

Radioluminescence mechanism of magnesium aluminate spinel transparent ceramics

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Radioluminescence (RL) of magnesium aluminate spinel transparent ceramics has been studied. The ceramics were obtained by hot-pressing technique using $\text{MgAl}_2\text{O}_4:\text{LiF}$ powders prepared by dry or sonic mixing of components. It is shown that the RL spectra contain a wide band with maximum at 4.9 eV related to recombination luminescence of electrons with localized holes, a band at 2.39 eV which is assigned to Mn^{2+} ion emission, and red luminescence with sharp lines related to emission of Cr^{3+} ions. Resolution of the UV band into Gaussians results in two bands with maxima at 5.05 and 4.7 eV, which are tentatively identified with electron-hole recombination luminescence at hole centers and anti-site defects. Investigation of the RL intensity increase kinetics for different bands suggests the competing processes of the excitation transfer to impurity ions and recombination of electrons with localized holes.

Изучена рентгенолюминесценция (РЛ) прозрачной керамики магний-алюминиевой шпинели. Керамика получена методом горячего прессования порошков $\text{MgAl}_2\text{O}_4:\text{LiF}$, приготовленных сухим или ультразвуковым перемешиванием компонентов. Показано, что спектры РЛ содержат полосу с максимумом при 4.9 эВ, обусловленную рекомбинационной люминесценцией электронов на локализованных дырках, полосу при 2.39 эВ, идентифицированную с излучением ионов Mn^{2+} , а также красную люминесценцию с линейчатым спектром, обусловленную излучением ионов Cr^{3+} . Разложением на гауссианы широкой УФ полосы получены две элементарные полосы с максимумами при 5.05 и 4.7 эВ, которые предположительно идентифицированы с рекомбинационной люминесценцией на дырочных центрах и дефектах антиструктуры. Исследование кинетики роста интенсивности полос РЛ указывает на конкурирующие процессы передачи возбуждения на примесные ионы и рекомбинации электронов на локализованных дырках.

Due to high melting point, high hardness, and resistance to chemical attack, the magnesium aluminate spinel ($\text{MAS-MgAl}_2\text{O}_4$) has found use in a variety of technological applications. The spinel single crystals and transparent ceramics show excellent dielectric and optical properties and are of good promise in electronic and optical devices, such as insulators, windows, and sensors. Many applications of this material are based

on luminescence properties of nominally pure spinels or those doped with different ions. The spinel single crystals doped with chromium are potentially useful sensor probes for the fiber-optic thermometers due to long photoluminescence lifetime and large temperature coefficient [1]. The spinel serves also as matrix for preparation of luminescent nanoparticles of $\text{MgAl}_2\text{O}_4:\text{Eu}$, Dy with green persistent luminescence after ex-

posure to UV radiation [2]. Searching for dosimetric materials based on the thermoluminescence (TL) or optically stimulated luminescence (OSL) results in conclusion that MAS is a prospective material for radiation dosimetry due to a high OSL signal linearly related to the absorbed dose [3]. It should be noted that the centers responsible for OSL signal are not identified. Unlike simple constituent oxides (MgO and Al_2O_3) having intense emission bands related to F^- and F^+ -centers, the quantum efficiency of these centers in MAS is very low. The investigations of TL spectral composition of nominally pure MAS irradiated with X-rays and X-ray stimulated luminescence (XRSL) at different temperatures show several emissions related to impurity ions such as Cr^{3+} (zero-phonon line at 688.7 nm) and Mn^{2+} ions with emission band at 520 nm. Moreover, an intense emission in UV-range was registered which is attributed to electron-hole recombination processes including mainly anti-site defects [4, 5].

In this work, we provided the detailed investigations of X-ray stimulated luminescence in optical ceramics obtained by different preparation methods to elucidate the emission processes and origin of the luminescence centers. The stationary luminescence and the increase kinetics were measured for different emission bands on the irradiation time.

