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SPECTROSCOPIC STUDIES OF DEFECTS IN GAMMA- AND NEUTRON-IRRADIATED MAGNESIUM ALUMINATES SPINEL CERAMICS

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The spectroscopic investigations of defects in optical spinel ceramics irradiated with gamma-rays from ^{60}Co source and mixed neutron-gamma field in WWR reactor to neutron fluences of $1\cdot10^{13}$ and $5\cdot10^{13}$ n/cm^2 were provided. The obtained data on the dose dependence of intensity of absorption bands in the visible range allow to identify the origin of optical centers formed under irradiation. Absorption in IR range indicates on the presence in ceramics carbon-related complexes that become active after irradiation. The registered EPR signal of g = (2.0174±0.0005) and width of (46.1±1.5) G which corresponds to HO_2^- or O_3^- radicals. The dependences of the investigated centers on annealing temperature of the irradiated spinel ceramics show unusual increase in intensity of absorption and steady-state radio-luminescence in the temperature range of 200…400 °C. The role of complexes of defects including anti-site defects in formation and healing of defects in different temperature ranges are analyzed taking into account different mobility of cations and anions and specific mechanism of radio-luminescence.

INTRODUCTION

Magnesium aluminates spinel ($MgAl_2O_4$ – MAS) ceramics due to the high radiation resistance and specific physical-chemical properties (wide spectral range of transparency, high melting temperature and chemical resistivity) is considered as prospective material for application in different nuclear devices [1]. The nature of radiation tolerance of MAS is still not understood due to abundance of the native defects in these crystals [2]. The structure of spinel lattice contains two types of cationic sites: octahedral positions occupied by Al^{3+} ions and tetrahedral ones occupied by Mg^{2+} ions. Structure of synthetic crystals of MAS is partially inverse one, i.e. Al^{3+} ions on tetrahedral sites forms locally charged defect $[Al_{Mg}]^+$ which can serve as electron traps and Mg^{2+} ions on octahedral sites forming also charged defects $[Mg_{Al}]^-$ capturing holes. The calculation of the energy formation of the native defects shows that along with isolated point defects the energetically preferable also the formation of different complexes of defects which can become apparent in the optical spectroscopy [3].

Previously [4] we have investigated the spinel single crystals of different compositions after irradiation with UV-light and X-rays and found a set of absorption bands some of them can be attributed to the corresponding calculated transitions. The practical use of spinel single crystals is questionable due to small size and high cost of crystals. Recently the technology of the optical spinel ceramics of high volumes was developed [5, 6] and the nature of defects responsible for the radiation tolerance of this material has to be investigated.

Therefore, the complex of techniques was used for investigation of the native defects in transparent spinel ceramics obtained by the high temperature technique. We present results on investigation of the optical absorption in the visible and IR-ranges of spectra, thermo- and steady-state radio-luminescence (TSL and SSRL) and electron paramagnetic resonance (EPR) spectra measurements in spinel ceramics subjected to gammas and to low fluences neutron irradiation.

1. EXPERIMENTAL DETAILS

Spinel ceramics were prepared by a conventional hot-pressing technique. Disks of 50 mm in radius and 7 mm in thickness were produced by sintering of spinel powder $MgAl_2O_4$:LiF (1 wt.%) at 1550 °C, at 35 MPa in a vacuum. Slices of 0.7 mm in thickness were cut from this disk and polished to optical finish. Irradiation of samples with gammas was carried out using ^{60}Co source at the dose rate of 2.4 Gy/min. Mixed gamma and neutron irradiation were provided in WWR reactor to thermal neutron fluences of $1\cdot10^{13}$ and $5\cdot10^{13}$ n/cm^2. Temperature of samples at irradiation was from 30 to 50 °C. Irradiated samples were annealed up to 550 °C with a step of 50 °C and cooled to room temperature for measurements of spectroscopic characteristics. Another set of spinel ceramics was irradiated with 16 MeV electrons to fluence of $1.1\cdot10^{17}$ el/cm^2 and also annealed with the same step up to 700 °C and cooled to room temperature for measurements of the SSRL.

Optical absorption spectra were measured using spectrophotometers SF-29 in UV and visible, and Specord 75 in IR range. EPR spectra were taken at RE 1306 spectrometer. The thermo-stimulated luminescence of irradiated samples was measured in the temperature range of 150…400 °C from the sample at heating rate of 1 °C/s. SSRL was measured in the spectral range of 200…900 nm at the excitation with X-rays from Cu-anode X-rays tube working at the voltage of 40 kV and current of 400 μA.

