



## Effect of Flux on (Dy<sup>3+</sup>) Photoluminescence Behaviour in Sr<sub>2</sub>CeO<sub>4</sub> Phosphor

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This paper reports the studies on the Role of flux on Photoluminescence (un-doped and Dy doped) behavior in Sr<sub>2</sub>CeO<sub>4</sub> phosphors prepared by standard solid-state reaction method. The luminescence spectra of both have been measured to examine the influence of the flux on intensity of yellow emission. Additionally, The luminescence spectrum of Sr<sub>2</sub>CeO<sub>4</sub>: Dy<sup>3+</sup> phosphors, characteristic lines of Dy<sup>3+</sup> have been observed. This result indicates that there also exists energy transfer process between Sr<sub>2</sub>CeO<sub>4</sub> and Dy<sup>3+</sup>.

**Keywords**— Photoluminescence; Solid state reaction method; Phosphor; flux.

### INTRODUCTION

Rare-earth doped matrices have many optical properties because of their special electronic transition among 4f energy levels [1]. Powder phosphors doped with Dy<sup>3+</sup> are of particular importance for observing yellow color images on the monitors of CRD, TV, and other related electronic devices; hence research on the production and characteristics of these inorganic compounds doped with Dysprosium ions was extensively increased [2–7]. In 1998, Danielson et al. [8] synthesized a new rare-earth luminescent material Sr<sub>2</sub>CeO<sub>4</sub>, possessing one-dimensional chain structure of edge-sharing CeO<sub>6</sub> octahedron, studied its optical properties, and determined that the emission of Sr<sub>2</sub>CeO<sub>4</sub> displays a broad band with a peak position at 475 nm, which can be ascribed to the charge-transfer transition Ce<sup>4+</sup>–O<sup>2-</sup>. Since then, lots of scientists took great interest in studying the special structure and fluorescent properties of this novel material [9–19].

Due to its broad emission band Sr<sub>2</sub>CeO<sub>4</sub> can be used as the matrix material, which may provide a new method to search for future attracting luminescence hybrids. According to the literatures, the luminescence properties of rare-earth doped Sr<sub>2</sub>CeO<sub>4</sub> have been affected by energy transfer from the triplet excited state of the metal to ligand charge transfer (MLCT) state for Sr<sub>2</sub>CeO<sub>4</sub> to the rare-earth ions [20–23]. Several methods have been employed in the synthesis of rare-earth ion doped Sr<sub>2</sub>CeO<sub>4</sub> phosphors, such as the conventional high-temperature solid-state method, chemical co-precipitation, citrate–gel method, and ultrasonic spray pyrolysis technique [8, 13, 16, 24–26].

It is well known that phosphor particles of the morphology and narrow particle size distribution with maximum in the sub-micrometer size give higher packing densities than commercial products, which are usually a few micrometers in size and are fabricated by solid-state reaction method. Thus, the smaller size enhances the overall luminescence [27]. This synthesis route is very easy and does not require expensive as well as sophisticated equipments. Solid-state reaction method (SSR) is recommended as a promising method for preparing phosphor particles to achieve good homogeneity and uniform morphology with fine particle size distribution, and non-aggregation characteristics [28]. 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.

In the present work, un-doped and Dy doped  $\text{Sr}_2\text{CeO}_4$  with different fluxes of powder phosphors were prepared by standard solid-state reaction method. XRD, SEM, photoluminescence (PL) excitation and emission, Thermoluminescence (TL) properties and CIE-co-ordinates (1931- chart) of un-doped and Dy doped  $\text{Sr}_2\text{CeO}_4$  phosphors have been investigated on the prepared samples.