The spinel ceramics were prepared by hot-pressing technique in the shape of 9 mm thick disks 50 mm in radius. The ceramics was produced by hot pressing of spinel powder $\text{MgAl}_2\text{O}_4:\text{LiF}$ (1 wt. %) at 1550°C and 35 MPa pressure in vacuum. The spinel powder was prepared of pure magnesium aluminate spinel (Baikalox S30SR) and lithium fluoride by dry mixing (the DM series) or sonic mixing (the SM series). The main impurities declared by supplier were (ppm): Na-10, K-200, Fe-20, Si-50, Ca-30. The samples for studies were cut from a segment of the disk that we could search for differences in optical properties along the radius from center to periphery. The 1.2 mm thick slices were polished to optical finish. It was revealed that the slices were optically inhomogeneous in a radial direction. Near the arc rim, there is a transparent area (a); further towards the center of the slice exists a smoke-colored strip which transforms into a diffusive U-type shape with a transparent area (c) inside the U shape (picture is shown in Fig. 1).

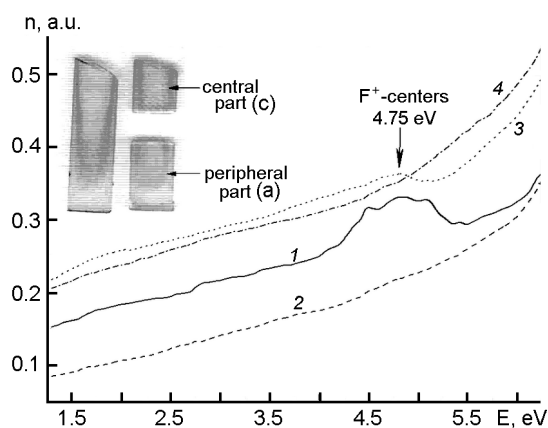


Fig. 1. Absorption spectra of ceramic samples taken from peripheral (a) and central (c) parts of disks obtained from spinel powder prepared using dry mixing (DM) and sonic mixing (SM) methods: 1 – sample DM, part (a); 2 – DM, part (c); 3 – SM part (a); 4 – SM part (c).

To characterize the properties of samples for RL investigations, the optical absorption spectra were measured using a single beam SF-46 spectrophotometer in the wavelength range of 186–960 nm (1.3–6.6 eV). We have measured the optical absorption over the length of a strip in spots (a) and (c) to obtain information on the radial distribution, the nature, and concentration of point defects in the ceramic disc. The obtained spectra show a quite different absorption (Fig. 1) in absolute values of absorption coefficient. In periphery part of the disk, there is an indication on the existence of wide absorption band at 4.75 eV which is usually identified with absorption of F^+ -centers. The stationary RL was measured under X-irradiation from X-ray tube with Cu anode operated at 37 kV and 400 μA . The emission was measured directly from irradiated surface using an MDR-1 monochromator and registered with FEU-106 PMT. The spectra were corrected for spectral sensitivity of the photomultiplier.

The review RL spectra of a sample cut from spinel ceramics disk pressed from a dry-mixed powder is shown in Fig. 2. Similar to the nominally pure spinel single crystals, the RL spectra of spinel ceramics contain three main bands: a wide UV-band with maximum at 4.9 eV, green band at 2.39 eV, and a discrete spectrum of red emission with the main zero-phonon line at 1.8 eV.

The previous investigations [8] have shown that RL in UV range is the most intense in nominally pure crystals. The

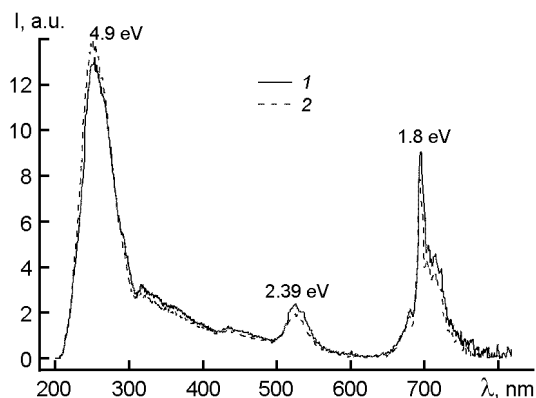


Fig. 2. The review RL spectra of samples cut from spinel ceramics disk pressed from dry mixed powder (DM): 1 – part (a); 2 – part (c).

characteristics of this emission (intensity and spectral composition) depend on the crystal growth method or ceramics production technology. Taking into account the data on RL in other oxide crystals of comparable composition and structure, this emission was assigned to the recombination luminescence of electrons with localized holes. The temperature dependence of this emission indicates this mechanism [4]. The UV emission intensity drops sharply at the temperature at which holes start to be mobile.