2. RESULTS AND DISCUSSIONS

The radiation-induced absorption spectra of gamma-irradiated ceramics to different doses are presented in Fig. 1. These spectra were obtained by subtracting the non-irradiated spectra from that of irradiated to different doses. Despite of the low resolution of indicated spectral bands the appearance if given peak in every of fifth spectra allow us to believe the existence of these bands. Therefore we can indicate the bands at 2.7; 3.3; 3.7; 4.2, and 4.75 eV, which increases in intensity after gamma irradiation, and those bands at 5.3 and 5.6 eV which decreases in intensity after irradiation.

In the spectra taken from spinel ceramics irradiated with gamma-neutrons in reactor channel we also observe bands which coincide on the spectral position with that bands observed in gamma-irradiated samples (Fig. 2). As it was shown before [4] the spectral bands in energy range of ≤ 4 eV are related to hole centers formed at near cationic vacancies, the bands in the range of ≥ 4 eV usually are ascribed to electron centers.

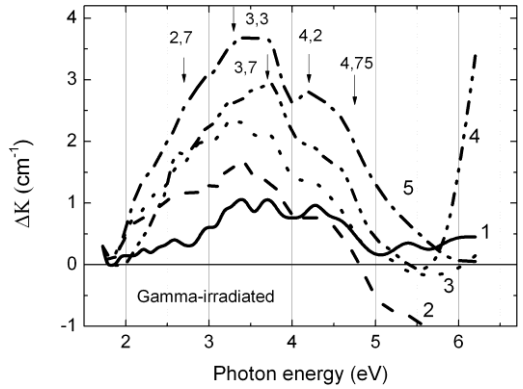

Fig. 1. Gamma-radiation-induced absorption spectra spinel ceramics irradiated to different doses: 1 – 0.5; 2 – 1.0; 3 – 3.0; 4 – 6.0; 5 – 10.0 kGy

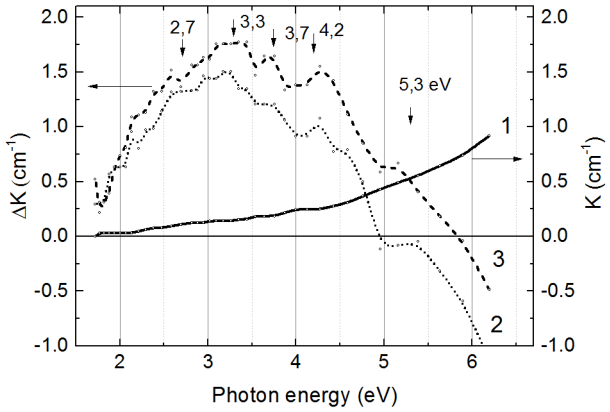

Fig. 2. Absorption spectra of spinel ceramics before irradiation (1), and gamma-neutron irradiation-induced absorption spectra of spinel ceramics irradiated to: 2 – $1.0 \cdot 10^{13}$, 3 – $5.0 \cdot 10^{13}$ n/cm^2

Most prominent 2.7 and 3.3 eV overlapping bands are related to V-type centers formed on different cationic vacancies; in the higher photon energy bands at 4.75 and 5.3 eV were identified with F^+ and F-centers formed by capturing one or two electrons at anionic vacancies, respectively; finally, the bands at 3.7 and 4.2 eV, most probably, are related to hole and electron centers at anti-site defects.

The negative absorption in Figs. 1 and 2 signifies that absorption at the wavelength of 5.3 and 5.6 eV in irradiated samples decreases. Indeed, in the spectra of non-irradiated ceramics there were found F-type centers, which were formed at anionic vacancies created due to presence of LiF according to reaction [5]

$$3LiF \xrightarrow{MgAl_2O_4} (Li_{Mg})^- + 2(Li_{Al})^{2-} + 3(F_O)^+ + V_O^{2+}. \quad (1)$$

Therefore, the anionic vacancies capture one or two electrons form F-type centers in the virgin samples of ceramics and irradiation leads to ionization of these centers.

