JSR Publications

Available Online

J. Sci. Res. **5** (1), 1-11 (2013)

JOURNAL OF SCIENTIFIC RESEARCH

www.banglajol.info/index.php/JSR

Synthesis and Luminescent Properties of Strontium Cerium Oxide Phosphors Doped with Rare Earths

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Received 22 June 2012, accepted in final revised form 21 December 2012

Abstract

In this paper we report the synthesis and luminescent properties of Sr_2CeO_4 doped with rare earths (0.5% concentration of La, Eu and Dy ions) are reported. The powder samples of rare earths doped strontium cerium oxide (Sr_2CeO_4: La, Eu and Dy ions) was synthesized by a standard solid state reaction method in air at 1200^0C. These samples were characterized by X-ray diffraction, scanning electron microscope (SEM) and photoluminescence (PL) techniques, particle size analysis**.** The XRD data revealed that the structure of the Sr_2CeO_4 as orthorhombic and the calculated average crystallite size is ~10nm. Scanning electron microscopy revealed that the Sr_2CeO_4 phosphor particles had non-spherical shape and the irregular shaped particles are highly agglomerated. PL excitation and emission spectra of Sr_2CeO_4 doped with rare earths are recorded at room temperature. The CIE coordinates depicted on 1931 chart of Eu (0.5%) doped Sr_2CeO_4 shown that the emission colour varies from blue to white. This phosphor has a good potential for application in white light LEDs.

Keywords: Inorganic compounds; Solid-state reaction; X-ray diffraction; Photoluminescence; CIE; LED; SEM; Particle size analysis.

doi: http://dx.doi.org/10.3329/jsr.v5i1.10965 J. Sci. Res. **5** (1), 1-11 (2013)

1. Introduction

Recently various phosphor materials have been actively investigated to improve their luminescent properties and to meet the development of different display and luminescence devices. Inorganic compounds doped with rare earth ions form an important class of phosphors as they possess a few interesting characteristics such as excellent chemical stability, high luminescence efficiency, and flexible emission colors with different

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activators[1,2]. Rare earth ions doped phosphors have been used in varied fields based on their electronic and optical characters arising from their 4f electrons. Among the rare earth elements, europium is a special element as dopant, because it exhibits the property of valence fluctuation, i.e., the valence state is divalent or trivalent [3]. In 1998, a blue phosphor compound, Sr_2CeO_4 possessing one-dimensional chain of edge-sharing CeO_6 octahedra, was identified by Danielson and his co-workers with combinatorial chemistry [4]. It exhibited a blue–white emission band that peaks at 485nm at 254nm excitation and the luminescence was suggested to originate from a ligand-to-metal Ce^{4+} charge transfer. This material was analyzed by Rietveld structural refinement, and the luminescent phase was characterized as Sr_2CeO_4 with orthorhombic structure containing one-dimensional chains of edge-sharing CeO_6 octahedra that are linked together by Sr^{2+} ions. This material exhibits excellent luminescent property and maximum emission band around 485nm, whose intensity changes depending on the employed heat treatment. Some impurity phases such as $SrCO_3$, $SrCeO_3$ and CeO_2 were also detected [5-7]. Some authors [8-10] have assigned the luminescence of the Sr_2CeO_4 material to the charge transfer between Ce^{4+} and O^{2-} because the position and shape of the absorption band and the emission band width are characteristic for this type of transition. Some authors have observed that the strong luminescence of Sr_2CeO_4 makes it potentially applicable as blue phosphor material in low pressure mercury vapor lamps [11] and FED [12, 13] as well as other types of luminescence devices [14]. Following this observation, several studies about this luminescent material have been conducted, and some synthetic routes have been developed for the preparation of Sr_2CeO_4 powders. Here we report the preparation and characterization of blue phosphor Sr_2CeO_4 doped with rare earths (0.5 mol% concentration only) La, Eu and Dy ions via standard solid state reaction method in air.

