex centers, which serve as stable (up to 620 K) seeds for nanosize Li colloids [5]. Absorption spectroscopy was performed to study the effects of thermal annealing on the aggregation of color centers in LiF crystals irradiated with different ions between carbon and uranium of MeV-GeV energy. The beam parameters such as energy, energy loss, and fluency have a pronounced influence on the initial defect composition and concentration as well as their evolution upon thermal annealing. A distinct phenomenon was observed, viz., the enhancement of F_n centers for annealing temperatures between 500 and 700 K, followed by Li colloid formation above 700 K. The phenomenon requires specific irradiation conditions whereas the formation of Mg colloids from Mg impurities occurs in all irradiated crystals [6]. The authors of [7] investigated the influence of thermal treatment at temperatures up to 400 °C on absorption and photoluminescence (PL) spectra as well as fluorescent nuclear tracks in irradiated LiF crystals. They found that PL spectral measurements in the irradiated crystals kept at a temperature about 80 °C show a considerable increase in PL intensity at 525 nm of F_3^+ color centers. This enhancement of PL intensity allows for the microscopic imaging of the fluorescent nuclear tracks using only F_3^+ emission, which is possible only at 80 ^{o}C. It was also found that heating the irradiated crystals before measurement at temperatures from 100 °C to 200 °C increases the concentration of F_3^+centers. Others reported the growth of complex color center concentrationafter thermal annealing at 130 °C [8, 9]. Such effects were explained by the enhancement of F_2 and F_3^+ concentrations caused by the interaction of single F and F_2 centers [6, 8]. Optical absorption and PL spectra were measured in lithium fluoride crystals after coloration with gamma irradiation to five different doses for dosimetric applications [10]. By accurate Gaussian best-fit procedures of the absorption measurements the peak intensity of F and M bands and the concentrations of F, F_2 and F_3^+ color centers in gamma irradiated LiF crystals at different doses were obtained. A quadratic relationship between F and F_2 defect concentrations as a function of the irradiation dose was found [10].

Previously, we [11] studied the absorption and PL spectra, micro hardness, and also conducted an X-ray structural analysis of LiF crystals irradiated with gamma-quanta flux in an active zone of shut-down reactor and in the ^{60}Co source at the gamma dose rate of 7.65 Gy/s. In addition to the known absorption bands of defects induced by the irradiation in the fluorine sub lattice, the structure phase analysis revealed the gamma-irradiation-induced nanoparticles of the LiOH phase and it was shown that the nano-phase and color centers were generated more efficiently in shut-down reactor due to the higher gamma-energy range and dose rate than in the monochromatic ^{60}Co source. Later in [12], we detected the broadening of the absorption band of 300–340 nm (growth of the R_1 band) and found the R_2 band in the region of 370–380 nm after irradiation by 4 MeV electrons at room temperature, which did not reach saturation in the electron dose range of 10^{13}–10^{15} cm^{-2}. The both bands are associated with F_3 centers by the most researchers [7-12]. This list of references presented the effect of elevated temperatures on aggregation of fluorine vacancies and metal nanocolloids.

The aim of this work is a comparative study of radiation defects created by an electron beam in LiF crystals at different temperatures much lower than the room temperature so as to minimize the effect of thermal diffusion and distinguish the radiation enhanced migration of vacancies or interstitials to assemble point defects into complexes.

Objects and experimental techniques. Since extinction densities differ very much for a metallic nano-colloid and insulating wide band crystal, they can be identified by the absorption contrast. The nano-colloid sizes and volume fraction are determined by the absorption band wavelength, width and maximum [13]. Their evolution can be followed by means of irradiations to various doses in a proper temperature interval [14]. Optically pure (no metal impurities above 10^{15} cm^{-3}) LiF crystals were irradiated on the top of the sample holder loaded in the liquid nitrogen filled dewar, while the open sample surface was cooled to ~165 K, and at a temperature of ~288 K during the irradiationat the electron accelerator "Elektronika U-003". The accelerator operated under the following conditions: average electron energy 5 MeV, current pulses $4.5 \cdot 10^{-6}$ s, beam current density 400 nA/cm^2, distance from exit accelerator window to the sample holder 48.5 cm, integral fluences $5 \cdot 10^{14}$ cm^{-2} and 10^{15} cm^{-2}. Optical absorption spectra were recorded on a Perkin Elmer Lambda-35 UV/VIS Spectrophotometer in the range of 190–1100 nm. Immediately after completing the irradiation by turning off the electron beam, the sample holder was turned up-down so as to cool the irradiated samples to 77 K until the optical measurements and conserve the shallowest electron and hole charge traps.

