Synthesis of Sr_2CeO_4: Eu^{3+} Phosphor and Characterization
A Candidate of white LED Phosphor

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Abstract

The photoluminescence (PL) spectra of Sr_2CeO_4 and Eu^{3+} ion doped Sr_2CeO_4 with different concentrations (0.1%, 0.5%, 1.0%, 1.5%, and 2.0%) are reported. The powder phosphors have been synthesized using a conventional solid state reaction method using inorganic materials like Strontium Carbonate ($SrCO_3$), Cerium Oxide (CeO_2) and Europium Oxide (Eu_2O_3). XRD, SEM, Photoluminescence (PL) spectra, TL and CIE techniques were used to investigate the formation process, crystal structure, phase, morphology and luminescent properties of the synthesized phosphors. From the XRD analysis it was found that the prepared phosphor is mostly in single phase of Sr_2CeO_4 with an orthorhombic structure. From XRD data by using the Scherer's formula the calculated mean crystallite size of Sr_2CeO_4 and Eu (0.5%) doped Sr_2CeO_4 is 28, 31nm respectively. The photoluminescence spectra were recorded at room temperature under different excitations. The Sr_2CeO_4 shows broad emission peak observed at 467nm and emission peaks of Sr_2CeO_4:Eu^{3+} of different concentrations were observed around 467, 490, 512, 537, 556, 587 and 616nm. Emission intensity is high for Eu (0.5%) under 280nm excitation.

Keywords: Ceramics, Chemical synthesis, X-ray diffraction, Photoluminescence

1. INTRODUCTION

Nowadays a great attention is paid to the research and development in the field of lighting technology in relation to the global problem of saving energy. One of the rapidly developing technologies is based on using very efficient light emitting diodes [LED] in light sources for general lighting. There has been much interest in light emitting diodes (LEDs) with emission wavelengths in the ultraviolet to infrared range. Major developments in wide band gap III-V nitride compound semiconductors have led to the commercial production of high efficiency LEDs [1-3]. Traditional colored LEDs have proven effective in signal applications, as indicator lights, and in automotive lightning. The development of white LEDs as a cost-competitive, energy-efficient alternative to conventional electrical lightning is very important for expanding LED applications toward general white lightning [4-8]. The first reported white light LEDs were based on blue InGaN technology, which uses a combination of blue emission from a blue LED and yellow emission from $Y_3Al_5O_{12}$: Ce. However, these two-band white LEDs suffer from limited color rendering and color temperature, and are unable to produce all nature-equivalent colors, especially in the red region. To improve the color temperatures and the rendering index of phosphor-converted white LEDs, various phosphors with different components of $(Y_{1-x}Gd_x)_3(Al_{1-y}Ga_y)_5O_{12}$:Ce have been developed. Another type of phosphor-combined white LED uses a blue chip as a pump source with a blend of a green and a red phosphor to generate high-quality white light.

The luminescence associated with Eu^{3+} contained in different host lattices has found applications related to its red light emission which is important in the fields of displays, sensors, lasers and LEDs. The past few decades have seen a lot of work reported on the use of divalent/trivalent europium as a dopant in phosphors, as they have very good optical properties in the blue to red regions which make them part of many display devices. Among all the rare-earth ions, Eu^{3+} is the most extensively studied owing to the simplicity of its spectra and also its use in commercial red phosphors. The luminescence spectrum of Eu^{3+} reveals spectroscopic transitions from the visible to the near-infrared region. Sr_2CeO_4 and Sr_2CeO_4:Eu^{3+} phosphor samples were prepared by the solid state

reaction. Phase identification of all the samples were carried out by X-ray powder diffraction.

2. MATERIALS AND METHODS

Sr_2CeO_4 and Sr_2CeO_4:Eu^{3+} phosphor samples were prepared by the conventional solid state reaction method. Strontium carbonate $SrCO_3$ and Cerium Oxide CeO_2 of high purity chemicals were used as starting materials by added them in stoichiometric proportions of Sr:Ce as 2:1. The compound obtained was grounded into a fine powder and fired at 1200°C for 3 hours in a muffle furnace with a heating rate of 5°C/min. The obtained powders were characterized by means of scanning electron microscopy (CP 30 Philips) and powder X-ray diffraction (XRD, Rigaku-D/max 2500 and Cu Kα radiation). The emission and excitation spectra were recorded at room temperature using Spectrofluorophotometer (SHIMADZU, RF-5301 PC) using Xenon lamp as excitation source.

