The luminescence properties of nanocrystalline phosphors
Mg$_2$SiO$_4$:Eu$^{3+}$

A Y Kolomytsev$^1$, D V Mamonova$^2$, A A Manshina$^3$, I E Kolesnikov$^4$

$^1$ Physics Department, Saint Petersburg State University, 3 Ulyanovskaya Street, Peterhof, Saint Petersburg, Russia
$^2$ Scientific and Technological Institute of Optical Material Science, VNTs S. I. Vavilov State Optical Institute, 36-1 Babushkina, Saint Petersburg, Russia
$^3$ Institute of Chemistry, Saint Petersburg State University, 26 Universitetskii prospekt, Peterhof, Saint Petersburg, Russia
$^4$ Centre for Optical and Laser Materials Research, Saint Petersburg State University

Contact information (e-mail): kau210296@mail.ru (Anton Kolomytsev)

**Abstract.** Nanocrystalline Eu$^{3+}$-doped Mg$_2$SiO$_4$ powders were prepared with combined Pechini-solid phase synthesis. The structural properties were investigated with XRD, SEM and Raman spectroscopy. XRD pattern indicated that Mg$_2$SiO$_4$:Eu$^{3+}$ were obtained with formation of other phase: MgO. Raman spectrum revealed good homogeneity and crystallinity of synthesized nanopowders. The luminescence properties were studied with measurement of excitation and emission spectra and decay curves. The effect of Eu$^{3+}$ concentration on $^5$D$_0$ level lifetime was studied. Most probably, the observed shortening of $^5$D$_0$ level lifetime with Eu$^{3+}$ concentration is caused by increase of nonradiative process probability.

1. Introduction
The study of inorganic nanomaterials doped with rare earth ions has attracted great interest. Phosphors based on silicates, phosphates, arsenates, chalcogenides doped with rare earth ions despite their widespread use do not fully satisfy the demands of modern technology. For example, forsterite (Mg$_2$SiO$_4$) is being currently studied as a potential matrix for bioimplants owing to its superior mechanical properties or as biomarkers for the detection of various diseases owing to its non-toxicity and high resistance to external factors, as well as the relatively low cost of synthesis of this compound [1-2].

Present article is devoted to investigation of nanocrystalline powder Mg$_2$SiO$_4$:Eu$^{3+}$ synthesized with combined Pechini-solid phase method. We examined structural and luminescence properties by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy and fluorescence spectroscopy, respectively. A lot of attention is paid to the study of Eu$^{3+}$ doping concentration on the luminescent properties.

2. Experimental
Nanocrystalline powders Mg$_2$SiO$_4$ doped with europium were prepared with combined Pechini-solid phase synthesis. Magnesium oxide powder containing a predetermined concentration of rare earth ions
is synthesized with Pechini method. For this purpose we prepare magnesium nitrate solution with europium. Then we get citrate complex metals with addition citric acid.

\[ \text{Me(NO}_3\text{)}_3 + 3 \text{C}_6\text{H}_8\text{O}_7 = [\text{Me(C}_6\text{H}_8\text{O}_7)_3]\text{(NO}_3\text{)}_3 (\text{Me: Mg, Eu}) \] (1)

After that we turn it to polymer gel with etherification reaction:

\[ 3[\text{Me(C}_6\text{H}_7\text{O}_5\text{COO})_3]\text{(NO}_3\text{)}_3 + \text{C}_2\text{H}_6\text{O}_2 \rightarrow \]
\[ \rightarrow \text{MeOOCC}_4\text{H}_4\text{COOC}_2\text{H}_2\text{OOCCC}_4\text{H}_4\text{COOMe} \text{CCOOMe} + (\text{NO}_2^+ + \text{CO}_2^+) + \text{H}_2\text{O} \] (2)

This gel was calcinated at 850 °C to form MgO:Eu$^{3+}$. The resulting powder is dispersed in ethanol solution. Then we add corresponding quantity of tetraethyl orthosilicate (TEOS) to reach stoichiometric composition of future complex oxide. The slip is dispersed again, and after that TEOS hydrolysis is carried out.

\[ \text{SiO}_4(\text{C}_2\text{H}_5)_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_5\text{OH} \] (3)

The resulting mixture is dried at 40 °C for a day. Then it is calcinated at high temperature (1000 °C) to form a complex oxide according to the principle of solid phase synthesis.

