LATVIAN JOURNAL OF PHYSICS AND TECHNICAL SCIENCES
2010, N 4
10.2478/v10047-010-0019-9

PHOTOLUMINESCENCE OF NEUTRON-IRRADIATED LiF SINGLE CRYSTALS

I. Jonane, A. Podins, A. Ivanova

Daugavpils University,
1 Parades Str., Daugavpils, LV-5401, LATVIA
e-mail: inform_parbaude@inbox.lv

In 1980, a single LiF crystal was irradiated by thermal neutrons up to the exposition dose 10^{19} n/cm^2 at the Salaspils nuclear reactor. The crystal has been kept at room temperature for 29 years. Samples in size of 5×4×1 mm^3 were cut from the crystal and some of them annealed at 920 K for 30 min. To study photoluminescence, measurements with a confocal laser scanning microscope Leica TCS SP5 were performed, during which 3D-defects of size of ~1μm^3 were revealed. Photoluminescence was observed in the red spectral region with the peak of ~ 655 nm when excited with an argon laser (λ = 458 nm).

Key words: *LiF crystals, dose 10^{19} n/cm^2, luminescence, annealing.*

1. INTRODUCTION

Lithium fluoride crystals as a research object have steadily attracted scientists' attention. The volume changes, formation of macropores, annealing of radiation defects in neutron-irradiated LiF crystals were subjected to investigation [1−7]. It was found that increasing the absorbed dose not only increases the concentration of radiation point defects (the color centers), but also creates some new more comlpex radiation defects. The formation of color centers and composite defects (colloidal centers, macrovoids, etc.) depends on the absorbed dose, its capacity, and on the irradiation temperature. Although the results of the national scientific research allowed the mechanisms of radiation defect formation to be established, the processes of defect accumulation and transformation during the annealing process in wide temperature and dose ranges are still unclear. In particular, some annealing characteristics of LiF crystals irradiated in a reactor with large doses are not understood well enough. This is associated with formation of pores and metallic colloids, which leads to destruction of the crystal at an advanced annealing stage. Unlike other alkali-halide crystals, in which the primary interaction of radiation effects is associated with the ionization and the elastic collisions, in LiF crystals a nuclear reaction with thermal neutrons ^{6}Li (n, α) ^{3}H occurs. The reaction disrupts the stoichiometric balance and, in addition to the color centers and other defects, introduces new elements: ^{3}H, ^{4}He (which arises from alpha-particles), and ^{3}He, which is the product of ^{3}H decay. As the half-life of tritium is 12.26 years, the ratio of different radiation defects is changing in time (during the 29 years of storage about 80% of ^{3}H was converted into ^{3}He). An electron emitted in the β-decay of ^{3}H has the energy of 17.95 keV and is absorbed

in the crystal. As far as we know there are no studies about the internal radiation influence on the radiation defects during a long storage.

In the paper, the results of the electron microscopy and photoluminescence studies are reported for LiF crystals irradiated at the Salaspils nuclear reactor in 1980 by thermal neutrons with the exposition dose of 10^{19} n/cm^2 and stored at room temperature for 29 years.

2. EXPERIMENTAL

A single crystal of LiF grown at the Leningrad Optical Mechanical Association (LOMO) cleaved to the size of 12×5×4 mm^3 was irradiated at the Salaspils nuclear reactor in 1980 by thermal neutrons with the exposition dose of 10^{19} n/cm^2. Radiation of the Salaspils reactor (ИРТ-2000) consists of thermal neutrons, gamma rays and fast neutrons, with the greatest contribution to the absorbing dose given by the nuclear reaction with thermal neutrons (^{6}Li(n,α)^{3}H). The total dose absorbed by the LiF crystal was 0.9×10^6 Mrad = 0.9×10^4 MGy. The radioactivity of the crystal after 29 years' storage was much lower than the radiation background of the environment. The additional absorbed dose accumulated from the radioactive decay of tritium in the samples during storage was about 9 MGy. The densities of uncompensated ions and introduced atoms in the irradiated crystal by approximate evaluation were:

a) 1.11×10^{19} 1/cm^3 for uncompensated ions, $^{19}F^-$;

b) 1.11×10^{19} 1/cm^3 for introduced atoms, ^{4}He (alfa-particles);

c) 0.83×10^{19} 1/cm^3 for introduced atoms, ^{3}He (product of ^{3}H decay), and

d) 0.19×10^{19} 1/cm^3 for introduced atoms (ions), ^{3}H.