2. Experimental Method

Strontium nitrate [$Sr(NO_3)_2$], Cerium oxide (CeO_2), Lanthanum oxide (La_2O_3), Europium oxide (Eu_2O_3) and Dysprosium oxide (Dy_2O_3) were used as starting materials to prepare Sr_2CeO_4 and rare earth doped phosphors.Every starting material was of greater than 99.9% purity. All the starting materials were weighed according to the stoichiometric ratio. Sr_2CeO_4 phosphor and other samples of Sr_2CeO_4 doped with rare earths (0.5% concentration of La, Eu and Dy ions) were prepared via solid state reaction method (SSR). A stoichiometric mixture of these staring powders was thoroughly homogenized in an agent mortar for 1hr and then put into an alumina crucible. The homogenized mixture was heated in air at 12000C for 3h in a muffle furnace with a heating rate of 50C/min. Finally the samples were allowed to cool down to room temperature for about 20h [15,16]. All the samples were again ground into fine powder using agate mortar and pestle about an hour.

Several complementary methods were used to characterize the prepared phosphors. To identify the crystal phase, X-ray diffraction (XRD) analysis was carried out with a powder X-ray diffractometer (Indus beam line-II (ADXRD BL-12),RRCAT, Indore, India), Photoluminescence (PL) emission spectra were measured by a Spectrofluorophotometer

(SHIMADZU, RF-5301 PC using Xenon lamp as excitation source. The morphologies of particles were investigated by using Scanning electron microscope (PHILIPS XL 30 CP). The particle size was measured by using Laser based particle size analysis (Malvern Instrument Ltd (U.K), The CIE (Commission International de l'Eclairage) co-ordinates were calculated by the Spectrophotometric method using the spectral energy distribution.

3. Results and Discussion

3.1. *X-ray diffractometry*

The typical XRD pattern of Sr_2CeO_4 is shown in Fig. 1 and all the diffraction peaks can be well indexed based on the ICDD No.89-5546 [17]. All the prepared samples are characterized to be single phase Sr_2CeO_4 of orthorhombic structure. Except this, no other phase exists in the XRD spectra, indicating that the as-prepared Sr_2CeO_4 phosphor is single phase.XRD study confirms the single phase Sr_2CeO_4 with the orthorhombic structure.The calculated crystallite sizes using Scherer's formula $D = K.\lambda/\beta \cos\theta$, where k the constant (0.94), λ the wavelength of the X-ray (0.895 Å), β the full-width at half maxima (FWHM), θ the Bragg angle of the XRD is around ~9nm (un-doped), La doped Sr_2CeO_4 is around ~ 11nm, Eu and Dy doped Sr_2CeO_4 is around ~ 10nm. No change in the crystal structure on doping rare earths in host material.

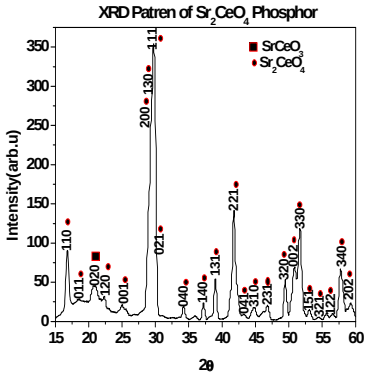

Fig. 1. XRD Pattern of Sr_2CeO_4 heated at 1200°C.

3.2. *SEM analysis*

Fig. 2 shows the SEM photograph of Sr_2CeO_4 phosphor particles. The Sr_2CeO_4 phosphor particles had non-spherical shape and the irregular shaped particles are highly agglomerated. Fig. 3 is the typical SEM photograph of the synthesized Sr_2CeO_4: Dy phosphor. The multi layered structure was observed. The prominent characteristic of Sr_2CeO_4: Dy crystal growth is a serious anisotropic growth rate. The growth rate along the

ab plane is ~5 times larger than that along *c*-axis. This phenomenon can be easily understood from the periodic bond chain (PBC) theory. The fundamental building units are in the orthorhombic structure. Fig. 4 shows the SEM photograph of Sr_2CeO_4: Eu (0.5%) and it exhibits the grains like irregular sizes and shapes which are highly agglomerated.