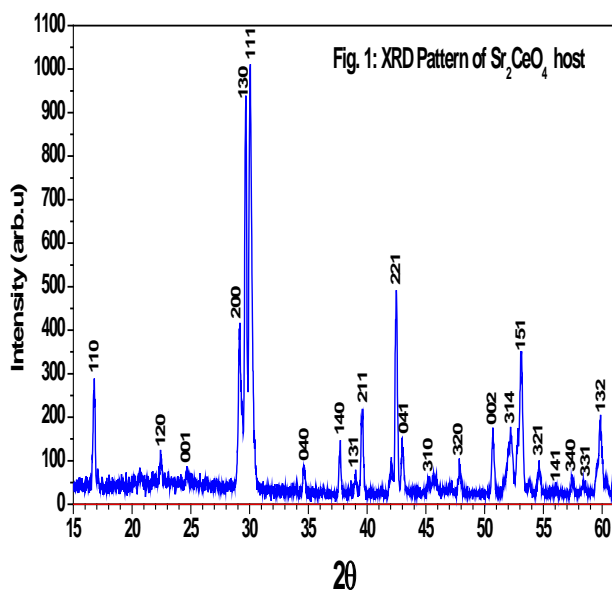## 3. RESULTS AND DISCUSSION
3.1 XRD Analysis:

Fig. 1: XRD pattern of Sr_2CeO_4

In order to determine the crystal structure, phase purity, chemical nature and homogeneity of the Sr_2CeO_4 phosphor, X-ray diffraction analysis was carried out. Figure-1 shows the XRD pattern of Sr_2CeO_4 host. The XRD pattern of Sr_2CeO_4:Eu^{3+} (0.5%) shows the same pattern with less intensity. From the XRD pattern analysis it was found that there is a prominent phase of Sr_2CeO_4 and well matched with the JCPDS card No 050-0115. This reveals that the

structure of Sr_2CeO_4 is Orthorhombic with a space group of Pbam 55, which agrees with the findings of previous research works of Danielson et al [9], Sankar et al [10] and Shu-Jian Chen et al [11]. The calculated lattice parameters are a = 6.094 Å, b = 10.232 Å, c = 3.566 Å, and volume V = a*b*c = 6.094*10.232*3.566 = 222.354 Å³. The crystallite size was determined using the Scherrer equation D = kλ /β cos θ, where k the constant (0.94), λ the wavelength of the X-ray (0.154 nm or 1.54 Å), β the full-width at half maxima (FWHM) and θ the Bragg angle of the XRD peak (1,1,1). From XRD data by using the Scherer's formula the calculated mean crystallite size of Sr_2CeO_4 and Eu (0.5%) doped Sr_2CeO_4 is 28, 31nm respectively.

3.2 SEM Analysis

SEM images for Sr_2CeO_4 particles obtained by solid state reaction at 1200⁰C the particles accelerated aggregation and sintering of the particles. Figure-2 shows the SEM micrograph of the pure Sr_2CeO_4 phosphor. The microstructure appears to consist of ellipsoidal flakes type particulates having an average basal diameter of ~450nm and a length of ~2µm.
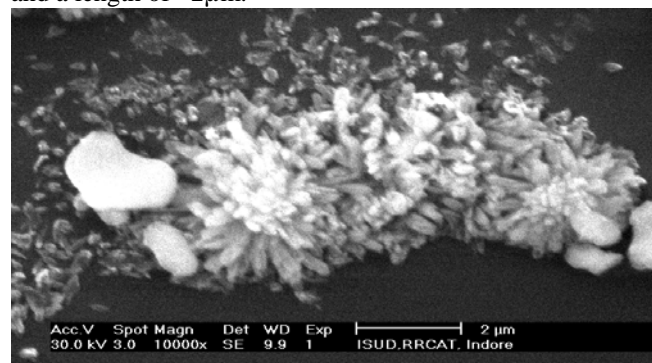
3.3 Photoluminescence Analysis