## **EXPERIMENTAL DETAILS**

Analytical grade Strontium nitrate [ $\text{Sr}(\text{NO}_3)_2$ ], Cerium oxide ( $\text{CeO}_2$ ) and Dysprosium oxide ( $\text{Dy}_2\text{O}_3$ ) of assay 99.9% were used as starting materials. All the phosphor samples are prepared via solid state reaction method (SSR). First we prepared un-doped  $\text{Sr}_2\text{CeO}_4$  phosphor by weighing, mixing inorganic salts, Strontium nitrate [ $\text{Sr}(\text{NO}_3)_2$ ], Cerium oxide [ $\text{CeO}_2$ ] in 2:1 molar ratio. We ground into fine powder using agate mortar and pestle about an hour. Different fluxes like as Urea ( $\text{NH}_2\text{CONH}_2$ ) (Qualigens fine chemicals; A division of GLAXO pharmaceuticals, Mumbai- 400030, Product No. 22585, Assay (99.9%), Glycin ( $\text{NH}_2\text{CH}_2\text{COOH}$ ) (Made in Germany; E. Merck, Darmstadt. Assay (99.95%) and Citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) (Qualigens fine chemicals-Mumbai) are added with 10wt% and stirred for 5min. The samples were fired at  $1200^\circ\text{C}$  for 3 hours with a heating rate of  $5^\circ\text{C}/\text{min}$  in a muffle furnace by keeping in an alumina crucible closed with lid. After heating at  $1200^\circ\text{C}$  and cooling to room temperature in the furnace, the sample appears in light cream colour as well as very smooth and looks like pulpy. All the samples were again ground to make in to fine powder.

The prepared phosphor powders were characterized via a scanning electron microscope (PHILIPS XL 30 CP) was used to examine the morphology of the samples at 20kv. Photoluminescence (PL) emission and excitation spectra taken with Spectrofluorophotometer (SHIMADZU, RF-5301 PC) using Xenon lamp as excitation source with both excitation and emission slit width of 1.5nm, at room temperature. Thermoluminescence study (TLD 1006) and Radiant Imaging colour calculations (CIE- 1931 colour) chart analysis were also done on prepared phosphors.

## **RESULTS AND DISCUSSION**

### **XRD Study**

The crystal structure, phase and the crystallite size were studied by means of X-ray diffraction technique. Fig.1 shows the XRD patterns of Dy doped  $\text{Sr}_2\text{CeO}_4$  phosphor with and with out fluxes. The peaks were indexed to the orthorhombic structure corresponding to ICDD Card (89-5546), [29]. The powders derived from the solid-state reaction method was heated at  $1200^\circ\text{C}$  in air for 3hrs shows the starting materials disappeared completely and  $\text{Sr}_2\text{CeO}_4$  was formed as the predominant product. Except this, no other phase exists in the XRD spectra, indicating the formation of the final product. In addition, the refined

crystallographic unit cell parameters were obtained and are listed in table- 1. These values are compared with ICDD and Li et al. [30]. The calculated average crystallite size of Dy doped is ~10nm. When compared with ICDD and other workers, the reduction in unit cell volume was observed and confirms the formation of nano crystallite phosphor, via solid-state method. From the XRD patterns it is observed that by adding different fluxes there is no change in the peaks position except intensities that means keeping the same structure and phase, it may be temperature conditions are in sufficient for preparing phosphor, via solid-state method.

**Table 1**

Crystal name	a (Å)	b (Å)	c (Å)	Cell volume (Å <sup>3</sup> )
ICDD No. 89-5546 [29]	6.119	10.350	3.597	227.79
Our sample	5.964	8.279	4.472	220.81
Li et al [30]	6.1153	10.3473	3.5957	227.52

### SEM Analysis

Figure-2 (A, B, C and D) shows the SEM images of Sr<sub>2</sub>CeO<sub>4</sub>: Dy (0.5mol %) with and with out fluxes. From the SEM images the morphology of the phosphors is changing according to the flux. In the case of with out flux the crystals are highly agglomerated with irregular shape. As the fluxes were added, the agglomeration is decreased by keeping irregular shape.

### Photoluminescence Study

Fig.3 shows the PL Excitation spectrum of un-doped and Dy doped Sr<sub>2</sub>CeO<sub>4</sub> monitored under 400nm wave length. It is observed that the excitation spectrum in the case of un-doped phosphor is broad one having peaks at 250 and a hump at 270nm which is attributed to the Ce<sup>4+</sup>- O distances in the lattice [31]. Where as in the case of Dy doped phosphor, the same excitation spectrum is observed with out hump and with less intensity. The phosphors are having different absorptions but the corresponding emission is high only under 270nm excitation.

Fig.4 shows the Emission Spectrum of un-doped Sr<sub>2</sub>CeO<sub>4</sub> with different fluxes under 270nm excitation. The phosphor shows broad band emission from 350 – 650nm with a peak at 470nm. The CT band can be assigned to the f→t<sub>1g</sub> transitions of Ce<sup>4+</sup> ions. It is observed that the emission under different fluxes, the phosphor with citric acid as flux shows high intensity when compared with others. The order of emission is as follows (Citric acid > Urea > Glycin > with out flux).

