

Photoluminescence of un-doped Sr_2CeO_4 and Eu^{3+} doped Sr_2CeO_4 phosphor

D.R.Taikar

Department of Physics
Shri Lemdeo Patil Mahavidyalaya,
Mandhal, Nagpur, India
deepak_taikar@rediffmail.com

C.P.Joshi

Department of Physics
R.K.N.E.C
Nagpur, India

S.V.Moharil

Department of Physics
P.G.T.D., Nagpur University,
Nagpur, India

Abstract— Photoluminescence studies on un-doped and Eu^{3+} doped Sr_2CeO_4 phosphor was investigated. The phosphor was prepared by conventional solid state reaction method. X-ray powder diffraction (XRD) analysis confirmed the formation of Sr_2CeO_4 . The un-doped Sr_2CeO_4 displays a broad band in its emission spectrum when excited with 254 nm, which peaks at 470 nm and is due to the energy transfer between the molecular orbital of the ligand and charge transfer state of the Ce^{4+} ion. The excitation spectrum shows a broad band which peaks at 290 nm. From the spectral properties, it is established that Sr_2CeO_4 has good potential for application as a blue phosphor in low pressure mercury vapor lamps and in TV tubes. The emission spectra of Eu^{3+} doped Sr_2CeO_4 show same emission spectra with sharp Eu^{3+} emission peaks and slight increase in the intensity.

Keywords- Photoluminescence; solid state reaction; Sr_2CeO_4 ; low pressure mercury vapor lamps

I. 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]. Danielson et al.[3] first reported blue luminescence in the relatively simple mixed oxide of the formula Sr_2CeO_4 in the SrO-CeO_2 system. Under excitation by UV light (254 nm), this compound exhibits photoluminescence due to the charge transfer mechanism, but this is not seen in SrCeO_3 or in any other Ce^{4+} containing oxidic compound with octahedral coordination. In addition, Sr_2CeO_4 was found to exhibit efficient luminescence under excitation with cathode and X-rays.

Sr_2CeO_4 phosphor has been confirmed to have an orthorhombic crystal structure with one-dimensional chains of edge-sharing $[\text{CeO}_6]$ octahedra linked by strontium ions [4]. Its luminescence was generally considered to originate from a ligand-to-metal charge transfer (LMCT) [4,5] and the quantum efficiency is high. Recently, intensive studies of the Sr_2CeO_4 host were focused on its synthesis [6], emission mechanism [7], and potential applications, such as usage in field emission displays [8]. In addition, Sr_2CeO_4 is an attractive host lattice for several lanthanide ions to produce efficient phosphors emitting a variety of colors because of efficient resonant ET from the host to lanthanide ions [6,9-12]. Sankar and Subba Rao [13] have proposed potential applications of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ in low-pressure mercury vapor lamps, high-pressure mercury vapor lamps, and TV tubes.

In this paper, synthesis and luminescence study of un-doped Sr_2CeO_4 and Eu^{3+} doped Sr_2CeO_4 phosphor reported.

