



## Synthesis, Characterization and Photoluminescence study of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ phosphor

Ch. Atchyutha Rao<sup>\*</sup>, K. Suresh<sup>1</sup>, K. V. R. Murthy<sup>2</sup> and N. V. Poornachandra Rao<sup>3</sup>

<sup>\*</sup>Department of Physics, VRS & YRN College, Chirala, A.P, India

<sup>1</sup>Department of physics, CSR Sarma, College, Ongole, A.P, India

<sup>2</sup>Display Materials Laboratory, Applied Physics Department, Faculty of Technology & Engineering, M.S University of Baroda, Baroda, India

<sup>3</sup>NVR College of Engineering and Technology, Tenali, Guntur District, A.P, India

---

### ABSTRACT

Photoluminescence studies of undoped  $\text{Sr}_2\text{CeO}_4$  phosphor and Eu rare earth ion doped  $\text{Sr}_2\text{CeO}_4$  phosphor with different concentrations are reported in the present paper. All the samples were prepared through standard solid state reaction method. Analytical grade inorganic salts like  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{CeO}_2$  and  $\text{Eu}_2\text{O}_3$  were used as raw materials of assay 99.9%. All the required chemicals were weighed in molar ratio 2:1 and thoroughly mixed in agate mortar and pestle. The final mixture was heated at 1200 °C for 3 hour in a muffle furnace with heating rate of 5°C/min. The XRD study reveals the formation of the material mostly in single phase and also particle size was measured by using laser based system. The Commission International de l'Eclairage coordinates of undoped  $\text{Sr}_2\text{CeO}_4$  is  $x = 0:158$  and  $y = 0:192$ , and Eu doped  $\text{Sr}_2\text{CeO}_4$  (0.1%, 0.5%, 1%) are  $x = 0.174$  and  $y = 0.143$ ,  $x = 0.26$  and  $y = 0.28$ ,  $x = 0.425$  and  $y = 0.241$ . The PL was recorded with 250nm excitation and the PL emission was observed at 470 for pure specimen, when the excitation is changed to 260nm the emission did not change but the intensity is increased by 40%. From this study it can be inferred the solid state reaction method is adequate for synthesis of  $\text{Sr}_2\text{CeO}_4$  nano crystallite phosphors. This phosphor can be useful for many display applications.

**Keywords:** Photoluminescence; Solid state reaction method; Phosphor; Nano particle.

---

### 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 activators [1, 2]. As a new blue luminescent material,  $\text{Sr}_2\text{CeO}_4$  phosphor has been widely studied since it was found by combinatorial chemistry method in 1998 [3, 4].  $\text{Sr}_2\text{CeO}_4$  consists of infinite edge-sharing  $\text{CeO}_6$

octahedral chains separated by Sr atoms. The luminescence originates from a ligand-to-metal  $Ce^{4+}$  charge transfer. The broad emission band (at ca. 475 nm) is suitable for the doping of rare earth ions in pursuing new luminescent materials and some research work has been carried out by traditional solid-state reaction [5, 6], namely the metal oxides are used as precursors and the reaction reagents have to be calcined at very high temperature for a long time. Growing interest has been focused on the synthesis and investigation of the properties of rare earth ions doped  $Sr_2CeO_4$ , which has been synthesized by many wet chemistry routes, including emulsion liquid membrane system [7], co precipitation process [8], assembling hybrid precursors [9] and citrate-gel method [10]. Sol-gel process is well accepted as a typical strategy to prepare nano scale complex oxides [11, 12]. In this study we presented the standard Solid state reaction method for the preparation of series of various concentrations of the rare earth ions doped  $Sr_2CeO_4$  at 1200°C temperature. The effect of calcinations temperature, and different amounts of doping ions on the structural, morphology and luminescent properties were investigated. The obtained phosphors were characterized by different techniques.