Fig.5 shows the emission spectrum of Dy (0.5mol %) doped Sr<sub>2</sub>CeO<sub>4</sub> phosphor with different fluxes under 270nm excitation. It is observed that the Dy (0.5mol %) concentration with citric acid as flux shows high intensity at 476 and 575nm. These peaks were well resolved and depicted in the spectra is from the transitions <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>15/2</sub>, <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub> in Dy<sup>3+</sup> respectively the results indicates the presence of energy transfer from the triplet excited state of the MLCT state for Sr<sub>2</sub>CeO<sub>4</sub> (sensitizer) to Dy<sup>3+</sup> (activator). These may be assigned to the transitions from <sup>4</sup>F<sub>9/2</sub>→<sup>4</sup>H<sub>15/2</sub>. When the dominating lines are from the <sup>6</sup>H<sub>13/2</sub> (575nm) transitions, then in this condition ΔJ = 2, so it is hypersensitive transition, hence we can say that the host lattice is hypersensitive [1]. This visible transition of dysprosium in the yellow region makes it an important material for technological applications, which require yellow light as emission. Therefore, it is possible that we can prepare a novel phosphor Sr<sub>2</sub>CeO<sub>4</sub>: Dy<sup>3+</sup> with different fluxes obtained from the SSR

method for emitting the pure blue and yellow luminescence in a single-host lattice, which can be provide important application in the field of luminescent materials.

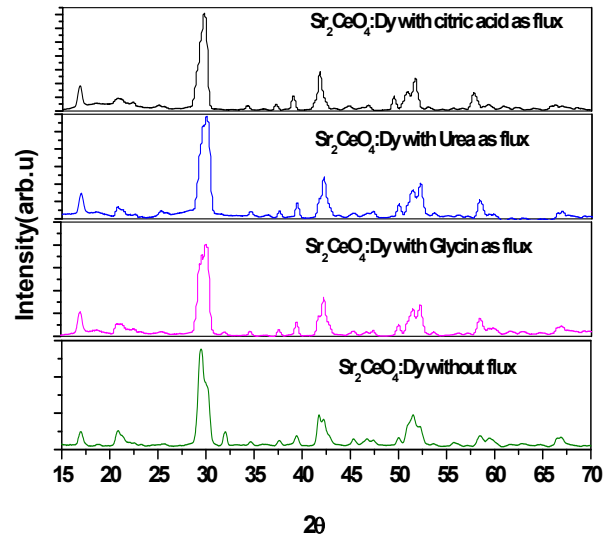
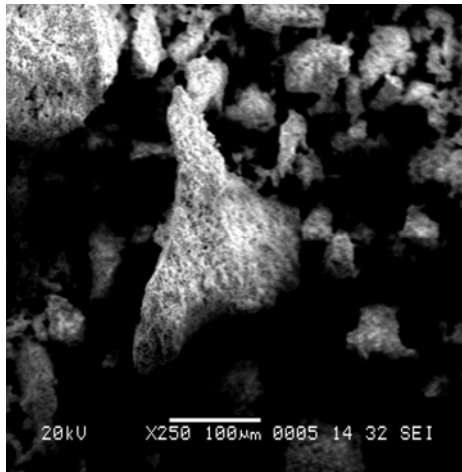
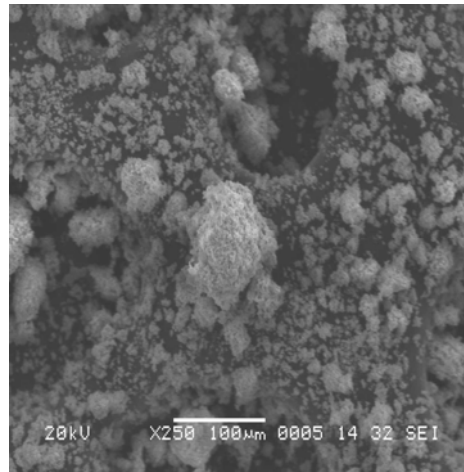


