sciendo

LATVIAN JOURNAL OF PHYSICS
AND TECHNICAL SCIENCES
2018, N 6

DOI: 10.2478/lpts-2018-0043

LUMINESCENCE PROPERTIES AND DECAY KINETICS OF Mn^{2+} AND Eu^{3+} CO-DOPANT IONS IN $MgGa_2O_4$ CERAMICS

A. Luchechko[1,a], Ya. Zhydachevskyy[2,3], D. Sugak[2,b], O. Kravets[1], N. Martynyuk[2], A.I.Popov[4,c], S. Ubizskii[2], A. Suchocki[3,5]

[1] Ivan Franko National University of Lviv,
107 Tarnavskogo St., Lviv 79017, UKRAINE

[2] Lviv Polytechnic National University, 12 Bandera St.,
Lviv 79646, Ukraine

[3] Institute of Physics, Polish Academy of Sciences,
32/34 Al. Lotnikow, Warsaw 02-668, POLAND

[4] Institute of Solid State Physics, University of Latvia, LATVIA

[5] Institute of Physics, University of Bydgoszcz, Weyssenhoffa 11,
Bydgoszcz 85-072, POLAND

E-mail: [a]andriy.luchechko@lnu.edu.ua,
[b]dm_sugak@yahoo.com, [c]popov@latnet.lv

The $MgGa_2O_4$ ceramics co-doped with Mn^{2+} and Eu^{3+} ions were synthesized via a high-temperature solid-state reaction technique. The samples with various Eu^{3+} concentrations were characterised using high-resolution photoluminescence (PL) spectroscopy. The PL spectra show weak matrix emission in a blue spectral region with dominant excitation band around 380 nm. Manganese ions are highly excited deeply in UV region and exhibit emission band peaked at 502 nm. The Eu^{3+} ions show characteristic f-f excitation and emission lines. The energy transfer between host defects and activator ions was observed. Luminescence decay curves of Mn^{2+} and Eu^{3+} emission showed complex kinetics with both Eu^{3+}-ion concentration and excitation wavelength changes.

Keywords*: energy transfer, europium (Eu^{3+}) and manganese (Mn^{2+}) ions, decay kinetics, magnesium gallate $MgGa_2O_4$, photoluminescence*

1. INTRODUCTION

Complex oxides with crystalline structures of perovskite, garnet and spinel have many important properties that determine their successful application in science and technology, in such areas as ferroelectricity, semiconductor electronics, optoelectronics, luminescence and radiation technology etc. [1]–[11]. In particular,

transition metal or rare earth ion doping of these materials creates excellent emitting phosphor materials [11]–[27]. Among these ions, the Mn^{2+} and Eu^{3+} ions are known as the main sources of green and red light emission, respectively. Thus, such materials are often used in display technologies, such as field emission displays, vacuum fluorescent displays etc. [12], [14].

At the same time, the Eu^{3+} ions are active in crystal sites with low point symmetry caused by the large degree of inversion of the spinel structure (e.g., magnesium gallate $MgGa_2O_4$) and other structural perturbations. In order to obtain efficient phosphors, the coexistence of tetrahedral and octahedral cation sites is the key factor for host materials [15]. As far as we know, there are only a few reports of photoluminescence (PL) decay investigations in $ZnGa_2O_4$: Eu^{3+} spinel obtained by different methods [12], [14]. Simultaneously, no detailed study has been reported about decay profiles and energy transfer process in $MgGa_2O_4$: Eu^{3+}. Only Tsai et al. 2006 [28] reported about the decay curve of $^5D_0 \rightarrow {}^7F_2$ transition of $MgGa_2O_4$: 5% Eu^{3+} nanopowder. Moreover, no PL decay kinetics investigations have been yet reported for $MgGa_2O_4$ co-doped with Mn^{2+} and Eu^{3+}.

In the present research, the high-resolution PL excitation and emission spectra, as well as decay characteristics of Mn^{2+} and Eu^{3+} co-doped magnesium gallate ceramics are presented.

