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Archives of Physics Research, 2012, 3 (2):123-129
*(http://scholarsresearchlibrary.com/archive.html)*

ISSN : 0976-0970
CODEN (USA): APRRC7

# Luminescence characterization of $Sr_2CeO_4:La^{3+}$, $Eu^{3+}$ phosphor

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**ABSTRACT**

*The present paper reports on the synthesis and characterization of $Sr_2CeO_4$ doped with $La^{3+}$ and $Eu^{3+}$ rare earth ions with (0.5%) concentration. The phosphor samples were synthesized using the standard solid state reaction technique. Analytical grade inorganic salts like $Sr(NO_3)_2$, $CeO_2$, $La_2O_3$ and $Eu_2O_3$ were used as raw materials of assay 99.9% were weighed, mixed and ground in to fine powder using agate mortar and pestle. The samples were heated to 1200°C for 3 hours using muffle furnace with a heating rate of 5°C/min. All the samples were allowed to cool at room temperature in the same furnace. We have studied the effect of La: Eu co-dopant on the structural, morphological, and Photo luminescent properties of the samples using X-ray diffraction (XRD), SEM, PL, particle size analysis and CIE coordinates.*

**Keywords**: *photoluminescence, solid state reaction method, light emitting diodes, Phosphor, nano-crystallite particles*

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## 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. 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). 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 [**1, 4**]. 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. **[5]** 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 **[6-10]**. $Sr_2CeO_4$ 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 Ce4+ charge-transfer (CT).

In this work, fine particles of the blue phosphor $Sr_2CeO_4$ and, La, Eu rare earth ions doped $Sr_2CeO_4$, in different concentrations are prepared via solid state method and a spectroscopic study is reported.

## MATERIALS AND METHODS

Analytical grade Strontium nitrate [$Sr(NO_3)_2$], Cerium oxide ($CeO_2$), Lanthanum oxide ($La_2O_3$), 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 (SSR).

First we prepared undoped $Sr_2CeO_4$ phosphor by weighing, mixing inorganic salts, Strontium nitrate [$Sr(NO_3)_2$], Cerium oxide ($CeO_2$) in 2:1 molar ratio. We ground into fine powder using agate mortar and pestle about an hour. The samples were fired at 1200 ºC for 3 hours with a heating rate of $5^oC$/min in a muffle furnace by keeping in an alumina crucible closed with lid. In the same way La, Eu rare earth ions doped and co- doped in $Sr_2CeO_4$ phosphor concentration (0.5mol %) was prepared.

All the phosphor samples were characterized by X-ray diffraction using (Synchrotron Beam Indus -II), Particle size analysis was done using, laser particle size analysis Malvern Instrument Ltd (U.K) and Photoluminescence study using Spectrofluorophotometer (JOBIN VYON, Fluoromax-3), recorded at room temperature.

## RESULTS AND DISCUSSION

***3.1 Physical properties***

After heating at $1200^0C$ and cooling to room temperature in the furnace, the samples appears light cream in colour and light hard crystalline into material was observed. All the samples were again ground to make powder.

***3.2 X-ray Diffractometry (XRD)***

The phase and purity of the products were identified by X-ray diffraction (XRD). XRD of the present phosphors were done on Indus beam line-II at RRCAT, Indore, India. The wave length of beam line X-ray is 0.895Å. Fig.1 is the XRD pattern of undoped $Sr_2CeO_4$ phosphor. On comparison with literature most of the peaks are matching and the majority of the material is in single phase and is good agreement with the findings of the previous workers like Chia-Hao-Hsu et al. **[11]**. The calculated crystallite size using Scherer's formula $D = K.\lambda \backslash B\cos\theta$ for undoped $Sr_2CeO_4$ is around ~ 9nm, for La doped 76Ǻ**.** 7.6nm and Eu doped 98Ǻ 10nm. This confirms the formation of nano phosphor, via solid state reaction method (SSR)**.**

***3.3 SEM Analysis***

Fig.2 is the typical SEM photograph of the synthesized $Sr_2CeO_4$: La: Eu phosphor. The multi layered structure was observed and the prominent characteristic of $Sr_2CeO_4$: La: Eu crystal growth is the serious anisotropic growth rate. The growth rate along the *ab* plane is ~5 times larger than that along the *c*-axis. This phenomenon can be easily understood from the periodic bond chain (PBC) theory. The fundamental building units are in the orthorhombic structure.

