

Eu⁺³ Ion as a Luminescent Probe in ZrO₂: Gd⁺³ Co-Doped Nanophosphor

S. Manjunatha, M.S. Dharmaprakash

Abstract—Well-defined 2D Eu⁺³ co-doped ZrO₂: Gd⁺³ nanoparticles were successfully synthesized by microwave assisted solution combustion technique for luminescent applications. The present investigation reports the rapid and effective method for the synthesis of the Eu⁺³ co-doped ZrO₂:Gd⁺³ nanoparticles and study of the luminescence behavior of Eu⁺³ ion in ZrO₂:Gd⁺³ nanostructures. The optical properties of the prepared nanostructures were investigated by using UV-visible spectroscopy and photoluminescence spectra. The phase formation and the morphology of the nanoplatelets were studied by XRD, FESEM and HRTEM. The average grain size was found to be 45-50 nm. The presence of Gd³⁺ ion increases the crystallinity of the material and hence acts as a good nucleating agent. The ZrO₂:Gd³⁺ co-doped with Eu⁺³ nanoplatelets gives an emission at 607 nm, a strong red emission under the excitation wavelength of 255 nm.

Keywords—Nanoparticles, XRD, TEM, photoluminescence.

I. INTRODUCTION

LUMINESCENT nanosized metal oxide materials, a newly emerging field at the frontier of science, provide challenges to both fundamental research and breakthrough development of technologies. Among the metal oxides, ZrO₂ is the most studied material for various applications. It is known that ZrO₂ exists in three polymorphic states namely, monoclinic, tetragonal and cubic. In the temperature region less than 1170 °C, the stable phase is monoclinic. Therefore, at room temperature and atmospheric pressure only the monoclinic phase is in thermodynamic equilibrium. In the temperature region 1170-2370 °C, the tetragonal phase is stable, but over 2370 °C, the cubic phase is detected [4]. Recently ZrO₂ has gained more attention in various technological applications based on its phase dependent applications, such as solid oxide fuel cells [5], oxygen sensors [6], thermal barrier coatings [7], corrosion resistance [8] and so on. Among the three polymorphic phases, cubic ZrO₂ has attracted more interest in applications such as oxygen sensors [9] and high thermal catalysis [10]. Hence, it is important to synthesize ZrO₂ in cubic phase for industrial application. However, it is possible to stabilize ZrO₂ cubic phase by either choosing the method of synthesis [11] or by adding different dopants (Y, Ca, Ce, Mg and others) [12]. From the luminescence point of view, to obtain the emissions in the visible range, the Eu⁺³ ion plays an important role as it gives

emissions in the red region of electromagnetic spectrum. For the same reason, ZrO₂ has gained lot of interest in the optical applications. It is significant that in many papers it is shown that ZrO₂ is a good material for RE ions incorporation and for further applications as RE ions build into ZrO₂ crystal with charge state of +3 [1]-[3].

In the present study, the synthesis of ZrO₂: Gd⁺³, Eu⁺³ nanophosphors (Gd⁺³= 2.5% and Eu⁺³ = 2.5 mol%) by microwave assisted solution combustion method and its photoluminescence properties are reported. Here Gd⁺³ is employed as the good nucleating agent for the preparation of the ZrO₂:Gd⁺³, Eu⁺³ nanoplatelets.

II. MATERIALS AND METHOD

Microwave assisted solution combustion technique was employed for the synthesis of ZrO₂ doped with Eu⁺³ and Gd⁺³. These nanoparticles are synthesized by using 2.1967 g of ZrO(NO₃)₂ · H₂O, 0.1128 g of Gd(NO₃)₃ · 6H₂O, 0.1115 g of Eu(NO₃)₃ · 6H₂O as the source of metal precursors. 0.8285 g L-Serine amino acid, a good reducing agent is used as the fuel for the combustion. To ensure the complete combustion of the precursors, the fuel to oxidizer (F/O) ratio was maintained to be unity. All the precursors are dissolved in de-mineralized water and excess water was evaporated on a hot plate. This viscous transparent gel was transferred to a domestic microwave oven (SamsungCE73JD/XTL model working at 2.45 GHz, connected to a 50 Hz source, with a rated power output 100-800 Watt). The gel was exposed to microwave irradiation for 30 seconds maintained at 800 Watt power output. Initially, the solution vigorously boils and undergoes dehydration followed by ignition leading to liberation of enormous amount of gases most likely composed of CO₂, N₂ and water vapours. This finally leads to the formation of a highly porous and voluminous puffy white powder of ZrO₂: Gd⁺³, Eu⁺³ nanoparticles.

