

# Photoluminescence Studies of $\text{Sr}_2\text{CeO}_4$ Phosphor without and with Flux under Different Excitation Wavelengths

Ch. Atchyutha Rao<sup>1</sup>, K.V.R. Murthy<sup>2</sup>

<sup>1</sup>Department of Physics, Bapatla College of Arts & Sciences, Bapatla - 522101, A.P, India (Corresponding author)

<sup>2</sup>Display Materials Laboratory, Applied Physics Department, Faculty of Technology and Engineering, M. S. University of Baroda, Vadodara-390001, India

**Abstract:** *The present paper reports the synthesis and Photoluminescence (PL) studies of  $\text{Sr}_2\text{CeO}_4$  phosphor without and with fluxes under different excitations. The inorganic compounds like Strontium Carbonate ( $\text{SrCO}_3$ ), Cerium Oxide ( $\text{CeO}_2$ ) were used as raw materials for the host. The samples were prepared by the conventional solid-state reaction method, which is the most suitable for large-scale production. The PL and CIE techniques were used to characterize received phosphor samples. Without flux and with flux  $\text{Sr}_2\text{CeO}_4$  phosphor exhibits good photoluminescence emission due to the charge transfer (CT) mechanism. The PL emission mainly concentrates around 470nm, when excited with 254, 267, 275, 302 and 340nm wavelengths. The  $\text{Sr}_2\text{CeO}_4$  phosphor, when prepared with urea, glycin and citric acid as fluxes, the PL emission was observed from 350 – 650 nm range, broad emission 470nm with high intensity was observed.*

**Keywords:** Photoluminescence (PL), Solid state reaction method (SSR), compact fluorescent (CFL)

## 1. Introduction

Phosphors are used in cathode ray tubes (CRTs), projection televisions (PTVs), fluorescent tubes, X-ray detectors and field emission displays (FED) etc.[1-6]. Concerning many of these applications, 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. Rare earth ions are widely employed in the development of luminescent materials for exhibiting monochromatic emission colors due to their intrinsic optical properties [7-10]. Therefore it is very significant to know the optical transitions of the 4f levels of the rare earth ions involved [11-13]. Rare earth applications in the field of display devices is still a warm topic much of the research around the world is to improve the phosphor efficiency and to improve the luminescence properties of the phosphor with discovery of blue light emitting  $\text{Sr}_2\text{CeO}_4$  by combinatorial chemistry method in 1998 by Danielson.  $\text{Sr}_2\text{CeO}_4$  consist of infinite edge-shearing  $\text{CeO}_6$  octahedral chains separated by Sr atoms. The luminescence originates from a ligand-to metal  $\text{Ce}^{4+}$  charge transfer [14, 18]. The broad emission band is proper for the doping of rare earth ions in pursuing new luminescent materials. The blue phosphors are very few and if a suitable blue phosphor is found then it can be added to the well studied red and green combination for white light emission from the phosphor. If blue phosphor  $\text{Sr}_2\text{CeO}_4$  doped with trivalent rare earths europium and samarium emit in the red region of the visible spectra [19-21]. The rare earth materials display excellent sharp- emission luminescence properties with suitable sensitization and effectively used in designing of white light emitting materials. Solid state lighting have a very bright future in various lighting applications because of their high energy efficiency and cost effectiveness compared to incandescent bulbs [22-26].

Recently, a new promising blue phosphor,  $\text{Sr}_2\text{CeO}_4$ , was developed by combinatorial synthesis and prepared by different routes. The effect of fluxes on the PL emission/excitation was also studied. In this study, we prepared Strontium Cerate phosphor that exhibits broad excitation ranges of 240–350 nm using high temperature solid state reaction method.