***3.4 Photoluminescence analysis***

Fig.3 shows the excitation spectrum of La, Eu and La: Eu doped $Sr_2CeO_4$ blue phosphor which is monitored under 400nm wavelength. It is a broad excitation range from 220 to 370 shows peaks around 250 and 365nm. The 365nm peak belongs to crystal field.

Fig.4 shows the emission spectrum of La, Eu and Eu: La doped $Sr_2CeO_4$ blue phosphor under 250nm excitation. Pure $Sr_2CeO_4$ shows emission peak at 470nm with high intensity**.** La doped sample shows peak at 470nm with less intensity when compared with pure $Sr_2CeO_4$. The emission peaks of Eu doped sample are around 466, 490, 509, 536, 542, 556, 584, 589, 614, 617 and 632nm. This result is compared with the results of Rahul et al **[12]**. Where as emission spectrum of La: Eu when co-doped with $Sr_2CeO_4$ phosphor shows the same peaks in addition a new peak around 601nm is observed with good intensity. The corresponding energy along with the transitions has been shown in table-1. Not only that as per the CIE co-ordinates (x=0.32, y=0.33) the sample emitting white light with good intensity. It is also observed that the emission intensity at 470nm is decreases gradually as the dopant concentration increases. Under the excitation of 260nm all the samples shows the same peaks but the intensity is high.

***3.5 Particle size analysis***

The Particle size distribution histograms of the undoped $Sr_2CeO_4$ & La:Eu (0.5%) doped $Sr_2CeO_4$ particles as shown in fig.5 & 6. The prepared phosphor specimen particle size was measured by using laser based system Malvern Instrument U.K. The mean diameter of the particle size as follows. $Sr_2CeO_4$:26µm, La: 18.31µm, Eu: 17µm and La: Eu 27.28 µm from the above data the average particle diameter of Europium doped phosphor is 17 µm and the crystallite size is around 10nm. As such many molecular particles agglomerate and from as a crystallite and many crystallites together become a particle. In the present case approximately 2000 crystallites (10nm) together forms a particle of diameter is 17μm in Eu doped $Sr_2CeO_4$ system.

### *3.6 CIE Coordinates*

The CIE co-ordinates of (chart -1931) were calculated by the Spectrophotometric method using the spectral energy distribution of the undoped $Sr_2CeO_4$, La doped $Sr_2CeO_4$, Eu doped $Sr_2CeO_4$ and La: Eu doped $Sr_2CeO_4$ samples shown in fig.7. The colour co-ordinates for the undoped $Sr_2CeO_4$ samples are x = 0.16 and y = 0.18 this does not match with the coordinates reported by Danielson et al. (x = 0.20, y = 0.30) [**13**] and those of Jiang et al. (x = 0.19, y = 0.26) [**14**]. But these are closer to the values of Serra et al. (x = 0.16, y = 0.21) **[15]** and Liu et al.(x =0.15 and y =0.21**[16]**. La doped $Sr_2CeO_4$ (0.5%) x = 0.16 and y = 0.19, Eu doped $Sr_2CeO_4$ (0.5%) x = 0.268 and y = 0.31, and Eu: La co-doped $Sr_2CeO_4$ (0.5%) x=0.32 and y=0.33. This phosphor is having excellent colour tunability from blue to cyan and emitting white light.