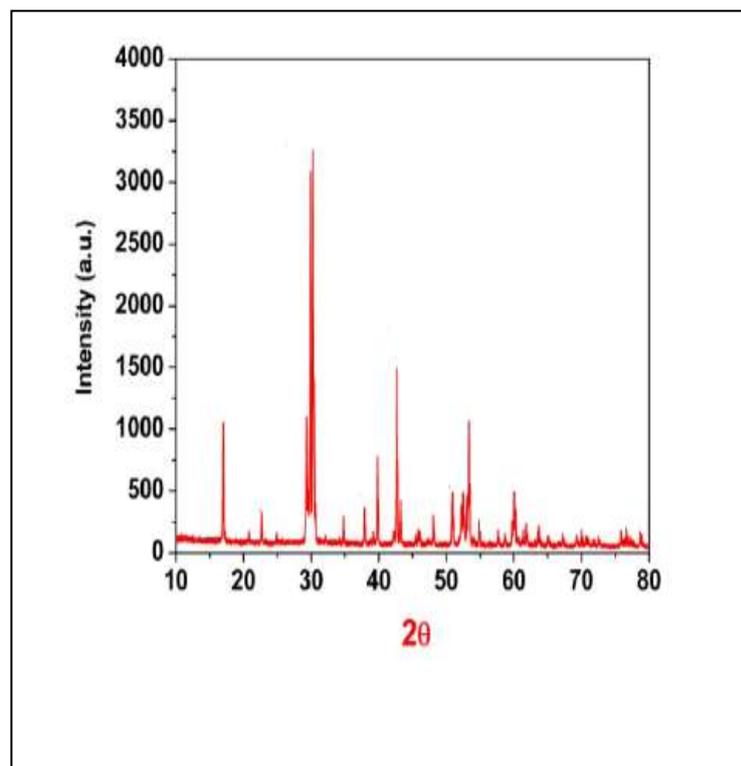
II. EXPERIMENTAL

Sr_2CeO_4 compound was synthesized by the conventional solid state reaction method. The starting materials were: SrCO_3 (of 99.5% purity, Merck Ltd.), and CeO_2 (of 99.99% purity,

Indian Rare Earths Ltd.). A stoichiometric mixture of the raw materials was ground for 45 min. to obtain a homogeneous powder and then calcined in an alumina crucible in a muffle furnace at 1000°C for 5hrs in air. Eu^{3+} doped Sr_2CeO_4 phosphor are prepared by same mentioned method. X-ray diffraction patterns were recorded on Philips PANalytical X'pert Pro diffractometer. Photoluminescence (PL) spectra in the spectral range 220-700 nm were recorded at room temperature on Hitachi F-4000 spectro-fluorimeter.

III. RESULTS AND DISCUSSION

Fig.1 shows the XRD analysis patterns of Sr_2CeO_4 phosphor. The pattern matches well with ICDD file no. 50-0115.



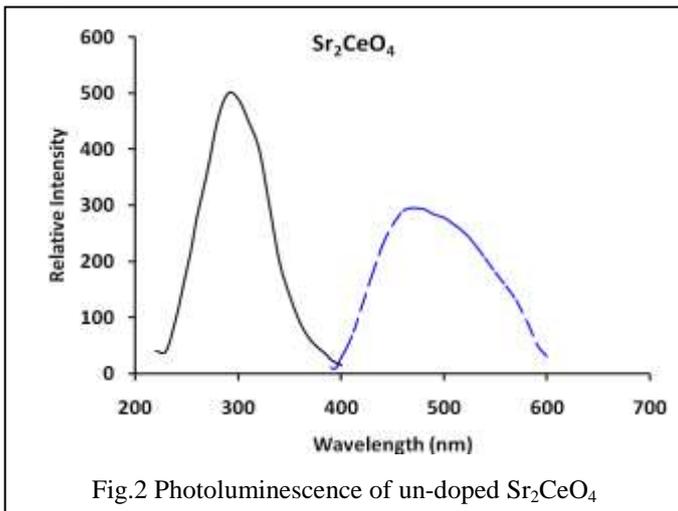


Fig.2 Photoluminescence of un-doped Sr₂CeO₄

Photoluminescence of un-doped Sr₂CeO₄

Fig 2 shows the PL excitation and emission spectra of un-doped Sr₂CeO₄ phosphor. The excitation spectrum shows a broad band ranging from 220 to 400 nm peaking around 290 nm. This band could be assigned to the transition $t_{1g} \rightarrow f$, where f is the lowest excited charge transfer state of the Ce⁴⁺ ion and t_{1g} is the molecular orbital of the surrounding ligand in six fold oxygen coordination [3,14]. This broad band is the charge transfer (CT) band of the Ce⁴⁺ ion and extends from 220-400 nm. Hence, it is possible to excite the Ce⁴⁺ ion in this lattice with 254 nm to check for its suitability for application in low pressure mercury vapour lamps. When excited with the radiation of wavelength 254 nm, Sr₂CeO₄ emits a broad band in the blue region which extends from 390-600 nm with a peak around 470 nm. This is in agreement with the results of Danielson et al.[3], and the band can be assigned to the $f \rightarrow t_{1g}$ transition of Ce⁴⁺ ion.

