

Synthesis, Characterization and Photoluminescence Study of $\text{CaZrO}_3:\text{Eu}^{3+}$ Phosphor

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Abstract: $\text{CaZrO}_3:\text{Eu}^{3+}$ phosphors were successfully synthesized by solid state reaction technique. The samples were characterized by X-ray Diffraction (XRD) and photoluminescence (PL) studies. The XRD pattern sample confirms the formation of CaZrO_3 and belongs to orthorhombic perovskite type structure. Under UV excitation the $\text{CaZrO}_3:\text{Eu}^{3+}$ shows photoluminescence emission peaks at 589 nm, 595 nm, 613 nm and 633 nm due to the Eu^{3+} transition ${}^5\text{D}_0-{}^7\text{F}_J$ (where $J = 0, 1, 2, 3$). The red luminescence of Eu^{3+} ion corresponding to the electric dipole (ED) transition is dominant for all concentration of dopant. The concentration quenching occurs when the concentration of dopant (Eu^{3+}) exceeds 1 mol%. Eu^{3+} doped CaZrO_3 is a promising phosphor for applications in displays and optical devices.

Keywords: Photoluminescence, XRD, Phosphors.

I. INTRODUCTION

Rare earth doped calcium zirconate (CaZrO_3) is a fascinating topic and drawn so much attention in research because of its wide range of application in electronic ceramic industry, gas sensors, optical coatings, filters etc [1, 28-33]. ABO_3 -like (where $A = \text{Ca, Ba, Sr}$ and $B = \text{Zr, Ti}$) compound with the perovskite structure showed interesting luminescent properties. CaZrO_3 is having an orthorhombic perovskite type structure [2, 27] and has unique properties like high chemical and thermal stability, single phase crystalline structure, high refractive index, wide band gap, high permittivity, high ionic conductivity and insulation resistance which make it suitable compound for use in oxide fuel cells and microwave dielectric substance [3, 28]. The zirconates are used as a special class in crucibles for superconductor synthesis, deposition substrates and refractory materials because it is one of high temperature materials [4, 29]. A large number of rare earth dopant like Eu^{3+} , Er^{3+} , Ce^{3+} , Yb^{3+} and Dy^{3+} for doping in zirconates have been investigated. There are many methods of synthesize phosphor like combustion, solid state reaction, hydrothermal and sol gel method [5]. In present paper we report the synthesis of $\text{CaZrO}_3:\text{Eu}^{3+}$ phosphors by modified solid state reaction

technique. The photoluminescent properties of $\text{CaZrO}_3:\text{Eu}^{3+}$ phosphors as a function of different doping concentrations were investigated.

II. EXPERIMENTAL

$\text{CaZrO}_3:\text{Eu}^{3+}$ phosphors with various concentrations of europium (0.1–1.5 mol%) were synthesized using the modified solid-state reaction technique. CaCO_3 , ZrO_2 and Eu_2O_3 were used as starting raw materials and taken in stoichiometric amounts to prepare the $\text{CaZrO}_3:\text{Eu}^{3+}$ phosphors. A mixture of these compounds was ground together using an agate pestle and mortar for 45 min to obtain the best homogeneity and reactivity in the powder. After being ground thoroughly, the powder was placed in an aluminium crucible and fired in a muffle furnace at 1300 °C for 2 h [16-25] in ambient air. The samples were characterized by X-ray diffraction (XRD) and. XRD measurements carried out using Bruker D8 Advanced X-ray Diffractometer with $\text{CuK}\alpha$ (wavelength $\lambda = 0.154\text{nm}$) radiation to analyse the crystalline structure and crystallite size of the phosphor powder. The crystallite size was calculated using the well-known Scherer formula. The PL excitation and emission spectra were recorded using SHIMADZU 5301R spectrophotofluorometer at room temperature [1-15].

III. CHARACTERIZATION

X-ray Diffraction (XRD)

The XRD pattern of $\text{CaZrO}_3:\text{Eu}^{3+}$ phosphors for doping concentrations of 1 mol% synthesized by solid-state reaction technique is shown in Figure 1. CaZrO_3 has an orthorhombic perovskite type structure. Crystallite size was computed from the full-width half-maxima (FWHM) of the all peaks of XRD pattern of sample using the well known Scherer's formula [26-30] which is given by:

$$D = 0.9 \lambda / \beta \cos \theta$$

Where, D is the average crystallite size perpendicular to the reflecting planes, $\lambda = 0.154\text{nm}$ is the wavelength of the X-ray, θ is the angle of diffraction and β represents the FWHM of the diffraction peak. Table 1 summarizes the angle of diffraction, FWHM, d-spacing and crystallite size of prepared $\text{CaZrO}_3:\text{Eu}^{3+}$. From Table 1 it is can be seen that crystallite size decreases as the FWHM of the peak increases. The crystallite size for the intense peak in the XRD pattern of the prepared phosphor is:

