



Preparation and Investigation on New Generation Peaks of Eu Doped Sr_2CeO_4 Phosphor

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This paper reported that the preparation and Investigation on new generation peaks of (585&611nm) Eu doped Sr_2CeO_4 phosphor were prepared by standard solid state reaction method. The obtained phosphors were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) and The Commission International de l'Eclairage co-ordinates (CIE). XRD reveals that except Sr_2CeO_4 , no other phase exists in the XRD spectra. SEM image is exhibits the grains like morphology with different sizes and shapes. PL emission spectrum of un-doped Sr_2CeO_4 phosphor shows broad emission from 350 – 650nm. This broad band is due to $f \rightarrow t_{1g}$ transition of Ce^{4+} . The emission spectra of Sr_2CeO_4 phosphor doped with Eu(0.5%) with citric acid($\text{C}_6\text{H}_8\text{O}_7$) as flux shows peaks at 467, 491, 512, 537,557, 585, 590, 601, 611 and 616nm under 254 & 270nm excitation. The CIE co-ordinates were calculated by the Spectrophotometric method using the spectral energy distribution of un-doped Sr_2CeO_4 and Eu doped Sr_2CeO_4 [(A) $x = 0.158$ and $y = 0.192$, (B) $x = 0.313$ and $y = 0.325$, (C) are $x=0.469$ and $y=0.295$].

Keywords— Photoluminescence, Solid state reaction method, crystallite, phosphor, CIE, SEM, XRD analysis.

INTRODUCTION

There is growing interest in the development of new full color emitting phosphor materials that combine thermal and chemical stability in air with high emission quantum yield at room-temperature [1]. The search for blue phosphor emitters has been increasing due to their applicability in many fields, such as cathode ray tubes (CRTs), projection televisions (PTVs), fluorescent tubes, X-ray detectors and field emission displays (FED). It is well known that the phosphors for field emission displays (FEDs) are required to have a high efficiency at low voltages, a high resistance to current saturation, a long service time and equal or better chromaticity than cathode ray tube (CRT) phosphors. Very satisfactory red and green commercial materials are being produced, but comparable materials for the blue emission are still lacking and are under development for practical applications [2]. Even in the paper industry, fluorescent dyes that absorb UV and emit in blue color are widely used as organic optical brightening agents (OBA) and new inorganic ones have been under investigation. Concerning many of these applications, such as FED and OBA, the availability of systems consisting of uniform particles in size and shape is also an essential prerequisite for improved performance, and new synthetic routes are been developed in order to

reach these systems. Most recently Danielson et al. [3] invented a new blue luminescent material, Sr_2CeO_4 , using combinatorial techniques. Not only that the same phosphor was prepared by different routes, such as conventional solid state reaction, chemical co-precipitation, microwave calcinations, pulsed laser deposition, polymeric precursors and ultrasonic spray pyrolysis methods [4-10]. Sr_2CeO_4 was found to exhibit efficient blue-white luminescence under excitation with UV light, cathode rays or X-rays. The excited-state lifetime, electron spin resonance, magnetic susceptibility and structural data suggest that luminescence of Sr_2CeO_4 originates from a ligand-to-metal Ce^{4+} charge-transfer (CT).

EXPERIMENTAL

Analytical grade Strontium nitrate [$\text{Sr}(\text{NO}_3)_2$], Cerium oxide (CeO_2), Europium oxide (Eu_2O_3) of assay 99.9% were used as starting materials. All the phosphor samples are prepared via solid state reaction method. First we prepared un-doped Sr_2CeO_4 phosphor by weighing inorganic salts, Strontium nitrate [$\text{Sr}(\text{NO}_3)_2$], Cerium oxide (CeO_2) in 2:1 molar ratio. Then mixing and ground into fine powder using agate mortar and pestle about an hour. The sample was fired at 1200 °C for 3 hours in a muffle furnace with a heating rate of 5°C/min by keeping in an alumina crucible closed with lid [7, 12]. In the same way Eu (0.5 mol %) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) at 10 wt % as flux were added in the Sr_2CeO_4 phosphor.

