

LaYO₃:Sm³⁺ Nanocrystalline Phosphor: Preparation and Emission Properties

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Samarium doped LaYO₃ nanocrystalline phosphor powders are obtained by polymer complex solution method. Stoichiometric quantities of La₂O₃, Y₂O₃ and for dopant ions Sm₂O₃ were dissolved in hot nitric acid. Polyethylene glycol was added in solutions in 1:1 mass ratio to corresponding metal nitrates to form gel. The gel is combusted and annealed at 800 °C for two hours to form nanopowder samples. Crystalline structure and phase purity is checked by X-ray diffraction and show that this material is synthesized in cubic bixbyite type structure for the first time. Luminescence properties of Sm³⁺ doped LaYO₃ exhibited characteristic orange-red emission coming from the intra-4f-shell ⁴G_{5/2} → ⁶H_J electron transitions with emission decay of 1.5 ms. Energy level positions are derived from emission and excitation spectra.

PACS: 71.20.Eh, 78.55.Hx, 81.20.Ka, 81.07.Bc

1. Introduction

Alternative procedures for the separation of lanthanoid elements [1] lowered the production costs of high purity rare earth oxides which increased both fundamental and applied research on these materials. The use of lanthanide ions as activators in phosphor materials is common for various applications [2–4].

Due to electronic configuration and the size of the lanthanoid atoms, their oxides are the most thermally stable of all known substances [5]. Among them rare-earth sesqui-oxides are well recognized due to good chemical stability, adequate thermal conductivity and wide electron band gap. Such materials are often used as hosts for phosphor materials. Nanophosphors present a type of phosphors reduced in at least one dimension below 100 nm and includes nanopowders, pressed compacts, nanoceramic materials, films, glasses, nanoclusters, and nanopowder coatings. Preparation of nanoparticles has been studied for about two decades and since then the quality of the nanophosphors has been greatly improved. The effort in making nanophosphors is justified by stronger luminescence emission in nanocrystalline materials compared to bulk materials and modification of radiative lifetime [6].

Synthesis techniques for nanomaterials, in general, can be divided into two broad categories as chemical methods and physical methods. Under chemical methods different routes are colloidal, capping, cluster formation, sol-gel, electrochemical, *etc.* Physical methods mostly used are molecular beam epitaxy, ionized cluster beam, liquid metal ion source, consolidation, sputtering and gas aggregation of monomers [7].

Preparation of low dimension phosphors has become highly significant because of its potential application in

various optical devices. Since Y₂O₃:Eu³⁺ is a well known red commercial phosphor, there have been many work published regarding Y₂O₃ as a single host or as a component in multi-oxide host. Only few Y₂O₃-La₂O₃ systems were reported, mostly studied as a potential candidate for anode material in solid oxide fuel cells [8], solid solutions of rare earth oxide mixtures at high temperatures [9] or as a material for diode-pumped solid-state lasers [10]. A phase diagram of the system was calculated and compared with scarce experimental data [11]. Kodaira *et al.* reported lifetime for ⁴G_{5/2} → ⁶H_{7/2} transition of Sm³⁺ in cubic bixbyite Y₂O₃: nanophosphor lifetime values around 1.0 ms at 298K for samples prepared by combustion and Pechini methods [12].

In this paper we present polymer complex solution method (PCS) [13] for synthesis of LaYO₃:Sm³⁺. The method was derived from classical combustion process [14] and Pechini process [15]. In the method polyethylene glycol (PEG) was used for combustion fuel compared to classical fuel such as urea, glycine or carbonylhydrazide. At the same time PEG is chelating agent for precursor cations compared to citric acid in Pechini process while no addition polymerization reaction is necessary. The PCS method is mixing constituting elements at the ionic level that allows homogenous distribution of the dopant cations as well as host cations in polymeric precursor. The method is proven to be a successful procedure for synthesis of single and mixed rare earth oxide nanopowders with nearly spherical shape of particles and good crystalline oxide phosphor characteristics [16–18].