## MATERIALS AND METHODS

Analytical grade Strontium nitrate [ $Sr(NO_3)_2$ ], Cerium oxide ( $CeO_2$ ) and 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 °C for 3 hours with a heating rate of 5°C/min in a muffle furnace by keeping in an alumina crucible closed with lid. In the same way Eu rare earth ion doped  $Sr_2CeO_4$  phosphor at 0.1, 0.5 and 1.0% concentrations 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), CIE analysis and the Photoluminescence (PL) emission and excitation spectra were measured by Spectrofluorophotometer (SHIMADZU, RF-5301 PC) using Xenon lamp as excitation source, recorded at room temperature.

## RESULTS AND DISCUSSION

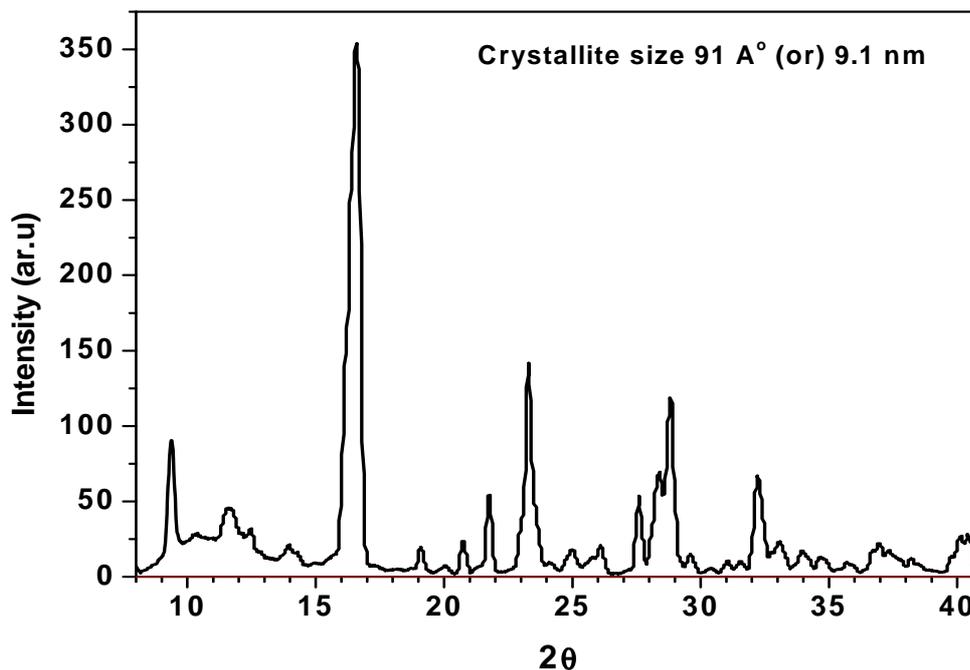
### 3.1 Physical properties

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

### 3.2 X-ray Diffractometry (XRD)

The crystalline structure of the powders was analyzed by X-ray powder diffraction (XRD). The present XRD 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. The crystalline phases were identified with the International Centre for Diffraction Data (ICDD) database card number 89-5546 [13]. All the diffraction peaks were well indexed and confirms the  $Sr_2CeO_4$  single phase. It clearly indicates that the heat treatment temperature and time were sufficient to form single phase. The calculated crystallite size using Scherer's formula  $D=K.\lambda/\beta\cos\theta$ , where k the constant (0.94),  $\lambda$  the wavelength of the X-ray (0.895 Å),  $\beta$  the full-width at half maxima (FWHM) (0.53),  $\theta$  the Bragg angle of the XRD big peak,  $\cos\theta=0.99$  and

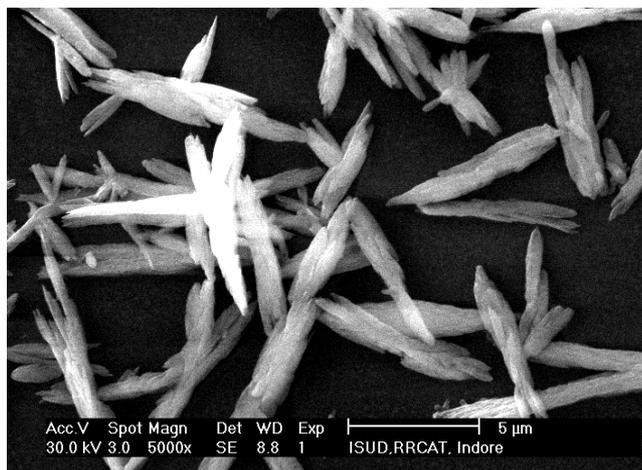
for undoped  $\text{Sr}_2\text{CeO}_4$  is around  $\sim 9\text{nm}$  and Eu doped  $\text{Sr}_2\text{CeO}_4$  is around  $12\text{nm}$ . This confirms the formation of nano crystallite phosphor, via solid state method.