The IR absorption spectra non-irradiated samples contains single band at 1445 cm^{-1} (Fig. 3). After irradiation the intensity of this band slightly decreases and the new weak bands at wave numbers of 1291 and 1576 cm^{-1} were registered. The band at 1445 cm^{-1} was observed also in spinel single crystals and spinel ceramics obtained by different technological conditions [7]. Because the technology installation of ceramic preparation includes carbon parts the carbon atoms at high temperature can be incorporated in spinel body in different forms. The most ubiquitous parasitic absorbers able to affect optical transmission have been identified for the case of spinel ceramics are carbon atom clusters [8]. The value of wave number of 1445 cm^{-1} matches the band related to the C-C stretching vibrations [9].

After the irradiation two absorption bands appear as a consequence of the irradiation-induced changes inter-atomic bonding between carbon and oxygen. The absorption band at 1291 cm^{-1} was identified with symmetrical stretching vibration of C-O-C group. Another band at 1556 cm^{-1} are related to skeletal C = C vibrations formed by ionizing irradiation [10]. The weak band at ~ 3400 cm^{-1} (3360 cm^{-1}) could belong to O-H stretching vibration, but slightly shifted to higher wave numbers.

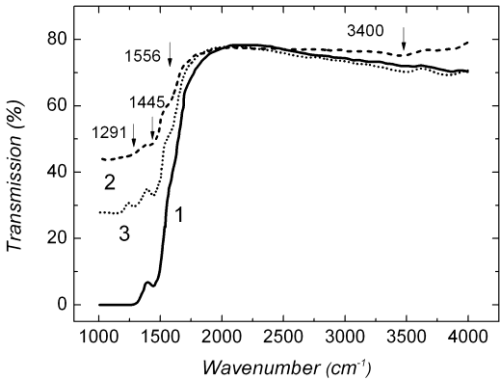

Fig. 3. IR transmission spectra of MAS ceramics: 1 – before irradiation; 2 – irradiated with gammas (8.0 kGy); 3 – after gamma-neutron irradiation ($5 \cdot 10^{13}$ n/cm^2)

In EPR spectra there was observed line of g = (2.0174±0.0005) and width of (46.1±1.5) G, intensity of which at high gamma doses riches saturation. This line also was registered in (n,γ)-reactor

irradiated samples. The line of such parameters corresponds to HO_2^- or O_3^- radicals [11].

The dependences of intensities of observed absorption bands in visible and IR range spectra together with EPR line on the dose of gamma irradiation are shown in Fig. 4. All three bands 2.7, 3.3, and 3.7 eV depend on the dose of gamma irradiation in the same manner. Moreover, the dependences of the intensity of these bands correlates to dependence of EPR signal on the dose of the gammas irradiation (curves 2 and 3). For formation of the hole centers responsible for absorption bands bands at 2.7; 3.3, and 3.7 eV we needs some source of holes and this source could be complexes of defects HO_2^- or O_3^- radicals.

As to dose dependence of IR absorption bands which are determined by presence of technological impurities they experience inter-conversion and measurements only one band 1576 cm^{-1} demonstrates growth up to saturation and than transformation in another type of center (appearance of different bonds).

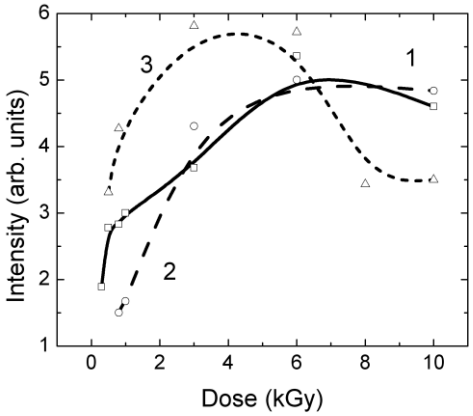

Fig. 4. Dose dependences of 1556 cm^{-1} (1), (2) intensity bands at 3.7 eV and EPR signal (3) on the gamma-irradiation dose