2. Experimental and methods

Stoichiometric quantities of La₂O₃, Y₂O₃ and Sm₂O₃ (all ≥ 99.9% Alfa Aesar) were dissolved in hot ni-

tric acid *pro analysis* (Zorka Šabac, Serbia). When cooled, polyethylene glycol of average molecular weight 200 (PEG 200, Alfa Aesar) was added in solution in 1:1 mass ratio to corresponding metal nitrates. After several hours of heating at 80 °C and steering on magnetic stirrer clear viscous gel was formed. The gel is combusted and annealed in a porcelain crucible at 800 °C for two hours. As prepared white nanopowder samples were used for all characterizations. X-ray diffraction (XRD) measurements were obtained on Philips PW 1050 instrument, using Ni filtered Cu $K_{\alpha 1,2}$ radiation, in a 2θ range from 10 ° to 120 °, counting for 12 seconds in 0.02 ° step. For luminescence experiments circular pellets were prepared from the powders, without any additives and under the load of 5 tones. Excitation measurements were performed on Fluorolog-3 Model FL3-221 spectrofluorometer system (Horiba Jobin-Yvon). Emission measurements were performed on High resolution spectrofluorometer system which comprises of OPO excitation source (EKSPLAN T 342 (210-2300 nm)), Cryostat 10 K (Advance Research Systems), Spectrometer FHR 1000 (Horiba Jobin-Yvon) with 1800 grooves/mm grating and ICCD detector (HJY-ICCD System).

3. Results

XRD analysis confirms that LaYO_3 powder sample crystallize in a cubic bixbyite type, space group Ia-3 (No.206), forming C-type solid solution of $(\text{La}_{0.5}\text{Y}_{0.5})_2\text{O}_3$. Crystal coherence size of 57.55 Å was calculated by Debay-Sherrer formulae using FWHM of (222) reflection. Cell parameter $a = 11.006$ Å was estimated from PowderCell 2.4 software.

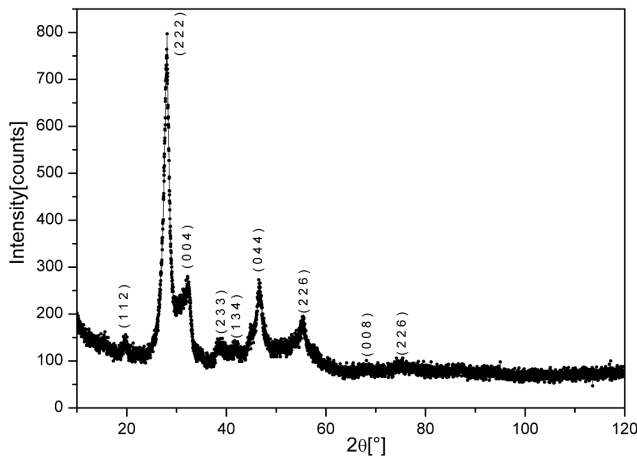


Fig. 1. XRD pattern of LaYO_3 . Main reflections indexed on JCPDS No. 43-0661.

Electron configurations of rare earth ions are characterized by an incompletely filled $4f$ shell. The $4f$ orbital lies inside the ion and is shielded from the surroundings by the filled $5s^2$ and $5p^6$ orbitals. Therefore the influence of the host lattice on the optical transitions within

$4f^n$ configuration is small, but essential, and emission transition yield sharp lines in the spectra. The emission of Sm^{3+} ($4f^5$) is situated in the orange-red spectral region and consist of transitions from the $^4G_{5/2}$ level to the ground state $^6H_{5/2}$ and higher levels 6H_J ($J > 5/2$). The emission spectrum of cubic LaYO_3 doped with 0.3 at% Sm^{3+} , measured at 10K with laser excitation at 477 nm, is given in Fig. 2. One can observe that the intra-configurational transitions of Sm^{3+} ion split in a maximum number of $(J+1/2)$ -manifolds, which is expected for Sm^{3+} ion occupying a local site with C_2 symmetry [18].

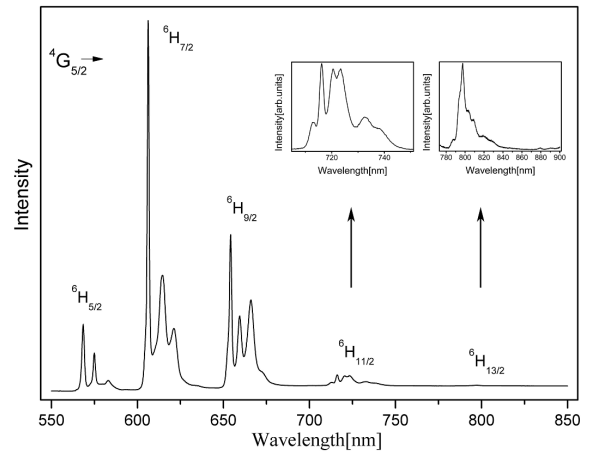


Fig. 2. Emission spectrum for LaYO_3 : 0.3 at% Sm^{3+} at 10 K, $\lambda_{ex} = 477$ nm.