The comparative RL spectra in UV-range for peripheral and central parts of disks of both series are shown in Fig. 3. The shape deviation of the UV emission band for different samples, and its large width indicates the nonelementary composition of this band. All the spectra were expanded into three Gaussian bands of about 0.8 eV half-width, which is typical of luminescence involving the lattice defects. Therefore, we obtained three bands with maxima at 5.05, 4.7, and 3.7 eV. The first two bands of slightly different spectral position were observed in thermoluminescence and in RL spectra. These bands were identified with electron-hole recombination on different types of V-centers [6]. The band at 4.95 eV was also observed in RL of MgO crystals which is also attributed to electron recombination on V-type centers [7]. Also, the band of lower energy has been ascribed to recombination of electrons with holes trapped at anti-site defects ($[\text{Mg}]_{\text{Al}}^-$ -centers) [8]. Therefore, we assign the band at 4.7 eV to recombination luminescence on anti-site defects and the 5.05 eV one, to recombination luminescence on V-type centers. Because the intensity ratio of RL bands at 5.05 and 4.7 eV in

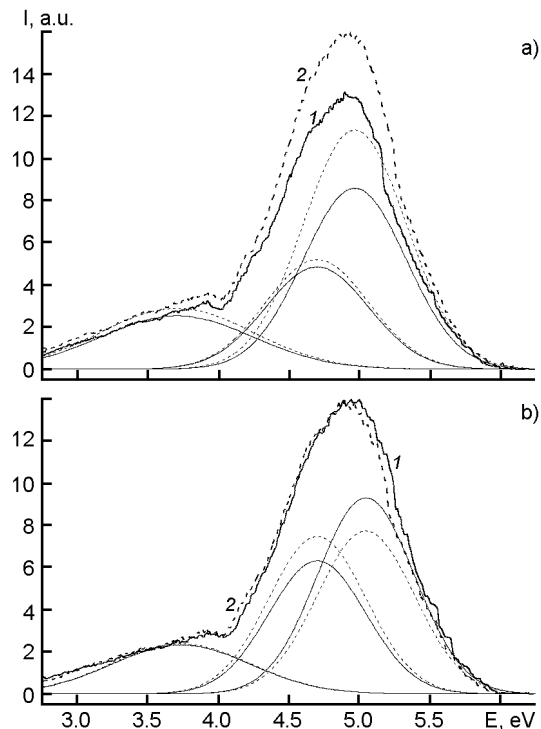


Fig. 3. The comparative RL spectra in UV range for peripheral (a) and central (c) parts of disks for both series and deconvolution into Gaussians: a) part (c), curve 1 – DM and 2 – SM; b) part (a), curve 1 – DM and 2 – SM..

spinel ceramic disk is higher as compared to that of periphery, we may conclude that concentration of hole centers in central part is much higher. The third emission band with maximum at 3.7 eV appeared mainly in ceramics and it can be related to presence of lithium fluoride in the investigated spinel ceramics.

In the spectra of photo-, radio-, and cathodoluminescence of both nominally pure and manganese doped spinel, there appears green luminescence with main band at 2.38–2.4 eV which is ascribed to transition of ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ in Mn^{2+} ions. Numerous spectroscopic investigations suggest that Mn^{2+} ions of $(3d)^5$ electron structure in spinel lattice are situated in oxygen tetrahedral position [9]. Under X-ray irradiation, there are two channels resulting in luminescence of Mn^{2+} ions. When electron-hole pair is created, Mn^{2+} ion attracts at first a hole forming Mn^{3+} ions, while subsequent electron capturing from the conduction band results in radiative recombination and transition of Mn^{2+} ions into ground state. In another channel, in contrast, there exists a possibility for electron to be trapped from