Photoluminescence of Sr₂CeO₄:Eu³⁺

Fig. 3 shows PL spectra of Sr₂CeO₄:Eu³⁺ (1mol%) phosphor. Eu³⁺ PL is in general weak, unless there is excitation by charge transfer or energy transfer from a sensitizer. Eu³⁺ excitation usually occurs through CT band or from host lattice absorption and energy transfer, rather than through 4f-5d absorption, though this is also possible in some solids by UV radiation in the region 200 – 250 nm. Sometimes, absorption within 4f shell also takes place as the spin and parity prohibitions are partially lifted by mixing of levels promoted by crystal field. Blasse et. al. [15-18] studied Eu³⁺ emission extensively in various hosts. In general, narrow emission bands may be observed at about 570, 590, 610, 650 and 700nm corresponding to transitions $^5D_0 \rightarrow ^7F_0, ^7F_1, ^7F_2, ^7F_3, ^7F_4$, respectively. Eu³⁺ emission usually occurs from $^5D_0 \rightarrow ^7F_j$ transitions. There are three transitions which are of prime importance $^5D_0 \rightarrow ^7F_0$ (around 570 nm), $^5D_0 \rightarrow ^7F_1$ (around 595 nm) and $^5D_0 \rightarrow ^7F_2$ (around 610 nm). The first one is strongly forbidden transition and yet observed with appreciable intensity in some hosts. $^5D_0 \rightarrow ^7F_1$ transition is forbidden as electric dipole, but allowed as magnetic dipole. This is the only transition when Eu³⁺ occupies a site coinciding with a centre of symmetry. When Eu³⁺ ion is situated at a site, which lacks the inversion symmetry, then the transitions corresponding to even values of J (except 0) are electric dipole allowed and red emission can be observed. $^5D_0 \rightarrow ^7F_1$ transition

can also be observed as magnetic dipole allowed transition. Further, all the lines corresponding to these transitions split into number of components decided by the local symmetry [19]. The spectra are also sensitive to sizes of cations [20] and chemical bonding [21].

The excitation spectra is very much similar to un-doped Sr₂CeO₄ excitation spectra, except some small sharp peak attributed to f-f transition are present. The strongest of these around 395 nm corresponds to $^7F_0 \rightarrow ^5L_6$ transition. The emission spectra of Eu³⁺ doped Sr₂CeO₄ phosphor shows broad band emission originates from Sr₂CeO₄ host itself and Eu³⁺ ion. It consists of some sharp lines around 570, 588, 594, 615, and 626 nm. 570 nm emission line is due to $^5D_0 \rightarrow ^7F_0$ transition, 588 nm and 594 nm emission lines are attributed to $^5D_0 \rightarrow ^7F_1$ transition, which is forbidden as electric dipole but allowed as a magnetic dipole. This is the only transition when Eu³⁺ occupies a site coinciding with a centre of symmetry. The 615 nm and 626 nm emission lines are attributed to $^5D_0 \rightarrow ^7F_2$ transition, which is allowed as electric dipole. In addition to these a small emission peak at 655 nm attributed to $^5D_1 \rightarrow ^7F_5$ transition.

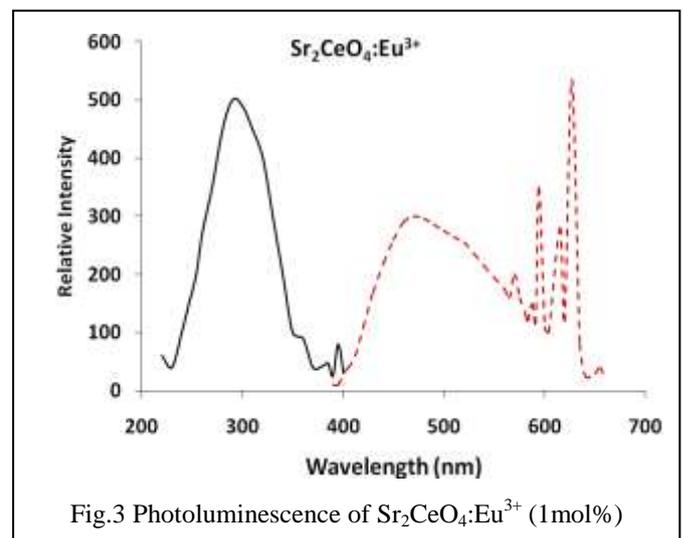


Fig.3 Photoluminescence of Sr₂CeO₄:Eu³⁺ (1mol%)

