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Blue light emitting UV excited photoluminescence in sonochemically synthesized ceria-zirconia nanocomposites

Divinah Manoharan[1]*, Aswaghosh L.[1], Victor Jaya N.[1]

[1]Department of Physics, Anna University, Chennai – 600025, India

Abstract: The present work brings forth an attempt to synthesize ceria-zirconia nano composites by sonochemical synthesis and the as-prepared nanopowder was heat treated at different calcination temperatures say 600°C, 700°C and 800°C. The structural and optical characteristics of the $Ce_{0.5}Zr_{0.5}O_2$ nanocomposites were studied. Phase segregation is observed due to formation of dual phase binary oxide system. Zirconia is stabilized to tetragonal phase forming tetragonally stabilized zirconia polycrystals (TZP) whereas ceria is in cubic phase. The crystallite size and crystallinity of the nanocomposites increases with increasing calcination temperature. The average crystallite size of ZrO_2 and CeO_2 are in the range 7-10 nm and 11-57 nm respectively in the nanocomposite. The photonic band gap energy was determined to be 5.08 eV from the Kubelka-Munk plot using UV Diffuse Reflectance Spectroscopy. The $Ce_{0.5}Zr_{0.5}O_2$ nanocomposite exhibits photoluminescence at room temperature with a broad emission in the blue region of the visible spectrum.
Keywords: Blue light emitting, UV excited photoluminescence, sonochemically synthesized ceria-zirconia nanocomposites.

Introduction

Nanoscale phosphors are likely to be more advantageous and beneficial than micron-sized phosphors, because the nanomaterials often show significant differences in the physical and chemical properties compared to the bulk. These inimitable properties are associated to the large number of surface atoms. Obviously, the quantum effects due to the high surface to volume ratio are expected to improve the luminescence characteristics[1]. This has presently besought advanced research in new inorganic nano-phosphor materials for new lighting devices. In recent years, inorganic oxide nanophosphors have gained much attention and are considered as the most potential candidate material for wide application in optical communication fields, fluorescent lamps, solid-state lasers, lighting and displays. Owing to the importance in optical applications, the studies on luminescence properties in inorganic nanocomposites have gained much interest in the past decade. Materials science research has provoked identification of new materials with shorter wavelength light emitting property for application in short-wavelength lasers which play important roles in laser printing and information storage. This is because of the fact that shorter the wavelength of the laser, the higher the information storage density of the compact disc[2]. Furthermore, it is suggested that the luminescence properties are dependent on the size, crystallinity and morphology of the nanoparticles which in turn is dependent on the synthesis procedure and reaction conditions[3,4,5,6].

Experimental

The ceria-zirconia nanocomposite was synthesized by the sonochemical method reported elsewhere6 using the precursor salts, AR grade Zirconium oxychloride (Himedia) and Cerium nitrate (Himedia) in the molar ratio Zr:Ce::1:1 The synthesized powders were calcined at 600˚C, 700˚C and 800˚C for 2 h.

Results and Discussion

The identification of phases in the synthesized ceria-zirconia powder samples was carried out by X-ray powder diffraction studies using Cu Kα radiation (1.54 Å), and comparing the interplanar distances and intensity values with those of the corresponding standard peaks using JCPDS files. The crystallite size of the nanomaterials was evaluated from X-ray powder diffraction data using Scherrer formula[7] for the most intense peak (111) in the case of ceria and (101) in the case of zirconia using the equation, $\boldsymbol{D = k\lambda / (\beta \cos \theta)}$ where *D* is the crystallite size; k = 0.89, a correction factor to account for particle shape; β is the full width at half maximum (*FWHM*) of the most intense diffraction plane; λ is the wavelength of Cu target = 1.54 Å; and θ is the Bragg angle.

