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Microstructure and luminescent properties of Eu$^{3+}$-activated MgGa$_2$O$_4$:Mn$^{2+}$ ceramic phosphors

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Abstract: Mn$^{2+}$ and the trivalent europium (Eu$^{3+}$)-doped MgGa$_2$O$_4$ ceramics are characterized using a multi-experimental approach. The formation of spinel-structured ceramics is ascertained from X-ray diffraction (XRD) analysis. Morphology investigations with transmission electron microscopy (TEM) show irregularly shaped grains and grain boundaries with a homogeneous distribution of Eu$^{3+}$ ions. The inability of Eu activator to penetrate the bulk of ceramic grains is inferred from positron annihilation lifetime spectroscopy data. The Eu doping is shown to enhance the positron trapping rate due to the occupancy of vacancy-type defects at ceramic grains by Eu$^{3+}$ ions. Both Mn$^{2+}$ and Eu$^{3+}$ doped samples show a broad multi-color luminescence in 350–650 nm range under 240 nm and 270–300 nm excitations. Blue emission is concluded to originate from host defects, whereas green emission and narrow lines in the red region of the spectrum are attributed to Mn$^{2+}$ and Eu$^{3+}$ ions, respectively. High asymmetry around Eu$^{3+}$ ions can be concluded from the photoluminescence and positron annihilation lifetime spectra analysis.

Keywords: spinel structure; magnesium gallate MgGa$_2$O$_4$; X-ray diffraction (XRD); positron annihilation; Mn$^{2+}$ and Eu$^{3+}$ luminescence

1 Introduction

Flat-panel displays (plasma, field-emission, electroluminescence, etc.) have drawn much interest recently due to their ultimate importance for modern electronics. The spinel oxide compounds are shown to be very appealing candidates for such applications due to their superior optical transparency, high thermal, and chemical stability, as well as electronic and magnetic properties [1–4]. As a result, the luminescent spinel-structured phosphors have emerged as one of the key materials
comprising an archetypal research challenge in nowadays optoelectronics [1–5]. For a long period, the 380 nm pumping radiation obtained from conventional ZnO electroluminescence or ultraviolet light-emitting diode (UV-LED) technology was used for the excitation of phosphors in flat-panel display systems. Recent optimization of micropillar approaches has boosted the deep UV-LED (DUV-LED) technologies, which enabled a new class of materials to be used in flat-panel display applications. The novel DUV-LEDs usually provide a quite powerful pumping (~150 mW) in UV spectral range with a maximum at 265 nm [6]. Currently, DUV-LED technology is on the way to be improved in terms of stability and power consumption [6].

The trivalent europium (Eu$^{3+}$) plays an important role as photoluminescent (PL) ion in phosphors due to its narrow emission bands in the orange region [5,7]. The PL of MgGa$_2$O$_4$ ceramics doped with Eu$^{3+}$ has been studied in Refs. [1,8,9], while those activated by Mn$^{2+}$ dopants were analyzed in Refs. [2,3,10–13]. It was shown that PL properties of such phosphors are strongly dependent on calcination temperature during synthesis procedure [1,3], affecting both the grain size [1] and the concentration of doping ions [2,8,10,11,13]. The combination of orange PL associated with Eu$^{3+}$ dopants with blue intrinsic PL of host lattice and green PL of Mn$^{2+}$ ions makes it possible to obtain phosphors in the visible range of spectrum using spinel-type compounds alone [8,9]. Despite a vast interest in the magnesium gallate spinels (including MgGa$_2$O$_4$) in view of their possible applications, the PL mechanisms of Eu$^{3+}$ ions and their incorporation into spinel host matrix is still a matter of hot debates. To our best knowledge, the correlation between PL and structure of spinel gallates has not been studied. There are only a few papers concerning the relationship between defect structure and PL in zinc gallate (ZnGa$_2$O$_4$) spinel [14,15], while similar studies for MgGa$_2$O$_4$ spinel have not been reported yet.

In this study, spinel-structured non-transparent MgGa$_2$O$_4$ ceramic phosphors prepared by solid-state reactions and doped with Mn$^{2+}$ and Eu$^{3+}$ activators are comprehensively characterized with X-ray diffraction (XRD), scanning transmission electron microscopy (STEM) with energy-dispersive X-ray spectroscopy (EDS) analysis, positron annihilation lifetime (PAL) spectroscopy, and photoluminescence (PL) methods. The use of a multi-experimental approach allowed us to shed more light on the correlation between PL mechanism and preferential surroundings of Eu$^{3+}$ activators in these ceramic phosphors.

2 Experimental

2.1 Sample preparation

The MgGa$_2$O$_4$: 0.05 mol% Mn$^{2+}$ and MgGa$_2$O$_4$: 0.05 mol% Mn$^{2+}$, 4 mol% Eu$^{3+}$ ceramics were prepared using standard high-temperature ceramic technology. The host material was prepared from simple oxides of magnesium and gallium (MgO, β-Ga$_2$O$_3$). The doping was implemented by substitution of magnesium and gallium oxides with manganese (II) oxide (MnO) and europium (III) oxide (Eu$_2$O$_3$) of the same molar amount. The optimal concentration of Mn$^{2+}$ and Eu$^{3+}$ activator ions was chosen to have a maximum yield of luminescence in green and orange-red spectral regions, respectively. The initial powders were at least of 4N purity. The mixing of the powders was carried out in agate mortar for 6 h with further pressing in a steel mold. The obtained pellets were heated with 5 °C/min ramp up to 1200 °C (±5 °C), held at this temperature for 8 h and cooled down to room temperature in the regime of the switched-off furnace.