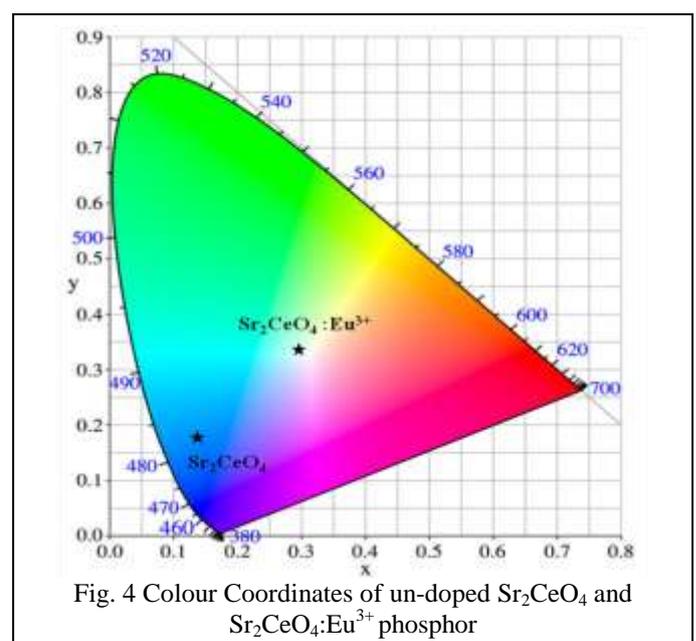


Fig. 4 Colour Coordinates of un-doped Sr₂CeO₄ and Sr₂CeO₄:Eu³⁺ phosphor

Fig.4 shows colour coordinates of un-doped Sr_2CeO_4 and $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ phosphors. Un-doped Sr_2CeO_4 gives blue colour light having coordinates are $x= 0.135$ and $y=0.18$, whereas $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ phosphor gives nearly white colour having colour coordinates $x=0.295$ and $y= 0.33$ as shown in fig.4.

IV. CONCLUSION

Un-doped and Eu^{3+} doped Sr_2CeO_4 phosphor was successfully prepared by conventional solid state reaction method. X-ray powder diffraction (XRD) analysis confirmed the formation of Sr_2CeO_4 compound. The un-doped Sr_2CeO_4 displays a broad band in its emission spectrum when excited with 254 nm, which peaks at 470 nm and is due to the energy transfer between the molecular orbital of the ligand and charge transfer state of the Ce^{4+} ion. The excitation spectrum shows a broad band which peaks at 290 nm. From the spectral properties, it is established that Sr_2CeO_4 has good potential for application as a blue phosphor in low pressure mercury vapor lamps and in TV tubes. The emission spectra of Eu^{3+} doped Sr_2CeO_4 shows broad band emission originates from Sr_2CeO_4 host itself and Eu^{3+} ion. The sharp Eu^{3+} emission peaks corresponding ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ and ${}^5\text{D}_1 \rightarrow {}^7\text{F}_j$ transition of Eu^{3+} ion which exhibit white light as indicated in colour coordinate diagram.