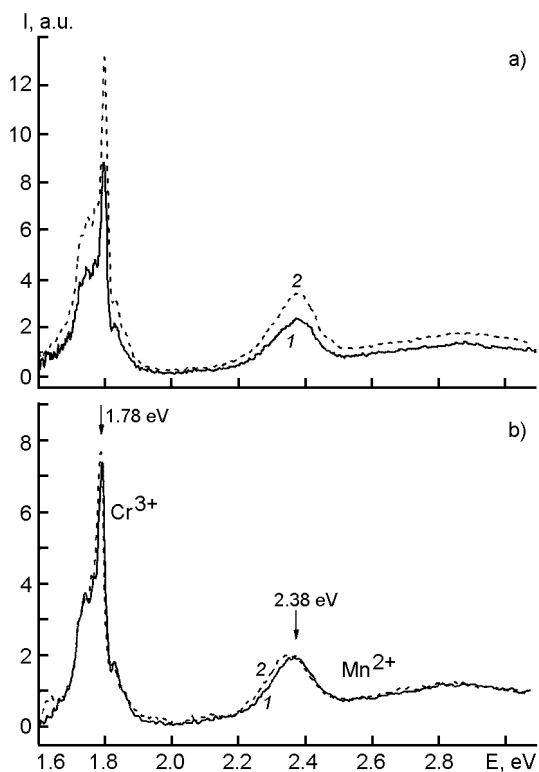


Fig. 4. The comparative RL spectra of Mn^{2+} and Cr^{3+} bands for peripheral (a) and central (c) parts of disks of both series : a) part (c), curve 1 – DM and 2 – SM; b) part (a), curve 1 – DM and 2 – SM..

conduction band by Mn^{2+} ion, then a hole from valence band radiatively recombines forming Mn^{2+} ion in ground state.

In both channels, the electron or hole trapping processes occur at a high probability because (i) the ($3d$)-orbitals of Mn^{2+} ion are well overlapped with $\text{O}-2p_{\sigma}$ ones which compose the valence band, and (ii) the conduction band consisting mainly of Al^{3+} ($3s$) and ($3p$) and/or Mn^{2+} ($3s$) orbitals is well hybridized with higher energy orbitals of Mn^{2+} ion substituting Mg^{2+} ion. That are the reasons for the high transfer efficiency of ionizing irradiation excitation energy to Mn^{2+} luminescence center.

The RL in the red spectral region consists of several narrow lines, the most intense one being at about 1.8 eV and related to ${}^2E(t_2^3) \rightarrow {}^4A_2(t_2^3)$ transition in Cr^{3+} ($3d^3$) ions in octahedral sites. Under X-irradiation, the formation of Cr^{4+} or Cr^{2+} ions takes place and subsequent electron or hole trapping causes the excited state of Cr^{3+} ions [10, 11]. The most intense RL bands of Mn^{2+} and Cr^{3+} ions are observed in the central part of disc prepared from sonic-mixed

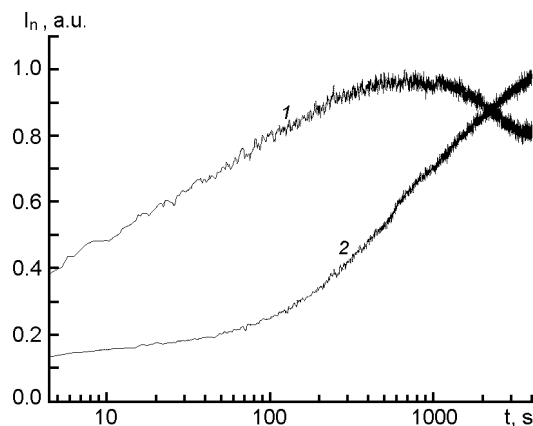


Fig. 5. The growth of RL intensity for UV-emission (1) and emission of Mn^{2+} -ions (2) under X-ray irradiation.

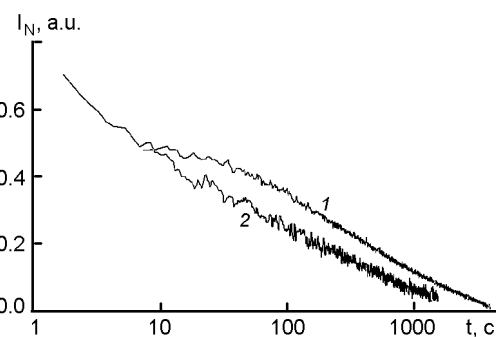


Fig. 6. Fluorescence decay after termination of X-ray irradiation of UV-emission (1) and emission of Mn^{2+} -ions (2).

powder which corresponds to perfect crystal spinel structure (see Fig. 4).

