

Low temperature photoluminescence emission of $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$ phosphor powder

S. R. LUKIĆ - PETROVIĆ^{a*}, D. M. PETROVIĆ^a, M. NIKOLIĆ^b, L. ĐAČANIN^a, M. D. DRAMIĆANIN^b

^aUniversity of Novi Sad, Department of Physics, Faculty of Sciences, Trg Dositeja Obradovića 4, 21000 Novi Sad, Serbia

^bVinča Institute of Nuclear Sciences, University of Belgrade, P.O. 522, 11001 Belgrade, Serbia

Phosphor materials are of special interest due to their important applications ranging from solid state lightning and displays to biomedicine. Understanding the spectroscopic properties of these materials is important for optimizing their emission for technological applications. Zinc silicate (Zn_2SiO_4) has been identified as a very suitable host matrix for many rare-earth and transition metal dopant ions with excellent luminescent properties in the blue, green and red spectral zones. Here, we present high resolution measurements of low-temperature photoluminescence of trivalent europium doped zinc silicate particles prepared by combination of sol-gel and combustion synthesis route. We observed and analyzed $^5\text{D}_0 \rightarrow ^7\text{F}_J$ spin forbidden f-f electronic transitions at low temperatures, as well as emission kinetics from $^5\text{D}_0$ level and lifetime-temperature dependence.

(Received March 18, 2013; accepted April 11, 2013)

Keywords: Phosphors, Zinc silicate, High resolution spectroscopy, Europium luminescence

1. Introduction

Phosphors are composed of an inert host lattice and an optically excited activator, typically a 3d or 4f electron metal. For application in the emerging full color, flat panel display industry, thermally stable, high luminous efficiency, radiation resistant, fine particle size powders are required. The demands of these newer technologies have produced a search for new materials and synthesis techniques to improve the performance of phosphors [1]. When used as luminescent activators in phosphor materials rare-earths possess excellent luminescent characteristics, with high color purity and high emission efficiency, which is a consequence of their specific electronic configuration. That is why rare-earths doped zinc-silicate phosphors are being used in optical display and lighting applications [2, 3]. Also, they are good candidates for field emission displays (FEDs).

In this paper we present high resolution measurements of low-temperature photoluminescence of trivalent europium ions in zinc-silicate matrix. Europium-doped Zn_2SiO_4 was synthesized using a novel procedure of sol-gel technique combined with combustion processing initiated in a microwave oven. This process enables fast and energetically efficient production of $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$ phosphor particles. We observed and analyzed $^5\text{D}_0 \rightarrow ^7\text{F}_J$ spin forbidden f-f electronic transitions of Eu^{3+} ion. Emission kinetics from $^5\text{D}_0$ level and lifetime-temperature dependence is also presented.

2. Experimental

Zn_2SiO_4 powder doped with 1 at% europium ions was prepared using polymer-assisted salted sol-gel method,

described in detail elsewhere [4], where the precursor for Eu^{3+} ions was europium nitrate (Alfa Aesar, p.a.). Polyethylene glycol with average molecular weight 4000 (PEG 4000, Alfa Aesar) was used not only as chelating agent and a resin vehicle, but also as fuel to provide the combustion reaction. PEG was added in the formed sols before gelling, in 1:1 mass ratio to the expected mass of the final product. After gelling and drying at 100°C for 5 days, obtained dry gel was combusted in a microwave oven (800 W for 5 min), and then thermally treated in a furnace at 1180°C for 1h.

Sample was characterized by X-ray diffraction technique for phase identification and peak broadening analysis. XRD measurements were obtained by Philips PW 1050 instrument, using Ni filtered $\text{Cu K}_{\alpha 1,2}$ radiation. Diffraction data was recorded in a 2θ range from 10° to 80° counting for 10 s in 0.02° steps.

Low-temperature photoluminescence emission spectra and lifetime measurements were performed on high resolution spectrofluorometer system which comprises of optical parametric oscillator excitation source (EKSPLA NT 342, emission range 210-2300 nm), Cryostat (Advance Research Systems), spectrograph FHR 1000 (Horiba Jobin-Yvon, 1800 groove/mm grating) and ICCD detector (Horiba Jobin-Yvon).

3. Results and discussion

Under ordinary conditions Zn_2SiO_4 crystallizes in phenacite structural type and belongs to the rhombohedral space group $R\bar{3}$ (No. 148), with both Zn^{2+} and Si^{4+} tetrahedrally coordinated to four oxygen ions. This is important for understanding the luminescence of

$\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$ because it is safe to assume that europium ions substitute zinc in this structure. The Zn_2SiO_4 structure is schematically presented in Fig. 1.