**Fig.1: XRD Pattern of  $\text{Sr}_2\text{CeO}_4$**

### 3.3 SEM Analysis

Fig.2 shows the SEM image of Eu doped  $\text{Sr}_2\text{CeO}_4$  phosphor, the morphology look like baby cornflake structure having length of  $5\mu\text{m}$  and diameter  $500\text{nm}$ , which are agglomerated randomly.



**Fig.2: SEM image of  $\text{Sr}_2\text{CeO}_4$**

### 3.3 Photoluminescence Study

Fig.3 shows PL emission spectrum of undoped  $\text{Sr}_2\text{CeO}_4$  phosphor, it is observed that under  $250\text{nm}$  excitation, phosphor shows broad emission from  $350 - 650$  peaking at  $470\text{nm}$ . This broad band is due to  $f \rightarrow t_{1g}$  transitions of  $\text{Ce}^{4+}$  [3] as shown in fig.10. When excitation was varied from  $250$  to  $260$ , the observed emission is same but intensity is high. The observed emission at  $370\text{nm}$  with good intensity is due to the crystal field.

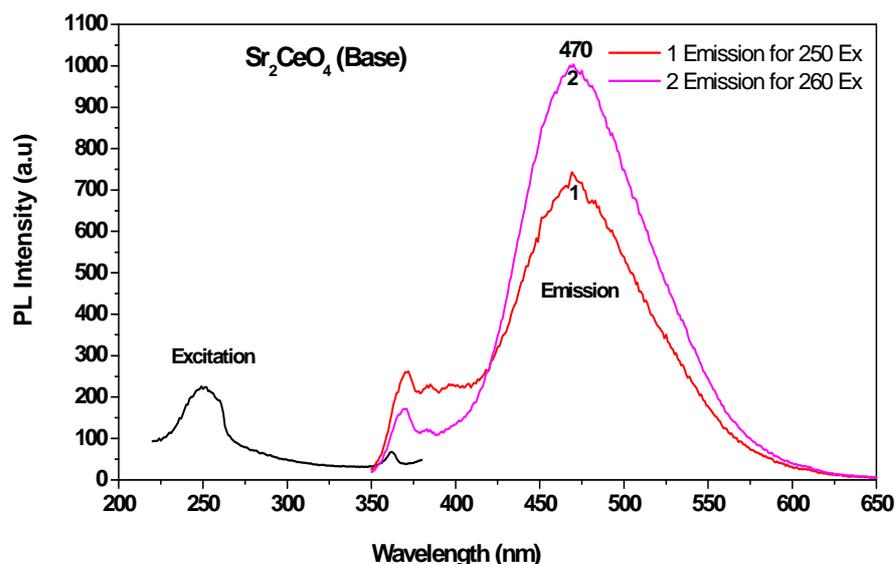


Fig.3: Excitation and emission spectra of undoped  $\text{Sr}_2\text{CeO}_4$  phosphor

Fig.4, 5 and 6 are the Eu (0.1, 0.5 & 1%) doped  $\text{Sr}_2\text{CeO}_4$  under excitation of 250 & 260nm. The blue emission band at 467 nm is attributed to the  $\text{Ce}^{4+}-\text{O}^{2-}$  charge transfer transitions in  $\text{Sr}_2\text{CeO}_4$  host. After doping 0.5 mol%  $\text{Eu}^{3+}$ , the phosphors shows white emission due to the overlap of host blue emission band and  $\text{Eu}^{3+}$  intra-  $4f^6$  lines.