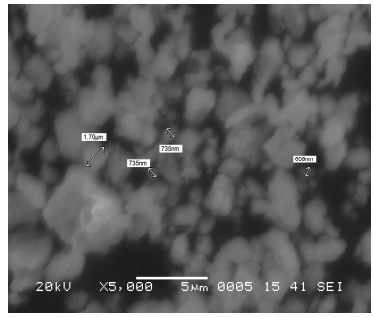

Fig. 2. SEM photograph of Sr_2CeO_4 prepared from solid state reaction method.

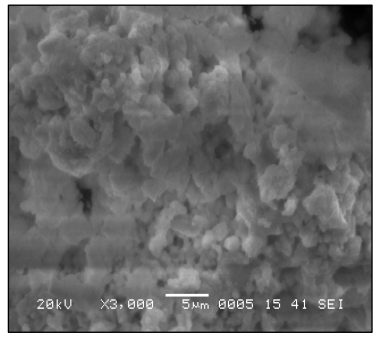

Fig. 3. SEM photograph of Sr_2CeO_4 doped with Dy (0.5%).

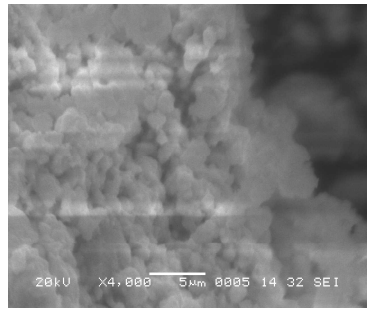

Fig. 4. SEM photograph of Sr_2CeO_4 doped with Eu (0.5%).

3.3. *Photoluminescence study*

Fig. 5 shows the PL excitation and emission spectra of Sr_2CeO_4 particles recorded at room temperature. The emission spectra of Sr_2CeO_4 excited at 250nm show a broad band in the region of 350-650nm with a peak at 470nm. The CT band can be assigned to the f→t_1g transitions of Ce^{4+} ions. The emission spectra of Sr_2CeO_4 observed with 260nm excitation is similar to that observed with 250nm excitation. The only difference is the emission intensity under 260nm excitation is higher than 250nm. The emission at 470nm is considered as a potential blue emitting phosphor. The excitation spectrum recorded for Sr_2CeO_4 displays a broad band and peaks at 250nm and 260nm which is attributed to the Ce^{4+}–O distances in the lattice.

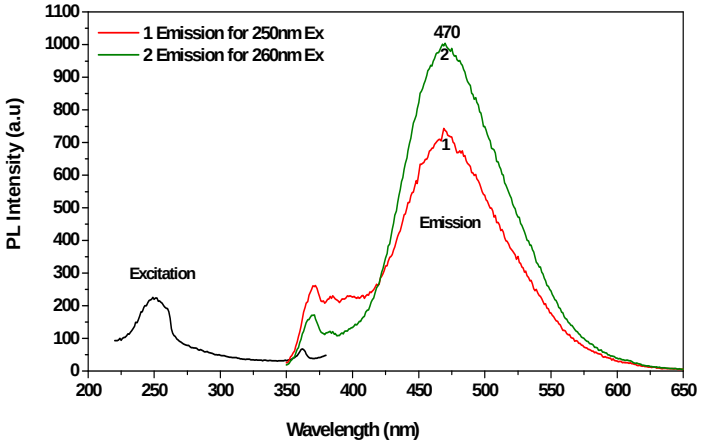

Fig. 5. Excitation and emission spectra of Sr_2CeO_4 phosphor.