$$D = 0.9 \times 0.154 / 0.0042 \times \cos 15.86^\circ = 35 \text{ nm.}$$

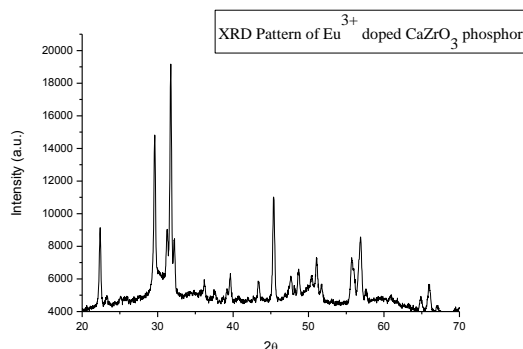


Fig. 1. Example of a figure caption.

Table I. Summarization Of Fwhm, Crystallite Size Bragg Angle And D-Spacing

S. No.	Summarization Of Fwhm, Crystallite Size Bragg Angle And D-Spacing		
	2 THETA 2θ ($^\circ$)	FWHM 2θ ($^\circ$)	Crystallite size (nm)
1	22.36	0.2263	37.39
2	29.61	0.2468	34.79
3	31.73	0.2463	35
4	45.09	0.2472	36.36
5	45.38	0.2392	37.61
6	48.69	0.2308	39.47
7	55.83	0.4963	18.93
8	56.84	0.4229	22.32

IV. PHOTOLUMINESCENCE (PL) STUDY

The excitation and emission spectra of $\text{CaZrO}_3:\text{Eu}^{3+}$ phosphors were shown in fig. 2 and fig. 3 respectively. The excitation spectrum shows a broad band region (220–300 nm) located at 271 nm attributed to charge transfer transition from 2p orbital of O^{2-} ions to 4f orbital of Eu^{3+} ions [7]. Upon 271 nm UV excitation the $\text{CaZrO}_3:\text{Eu}^{3+}$ shows photoluminescence emission peaks at 589 nm, 595 nm, 613 nm and 633 nm corresponding to Eu^{3+} transition ${}^5\text{D}_0\text{-}{}^7\text{F}_j$ (where $J = 0\text{-}3$). Among these all photoluminescence peaks the dominant red emission

at 613 nm corresponds to the transition ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ is sensitive to local symmetry while emission peak due to the magnetic dipole transition ${}^5\text{D}_0\text{-}{}^7\text{F}_1$ is partially allowed and insensitive to site symmetry of Eu^{3+} ions in sample [7]. However, the photoluminescence intensity of phosphor is found to increase with increase in doping concentration of Eu^{3+} ion and reaching a maximum for 1 mol% then decreases due to the occurring of concentration quenching.

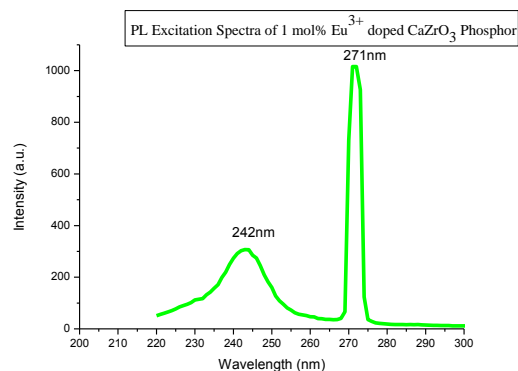


Fig. 2. PL excitation spectrum of $\text{CaZrO}_3:\text{Eu}^{3+}$ (1 mol%)

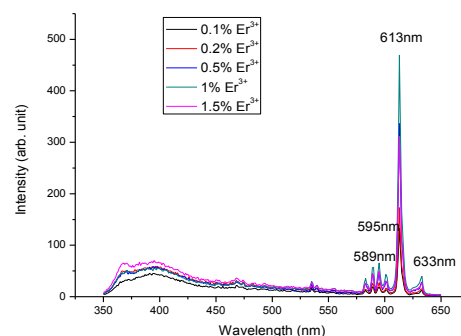


Fig. 3. Emission spectra of $\text{CaZrO}_3:\text{Eu}^{3+}$ phosphors with different concentration of Eu^{3+} ion.

VI. CONCLUSION

$\text{CaZrO}_3:\text{Eu}^{3+}$ were success fully prepared by solid state reaction technique. Upon 271 nm excitation the phosphor shows an intense photoluminescence emission peak at 613 nm due to the electric dipole (ED) transition ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ of Eu^{3+} ions and three other shoulder peaks at 589, 595 and 633 nm. From XRD pattern of sample the crystallite size for intense peak is found 35 nm. The photoluminescence result indicates this phosphor as a promising red light emitting phosphor and is useful in LEDs and other display devices.

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