2.2 Microstructure characterization

The structure of prepared ceramics was studied with XRD analysis. Experimental XRD patterns were collected using the STOE STADI P diffractometer equipped with a linear position-sensitive detector and X-ray tube with Cu anode (Kα$_1$-radiation, $\lambda$ = 1.5406 Å). The measurements were carried out with 0.005° scanning step and the diffraction peaks were analyzed with the STOE WinXPOW software package.

Morphology of intrinsic grains in the ceramics was investigated using the TEM method complemented by EDS analysis (FEI Tecnai Osiris device). The atomically resolved information was obtained through a combination with a high-angle annular dark-field (HAADF) detector. The investigated samples were powdered with agate mortar and pestle, suspended in ethanol, sonicated for 5 min, placed onto the TEM Cu grid, and dried at the ambient temperature.

The free-volume structure on the atomic scale was studied with PAL spectra analysis. These spectra were recorded using a fast-fast coincidence system of 230 ps
resolution (full width at half maximum) equipped with two Photonis XP2020/Q photomultiplier tubes coupled to BaF2 scintillator detectors. The 22Na isotope (~50 kBq) sealed in Kapton film was used as a positron source, which was sandwiched between 2 identical samples. The experiments were performed in controlled conditions (22 °C ambient temperature and 35% humidity) collecting the normal statistics of 1M annihilation events. Three measurements for each sample were performed to ensure reproducibility of the results. The software LT 9.0 program [16] was used to decompose the raw PAL spectra into three exponentials, which contain information about the annihilation of positrons within defect-free bulk, trapped in free-volume defects, and forming bound positron-electron states (positronium Ps). The resultant accuracy in lifetime (τ) and intensity (I) was ±0.005 ns and ±5%, respectively. The positron trapping was parameterized by mean positron lifetime (τm), defect-free bulk lifetime (τb), trapping rate in defects (κ), and fraction of trapped positrons (η) defined within two-state simple trapping model (STM) [17–19], applied in addition to Ps-decay contribution [20]. Following the interpretation of free-volume positron trapping [17], the difference between defect-specific and defect-free lifetime (τ2 – τb) was accepted as a signature of positron traps in terms of the equivalent number of vacancies, whereas τ2/τb ratio was ascribed to the nature of these defects.

2.3 Optical-PL characterization

Optical absorption spectra of the ceramics in 200–800 nm range were recorded at room temperature using a double-beam spectrophotometer Agilent Cary 5000. The optical absorption setup was equipped with Agilent diffuse reflectance accessory focusing an integrated signal to the detector.

PL characterization of the studied ceramics was carried out at room temperature employing SM 2203 spectrofluorometer operated in 230–820 nm range. The PL excitation was performed with a 150 W Xenon lamp, the Hamamatsu R928 photomultiplier being used for spectra detection. Both PL excitation and emission spectra were registered with a resolution of 0.5 nm and automatically corrected by lamp intensity and photomultiplier tube sensitivity. Additional PL measurements at room (T_R = 298 K) and liquid nitrogen (T_LN = 77 K) temperatures were performed for Eu3+ doped MgGa2O4:Mn2+ ceramics using Horiba Fluorolog-3 spectrofluorometer equipped with Xenon short-arc lamp as a light source. The PL emission spectra were collected in 300–640 nm range with excitation wavelength in 235–585 nm range.

3 Results and discussion

3.1 Phase composition and atomic-specific structure

The Rietveld refinement analysis of ceramic samples with nominal compositions of MgGa2O4: 0.05 mol% Mn2+ and MgGa2O4: 0.05 mol% Mn2+, 4 mol% Eu3+ was carried out for XRD patterns shown in Fig. 1. Besides the main MgGa2O4 phase (MgAl2O4 structure type, Pearson symbol cF56, space group Fd-3m (227)), a negligible amount of Ga2O3 phase (Pearson symbol mS20, space group C2/m(12)) was found in MgGa2O4:Mn2+ ceramics (Table 1). In Eu-doped MgGa2O4:Mn2+ samples, about 2.3 mol% of additional Eu3Ga5O12 phase (Y3Al5O12 structure type, Pearson symbol cI160, space group Ia-3d (230)) was revealed to coexist with the main MgGa2O4 spinel phase (Table 2).

![Fig. 1 Experimental XRD patterns of MgGa2O4:Mn2+ and MgGa2O4:Mn2+,Eu3+ ceramics (cell parameter, a = 8.2704(1) Å, R-factor = 2.44)](image)

Table 1 Atomic coordinates of spinel phase in MgGa2O4:Mn2+ ceramics (cell parameter, a = 8.2704(1) Å, R-factor = 2.44)

| Site | Wyckoff position | Atomic coordinates | Occupancy |
|------|-----------------|-------------------|-----------|
| O    | 32e             | x = 0.2441        | y = 0.2441| z = 0.2441| 1          |
| Mg1  | 16c             | 0                 | 0         | 0         | 0.46(1)    |
| Ga1  | 16c             | 0                 | 0         | 0         | 0.54(1)    |
| Mg2  | 8b              | 3/8               | 3/8       | 3/8       | 0.18(1)    |
| Ga2  | 8b              | 3/8               | 3/8       | 3/8       | 0.82(1)    |