2. EXPERIMENTAL DETAILS

The synthesis had been carried out via high-temperature solid-state ceramic technique from simple oxide powders of at least 4N grade of purity. The powders were mixed with the stoichiometric composition in an agate mortar for 6 h with further pressing. The obtained tablets were annealed at 1200 °C for 8 hours in the air. The concentration of Mn^{2+} was set constant at 0.05 mol.% and concentration of Eu^{3+} ions was changed from 2 mol.% to 4 mol.%. The phase and structure analysis were described earlier [13], [29].

PL and appropriate PL excitation (PLE) spectra were measured at room temperature using a Horiba/Jobin-Yvon Fluorolog-3 spectrofluorometer with a 450 W continuous xenon lamp as an excitation source, while a Hamamatsu R928P was used as a detector. The measured PLE spectra were corrected for the xenon lamp emission spectrum. The PL spectra were corrected for the spectral response of the spectrometer system. The PL decay kinetics was recorded using an Edinburgh FS5-MCS spectrofluorometer equipped with a 5 W/ms Xenon flash lamp.

3. RESULTS AND DISCUSSION

PL excitation spectra of $MgGa_2O_4$ co-doped with 0.05 mol.% Mn^{2+} and 4 mol.% Eu^{3+} ions registered at several emission wavelength are shown in Fig. 1a. Two excitation bands of the matrix emission in the $MgGa_2O_4$ ceramics co-doped with Mn^{2+} and Eu^{3+} ions were observed in the UV and near UV regions of spectra. Deeper UV excitation band peaking around 260 nm shows a lower intensity with respect to near UV band at about 380 nm. The excitation spectrum of Mn^{2+} ion registered at

502 nm demonstrates intense excitation deeply in the UV spectral region indicating the recombination process as it corresponds to the region of fundamental absorption edge (E_g = 5 eV) [28]. The tail in the exitation of manganese ions from 260 to 320 nm shows that the charge transfer ($O^{2-} \rightarrow Mn^{2+}$) also occurs [1], [13], [14].

The europium ions are excited with the charge transfer from oxygen anions to Eu^{3+} ions (240–340 nm) and the *4f-4f* intra-shell transitions of Eu^{3+} ions corresponding to the sharp lines (350–420 nm) under 615 nm registration [13], [29]. The remarkable sharp declines of the excitation intensities in the range of *f-f* lines on the excitation spectra registered at 440 nm and 502 nm indicate that the energy transfer occurs through excitation mechanisms between host defects and activator ions.