The structure and the particle size were determined by means of X-ray diffraction using SYNCHROTRON BEAM LINE-II, λ of beam line =0.895Å. The microstructures of the prepared powders were observed using (SEM) a scanning electron microscope (PHILIPS XL 30 CP) to examine the morphology of the samples at 20KV. Luminescence spectra were measured at room temperature by SHIMADZU, RF-5301 PC model Spectrofluorophotometer (Xenon lamp as excitation source) excitation and emission slit width=1.5mm.

RESULTS AND DISCUSSION

The structure and the crystallite size were determined by means of X-ray diffraction technique. Fig.1 is the XRD pattern of Eu doped Sr_2CeO_4 phosphor and was indexed to crystallize in the orthorhombic phase corresponding to JCPDS Card no - 89-5546 [13]. In addition, the refined crystallographic unit cell parameters were obtained and are listed in table 1. These values are compared with L. Li et al. [14] and R. Seema et.al. [15]. The powder derived from the solid state reaction method was heated at 1200°C in air for 3hrs shows the starting materials disappeared completely and Sr_2CeO_4 was formed as the predominant product with a tiny amount of SrCeO_3 . Except this, no other phase exists in the XRD spectra, indicating the formation of the final product. The calculated average crystallite size using Scherer's formula ($t = K \cdot \lambda / \beta \cos\theta$) where 'k' the Scherer's constant (0.94), ' λ ' the wavelength of the X-ray (0.895 Å), ' β ' the full-width at half maxima (FWHM) and ' θ ' the Bragg angle, of un-doped Sr_2CeO_4 is around ~9nm, and Eu doped is ~10nm. The reduction in unit cell volume was observed compared with previous workers as shown in table 1. Therefore this confirms the formation of nano crystallite phosphor, via solid state method.

Figure-2 shows the SEM image of Sr_2CeO_4 : Eu (0.5%). SEM image is exhibits the grains like morphology with different sizes and shapes and are highly agglomerated.

Fig.3a shows PL excitation and emission spectrum of un-doped and Eu (0.5%) doped Sr_2CeO_4 phosphor. The un-doped sample shows broad emission (curve 2) from 350 – 650nm peaks at 470nm which is attributed to the energy transfer between the molecular orbital of the ligand and charge transfer state of

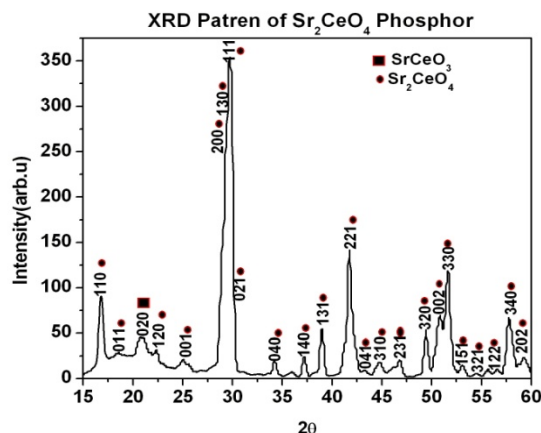
the Ce⁴⁺ ion. The emission band can be assigned to the f→t_{1g} transitions of Ce⁴⁺ ions. The excitation spectra were studied under 260 and 270nm, the observed emission peak was same but intensity is high for 270nm excitation. However our results were compared with the previous workers [16-21].