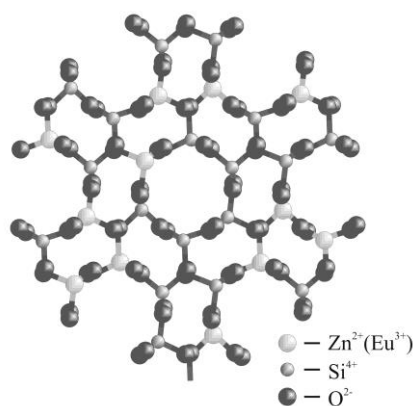


Fig. 1. Structure of zinc-silicate.

Using traditional synthesis procedures, even under high temperatures and long thermal treatments, Zn_2SiO_4 phase is accompanied by residual zinc-oxide and quartz phases [5, 6]. X-ray diffraction pattern of the obtained sample is shown in Fig. 2. Phase purity was confirmed according to the JCPDS No. 37-1485 diffraction data of Zn_2SiO_4 . This shows that the synthesis method we used enables fast and energetically efficient production of pure zinc-silicate powder. The average crystallite size of the powder, from Scherer's equation for the strongest peak (1 1 3) of reflection, is calculated to be around 300 nm.

High-resolution photoluminescence emission spectra of the sample ($\lambda_{\text{exc}} = 464.3$ nm), acquired at different temperatures, are presented in Fig. 3. Each spectrum shows five red emission bands, centered at around 578, 590, 613–625, 653 and 702 nm, associated to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($J = 0, 1, 2, 3, 4$) spin forbidden f-f electronic transitions of Eu^{3+} ion [7-10]. For ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition we observed just one peak, which is expected knowing that coordination difference between two non-equivalent Zn^{2+} crystallographic sites (where Eu^{3+} ion can be found) is practically negligible [4]. ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition is the parity allowed magnetic dipole transition ($\Delta J = 1$) and its intensity does not vary with the host. As opposed to this, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ electric dipole transition ($\Delta J = 2$) is very sensitive to the local environment around Eu^{3+} . Being in this case the most dominant one, it indicates that Eu^{3+} ion occupies a site without a center of symmetry [11]. Lower energy transitions, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$, are also clearly visible. Decreasing the temperature (elimination of phonon vibrations) leads to the significant increase of the emission intensity.

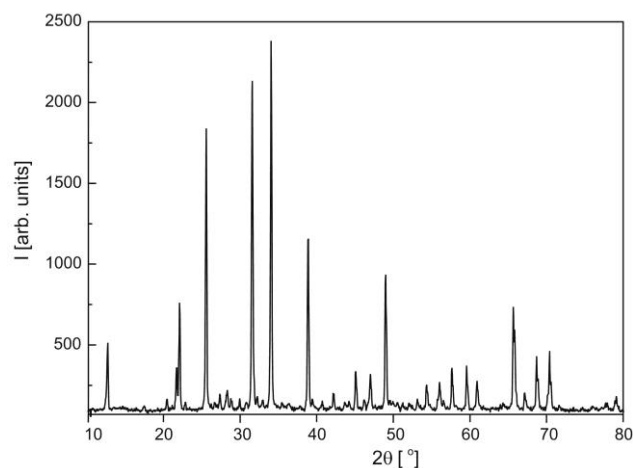


Fig. 2. X-ray diffraction pattern of the $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$ phosphor.

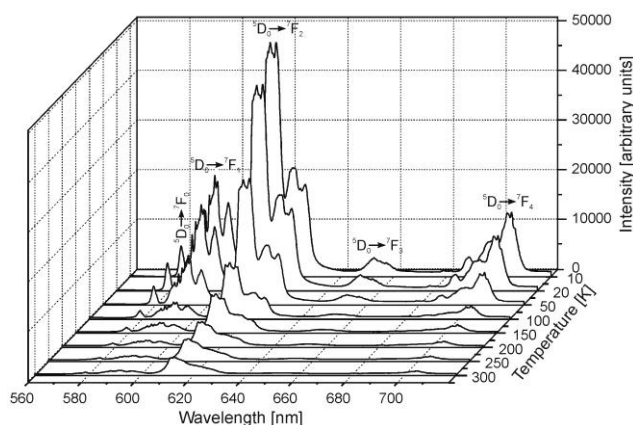


Fig. 3. Low-temperature photoluminescence emission spectra of the sample.

Emission kinetics from ${}^5\text{D}_0$ level was investigated by measuring luminescence emission decay of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. It is presented in $\ln(I) - t$ format, Fig. 4, and fitted with linear function, showing that only one de-excitation process is present. This indicates that there is only one emission source inside the sample – isolated Eu^{3+} ions, homogeneously distributed within the zinc-silicate matrix [8,12]. Lifetime of this transition (measured at 10 K) is calculated from the slope, 1.43 ms. We also examined lifetime-temperature dependence for the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. The result is shown in Fig. 5. One can say that emission lifetime does not depend on temperature decrease.