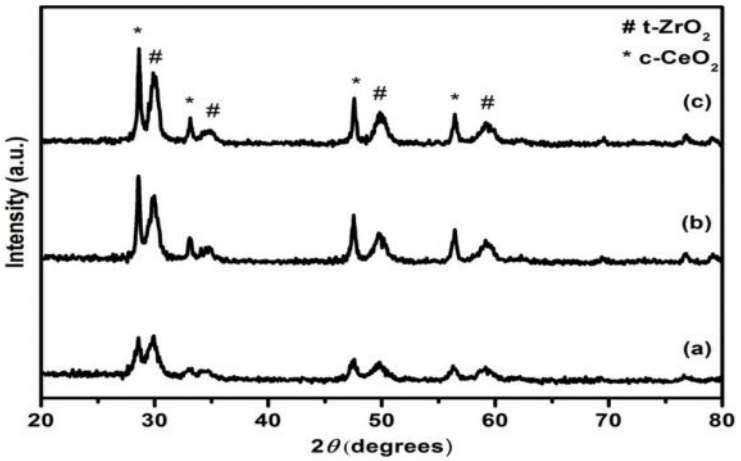

Figure 1. XRD of $Zr_{0.5}Ce_{0.5}O_2$ nanocomposite

Phase segregation is observed due to formation of dual phase binary oxide system. The ceria and zirconia peak are marked separately in Figure 1. In the dual phase $Zr_{0.5}Ce_{0.5}O_2$ nanocomposite, the ceria peaks correspond to the cubic phase and zirconia peaks correspond to the tetragonal phase. It may be noted that the crystallinity of ceria is higher than zirconia in $Zr_{0.5}Ce_{0.5}O_2$ as inferred from the peak intensity. The crystallite size and crystallinity of the nanocomposites increases with increasing calcination temperature. As the crystallite size decreases strain and dislocation density increases and vice versa.

Table 1. Lattice parameters of $Zr_{0.5}Ce_{0.5}O_2$ nanocomposite

Sample	Calcination Temperature ° C	Phase	Mean Crystallite size D nm	Strain x 10^{-4}	Dislocation density x 10^{15} lines/m^2
$Zr_{0.5}Ce_{0.5}O_2$	600	t-ZrO_2	7.17	63.19	20.95
		c-CeO_2	11.45	37.65	10.08
	700	t-ZrO_2	9.26	50.29	13.18
		c-CeO_2	30.09	14.40	1.29
	800	t-ZrO_2	9.53	46.87	12.08
		c-CeO_2	56.47	9.26	0.61

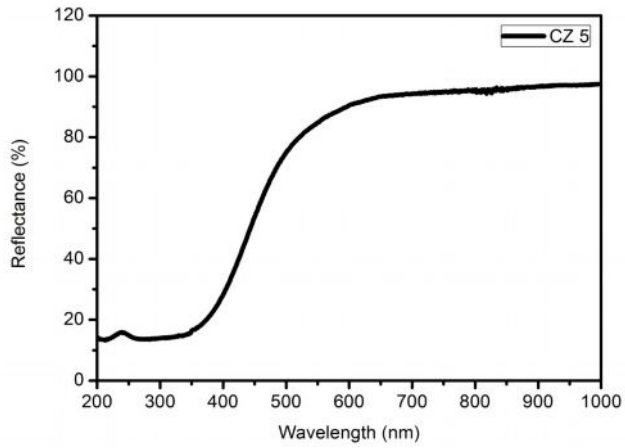

Figure 2. Diffuse Reflectance spectrum of $Zr_{0.5}Ce_{0.5}O_2$ nanocomposite

Figure 2 shows the diffuse reflectance spectrum of ceria-zirconia dual phase nanocomposite. It is evident that the spectra of the mixed binary oxides are almost similar to pure ceria nanopowders. Pure ceria and ceria containing systems show excellent transparency in visible region and high absorption in the UV region compared to pure ZrO_2. The characteristic wavelength components are nearly around 440 nm (CeO_2) and 240 nm (ZrO_2). The energy band gap is determined from UV Diffuse reflectance data by transforming it into a function of reflectance as proposed by Kubelka-Munk. The Kubelka-Munk plot for determining band gap energy is shown is Figure 3 for the ceria-zirconia nanocomposite. KM plot is plotted with the n^{th} power of product of function of reflectance F(R) and photonic energy ($E_g = h\upsilon$) against the photonic energy. Considering as a direct band gap semiconductor the value of n is taken as 2 for allowed transitions[8]. The energy band gap is found out by extrapolating the linear portion of the graph to the X-axis. The energy band gap was determined to be 5.08 eV.