The excitation spectra of Sr_2CeO_4 host and Sr_2CeO_4: Eu^{3+} (0.5%) monitored under 617nm wavelength may be divided in to two regions (1) the intense broad band centered at 280nm is attributed to the charge – transfer (CT) transition between Ce^{4+}– O^{2-} as described by Danielson et al [9]. (2) In the range from 380 to 500nm, the sample shows the characteristic intra configuration 4f – 4f transitions of the Eu^{3+} ion. $^7F_0 \rightarrow ^5L_6$ transition at 395nm and $^7F_0 \rightarrow ^5D_2$ transition at 467nm, of these two lines 467nm is the strongest and well matched with the blue LED chip.

But the emission spectrum of Sr_2CeO_4 shows a broad band due to f→ t_1g transitions of Ce^{4+} fig-3a. When the excitation was varied from 254 to 350 nm the observed emission is a broad one and a peak at 467nm for entire range. It is also observed that the emission intensity is high when excited with 280nm.
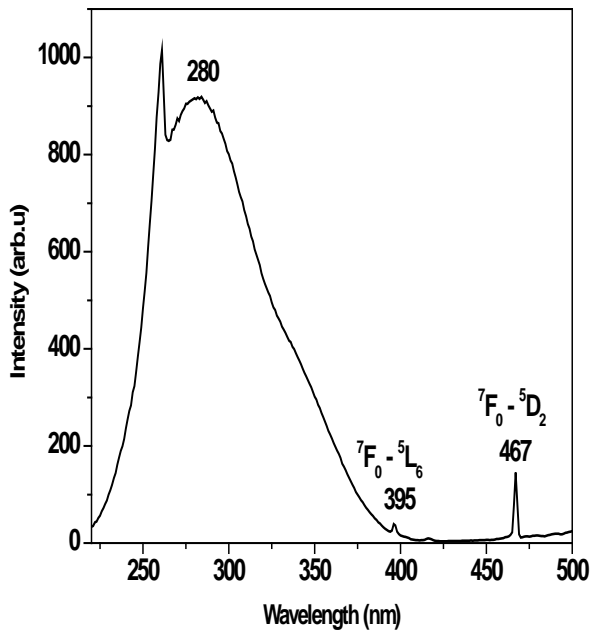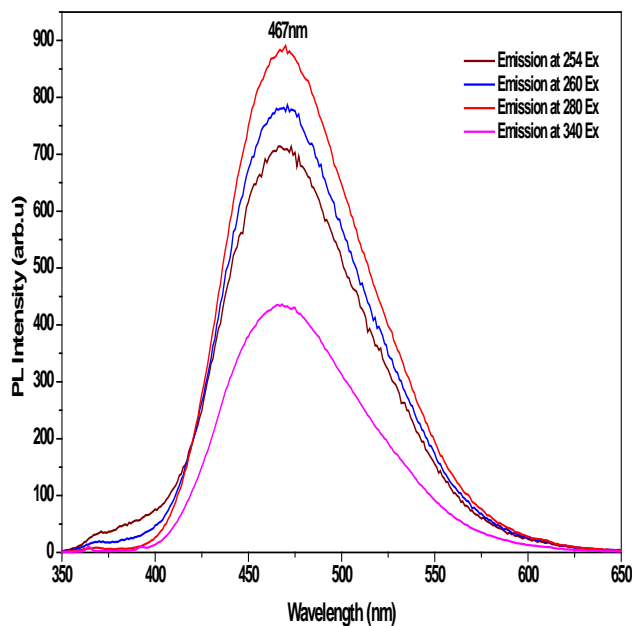
Fig.3: Excitation spectrum