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Table 2  Atomic coordinates of spinel phase in Eu-doped MgGa2O4:Mn2+,Eu3+ ceramics (a = 8.2726(1) Å, R-factor = 3.17)

| Site  | Wyckoff position | Atomic coordinates | Occupancy |
|-------|------------------|---------------------|-----------|
| O     | 32e              | x=0.2441 y=0.2441 z=0.2441 | 1         |
| Mg1   | 16c              | x=0 y=0 z=0 | 0.48(1) |
| Ga1   | 16c              | x=0 y=0 z=0 | 0.52(1) |
| Mg2   | 8b               | x=3/8 y=3/8 z=3/8 | 0.17(1) |
| Ga2   | 8b               | x=3/8 y=3/8 z=3/8 | 0.83(1) |

Similar content of additional garnet phase was also observed in Eu-doped ZnGa2O4:Mn2+ ceramics recently [14]. Zhang et al. [15] used a facile hydrothermal method to synthesize ZnGa2O4 ceramics doped with a small amount (< 5 mol%) of Mn2+ or Eu3+ ions, but no additional phase was detected. Li et al. [21] reported the Eu3Ga5O12 phase in Eu-doped MgGa2O4 ceramics at the concentration of Eu3+ ions above 5 mol%, whereas Sawada et al. [22] observed no Eu3+ emission for Eu3Ga5O12 garnet. Owing to low concentration in our samples, it looks like the additional garnet phase does not affect the properties of the investigated MgGa2O4 ceramics, and would not be discussed further.

The refined structural data show that both MgGa2O4:Mn2+ and Eu-doped MgGa2O4:Mn2+ ceramics possess a partially inversed spinel structure. However, a normal spinel structure without inversion has been reported recently for similar ceramics obtained with this technology and with identical concentrations of Mn and Eu dopants [14]. This apparent controversy is due to a high number of singly charged point defects [Ga₄₋₈⁺] and [Mg₇⁺] caused by cation exchange between tetrahedral and octahedral sites, which is the reason for inverse spinel structure of the investigated magnesium gallate compounds, as well as changes in their physical properties.

Embedding the Eu3+ ions into a spinel-structured MgGa2O4 host matrix leads to a small increase in cell parameters, whereas the rest of unsolvable europium oxide Eu2O3 forms an additional garnet phase. Additional process in the structure of Eu-doped MgGa2O4:Mn2+ ceramics can be suspected because of much higher R-factor concerning that observed in MgGa2O4:Mn2+ and Eu-doped MgGa2O4:Mn2+ spinel-structured ceramics are shown in Figs. 2(a) and 2(b), respectively. The observed grains of irregular shape seem to be a common feature of these ceramics prepared by solid-state synthesis [14,21].

The EDS maps of MgGa2O4:Mn2+ and MgGa2O4:Mn2+,Eu3+ ceramics are presented in Figs. 2(a), 2(c), 2(e), and 2(g), and Figs. 2(b), 2(d), 2(f), 2(h), and 2(i), respectively. Homogeneous distribution of Eu across grain surfaces is evident from the EDS map for Eu-doped ceramics (Fig. 2(i)). At the same time, the concentration of Mn2+ dopant is too low to be detected unambiguously by this technique.

The electron diffraction patterns of both MgGa2O4:Mn2+ and MgGa2O4:Mn2+,Eu3+ ceramics are shown in Figs. 3(a) and 3(b). Figure 3 demonstrates typical patterns of polycrystalline material with sharp reflexes from 400, 422, 440, 533, and 731 planes of spinel phase and no traces of other additional phases.

3.2 Grain morphology

The HAADF–STEM images of both MgGa2O4:Mn2+ and Eu-doped MgGa2O4:Mn2+ spinel-structured ceramics are shown in Figs. 2(a) and 2(b), respectively. The observed grains of irregular shape seem to be a common feature of these ceramics prepared by solid-state synthesis [14,21].

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3.3 Nanovoid structure

Based on the PAL spectroscopy data, it can be concluded that Eu3+ ions do not penetrate deeply into the grains of spinel-structured MgGa2O4:Mn2+ ceramics.

The raw PAL spectra of these ceramics are presented in Fig. 4, while corresponding parameters of the unconstrained three-exponential fits are gathered in Table 3. The results show only a slight growing tendency in τav of the Eu-doped ceramics (Fig. 5 compares PAL spectra of both ceramics).

In the developed approach to spinel-type ceramics [23], the second component (τ2, I2) in the decomposed PAL spectrum can be attributed to a positron trapping in vacancies and vacancy-like free-volume defects located preferentially near grain boundaries. The third long-lived lifetime component (τ3, I3) is responsible for Ps-decay through the “pick-off” annihilation of a positron with an electron from surrounding [17,20]. In spinel-structured ceramics, the Ps is known to be localized in free-volume holes within intergranular space [23], which means that radius R3 of these holes can be calculated using τ3 in the Tao–Eldrup approach [17]. Respectively, the intensity (I3) correlates with the number of Ps sites, so that the fractional free volume (f3) can be calculated in a spherical approximation with some empirical constant [20].