Table 1

Crystal name	a (Å)	b (Å)	c (Å)	Cell volume (Å ³)
JCPDS No. 89-5546[13]	6.119	10.350	3.597	227.79
Our sample	5.964	8.279	4.472	220.81
L.Li et al[14]	6.1153	10.3473	3.5957	227.52
R.Seema et al[15]	6.07	10.32	3.62	226.76

The Eu (0.5%) doped Sr₂CeO₄ phosphor without and with flux; under 270nm excitation (curve 3 & 4) shows peaks at 467, 491, 512, 537, 557, 585, 590, 601, 611 and 616nm with good intensity. Under 270nm excitation, the samples show same emission spectra with increase in the intensity by 60%. The observed peaks are from the transitions ⁵D₂→⁷F_{0, 2, 3}, ⁵D₁→⁷F_{1, 2} and also from ⁵D₀→⁷F_{1, 2}, respectively. The peak around 610-620nm is due to the electric dipole transition of ⁵D₀→⁷F₂, which is induced by the lack of inversion symmetry at the Eu³⁺ sites. It is well known that the ⁵D₀→⁷F₂ / ⁵D₀→⁷F₁ intensity ratio is a good measure of the site symmetry of rare-earth ions in a doped material. This is because the hypersensitive transition ⁵D₀→⁷F₂ tends to be much more intense at a site with no inversion symmetry, while the magnetic dipole transition ⁵D₀→⁷F₁ is constant, regardless of the environment Ch. Atchyutha Rao et.al [22-25].

The result indicated the presence of energy transfer is taking place from Ce to Eu ion. It is also observed that broad emission from Ce ion is not completely quenched even when the dopant are added to the host material. This may be because of the low concentration of the dopant. It is concluded that may be at high concentrations of Eu (5-10%) in Sr₂CeO₄ phosphor one can get red color emission. When compared with the sample without flux, it is also observed that the citric acid added sample shows the enhancement of 611nm peak, increased by 50% hence we can conclude that the citric acid plays an important role.

Fig. 1: XRD Pattern of Eu doped Sr₂CeO₄

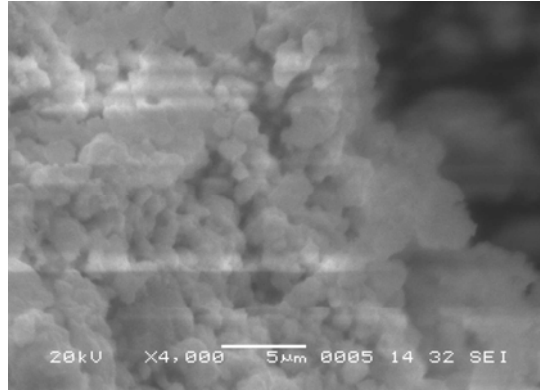


Fig. 2: SEM image of Sr₂CeO₄: Eu (0.5%)

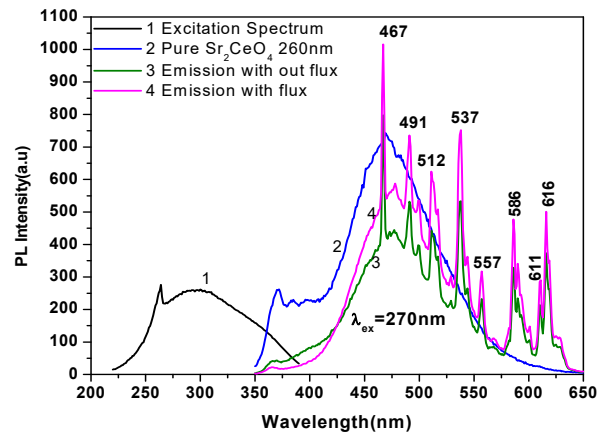


Fig. 3: (a) Shows excitation and emission spectrum of undoped Sr₂CeO₄ with and without fluxes

