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MONITORING OF RADIATION DEFECTS RECOVERY IN $MgAl_2O_4$ DURING ANNEALING BY OPTICAL SPECTROSCOPY[†]

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The extraordinary radiation resistance of single crystals and ceramics of magnesium-aluminum spinel to neutron irradiation is known, but the mechanisms that provide it are not yet fully understood. Irradiation of crystals with fast electrons creates defects partially similar to defects in neutron irradiation. The difference in the destructive effect is the significant level of ionization during electron irradiation. Therefore, to compare the results of irradiation by different sources, it is necessary to determine the parameters of radiation defects. One of them is the conditions of radiation damage recovery. When irradiating the crystals with electrons with an energy of 12.5 MeV to a fluence of $6.8 \cdot 10^{16}$ eV/cm^2, the concentration of defects such as F-centers $2.6 \cdot 10^{16}$ cm^{-3} and V-centers $3 \cdot 10^{17}$ cm^{-3} was obtained. TSL and optical absorption spectroscopy methods were used to determine the state of radiation defects in crystals during annealing. Since annealing at temperatures above 900 K leads to complete discoloration of all optically active centers, therefore, to determine the effect of annealing at higher temperatures, the crystals after annealing were irradiated with ultraviolet light. At temperatures above 900 K, cationic disorder begins to increase, but annealing at 1010 K for 30 minutes was not enough to completely restore the damage to the crystal lattice created by electron irradiation. This is expected, given the characteristic relaxation time of cation disorder, which reaches 1000 hours at this temperature. However, increasing the annealing temperature to 1050 K, in addition to the recovery of radiation defects, creates a noticeable additional difference in TSL, probably due to the formation of complexes from residual F-centers. However, determining the difference between irradiated and non-irradiated crystals gives a difference in the concentration of F-centers less than 10^{15} cm^{-3}.
Keywords: *Spinel; Electron Irradiation; Radiation Defects; Annealing; Thermoluminescence*
PACS: 61.80.Fe; 78.60.Kn; 61.72.jn

INTRODUCTION

Magnesium-aluminum spinel ($MgAl_2O_4$) is an extremely resistant to ion and neutron irradiation insulator with a wide bandgap. Crystals and ceramics can withstand neutron irradiation at moderate fluxes up to fluences of $2.49 \cdot 10^{23}$ n/cm^2 without appreciable change in sample size [1]. Although the optical and dielectric properties of spinel are very sensitive to ionizing irradiation [2] ceramics and spinel powders are considered for use [3] and are used [4] under conditions of powerful gamma, neutron and ion irradiation. Doses and levels of damage of 249 d.p.a., which were achieved at the FFTF reactor, are unattainable for other irradiation devices, except for ion irradiation, but it has its disadvantages related to the small depth of ion penetration. If the thin damaged layer can still be dealt with by experimental methods [5], there remains the implantation of ions that are not an element of the crystal and the temperature peaks when using heavy ions.

Irradiation by electrons compared to neutron irradiation is much more accessible. And because of the relatively small interaction cross-section of fast electrons, unlike ion irradiation, it makes it possible to obtain a practically uniform distribution of defects over the thickness of the samples. But the consequence is a relatively low rate of defect creation, which usually does not exceed one defect per electron. In addition, the beam current during irradiation is limited by the power of ionization losses of electrons in the crystal. The fact that the electrons predominantly (more than 99%) spend their energy on ionization and only a small fraction on defect creation is a feature to be taken into account when comparing experiments with different irradiation sources [6].

One of the characteristics of radiation defects is their destruction temperature. Since Schottky defects are the dominant type for spinel [7], the creation of Frenkel pairs during irradiation creates a complex set of pairs of defects of both types, some of which recombine during irradiation, preventing the creation of large complexes of defects and dislocations [8]. For neutron irradiated crystals, the temperature of the beginning of vacancy mobility and dislocation destruction is about 1000 K [9]. The trap depth for the vacancy mobility is determined as 2±0.7 eV.

Annealing of optically active centers in crystals allows the comparison of optical and ESR spectral data [10], but both techniques dealt with an electron bound to the defect rather than to the defect itself. In [11] annealing of spinel single crystals after electron irradiation at only 900 K resulted in complete bleaching of the radiation-induced absorption. In work [12] it is shown that after annealing to 750 K all optically active centers in the crystals after neutron irradiation are destroyed, but a significant concentration of defects remains. Therefore, elucidation of conditions and possibility of

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restoration of damages of crystals after irradiation by relativistic electrons has both fundamental and applied importance concerning possibility of prolongation of use of crystals in radiation conditions and reuse of crystals in experiments on irradiation.