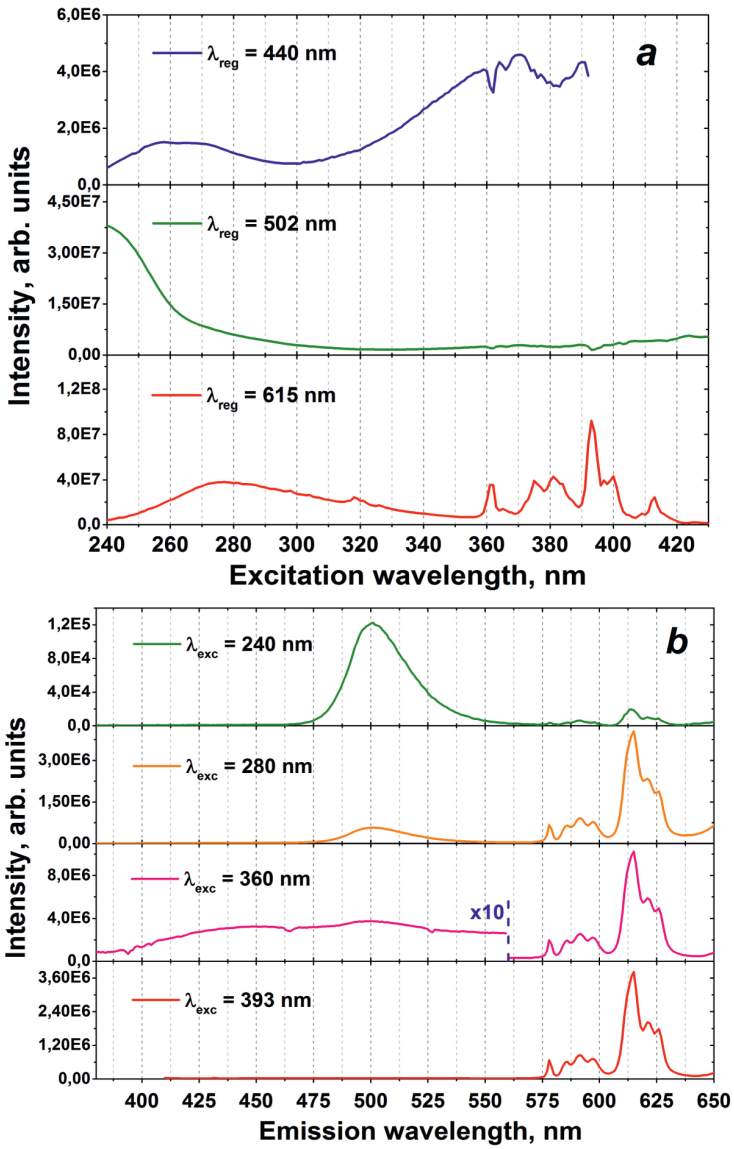

Fig.1. Photoluminescence excitation (a) and emission (b) spectra of $MgGa_2O_4$ co-doped with 0.05 mol.% Mn^{2+} and 4 mol.% Eu^{3+} ions.

PL spectra of $MgGa_2O_4$ co-doped with 0.05 mol.% Mn^{2+} and 4 mol.% Eu^{3+} ions at different excitations are shown in Fig. 1b. The luminescence of $MgGa_2O_4$:Mn^{2+},Eu^{3+} is represented by the UV-blue host emission and activator ions in green and orange-red regions, respectively. The host luminescence originating from structural defects is clearly seen under 360-nm excitation [29]. The decline of the host emission intensity at about 393 and 463 nm is due to reabsorption by Eu^{3+} ions in the near-surface ceramics layer [13]. The emission of Mn^{2+} ions peaked at ~ 502 nm is the most intense at 240-nm excitation due to the efficient energy transfer from $MgGa_2O_4$ host to the Mn^{2+} ions [30]. At the same time, the orange-red emission of Eu^{3+} ions is the most intense under the 280, 380 and 393 nm excitations. Only dominant emission of Eu^{3+} ions is obtained at 393-nm excitation, which corresponds to $^7F_0 \rightarrow {}^5L_6$ electron transitions in the activator ions. Note that redistribution of the emission intensities in hyperfine structure of $^5D_0 \rightarrow {}^7F_2$ transitions, and a change in excitation wavelength is found as well.

All PL decay curves of $MgGa_2O_4$:Mn^{2+}, x Eu^{3+} excited at 240 nm and monitored at 505 nm can be fitted with double-exponential function: $I(t) = A_1 exp(-t/\tau_1) + A_2 exp(-t/\tau_2)$, where I(t) is the emission intensity, A_1 and A_2 are the weighting constants, τ_1 and τ_2 are the fast and slow decay components of the luminescence lifetimes, respectively. The typical curve for $MgGa_2O_4$:Mn^{2+}, 4 mol% Eu^{3+} is shown in Fig. 2a. It has been established that fast and slow components are at about 3.2 and 5.6 ms, respectively. Moreover, the lifetime constants of manganese ions weakly depend on the europium concentration. One can assume that one of the components is related to Mn^{2+} ions in the tetrahedral sites of the spinel structure and the another with manganese ions near structural defects or in distorted tetrahedral sites, for example, by oxygen vacancies. At the same time, to reveal the nature of the fast and slow components more detailed investigation is needed. It should also be noted that $MgGa_2O_4$: Mn^{2+} shows a single-exponential decay with τ = 7.1 ms at the excitation in the region of *d-d* intraband transitions of Mn^{2+} ions [30].

The PL decay curves of Eu^{3+} ions have been measured at a different excitation wavelength in the emission peak at 615 nm. Figure 2b shows the PL decay curves of Eu^{3+} ions in $MgGa_2O_4$ ceramics co-doped with 0.05mol% Mn^{2+} and 2-8% Eu^{3+} at 393 nm excitation that corresponds to the *f-f* transitions in Eu^{3+} ions. The decay curves were also fitted using the double exponential function. The values of a lifetime are presented in Table 2. The lifetime decreases with growth of the Eu^{3+} ion doping level. Short component changes from 0.31 to 0.14 ms and a long one from 1.98 to 0.77 ms.