The samples in size of 5×4×1 mm^3 were cut from the crystal and some of them were annealed at 920 K for 30 min. The temperature was measured with a Cr−Al thermocouple. Some of the samples were etched in Fe_2Cl_3:H_2O solution for 5 min. A confocal laser scanning microscope Leica TCS SP5 was used to study the photoluminescence. Surfaces of some specimens were overlaid with carbon (C) and examined with an electron microscope (VEGA II LMU, TESCAN). Some non-radiated and gamma-ray-irradiated samples with the absorbed dose of 0.1 MGy were used as the control samples. A JENWAY 63000 spectrophotometer was employed for the optical density measurements.

The simplest method for obtaining the information on the bulk defects is to cut through a crystal and examine the cut surface. The defects were observed on the specimen surface at different magnifications using a scanning electron microscope (Fig. 1). At magnification 2.41 kX the macro-defects associated with cutting planes, irregular network and etching pits could be seen (Fig. 1*a*). At magnification 52.59 kX it is seen that the pits have a square (rectangular) shape with dimensions of 0.2 μm (Fig. 1*b*). The pits do not have a pyramidal shape characteristic of the etched dislocations, therefore they can be related to micro-voids formed in the neutron-irradiated LiF crystals. In Fig. 1*c,d* some single pits of about 20 μm are discernable. We think that the defects on the surface (pits) might be responsible for the luminescence observed in the sample bulk.

The electron microscopy studies of surfaces of the LiF crystals neutron-irradiated with doses up to 10^{18} n/cm^2 were carried out earlier using the replica method [1, 4, 5].

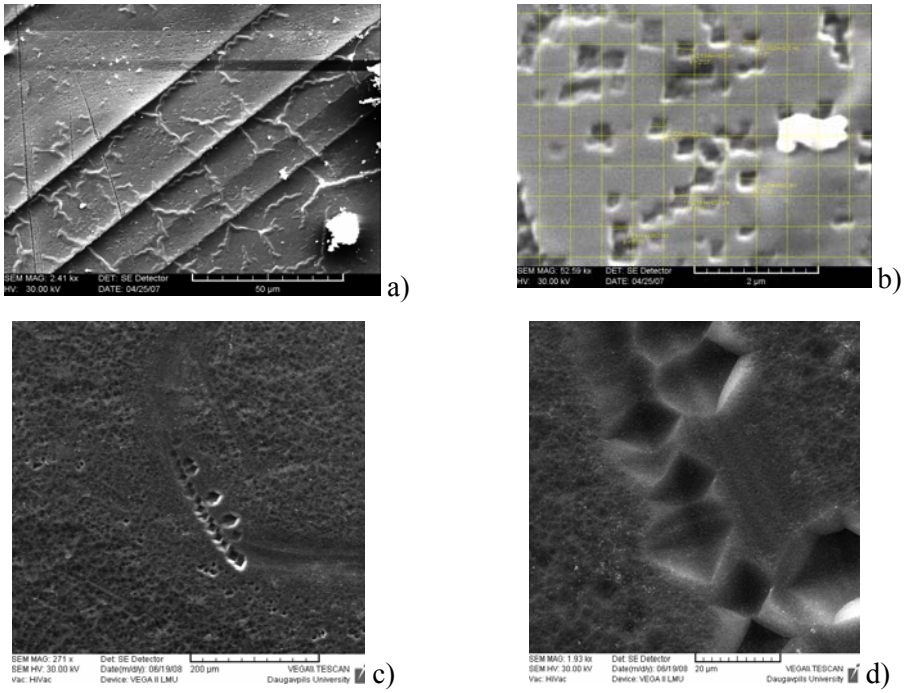

Fig.1. Neutron-irradiated LiF crystal surface image taken by a scanning electron microscope (SEM): *a*) at magnification 2.41 kX (chemically etched); *b*) at magnification 52.59 kX |(chemically etched), *c*) at magnification 271 X, *d*) at magnification 1.93 kX.

The most obvious difference between the earlier surface images and the images of the stored crystal is in the shape of defects: in our case the defects (pits) have a more distinct rectangular shape. One reason for that could be different doses: the previously studied crystals were irradiated with lower doses. Another reason is probably thermo- and radiation-stimulated diffusion during the storage.