The above shown results demonstrate mostly the role of charge carriers rearrangement in spinel ceramics at irradiation with gamma- and gamma-neutron irradiation in dependence on gamma dose and low neutron fluences. All spectroscopic characteristics indicate the existence of native defects and impurities which under ionizing irradiation capture (or lost) charge carriers and becoming optically or paramagnetic active centres. The numerous of the overlapped absorption band at photon energy ≤ 4 eV corresponds to two types of cationic vacancies in tetrahedral and octahedral positions captured one or several holes. As can be seen from Fig. 4 all bands demonstrate the saturation at high dose that support their formation at native defects, impurity ions or their complexes. As was mentioned in Introduction magnesium aluminates spinel has partially inverse structure. The degree of inversion in spinel ceramics is about 10…15% [12], that causes the anti-site defects concentration of about 1.5…2 at.% which corresponds to average distance between defects of about lattice parameter (7.9 Å). Such concentration of the anti-site defects is much higher the concentration of the impurity ions in ceramics [13] and the formation of complexes of the anti-site defects – impurity ions is highly probable. It was shown [14] that Mn^{2+} ions stimulate the formation form anti-sites defects for elastic stress compensation caused by place of the over dimensioned impurity ions ($r(Mn^{2+}) > r(Mg^{2+})$) in tetra-position [15]. In paper [16] there was establish that in natural crystals the manganese and chromium ions after annealing to 1010 °C become disordered as in synthetic crystals and manifest ion luminescence typical to emission from ions in distorted tetrahedral or octahedral environment [17]. The minimal energy of defects formation is 0.8 eV for the case when the pair of Mg and an Al anti-site was nearby, only 3.35 Å apart [18]. Therefore, we suggest that every luminescent impurity ions form complex with pair anti-site defects.

Electron or neutron irradiation lead to increase of concentration of the isolated and nearby complexes of anti-site defects [3], that inevitable modify the structure of such defective complexes and change their luminescent and optical properties. Due to the high concentration of anti-site defects there exists the high probability of the creation under irradiation of the anionic vacancy between the components of anti-site defects. In this case for both centers at anti-site defects $[Al_{Mg}]^+$ и $[Mg_{Al}]^-$ the anionic surroundings are changed and these centers lost ability to be the traps for charge carriers.

The most radiation created defects ate thermally unstable and under elevated temperature the radiation induced changes may disappear. At the subsequent heating of the irradiated samples two processes take place simultaneously: the change of charge states of defects due to release of the charge carriers from shallow traps and secondly recapture by more deep traps which are stable at given temperature, and also relaxation of radiation damages which leads as to recovery of the initial crystal structure and transformation of defects in more thermally stable ones. To resolve these two phenomena the measurements of the TSL of gamma irradiated to different doses were provided (Fig. 5).

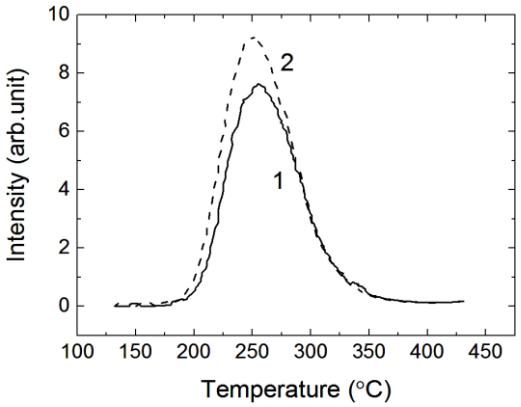

Fig. 5. TSL curves of γ-irradiated spinel ceramics (curves 1 – 8 and 2 – 10 kGy)

Because of the heating rate at TSL measurements was 1 °C/s the warm-up time of sample was less 8 minutes. During this time the relaxation of electron subsystem takes place and traps of depth of up to 1 eV are becoming empty [19]. Since the rearrangement of atomic structure at given temperature occurs much

slowly then relaxation of electron sub-system (for example, the time constant of changing inversion parameter at 700 °C is about one hour [20]), we conclude that crystal structure was change negligible at such short time warm-up.

The influence of the subsequent stepwise annealing on the intensity of optical absorption of F-centers is shown in Fig. 6 (curves 1, 2). The enhancement of absorption after annealing to 200 °C can not be due to capture of electrons by anionic vacancies because all shallow traps are empty. But in this temperature range the annealing of radiation defects after neutron [21] or ion [22] irradiation are already realized due to the low activation energy of the ion diffusion spinel crystals or ceramics [23]. For the F-center formation the anionic vacancy should have normal cationic surroundings which were disordered during the irradiation process. Thermally stimulated recombination of the cationic Frenkel pairs leads to growth of anionic vacancies and formation of F-centers. Also the total concentration of defects capable to capture of free charge carriers is becoming lower. The EPR signal decreases very steeply with increasing temperature and about 200 °C the EPR centers disappeared. It indicates that at elevated temperature the charges of HO_2^- or O_3^- radicals [11] undergo rearrangement becoming paramagnetically non-active. This process does not generate the free charge carriers because we do not observe TSL signal up to temperature of 200 °C.