Table 1

Decay Profiles of Double Exponential Fitting of $MgGa_2O_4$ Co-doped with 0.05 mol.% Mn^{2+} and 2-8 mol.% Eu^{3+} Ions at 615 nm Registration and Excition 270 nm

x mol.% Eu^{3+} ions	τ_1, ms	A_1, %	τ_2, ms	A_2, %	Adj.R^2
2	0.26	94.8	0.98	5.2	0.99981
4	0.19	77.2	0.78	22.8	0.99983
6	0.17	72.4	0.76	27.6	0.99952
8	0.11	80.6	0.58	19.4	0.99934

Table 2

Decay Profiles of Double Exponential Fitting of $MgGa_2O_4$ Co-doped with 0.05 mol.% Mn^{2+} and 2-8 mol.% Eu^{3+} Ions at 615 nm Registration and Exitation 393 nm

x mol.% Eu^{3+} ions	τ_1, ms	A_1, %	τ_2, ms	A_2, %	Adj.R^2
2	0.31	98.3	1.98	1.7	0.99875
4	0.25	81.5	0.82	18.5	0.99914
6	0.18	67.1	0.79	32.8	0.99896
8	0.14	52.4	0.77	47.3	0.99862

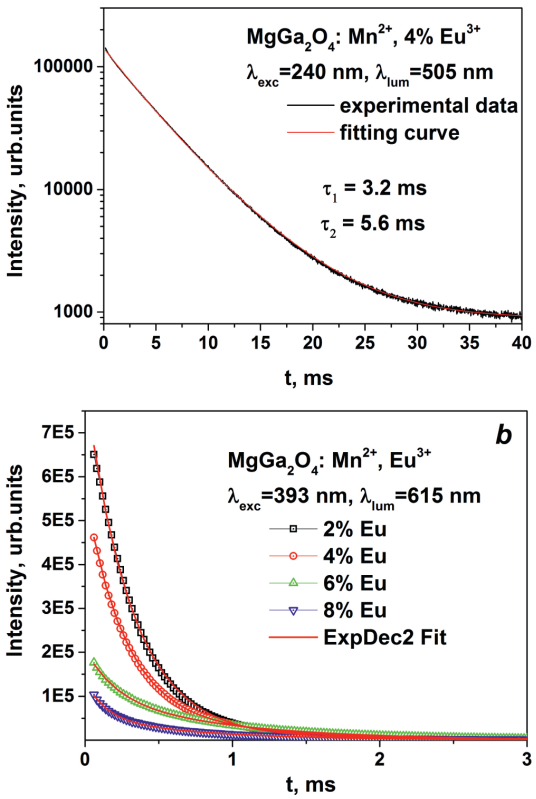

Fig. 2. Decay kinetic curves of Mn^{2+} ions (a) and Eu^{3+} ions (b) in magnesium gallate spinel.

The decay curves for $ZnGa_2O_4$: 4%Eu^{3+} nanospheres and $MgGa_2O_4$: 5%Eu^{3+} nanopowders were fitted with a single exponential function with lifetimes 0.472 ms [12] and 0.934 ms [28], respectively. At the same time, the double exponential function was used for the decay profiles in $ZnGa_2O_4$: Eu^{3+} nanopowders [14], [15]. It was suggested [28] that only one mechanism was involved in the luminescence process, and most of the Eu^{3+} ions occupied distorted octahedral sites in the $Mg_xZn_{1-x}Ga_2O_4$ crystallites. In $MgGa_2O_4$: Mn^{2+}, Eu^{3+}, the decay kinetics was more complicated, which suggested involvement of at least two mechanisms in the luminescence process. The fast component was tentatively related to Eu^{3+} located on grain boundaries. The second process could be attributed to the Eu^{3+} ions in crystallite bulk.