## 2. Experimental Work

Strontium Carbonate ( $\text{SrCO}_3$ ), Cerium Oxide ( $\text{CeO}_2$ ) of high purity (99.9%) chemicals was used as starting materials to prepare  $\text{Sr}_2\text{CeO}_4$ . Strontium carbonate ( $\text{SrCO}_3$ ), Cerium Oxide ( $\text{CeO}_2$ ) in stoichiometric proportions of Sr:Ce as 2:1 is weighed and ground into a fine powder using agate mortar and pestle. The samples of synthesized phosphor were heated up to 1200°C for three hours in a furnace made by 'Precision Control', Mumbai having 12 Molybdenum heating elements. The furnace has a very precise temperature controller of 'Eurotherm' make, with a resolution of  $\pm 1^\circ\text{C}$ . A mechanical protection system is provided so that the input current to the heating elements would be cut-off, once the temperature reaches 1200°C. However in the present investigation heating required is 1200°C. The grounded samples was placed in an alumina crucible and fired at 1200°C for 3 hours in a muffle furnace with a heating rate of 5°C/min. The samples are allowed cool to room temperature in the same furnace for about 20 hours. Spectrofluorophotometer (SHIMADZU, RF-5301 PC) was used for PL studies. The 1200°C fired samples show good PL. All the spectra were recorded at room temperature [27].

### 3. Results and discussion

#### 3.1 Preparation of pure and rare earths doped $\text{Sr}_2\text{CeO}_4$ phosphors with and without fluxes

Another important aspect of solid-state reaction is that its reaction rates are greatly influenced by flux. The purpose of adding flux is to enhance the crystal growth during the solid-state reaction. The formation temperature of some of the phases is reduced to a large extent with use of flux and it facilitates the reaction by reducing the activation energy. A suitable flux increases the reactivity by dissolving at least reactants and promotes the crystallization of phosphors. There are two types of fluxes viz., volatile and non-volatile. Volatile flux reacts with starting materials and leaves the reaction mixture spontaneously. While using the flux it is necessary to optimize the amount of flux materials because any excess amount of that would lead to phase segregation. Generally, the amount of flux is used very small and it is the order of few mole percent. Some phosphors such as phosphates and borates in general do not need flux. The powder obtained from solid-state reaction is normally in the order of  $100\mu\text{m}$  due to high temperature and prolonged firing time. The purpose of firing is not only to cause solid-state reactions but also to form well crystallized particles with an appropriate average diameter. The substance added to the raw material mixture to help crystal growth is called a flux. Fluxes are usually compounds of alkali or alkaline earth metals having low melting points. The halides are most frequently used. The flux used plays a determining role in the particle growth process. Each flux influences the particle size and the shape in a different way. Therefore, a combination of fluxes is sometimes used to obtain products with desired morphology. Another important function of the

flux is that it acts as a source of the co-activator. The advantages of solid-state reactions are easy availability of oxide precursors and the less expensive powder production on the industrial scale. This method is also convenient for laboratory scale preparation. One more advantage of the use of flux is the firing temperature can be reduced. However, it has some inherent disadvantages. In solid-state reaction, the homogenous distribution of dopants, important phosphors is sometimes difficult to achieve. Finally, the formation of undesirable phases and agglomeration take place due to high temperature firing.

#### 3.2 Excitation Study

Fig.1 shows the excitation spectra of  $\text{Sr}_2\text{CeO}_4$  phosphor for different excitations. The excitation spectrum is monitored under 470nm wavelength measured range from 200 to 450nm with the intensity is out of range of instrument monitored at 470nm wavelength. The intense broad band centered at 275nm is attributed to the charge – transfer (CT) transition between  $\text{Ce}^{4+}$ –  $\text{O}^{2-}$  as described by Danielson et al [5]. The two excitation peaks may be assigned to the two kinds of  $\text{Ce}^{4+}$  ions present in  $\text{Sr}_2\text{CeO}_4$ . There are two different  $\text{Ce}^{4+}$ –  $\text{O}^{2-}$  bond lengths in the lattice, thus two excitation peaks are attributed to the two different charge transfer transitions. The hump around 275nm evident from the excitation curve may be attributed to the above-defined mechanism. Though the intensity of two excitations is not same this is in good agreement with those reported by Serra et al. [23]. It is decided to measure the emission under 254, 267, 275, 302 and 340nm excitations and presented in this paper.