Results and discussion. The absorption spectra of LiF crystals taken before and after irradiation at 165 and 288 K are shown in Fig.1, Fig.2. It can be seen that the spectrum of the non-irradiated sample contains only a weak band at 205 nm, probably due to α-centers [5]. When irradiated with an electron beam, LiF crystals acquired a green color more intensive and stable after irradiation at 165 K than 288 K. In the absorption spectrum of crystals irradiated at 165 K with an electron fluence of $5 \cdot 10^{14}$ cm^{-2} and heated to 300 K (Fig.1, Fig.2, curve 3), *F*- (band with a maximum at 250 nm) and $F_2(M)$ - centers (band at 445 nm) appear.

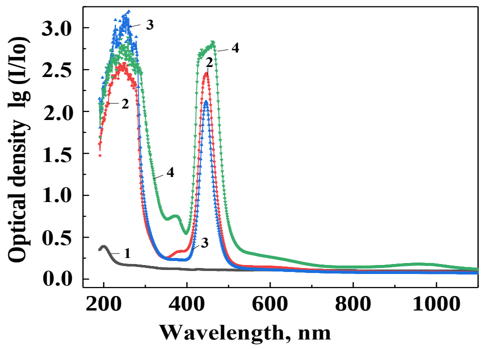

Fig. 1. Absorption spectra of LiF crystals: 1–non-irradiated, 2–irradiated at 288 K, fluency $5 \cdot 10^{14} cm^{-2}$; 3–165 K, $5 \cdot 10^{14}$ cm^{-2}; 4 – 165 K, 10^{15} cm^{-2}.

The intensity of *F*-band is almost 1.5 times greater than that of *M*-band (curve 3). Other bands are not detected. In contrast, in the spectrum of samples irradiated at 288 K to the same electron fluency (curve 2), in addition to the *F*- and *M*- bands, a low-intensity band at 375 nm also appears, caused by the $F_3(R)$-centers. This experiment proves that at 165 K *R*-centers can not be assembled from *F*- and *M*- due to localization of charge carriers in shallow traps, while at 288 K these traps are empty and *R*- centers can be produced by assembling *F*- and *M*-centers. Comparison of spectra 2 and 3 shows, that increasing the irradiation temperature from 165 to 288 K decreases *F*-centers and increases F_2 or *M*- (440 nm) and F_3 or *R*- (375 nm), i.e. temperature assisted aggregation of separated centers.

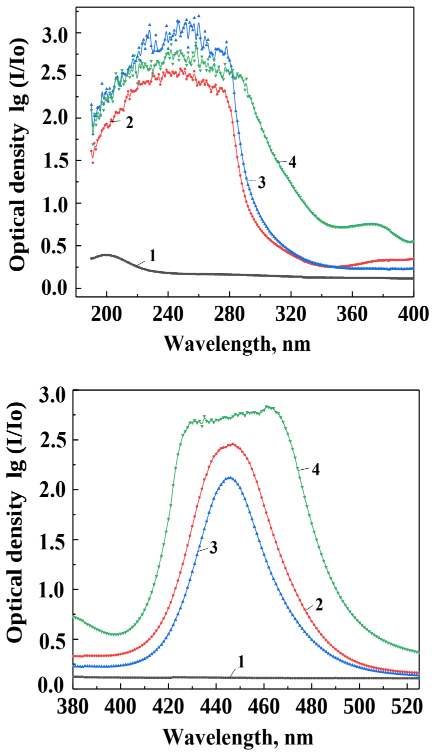

Fig. 2. Absorption spectra fragments of LiF crystals: *1–non-irradiated (21×15.1×3 mm), 2–irradiated on 15.03.2023 at 288 K to the fluency of $5 \cdot 10^{14}$ cm^{-2}, 200 s; 3–on 15.01.2025 (26×13×38 mm) at 165 K to $5 \cdot 10^{14}$ cm^{-2}, 200 s; 4–on 22.01.2025 (16×16×3 mm) at 165 K to 10^{15} cm^{-2}, 400 s.*

Comparison of the spectra (curves 2 and 3) obtained under the same irradiation conditions but at different temperatures (165 and 288 K) and recorded at room temperature 300 K showed a noticeable decrease in the intensity of the *F*- and an increase in the intensity of the *M*-absorption bands and the appearance of $F_3(R)$-centers under high-temperature irradiation, associated with the suppression of the mobility of point defects and an increase in the probability of their aggregation at 288 K than at 165 K, which ensures more efficient accumulation of F_2- and F_3-centers at high temperatures. With a further increase in the irradiation dose at a temperature of 165 K (curve 4), not only is a slight decrease in *F*- and an increase in *M*-and *R*- centers observed, but also the appearance of additional wide bands of $R^+(F_3^+)$ centers (in the region of 460 nm), $M^+(F_2^+)$ centers (in the region of 620 nm) and $M^-(F_2^-)$ centers (in the region of 960 nm), associated with charge exchange at *M*- and *R*- centers [15-17]. The anomalous broadening of the *F*-absorption band in the long-wavelength region (curve 4) indicates an increase in the formation of nanoparticles at high irradiation doses even at low irradiation temperatures.