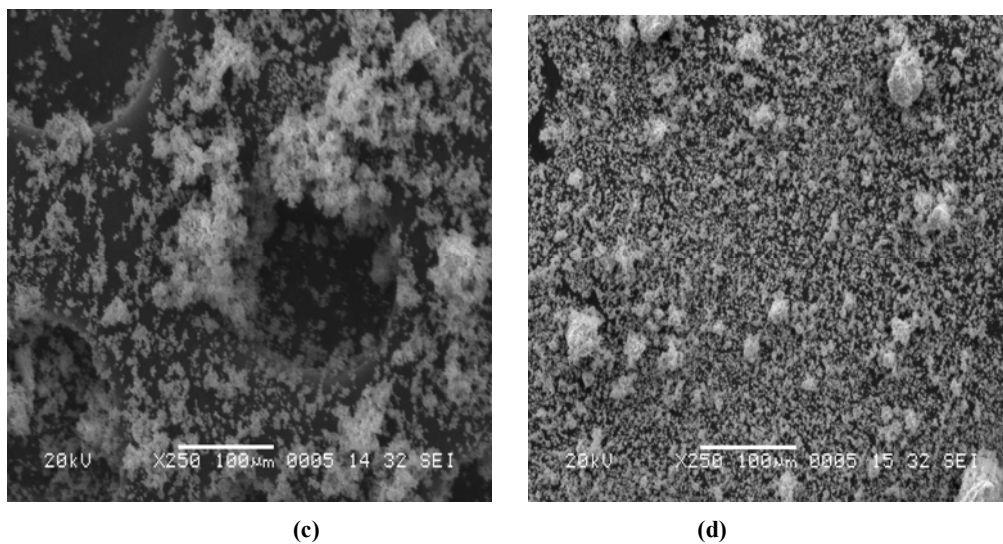
Fig. 1: XRD Pattern of  $\text{Sr}_2\text{CeO}_4:\text{Dy}$  with and with out fluxes



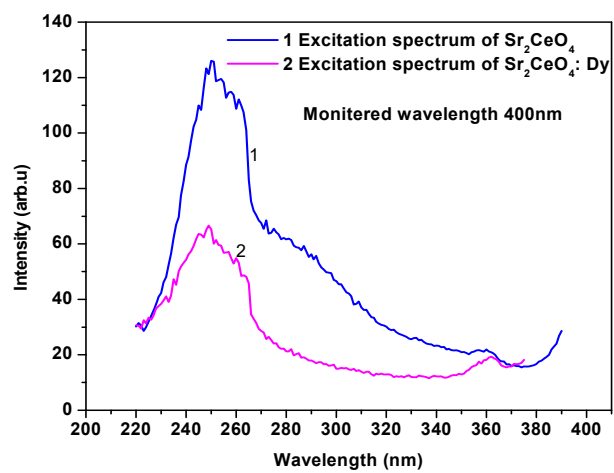
(a)



(b)



**Fig.2: SEM images of  $Sr_2CeO_4$ : Dy with and with out fluxes**  
(a) Dy doped  $Sr_2CeO_4$  (b) Dy doped  $Sr_2CeO_4$  with Urea as flux (c) Dy doped  $Sr_2CeO_4$  with Glycin as flux  
(d) Dy doped  $Sr_2CeO_4$  with Citric acid as flux



**Fig. 3: Excitation spectrum of un-doped and dy doped  $Sr_2CeO_4$**

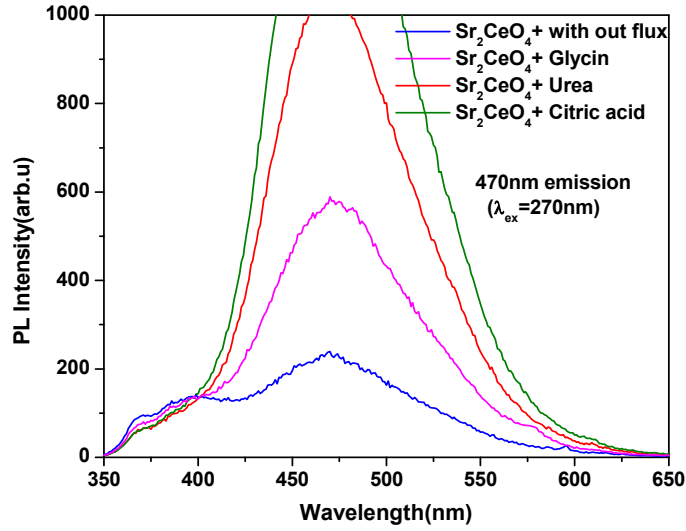


Fig. 4: Emission Spectrum of un-doped  $\text{Sr}_2\text{CeO}_4$  with different fluxes under 270nm excitation

