EU$^{3+}$ ION AS A LUMINESCENT PROBE IN ZRO$_2$: GD$^{3+}$ CO-DOPED NANOPHOSPHOR

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ABSTRACT—Well-defined 2D EU$^{3+}$ co-doped ZrO$_2$: 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 ZrO$_2$:Gd$^{3+}$ nanoparticles and study of the luminescence behavior of Eu$^{3+}$ ion in ZrO$_2$:Gd$_2$ nanosstructures. 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 Gd$^{3+}$ ion increases the crystallinity of the material and hence acts as a good nucleating agent. The ZrO$_2$:Gd$^{3+}$ 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, ZrO$_2$ is the most studied material for various applications. It is known that ZrO$_2$ exists in three polymorphic states namely, monoclinic, tetragonal and cubic. In the temperature region less than 1170 ºC, 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 ºC, the tetragonal phase is stable, but over 2370 ºC, the cubic phase is detected [4]. Recently ZrO$_2$ has gained more attention in various technological applications based on its phase dependent properties. Among various applications, ZrO$_2$ is used in oxygen sensors [5], as solid oxide fuel cells [6], in thermal barrier coatings [7], as an electronic material for gas sensors [8] and so on. Among the three polymorphic phases, cubic ZrO$_2$ has attracted more interest in applications such as oxygen sensors [9] and high thermal catalysis [10]. Hence, it is important to synthesize ZrO$_2$ in cubic phase for industrial application. However, it is possible to stabilize ZrO$_2$ 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, ZrO$_2$ has gained lot of interest in the optical applications. It is significant that in many papers it is shown that ZrO$_2$ is a good material for RE ions incorporation and for further applications as RE ions build into ZrO$_2$ crystal with charge state of +3 [1]-[3].

In the present study, the synthesis of ZrO$_2$: 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 ZrO$_2$:Gd$^{3+}$, Eu$^{3+}$ nanoplatelets.

II. MATERIALS AND METHOD

Microwave assisted solution combustion technique was employed for the synthesis of ZrO$_2$ doped with Eu$^{3+}$ and Gd$^{3+}$. These nanoparticles are synthesized by using 2.1967 g of ZrO(NO$_3$)$_2$. H$_2$O, 0.1115 g of Gd(NO$_3$)$_3$. 6H$_2$O, 0.1115 g of Eu(NO$_3$)$_3$. 6H$_2$O 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 (SamsungCE73JDXTL 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 CO$_2$, N$_2$ and water vapours. This finally leads to the formation of a highly porous and voluminous puffy white powder of ZrO$_2$: Eu$^{3+}$, Gd$^{3+}$ nanoparticles.

The ZrO$_2$ 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-Ka, 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 ZrO$_2$ 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 ZrO$_2$ nanoparticles were recorded using high resolution transmission electron microscopy (HRTEM).
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

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-Scherer formula \( D = K \lambda / \beta \cos \theta \) where \( K = 0.94 \) which stands for shape factor, \( \lambda = 1.5405 \text{A} \) represents the wavelength of Cu K\( \alpha \) radiation, \( \beta \) is the half width if each diffraction peak and \( \theta \) 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. 3 (a) TEM of \( \text{ZrO}_2: \text{Gd}^{3+}, \text{Eu}^{3+} \) nanophosphors (b) HRTEM showing lattice fringes (c) SAED pattern
In order to confirm the doping gadolinium and europium in the synthesized ZrO$_2$: Gd$^{3+}$, Eu$^{3+}$ nanoparticles, EDS measurements were performed. Fig. 2 (b) shows the EDS spectra of ZrO$_2$: Gd$^{3+}$, Eu$^{3+}$ nanoparticle. From EDS analysis, it is clear that after the synthesis process, gadolinium and europium are homogenously distributed inside the ZrO$_2$ matrix.

Fig. 3 (a) represents the TEM image of the ZrO$_2$: Gd$^{3+}$, Eu$^{3+}$ nanophosphors, which shows that the majority of the particles are crystallizes 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 ZrO$_2$: Gd$^{3+}$, 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 ZrO$_2$: Gd$^{3+}$, 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 $^5D_0 \rightarrow ^7F_1$ transition. The 592 nm orange emission was originated due to $^5D_0 \rightarrow ^7F_1$ transition is typically because of magnetic dipole transition. The most intense emission peak at 607 nm is due to the transition of $^5D_0 \rightarrow ^7F_2$, 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 $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ 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, 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 ZrO$_2$: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 ZrO$_2$: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 ZrO$_2$: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


