

Photoluminescent properties of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ and $\text{Sr}_2\text{CeO}_4:\text{Eu}^{2+}$ phosphors suitable for near ultraviolet excitation

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Abstract. Powder phosphors of 1 mol% Eu^{3+} - and Eu^{2+} -doped strontium cerium oxide (Sr_2CeO_4) were synthesized by standard solid-state reaction method. Eu^{3+} - and Eu^{2+} -doped Sr_2CeO_4 phosphors fired at 1100 °C for 2 h were analysed by X-ray diffraction (XRD) and photoluminescence (PL) techniques. The XRD patterns confirm that the obtained phosphors are a single phase of Sr_2CeO_4 composed of orthorhombic structure. Room temperature PL excitation spectrum of air-heated $\text{Sr}_2\text{CeO}_4:\text{Eu}$ phosphor has exhibited bands at 260, 280 and 350 nm. Whereas the excitation spectrum of $\text{Sr}_2\text{CeO}_4:\text{Eu}$ phosphor heated under reducing (carbon) atmosphere exhibited single broadband range from 260 to 390 nm. The (PL) emission peaks of both the phosphors at 467 (blue), 537 (green) and 616 nm (red) generate white light under 260, 280 and 350 nm excitation wavelengths. The Commission International de l'Eclairage (CIE) colour coordinates conforms that these phosphors emitting white light. The results reveal that these phosphors are multifunctional phosphors which emit white light under these excitations that they could be used as white components for display and lamp devices and as well as possible good light-conversion phosphor LEDs under near-ultraviolet (nUV) chip.

Keywords. White light emitting diode; phosphor; excitation; emission; solid state reaction.

1. Introduction

In recent years, research on these phosphors used for white light emitting diodes (LEDs) have become a hot topic and gained maturity. When excited, the oxide-based phosphors convert absorbed energy into electromagnetic radiation in the ultraviolet, visible and infrared regions and the luminescence of rare earth-doped phosphors also permits the evolution of trichromatic luminescence lighting. In 1998, a blue phosphor compound, Sr_2CeO_4 phosphor possessing one-dimensional chain of edge-sharing CeO_6 octahedron, was identified by Danielson and his co-workers (1998) by combinatorial chemistry method. The study on white light phosphors suitable for near-ultraviolet (nUV) excitation has been attracting more attention for fabricating white LED with nUV GaN chip for white lighting (Kuo *et al* 2003; Kim *et al* 2004a,b,c). In comparison with the commercial white LED fabricated with a blue chip and yellow phosphor $\text{YAG}:\text{Ce}^{3+}$, the white LED fabricated with nUV chip and corresponding phosphor has higher colour stability because all the colours are determined by the phosphors.

Rare earth ion-doped hosts have demonstrated good photoluminescence (PL) properties and chemical–physical stabilities. Eu^{2+} in such kinds of host may emit various colours demanded by white lighting. Rare earth ion-doped phosphors have been used in varied fields based on their electronic and optical characters arising from their 4*f* electrons. Among the rare earth elements, europium is a special element as dopant, because it exhibits the property of valence fluctuation, i.e. the valence state is divalent or trivalent. And it exhibits different characteristics luminescence due to the different valence. The red light emission of Eu^{3+} which is due to intra-4*f* transition. While the emission of Eu^{2+} from the dipole allowed 5*d*–4*f* transition, varies in a wide range from red to ultraviolet which depends on the crystal structure of host materials. It is well known that the optical properties of rare earth ion-doped luminescent materials are greatly influenced by the matrix. It has been reported that Eu^{2+} ions or Eu^{3+} ions exhibit favourable luminescence behaviour in many matrices (Vijay Singh *et al* 2006; Sharma *et al* 2009). It absorbs ultraviolet radiation and emits white light, when activated by Eu^{2+} ions. It is anticipated that the dual behaviour of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ and $\text{Sr}_2\text{CeO}_4:\text{Eu}^{2+}$ phosphors as a single host may play a positive role in practical applications.

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In this research paper, we have studied the synthesis and PL properties of Eu^{3+} - and Eu^{2+} -doped Sr_2CeO_4 phosphors prepared by the solid-state reaction method fired at 1100°C for 2 h. The prepared phosphors were characterized by X-ray diffraction (XRD) and PL techniques. PL studies and Commission International de l'Eclairage (CIE) colour coordinates reveal that these phosphors emit white light under 260, 280 and 350 nm excitation wavelengths.