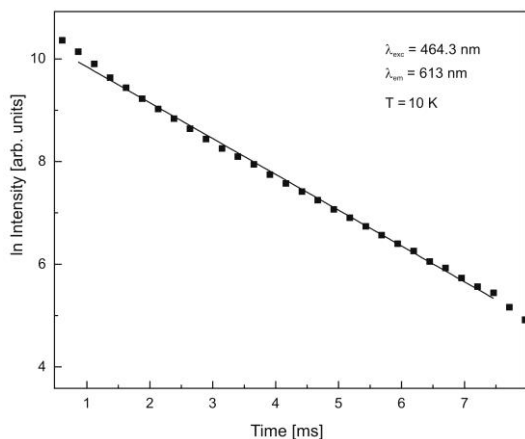


Fig. 4. Luminescence emission decay of ${}^5D_0 \rightarrow {}^7F_2$ transition.

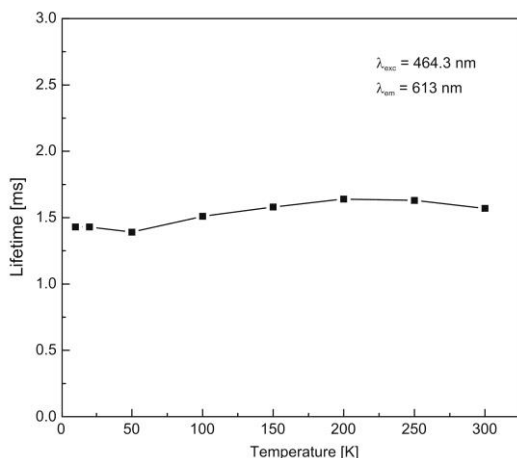


Fig. 5. Lifetime versus temperature for the ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ion.

4. Conclusion

Pure phase and well crystallized $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$ phosphor particles, with crystallite size of 300 nm, were successfully obtained using novel synthesis procedure based on the combination of sol-gel and combustion method. Sample exhibits intense red emission characteristic for the Eu^{3+} ion in tetrahedral environment. Emission intensity rapidly increases with the decrease of temperature. Lifetime of the ${}^5D_0 \rightarrow {}^7F_2$ emission transition

is around 1.5 ms and does not change with the temperature decrease.

Acknowledgements

Authors acknowledge the financial support of the of Education, Science and Technological Development of the Republic of Serbia (project No OI171022 and project No III45020), and Provincial Secretariat for Science and Tehnological Development of the Automomous Province of Vojvodina.

References

- [1] J. McKittrick, L. E. Shea, C. F. Bacalski, E. J. Bosze, *Displays* **19**, 169 (1999).
- [2] H. X. Zhang, C. H. Kam, Y. Zhou, X. Q. Han, S. Buddhudu, Y. L. Lam, C. Y. Chan, *Thin Solid Films* **370**, 50 (2000).
- [3] Q. Y. Zhang, K. Pita, W. Ye, W. X. Que, *Chem. Phys. Lett.* **351**, 163 (2002).
- [4] S. R. Lukić, D. M. Petrović, M. D. Dramićanin, M. Mitrić, Lj. Đačanin, *Scripta Mater.* **58**, 65 (2008).
- [5] A. Fores, M. Llusar, J. A. Badenes, J. Calbo, M. A. Tena, G. Monros, *Green Chem.* **2**, 93 (2000).
- [6] M. Llusar, A. Forés, J.A. Badenes, J. Calbo, M. A. Tena, Guillermo Monrós, *J. Eur. Ceram. Soc.* **21**, 112 (2001).
- [7] Q. Y. Zhang, K. Pita, C. H. Kam, *J. Phys. Chem. of Solids* **64**, 333 (2003).
- [8] A. Patra, G. A. Baker, S. N. Baker, *Opt. Mater.* **27**, 15 (2004).
- [9] Y. C. Li, Y. H. Changa, Y. F. Lin, Y. S. Changb, Y. J. Lin, *J. All. Comp.* **439**, 367 (2007).
- [10] V. Natarajana, K. V. R. Murthyb, M. L. Jayanth Kumar, *Solid State Comm.* **134**, 261 (2005).
- [11] G. Blasse, B. C. Grabmaier, *Luminescent Materials*, Springer Verlag, Berlin, (1994).
- [12] A. Morell, N. Elkhiahi, *J. Electrochem. Soc.* **140**, 2019 (1993).

*Corresponding author: svetlana@df.uns.ac.rs