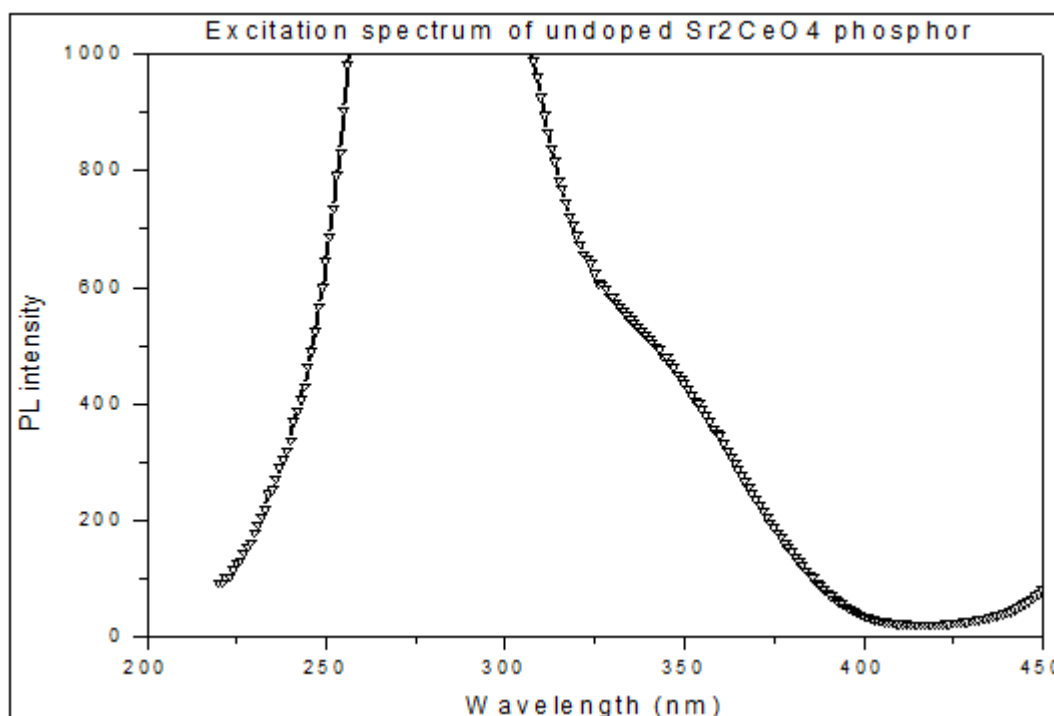


Figure 1: Excitation spectrum of  $\text{Sr}_2\text{CeO}_4$  phosphor monitored at 470nm wavelength