Table 3

Decay Profiles of Double Exponential Fitting of $MgGa_2O_4$ Co-doped with 0.05 mol.% Mn^{2+} and 4 mol.% Eu^{3+} Ions at Different Excitations and 615 nm Registration

λ_{exc}, nm	τ_1, ms	A_1, %	τ_2, ms	A_2, %	Adj.R^2
240	0.14	80.4	0.78	19.6	0.99943
270	0.19	77.2	0.78	22.8	0.99983
300	0.20	76.3	0.74	23.7	0.99978
380	0.23	78.9	0.76	21.1	0.99962
393	0.25	81.5	0.82	18.5	0.99914

4. CONCLUSIONS

The excitation spectrum of Eu^{3+}-emission shows dominance of *4f-4f* transitions over the charge transfer band despite it is also very intense. Emission spectra demonstrate that the $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} ions in the orange-red spectral region are the most intense ones. The energy transfer from the host and Mn^{2+} ions to Eu^{3+} ions has been demonstrated by the excitation/emission spectra as well as PL decay curves. The luminescence decay time of Mn^{2+} emission has been determined to be ~ 4.7 ms and independent of Eu^{3+} ions concentration. The emission decay profiles of Eu^{3+} emission ions in $MgGa_2O_4$ co-doped with 0.05 mol.% Mn^{2+} and 2-8 mol.% Eu^{3+} ions have been observed to be non-exponential, depending on different europium concentrations and excitation wavelengths.

ACKNOWLEDGMENTS

The research has partly been supported by the Ukrainian Ministry of Education and Science within the Latvian–Ukrainian Joint Research Project (LV-UA/2016/1 in Latvia, and M/.8-2018 in Ukraine) and the project DB/RIDER (No. 0117U004443). A. Luchechko gratefully acknowledges a grant from the Institute of Physics PAS for a research visit to the institute, while A.I. Popov has been supported by project LZP-2018/1-0214 from the Latvian Council of Science.

REFERENCES

1. Brik, M. G., Suchocki, A., & Kaminska, A. (2014). Lattice parameters and stability of the spinel compounds in relation to the ionic radii and electronegativities of constituting chemical elements. *Inorganic chemistry*, *53*(10), 5088–5099.
2. Suchocki, A., & Powell, R.C. (1988). Laser-induced grating spectroscopy of Cr^{3+}-doped $Gd_3Ga_5O_{12}$ and $Gd_3Sc_2Ga_3O_{12}$ crystals. *Chemical Physics*, 128(1), 59–71.
3. Matkovski, A., Durygin, A., Suchocki, A., Sugak, D., Neuroth, G., Walrafend, F., ... Solski, I. (1999). Photo and gamma induced color centers in the $YAlO_3$ and $YAlO_3$:Nd single crystals. *Optical Materials*, 12(1), 75–81.