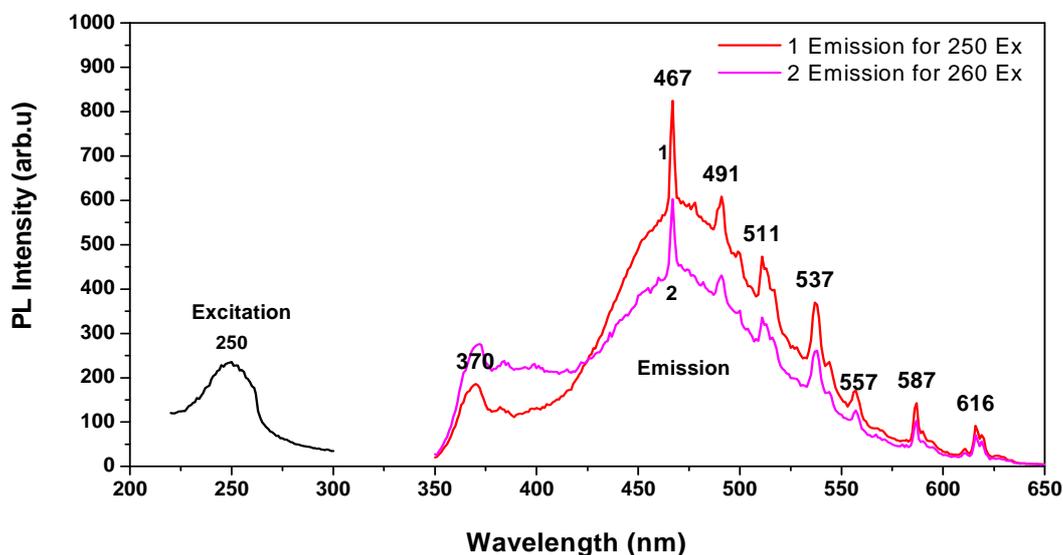


Fig.4: Excitation and emission spectra of Eu (0.1%) doped  $\text{Sr}_2\text{CeO}_4$  phosphor

The  $\text{Sr}_2\text{CeO}_4$  phosphor doped with  $\text{Eu}^{3+}$  (0.1, 0.5 & 1%) excited under 250nm wavelength shows main emission peaks at 467, 491, 511, 538, 557, 587 and 616nm. The emission spectra of  $\text{Eu}^{3+}$  contain not only the characteristic transition lines from the lowest excited  $^5\text{D}_0$  level but also those from higher energy levels  $^5\text{D}_1$  and  $^5\text{D}_2$ . As the  $\text{Eu}^{3+}$  concentration increases, the relative intensity

of both  $^5D_0 \rightarrow ^7F_1$  transition at 587 nm and the  $^5D_0 \rightarrow ^7F_2$  transition at 616 nm increased whereas the intensity of  $^5D_0 \rightarrow ^7F_1$  and  $^5D_1, ^5D_2 \rightarrow ^7F_J$  transition decreased. This observation suggests that most of  $\text{Eu}^{3+}$  ions are located in a site without inversion symmetry. At  $\text{Eu}^{3+}$  concentration above 5 mol %, phosphors have a red emission spectra pattern due to the vanishing of blue emission and the dominance of  $^5D_0 \rightarrow ^7F_2$  transition. The PL emission intensity vs wavelength of the phosphors studied are presented in table 1. Table 2 shows the energy values of corresponding transitions.