EXPERIMENTAL DETAILS

Electron irradiation was performed on an M-30 microtron at Institute of Electron Physics of NAS of Ukraine [13] with an electron energy of 12.5 MeV and a current density of 3 μA/cm^2 up to a fluence of $6.8 \cdot 10^{16}$ e/cm^2. The sample was glued with thermal grease KTP-19 on an aluminum plate with a thickness of 2 mm and located at a distance of 5 cm from the exit window of the accelerator. With addition of intense air blowing, this ensured that the temperature of the sample during irradiation did not exceed 20°C.

Measurements of the curves of thermostimulated luminescence (TSL) induced by heating samples at a rate of 0.5 K/s up to 575 K were performed after the half hour delay to partial decay of phosphorescence. The integral thermoluminescence yields were performed using a FEU-106 photoelectron multiplier (spectral response 180-800 nm) operating in the photon count mode.

Before TSL measurements (except for electron irradiated sample) samples were irradiated with UV lamp DDS-30 (analogue of L2(D)2) for filling electron and hole traps. Distance between lamp and samples was 50 mm.

High-temperature annealing was carried out in a tubular quartz furnace insulated from the ends with fireclay. The temperature of the samples was controlled by a chromel-alumel thermocouple located in the sample holder. Cooling from the maximum temperature to 200°C took place in the furnace for an hour, and then in the open air.

Optical absorption was measured in the range 1.2–6.4 eV using a single beam spectrophotometer SF-46 with manual correction of residual phosphorescence.

RESULTS AND DISCUSSION

The optical absorption spectra of single crystals before and after irradiation with electrons with energy of 12.5 MeV and fluence of $6.8 \cdot 10^{16}$ cm^{-2} are shown in Fig. 1. As can be seen, the spectrum shows two well-known absorption bands at 3 eV - hole centers on cation vacancies and 5.3 eV - F-centers. The integrated glow curve of this sample is also quite typical for nominally pure spinel single crystals of stoichiometric composition (Fig.2). It contains one high-intensity broad maximum at 500 K which is very similar to the TSL curve after gamma irradiation [14,15]. In neutron-irradiated crystals, the spinel light curve has weak peaks at 440, 490 K and a prominent peak at 630 K [16]. This difference could be caused by the high level of ionization during electron and gamma irradiation.

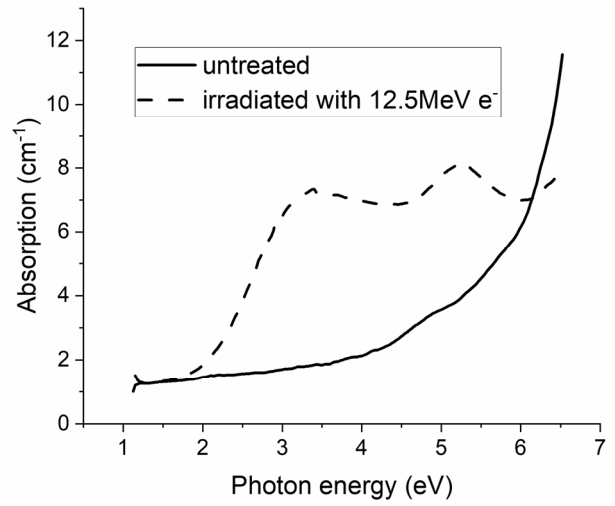

Figure. 1. Optical absorption spectra of $MgAl_2O_4$ single crystal before and after irradiation with 12.5 MeV electrons to fluence $6.8 \cdot 10^{16}$ e/cm^2

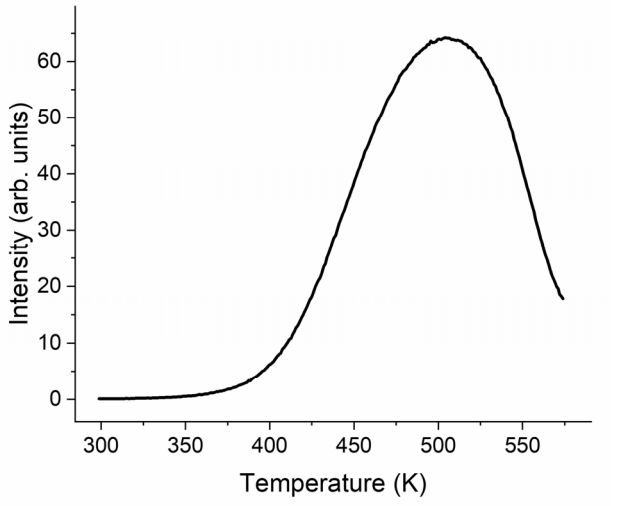

Figure. 2. TSL glow curve of $MgAl_2O_4$ single crystal irradiated with 12.5 MeV electrons to fluence $6.8 \cdot 10^{16}$ e/cm^2