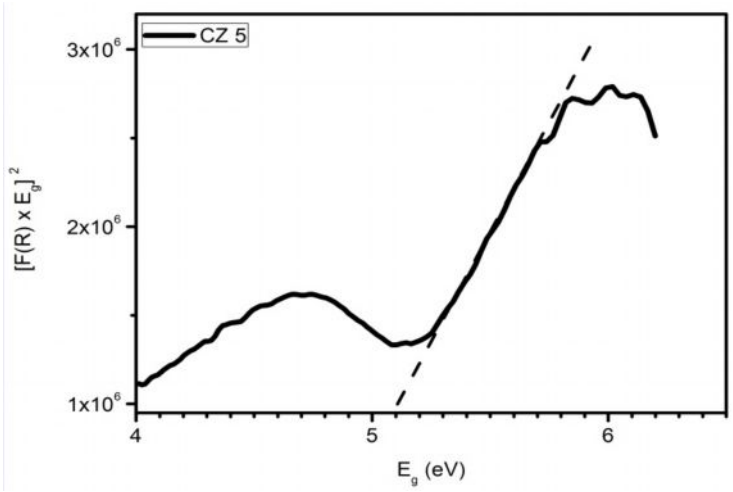

Figure 3. Kubelka-Munk plot of $Zr_{0.5}Ce_{0.5}O_2$ nanocomposite

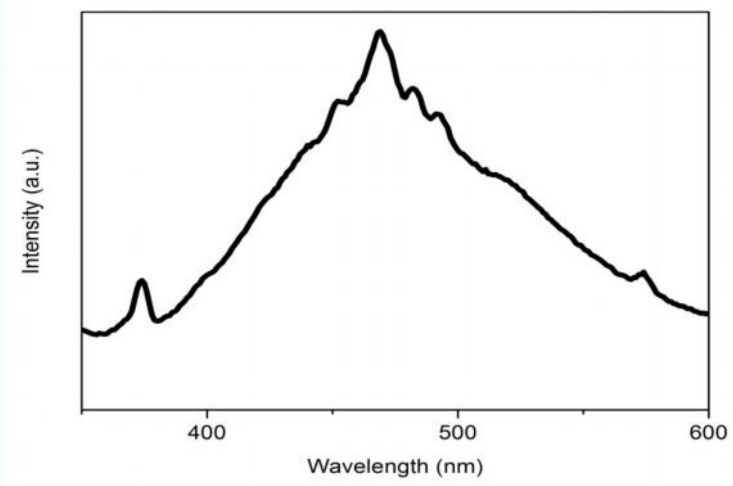

Figure 4. Photoluminescence spectrum of $Zr_{0.5}Ce_{0.5}O_2$ nanocomposite

The $Zr_{0.5}Ce_{0.5}O_2$ nanocomposite show two prominent peaks in the UV and blue region of the electro-magnetic spectrum with emission wavelength centered around 374 nm and 470 nm corresponding to excitation at 325 nm as shown in Figure 4. Varying the excitation wavelength from 270 to 325 nm does not show much difference in emission spectra except little intensity variation.The intense zirconia emission peak at 374 nm in the samples calcined in air can be due to the ionized oxygen vacancies (F+ and F− centers) from the conduction band[9]. Here UV emission can arise as a result of the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy. It is reported that there is formation of surface traps in the material leading to electron transitions, even with a small amount of excitation energy[10]. The PL emission band observed at 470 nm might be due to the transitions from the surface trap states in the conduction band to lower energy levels close to the valance band. This is in agreement with the results reported in the literature[10, 11]. The broad band may be due to the inhomogeneous broadening from a distribution of surface or defect states because of the narrow particle size distribution[12].

Conclusion

Nanostructured dual phase ceria-zirconia nanocomposite was successfully prepared by sonochemical method. The increase in crystallite size of c-CeO_2 phase with calcination temperature is almost linear. There is no much increase in crystallite size of t-ZrO_2 phase with calcination temperature as grain growth is hindered by the ceria presence. As the crystallite size decreases strain and dislocation density increases and vice versa. Compositional heterogeneity is observed in all calcined samples. The nanocomposite exhibits a wide band gap of 5.08 eV. Upon 325 nm excitation, the materials exhibit emission in the UV and blue region of the electromagnetic spectrum.

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