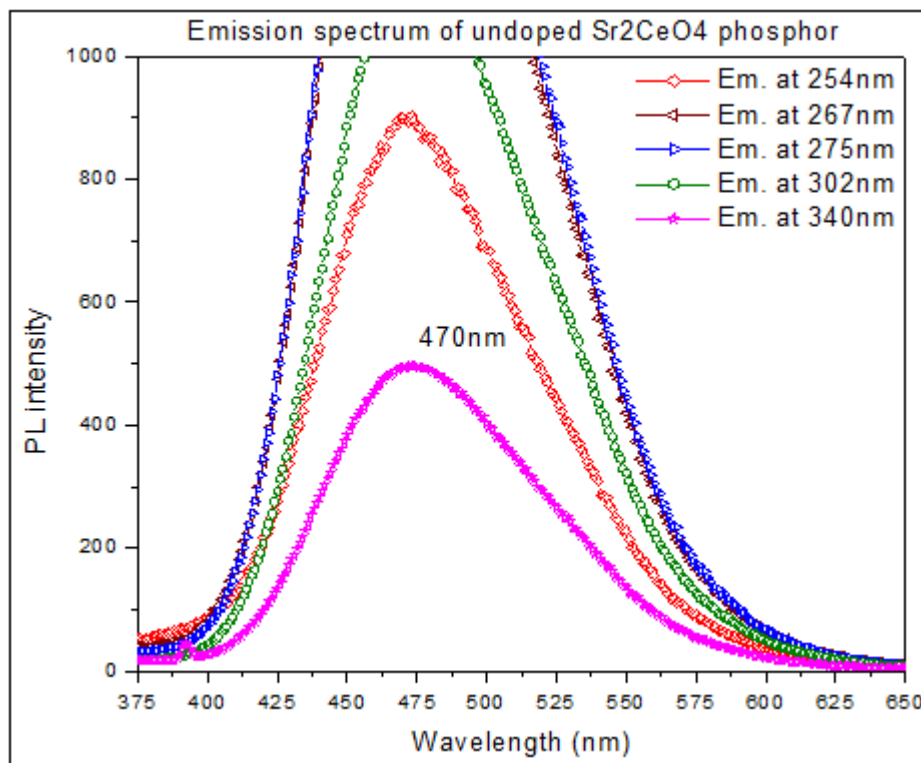
### 3.2 Emission Study

Figures 2-5 are the PL emission spectra of the prepared phosphors. The main PL emission under 254, 267, 275, 302 and 340nm excitations is a broad emission range from 375 – 650nm peaked at 470nm (blue band), which is deep blue originated from  $Ce^{4+}$  ion. These bands in the excitation and emission spectra have been assigned to the  $Ce^{4+}-O^{2-}$  charge-transfer transition [5]. Considering that an electron can be transferred from an oxygen ligand to the empty 4f shell of  $Ce^{4+}$ , a high spin triplet excited state is formed via a spin-forbidden transition. Therefore, the PL can be assigned to a ligand-to-metal charge-transfer transition of  $Ce^{4+}$ . However the effect of different fluxes i.e. citric acid, glycin, and urea did not see any change on PL emission except slight decrease/increase of FWHM value only. It is observed from all figures the maximum emission intensity is observed for 275nm excitation. However when the phosphor is excited with 267 and 275nm the emission at 470nm wavelength is gives raise maximum PL output in deep blue region is out of range of the instrument.

Table.1 is shows the PL emissions for various excitations of  $Sr_2CeO_4$  phosphor prepared with and without flux. The role of flux on  $Sr_2CeO_4$  is not much affected the PL output at 472nm. Therefore we conclude that we successfully synthesized the  $Sr_2CeO_4$  with and without flux which are giving deep blue emissions around 472nm for excitations between 254nm – 340nm. It is also concluded the flux did not affect and influence the PL emission peaking at 470nm except minor variations in intensity for different excitations.

**Table 1**

S.No	Name of the Sample	Excitation Wavelength (nm)	Intensity of Emission wavelength (472nm) (arb. Units)			
			Without flux	Citric Acid	Glycin	Urea
1	$Sr_2CeO_4$	254	902	814	782	803
2		267	>1200	>1200	>1200	>1200
3		275	>1200	>1200	>1200	>1200
4		302	1100	1000	1020	1000
5		340	498	481	458	481