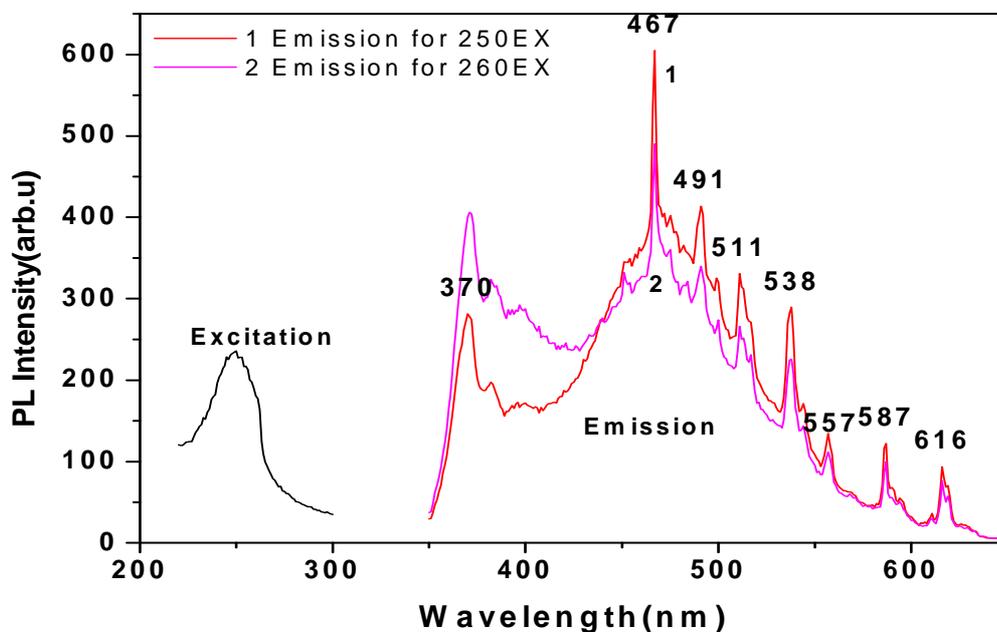


Fig.5: Excitation and emission spectra of Eu (0.5%) doped  $\text{Sr}_2\text{CeO}_4$  phosphor

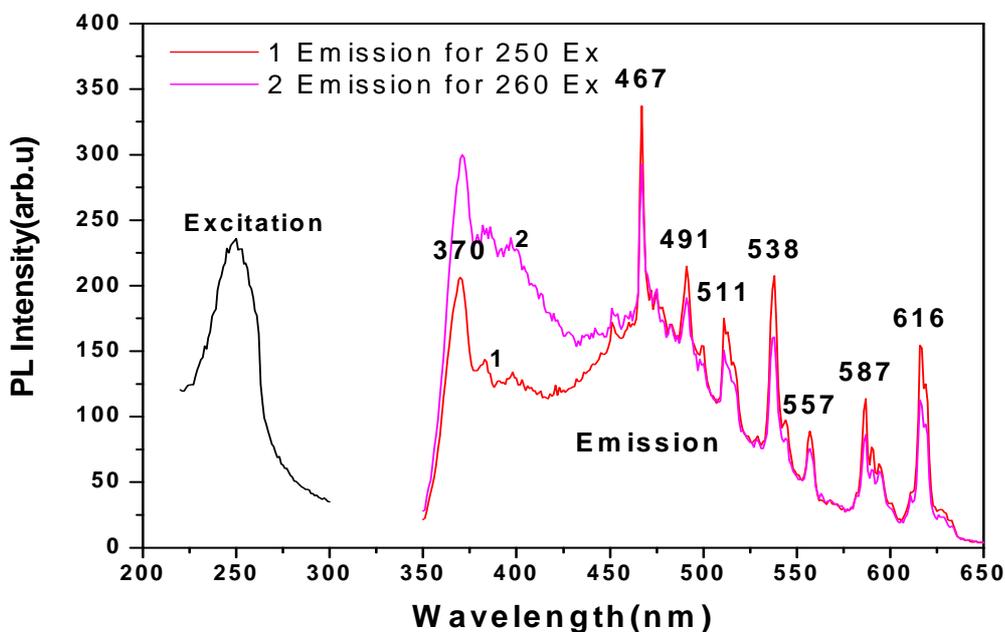


Fig.6: Excitation and emission spectra of Eu (1%) doped  $\text{Sr}_2\text{CeO}_4$  phosphor

**Table -1: Peak intensity of a particular colour wavelength**

S. No	$\lambda$ (nm)	Eu (0.1%)	Eu (0.5 %)	Eu (1%)
1	467	826	609	336
2	491	609	414	214
3	511	471	336	184
4	537	370	287	206
5	558	172	133	93
6	587	145	121	113
7	616	93	93	155