As a result of annealing to 575 K, the absorption spectrum of the crystal partially discolored. The spectra of radiation stimulated absorption after irradiation and annealing are shown in Fig. 3. Also, thin lines show the decomposition of the spectra into separate bands according to [17]. As can be seen, partial annealing caused 50% loss of absorption of V-centers, and almost complete decolorization of F^+ and F-centers. Since an annealing at a temperature of at least 970 K is required to fully restore the absorption spectrum, the sample irradiated by electrons was annealed at 1010 K for 30 min.

To analyze the results of such annealing, the crystal after slow cooling was irradiated with UV light for 30 min. and after an additional 30 min. the thermoluminescence was measured (see Fig. 4). For comparison, the thermal luminescence curve of the crystal without electron irradiation and annealing is also shown. It can be seen that the first peak at 410 K is almost the same, but at higher temperature (peak at 650-700 K) the crystal irradiated by electrons has much more intense

luminescence. In order to return the crystal to the initial state, an additional annealing was carried out at a temperature of 1050 K. This significantly reduced the intensity of the high-temperature maximum and it became even smaller than the corresponding maximum in the initial crystal. But it caused a shift of the first maximum towards higher temperatures.
To further verify the effect of irradiation and annealing on the crystal state, both samples were irradiated with UV light after annealing at 1050 K. Fig. 5 shows the absorbance for both samples, where it can be seen that the absorbance (concentration of optically active centers) due to hole centers on cation vacancies and anti-structure defects is identical. There is a very weak difference in the absorption of electron-type optically active centers: antisite defects and anion vacancies.

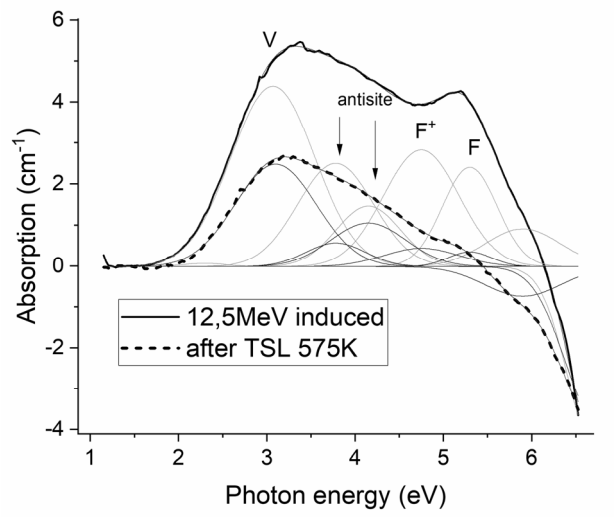

Figure. 3. Optical absorption spectra of $MgAl_2O_4$ single crystal irradiated with 12.5 MeV electrons to fluence $6.8 \cdot 10^{16}$ e/cm^2 and after annealing to 575 K during TSL measurement

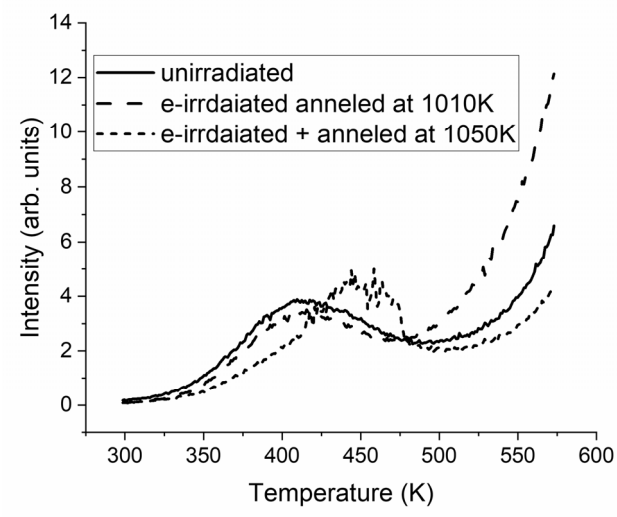

Figure. 4. TSL glow curve of UV irradiated $MgAl_2O_4$ single crystals: unirradiated and irradiated with 12.5 MeV electrons to fluence $6.8 \cdot 10^{16}$ e/cm^2 and annealed to different temperatures during 30 min

It is shown in more detail in Fig. 6 in the form of difference of absorption spectra of two crystals (with and without irradiation) in the same state. It can be seen that the effect of electron irradiation after annealing to 1050 K on the formation of optically active centers is very weak both for the annealed state and after UV irradiation.