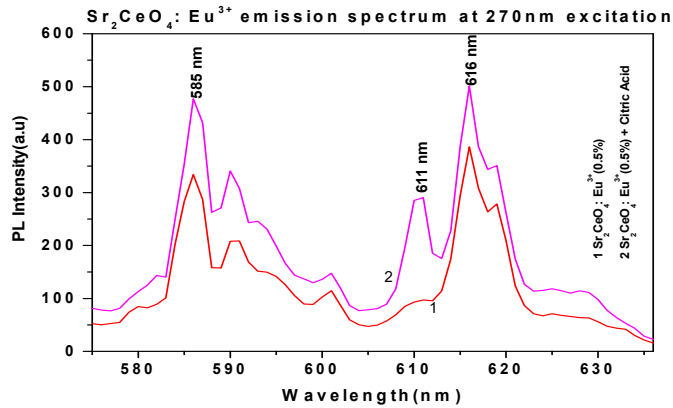


Fig. 3: (b) Shows emission spectrum of Eu doped Sr₂CeO₄ with and without fluxes range from 575-645nm

Table 1: Energy values of the corresponding transitions of Eu doped Sr₂CeO₄ phosphor

Wavelength (nm)	Transitions	Energy (eV)
467	⁵ D ₂ → ⁷ F ₀	2.657
491	⁵ D ₂ → ⁷ F ₂	2.528
512	⁵ D ₂ → ⁷ F ₃	2.429
537	⁵ D ₁ → ⁷ F ₁	2.307
557	⁵ D ₁ → ⁷ F ₂	2.228
585	⁵ D ₀ → ⁷ F ₁	2.118
611	⁵ D ₀ → ⁷ F ₂	2.031
616	⁵ D ₀ → ⁷ F ₂	2.015

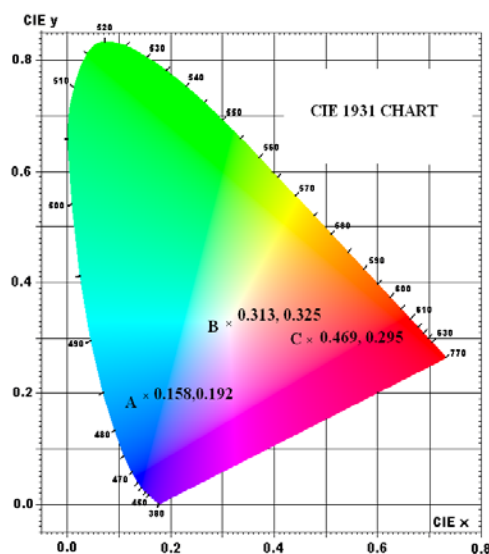


Fig. 4: CIE Coordinates of A) Undoped Sr₂CeO₄ B) Eu (0.5%) doped with citric acid as flux C) Eu (1.0%) doped with citric acid as flux

Fig.4 illustrates the CIE chromaticity diagram depicted on 1931 chart. . The CIE co-ordinates were calculated by the spectrophotometric method using the spectral energy distribution. The colour co-ordinates for the un-doped Sr₂CeO₄ sample (A) are x = 0.158 and y = 0.192, Eu(0.5%) doped Sr₂CeO₄ sample (B) are x=0.313 and y=0.325. Eu(1.0%) doped Sr₂CeO₄ sample (C) are x=0.469 and y=0.295. It is observed that the emission varies from blue to white and then to red with increasing of the Eu(1.0%) concentration.

CONCLUSIONS

The synthesis of phosphors Sr₂CeO₄ and Eu³⁺doped Sr₂CeO₄ with and with out flux via solid state reaction method and measured their fluorescence spectra is reported. XRD and SEM of the phosphors have shown that the average crystallite size of un-doped Sr₂CeO₄ is around~9nm, and Eu doped is ~10nm

and the phosphors exhibit the grains like morphology with different sizes and shapes of highly agglomerated. By studying the optical properties we found that the emission transition of 5D_0 - 7F_2 intensity was the strongest among the main lines and the emission from ${}^5D_{1,2}$ was also observed due to the low-energy vibration of the host lattice. Besides, the red emission 5D_0 - 7F_2 intensity was increased when the Eu ion concentration was increased from 0.01 to 1.0 mol%. From CIE study this single host phosphor emitting perfect white light. Therefore the application is as multicolor emitting fluorescence powder in many display devices, technological applications and in the fluorescent lamps.

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