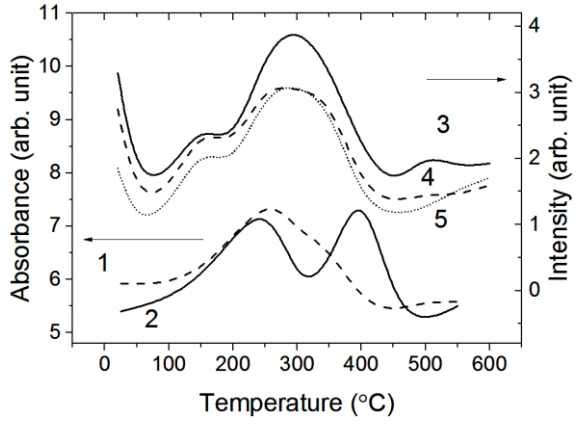

Fig. 6. Correlation of temperature dependence of absorption band at 5.3 eV for gamma-neutron irradiated spinel ceramics to different neutron fluences (curves 1 – $1.0 \cdot 10^{13}$ and 2 – $5.0 \cdot 10^{13}$ n/cm^2) and the SSRL intensity at 260 (3), 520 (4), 689 nm (5) for electron irradiated spinel ceramics

To support of the reliability of the above discussed processes we also provided the measurement of SSRL in electron irradiated and stepwise annealed spinel samples and compared with absorption (see Fig. 6, curves 3, 4, 5). As it was shown before the spectra of SSRL contains three prominent bands at 260 nm related to electron-hole recombination, 520 nm identified with emission of Mn^{2+}-ions, and 689 nm emission of the excited Cr^{3+}-ions [24]. In contrast to photoluminescence where the luminescence centers are excited at internal transitions the X-ray excitation of impurity ions take place mainly by the capture of relaxed electrons and holes formed at the absorption of the X-ray quanta. The kinetics of the X-ray luminescence rise of all emission bands indicates on the competitive process of capture channels of the excitation and so far on the existence of group complexes for UV emission band and luminescence of the impurity ions [25].

Intensity of luminescence excited with ionizing irradiation is defined by parameters of luminescence centers and the charge transport properties of crystal. When crystal is irradiated with X-rays the isolated excited area is created, and its size (volume) is inversely depend on the concentration of the traps of charge carriers [25]. The luminescence intensity depends on the number of luminescence centers concentrated in the volume of excitation. Synchronous change of SSRL intensity of all emission bands can be explained by variation of the size of the volume of excitation which depends only on the traps concentration.

The high intensity of the SSRL in the nonannealed irradiated samples (T = 30 °C) is caused by the filling during preliminary electron irradiation most initial traps that leads to formation at the X-ray irradiation the large size of excitation volumes. The sharp decrease of the SSRL intensity of all three bands is caused by thermally stimulated trap depletion at the first annealing step. Such effect is not observed in dependence of absorption band (see curves 1, 2 in Fig. 6) on annealing temperature due to preliminary annealing by measuring TSL.

The annealing at elevated temperature (> 150 °C) causes the recombination of radiation induced lattice defects and decrease the concentration of traps, so, we observe the enhancement of luminescence intensity. Due to the higher mobility of defects in cationic sub-lattice the radiation-induced complexes of defects $V_O + Al_{Mg}$ and $V_O + Mg_{Al}$ dissociate forming isolated anionic vacancies and F-type centers. Therefore we observe the growth of absorption band related F-type centers (Borges). The growth of absorption in annealing temperature range of 200…250 °C also could be due to healing of cationic vacancy in the Schottky defects forming isolated anionic vacancy and consequences of F-type centers. In both cases the concentration of traps decreases and intensity of SSRL increases.

Finally, the negative-going slope of dependences (see Fig. 6) in the temperature range of 250…400 °C the most probably is caused by thermally stimulated recombination of oxygen interstitial with anion vacancy. It is consistent with temperature dependence of absorption of F-type centers on the annealing temperature. In the case of the restoring of complexes of defects consisting of the anionic vacancy between anti-site defects the filling vacancy with oxygen the concentration of traps increases due to recovery of the broken by irradiation the anionic surroundings for two centers – components of anti-site defects Al_{Mg} and Mg_{Al}.

CONCLUSIONS

There were investigated the spectroscopic properties of magnesium aluminates spinel ceramics irradiated with gamma rays from ^{60}Co source and mixed gamma-

neutron irradiation from nuclear reactor. It was revealed that in spinel ceramics the optical absorption spectra contains the same set of bands at 2.7; 3.3, and 3.7 eV as in single crystals, which were identified with hole centers at cation vacancies and bands at 4.2; 4.75, and 5.3 eV related to electron centers at anion vacancies. Data on the γ-dose dependences of the intensity of optical absorption bands in the visible range and the EPR signal at g = 2.0174 indicates the existence of some correlation between these two types of centers having different spectroscopic parameters.

