Journal of Ovonic Research Vol. 20, No. 2, March - April 2024, p. 155 - 161

$Sr_{0.99}Zr(PO_4)_2$:0.01Eu^{3+} ceramic glass for photoluminescence applications

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This paper reports the first-time synthesis of $Sr_{0.99}Zr(PO_4)_2$:0.01Eu^{3+} nanophosphor via solution combustion method using glycine as fuel at a fuel-to-oxidizer ratio of 1:1. The PXRD pattern confirmed the formation of the desired phase, while the Scherrer calculation revealed an average particle size of approximately 60 nm. Scanning electron microscopy (SEM) further corroborated the particle size, estimating it around 75 nm. The material exhibited a characteristic mesoporous structure, a hallmark of the solution combustion synthesis technique. Photoluminescence (PL) spectroscopy revealed two intense emission peaks at 590 nm and 615 nm, attributed to Eu^{3+} ions, suggesting potential applications in LED technology. CIE coordinates indicated emission close to the white region defined by the NTSC standard.

(Received December 24, 2023; Accepted March 11, 2024)

Keywords: SZO nanophosphor, Solution combustion synthesis, Photoluminescence, LEDs

1. Introduction

Phosphates have captivated researchers for decades due to their vast array of applications, ranging from phosphors and nuclear waste forms to thermal barrier coatings, catalysts, and solid electrolytes [1]. They boast remarkable chemical stability, low thermal conductivity, a high melting point, a high thermal expansion coefficient, and an exceptional ability to accommodate defects [2]. Recently, zirconia-based phosphates have garnered significant attention for their potential as phosphor and energy storage materials, leading to a surge in research focused on their preparation and functional properties [3]. Diverse synthesis methods have been developed, including solid-state reaction, sol-gel, combustion, stearic acid, solution combustion, and hydrothermal methods. While solid-state synthesis remains prevalent due to its simplicity, it suffers from limitations such as high preparation temperatures (often exceeding 1200°C) and lengthy reaction times (lasting several days), resulting in large agglomerates and reduced luminescence efficiency [4].

In our previous work, we successfully addressed these drawbacks by employing the solution combustion route to synthesize $Sr_{0.99}Zr(PO_4)_2$:0.01Eu^{3+} nanopowders at a significantly lower temperature (400°C) and shorter reaction time (approximately 10 minutes) [5]. This method yielded nanopowders with a characteristic mesoporous structure and superior chemical homogeneity, making it a simpler and more cost-effective alternative to conventional methods [6]. This present work focuses on the preparation and characterization of Europium-doped $Sr_{0.99}Zr(PO_4)_2$:0.01Eu^{3+}. Eu3^{+} ions play a crucial role in the luminescence properties of phosphates, exhibiting distinct PL emissions associated with the 5d-4f transitions. The intensity and position of these emissions, highly sensitive to the local environment of the Eu3^{+} ions, provide valuable information about the structure and defects within the matrix. Notably, the 5d-4f^{2} transitions are sensitive to the coordination number of Eu3^{+} ions, while the 5d-4f^{1} transitions are sensitive to the local symmetry [7].

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https://doi.org/10.15251/JOR.2024.202.155

The growing demand for highly efficient, durable, sustainable, and cost-effective energy storage solutions necessitates the exploration of novel materials with exceptional properties. Supercapacitors, bridging the gap between capacitors and batteries, offer promising possibilities for applications with rapid energy cycling needs, due to their fast charging/discharging capabilities [8]. This has sparked significant research interest in materials exhibiting supercapacitive properties. Preliminary studies suggest that $SrZr(PO_4)_2$ possesses promising supercapacitive properties, making it a promising candidate for further exploration and optimization [9]. $SrZr(PO_4)_2$, in general, present themselves as versatile and highly functional material with a wide range of potential applications, particularly in the fields of energy storage and luminescence [10]. Their unique combination of desirable properties, including high stability, low thermal expansion, and superionic conductivity, makes them attractive candidates for various technological advancements [11]. Continued research and development are crucial to unlock the full potential of these materials and contribute to the advancement of diverse industries [12].