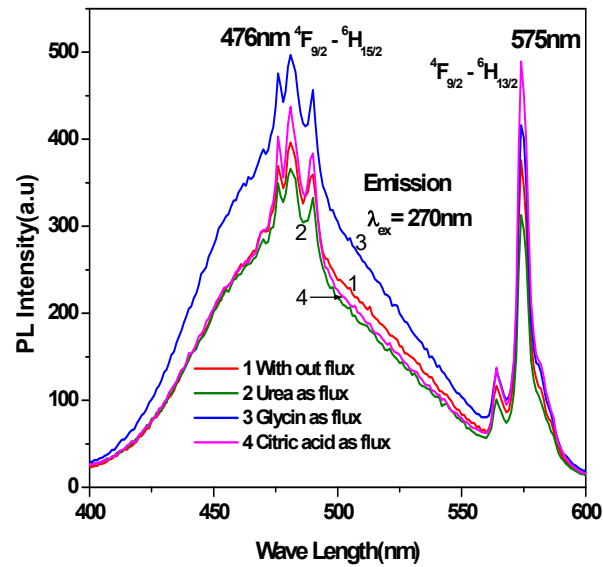


Fig. 5: Emission Spectrum of Dy(0.5%) doped  $\text{Sr}_2\text{CeO}_4$  With different fluxes under 270nm excitation

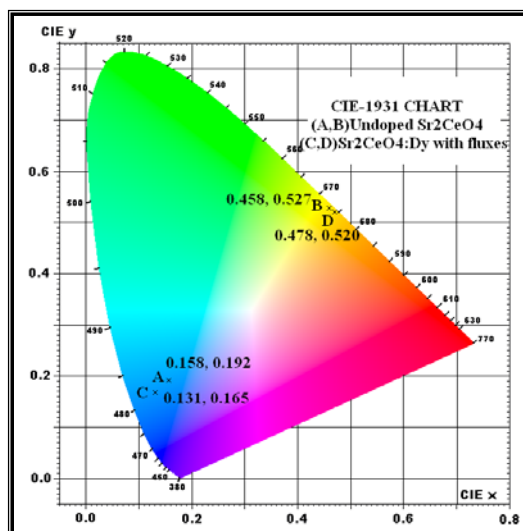


Fig. 6: CIE Co-ordinates of Un-doped and  $Sr_2CeO_4:Dy$  (0.5%) with fluxes depicted on 1931

### Thermoluminescence Study

Thermoluminescence (TL) of prepared phosphor was studied using the equipment described by Murthy et al [32]. 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 heating conditions is sufficient in the formed compounds are in nano crystallite size form. During heating process,  $Sr_2CeO_4$  tends to thermally decompose at elevated temperatures.

### CIE Coordinates

The CIE co-ordinates of (chart -1931) were calculated by the Spectrophotometric method using the spectral energy distribution of un-doped  $Sr_2CeO_4$  and Dy (0.5%) doped  $Sr_2CeO_4$  with fluxes samples are shown in fig.6. The colour co-ordinates for the A, B are un-doped  $Sr_2CeO_4$  samples are (A)  $x = 0.158$  and  $y = 0.192$ , (B)  $x = 0.458$  and  $y = 0.527$  and C, D are Dy (0.5%) doped  $Sr_2CeO_4$  with fluxes samples are (C)  $x = 0.131$  and  $y = 0.165$ , (D)  $x = 0.478$  and  $y = 0.520$

### CONCLUSIONS

The synthesis and luminescent properties of  $Sr_2CeO_4$  were explored in this study, and these results can serve to provide better understanding for preparing  $Sr_2CeO_4$  with high luminescent intensity and for its future application in luminescence devices. By studying the optical properties of  $Dy^{3+}$ -doped  $Sr_2CeO_4$  phosphor powder with different fluxes is good PL intensity, we found that the emission transitions of  ${}^4f_{9/2} \rightarrow {}^6H_{15/2}$  and  ${}^4f_{9/2} \rightarrow {}^6H_{13/2}$  intensity was the strongest among the main lines and the emission was observed due to exists energy transfer process between  $Sr_2CeO_4$  and  $Dy^{3+}$ , which can provides an opportunity to find a novel phosphor for emitting blue & yellow luminescence in a single host. According to the CIE coordinates, the addition of Dy (0.5%) ions to  $Sr_2CeO_4$  exhibit excellent yellow emission,

which can be useful in many technological display devices. It is concluded that the citric acid plays a major role in formation of un-doped and Dy doped  $\text{Sr}_2\text{CeO}_4$  phosphor.