To derive information about the distribution of macro-defects in the bulk, the luminescence and transmittance measurements with a confocal scanning microscope Leica TCS SP5 were performed. Figure 2 shows the bulk image in the reflected (*a*) and transmitted (*b*) light. The 2 μm-sized macro-defects are clearly seen in the reflected light

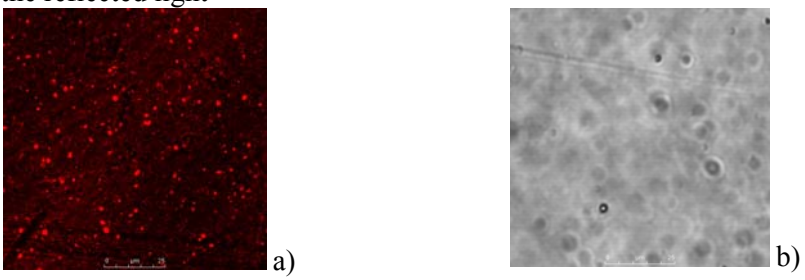

Fig.2. Neutron-irradiated LiF crystal bulk image taken by the confocal scanning microscope: *a*) in the reflected light, *b*) in the transmitted light.

Useful information about the presence of defects can be derived from the absorption spectra. Unfortunately, the LiF crystals with high dose neutrons contain so many color centers that the crystal is opaque in the visible region [8]. The

absorption spectra of gamma-ray-irradiated and neutron-irradiated and annealed LiF crystals are presented in Fig. 3, which shows an intensive absorption band with the peak at ~ 445 nm (ascribed to F_2 centers) and less intensive absorption bands with peaks at ~ 375, ~ 520 and ~ 540 nm (ascribed to F_3 (R_2), F_4 (N_1) and $F_4(N_2)$ centers, respectively [5]). The absorption spectra of neutron-irradiated and annealed LiF crystals do not contain significant peaks; instead, minor bulges are observed, one of them (peaking at ~ 440 nm) could be ascribed to the F_2 center. The optical density increases in the direction of the shortest wavelength. This could be caused by Rayleigh scattering from macro-defects. The crystals are translucent in the region from 570 nm to 800 nm.

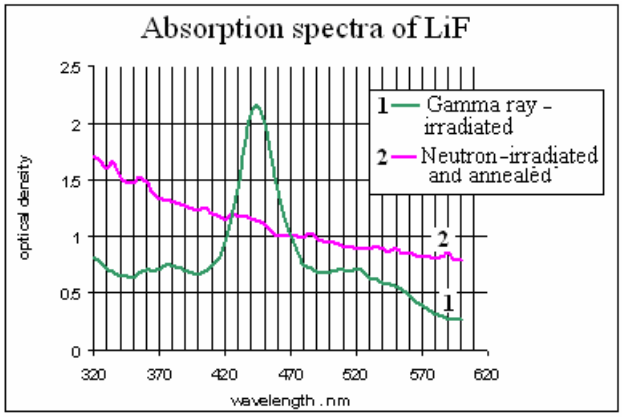

Fig. 3. Absorption spectra of LiF crystals:
1 – gamma-ray-irradiated (specimen thickness d = 0.4 mm),
2 – neutron-irradiated and annealed (specimen thickness d = 1.0 mm)

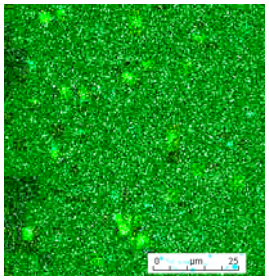

Fig. 4. Photoluminescence image of the neutron-irradiated and annealed LiF crystal (taken with a confocal scanning microscope and excited by Ar laser (λ = 458 nm)).

Figure 4 shows the photoluminescence image of the neutron-irradiated and annealed LiF crystal taken with a confocal scanning microscope and excited by Ar laser (λ = 458 nm) [9]. As is seen, the intensity distribution of the luminescence is not uniform, with spots of 0.2–2.0 μm size which corresponds to the dimensions of 3D defects (Fig. 2). The spectral distribution of luminescence intensity of the LiF crystal excited by Ar laser (λ = 458 nm) is shown in Fig. 5. Three different LiF crystals are compared: the gamma-ray-irradiated with the absorbed dose of 0.1 MGy (curve *1*), the neutron-irradiated and annealed (curve *2*) and the neutron-irradiated non-annealed (curve *3*). The neutron-irradiated crystal is opaque in the visible region, so the excitation of luminescence occurs only in a thin layer of the

crystal surface; therefore, the luminescence intensity is weaker (curve *3*). The luminescence of the neutron-irradiated specimens is weak; therefore, it is displayed on a 50 times larger scale (curves *2* and *3*). The luminescence spectra in all three cases are similarly shaped, with weak peaks at ~ 630, ~ 655, ~ 680 and ~ 720 nm. The most intense luminescence is observed for gamma-ray-irradiated specimen.