Fig. 6 shows the PL excitation and emission spectra of La (0.5%) doped Sr_2CeO_4 phosphor. The sample exhibit the emission peak at 470nm upon the excitation at 250nm and 260nm.The PL emission intensity at 260nm excitation is 40% more than that of 250nm excitation. Due to the Ce sites were replaced by La ions, the charge transfer emission intensity decreased by 60% than that of Sr_2CeO_4 phosphor. Fig. 7 shows the PL excitation and emission spectra of Dy (0.5%) doped Sr_2CeO_4 phosphor. The sample exhibit the peaks at 469nm and 575nm upon the excitation at 250nm and 260nm.These peaks are assigned to the $^4F_{9/2}$–$^6H_{15/2}$ and $^4F_{9/2}$–$^6H_{13/2}$ transitions, respectively. Dy is well resolved in the host phosphor at 575nm in yellow region. The PL emission intensity at 260nm excitation is sharper than that of 250nm excitation.

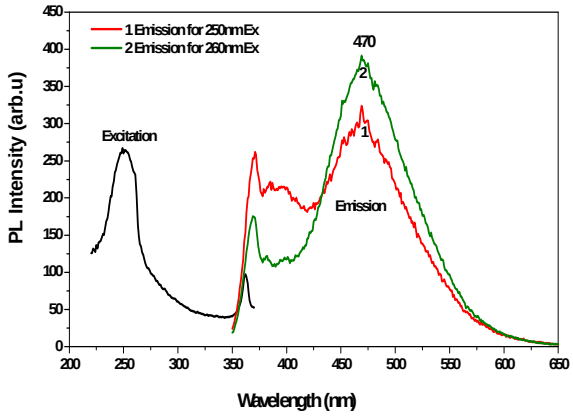

Fig. 6. Excitation and emission spectra of La (0.5%) doped Sr_2CeO_4 phosphor.

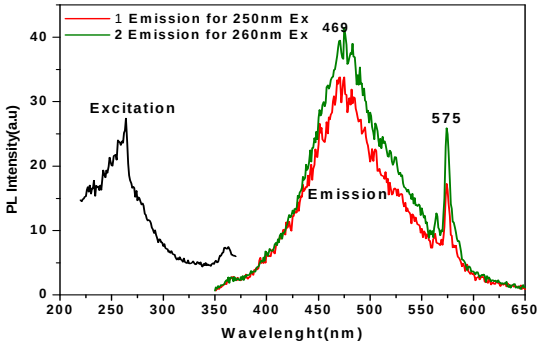

Fig. 7. Excitation and emission spectra of Dy (0.5%) doped Sr_2CeO_4 phosphor.

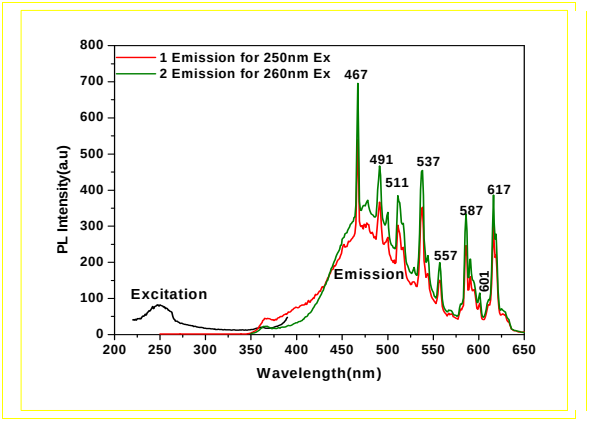

Fig. 8. Excitation and emission spectra of Eu (0.5%) doped Sr_2CeO_4 phosphor.

Fig. 8 shows the PL excitation and emission spectra of Eu (0.5%) doped Sr_2CeO_4 phosphor. The sample exhibit the emission peaks at 467, 491, 511, 537, 557, 587,601 and 617nm upon the excitation at 250nm and 260nm. These peaks are assigned to the $^5D_2 \rightarrow {}^7F_{1,\ 2,\ 3}$, $^5D_1 \rightarrow {}^7F_{1,\ 2,}$ and also from $^5D_0 \rightarrow {}^7F_{\ 1,\ 2}$ transitions respectively. The peak around 610 - 620nm is due to the electric dipole transition of $^5D_0 \rightarrow {}^7F_2$, which is induced by the lack of inversion symmetry at the Eu^{3+} sites. It is well known that the $^5D_0 \rightarrow {}^7F_2$ / $^5D_0 \rightarrow {}^7F_1$ intensity ratio is a good measure of the site symmetry of rare-earth ions in a doped material. The observed PL emission of Eu doped Sr_2CeO_4 may be due to crystal field effect and unusual luminescent property due to low vibration energy of Sr_2CeO_4 host lattice and different energy transfer process from host to dopant. The high efficiency energy transfer allows us to expect that the Sr_2CeO_4 crystal structure could form the base for phosphors with different spectral emissions [18-21]. The Eu (0.5%) doped Sr_2CeO_4 phosphor displays all the colours led to white light emission. Therefore this phosphor can be good has a good potential for application in white light LED's.