Barycenters of these transitions are 575.49 nm ($^4G_{5/2} \rightarrow ^6H_{5/2}$), 619.23 nm ($^4G_{5/2} \rightarrow ^6H_{7/2}$), 663.05 nm ($^4G_{5/2} \rightarrow ^6H_{9/2}$), 724.02 nm ($^4G_{5/2} \rightarrow ^6H_{11/2}$), 805.73 nm ($^4G_{5/2} \rightarrow ^6H_{13/2}$).

The excitation spectrum of cubic LaYO_3 doped with 0.3 at% Sm^{3+} , measured at 10K with emission detected at 606 nm, is given in Fig. 3. The spectrum is comprised from lines coming from $^6H_{5/2} \rightarrow ^4L_{17/2}$, $^6H_{5/2} \rightarrow ^4P_{5/2}$, $^6H_{5/2} \rightarrow ^4F_{7/2}$, $^6H_{5/2} \rightarrow ^6P_{3/2}$, $^6H_{5/2} \rightarrow ^6P_{5/2}$, $^6H_{5/2} \rightarrow ^4I_{9/2}$, $^6H_{5/2} \rightarrow ^4I_{11/2}$, $^6H_{5/2} \rightarrow ^4I_{13/2}$ and $^6H_{5/2} \rightarrow ^4G_{7/2}$ transitions [19, 20]. Emission decay of the $G_{5/2}$ excited state of Sm^{3+} ions in the cubic LaYO_3 is measured both at room temperature and low (10 K) with laser excitation at 477 nm and detection at 606 nm. Experimental data follow pure single exponential decay and the lifetime values are obtained by linear regression of logarithm of emission intensity versus decay time. In both cases lifetime value of about 1.5 ms is found. This value is considerably longer compared to bulk $\text{Y}_2\text{O}_3:\text{Sm}^{3+}$ (1.0 ms) [21] and nanopowder $\text{Y}_2\text{O}_3:\text{Sm}^{3+}$ (1.0 ms) [12], and similar to one obtained on nanopowder $\text{Y}_2\text{O}_3:\text{Sm}^{3+}$ (1.5 ms) prepared by combustion method [21]. Higher lifetime values in nanocrystals compared to bulk may be attributed to changes in refractive index as first suggested by Meltzer and co-workers [22].

From low-temperature excitation and emission spectra we derived energy levels of trivalent Sm ion in C₂ site of cubic LaYO₃, Fig. 4. Crystal field splitting is successfully resolved in case of lower energy levels and values are given in the right part of Fig. 4. To the best of our knowledge this is the first energy level diagram of Sm³⁺ ion in any cubic La₂O₃-Y₂O₃ host.

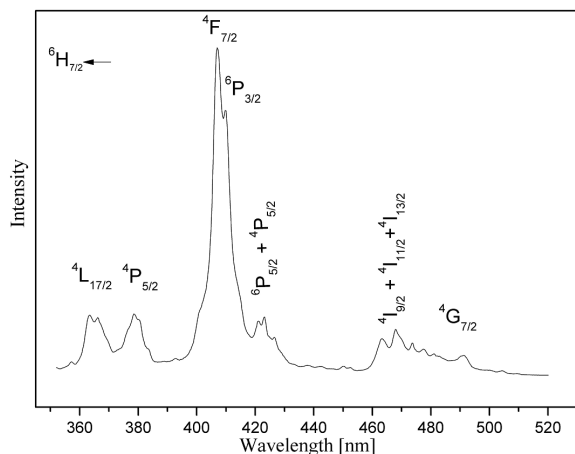


Fig. 3. Excitation spectrum for LaYO₃: 0.3 at% Sm³⁺ at 10 K, λ_{em} =606 nm.

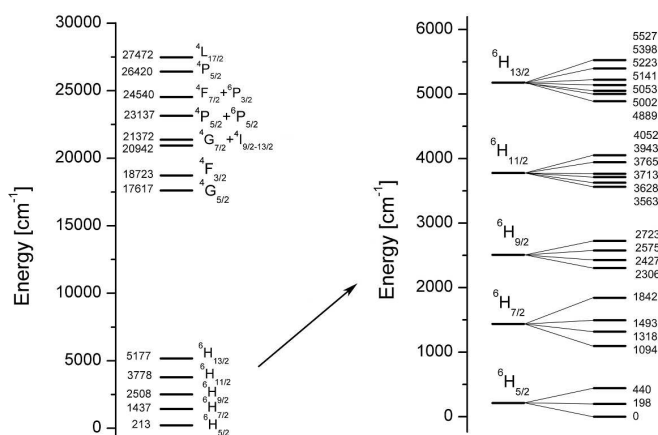


Fig. 4. Energy levels diagram for Sm³⁺ in C₂ site of cubic LaYO₃ host.