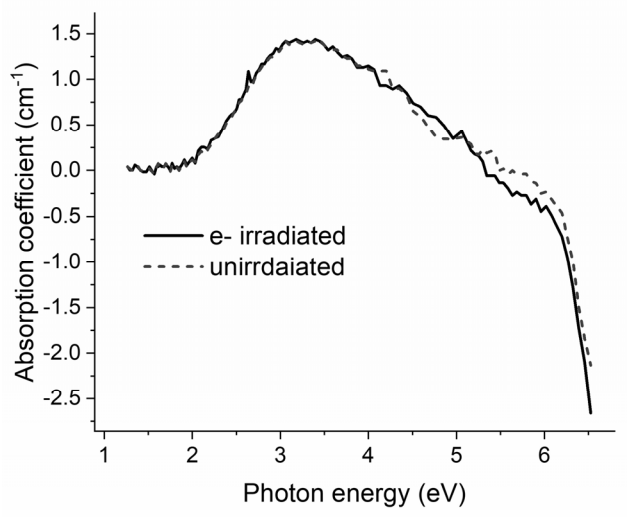

Figure 5. UV induced optical absorption spectra of $MgAl_2O_4$ single crystal with and without irradiation with 12.5 MeV electrons to fluence $6.8 \cdot 10^{16}$ e/cm^2 and annealing at 1050 K for 30 min

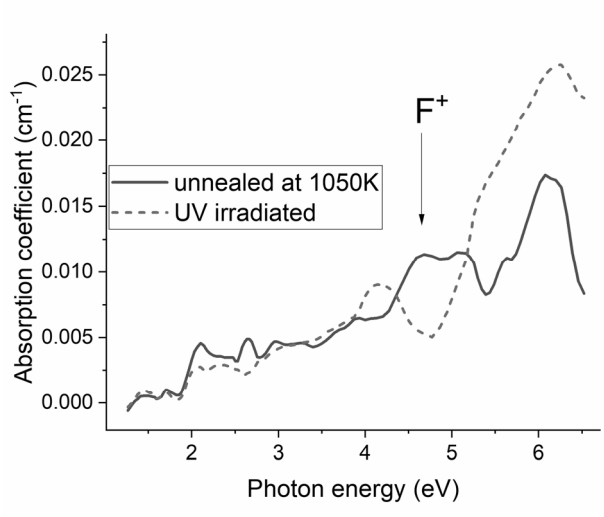

Figure 6. Difference optical spectra of irradiated and unirradiated $MgAl_2O_4$ crystals after annealing to 1050 K and subsequent UV irradiation

The difference between irradiated and non-irradiated crystals is small, slightly exceeding the measurement error of the spectrophotometer. Only one very weak band corresponding to F^+-centers can be approximately identified in the spectra, but their concentration determined by the Smakula formula [18] does not exceed $1.5 \cdot 10^{14}$ cm^{-3}. Absence of differences in induced absorption spectra in the region of maxima corresponding to antisite defects indicates that although

the annealing temperature exceeded the threshold of cation mobility and increasing of inversion the changes in TSL glow curve (Fig. 4) are rather related to the formation of complexes from residual defects.

CONCLUSIONS

Sequential annealing of defects in $MgAl_2O_4$ single crystals after 12.5 MeV electron irradiation was carried out. It was found that 30 min. of annealing at 1010 K was not sufficient for the complete recovery of radiation defects. Additional annealing at 1050 K of $MgAl_2O_4$ single crystals irradiated with intermediate fluence electrons practically restores the crystal state to the initial level.

It is also shown that annealing at 1050 K for 30 min., besides the restoration of defects, introduces noticeable changes in the crystal, which may be associated with an increase in inversion. However, the residual difference in F-centers concentration at $1.5 \cdot 10^{14}$ cm^{-3} rather indicates the formation of complexes from residual defects. Therefore, the optimization of the annealing process with respect to temperature, duration and cooling regime requires further investigation.