**Figure 2:** Emission spectrum of  $Sr_2CeO_4$  phosphor under different excitation wavelengths

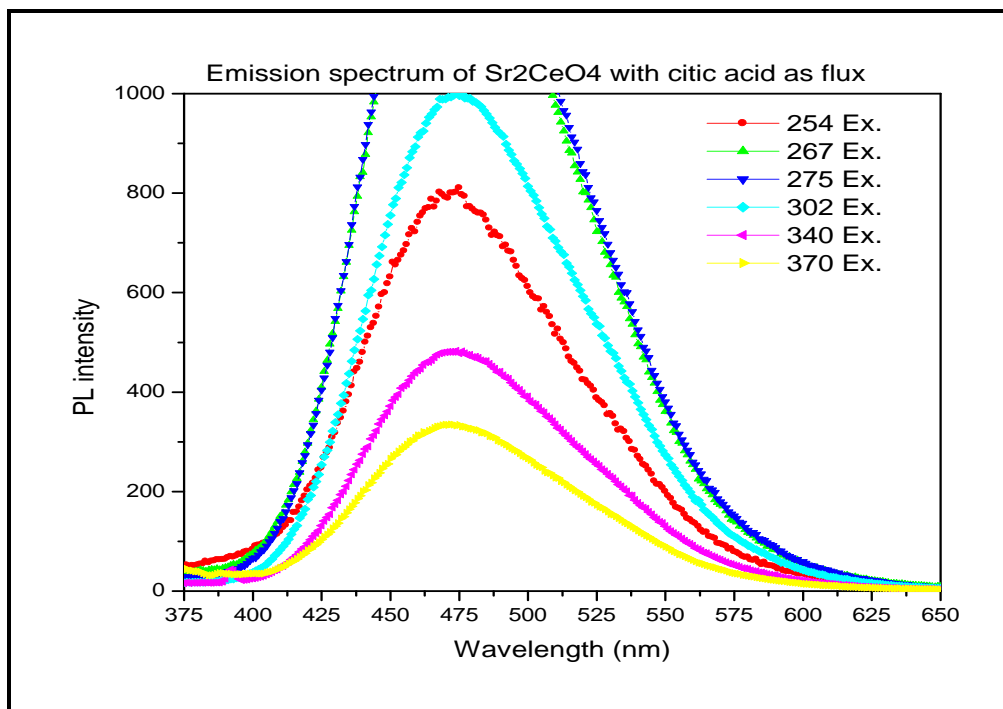


Figure 3: Emission spectrum of Sr<sub>2</sub>CeO<sub>4</sub> phosphor with citric acid as flux under different excitation wavelengths

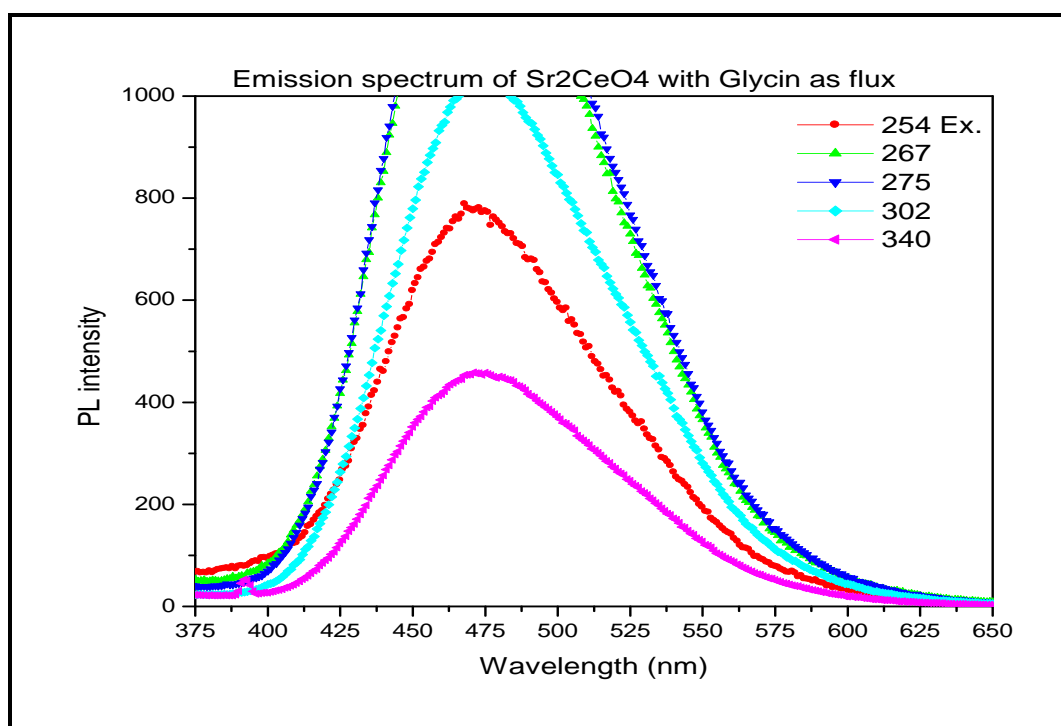


Figure 4: Emission spectrum of Sr<sub>2</sub>CeO<sub>4</sub> phosphor with glycin as flux under different excitation wavelengths