The ZrO₂ nanoparticles synthesized from microwave combustion method were characterized by various analytical techniques. The X-ray diffraction (XRD) of powder samples was measured using X-ray powder diffractometer (Bruker D8 Diffractometer, source Cu-K α , λ = 1.5418Å) operated in the reflection mode. Fourier Transform Infrared (FTIR) was recorded (Perkin-Elmer spectrometer) with KBr pellet technique. The morphology of the ZrO₂ nanoparticles was studied using field emission scanning electron microscope (FESEM) with energy dispersive spectroscopy (EDS) using Gemini, Ultra 55. The particle size and microstructure of ZrO₂ nanoparticles were recorded using high resolution transmission electron microscopy (HRTEM). The phase

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formed was reconfirmed by using selective area electron diffraction (SAED) pattern using JEOL 2100. The excitation and the emission spectra were recorded using photoluminescence spectra. The spectra were collected using Jobin Yvon spectrofluorimeter Fluorolog-3, which uses a 450W xenon lamp as an excitation source.

III. RESULTS AND DISCUSSION

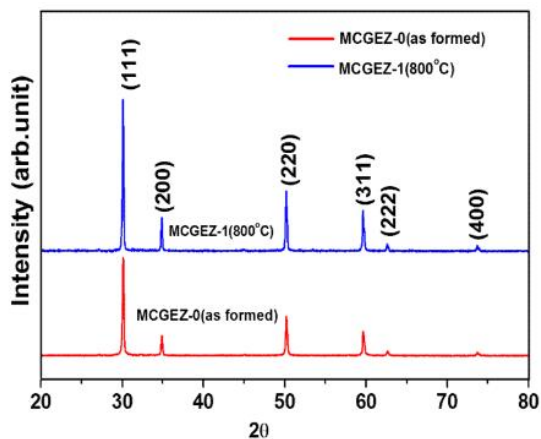


Fig. 1 XRD pattern of cubic $\text{ZrO}_2: \text{Gd}^{+3}, \text{Eu}^{+3}$ nanophosphors

The power XRD pattern of the prepared nanoparticles is shown in Fig. 1. From XRD pattern, it is clear that, all the samples including the as prepared sample, exhibit only the cubic phase though calcined at temperatures as high as 800 °C. The synthetic method has important role to play in the formation of crystalline phase and the particle size [13]. The $\text{ZrO}_2: \text{Gd}^{+3}, \text{Eu}^{+3}$ nanophosphors are crystalline in nature and are mesoporous. The particle size is calculated by Debye-Scherrer formula $D = K / \cos \theta$ where $K=0.94$ which stands for shape factor, $\lambda = 1.5405 \text{ \AA}$ represents the wavelength of Cu K radiation, β is the half width of each diffraction peak and θ represents the half angle of the diffraction peak. The mean crystallite size of the nanoparticles found in the range of 45-50 nm.

Fig. 2 (a) shows the scanning electron micrographs of $\text{ZrO}_2: \text{Gd}^{+3}, \text{Eu}^{+3}$ hexagonal nanoplatelets synthesized by the microwave solution combustion method. The as synthesized nanoparticles of $\text{ZrO}_2: \text{Gd}^{+3}, \text{Eu}^{+3}$ is found to be uniform and porous. The porous nature is due to the escaping of the gases liberated during the combustion process.