The described synthesis procedure was used for preparation of powder series with different Eu concentration: 2, 4, 8 and 12 at.%. For luminescence studies the synthesized powders samples of quantity 5 mg were pressed with KBr into pellets.

X-ray phase analysis of the samples was carried out using Bruker «D8 DISCOVER X-ray diffractometer with CuKα -radiation (λ = 1.5406 Å). Electron micrograph images were obtained with Zeiss Merlin scanning electron microscope with the resolution of 1 nm. Raman spectra were investigated on Bruker SENTERRA Raman Microscope with semiconductor laser 488 nm as an excitation source. Photoluminescence spectra of Mg$_2$SiO$_4$:Eu$^{3+}$ nanophosphors were recorded with a fluorescence spectrometer Lumina with a Xe lamp (150W power) and the decay curves were obtained with the fluorescence spectrometer Fluorolog-3 with a Xe-flash lamp (150W power). All the measurements were performed at room temperature.

3. Results and discussion
3.1. Structural properties

Figure 1 shows the XRD pattern of Mg$_2$SiO$_4$:Eu$^{3+}$ 8 at.% nanophosphors synthesized with combined Pechini-solid phase method. This XRD pattern reveals presence of both orthorhombic Mg$_2$SiO$_4$ (JCPDS 34-0189) and MgO (JCPDS 77-2364) phase. It should be noted that presence of MgO phase does not affect luminescence properties as far as Eu$^{3+}$ ions replace only Mg$^{2+}$ ions in Mg$_2$SiO$_4$ host. Such conclusion can be drawn due to different shape and spectral position of bands at emission spectra of MgO:Eu$^{3+}$ [3]. Partial substitution of Mg$^{2+}$ for Eu$^{3+}$ does not affect the orthorhombic structure of Mg$_2$SiO$_4$ phase, indicating that the Eu$^{3+}$ ions locate in the Mg position in the Mg$_2$SiO$_4$ crystal lattice.
Figure 1. XRD pattern of $\text{Mg}_2\text{SiO}_4:\text{Eu}^{3+}$ 8 at.% phosphor and standard cards for $\text{Mg}_2\text{SiO}_4$ (JCPDS 34-0189) and MgO (JCPDS 77-2364)

Figure 2. SEM image of $\text{Mg}_2\text{SiO}_4:\text{Eu}^{3+}$ 8 at.% phosphor

The scanning electron micrograph of the prepared $\text{Mg}_2\text{SiO}_4:\text{Eu}^{3+}$ 8 at.% phosphor is shown in Figure 2. $\text{Mg}_2\text{SiO}_4:\text{Eu}^{3+}$ powder consists of stable agglomerates of nanocrystalline particles with average size about 100 nm.

Raman spectrum of $\text{Mg}_2\text{SiO}_4:\text{Eu}^{3+}$ 8 at.% is presented in Figure 3. The spectrum was measured in spectral region from 80 to 1150 cm$^{-1}$. The narrow width of Raman lines indicates good homogeneity and crystallinity of synthesized powders that coincide with results of X-ray diffraction and scanning electron microscopy. The $\text{Mg}^{2+}$ ions are mainly involved in external vibrations ($\text{Mg} - \text{SiO}_4$) in the spectral range $\sim$150 – 400 cm$^{-1}$, whereas the contributions of internal vibrations of $\text{SiO}_4$ group is significant in the whole frequency region except the low frequency region (0–150 cm$^{-1}$). The most intense bands are centered at 420, 824, 857, 920, 966 and 1005 cm$^{-1}$. These vibrations are probably attributed to the $\text{SiO}_4$ stretching mode. It should be noted that Raman spectrum is dominated by line centered at 857 cm$^{-1}$, whereas band centered at 1005 cm$^{-1}$ has rather small intensity. The obtained results agree well with the theoretical and experimental data from Ref. 4.
3.2. Luminescence properties

Figure 4 shows the absorption spectrum of Mg$_2$SiO$_4$:Eu$^{3+}$ 8 at.% powder. The wide band in the region of low wavelengths corresponds to absorption of Mg$_2$SiO$_4$ host. The narrow lines correspond to the transitions inside Eu$^{3+}$ ion.