3.4. *Particle size analysis*

The particle size distribution histogram of Sr_2CeO_4 and La, Eu, Dy doped Sr_2CeO_4 phosphors shown in Figs. 9 to 12. The particle size of prepared phosphor specimen was measured by using laser based system, Malvern Instrument, U.K. The mean diameter of the particle size of Sr_2CeO_4 phosphor specimen is 26μm, La doped Sr_2CeO_4 specimen is 18.31μm, Eu doped Sr_2CeO_4 specimen is 17μm and Dy doped Sr_2CeO_4 specimen is 32μm. The average particle diameter of europium doped Sr_2CeO_4 phosphor is 17μm and the crystallite size is around~ 10nm.

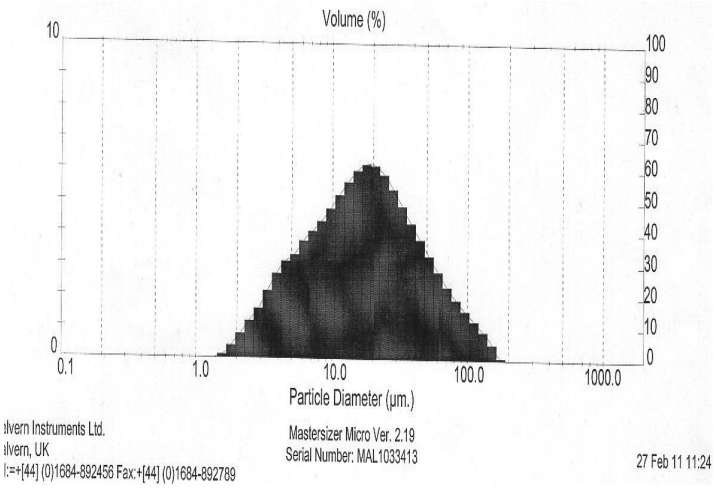

Fig. 9. Particle size distribution histogram of Sr_2CeO_4.

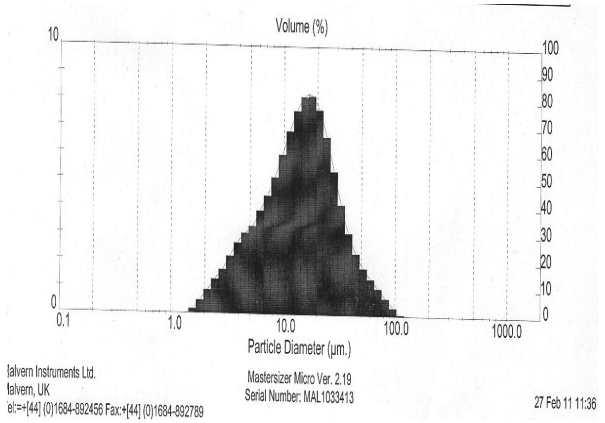

Fig. 10. Particle size distribution histogram of La doped Sr_2CeO_4.