depicted in the spectra are from the transitions $^5D_2 \rightarrow {}^7F_{0,1,2,3}$, $^5D_1 \rightarrow {}^7F_{1,2}$ and also from $^5D_0 \rightarrow {}^7F_{1,2,}$. In this composition, the $^5D_2 \rightarrow {}^7F_0$ line appears as the most intense emission in the blue region followed by $^5D_1 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ lines in green and orange-red regions in the order of decreasing intensities. The $Ce^{4+} - O_2^{2}$ CT emission band completely disappears for Sr_2CeO_4 and the intensity of $^5D_0 \rightarrow {}^7F_2$ line starts increasing whereas the intensity of $^5D_2 \rightarrow {}^7F_0$ diminishes. The $^5D_0 \rightarrow {}^7F_2$ line in the red region becomes the most intense line for Sr_2CeO_4: Eu 2% followed by $^5D_0 \rightarrow {}^7F_1$, $^5D_1 \rightarrow {}^7F_1$ and $^5D_2 \rightarrow {}^7F_0$ in decreasing order of intensity. If we go to higher concentrations of Eu may be at 5% the $^5D_0 \rightarrow {}^7F_2$ line become the most intense with no other emission lines involving $^5D_2$ levels. The peak around 610- 620nm is due to the electric dipole transition of $^5D_0 \rightarrow {}^7F_2$ which is induced by the lack of inversion symmetry at the Eu^{3+} sites and is much stronger than the $^5D_0 \rightarrow {}^7F_1$ transition. It is well known that the $^5D_0 \rightarrow {}^7F_2$ / $^5D_0 \rightarrow {}^7F_1$ intensity ratio is a good measure of the site symmetry of rare-earth ions in a doped material. This is because the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ tends to be much more intense at a site with no inversion symmetry, while the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ is constant, regardless of the environment (11). However in the present study on Sr_2CeO_4: Eu the observed intensity is very high when compared with previous workers prepared under different routes [12-15].

Fig.3a: Emission spectra of Sr_2CeO_4 phosphor

The Sr_2CeO_4 phosphor doped with Eu^{3+} (0.5%) does not show any change in the excitation spectrum. Figure-3b shows emission spectrum with peaks at 467, 490, 512, 537, 556, 587 and 616nm under 350nm excitation. The peaks
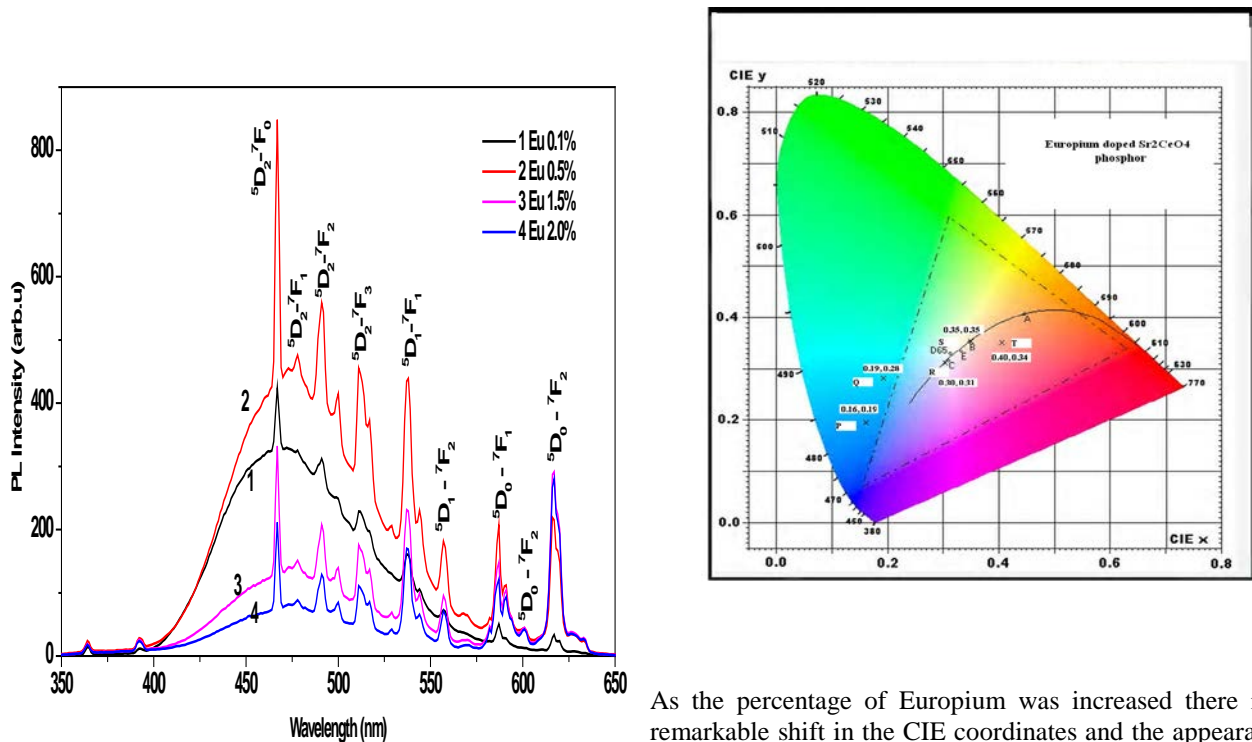
Fig.3b: Transitions in Emission spectra of Sr_2CeO_4: Eu^{3+} (0.1%, 0.5%,,1.0%,1.5%,,2.0%)