For each luminescence bands, there were measured the RL increase under prolonged X-ray irradiation and the luminescence decay after the irradiation is over. The typical kinetics of the RL increase represented in semi-log scale is shown in Fig. 5. The comparison of luminescence increase curves at lattice defects and impurity ions gives information on processes causing the luminescence. Initially, the direct excitation of Mn^{2+} ions results in a sharp increase of RL intensity. The further intensity increase occurs according to two channels described before through the subsequent trapping of charge carriers generated by irradiation. Simultaneously, the accumulation of hole centers at cation vacancies and anti-site defects takes place and radiative recombination of electrons with holes causes a gradual increase of UV-band intensity. At a high concentration of hole centers (irradiation time exceeding 500 s), the electrons released

under irradiation primarily recombine with holes localized at lattice defects, thus causing the decreasing luminescence intensity of impurity ions.

The irradiated spinel samples demonstrated a long afterglow for all emission bands. The fluorescence decay law cannot be described by one exponent; thus indicating the complex process of energy relaxation in irradiated samples. We have presented the decay kinetics also in semi-log scale and found these dependences to be also different for UV-luminescence and luminescence of impurity ions. Now we are under way to develop a model which could be applied to explain this difference.

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References

1. H.Aizava, N.Ohoshi, S.Ogawa et al., *Rev. Sci. Instr.*, **73**, 3089 (2002).
2. A.S.Maia, R.Stefani, C.A.Kodaira et al., *Opt. Mat.*, **31**, 440 (2008).
3. E.M.Yushimura, E.G.Yukihara, *Radiat. Measur.*, **41**, 163 (2006).
4. V.T.Gritsyna, Yu.G.Kazarinov, V.A.Kobyakov, I.E.Reimanis, *Nucl. Instr. Meth. Phys. Res*, **B250**, 342 (2006).
5. A.Lushchik, M.Kirm, A.Kotlov et al., *J. Luminescence*, **102–103**, 38 (2003).
6. A.Ibarra, D.F.Mariani, M.J.de Castro, *Phys. Rev.*, **B44**, 12158 (1991).
7. K.H.Lee, J.H.Crawford, *J. Luminescence*, **20**, 8, (1979).
8. V.T.Gritsyna, Yu.G.Kazarinov, V.B.Kol'ner et al., *Functional Materials*, **12**, 652 (2005).
9. A.Tomita, T.Sato, K.Tanaka et al., *J. Luminescence*, **109**, 19 (2004).
10. V.T.Gritsyna, I.V.Afanasyev-Charkin, V.A.Kobyakov, *J. Am. Ceram. Soc.*, **82**, 3365 (1999).
11. T-L.Phan, M-H.Phan, S-C.Yu, *Phys. Stat. Sol. (b)*, **241**, 434 (2004).

Механізм рентгенолюмінесценції прозорої кераміки магній-алюмінієвої шпінелі

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Досліджено рентгенолюмінесценцію (РЛ) прозорої кераміки магній-алюмінієвої шпінелі. Кераміку виготовлено методом гарячого пресування порошків $MgAl_2O_4:LiF$, приготованих сухим або ультразвуковим змішуванням компонентів. Знайдено, що спектри РЛ містять смугу при 4,9 еВ, зумовлену рекомбінаційною люмінесценцією електронів на локалізованих дірках, смугу при 2,39 еВ, ідентифіковану з випромінюванням іонів Mn^{2+} , а також червону люмінесценцію з лінійчатим спектром, зумовлену випромінюванням іонів Cr^{3+} . Розкладом широкої УФ смуги на гаусіани виявлено дві елементарні смуги з максимумами при 5,05 та 4,7 еВ, що вірогідно ідентифіковано з рекомбінаційною люмінесценцією на діркових центрах та дефектах антиструктури. Дослідження кінетики росту інтенсивності смуг РЛ вказує на конкуруючі процеси передачі збудження на іони домішок та рекомбінації електронів на локалізованих дірках.