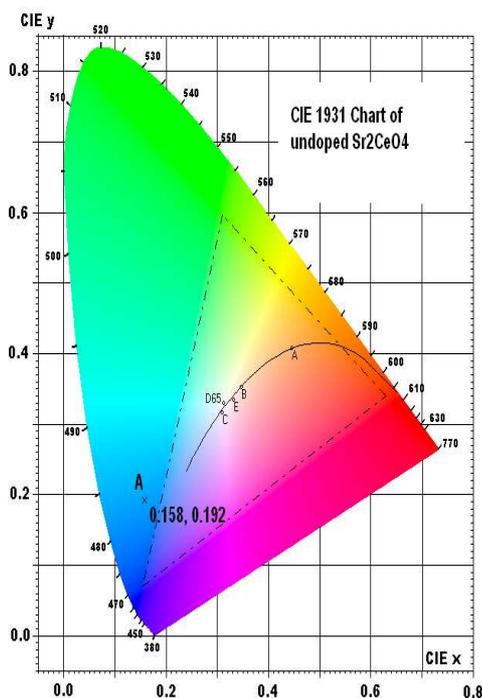
**Table-2: Energy values of the corresponding transitions**

Transition	Wavelength (nm)	Energy ( $\text{cm}^{-1}$ )
$^5D_2 \rightarrow ^7F_0$	467	21459
$^5D_2 \rightarrow ^7F_2$	491	20408
$^5D_2 \rightarrow ^7F_3$	511	19646
$^5D_1 \rightarrow ^7F_1$	538	18726
$^5D_1 \rightarrow ^7F_2$	557	18018
$^5D_0 \rightarrow ^7F_1$	587	17123
$^5D_0 \rightarrow ^7F_2$	617	16207

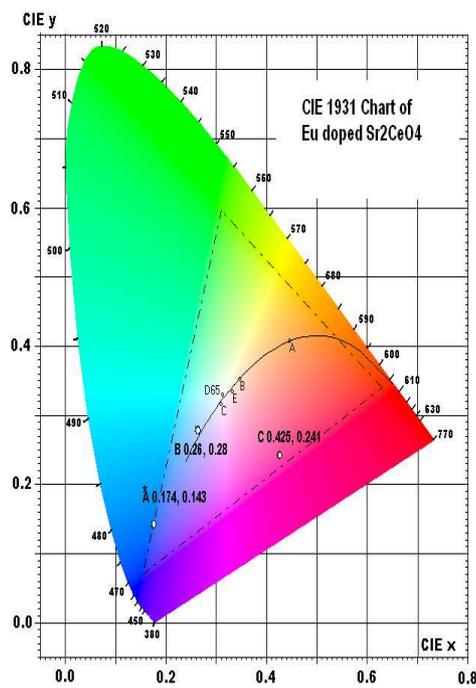
These above PL observed luminescent properties are due to low vibration energy of  $\text{Sr}_2\text{CeO}_4$  host lattice and different energy transfer process from host to dopant. The high efficiency energy transfer allows us to expect that the  $\text{Sr}_2\text{CeO}_4$  crystal structure could form the base for the creation of phosphors with different spectral emissions [14-19].

### 3.4 Thermoluminescence study

Thermoluminescence (TL) of prepared phosphor was studied using the equipment described by Murthy et al [18]. TL of all the phosphors is studied with beta dose of 10Gy given prior to TL recording. Every time for TL measurement 5mg of irradiated weighted powder phosphor was taken. There is no TL observed, irradiated using Sr-90,  $\beta$  source, because may be the formed compounds are in nano crystallite form.