4. Dimza, V., Popov, A. I., Lāce, L., Kundzins, M., Kundzins, K., Antonova, M., & Livins, M. (2017). Effects of Mn doping on dielectric properties of ferroelectric relaxor PLZT ceramics. *Current Applied Physics*, *17*(2), 169–173.
5. Porotnikova, N. M., Anan'ev, M. V., & Kurumchin, E. K. (2011). Effect of defect structure of lanthanum manganite on oxygen exchange kinetics and diffusion. *Russian Journal of Electrochemistry*, *47*(11), 1250–1256.
6. Porotnikova, N. M., Eremin, V. A., Farlenkov, A. S., Kurumchin, E. K., Sherstobitova, E. A., Kochubey, D. I., & Ananyev, M. V. (2018). Effect of AO segregation on catalytical activity of $La_{0.7}A_{0.3}MnO_{3\pm\delta}$ (A= Ca, Sr, Ba) regarding oxygen reduction reaction. *Catalysis Letters*, *148*(9), 2839–2847.
7. Piskunov, S., Isakoviča, I., & Popov, A. I. (2018). Electronic structure of Mn^{3+}_{Al} and Mn^{2+}_{Al}-doped $YAlO_3$: Prediction from the first principles. *Optical Materials*, *85*, 162–166.
8. Klym, H., Ingram, A., Shpotyuk, O., Hadzaman, I., Solntsev, V., Hotra, O., & Popov, A. I. (2016). Positron annihilation characterization of free volume in micro-and macro-modified $Cu_{0.4}Co_{0.4}Ni_{0.4}Mn_{1.8}O_4$ ceramics. *Low Temperature Physics*, *42*(7), 601–605.
9. Piskunov, S., Isakoviča, I., & Popov, A. I. (2018). Atomic structure of manganese-doped yttrium orthoaluminate. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, *434*, 6–8.
10. Porotnikova, N.M., Ananyev, M.V., Eremin, V.A., Molchanova, N.G., & Kurumchin, E.K. (2016). Effect of acceptor substitution in perovskites $La_{1-x}A_xMnO_{3\pm\delta}$ (A = Ca, Sr, Ba) on the kinetics of interaction of gas-phase oxygen. *Russian Journal of Electrochemistry, 52(*8), 717–722.
11. Zhydachevskyy, Ya., Martynyuk, N., Popov, A.I., Sugak, D., Bilski, P., Ubizskii, S., … Suchocki, A. (2018). Thermally induced fading of Mn-doped YAP nanoceramics. *Journal of Physics: Conference Series*, 987(1), 012009.
12. Zhang, Y., Wu, Z., Geng, D., Kang, X., Shang, M., Li, X., … Lin, J. (2014). Full color emission in $ZnGa_2O_4$: Simultaneous control of the spherical morphology, luminescent, and electric properties via hydrothermal approach. *Advanced Functional Materials*, *24*(42), 6581–6593.
13. Luchechko, A., & Kravets, O. (2017). Novel visible phosphors based on $MgGa_2O_4$-$ZnGa_2O_4$ solid solutions with spinel structure co-doped with Mn^{2+} and Eu^{3+} ions. *Journal of Luminescence*, *192*, 11–16
14. Duan, X., Yu, F., & Wu, Y. (2012). Synthesis and luminescence properties of $ZnGa_2O_4$ spinel doped with Co^{2+} and Eu^{3+} ions. *Applied Surface Science*, *261*, 830–834.
15. Huo, Q., Tu, W., & Guo, L. (2017). Enhanced photoluminescence property and broad color emission of $ZnGa_2O_4$ phosphor due to the synergistic role of Eu^{3+} and carbon dots. *Optical Materials*, *72*, 305–312.
16. Polisadova, E. F., Vaganov, V. A., Stepanov, S. A., Paygin, V. D., Khasanov, O. L., Dvilis, E. S., ... Kalinin, R. G. (2018). Pulse cathodoluminescence of the impurity centers in ceramics based on the $MgAl_2O_4$ spinel. *Journal of Applied Spectroscopy*, *85*(3), 416–421.
17. Martynyuk, N.V., Ubizskii, S.B., Buryy, O.A., Becker, K.D., & Kreye, M. (2005). Optical *in-situ* study of the oxidation and reduction kinetics of Yb-substituted YAG epitaxial films. *Physica Status Solidi C: Conferences*, *2*(1), 330–333.
18. Zhydachevskii, Y., Syvorotka, I.I., Vasylechko, L., Sugak, D., Borshchyshyn, I.D., Luchechko, A.P., … Suchocki, A. (2012). Crystal structure and luminescent properties of nanocrystalline YAG and YAG:Nd synthesized by sol-gel method. *Optical Materials, 34*(12), 1984–1989.