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## **REFERENCES**

- [1] G. Blasse, B.C. Grabmaier, *Luminescent Materials*, Springer, Berlin, 1994.
- [2] U. Rambabu, T. Balaji, S. Baddhudu, *Mater. Res. Bull.* 30 (1995) 891
- [3] U. Rambabu, D.P. Amalnerkar, B.B. Kale, S. Budduhu, *Mater. Res. Bull.* 35 (2000) 929
- [4] M. Haase, K. Riwozki, H. Meyssamy, A. Kornowski, *J. Alloy Compd.* 303 (2000) 191
- [5] A. Huignard, T. Gacoin, J.P. Boilot, *Chem. Mater.* 12 (2000) 1090
- [6] M.G. Kwak, J.H. Park, S.H. Shon, *Solid State Commun* 130 (2004) 199
- [7] B. Yan, L. Zhou, *J. Alloys Compd.* 372 (2004) 238
- [8] E. Danielson, M. Devenney, D.M. Giaquinta, J.H. Golden, R.C. Haushalter, E.W. McFarland, D.M. Poojary, C.M. Reaves, W.H. Weinberg, X.D. Wu, *J. Mol. Struct.* 470 (1998) 229
- [9] G.Y. Hong, L. Zhang, X.L. Sun, *Chin. J. Lumin.* 4 (2002) 381
- [10] X.H. Chuai, H.J. Zhang, F.S. Li, G.Z. Zhou, *Chin. J. Inorg. Chem.* 5 (2003) 463
- [11] M. Yu, J. Lin, Y.H. Zhou, M.L. Pang, X.M. Han, S.B. Wang, *Chin. J. Lumin.* 1 (2003) 91
- [12] X.B. Yu, X.H. He, S.P. Yang, X.F. Yang, X.L. Xu, *Mater Lett* 58 (2003) 48
- [13] E. Danielson, M. Devenney, D.M. Giaquinta, J.H. Golden, *Science* 279 (1998) 837.
- [14] C.H. Park, C.H. Kim, C.H. Pyun, J.H. Choy, *J. Lumin* 87 (2000) 1062
- [15] A. Huignard, V. Buissette, A.C. Franville, J.P. Boilot, *J. Phys. Chem. B* 107(2003) 6754
- [16] Y.D. Jiang, F. Zhang, J. Christopher, *Appl. Phys. Lett.* 72 (1999) 1677
- [17] Y.E. Lee, D.P. Nortor, J.D. Dudai, *Appl. Phys. Lett.* 77 (2000) 678
- [18] Y.X. Tang, H.P. Guo, Q.Z. Qin, *Solid State Commun.* 121 (2002) 351
- [19] P.V. Pieterston, S. Soverna, A. Meijerink, *J. Electrochem. Soc.* 147 (2000) 4688
- [20] T. Hirai, Y. Kawamura, *J. Phys. Chem. B* 109 (2005) 5569
- [21] A. Nag, T.R. Narayanan Kutty, *J. Mater. Chem.* 13 (2003) 370
- [22] R. Sankar, G.V. Subba Rao, *J. Electrochem. Soc.* 147 (2000) 2773
- [23] T. Hirai, Y. Kawamura, *J. Phys. Chem. B* 108 (2004) 12763
- [24] L. Van Pieterston, *J. Electrochem. Soc.* 147 (2000) 4688
- [25] T. Masui, et al., *Mater. Res. Bull.* 38 (2003) 17
- [26] M.-J. Kang, et al., *J. Mater Sci.* 37 (2002) 2721
- [27] T. Masui, T. Chiga, N. Imanaka, G.Y. Adachi, *Mater. Res. Bull.* 38 (2003) 17
- [28] Y.C. Kang, E.J. Kim, D.Y. Lee, H.D. Park, *J. Alloys Compounds* 347 (2002) 266
- [29] ICDD Powder Diffraction, Card No.89-5546
- [30] Li, L. et.al *Chemical physics Letters* 453 (2008) 283-289.
- [31] Nag, A, Kutty TRN (2003) *J. Mater Chem* 13:370
- [32] K.V.R. Murthy et al, *Journal of Luminescence*, Vol.124, Issue 2, (2007), Pages 217-220