2. Experimental

Strontium cerium oxide (Sr_2CeO_4) doped with Eu (1 mol%) phosphors was developed by conventional solid-state reaction method. SrCO_3 (Sigma-Aldrich Chemie Inc., Germany), CeO_2 (National Chemicals, Vadodara, India) were used as starting materials for the host material taken in stoichiometric proportions (Sr:Ce is 2:1) and Eu_2O_3 (National Chemicals, Vadodara, India) as an activator ion. The samples were doped with 1 mol% of Eu ion. All the above materials were of analytical grade exceeding 99.9% assay. These materials in the desired ratio were well homogenized in an agate mortar and pestle at room temperature for 1 h.

Eu -doped Sr_2CeO_4 mixture is placed in a clean alumina crucible and fired from room temperature (35°C) to 1100°C in a muffle furnace with a heating rate of $5^\circ\text{C}/\text{min}$ for 2 h. Then, the phosphor was allowed to cool down to room temperature for 20 h. The heating process was done in the air atmosphere. Thus, $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ phosphor was obtained. In the same way, $\text{Sr}_2\text{CeO}_4:\text{Eu}^{2+}$ phosphor was successfully prepared but heated in a reducing atmosphere. This heating was carried out using a double crucible configuration, in which one crucible was nestled in the other with carbon in between.

To identify the crystal phase, XRD analysis was carried out with a powder diffractometer (Rigaku-D/max 2500 X-ray diffraction) with $\text{CuK}\alpha$ radiation ($\lambda = 0.154060\text{ nm}$) as the incident radiation. The PL emission and excitation spectra were recorded with a spectrofluorophotometer (Shimadzu, RF-5301 PC) using xenon lamp as excitation source. All the spectra were recorded at room temperature. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. The CIE colour coordinates were calculated by the spectrophotometric method using the spectral energy distribution using Radiant Imaging (version 2) Software (2007).

3. Results and discussion

3.1 XRD analysis

The synthesized phosphors were characterized by powder XRD using $\text{CuK}\alpha$ radiation shown in figure 1. From the XRD pattern analysis, it was found that the diffraction

peaks are well indexed based on the JCPDS no. 50-0115 and conforms single phase Sr_2CeO_4 compound is formed. This reveals that the structure of Sr_2CeO_4 is orthorhombic and is in agreement with the findings of the previous workers like Danielson *et al* (1998), Sankar and Subba Rao (2000) and Chen *et al* (2004). The incorporation of Eu ion did not affect the host structure and +3 and +2 oxidation states have been ascertained from PL measurements. Besides this, no other peaks of un-reacted SrCO_3 and CeO_2 were observed, suggesting that the reaction of raw materials is complete. The diffraction peaks are in good agreement with other results like Li *et al* (2008), Jie Li *et al* (2010), Pallavi Page and Murthy (2010), Hong *et al* (2006) and Zhang *et al* (2009). However, the data reported by Jiang *et al* (1999) and Serra *et al* (2001) indicate triclinic structure.

The divalent or trivalent europium ion is expected to occupy the strontium site in the Sr_2CeO_4 matrix, because the ionic radius of Eu^{2+} (1.29 \AA) differs slightly from the ionic radius of Sr^{2+} (1.12 \AA). The calculated lattice parameters are $a = 6.094$, $b = 10.232$, $c = 3.566\text{ \AA}$ and volume $V = a \times b \times c = 6.094 \times 10.232 \times 3.566 = 222.354\text{ \AA}^3$. These parameters are compared with the data of JCPDS and Danielson *et al* (1998), which are shown in table 1, found that the remarkable decrease in unit cell volume indicates the crystallite size is in nanoscale.

3.2 $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ phosphor luminescent properties

Figure 2 represents the excitation spectrum of Eu^{3+} -doped Sr_2CeO_4 phosphor obtained at 1100°C in air for 2 h. The