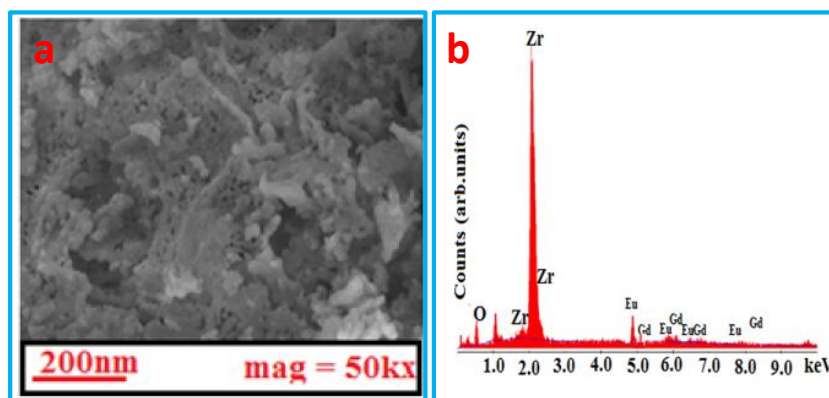


Fig. 2 (a) FESEM of the porous $\text{ZrO}_2: \text{Gd}^{+3}, \text{Eu}^{+3}$ nanophosphors (b) EDS elemental analysis of $\text{ZrO}_2: \text{Gd}^{+3}, \text{Eu}^{+3}$ nanoparticles

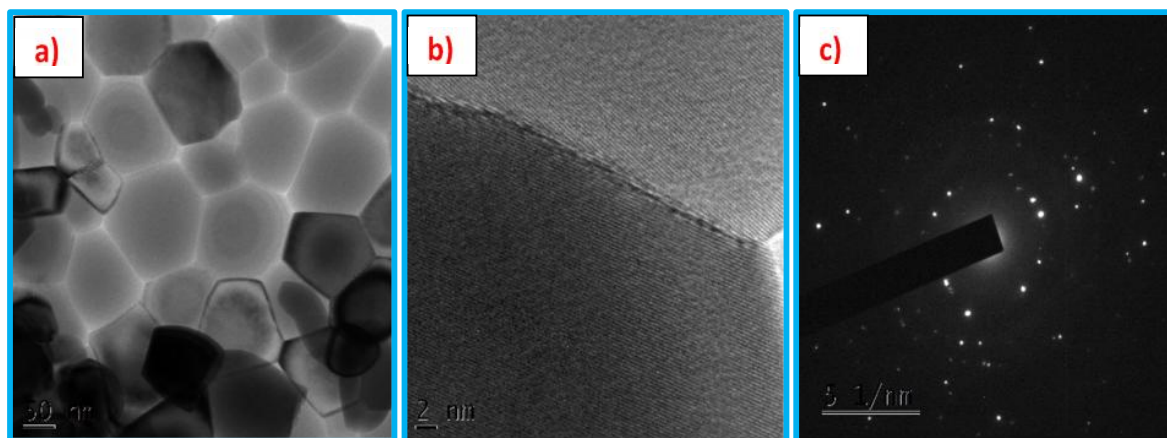


Fig.3 (a) TEM of $\text{ZrO}_2: \text{Gd}^{+3}, \text{Eu}^{+3}$ nanophosphors (b) HRTEM showing lattice fringes (c) SAED pattern

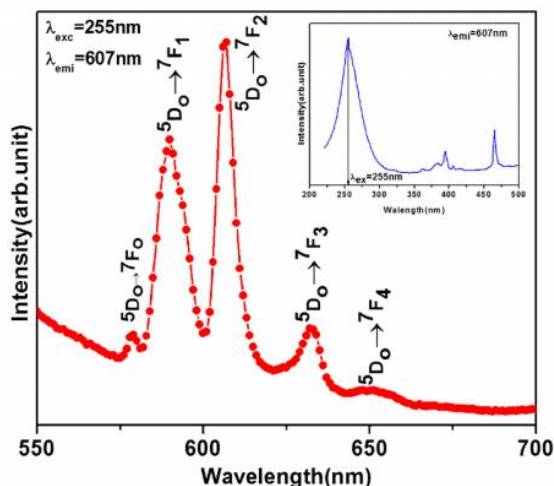


Fig. 4 Photoluminescence emission of the $\text{ZrO}_2: \text{Gd}^{3+}, \text{Eu}^{3+}$ nanophosphors (inset: Excitation spectra of the $\text{ZrO}_2: \text{Gd}^{3+}, \text{Eu}^{3+}$)