4. Conclusions

Polymer complex solution synthesis method utilizing polyethylene glycol as a fuel can be used for preparation of pure phase cubic LaYO₃:Sm³⁺ nanophosphor. Powder with crystallite size of around 6 nm in a cubic bixbyite type crystal structure is produced at low temperatures (800 °C) in a simple and energy efficient way. Powder exhibited intense orange-red emission, with the most intense peak at 619.2 nm from ⁴G_{5/2} → ⁶H_{7/2} intraconfigurational transitions of Sm³⁺ ions. Observed emission

lifetime of 1.5 ms is much higher compared to the case of standard bulk Y₂O₃:Sm³⁺ phosphors (1 ms) and similar to Y₂O₃:Sm³⁺ nanophosphors (1.5 ms) indicating promising applicability of this material.

Acknowledgments

Authors acknowledge the financial support of the Ministry of Science of the Republic of Serbia (Project 141026).

References

- [1] T. Uda, K.T. Jacob, M. Hirasawa, *Science* **289**, 2326 (2000).
- [2] G. Blasse, *Chemistry of Materials* **1**, 294 (1989).
- [3] L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini, E. Tondello, *Coordin. Chem. Rev.* **254**, 487 (2010).
- [4] H. Wang, J. Yang, C.M. Zhang, J. Lin, *J. Solid State Chem.* **182**, 2716 (2009).
- [5] G.-Y. Adachi, N. Imanaka, *Chem. Rev.* **98**, 1479 (1998).
- [6] R.S. Meltzer, S.P. Feofilov, R. Tissue, H.B. Yuan, *Phys. Rev.* **B60**, 14012 (1999).
- [7] H. Chander, *Mat. Sci. Eng.* **R49**, 113 (2005).
- [8] E. Ruiz-Trejo, J.A. Kilner, *Solid State Ion.* **97**, 529 (1997).
- [9] M. Yoshimura, X.-Z. Rong, *J. Mater. Sci. Lett.* **16**, 1961 (1997).
- [10] B.-X. Jiang, T.-D. Huang, Y.-S. Wu, W.-B. Liu, Y.-B. Pan, T. Feng, Q.-H. Yang, *Chinese Phys* **B17**, 3407 (2008).
- [11] M. Chen, B. Hallstedt, L.J. Gauckler, *CALPHAD* **29**, 103 (2005).
- [12] C.A. Kodaira, R. Stefani, A.S. Maia, M.C.F.C. Felinto, H.F. Brito, *J. Lumin.* **127**, 616 (2007).
- [13] S. Yamamoto, M. Kakihana, S. Kato, *J. Alloy. Compd.* **297**, 81 (2000).
- [14] T. Ye, Z. Guiwen, Z. Weiping, X. Shangda, *Mater. Res. Bull.* **32**, 501 (1997).
- [15] M.U. Pechini, US Patent No. 3330697, 1967.
- [16] R. Krsmanović, Ž. Antić, I. Zeković, B. Bártová, M.D. Dramićanin, *Radiat. Meas.* **45**, 438 (2010).
- [17] Ž. Antić, R. Krsmanović, M. Wojtowicz, E. Zych, B. Bártová, M.D. Dramićanin, *Opt. Mater.* **32**, 1612 (2010).
- [18] R. Krsmanović, Ž. Antić, B. Bártová, M.D. Dramićanin, *J. Alloy. Compd.* **505**, 224 (2010).
- [19] G. Lakshminarayana, Rong Yang, Mengfei Mao, Jianrong Qiu, I.V. Kityk, *J. Non-Cryst. Solids* **355**, 2668 (2009).
- [20] J-P.R. Wells, A. Sugiyama, T.P.J. Han, H.G. Gallagher, *J. Lumin.* **87**, 1029 (2000).
- [21] F. Vetrone, J.-C. Boyer, J. Capobianco, A. Speghini, M. Bettinelli, *Nanotechnology* **15**, 75 (2004).
- [22] R.S. Meltzer, S.P. Feofilov, B. Tissue, H.B. Yuan, *Phys. Rev. B* **60**, R14012 (1999).