Since only low contribution in the PAL spectra shown in Fig. 4 arises from the third component (the corresponding intensity I3 in Table 3 does not exceed
the realistic annihilation scheme in this ceramics can be quite adequately described within two-state STM [17–19], thus ignoring Ps-decay contribution [20]. The results of such parameterization are gathered in Table 4. This simplification allows us to conclude that Eu$^{3+}$ doping enhances positron trapping in the studied MgGa$_2$O$_4$:Mn$^{2+}$ ceramics (due to increased $\kappa_d$ from 0.50 to 0.72 ns$^{-1}$). Realistically, this enhancement is counterbalanced by a decrease in $f_{x3}$ calculated from Ps-related components. The high values of ($\tau_2 - \tau_b$) reaching ~0.13–0.15 ns and

![Image](https://example.com/image1.png)

**Fig. 2** HAADF–STEM images of (a) MgGa$_2$O$_4$:Mn$^{2+}$ and (b) MgGa$_2$O$_4$:Mn$^{2+}$,Eu$^{3+}$ grains, with corresponding chemical composition EDS maps of (c, e, g) MgGa$_2$O$_4$:Mn$^{2+}$ and (d, f, h, i) MgGa$_2$O$_4$:Mn$^{2+}$,Eu$^{3+}$ grains, representing location of each element in the grain.

![Image](https://example.com/image2.png)

**Fig. 3** Electron diffraction patterns of (a) MgGa$_2$O$_4$:Mn$^{2+}$ and (b) Eu-doped MgGa$_2$O$_4$:Mn$^{2+}$,Eu$^{3+}$ ceramics.

![Image](https://example.com/image3.png)

**Fig. 4** Raw PAL spectra of spinel-structured (a) MgGa$_2$O$_4$:Mn$^{2+}$ and (b) MgGa$_2$O$_4$:Mn$^{2+}$,Eu$^{3+}$ ceramics, reconstructed from unconstrained x3-term fitting and source contribution (bottom insets show statistical scatter of variance).
traps in both types of the studied ceramics. The role of quadruple vacancies \[17,23\] as prototypes of positron clusters with free volumes comparable to triple or even trapping and Ps-decay contributions into the resulting form for both non-modified (MgGa\(_2\)O\(_4\):Mn\(^{2+}\)) and PAL spectra are transformed into generalized \(x^2\)-term this formalism, the unconstrained \(x^3\)-term reconstructed

\[
\tau \approx 0.3 \text{ nm (radius) by positron}
\]

\[
I_{\text{int}}(a.u.) = R_3(nm) = \frac{I_{\text{int}}}{3}\text{ratio approaching } \sim 2.1 \text{ are located deeply in ceramic grains. Therefore, the holes associated with Ps decay should stabilize predominantly at the ceramic grain boundaries.}
\]

The obtained results suggest that relative input of positron traps in an overall annihilation process in Eu-doped MgGa\(_2\)O\(_4\):Mn\(^{2+}\) spinel-structured ceramics is enhanced as a result of Eu\(^{3+}\) ions localization in the Ps-decaying holes near ceramic grain boundaries. This should decrease their effective number, and consequently, depress the Ps-related component in the PAL spectra.

3.4 Optical absorption

The optical absorption spectra of both ceramics are shown in Fig. 6. The MgGa\(_2\)O\(_4\):Mn\(^{2+}\) spinel-structured ceramics show an intense absorption band in the UV region of

\[
\tau_b = -1.7\text{–}1.8 \text{ (Table 4) suggest multivacancy clusters with free volumes comparable to triple or even quadruple vacancies \[17,23\] as prototypes of positron traps in both types of the studied ceramics. The role of Ps-decay input is somewhat depressed in Eu\(^{3+}\)-doped ceramics due to decreased probability of Ps formation, as it follows from opposite trends in } I_3 \text{ and } I_1 \text{ compared to } I_2 \text{ [24].}
\]

In the case of well-separated inputs from positron trapping and Ps-decay contributions into the resulting PAL spectra, the Ps-positron trapping conversion can be analyzed with \(x^3\)-\(x^2\)-CDA (coupling decomposition algorithm) [25,26]. A similar approach was successfully used recently to analyze the reverse positron-to-Ps trapping interplay in zinc gallate ceramics [14]. Within this formalism, the unconstrained \(x^3\)-term reconstructed PAL spectra are transformed into generalized \(x^2\)-term form for both non-modified (MgGa\(_2\)O\(_4\):Mn\(^{2+}\)) and modified (Eu-doped MgGa\(_2\)O\(_4\):Mn\(^{2+}\)) ceramics assuming all possible trapping contributions (including ortho-Ps decay and para-Ps self-annihilation). This allows to resolve additional component in the generalized \(x^2\)-term PAL spectrum for modified matrix (with defect-related positron lifetime (\(\tau_{\text{int}}\)) and intensity (\(I_{\text{int}}\)) and compensating (\(\tau_m, I_n\)) input to the first channel. The \(\tau_{\text{int}}\) in this model reflects appeared/disappeared defect-related traps depending on the positive/negative sign of both \(I_n\) and \(I_{\text{int}}\) [14,25,26].