**Fig.7: CIE coordinates depicted on 1931 chart undoped  $\text{Sr}_2\text{CeO}_4$  phosphor**



**Fig.8: CIE coordinates depicted on 1931 chart where A=0.1%, B=0.5% & C=1% of Eu doped  $\text{Sr}_2\text{CeO}_4$  phosphor**

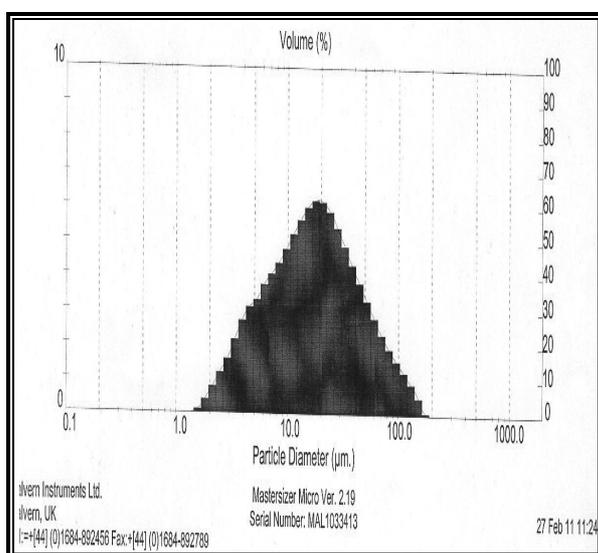
### 3.5 CIE Coordinates

The CIE co-ordinates of (chart -1931) were calculated by the Spectrophotometric method using the spectral energy distribution of undoped  $\text{Sr}_2\text{CeO}_4$  and Eu doped  $\text{Sr}_2\text{CeO}_4$  sample is shown in fig.7 & 8. The color co-ordinates for the undoped  $\text{Sr}_2\text{CeO}_4$  sample are  $x = 0.158$  and  $y = 0.192$  this does not match with the coordinates reported by Danielson et al. ( $x = 0.20$ ,  $y = 0.30$ ) [3] and

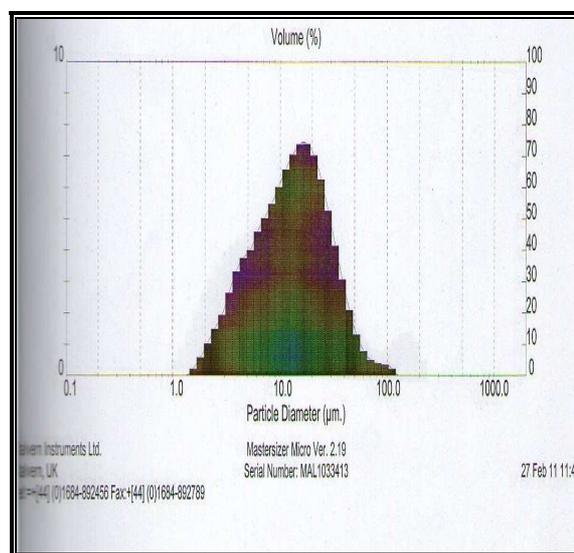
those of Jiang *et al.* ( $x = 0.19$ ,  $y = 0.26$ ) [20]. But these are closer to the values of Serra *et al.* ( $x = 0.16$ ,  $y = 0.21$ ). Eu doped  $\text{Sr}_2\text{CeO}_4$  (0.1%, 0.5%, 1%) samples are  $x = 0.174$  and  $y = 0.143$ ,  $x = 0.26$  and  $y = 0.28$ ,  $x=0.425$  and  $y=0.241$ . This phosphor is having excellent color tunability from blue to red and emitting white light.

### 3.6 Particle size analysis

The particle size distribution histogram of undoped  $\text{Sr}_2\text{CeO}_4$  and Eu doped  $\text{Sr}_2\text{CeO}_4$  shows in fig.9 & 10. The prepared phosphor specimen particle size was measured by using laser based system Malvern Instrument U.K. The mean diameter of the particle size of undoped  $\text{Sr}_2\text{CeO}_4$  is  $26\mu\text{m}$  and Eu doped  $\text{Sr}_2\text{CeO}_4$  is  $17\mu\text{m}$ , from the above data the average particle diameter of Europium doped phosphor is  $17\mu\text{m}$  and the crystallite size is around  $12\text{nm}$ . As such many molecular particles agglomerate and form as a crystallite and many crystallites together becomes a particle. In the present case approximately 2000 crystallites ( $12\text{nm}$ ) together forms a particle of diameter is  $17\mu\text{m}$  in Eu doped  $\text{Sr}_2\text{CeO}_4$  system.