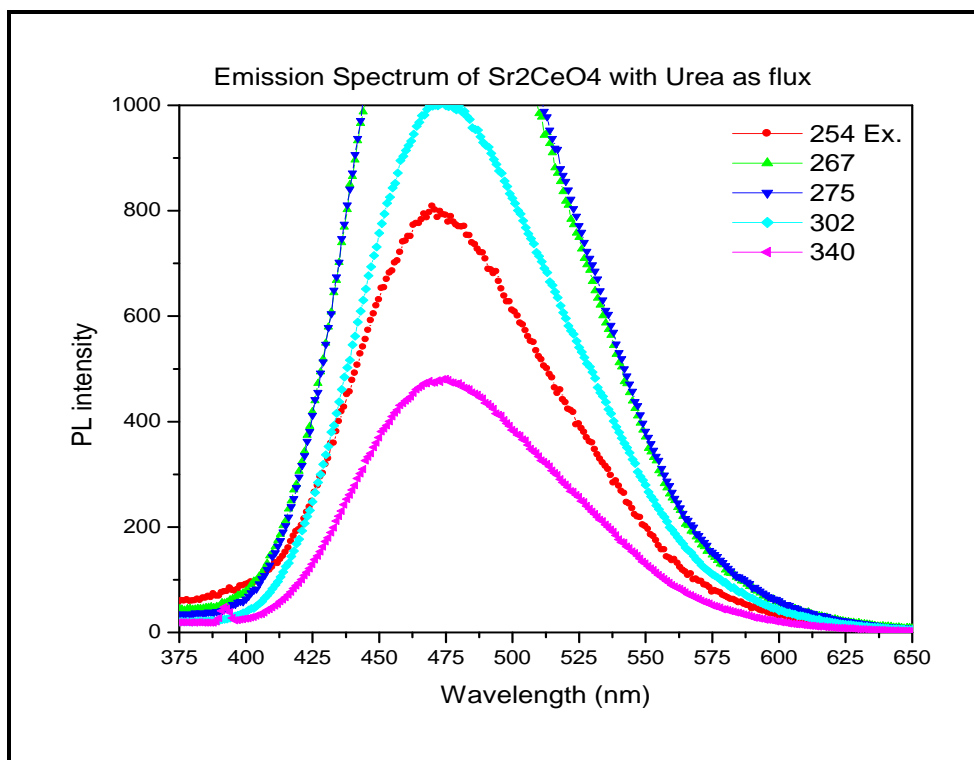


Figure 5: Emission spectrum of Sr<sub>2</sub>CeO<sub>4</sub> phosphor with urea as flux under different excitation wavelengths

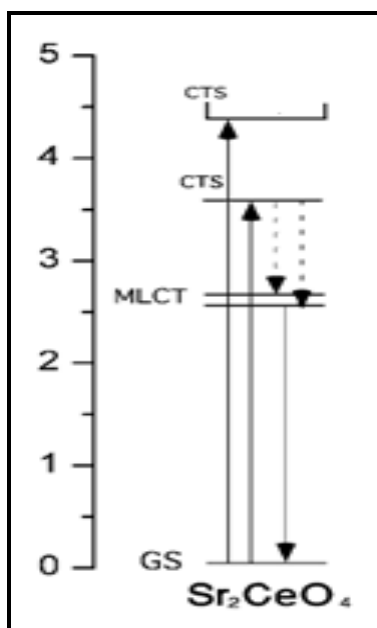


Figure 6: Charge transfer mechanism of Sr<sub>2</sub>CeO<sub>4</sub> phosphor

However the present observed PL in our samples are compared with the previous workers synthesized by different routes. Fig.6 shows the charge transfer mechanism of Sr<sub>2</sub>CeO<sub>4</sub> phosphor.