Conclusion. This study demonstrates that electron irradiation of LiF crystals leads to the formation of various color centers, whose optical characteristics depend on both irradiation dose and temperature. Comparison of spectra obtained under the same irradiation conditions but at different temperatures (165 and 288 K) and recorded at room temperature showed a noticeable decrease in the intensity of the *F*- and an increase in the intensity of the *M*-absorption bands and the appearance of F_3 (*R*)-centers under high-temperature irradiation, associated with the suppression of the mobility of point defects and an increase in of their aggregation at 288 K than at 165 K, which ensures more efficient accumulation of F_2- and F_3-centers at high temperatures. Splitting of the *F*-absorption band to the long-wavelength region indicates an increase in the formation of nanoparticles at high irradiation doses even at low irradiation temperatures. The stable color is associated with neutral F_n centers and Li colloids, the absorption of which can be used for dosimetry (at higher doses).

Acknowledgments. The researchis supported by basic funding allocated to the Institute of Nuclear Physics of the Academy of Sciences of the Republic of Uzbekistan by the decree PP-4526.

References

1. Daniels F., Boyd C.A., Saunders D.F. Thermoluminescence as a Research Tool. // Science. 1953. V. 117. – P. 343-349.
2. Bilski P. Lithium Fluoride: From LiF:Mg,Ti to LiF:Mg,Cu,P // Radiation Protection Dosimetry. 2002, Vol. 100, Nos 1-4. – P. 199-206.
3. Gusev Yu.L., Marennikov S.I., Chebotaev V.P. Generation at F_2^+ and F_2^- color centers in LiF crystal in the spectral region of 0.88-1.2 μm // Letters to the Journal of Technical Physics. 1977, Vol. 3, Issue 7. – P. 305-307.
4. Luminescence and related phenomena. Proceedings of the VII All-Russian School-Seminar / Edited by prof. E.F.Martynovich. – Irkutsk: Publishing house of Irkutsk University, 2001. – P. 214.
5. Lushchik A., Lushchik Ch., Schwartz K., Vasil'chenko E., Papaleo R., Sorokin M., Volkov A.E., Neumann R. and Trautmann C. Creation of nanosize defects in LiF crystals under 5- and 10-MeV Au ion irradiation at room temperature. // Physical Review B. 2007, V.76. – P. 054114.
6. Schwartz K., Volkov A.E., Sorokin M.V., Neumann R., Trautmann C. Effect of irradiation parameters on defect aggregation during thermal annealing of LiF irradiated with swift ions and electrons. // Phys. Rev. B, 2010, 82. – P.144116.
7. Sankowska M., Bilski P., Marczewska and B., Zhydachevskyy Y. Influence of Elevated Temperature on Color Centers in LiF Crystals and Their Photoluminescence. // Journal of Materials Science 2023, Vol. 16, Issue 4. – P.1489.
8. Dauletbekova A., Schwartz K., Sorokin M.V., Maniks J., Rusakova A., Koloberdin M., Akilbekov A., Zdorovets M. LiF crystals irradiated with 150 MeV Kr ions: Peculiarities of color center creation and thermal annealing. // Nucl. Instrum. Methods Phys. Res. Sect. B. 2013, 295 (Suppl. C). – P.89-93.
9. Akilbekov A.T., Russakova A.V., Dauletbekova A.K., Koloberdin M.V., Baijumanov M.Z., Zdorovets M.V. Generation of color centers when annealing LiF crystals irradiated by Kr ions with an energy of 150 MeV. // Bull. Russ. Acad. Sci. Phys. 2014, 78, – P. 535-539.
10. Vincenti M.A., Baldacchini G., Kalinov V.S., Montereali R.M. and Voitovich A.P. Spectroscopic investigation of *F*, F_2 and F_3^+ color centers in gamma irradiated lithium fluoride crystals. // IOP Conference Series: Materials Science and Engineering. 2010. – P. 1-6.
11. Mussaeva M.A., Ibragimova E.M., Kalanov M., Muminov M.I. Formation of nanodefects in LiF crystals under gamma irradiation. // Physics of the Solid State, 2006, V. 48, No. 12. – P. 2295-2299.
12. Mussaeva M.A., Ibragimova E.M., BuzrikovSh.N., Ismatov N.B. Mechanisms of creation of complex radiation defects in LiF crystals under electron irradiation. / International Conference, "Fundamental and Applied Issues of Physics", June 13-14, 2017 (Phys. Technology Inst.), 2017. – P. 62-67.
13. Mie G. Beiträge zur optik trüber medien speziell kolloidaler metallösungen // Annalen der Physik, 1908, Vol. 330, Issue 3. – P. 377-445.
14. Ibragimova E.M., Mussaeva M.A., Kalanov M.U., Mukhamedshina N.M. and Sandalov V.N. Lithium nanoparticles in lithium fluorite crystals. // J. Phys.: Conf. Ser. 2012. 391. – P. 012172.
15. Parfianovich I.A., Khulugurov V.M., Lobanov B.D., Maksimova A.T. and others. Luminescence and stimulated emission of color centers in LiF. // Izv. USSR Academy of Sciences, ser. Physics and Mathematics Sciences, 1979, Vol. 43, № 6. – P. 1125-1132.
16. Bosi L., Bussolati C., Spinolo G. Lifetime of the first excited state of the F_2^+ center in LiF. // Physics Letters A, 1970, Vol. 32. Issue 3. – P. 159-160.