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REFERENCES

[1] F.A. Garner, G.W. Hollenberg, F.D. Hobbs, J.L. Ryan, Z. Li, C.A. Black, and R.C. Bradt, "Dimensional stability, optical and elastic properties of $MgAl_2O_4$ spinel irradiated in FFTF to very high exposures", J. Nucl. Mater. **212–215**, 1087–1090 (1994). https://doi.org/10.1016/0022-3115(94)91000-6

[2] J.-M. Costantini, G. Lelong, M. Guillaumet, S. Takaki, and K. Yasuda, "Color-center formation and thermal recovery in X-ray and electron-irradiated magnesium aluminate spinel", J. Appl. Phys. **124**, 245901 (2018). https://doi.org/10.1063/1.5055230

[3] E.F. Daly, K. Ioki, A. Loarte, A. Martin, A. Brooks, P. Heitzenroeder, M. Kalish, C. Neumeyer, P. Titus, Y. Zhai, Y. Wu, H. Jin, F. Long, Y. Song, Z. Wang, R. Pillsbury, J. Feng, T. Bohm, M. Sawan, and J. Preble, "Update on design of the ITER in-vessel coils", Fusion Sci. Technol. **64**, 168–175 (2013). https://doi.org/10.13182/FST13-A18073

[4] J. Delauter, J.C. Dekamp, A.F. Zeller, C.Y. Gung, and J.V. Minervini, "Magnetic testing of a superferric dipole that uses metal-oxide insulated CICC", IEEE Trans. Appl. Supercond. **19**, 1092–1094 (2009). https://doi.org/10.1109/TASC.2009.2019217

[5] D. Simeone, C. Dodane-Thiriet, D. Gosset, P. Daniel, and M. Beauvy, "Order-disorder phase transition induced by swift ions in $MgAl_2O_4$ and $ZnAl_2O_4$ spinels", J. Nucl. Mater. **300**, 151–160 (2002). https://doi.org/10.1016/S0022-3115(01)00749-8

[6] T. Shikama, and G.P. Pells, "A comparison of the effects of neutron and other irradiation sources on the dynamic property changes of ceramic insulators", J. Nucl. Mater. **212–215**, 80–89 (1994). https://doi.org/10.1016/0022-3115(94)90036-1

[7] S.S. De Souza, F. Ayres, and A.R. Blak, "Simulation models of defects in Mg Al_2O_4:Fe^{2+}, Fe^{3+} spinels", Radiat. Eff. Defects Solids. **156**, 311–316 (2001). https://doi.org/10.1080/10420150108216911

[8] C. Kinoshita, K. Fukumoto, K. Fukuda, F.A. Garner, and G.W. Hollenberg, "Why is magnesia spinel a radiation-resistant material?", J. Nucl. Mater. **219**, 143–151 (1995). https://doi.org/10.1016/0022-3115(94)00388-2

[9] K. Yasuda, C. Kinoshita, K. Fukuda, and F.A. Garner, "Thermal stability and kinetics of defects in magnesium aluminate spinel irradiated with fast neutrons", J. Nucl. Mater. **283–287**, 937–941 (2000). https://doi.org/10.1016/S0022-3115(00)00118-5

[10] A. Lushchik, E. Feldbach, E.A. Kotomin, I. Kudryavtseva, V.N. Kuzovkov, A.I. Popov, V. Seeman, and E. Shablonin, "Distinctive features of diffusion-controlled radiation defect recombination in stoichiometric magnesium aluminate spinel single crystals and transparent polycrystalline ceramics", Sci. Rep. **10**, 1–9 (2020). https://doi.org/10.1038/s41598-020-64778-8

[11] A. Lushchik, S. Dolgov, E. Feldbach, R. Pareja, A.I. Popov, E. Shablonin, and V. Seeman, "Creation and thermal annealing of structural defects in neutron-irradiated $MgAl_2O_4$ single crystals", Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms, **435**, 31–37 (2018). https://doi.org/10.1016/j.nimb.2017.10.018

[12] V.T. Gritsyna, and Y.G. Kazarinov, "Thermal stability of radiation-induced optical centers in non-stoichiometric spinel crystals", Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms, **250**, 349–353 (2006). https://doi.org/10.1016/j.nimb.2006.04.136