### 3.3 CIE Coordinates

The CIE co-ordinates were calculated by the Spectrophotometric method using the spectral energy distribution of the Sr<sub>2</sub>CeO<sub>4</sub> sample is shown in Fig.7. The colour co-ordinates for the un-doped Sr<sub>2</sub>CeO<sub>4</sub> sample are x=0.152 and y=0.167 Hence this phosphor is having excellent blue-cyan colour which can be produce white light.

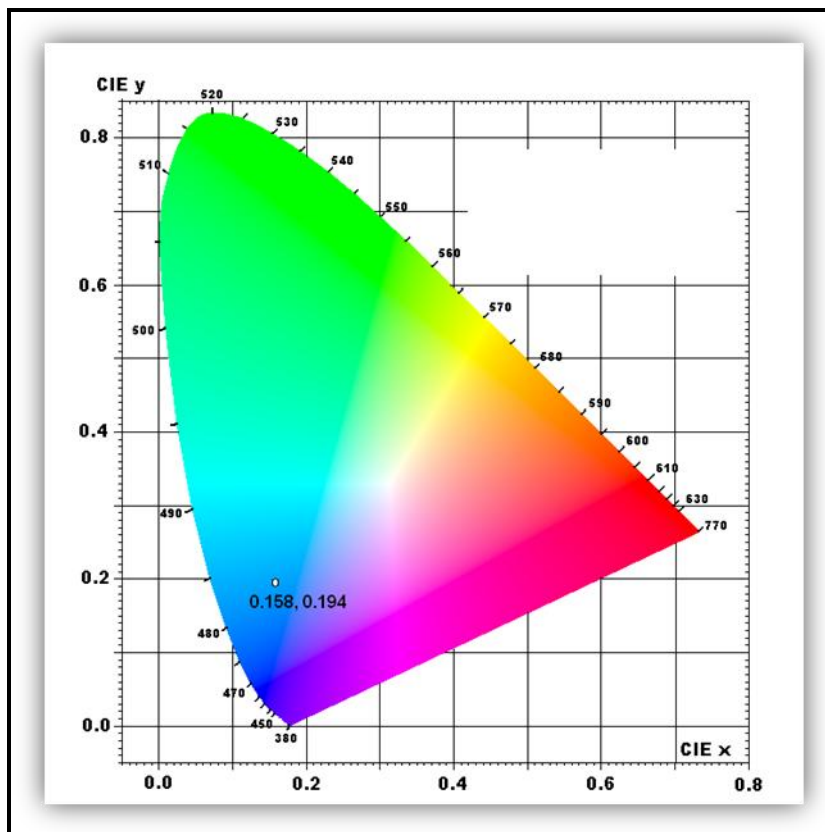


Figure 7: CIE coordinates of Sr<sub>2</sub>CeO<sub>4</sub> phosphor depicted on 1931 chart

#### 4. Conclusions

Pure Sr<sub>2</sub>CeO<sub>4</sub> phosphors without and with fluxes was synthesized via high temperature solid state reaction. The characteristic blue emission of the Sr<sub>2</sub>CeO<sub>4</sub> phosphor with high intensity is observed. It is concluded this may be due to the CT from Ce<sup>4+</sup> - O<sup>2-</sup>. From the PL studies, it is concluded that Sr<sub>2</sub>CeO<sub>4</sub> phosphor under 275nm excitation producing blue light with good intensity which is useful for all practical display devices in particular compact fluorescent lamps.