Figure 5 shows the excitation spectrum of Mg$_2$SiO$_4$:Eu$^{3+}$ 8 at.% powder for forced electric dipole transition $^5$D$_0$–$^7$F$_2$ with maximum at 614 nm. All observed lines are very sharp. As it is known, the most intensive line can be attributed to the $^7$F$_0$–$^7$L$_6$ with maximum at 393.5 nm. Other lines are also associated with typical transitions of the Eu$^{3+}$ ion: $^7$F$_0$–$^7$L$_5$ (319 nm), $^7$F$_0$–$^7$D$_4$ (362 nm), $^7$F$_0$–$^7$L$_7$ (379 nm), $^7$F$_0$–$^7$D$_3$ (417 nm), $^7$F$_0$–$^7$D$_2$ (465 nm), $^7$F$_0$–$^7$D$_1$ (527 nm), $^7$F$_0$–$^7$D$_0$ (590 nm).

Figure 6 presents emission spectra of the Mg$_2$SiO$_4$:Eu$^{3+}$ powders (2, 4, 8, 12 at. %). The spectra consist of bands corresponding to the transitions from the metastable excited state ($^5$D$_0$) to the ground $^7$F$_J$ ($J = 0$–4) under excitation at 393.5 nm.
Figure 5. Excitation spectrum of Mg$_2$SiO$_4$:Eu$^{3+}$ 8 at.% phosphor

Figure 6. Emission spectra of Mg$_2$SiO$_4$:Eu$^{3+}$ phosphors (2, 4, 8, 12 at.%)

Figure 7 shows concentration dependence of the luminescence intensity of the most intensive transition $^5$D$_0$-$^7$F$_2$ (614 nm). One can see that luminescence intensity grows with increasing number of Eu$^{3+}$ ions up to 8 at.%. Further increase of Eu$^{3+}$ concentration leads to intensity reduction. This decrease is due to the concentration quenching. Such behavior of the luminescence intensity is typical for rare earth doped materials [5-6].
Figure 7. Photoluminescence intensity of Mg$_2$SiO$_4$:Eu$^{3+}$ phosphors as a function of doping concentration.

Figure 8. Decay curves of Mg$_2$SiO$_4$:Eu$^{3+}$ phosphors (2, 4, 8, 12 at.%) suggests time dependence of the luminescence intensity of Mg$_2$SiO$_4$:Eu$^{3+}$ powders (2, 4, 8, 12 at %). Experimental curves for each compound were approximated with double exponential function.

$$I = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}$$

Fitting parameters for each sample are presented in Table 1.

**Table 1.** Fitting parameters for Mg$_2$SiO$_4$:Eu$^{3+}$ powders with different Eu$^{3+}$ ions concentration.

| C(Eu$^{3+}$), at.% | $A_1$       | $\tau_1$, ms | $A_2$       | $\tau_2$, ms |
|-------------------|-------------|--------------|-------------|--------------|
| 2%                | 0.21 ±0.01  | 1.69 ± 0.05  | 1.00 ±0.01  | 0.219 ± 0.003|
| 4%                | 0.18 ± 0.01 | 0.88 ±0.05   | 1.32 ± 0.02 | 0.103 ±0.002 |
| 8%                | 0.11 ± 0.02 | 0.87 ±0.09   | 1.13 ± 0.01 | 0.203 ±0.003 |
| 12%               | 0.34 ± 0.02 | 0.42 ±0.02   | 1.15 ± 0.02 | 0.092 ±0.004 |