The comparison of trapping parameters calculated with the \(x^3\)-\(x^2\)-CDA for studied samples of spinel-structured ceramics is given in Table 5. Taking into account positive values of \(I_n\) and \(I_{\text{int}}\) intensities, the overall free-volume evolution caused by Eu\(^{3+}\) doping can be described as the replacement of Ps-decaying holes with \(\tau = 2.142 \text{ ns (corresponding to spheres of approximately } \sim 0.30 \text{ nm in radius) by positron trapping free-volume defect with } \tau_{\text{int}} = 0.372 \text{ ns (the equivalent of multi-vacancy clusters \[17,23\]). Owing to close values of bulk positron lifetime for modified ceramics (\(\tau^m_{\text{bulk}} \approx 0.18 \text{ ns}) and defect-free bulk positron lifetime for spinel-structured compounds \[26\], we believe that respective positron traps (which should be quite extended due to large } \tau_{\text{int}}/\tau^m_{\text{bulk}} \text{ ratio approaching } \sim 2.1\) are located deeply in ceramic grains. Therefore, the holes associated with Ps decay should stabilize predominantly at the ceramic grain boundaries.

The obtained results suggest that relative input of positron traps in an overall annihilation process in Eu-doped MgGa\(_2\)O\(_4\):Mn\(^{2+}\) spinel-structured ceramics is enhanced as a result of Eu\(^{3+}\) ions localization in the Ps-decaying holes near ceramic grain boundaries. This should decrease their effective number, and consequently, depress the Ps-related component in the PAL spectra.

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\]
the spectrum with a maximum around 240 nm (Fig. 6, black dashed line), which corresponds to “band-to-band” absorption in host MgGa₂O₄ matrix. The band gap energy estimated by extrapolation of the fundamental optical absorption edge for MgGa₂O₄:Mn²⁺ gives a value of about 4.8 eV. A broad absorption band is observed for MgGa₂O₄:Mn²⁺ ceramics in a 400–600 nm range with a maximum of around 480 nm. One of the possible origins of this broadband is Mn in the “4+” state, which was observed earlier by Costa et al. [11]. However, we assume that Mn⁴⁺ ions have appeared in Ref. [11] due to a high sintering temperature of 1500 °C which caused strong evaporation of starting materials (primarily of gallium). The deficiency of host atoms led to the creation of vacancy defect and change in the valence state of a significant number of manganese ions. The conclusion on the substantial impact of sample preparation conditions on the manganese valence state is also supported by Moon et al. [2]. In our case, we have used lower sintering temperatures to avoid strong evaporation of initial precursors and obtained samples with minimal deviation from stoichiometry. We found no direct evidence on the existence of Mn⁴⁺ ions in the MgGa₂O₄:Mn²⁺ ceramics. Another explanation of a broad absorption band with a maximum at 480 nm is due to the resonant absorption in-between the levels formed by host defects. This explanation is supported by earlier results obtained on a series of MgGa₂O₄:Mn²⁺, Eu³⁺ samples with various content of Eu³⁺ ions [8]. It was shown that Eu³⁺ ions substantially suppress the matrix emission, which correlates with the disappearance of the broad absorption band in the absorption spectrum of Eu-doped MgGa₂O₄:Mn²⁺ ceramics (Fig. 6, red solid line) and the results of PAL spectroscopy presented above.

The optical absorption spectrum of the Eu-doped MgGa₂O₄:Mn²⁺ ceramics demonstrates similar features (Fig. 6, red solid line), except that the maximum UV band is red-shifted due to the overlap with the intense band visible as shoulder around 290 nm. This shoulder is associated with charge transfer from 2p shell of oxygen anions to 4f shell of Eu³⁺ ions [9]. Sharp absorption lines observed on the right side of the absorption spectrum (Fig. 6) originate from f–f transitions in 4f⁶ configuration of Eu³⁺ ions. The most prominent line at 393 nm is identified as ⁷F₀–⁵L₆ transition [1,9], while the rest of the lines observed at 414, 464, 525, and 583 nm are caused by ⁷F₀–⁵D₈ transitions with j value of 3, 2, 1, and 0, respectively. The energy-level diagram showing the observed absorption and emission are presented in Fig. 7.

3. 5 Photoluminescence at room and liquid nitrogen (LN) temperatures

The PL properties of the MgGa₂O₄:Mn²⁺ and MgGa₂O₄:Mn²⁺,Eu³⁺ ceramics were studied at room temperature, and the results are presented in Figs. 8 and 9, respectively. The magnesium gallate ceramics doped with manganese ions show strong excitation in deep UV spectral region with a maximum at about 240 nm related to the fundamental absorption of magnesium gallate host under 505 nm monitoring wavelength (Fig. 6). This aspect indicates a favorable contribution of the recombination mechanism to manganese ion excitation [8,12]. Also, the existence of a strong green emission band of MgGa₂O₄:Mn²⁺ ceramics with a peak at 505 nm under the excitation of 240 nm UV light shows an efficient energy transfer from the host to the manganese activator ions. The
shoulder at about 275 nm is assigned to charge transfer from oxygen to manganese ions. Another weak excitation found in the region of 325–450 nm is due to the matrix PL excitation [8] that partially overlaps with unresolved d–d excitation bands of Mn2+ ions [11–13]. The MgGa2O4:Mn2+ ceramics at 240 and 270 nm excitations show emission in two spectral regions of 320–470 nm and 470–550 nm related to host defects of the spinel structure and Mn2+ ions, respectively [2,8]. It should be noted that the relative intensity of the green emission associated with Mn2+ ions increases significantly with the excitation in the region of fundamental absorption edge, which is indirect evidence of the recombination mechanism. However, the relative intensity of PL from the matrix is comparable with activator PL at the excitation in the charge transfer band. According to Costa et al. [11] and Mironova et al. [27], luminescence at 505 nm is typical for divalent manganese cations in four-fold tetrahedrally coordinated sites corresponding to 4T1(4G)→6A1(6S) transition in Mn2+. The PL excitation and emission spectra of Eu-doped MgGa2O4:Mn2+ ceramics monitored at 505 and 617 nm are shown in Fig. 9. These spectra occurred to be similar to those detected in MgGa2O4:Mn2+ samples (Fig. 8). However, the host and Mn2+ excitation bands in the range of 325–450 nm are effectively suppressed by the incorporation of Eu3+ emission. This effect is explained by the redistribution of the energy between Mn2+ and Eu3+ activators. Broad excitation band (charge transfer from O2− to Eu3+ ions) and several excitation peaks in 350–550 nm region (f–f transition in Eu3+) ions, with two strongest ones at 393 (7F0→5L6) and 462 (7F0→5D2) nm were found under 617 nm monitored wavelength.