In order to confirm the doping gadolinium and europium in the synthesized $\text{ZrO}_2: \text{Gd}^{3+}, \text{Eu}^{3+}$ nanoparticles, EDS measurements were performed. Fig. 2 (b) shows the EDS spectra of $\text{ZrO}_2: \text{Gd}^{3+}, \text{Eu}^{3+}$ nanoparticle. From EDS analysis, it is clear that after the synthesis process, gadolinium and europium are homogeneously distributed inside the ZrO_2 matrix.

Fig. 3 (a) represents the TEM image of the $\text{ZrO}_2: \text{Gd}^{3+}, \text{Eu}^{3+}$ nanophosphors, which shows that the majority of the particles are crystallized in hexagonal shape and the particles are narrow size distribution and conjoined together through their edges. The TEM analysis is in agreement with FESEM results in which the evolution of hexagonal nanoplatelets is observed. The average particle size was measured to be 52 nm. Fig. 3 (b) shows HRTEM images of $\text{ZrO}_2: \text{Gd}^{3+}, \text{Eu}^{3+}$ nanophosphors. From the HRTEM, the interspacing between the lattice fringes are found to be equidistant and is equal to 0.24 nm, which corresponds to (200) plane of cubic ZrO_2 . The d-spacing value measured is close to the value mentioned in the ICSD reference number 00-049-1642. Fig. 3 (c) is the SAED pattern of the nanoparticles which supports the high crystalline nature of the material revealed by XRD analysis.

The optical emission property of the $\text{ZrO}_2: \text{Gd}^{3+}, \text{Eu}^{3+}$ nanophosphors is studied under the excitation of 255 nm. The inset of Fig. 4 is the excitation spectra of the nanophosphors which gives the emissions in the visible range. The sharp peak at 255 nm in the excitation spectra is due to the Eu-O charge transfer. The recorded emission spectra show well resolved peaks. These emissions are due to the intra f-f transitions occurred in Eu^{3+} ion only. The strongest red peak at 607 nm was due to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition. The 592 nm orange emission was originated due to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is typically because of magnetic dipole transition. The most intense emission peak at 607 nm is due to the transition of $^5\text{D}_0 \rightarrow ^7\text{F}_2$, which corresponds to the electric dipole transition in Eu^{3+} ion [14]. The ratio of red and orange peak intensity (R/O value) called asymmetric ratio strongly depends on local symmetry of

activator ion Eu^{3+} . The asymmetric ratio of the synthesized nanophosphors is equal to 1.40 which indicates the high symmetry of the crystal [15], which corroborates the cubic pattern of XRD reflections. Two more peaks at 630 nm and 652 nm corresponds to the transitions of $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ respectively. Further, it is also clear that Gd^{3+} ion is not influencing the characteristic emission spectra of Eu^{3+} ion as there is no shift observed, which is in agreement with reported literature [16]. In this phosphor material, $\text{Gd}^{3+}(4f^7)$ has half-filled shell ground state. Hence the Eu^{3+} ion is the probe for the luminescence emissions in the ZrO_2 host.

IV. CONCLUSION

The microwave assisted solution combustion technique provides a fast heating method to synthesize $\text{ZrO}_2: \text{Gd}^{3+}$ co-doped with Eu^{3+} nanoplatelets. This method required a very short heating time, and will be extended to synthesize some other oxide rods. The obtained $\text{ZrO}_2: \text{Gd}^{3+}$ co-doped with Eu^{3+} nanoplatelets have an average size of 45–50nm and stabilized in pure cubic phase. The crystallinity of the material is enhanced due to the presence of Gd^{3+} ion, as it acts as a good nucleating agent. Under 255nm excitation wavelength, the emission observed at 607nm for Eu^{3+} co-doped $\text{ZrO}_2: \text{Gd}^{3+}$ nanoplatelets corresponds to the emissions of Eu^{3+} . Strong red emission at 607nm indicating that this red phosphor is a potentially good candidate for luminescent devices.