Probably difference from exponential decay can be explained with location of Eu$^{3+}$ ions in two different positions: on the surface and inside the particles [7]. In order to compare lifetimes more convenient, the averaged luminescence lifetimes of Eu$^{3+}$ ions were calculated with obtained approximation parameters using the following formula:

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

Calculated luminescence lifetimes of Eu$^{3+}$ ions for different concentrations are presented in Table 2.
Table 2. Calculated luminescence lifetimes of Eu$^{3+}$ ions for different Eu$^{3+}$ concentrations

| Eu$^{3+}$ concentration (at. %) | 2   | 4   | 8   | 12  |
|--------------------------------|-----|-----|-----|-----|
| Luminescence lifetime (ms)     | 1.48| 0.46| 0.39| 0.26|

As one can see, the averaged lifetime is decreased along with increase of Eu$^{3+}$ doping concentration. Probably, it can be explained with increase of nonradiative decay rate of Eu$^{3+}$ ions because of decrease of distance between Eu$^{3+}$ ions with growth of doping concentration.

4. Conclusions

The nanocrystalline powders Mg$_2$SiO$_4$:Eu$^{3+}$ were prepared with combined Pechini – solid phase synthesis. XRD pattern revealed that synthesized samples contained both Mg$_2$SiO$_4$ and MgO phase. XRD and Raman spectroscopy confirmed that synthesized nanocrystalline powders had good homogeneity and crystallinity. The emission and excitation spectra consisted of characteristic lines which can be ascribed to the 4f–4f transitions of Eu$^{3+}$ and the most prominent transition is forced electric dipole $^5D_0$–$^7F_2$ transition (614 nm). Lifetime of excited state $^5D_0$ as a function of doping concentration was investigated. Most probably, the observed decrease of luminescence lifetime can be explained with increase of nonradiative decay rate.

Acknowledgments

This research has been supported by the Russian Foundation of Basic Research (RFBR 16-32-00091) and The Ministry of education and science of the Russian Federation (# 14.604.21.0078, RFMEFI60414X0078). Experimental investigations were carried out in "Center for Optical and Laser materials research", "Research Centre for X-ray Diffraction Studies", "Interdisciplinary Resource Centre for Nanotechnology" (St. Petersburg State University).

References

[1] Kolesnikov, I. E., Tolstikova, D. V., Kurochkin, A. V., Manshina, A. A., & Mikhailov, M. D. (2014). Eu$^{3+}$ concentration effect on luminescence properties of YAG: Eu$^{3+}$ nanoparticles. Optical Materials, 37, 306-310.
[2] Ramesh, S., Yaghoubi, A., Lee, K. S., Chin, K. C., Purboalaksono, J., Hamdi, M., & Hassan, M. A. (2013). Nanocrystalline forsterite for biomedical applications: synthesis, microstructure and mechanical properties. Journal of the mechanical behavior of biomedical materials, 25, 63-69.
[3] Devaraja P. B. et al. MgO: Eu 3+ red nanophosphor: Low temperature synthesis and photoluminescence properties //Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. – 2014. – T. 121. – C. 46-52.
[4] Iishi, K. (1978). Lattice dynamics of forsterite. American Mineralogist, 63(11-12), 1198-1208.
[5] Kolesnikov, I. E., Tolstikova, D. V., Kurochkin, A. V., Pulkin, S. A., Manshina, A. A., & Mikhailov, M. D. (2015). Concentration effect on photoluminescence of Eu$^{3+}$-doped nanocrystalline YVO$_4$. Journal of Luminescence, 158, 469-474.
[6] Kolesnikov, I. E., Golyeva, E. V., Kurochkin, A. V., & Mikhailov, M. D. (2016). Structural and luminescence properties of MgAl$_2$O$_4$:Eu$^{3+}$ nanopowders. Journal of Alloys and Compounds, 654, 32-38.
[7] Kolesnikov, I. E., Povolotskiy, A. V., Mamonova, D. V., Lähderanta, E., Manshina, A. A., & Mikhailov, M. D. (2016). Photoluminescence properties of Eu$^{3+}$ ions in yttrium oxide nanoparticles: defect vs. normal sites. RSC Advances, 6(80), 76533-76541.