In addition to the intense broadband PL centered at 505 nm associated with Mn2+ ions, the MgGa2O4:0.05Mn2+, Eu3+ ceramics show emission at 575–650 nm, which belongs to the transitions from excited 3D0 to ground 7Fj (j=1, 2) level of the Eu3+ ions [1,8,9]. The strongest red emission at about 617 nm associated with 5D0→7F2 transition of Eu3+ ions is dominated in the PL spectrum. It should be noted that the matrix luminescence was completely suppressed in these ceramics after doping with Eu3+ ions.

It is well known that the local symmetry of Eu3+ sites in the lattice is reflected by a form of Eu3+ emission spectrum. According to the Judd–Ofelt theory [28,29], the magnetic dipole transition at about 593 nm (3D0→3F1) is attributed to the ions with higher symmetry, while electric-dipole transitions at about 617 nm (3D0→3F2) originate mainly from the ions in sites with lower symmetry. The more asymmetric is the local surrounding around Eu3+ ion, the higher is the intensity of the electric-dipole transition (Fig. 9). The intense red emission of Eu3+ ions is caused by dominated electric-dipole transitions in Eu-doped MgGa2O4:Mn2+ spinel ceramics. Thus, the important parameter that has been used to identify site symmetry of Eu3+ ions is the intensity ratio between magnetic-dipole and electric-dipole transitions, emitting at about 595 and 617 nm, respectively. The calculated asymmetry ratio (3D0→3F2)/(3D0→3F1) for MgGa2O4:Mn2+,Eu3+ ceramics is equal to 3.4 for the intensities (I617/I593), and 2.7 for the areas of respective group lines (S605-640/S585-605). The above-obtained asymmetry values suggest that coordination polyhedron around Eu3+ ions is rather distorted or asymmetric, i.e., the Eu3+ ions occupy non-inversion symmetry sites in a spinel lattice of Eu3+.
these ceramics.

The three-dimensional (3D) fluorescence spectra of Eu\(^{3+}\) doped MgGa\(_2\)O\(_4\)::Mn\(^{2+}\) ceramics at room and LN temperatures are compared in Fig. 10. At LN temperature, the PL within 320–360 nm caused by the excitation at \(~240\) nm wavelength diminishes, while the PL within 370–440 nm region becomes more prominent (Figs. 10(a) and 10(b)). The PL intensity also increases at around 595 and 620 nm when excited with light of 468, 528, and 580 nm at LN temperature (\(T_{LN}\)) (Figs. 10(c) and 10(d)). At the same time, the intensity of PL at around 620 nm with excitation at \(~350\), \(~375\), and \(~395\) nm decreases compare to PL at room temperature (Figs. 10(c) and 10(d)).

The luminosity Commission Internationale de l'Éclairage (CIE) diagram of spinel-structured magnesium gallate ceramic samples is shown in Fig. 11. The solid blue curve represents the temperature emission of the black body. This curve is surrounded by A, B, C circles defining standard illuminants. The E corresponds to the point of achromatic white color, and \(D_{65}\) corresponds to the color of black body emission at 6500 K.

The respective emission colors of the prepared MgGa\(_2\)O\(_4\) ceramics are marked by squares 1–5 (Fig. 11). The first point represents the emission of MgGa\(_2\)O\(_4\)::Mn\(^{2+}\) ceramics with 240 nm excitation and shows a bluish-green color due to the strong emission of Mn\(^{2+}\) ions and weak matrix PL. The same sample with 270 nm excitation exhibits greenish-blue PL (point 2) that is caused by the dominant broad emission band of the spinel matrix and addition of green Mn\(^{2+}\) PL emission. Taking into account the previously reported PL excitation spectra of completely “pure” magnesium gallate MgGa\(_2\)O\(_4\) and manganese-modified MgGa\(_2\)O\(_4\)::Mn\(^{2+}\) spinel-structured ceramics [8], we conclude that both spectra are overlapped in the UV region. Thus, it is not possible to obtain only matrix or Mn\(^{2+}\) emission in the MgGa\(_2\)O\(_4\)::Mn\(^{2+}\) ceramics, since the first and second points, show edges of possible PL emission color in manganese-doped gallate spinel.

**Fig. 10** PL spectra of Eu-doped MgGa\(_2\)O\(_4\)::Mn\(^{2+}\) ceramics recorded at (a, c) room temperature and (b, d) LN temperature.