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REFERENCES

- [1] M.R.N. Soares, C. Nico, D. Oliveira, M. Peres, L. Rino, A.J.S. Fernandes, T. Monteiro, F.M. Costa, Red light From $\text{ZrO}_2: \text{Eu}^{3+}$ nanostructures Mat. Science and Engineering B, vol. 177, pp. 712–716, 2012.
- [2] C.M. Leroy, T. Cardinal, V. Jubera, C. Aymoniera, M. Treguer-Delapierre, C. Boissière, D. Grosso, C. Sanchez, B. Viana, F. Pellé, Luminescence properties of ZrO_2 mesoporous thin films doped with Eu^{3+} and Ag^+ , Microporous and Mesoporous Materials, vol. 170, pp. 123–130, 2013.
- [3] S.S. Syamchand, G. Sony, Europium enabled luminescent nanoparticles for biomedical applications, J. of Lumin., vol. 165, pp. 190–215, 2015.
- [4] Meijun Li and Zhaochi Feng, J.Phys. Chem.B, vol. 105, pp.8107–8111, 2001.
- [5] A Samson Nesaraj, “Recent developments in solid oxide fuel cell technology” – a review, J. of Scientific & Industrial Research, vol. 69, pp. 169–176, 2010.
- [6] Zhou M and Ahmad A, “Synthesis, processing and characterization of calcia-stabilized zirconia solid electrolytes for oxygen sensing applications,” Mater Res Bull vol. 41 pp.690–696, 2006.
- [7] M.D. Chambers and David R. Clarke, “Effect of long term, high temperature aging on luminescence from Eu-doped YSZ thermal barrier coatings Materials,” Surface & Coatings Technology, vol. 201 pp. 3942–3946, 2006.
- [8] M. Balog and M. Schieber, “The chemical vapour deposition and characterization of zrO_2 films from organometallic compounds,” Thin Solid Films, vol. 47, pp. 109–120, 1977.
- [9] E Haefele, K Kaltenmeier and U Schoenauer Sensors and Actuators, Chemicals B4, pp. 525, 1991.

- [10] Weigel, J. Koepfel, R. Baiker, Wokaun, "Surface species in CO and CO₂ hydrogenation over copper/zirconia: On the methanol synthesis mechanism," *Langmuir*, vol. 12, pp. 5319-5329, 1996.
- [11] S. Manjunatha and M.S. Dharmaprakash, "Microwave assisted synthesis of cubic Zirconia nanoparticles and study of optical and photoluminescence properties," *J of Luminescence*, vol. 180, pp. 20-24, 2016.
- [12] S. Manjunatha and M.S. Dharmaprakash, "Synthesis and characterization of Cerium doped ZrO₂ blue-green emitting nanophosphors," *Mat. Lett.* Vol. 164, pp. 476-479, 2016
- [13] Florence Boulch and Elisabeth Djurado, "Structural changes of rare-earth-doped, nanostructured zirconia solid solution," *Solid State Ionics*, vol. 157 pp. 335-340, 2003.
- [14] H. Zhanga, X. Fub, S. Niub, G. Suna, Q. Xin, "Synthesis and characterization of ZrO₂:Eu nanopowder by EDTA complexing sol-gel method," *Materials Chemistry and Physics*, vol.91, pp. 361-364, 2005.
- [15] S.D. Meetei, S. Dorendrajit Singh, "Effects of crystal size, structure and quenching on the photoluminescence emission intensity, lifetime and quantum yield of ZrO₂:Eu³⁺ nanocrystals," *J.of Luminescence*, vol.147, pp. 328-335, 2014.
- [16] Feng Huang, Daqin Chen, Jiangcong Zhou and Yuansheng Wang, "Modifying the phase and controlling the size of monodisperse ZrO₂ nanocrystals by employing Gd³⁺ as a nucleation agent," *CrystEng Comm*, vol.13, pp. 4500, 2011.