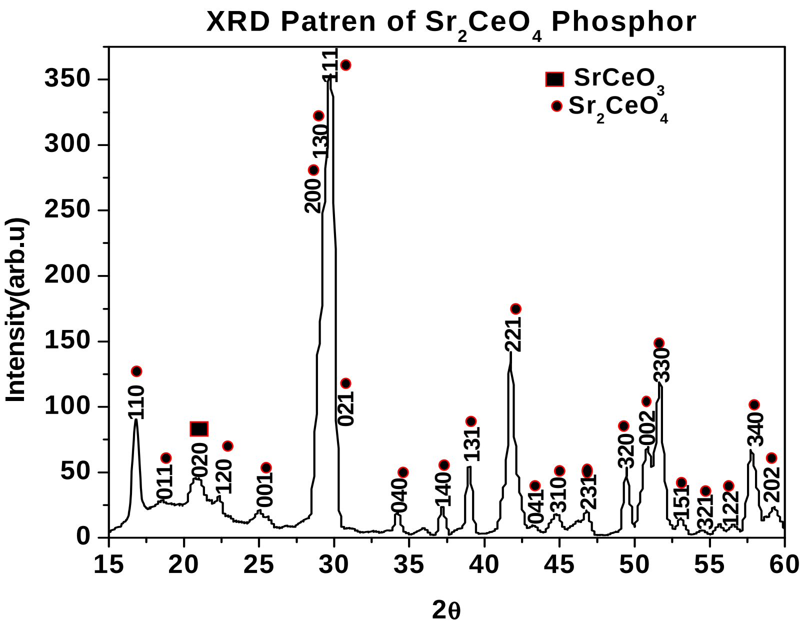


**Fig.1: XRD Pattern of undoped $Sr_2CeO_4$**

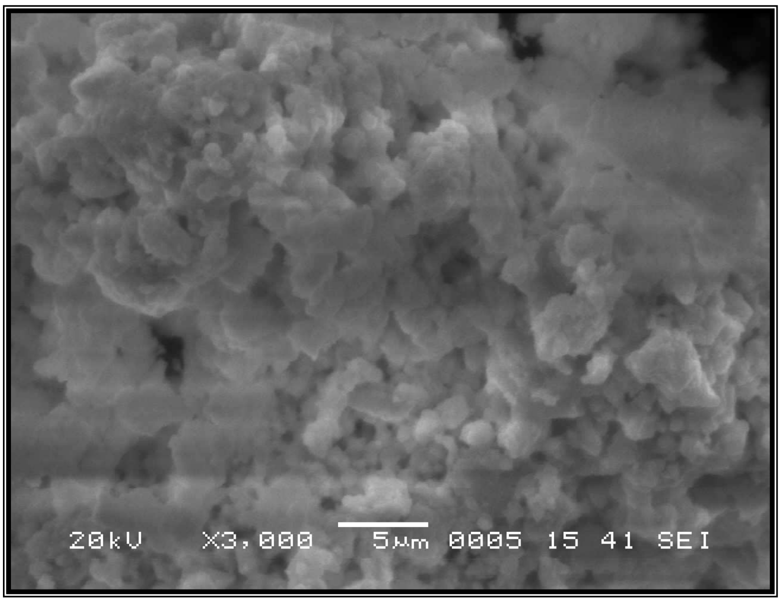


**Fig.2: SEM image of La,Eu doped $Sr_2CeO_4$**

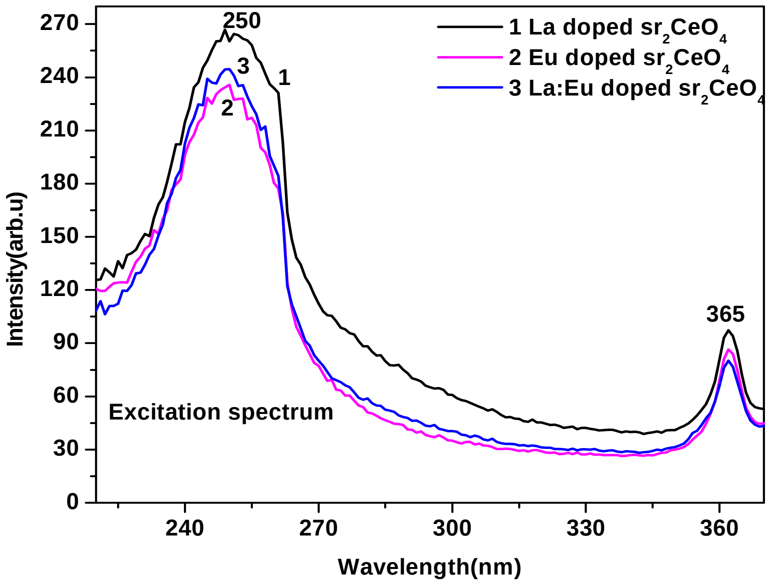