3.4 CIE coordinates

Fig.4 is the Commission Internationale de l'Eclairage (CIE) coordinates which are calculated using the spectral energy distribution (1931 chart). The CIE co-ordinates of the undoped Sr_2CeO_4 sample are x = 0.16 and y = 0.19. These values are closer to the values of Serra et al. and Rahul et al. The different CIE coordinates reported till date for the Sr_2CeO_4 with different synthesis technique have been tabulated in table-2. The colour co-ordinates of the Sr_2CeO_4: Eu (0.1%) sample are x = 0.19 and y = 0.28. When it is 0.5% the CIE was x=0.30 and y=0.31, at 1.5% the CIE was x=0.35 and y=0.35 and at 2% the CIE was x=0.40 and y=0.34.

As the percentage of Europium was increased there is a remarkable shift in the CIE coordinates and the appearance of blue color shifts to bluish green to white (perfect white being x=0.33 and y=0.33) and finally towards red with good CRI value of 96. The tuning of the color by proper doping of the Europium is a very important property and can be utilized for many applications. From a single host lattice the tuning of these many colors is an interesting phenomenon.

S. No.	CIE – X	CIE – Y	Reference
1.	0.198	0.292	Danielson et al [9]
2.	0.19	0.26	Jiang et al [8]
3.	0.16	0.21	Serra et al [12]
4.	0.16	0.25	Rahul et al [14]
5.	0.16	0.19	Present Sample

4. CONCLUSION

The Photoluminescence emission studies of undoped Sr_2CeO_4 phosphor and Eu doped Sr_2CeO_4 phosphor synthesized via high temperature solid state reaction method studies showed interesting results.

(1) The Eu doped Sr_2CeO_4 phosphor emission spectrum shows all the allowed transitions of Eu, which are well resolved with high intensity from nUV to red may be due to the nano size of the phosphor or may be due to the transitions are very sensitive to the crystal field wherein the splitting due to induced lattice.

(2) As the Eu concentration increases, the host emission intensity increased up to 0.5% and then decreases. This

luminescence quenching of host may be due to the activator (Eu) ions can begin to interact with one another by overlapping of the wave functions. As the Eu concentration increases, the emission intensity shift is observed. The shift in emission may be attributed to different symmetries of the Eu^{2+} and or Eu^{3+} ions at Ce and or Sr sites. The characteristic blue emission of the Sr_2CeO_4 phase was quenched in favor of the red emission of Eu ions indicating that europium must be close to cerium ions in the host – Eu energy transfer. Which led us to conclude the crystal host is a donor of energy and the doped Eu ion is an acceptor of energy.

(3) The single phase Sr_2CeO_4 phosphor synthesized via solid state reaction technique did not show any thermoluminescence (TL) when measured from room temperature to 300^oC, after 10Gy β irradiation, may be due to formation of nano size phosphor. Since the crystallite is in nano form having 30-35 molecules of the host, it is very difficult to create TL traps in a perfect crystal. Therefore it is concluded the nano materials will not yield any thermoluminescence in pure nano form.

(4) From the PL studies, it is concluded that Eu doped Sr_2CeO_4 phosphor can act as a single host for producing white light under 350nm excitation, for all practical display devices. All these favorable properties indicate that this phosphor might be a useful candidate to act as a single phosphor for producing white light under blue LED excitation.

ACKNOWLEDGEMENT

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