REFERENCES

- [1] Y. H. Wang, Z. Y. Wang, P.Y. Zhang, Z.L. Hong, X.P.Fan, "Preparation of Eu^{2+} and Dy^{3+} co-activated $\text{CaAl}_2\text{Si}_2\text{O}_8$ -based phosphor and its optical properties," *Mater.Lett.*, vol. 58, pp.3308, 2004.
- [2] C. Feldmann, T. Jüstel, C. R. Ronda, P. J. Schmidt, "Inorganic luminescent materials: 100 Years of research and application," *Adv. Funct. Material*, vol. 13, pp. 511, 2003
- [3] E. Danielson, M. Devenney, D. M. Giaquinta, J. H. Golden, R. C. Haushalter, and X. D. Wu, "X-ray powder structure of Sr_2CeO_4 : a new luminescent material discovered by combinatorial chemistry," *J. Mol. Struct.*, vol. 470, pp. 229, 1998.
- [4] E. Danielson, M. Devenney, D. M. Giaquinta, J. H. Golden, R. C. Haushalter, and X. D. Wu, "A rare-earth phosphor containing one-dimensional chains identified through combinatorial methods," *Science* vol. 279, pp. 837, 1998.
- [5] L. van Pieterse, S. Sovarna, and A. Meijerink, "On the Nature of the Luminescence of Sr_2CeO_4 ," *J. Electrochem. Soc.*, vol.147, pp. 4688, 2000.
- [6] Y. D. Jiang, F. L. Zhang, C. J. Summers, and Z. L. Wang, "Synthesis and properties of Sr_2CeO_4 blue emission powder phosphor for field emission displays," *Appl. Phys. Lett.*, vol. 74, pp. 1677, 1999.
- [7] C. H. Lu and C. T. Chen, "Luminescent characteristics and microstructures of Sr_2CeO_4 phosphors prepared via sol-gel and solid-state reaction routes," *J. Sol-Gel Sci. Technol.*, vol. 43, pp.179, 2007.
- [8] A. Nag and T. R. N. Kutty, "Photoluminescence of $\text{Sr}_{2-x}\text{Ln}_x\text{CeO}_{4+x/2}$ ($\text{Ln} = \text{Eu, Sm or Yb}$) prepared by a wet chemical method," *J. Mater. Chem.*, vol. 13, pp. 370, 2003.
- [9] L. L. Shi, C. Y. Li, and Q. Su, *Opt. Lett.*, vol. 36, pp. 582, 2011.
- [10] O. Viagin, A. Masalov, I. Ganina, and Y. Malyukin, "Mechanism of energy transfer in $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ phosphor," *Opt.Mater.*, vol. 31, pp. 1808, 2009.
- [11] N. Rakov, R. B. Guimaraes, and G. S. Maciel, "Strong infrared-to-visible frequency upconversion in Er^{3+} -doped Sr_2CeO_4 powders," *J. Lumin.*, vol. 131, pp. 342, 2011.
- [12] T. Hirai and Y. Kawamura, "Preparation of Sr_2CeO_4 blue phosphor particles and rare earth (Eu, Ho, Tm, or Er)-doped Sr_2CeO_4 phosphor particles, using an emulsion liquid membrane system," *J. Phys. Chem. B*, vol. 108, pp. 12763, 2004.
- [13] R. Sankar and G. V. Subba Rao, "Eu³⁺ Luminescence, Ce⁴⁺ → Eu³⁺ Energy Transfer, and White-Red Light Generation in Sr_2CeO_4 ," *J. Electrochem. Soc.*, vol. 147, pp.2773, 2000.
- [14] H. E. Hoefdraad, "Charge-transfer spectra of tetravalent lanthanide ions in oxides," *J. Inorg. Nucl. Chem.*, vol. 37, pp. 1917, 1975.
- [15] G. Blasse, "On the Eu³⁺ Fluorescence of Mixed Oxides. IV. The Photoluminescence Efficiency of Eu³⁺-Activated Oxides," *J. Chem. Phys.*, vol. 45, pp. 2356 1966.
- [16] G. Blasse, "On the Eu³⁺ Fluorescence of Mixed Oxides. III. Energy Transfer in Eu³⁺ Activated Tungstates and Molybdates of Type Ln_2WO_6 and Ln_2MoO_6 ," *J. Chem. Phys.*, vol. 45, pp. 2350, 1966.
- [17] G. Blasse, J. De Vries, "On the Eu³⁺ Fluorescence of Mixed Metal Oxides," *J. Electrochem. Soc.*, vol. 114, pp. 875, 1967.
- [18] G. Blasse, A. Brill, W. C. Nieuport, "On the Eu³⁺ fluorescence in mixed metal oxides part I-the crystal structure sensitivity of the intensity ratio of electric and magnetic dipole emission," *J. Phys. Chem. Solids*, vol. 27, pp. 1587, 1966.
- [19] G. Blasse, A. Brill, "Fast phosphors for colour television," *Tech. Rev.*, vol. 31, pp. 304, 1970.
- [20] C. G. Van Uitert, R. R. Soden, "Influence of ion size upon the intensity of Eu³⁺ fluorescence in the tungstates," *J. Chem. Phys.*, vol. 36, pp. 517, 1962.
- [21] G. Blasse, "The Eu³⁺ luminescence as a measure for chemical bond differences in solids," *Chem. Phys. Lett.*, vol. 20, pp. 573, 1973.