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The emission colors of Eu-doped MgGa₂O₄:Mn²⁺ spinel-structured ceramics are represented by the points 3–5 and corresponding squares 3–5 on Fig. 11. The PL emission of the Eu-doped sample with excitation at 240 nm is located close to point 1 but shifted a little bit towards the green region. The observed small shift is explained by the weakening of the host matrix PL concerning MgGa₂O₄:Mn²⁺ sample that causes an increase in the green color PL emission. The applied 300 nm excitation leads to further weakening of the PL emission from Mn²⁺ ions and the matrix PL. Point 4 shows the reddish-orange color, which is related to the emission of Eu³⁺ ions in the “orange-red” spectral region. The excitation at f–f lines (393 nm) is presented by the emission of Eu³⁺ ions only, and shows a red color with little addition of the orange (point 5, Fig. 11). The calculated CIE achromatic coordinates under different light excitations for MgGa₂O₄:Mn²⁺ and Eu-doped spinel-structured MgGa₂O₄:Mn²⁺ ceramics are listed in Table 6.

In the studied MgGa₂O₄:Mn²⁺,Eu³⁺ phosphors, the purity of the colors obtained at different excitation wavelengths ranges from 53% to 81%. The highest color purity is observed at the f–f intra-center excitation of Eu³⁺ ions ($\lambda_{exc} = 393$ nm, point 5 on the CIE diagram). It should be noted that most commercial phosphors activated by Eu³⁺ ions demonstrate a color purity of more than 90%. At the same time, in the case of MgGa₂O₄ spinel, there is a considerable inversion of the structure, and part of Eu³⁺ ions occupies inversion symmetry sites which can lead to a decrease in color purity.

### Table 6 CIE achromatic coordinates calculated for both MgGa₂O₄:Mn²⁺ and MgGa₂O₄:Mn²⁺,Eu³⁺ ceramics under different excitations

| Point number | Ceramics          | Excitation wavelength (nm) | CIE coordinates |
|--------------|-------------------|-----------------------------|-----------------|
| 1            | MgGa₂O₄:Mn²⁺      | 240                         | $x = 0.10$, $y = 0.51$ |
| 2            | MgGa₂O₄:Mn²⁺      | 270                         | $x = 0.14$, $y = 0.23$ |
| 3            | MgGa₂O₄:Mn²⁺,Eu³⁺ | 240                         | $x = 0.16$, $y = 0.54$ |
| 4            | MgGa₂O₄:Mn²⁺,Eu³⁺ | 300                         | $x = 0.51$, $y = 0.38$ |
| 5            | MgGa₂O₄:Mn²⁺,Eu³⁺ | 393                         | $x = 0.58$, $y = 0.35$ |

### 4 Conclusions

The Rietveld refinement analysis of XRD patterns confirms the existence of the spinel phase in the structure of magnesium gallate MgGa₂O₄:Mn²⁺ ceramics, whereas Eu-doped MgGa₂O₄:Mn²⁺ ceramics show a small amount of Eu₂Ga₃O₁₂ phase. The homogeneous distribution of Eu dopants is proven by TEM–EDS mapping. The TEM morphology images show that ceramics grain sizes range from hundreds of nanometers to few micrometers. The inability of Eu activator to penetrate deeply into the MgGa₂O₄ ceramic grains is assumed from PAL spectroscopy results. The preferential location of Eu³⁺ ions in Ps-decay sites of the intergranular space leads to the enhanced positron trapping rate in Eu-doped MgGa₂O₄:Mn²⁺ ceramics. Therefore, the overall structural evolution caused by Eu³⁺ doping in MgGa₂O₄:Mn²⁺ ceramics can be described as the disappearance of Ps-trapping holes (0.30 nm in a radius) and formation of positron traps with defect lifetime equivalent of multi-vacancy clusters.

The MgGa₂O₄:Mn²⁺ ceramics show intense green luminescence under 240 nm excitation, confirming the dominant contribution of the recombination mechanism. Selective excitation and excitation-dependent emission reveal few ways to excite the Eu³⁺ ions in MgGa₂O₄:Mn²⁺ ceramics, all leading to the characteristic f–f emission in these ions. The Judd–Ofelt parameters calculated as the ratio between electric-dipole to magnetic-dipole transition shows that Eu³⁺ ions occupy sites of low symmetry within spinel MgGa₂O₄ lattice. The chromaticity coordinate values of MgGa₂O₄:Mn²⁺ and Eu-doped MgGa₂O₄:Mn²⁺ ceramics indicate that these phosphors can effectively emit different colors of light when excited with UV wavelength in 240–400 nm range.
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References