#### 5. Acknowledgement

One of the authors (Ch. Atchyutha Rao) is grateful for the financial support from the University Grant Commission (UGC), New Delhi, India, under Minor research Project (MRP No: 4687/14-SERO/UGC), and the author expresses their sincere thanks to Prof. K. V. R. Murthy garu to provide Lab facility in M.S. University, Baroda. Also very much thankful to the Principal and management of the Bapatla College of Arts & Sciences, Bapatla for continuous encouragement during this project work.

#### References

- [1] T. Jüstel, H. Nikol, C. Ronda, *Angew. Chem., Int. Ed.* (1998), 37, 3084
- [2] B. S. Jeon, G. Y. Hong, Y. K. Yoo, J. S. Yoo, *J. Electrochem. Soc.* (2001), 148, H128
- [3] Y. D. Jiang, F. Zhang, C. J. Summers, *Appl. Phys. Lett.* (1999), 74, 1677
- [4] L. van Pieterse, S. Sovarna, A. Meijerink, *J. Electrochem. Soc.*, (2000), 147, 4688
- [5] Danielson, E. Devenney, M. Giaquinta, D. M. Golden, J. H. Haushalter, R. C. McFarland, E. W. Poojary, D. M. Reaves, C. M. Weinberg, *Science*, **279** (1998), 837-839.
- [6] G. Blasse, B.C. Grabmaier, *Luminescent Materials*, Springer, New York, 1994, p. 143.
- [7] R. Sankar et al, *Journal of Electrochem. Soc.* 147 (2000) page 2773.
- [8] S.J. Chen et al, *Solid state commun* 130 (2004) page 28.
- [9] J.-C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.*, 34, 1048 (2005)
- [10] J. P. Van der Ziel, L. G. Van Uitert, *J. Appl. Phys.* **60** (1986) 4262.
- [11] S. A. Pollack, D. B. Chang, N. L. Moise, *J. Appl. Phys.* **60** (1986) 4077.
- [12] P. W. France (ed.) *Optical Fiber Lasers and Amplifiers*, CRC, Boca Raton, FL, 1991.
- [13] W. J. Park, M.K. Jung, T. Masaki, *Materials Science and Engineering B* **146** (2008) 95-98.
- [14] Jiao Hai- Yan, Wahg Yu-Hua, Zhang -Chi J. of *Inorganic Materials*, **23**,3, (2008) 471-474.
- [15] Qiao Yanmin, Zhang Xinbo, et.al. *J. of Rare earths* **27**, 2, (2009), 323-326.
- [16] Chunxiang Zhang, Wenjun Jiang, et. al. *J. of Alloys and Compounds*, **474**, (2009) 287-291.
- [17] Zambare Pradip Z. et al. *Advanced in Applied Science Research* 2011, 2(3). 520-524
- [18] Zambare P. Z., Mahajan O. H. : *Journal of Pure and Applied Physics*, 2013, **4**(7), P577-581.
- [19] Niyaz Sk, N. V. Poorchandra Rao, K. V. R. Murthy, *World J. of Chem.* **6**,2, 11), 115-117.
- [20] Zhang Chunxiang, Shi Jianshe, Yang Xujie, Lu Lude, *J. of Rare earths*, **28** (2010) 513-518.



- [21] Chang-Hsin Lu, Chang-Tao Chen, J. sol-gel sci. Technol. **43**; (2007), 179-185.
- [22] Y.D.Jiang, F.Zhang, J.Summers, Applied Physics Lett, vol.74, No.12, 22, March 1999.
- [23] Serra et al, Journal of Alloys and compounds 323-324 (2001) p.667
- [24] K.V.R. Murthy et al, J. of Luminescence, Volume 124, Issue.2, (2007), Pages 217-220.
- [25] K.V.R. Murthy et al, Radiation Protection Dosimetry (2006), Vol. 120, No. 1-4, 238-241.
- [26] Jie Li, Li Wang et al, Journal Alloys and compounds, Manuscript no JALCOM-D-10-00619
- [27] AtchyuthaRao,Ch., PoornachandraRao.V.N., Murthy,K.V.R, J.Sci. Res, 5(1),1-11,(2013)