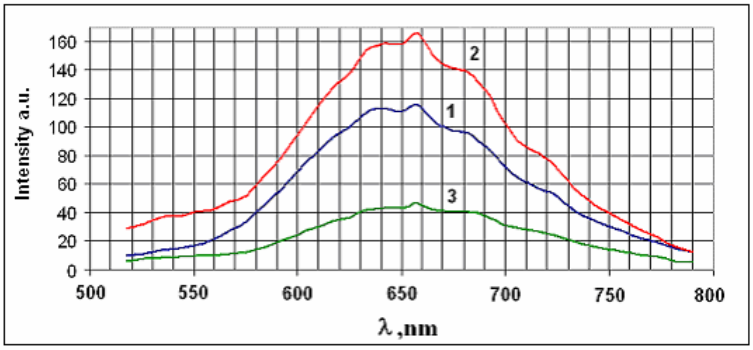

Fig. 5. Photoemission spectra of the LiF crystals: *1* – gamma-ray irradiated; *2* – neutron-irradiated and annealed (50x); *3* – neutron-irradiated, non-annealed (50x).The excitation was performed by the 458 nm line of an argon laser.

After annealing the neutron-irradiated specimen, it became translucent, so the excitation of the luminescence is in a thicker layer, and the intensity of the luminescence is greater than that of the non-annealed crystal (curve *2*). Therefore, a question arises: why is the annealed specimen luminescent at all? Indeed, the elementary F, F_2, F_3^+ color centers are destroyed in the annealing process − partly by recombination of electron and hole centers and partly by aggregation of centers, which leads to formation of colloids, clusters, dislocation loops, pores, etc. [5]. The spectrum was not measured immediately after crystal annealing, so it is possible that in this case we are dealing with color centers created during radioactive decay of tritium.

The luminescence peak at ~ 680 nm could arise due to the luminescence of F_2 centers, while that at 630 nm – due to the F_3^+ (two electrons bound to three neighboring anion vacancies) center luminescence [10, 11, 12]. The origin of the rest of the peaks is not yet clear.

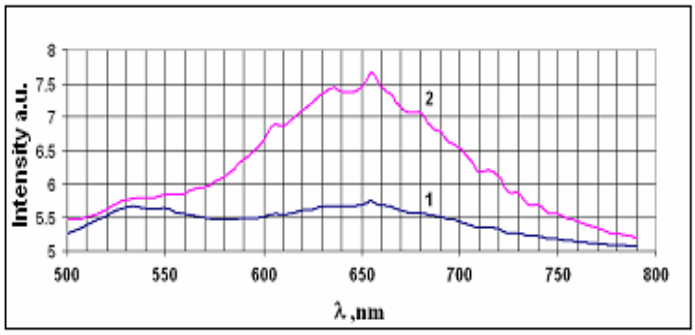

Fig.6. Photoemission spectra of the LiF crystal excited by an argon laser (the 458 nm line) at different excitation intensities: *1* – 30%; *2* –75%.

The luminescence of the neutron-irradiated and annealed LiF was excited by a laser (λ = 458 nm) at various excitation intensities (Fig. 6). Variation in the excitation intensity affects the intensity distribution of the luminescence spectrum. At the low excitation intensity a band can be seen in the region of 530–550 nm, which could be related to the F_3^+ centers [11, 13, 14].

The ultra-short high intensity laser pulses can produce a great number of F-centers in LiF single crystals that would give rise to the F_2, F_3, F_2^+, F_3^+ aggregates [10, 11]. After exciting a non-radiated LiF crystal with an argon laser (λ = 458 nm) no luminescence was revealed; consequently, in our case no color centers were produced. The conversion $F_2 \rightarrow F_3^+$ of color centers by femtosecond pulse laser irradiation in LiF: F_2 crystals has been studied [10] In our case there is little likelihood that the F_2 centers are converted to the F_3^+ ones during measurements of the luminescence spectra.

4. CONCLUSIONS

After a long storage of neutron-irradiated single LiF crystals, macro-defects of a rectangular shape have been revealed. The photoluminescence is observed in the red light spectral region, with a peak around 655 nm when excited with the argon laser (λ = 458 nm). The measured spectra have a composite structure, which includes the luminescence of F_2 and F_3^+ and other centers with peaks at ~680 nm and ~530, ~630 nm.