Orthophosphates have emerged as prominent host materials for luminescent applications due to their exceptional properties, including a large band gap, moderate phonon energy, high chemical stability, and exceptional optical damage resistance [13]. $Sr_{0.99}Zr(PO_4)_2{:}0.01Eu^{3+}$ceramic material was specifically chosen for this study due to its unique characteristics, including: Ionic conductivity: Facilitating efficient charge transport, Anisotropy: Tailoring material properties for specific applications, Lower thermal expansion: Enhancing material stability, Larger ionic radii: Enabling effective incorporation of rare-earth ions without altering the crystal structure, Presence of zirconium and phosphate: Providing a well-defined crystal field for structural applications [14]. Despite the promising potential of $SrZr(PO_4)_2$, limited research has been conducted on its luminescence properties, particularly regarding the doping of Eu3+ ions. Additionally, the dielectric properties of the material will be investigated to gain further insights into its potential applications. To the best of our knowledge no reports are available on the photo-luminesce studies.

2. Preparation

$Sr_{0.99}Zr(PO_4)_2{:}0.01Eu^{3+}$ was prepared by solution combustion method with F/O ratio maintained at unity. Stoichiometric amounts of $ZrO(NO_3)_2$, $NH_6(PO_4)_2$, $Eu(NO_3)_3$, $Sr(NO_3)_2$, and Glycine were dissolved in 50 ml of double distilled water to obtain a homogenous solution. The precursor solution was then transferred to a crystalline dish and placed in a preheated muffle furnace at 500°C. Upon completion of the reaction, the sample was removed from the furnace and allowed to cool to room temperature. Finally, the powder was calcined at 800°C for 6 hours.

3. Result and discussion

To ascertain the crystallinity, phase purity, and structural information of $Sr_{0.99}Zr(PO_4)_2{:}0.01Eu^{3+}$, powder X-ray diffraction (XRD) measurements were conducted, Fig. 1. The observed diffraction patterns aligned well with ICSD file number 150336 [15]. The crystalline sizes of the prepared samples were calculated using the Scherer method and were about 60nm.

The Scherer equation is given by:

$$D = k\lambda/\beta\cos\theta \tag{1}$$

where λ is the wavelength of X-rays (1.5406 Å), β is the full width half maxima of diffraction peaks, k is the Scherer's constant (0.9), and θ is the Bragg's angle.

FTIR analysis was conducted on the samples to gain insights into their molecular structure and functional groups. The FTIR spectra for all F/O ratios were measured within the range of 400 to 4000 cm^{-1}, Fig. 2. Broad bands observed in the region 3400–3200 cm^{-1} correspond to the stretching vibrations of -OH groups. The phosphate group $(PO4)^{3-}$ is characterized by the intense band at around 1050 cm^{-1}. In the range 700–500 cm^{-1}, vibrations of O-Sr-O and O-P-O groups occur. The peak around 1200–1210 cm^{-1} is attributed to PO4 asymmetric stretching [16].

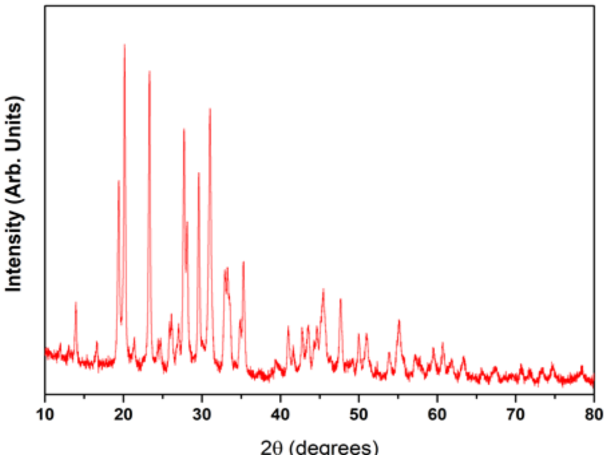

Fig. 1. PXRD spectrum of $Sr_{0.99}Zr(PO_4)_2$:0.01Eu.

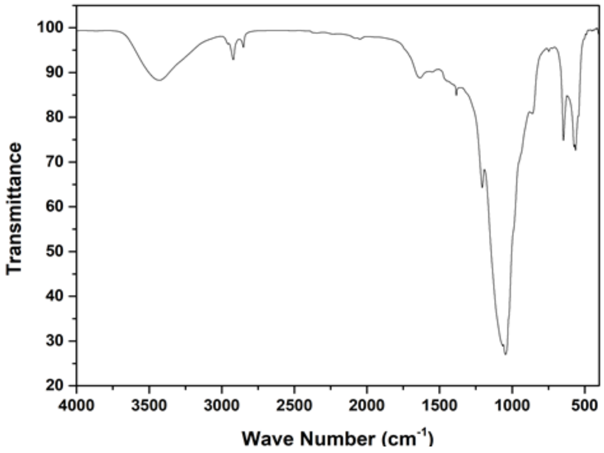

Fig. 2. FTIR spectra of $Sr_{0.99}Zr(PO_4)_2$:0.01Eu.