**Fig.3: Excitation Spectrum of La (0.5%), Eu (0.5%) doped $Sr_2CeO_4$ & La: Eu(0.5%) doped $Sr_2CeO_4$**

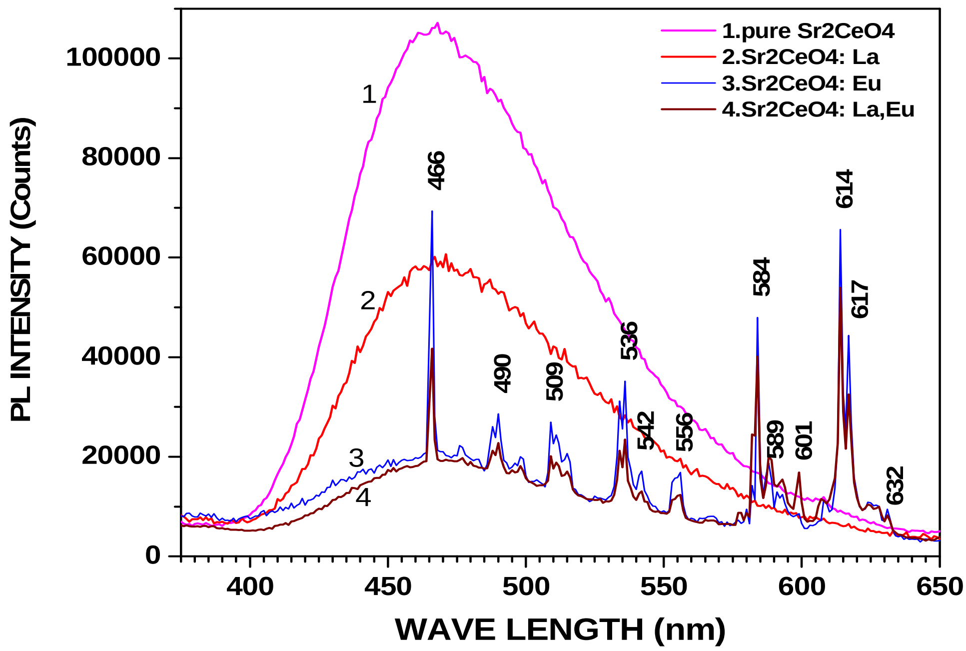


**Fig.4: Emission Spectrum of undoped $Sr_2CeO_4$, La (0.5%), Eu (0.5%) & La: Eu (0.5%) doped $Sr_2CeO_4$ under 250nm excitation**