**Fig.9 Particle size distribution histogram undoped  $\text{Sr}_2\text{CeO}_4$**



**Fig.10 Particle size distribution of histogram of Eu doped  $\text{Sr}_2\text{CeO}_4$**

## CONCLUSION

Superfine  $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$  phosphor was successfully prepared by solid state reaction method and the preparation temperature was lowered from at least  $1500$  to  $1200^\circ\text{C}$  and got single phase phosphor. The  $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$  emission could be tuned from blue to white and red light by varying the concentration of  $\text{Eu}^{3+}$  thereby controlling the emission intensity ratio of host and  $\text{RE}^{3+}$  transitions. The mean diameter of the particle size  $\text{Sr}_2\text{CeO}_4$  is  $26\mu\text{m}$  and doped with Eu is  $17\mu\text{m}$  which led as to conclude the Eu doped host reduces the average particle size. The calculated average crystallite size using Scherer's formula is  $\sim 10\text{nm}$ . This method is easy for the preparation of  $\text{Sr}_2\text{CeO}_4:\text{RE}^{3+}$  phosphors and can be potentially applied to the synthesis of other high quality rare earth ions doped oxides phosphor materials with micro/nano structure. This phosphor can be useful in many lamps and display devices.

### Acknowledgement

The authors Ch. Atchyutha Rao and K. Suresh are thanking University Grant Commission, New Delhi, India for financial support under Faculty Development Programme (FDP).

## REFERENCES

- [1] Y H Wang, Z Y Wang, P Y Zhang, Z L Hong, X P Fan, *Mater. Lett.*, **2004**, 58: 3308.
- [2] C Feldmann, T Jüstel, C R Ronda, P J Schmidt. *Adv. Funct. Mater* **2003**, 13, 511.
- [3] E Danielson et al., *J. Mol. Struct.*, **1998**, 470, 229.
- [4] E Danielson et al., *Science*, **1998**, 279: 837.
- [5] S Okada et al., *Chemical, Solid State Ionics*, **2004**, 175: 593.
- [6] Y Hinatsu, M Wakeshima, N Edelstein, I.Craig, *J. Solid State Chem.*, **1999**, 144: 20.
- [7] T Hirai, Y Kawamura., *J. Phys. Chem. B*, **2005**, 109: 5569.
- [8] A Nag, T R.Narayanan Kutty, *J. Mater. Chem.*, **2003**, 13: 370.
- [9] X Z Xiao, B. Yan, *J. Phys. Chem. Solids*, **2008**, 69: 1665.
- [10] X H Chuai, H J Zhang, F S Li, G Z.Zhou, *Chin. J. Inorg. Chem.*, **2003**, 19: 462.
- [11] J Yang, D Li, X Wang, X J Yang, *J. Solid State Chem. (in Chin.)*, **2002**, 165 193.
- [12] C X Zhang, W J Jiang, X J Yang, Q F Han, Q L Hao, *J. Alloys Compd.*, **2009**, 474: 287.
- [13] ICDD Powder Diffraction, Card No.89-5546.
- [14] K.V.R. Murthy et al, *Journal of Luminescence*, Vol.124, Issue 2, (2007), Pages 217-220.
- [15] K.V.R.Murthy et al., *Materials Research Bulletin*, Vol.41, 10, (2006), 1854-1860.
- [16] K.V.R.Murthy et al., *Philosophical Magazine Letters*, Vol.90, No.9, **Sept2010**, 653–662
- [17] G. Blasse and B.C.Grabmaier, *Luminescent Materials*, Springer-Verlag, Berlin **1994**.
- [18] Y.X.Tang, H.P.Guo, Q.Z.Qin, *Solid state Commun.*121 (2002) 352
- [19] Y.Zhai, et al *Journal of RE*, vol.24, issue3, june **2006**, 281-284.
- [20] Y.D. Jiang, F. Zhang, C.J. Summers, Z.L. Wang, *Appl. Phys. Lett.* 74 (12) (1999) 1677.