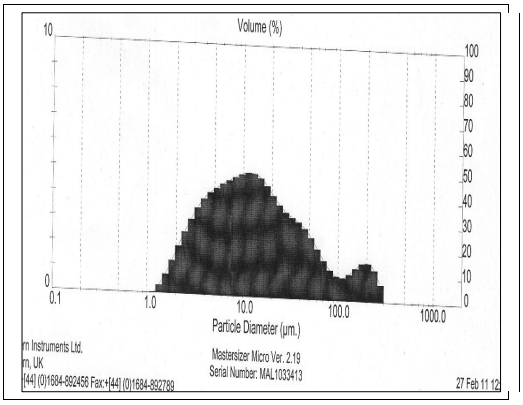

Fig. 11. Particle size distribution histogram Dy doped Sr_2CeO_4

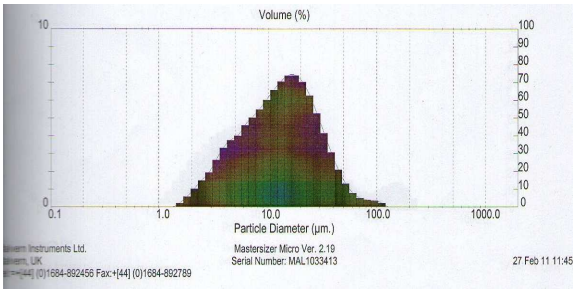

Fig. 12. Particle size distribution histogram of Eu doped Sr_2CeO_4.

3.5. *CIE coordinates*

Based on the emission spectra, it was possible to see the color of the emission of each sample in the CIE diagrams 1931. Fig. 13 shows the CIE diagram 1931. The CIE co-ordinates were calculated by the spectrophotometric method using the spectral energy distribution of Sr_2CeO_4 phosphor. The CIE chromaticity index for the Sr_2CeO_4 phosphor (A) are x = 0.16 and y = 0.18, which is better than that reported by Danielson (x=0.20 and y=0.30) [22] and Jiang (x=0.19 and y=0.26) [23], CIE chromaticity index for La (0.5%) doped Sr_2CeO_4 phosphor (B) are x=0.16 and y=0.19, for Dy (0.5%) doped Sr_2CeO_4 phosphor (C) are x=0.28 and y=0.31 and Eu (0.5%) doped Sr_2CeO_4 phosphor (D) are x=0.32 and y=0.33.The CIE coordinates depicted on 1931 chart reveals that the emission colour varies from blue to white with Eu (0.5%) doped Sr_2CeO_4.

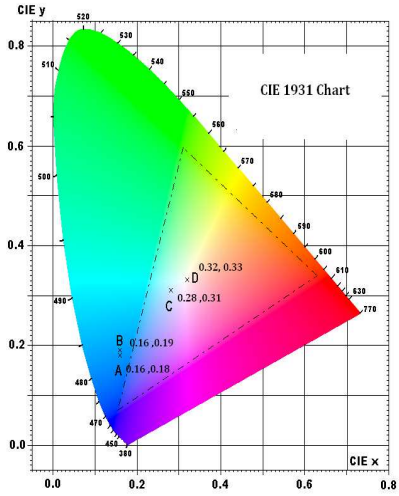

Fig.13. CIE coordinates depicted on 1931 chart where (A) Sr_2CeO_4, (B) La doped Sr_2CeO_4, (C) Dy doped Sr_2CeO_4, (D) Eu doped Sr_2CeO_4.

4. Conclusions

Sr_2CeO_4 phosphor sample is prepared by a standard solid state reaction method in air at 1200^0C. The XRD study confirms the structure of the system as orthorhombic and single phase was obtained due to the calcination temperature. The calculated average crystallite size using Scherer's formula is ~10nm. The excitation spectrum recorded for Sr_2CeO_4 displays a broad band and peaks at 250nm and 260nm which is attributed to the Ce^{4+}–O distances in the lattice The CIE coordinates depicted on 1931 chart reveals that the Sr_2CeO_4 and La doped phosphors exhibit blue colour, Dy doped phosphor exhibit Blue Yellow (cyan) colour and Eu doped Sr_2CeO_4 phosphor displays all colours. Therefore

Sr_2CeO_4 doped with rare earths have good potential applications in lamps, display devices and white light LED.

Acknowledgements

This work was supported by University Grant Commission (UGC), New Delhi, India, under Faculty Development Programme (FDP).

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