[1] Tsai BS, Chang YH, Chen YC. Nanostructured red-emitting MgGa2O4:Eu3+ phosphors. J Mater Res 2004, 19: 1504–1508.
[2] Moon YM, Choi S, Jung HK, et al. Sensitized photoluminescent properties of manganese-activated magnesium gallate phosphor. J Lumin 2008, 128: 1491–1495.
[3] Choi S, Kim K, Moon YM, et al. Rapid synthesis of spherical-shaped green-emitting MgGa2O4: Mn2+ phosphor via spray pyrolysis. Mater Res Bull 2010, 45: 979–981.
[4] Tang YX, Zhang DF, Qiu XX, et al. Fabrication of a NiCo2O4/ZnO/cd0,85-p-n heterojunction photocatalyst with improved separation of charge carriers for highly efficient visible light photocatalytic H2 evolution. J Alloys Compd 2019, 809: 151855.
[5] Gedekar KA, Wankhede SP, Moharil SV, et al. D-f luminescence of Ce3+ and Eu2+ ions in BaAl2O4, SrAl2O4 and CaAl2O4 phosphors. J Adv Ceram 2017, 6: 341–350.
[6] Inoue SI, Tamari N, Taniguchi M. 150 mW deep-ultraviolet light-emitting diodes with large-area AlN nanophotonic light-extraction structure emitting at 265 nm. J Lumin 2017, 186: 97–101.
[7] Xia C, Yu CY, Cao MM, et al. A Eu and Tb co-doped garnet (Eu3Ga5O12) and Eu 3GaO6: Synthesis and material characterization. Appl Phys Lett 2017, 110: 141106.
[8] Luchechko A, Kravets O, Kostyk L, et al. Luminescence spectroscopy of Eu3+ and Mn2+ ions in MgGa2O4 spinel. Radiat Meas 2016, 90: 47–50.
[9] Luchechko A, Kravets O. Novel visible phosphors based on MgGa2O4–ZnGa2O4 solid solutions with spinel structure co-doped with Mn2+ and Eu3+ ions. J Lumin 2017, 192: 11–16.
[10] Osada M, Takesada M, Isobe T. Comparison between MgGa2O4:Mn2+ and ZnGa2O4:Mn2+ nanophosphors synthesized by glycothermal method. ECS Transactions 2009, 16: 75–80.
[11] Costa GKB, Pedro SS, Carvalho ICS, et al. Preparation, structure analysis and photoluminescence properties of MgGa2O4:Mn2+. Opt Mater 2009, 31: 1620–1627.
[12] Luchechko A, Zhydachevskyy Y, Maraba D, et al. TL and OSL properties of Mn2+-doped MgGa2O4 phosphor. Opt Mater 2018, 78: 502–507.
[13] Ahn W, Im M, Kim YJ. Effects of flux on the luminescence of MgGa2O4:Mn2+ phosphors. Mater Res Bull 2017, 96: 254–257.
[14] Kravets O, Zaremba O, Shpotyuk Y, et al. Structure, morphology and optical-luminescence investigations of spinel ZnGa2O4 ceramics co-doped with Mn2+ and Eu3+ ions. Appl Nanosci 2019, 9: 907–915.
[15] Zhang Y, Wu ZJ, Geng DL, et al. Full color emission in ZnGa2O4: Simultaneous control of the spherical morphology, luminescent, and electric properties via hydrothermal approach. Adv Funct Mater 2014, 24: 6581–6593.
[16] Kansy J. Microcomputer program for analysis of positron annihilation lifetime spectra. Nucl Instrum Meth Phys Res Sect A: Accel Spectrometers Detect Assoc Equip 1996, 374: 235–244.
[17] Krause-Rehbberg R, Leipner HS. Positron Annihilation in Semiconductors. Berlin, Heidelberg: Springer Berlin Heidelberg, 1999.
[18] Tuomisto F, Makkonen I. Defect identification in semiconductors with positron annihilation: Experiment and theory. Rev Mod Phys 2013, 85: 1583–1631.
[19] Saarinen K, Hautojarvi P, Corbel C. Chapter 5 positron annihilation spectroscopy of defects in semiconductors. Semiconductor Semimetals, 1998, 51: 209–285.
[20] Jean YC, Mallon PE, Schradar DM. Introduction to positron and positronium chemistry. In Principles and Application of Positron and Positronium Chemistry. New Jersy: World Scientific, 2003: 1–15.
[21] Li YX, Niu PJ, Hu L, et al. Monochromatic blue-green and red emission of rare-earth ions in MgGa2O4 spinel. J Lumin 2009, 129: 1204–1206.
[22] Sawada K, Nakamura T, Adachi S. Europium gallium garnet (Eu3Ga5O12) and Eu3GaO6: Synthesis and material properties. J Appl Phys 2016, 120: 143102.
[23] Shpotyuk O, Ingram A, Klym H, et al. PAL spectroscopy in application to humidity-sensitive MgAl2O4 ceramics. J Eur Ceram Soc 2005, 25: 2981–2984.
[24] Vijay YK, Sate S, Awasthi DK, et al. Ion induced effects in polymers. Indian J Eng Mater Sci 2000, 7: 375–377.
[25] Shpotyuk O, Filipecki J, Ingram A, et al. Positronics of subnanometer atomistic imperfections in solids as a high-informative structure characterization tool. Nanoscale Res Lett 2015, 10: 77.
[26] Shpotyuk O, Ingram A, Shpotyuk Y. Free-volume characterization of Nanostructuredized substances by positron annihilation lifetime spectroscopy. Nucl Instrum Meth Phys Res Sect B: Beam Interactions Mater Atoms 2018, 416: 102–109.
[27] Mironova N, Skvortsova V, Smirnovs A, et al. Distribution

www.springer.com/journal/40145
of manganese ions in magnesium-aluminium spinels of different stoichiometries. Opt Mater 1996, 6: 225–232.

[28] Judd BR. Optical absorption intensities of rare-earth ions. Phys Rev 1962, 127: 750.

[29] Ofelt GS. Intensities of crystal spectra of rare-earth ions. J Chem Phys 1962, 37: 511–520.

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