REZYUME. Optik jihatdan toza LiF kristallarining yutilish spektrlari 5 MeV energiyali elektronlar bilan, 400 nA nur oqimi zichligida va $5{\cdot}10^{14}$ sm^{-2} hamda 10^{15} sm^{-2} flyuenslarda ~165 K va ~288 K haroratlarda nurlantirilgandan keyin o'rganildi. Bunday nurlantirishdan so'ng kristallar yorqin yashil rangga ega bo'ldi, bu rang 77 K da barqaror saqlanib, 300 K da so'ndi. Yutilish spektrlari *F*-markazlarning 250 nm da va F_2(*M*)-markazlarning 445 nm da ma'lum bo'lgan polosalarini o'z ichiga oladi, ularning intensivlik nisbati esa nurlantirish haroratiga bog'liq. 10^{15} sm^{-2} yuqori doza bilan hatto 165 K da ham, issiqlik diffuziyasi cheklangan sharoitda, F_2-markazlarining ko'paygan konsentratsiyasi kattaroq vakansiya agregatlarining shakllanishi uchun yetarli bo'ldi; ular 440 nm bo'lgan *M*- va 320 hamda 380 nm dagi yangi yutilish polosalarining paydo bo'lishiga, shuningdek, Li-nanokolloidlarning (~520, 600, 950 nm) hosil bo'lishiga sabab bo'ldi.

РЕЗЮМЕ. Исследованы спектры поглощения оптически чистых кристаллов LiF после облучения электронами с энергией 5 МэВ при токе пучка 400 нА до флюенсов $5{\cdot}10^{14}$ см$^{-2}$ и 10^{15} см$^{-2}$ при температурах ~165 К и ~288 К, которые ниже и выше температуры освобождения носителей заряда с ловушек. Сразу после такого облучения кристаллы приобретали ярко-зеленую окраску, устойчивую при 77 К и отжигаемую при 300 К. В спектрах поглощения присутствуют известные полосы *F*-центров при 250 нм и F_2(*M*)-центров при 445 нм, соотношение интенсивностей которых зависит от температуры облучения. При большей дозе облучения 10^{15}см$^{-2}$, даже при 165 К, затрудняющей термодиффузию, увеличение концентрации F_2-центров оказывается достаточным для образования более крупных агрегатов вакансий, ответственных за *M* -центры 440 нм и растущие полосы поглощения при 320, 380 нм, а также наноколлоидов Li (~520, 600, 950 нм).

SUMMARY. The absorption spectra of optical pure LiF crystals were studied after irradiation with 5 MeV electrons at a beam current 400 nA to fluencies $5{\cdot}10^{14}$ cm^{-2} and 10^{15} cm^{-2} at ~165 K and ~288 K, which are below and above the temperature of charge carrier release from traps. Immediately after such irradiation, the crystals acquired a bright green coloration, which was stable at 77 K and annealed at 300 K. The absorption spectra contain the known bands of *F*-centers at 250 nm and F_2(*M*)-centers at 445 nm with their intensity ratio depending on the irradiation temperature. At a higher irradiation dose of 10^{15} cm^{-2}, even at 165 K, which hinders thermal diffusion, the increase in the concentration of F_2 centers is sufficient to form larger aggregates of vacancies responsible for *M* centers of 440 nm and growing absorption bands at 320, 380 nm, as well as Li nanocolloids (~520, 600, 950 nm).