[13] M.I. Romanyuk, J.J. Hainysh, Y. Plakosh, V. Kovtun, O.M. Turhovsky, G.F. Pitchenko, I.G. Megela, M.V. Goshovsky, O.O. Parlag, V.T. Maslyuk, and N.I. Svatiuk, "Microtron M-30 For Radiation Experiments: Formation And Control Of Irradiation Fields", PAST, **3**, 137–143 (2022). https://doi.org/10.46813/2022-139-137

[14] A. Lorincz, M. Puma, F.J. James, and J.H. Crawford, "Thermally stimulated processes involving defects in γ- and x-irradiated spinel ($MgAl_2O_4$)", J. Appl. Phys. **53**, 927–932 (1982). https://doi.org/10.1063/1.330562

[15] Y. Kazarinov, V. Kvatchadze, V. Gritsyna, M. Abramishvili, Z. Akhvlediani, M. Galustashvili, G. Dekanozishvili, T. Kalabegishvili, and V. Tavkhelidze, "Spectroscopic studies of defects in gamma- and neutron-irradiated magnesium aluminates spinel ceramics", PAST, **5**, 8–13 (2017). https://vant.kipt.kharkov.ua/ARTICLE/VANT_2017_5/article_2017_5_8.pdf

[16] V.T. Gritsyna, I. V. Afanasyev-Charkin, V.A. Kobyakov, and K.E. Sickafus, "Neutron irradiation effects in magnesium-aluminate spinel doped with transition metals", J. Nucl. Mater. **283–287**, 927–931 (2000). https://doi.org/10.1016/S0022-3115(00)00196-3

[17] V.T. Gritsyna, I. V. Afanasyev-Charkin, Y.G. Kazarinov, and K.E. Sickafus, "Optical transitions in magnesium aluminate spinel crystals of different compositions exposed to irradiation", Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. **218**, 264–270 (2004). https://doi.org/10.1016/j.nimb.2004.02.002

[18] D.L. Dexter, "Absorption of light by atoms in solids", Phys. Rev. **101**, 48–55 (1956). https://doi.org/10.1103/PhysRev.101.48

МОНІТОРИНГ ВІДНОВЛЕННЯ РАДІАЦІЙНИХ ДЕФЕКТІВ В $MgAl_2O_4$ ПРИ ВІДПАЛІ МЕТОДОМ ОПТИЧНОЇ СПЕКТРОСКОПІЇ

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Відома надзвичайна радіаційна стійкість монокристалів і кераміки магнієво-алюмінієвої шпінелі до нейтронного опромінення, але механізми, які її забезпечують, ще остаточно не з'ясовані. Опромінення кристалів швидкими електронами створює дефекти, частково подібні до дефектів при нейтронному опроміненні. Відмінність у руйнівній дії полягає в значному рівні іонізації при електронному опроміненні. Тому, для порівняння результатів опромінення різними джерелами необхідно визначати параметри радіаційних дефектів. Одним з них є температурні умови відновлення радіаційних пошкоджень. При опроміненні кристалів електронами з енергією 12,5 МеВ до флюенсу $6{,}8\cdot10^{16}$ е/см^2 отримано концентрацію дефектів типу F-центрів $2{,}6\cdot10^{16}$ см$^{-3}$ та V-центрів $3\cdot10^{17}$ см$^{-3}$. Для визначення стану радіаційних дефектів у кристалах під час відпалу використовувались методи ТСЛ та оптичної абсорбційної спектроскопії. Оскільки відпал при температурах вище 900 К призводить до повного знебарвлення всіх оптично активних центрів, тому для визначення впливу відпалу при більш високих температурах кристали після відпалу опромінювали ультрафіолетовим світлом. При температурах вище 900 К починає зростати катіонне невпорядкування, але відпалу при 1010 К протягом 30 хвилин виявилося недостатньо для повного відновлення пошкоджень кристалічної гратки, створених електронним опроміненням. Це очікувано, враховуючи характерний час релаксації катіонного невпорядкування, який при цій температурі сягає 1000 годин. Однак підвищення температури відпалу до 1050 К, окрім відновлення радіаційних дефектів, створює помітну додаткову різницю в ТСЛ, ймовірно, за рахунок утворення комплексів із залишкових F-центрів. Однак визначення різниці між опроміненими і неопроміненими кристалами методом оптичної спектрофотометрії дає різницю в концентрації F-центрів менше за 10^{15} см$^{-3}$.

Ключові слова: *шпінель; електронне опромінення; радіаційні дефекти; відпал; термолюмінесценція*