**Table 1: Energy values of the corresponding transitions of Eu doped $Sr_2CeO_4$ phosphor**

| Wavelength (nm) | Transitions | Energy (eV) |
|---|---|---|
| 466 | $^5D_2 \rightarrow {}^7F_0$ | 2.657 |
| 490 | $^5D_2 \rightarrow {}^7F_2$ | 2.528 |
| 509 | $^5D_2 \rightarrow {}^7F_3$ | 2.429 |
| 536 | $^5D_1 \rightarrow {}^7F_1$ | 2.307 |
| 542 | $^5D_1 \rightarrow {}^7F_1$ | 2.281 |
| 556 | $^5D_1 \rightarrow {}^7F_2$ | 2.228 |
| 584 | $^5D_0 \rightarrow {}^7F_1$ | 2.118 |
| 589 | $^5D_0 \rightarrow {}^7F_1$ | 2.103 |
| **601** | $\mathbf{^5D_0 \rightarrow {}^7F_2}$ | **2.063** |
| 616 | $^5D_0 \rightarrow {}^7F_2$ | 2.015 |
| 619 | $^5D_0 \rightarrow {}^7F_2$ | 2.003 |
| 632 | $^5D_0 \rightarrow {}^7F_3$ | 1.961 |

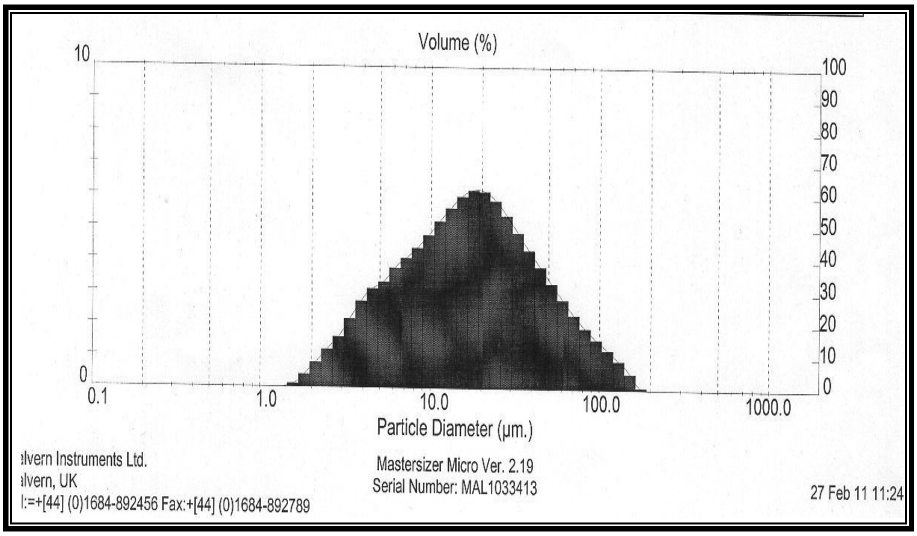


**Fig.5: Particle size of undoped $Sr_2CeO_4$**

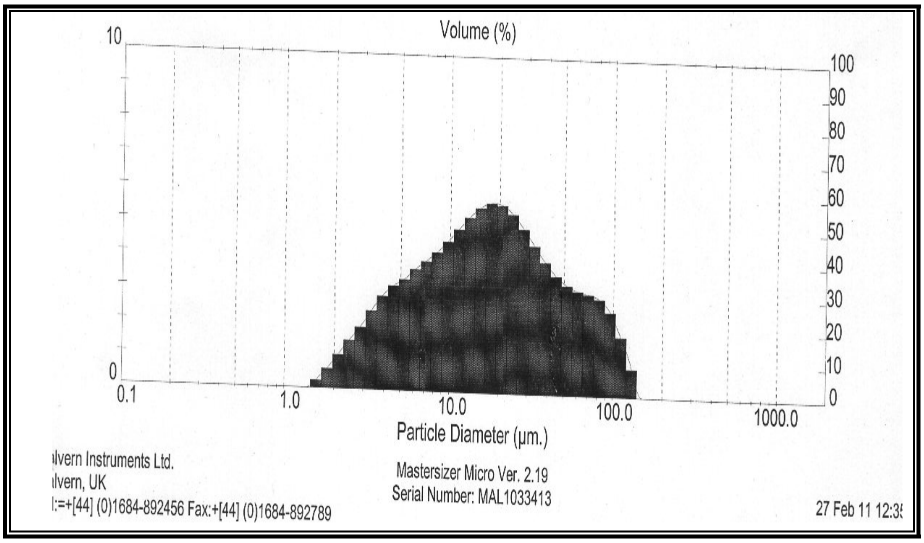


**Fig.6: Particle size of La:Eu (0.5%) doped $Sr_2CeO_4$**

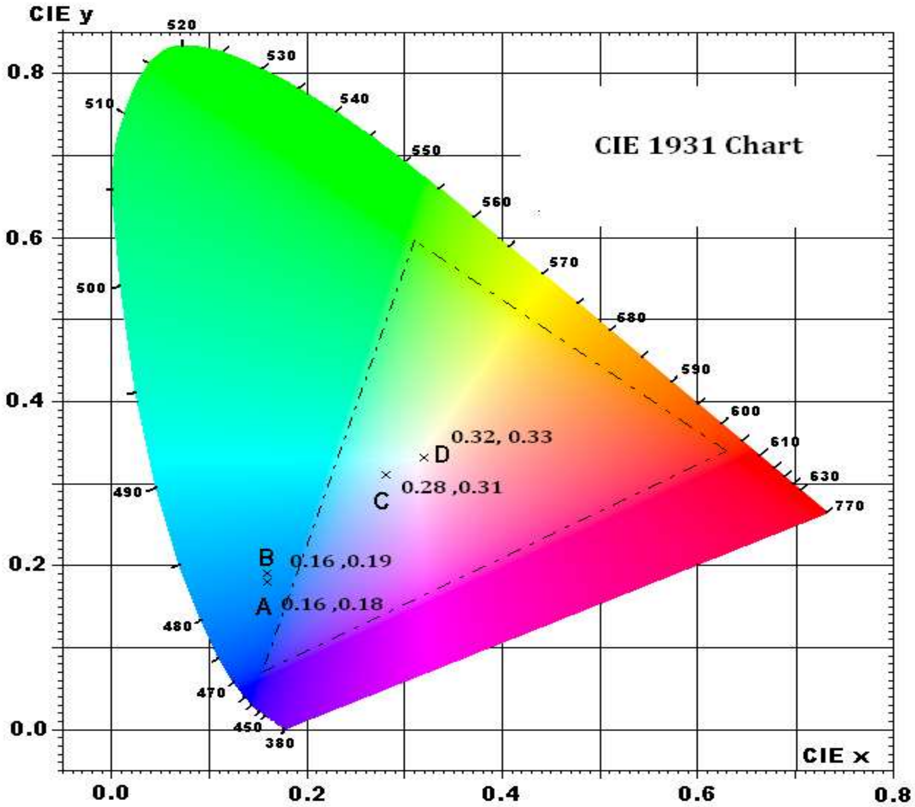


**Fig.7: CIE coordinates depicted on 1931 chart where (A) undoped $Sr_2CeO_4$, (B) La doped $Sr_2CeO_4$, (C) Eu doped $Sr_2CeO_4$, (D) La: Eu Co- doped $Sr_2CeO_4$**

## CONCLUSION

The present phosphor under study can be a good LED material if one can get good semiconductor LED emission in the range 240-280nm. The XRD pattern of $Sr_2CeO_4$ phosphor at $1200^0$c shows the formation of a single-phase compound. The calculated average crystallite size using scherrer's formula is ~9nm.This confirms the nano size. The Commission International de l'Eclairage co-ordinates are x = 0.16 and y = 0.18 for the undoped $Sr_2CeO_4$ sample and x = 0.32 and y = 0.33 for the La: Eu(0.5%) co-doped $Sr_2CeO_4$ sample. This confirms the PL studies& CIE co-ordinates revels that the present phosphor can be a good blue emitting phosphor material for lamps and white emitting phosphor for many display devices.

**Acknowledgement**
The author is gratefully thanking University Grant Commission, New Delhi, for financial support under Faculty Development Programme (FDP).

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