Scanning electron microscopy (SEM) was recorded for the sample, Fig.3. These images revealed significant changes in microstructure, including grain size, porosity, and particle distribution. The voids and porosity observed in the samples are attributed to the evolution of a large volume of gases during the combustion process. The particle size obtained in SEM micrographs was about 75 nm which matches with the PXRD studies.

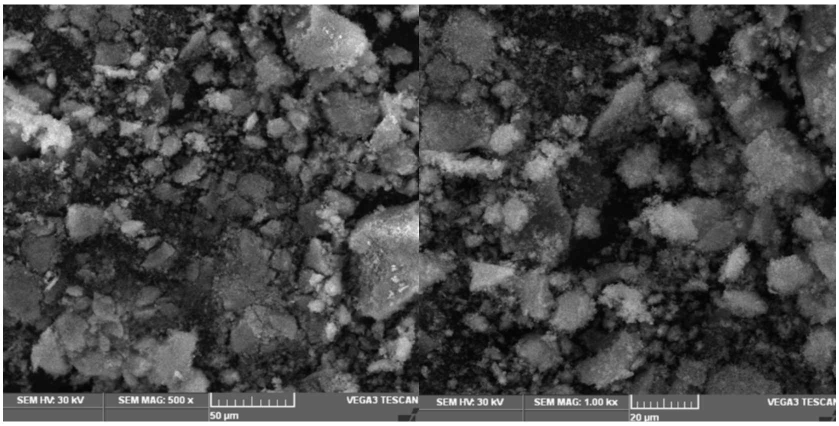

Fig. 3. SEM images of $Sr_{0.99}Zr(PO_4)_2$:0.01Eu at 50 different magnification.

The luminescence properties of RE ions are significantly impacted by the matrix in which RE is been hosed. Modifying luminescence properties can be achieved through various preparation techniques, such as employing different atmospheric conditions and fuels [17]. Fig. 4 depicts the PL excitation spectra of $Sr_{0.99}Zr(PO_4)_2:0.01Eu^{3+}$ by monitoring the emission at 615 nm. Excitation bands are observed at 362 nm ($^7F_0 \rightarrow {}^5D_4$), 381 nm ($^7F_0 \rightarrow {}^5L_7$), and 394 nm ($^7F_0 \rightarrow {}^5L_6$) [18]. Fig. 7 illustrates the emission spectra of the samples excited at 395 nm. The band at 410 nm is the charge transfer band. The peaks at 589, 615, and 653 nm correspond to $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_3$ transitions, respectively [19].

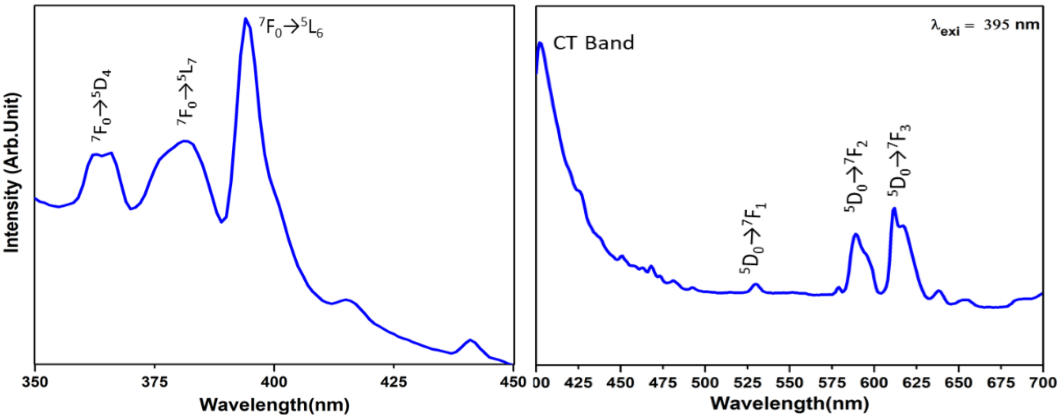

Fig. 4. (a) PL excitation spectrum $Sr_{0.99}Zr(PO_4)_2$:0.01Eu while monitoring emission at 615 nm.(b) PL emission spectrum of $Sr_{0.99}Zr(PO_4)_2$:0.01Eu exited at 395 nm.