19. Luchechko, A., Kravets, O., Kostyk, L., & Tsvetkova, O. (2016). Luminescence spectroscopy of $Eu^{3+}$and Mn^{2+} ions in $MgGa_2O_4$ spinel. *Radiation Measurements, 90*, 47–50.
20. Kirm, M., Feldbach, E., Lushchik, A., Lushchik, Ch., Maaroos, A., Savikhina, & T. (1997). Luminescent materials with photon multiplication. *Optical Inorganic Dielectric Materials and Devices* (eds. A. Krumins, D.K. Millers, A. Sternberg, J. Spigulis) *Proc. SPIE*, *2967*, 18–23.
21. Lushchik, A., Lushchik, Ch., Kotlov, A., Kudryavtseva, I., Maaroos, A., Nagirnyi, V., & Vasil'chenko, E. (2004). Spectral transformers of VUV radiation on the basis of wide-gap oxides. *Radiation Measurements*, *38*(4–6), 747–752.
22. Lushchik, A., Lushchik, C., Popov, A.I., Schwartz, K., Shablonin, E., & Vasil'chenko, E. (2016). Influence of complex impurity centres on radiation damage in wide-gap metal oxides. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, *374*, 90–96.
23. Lushchik, A., Dolgov, S., Feldbach, E., Pareja, R., Popov, A. I., Shablonin, E., & Seeman, V. (2018). Creation and thermal annealing of structural defects in neutron-irradiated $MgAl_2O_4$ single crystals. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, *435,* 31–37.
24. Kravets, O.P., Lys, R.M., Tsvetkova, O.V., Luchechko, A.P., & Pavlyk, B.V. (2018). Thermally stimulated luminescence and thermally stimulated depolarization currents in $MgGa_2O_4$ spinels. *Journal of Physical Studies, 22(1)*, 1602.
25. Luchechko, A., Kravets, O., & Syvorotka, I.I. (2017). Optical and luminescence spectroscopy of zinc gallate phosphors codoped with manganese and europium ions. *Spectroscopy Letters, 50(7)*, 404–410.
26. Luchechko, A., Kravets, O., Tsvetkova, O. (2017). Structure and optical-lumenescent characteristics of $Mg_{1-x}Zn_xGa_2O_4$: Mn^{2+} ceramics. *Journal of Nano- and Electronic Physics, 9(1)*, 01003.
27. Valiev, D., Khasanov, O., Dvilis, E., Stepanov, S., Polisadova, E., & Paygin, V. (2018). Luminescent properties of $MgAl_2O_4$ ceramics doped with rare earth ions fabricated by spark plasma sintering technique. *Ceramics International*, *44*(17), 20768–20773.
28. Tsai, B. S., Chang, Y. H., & Chen, Y. C. (2006). Preparation and luminescent characteristics of Eu^{3+}-activated $Mg_xZn_{1-x}Ga_2O_4$ nanocrystals. *Journal of Alloys and Compounds*, *407*(1–2), 289–293.
29. Luchechko, A., & Kravets, O. (2017). Synthesis and luminescent properties of magnesium gallate spinel doped with Mn^{2+} and Eu^{3+} ions. *Physica Status Solidi C*, *14*(1–2), 1600146.
30. Luchechko, A., Zhydachevskyy, Y., Maraba, D., Bulur, E., Ubizskii, S., & Kravets, O. (2018). TL and OSL properties of Mn^{2+}-doped $MgGa_2O_4$ phosphor. *Optical Materials*, *78*, 502–507.
31. Takesada, M., Osada, M., & Isobe, T. (2009). Glycothermal synthesis and photoluminescence of $MgGa_2O_4$: Mn^{2+} nanophosphors: Comparison to $ZnGa_2O_4$: Mn^{2+} nanophosphors. *Journal of the Electrochemical Society*, *156*(5), J97–J101.

AR Mn^{2+} UN Eu^{3+} JONIEM LEĢĒTĀS $MgGa_2O_4$ KERAMIKAS LUMINISCENCES ĪPAŠĪBAS UN SABRUKŠANAS KINĒTIKA

A. Lučečko, J. Žudačevski, D. Sugaks, O. Kravets, N. Martiņuks,
A.I.Popovs, S. Ubizski, A. Sučocki

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

Ar Mn^{2+} un Eu^{3+} joniem leģētā $MgGa_2O_4$ keramika tika sintezēta, izmantojot augstas temperatūras cietvielu reakcijas metodi. Paraugi ar dažādām Eu^{3+} koncentrācijām tika raksturoti, izmantojot augstas izšķirtspējas fotoluminiscences (PL) spektroskopiju. PL spektrā ir redzama vāja matricas emisija zilajā spektra zonā ar dominējošo ierosmes joslu ap 380 nm. Mangāna joni ir ierosināti UV zonā un izstaro emisijas joslu, kuras maksimums ir 502 nm. Eu^{3+} joniem ir raksturīgas f-f ierosmes un emisiju līnijas. Tika novērota enerģijas pārnese starp matricas defektiem un aktivatora joniem. Mn^{2+} un Eu^{3+} emisijas luminiscences dzesēšanas līknes parādījušas sarežģītu kinētiku saistībā ar Eu^{3+} jonu koncentrācijas un ierosmes viļņa garuma izmaiņām.

07.12.2018.