REFERENCES

1. Шварц, К.К., & Экманис, Ю.А. (1966). Электронномикроскопические исследования радиационных дефектов в кристаллах LiF и KCl. *Радиационная физика, 1V. Ионные кристаллы*, 111–116 (Рига).
2. Schwartz, K., Trautmann, C., & Neumann, R. (2003). Electronic excitations and heavy-ion-induced processes in ionic crystals. *Nuclear Instruments and Methods in Physics Research,* B, *209*, 73–84.
3. Фелдман, Э. (1976). *Исследование образования макропор в облучённых кристаллах фтористого лития.* Диссертация (Тарту).
4. Шварц, К.К., Калнинь, Д.О., Фелдмане, Э.Э., & Экманис, Ю.А. (1965). Изменение обьёма и поверхности облучённых в реакторе кристаллов LiF. *Радиационная физика, 111. Ионные кристаллы*, 3–16 (Рига).
5. Шварц, К., & Экманис, Ю. (1989). *Диэлектрические материалы: радиационные процессы и радиационная стойкость*. Рига: Зинатне.
6. Шварц, К.К., Подынь, А.В., & Балтмугур, К.К.(1966). Энергия образования F-центров в кристаллах LiF при возбуждении гамма- и реакторным облучением. *Радиационная физика, 1V. Ионные кристаллы*, 117–124 (Рига).
7. Manika, I., Maniks, J., Schwartz, K., Toulemonde, M., & Trautmann, C. (2003). Hardening and long-range stress formation in lithium fluoride induced by energetic ions. *Nuclear Instruments and Methods in Physics Research, B 209*, 93–97.
8. Shvarts, K.K., Vitol, A.Ya., & Podin, A.V. (1966). Radiation effects in pile-irradiated LiF crystals. *Phys. Status Solidi,18* (2), 897–909.
9. Leica TCS SP5 User Manual. http://www.biology.ed.ac.uk/research/groups/aebischer/confocal/Leica_SP5_docs/User%20Manual_TCS_SP5_V02_EN.pdf
10. Guanghua Cheng, Yishan Wang, JunFang He, Guofu Chen, & Wei Zhao (2007). Color center conversion by femtosecond pulse laser irradiation in LiF:F_2 crystals. *OPTICS EXPRESS 8938* 9 July, *15* (14).

11. Courrol, L.C., Samad, R.E., Martinez, O.E., Gomes, L., Ranieri, I.M., Baldochi, S.L., de Freitas, A.Z., & Vieira, N.D. (Jr) (2008). Determination of dose-like curve for active color centres produced in LiF single crystals by ultrashort high intensity laser pulses and a preliminary investigation of their spectral and spatial properties by confocal and atomic microscopies. *J. Opt. A: Pure Appl. Opt.,* (10), 104023.
12. Baldacchini, G., & Montereali, R.M. (2001). New perspectives of coloured LiF for optoelectronic devices. *Optical Materials, 16*.
13. Montereali, R.M., & Piccinini, M. (2002). Optical gain of F_2 colour centres in LiF confining structures realised by electron-beam lithography. *Optics Communications, 209*, 201–208.
14. Bonfigli, F., Jacquier, B., Montereali, R.M., Moretti, P., Mussi, V., Nichelatti, E., & Somma, F. (2003). Concentration of F_2 and F_3^+ defects in He^+ implanted LiF crystals determined by optical transmission and photoluminescence measurements. *Optical materials, 24*, 291–296.

AR NEITRONIEM APSTAROTA LiF KRISTĀLA FOTOLUMINISCENCE

I. Jonāne, A. Podiņš, A. Ivanova

K o p s a v i l k u m s

Ar konfokālā lāzerskenējošā mikroskopa Leica TCS SP5 palīdzību pētīti LiF kristāli, kas apstaroti Salaspils reaktorā (1980) ar dozu 10^{19} n/cm^2 (pēc termiskajiem neitroniem). Apstarotais kristāls tika uzglabāts pie istabas temperatūras 29 gadus. Tika pētīti atlaidinātie (atlaidināti 30 minūtes pie temperatūras 920 K) un neatlaidinātie izskaldītie paraugi. Atlaidinātu kristālu tilpumā novēroti 3D-defekti, kuru izmēri ir aptuveni 1 μm^3. Ierosinot ar argona lāzeri (λ = 458 nm), novērojama luminiscence sarkanās gaismas spektrālajā apgabalā. ar maksimumu ~ 655 nm.