Judd–Ofelt (J-O) intensity parameters and radiative properties were computed in order to probe into the site symmetry and luminescence property of Eu^{3+} ions in the $Sr_{0.99}Zr(PO_4)_2:0.01Eu^{3+}$. By J-O theory one can calculate radiation transition probability (A_T), branching ratios (B_r), stimulated emission cross-section (s) and radiative lifetime (t_r). symmetry around the Eu^{3+} ions and polarization can be obtained from the Ω_2 and Ω_4 values. Whereas, Ω_6 is influenced by long range effects [20].

Total emission amplitude is given by

$$A_T\,(\psi J) = \sum_{\psi' J'} A(\psi J, \psi' J') \qquad (2)$$

The relative amplitudes of the fluorescence transitions or fluorescence branching ratio is given by

$$A_R\,(\psi J) = A(\psi J, \psi' J') \tag{3}$$

The rate of depopulation of an excited state is given by the decay lifetime, $\tau_R\,(\psi J)$

$$\tau_R\,(\psi J) = \frac{1}{A(\psi J, \psi' J')} \tag{4}$$

The calculated radiative transition probabilities (A_R), decay lifetime, $\tau_R\,(\psi J)$, and radiative branching ratios (β_R), from the $^5D_0$ excited level to all its lower lying levels are presented in table 1.

$$\beta_R\,(\psi J, \psi' J') = A(\psi J, \psi' J') /\, A_T\,(\psi J) \tag{5}$$

Bonding parameter (σ) and Judd-Ofelt parameters Ω_2 and Ω_4 offer valuable insights into the electronic properties of Europium ions in various host materials. Large values obtained for the stimulated emission cross section (s) implies potential use of these material for LASER applications.

Table 1. Calculated branching ratios, radiative and J-O parameters of $Sr_{0.99}Eu_{0.01}Zr(PO_4)_2$.

Transition	**Branching Ratios**		**Radiative Parameters**	
	Expt	**Theory**	**υ/cm**	**σ** x10^{-22} **(cm^2)**
$^5D_0 \longrightarrow {}^7F_1$	0.280	0.261	16883	1.8
$^5D_0 \longrightarrow {}^7F_2$	0.389	0.378	16161	2.7
$^5D_0 \longrightarrow {}^7F_4$	0.329	0.360	14382	2.4
J-O Parameters x 10^{-20}		$\Omega_2 = 2.14$	$\Omega_4 = 4.03$	

Commercial phosphors should comply the color purity requirements as prescribed by the CIE [21]. To visualize the emission colors corresponding to different wavelengths and their combined effect in RGB space, a CIE chromaticity diagram is presented in Fig. 5. The emission color of the $Sr_{0.99}Zr(PO_4)_2$:0.01Eu^{3+} lies close to the standard white as shown in the figure [22]. The phosphor could possibly be used in solid state white light emitting diodes.

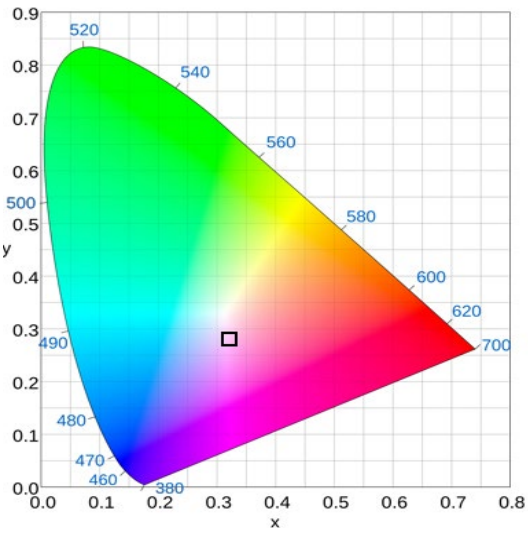

Fig. 5. CIE color co-ordinates of $Sr_{0.99}Zr(PO_4)_2$*:0.01Eu.*

4. Conclusion

For the first time, we report the synthesis of $Sr_{0.99}Zr(PO_4)_2$:0.01Eu^{3+} using a simple solution combustion method. XRD analysis confirms the triclinic phase of the synthesized materials, with particle sizes about 60 nm. SEM micrographs show mesoporous particle formation with lot of voids and agglomeration. PL excitation spectra exhibit three excitation bands at 362 nm ($^7F_0 \rightarrow {}^5D_4$), 381 nm ($^7F_0 \rightarrow {}^5L_7$), and 395 nm ($^7F_0 \rightarrow {}^5L_6$). Samples excited at 395 nm, the dominant excitation band, show three emission bands at 589, 615, and 653 nm corresponding to $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_3$ transitions, respectively. Calculated CIE values implies emission close to the white emission suggested by NTSC.

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