Comparison of dependences of absorption bands related to F-type centers and intensity of radio-luminescence on the annealing temperature of irradiated spinel ceramics leads to conclusion on the process of the thermally stimulated two step relaxation of complex defect structure involved anion vacancy and anti-site defects. Decreasing of concentration of radiation defects due to recombination of Frenkel pairs and structure restoration of defect complexes leads to enhancement of steady-state radio-luminescence in the temperature range of 200…400 °C.

The conception of complexes of native defects which include of the anionic and cationic vacancies, impurity ions and localized nearby anti-site defects was used for explanation of the spectroscopic characteristics of irradiated spinel ceramics. Gamma-irradiation causes mainly to exchange between defects and impurities leading to growth of the optical and paramagnetic centers up to saturation at the dose of 10 kGy.

Annealing of the irradiated samples causes the unusual behavior both absorption and SSRL bands on the annealing temperature having maximal intensity about 250 °C which was explained by decay of the complex defects into isolated anti-site defects and anionic vacancies. This annealing temperature coincide with temperature of the second stage of defect destruction in ion irradiated spinel ceramics [22].

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СПЕКТРОСКОПИЧЕСКИЕ ИССЛЕДОВАНИЯ ДЕФЕКТОВ В ГАММА- И НЕЙТРОН-ОБЛУЧЕННОЙ КЕРАМИКЕ МАГНИЙ-АЛЮМИНИЕВОЙ ШПИНЕЛИ

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Проведены спектроскопические исследования оптической керамики шпинели, облученной гамма-квантами источника ^{60}Co и смешанным гамма-нейтронным потоком в реакторе ВВР при потоках нейтронов $1\cdot10^{13}$ и $5\cdot10^{13}$ нейтр./см^2. Полученные данные из зависимости интенсивности полос поглощения в видимой области позволили определить природу оптических центров, созданных облучением. Поглощение света в инфракрасной области указывает на присутствие в керамике углеродсодержащих комплексов, которые становятся оптически активными после облучения. Зарегистрированный сигнал ЭПР с g = (2.0174 ±0.0005) и шириной (46.1±1.5) Гс, соответствующий HO_2^- - или O_3^- -радикалам. Зависимость концентраций исследованных центров от температуры отжига в облученной керамике шпинели демонстрирует необычный рост интенсивности поглощения и стационарной люминесценции в интервале температур 200…400 °С. Проанализирована роль комплексов дефектов, которые включают дефекты антиструктуры в образовании и отжиге дефектов в различных температурных областях с учетом различной подвижности катионов и анионов, а также специфики механизма рентгенолюминесценции.

СПЕКТРОСКОПІЧНІ ДОСЛІДЖЕННЯ ДЕФЕКТІВ У ГАММА- ТА НЕЙТРОН-ОПРОМІНЕНІЙ КЕРАМІЦІ МАГНІЙ-АЛЮМІНІЄВОЇ ШПІНЕЛІ

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Проведені спектроскопічні дослідження в оптичній кераміці шпінелі, опроміненій гамма-променями джерела ^{60}Co та змішаним гамма-нейтронним потоком у ВВР реакторі при потоках нейтронів $1\cdot10^{13}$ та $5\cdot10^{13}$ нейтр./см^2. Одержані дані із залежності інтенсивності смуг поглинання у видимій області дозволили ідентифікувати природу оптичних центрів, створених опромінюванням. Поглинання світла в інфрачервоній області вказує на присутність у кераміці комплексів, що містять вуглець та стають оптично активними після опромінення. Зареєстрований сигнал ЕПР з g = (2.0174 ±0.0005) і шириною (46.1±1.5) Гс, що відповідає HO_2^- - або O_3^- -радикалам. Залежність досліджених центрів від температури відпалу в опроміненій кераміці шпінелі демонструє незвичайне збільшення інтенсивності поглинання та стаціонарної люмінесценції в інтервалі температур 200…400 °С. Проаналізована роль комплексів дефектів, які включають дефекти антиструктури в створенні та відпалу дефектів у різних температурних областях з урахуванням різної рухливості катіонів та аніонів, а також специфіки механізму рентгенолюмінесценції.