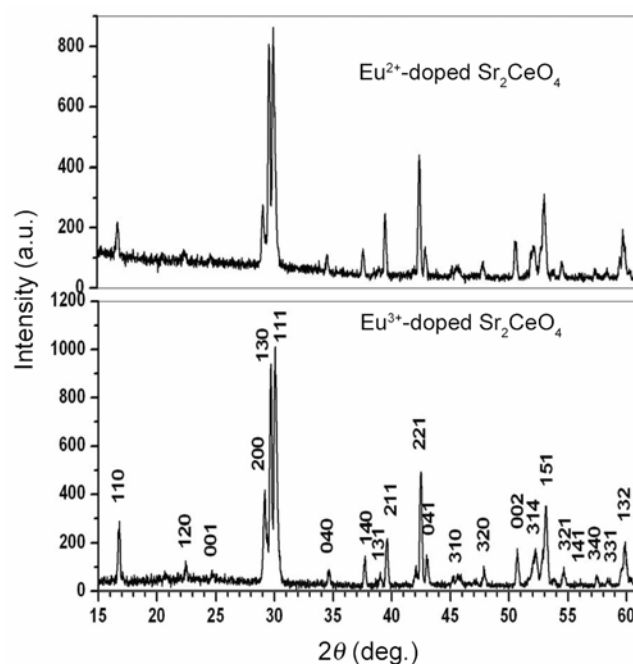
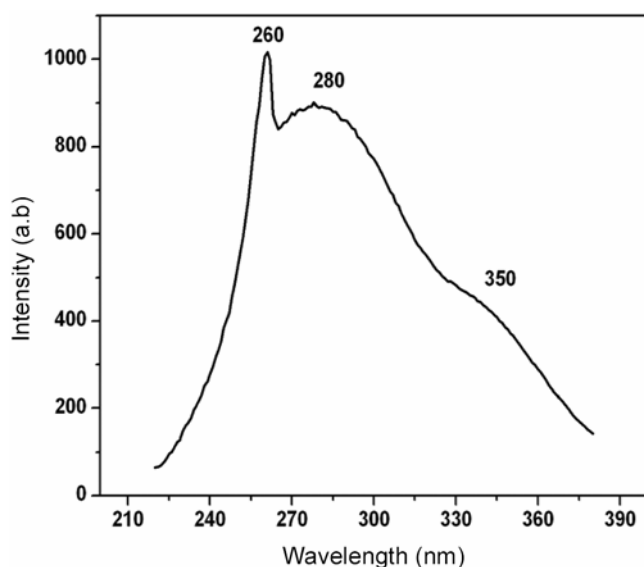
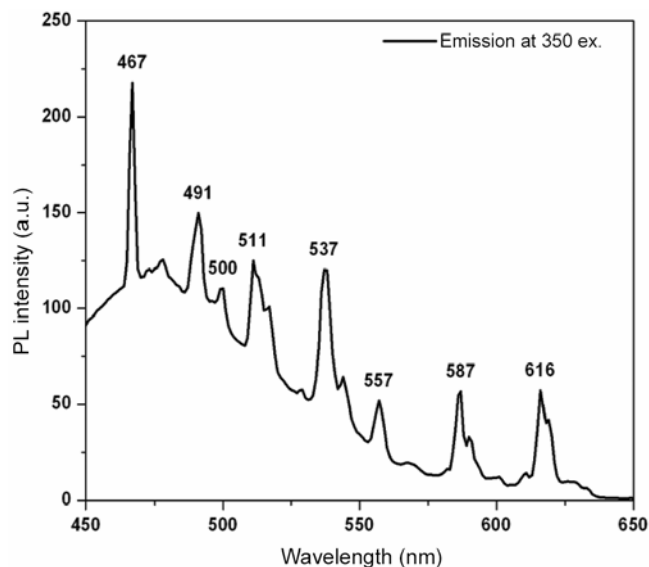


Figure 1. X-ray diffraction patterns of the phosphors.

Table 1. Crystallographic data for Sr_2CeO_4 .

Parameter	JCPDS (50-0115)	Ours (SSR)	Danielson <i>et al</i> (combinatorial chemistry)
a (Å)	6.119	6.094	6.1189
b (Å)	10.350	10.232	10.3495
c (Å)	3.597	3.566	3.597
V (Å ³)	227.79	222.354	227.789

**Figure 2.** Excitation spectrum of Eu^{3+} -activated Sr_2CeO_4 phosphor monitored under 470 nm wavelength.**Figure 3.** Emission spectrum of Eu^{3+} -activated Sr_2CeO_4 phosphor under 350 nm excitation wavelength.

excitation spectrum was obtained under 470 nm monitoring wavelength. An intense broad excitation band is observed having peaked maximum at 280 nm and a hump at 350 nm, which is attributed due to the charge transfer transition originating from O^{2-} to Eu^{3+} . The line positions are in good agreement with the other workers (Zhang *et al* 2009).

Figure 3 shows the emission spectrum of Eu^{3+} -doped Sr_2CeO_4 phosphor (scan range from 450 to 650 nm) measured under 350 nm excitation wavelength. The emission spectrum shows typical emissions of Eu^{3+} ions. In this matrix, the dopant emission is observed not only from low excited $^5\text{D}_0$ level of Eu^{3+} , but also from higher energy levels ($^5\text{D}_1$ and $^5\text{D}_2$) of Eu are detected with a higher intensity. These transitions are tabulated along with their energy values in table 2. The emission spectrum measured under 280 nm excitation wavelength shows similar spectrum with higher intensity by 5%, which is not reported.

In this composition, the $^5\text{D}_2 \rightarrow ^7\text{F}_0$ (467 nm) line appears as the most intense emission in the blue region followed by $^5\text{D}_1 \rightarrow ^7\text{F}_1$ (537 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (616 nm) lines in green and orange-red regions in the order of decreasing intensities. The emission spectrum,

Table 2. Transitions and energy values of the Eu ion peaks in Sr_2CeO_4 matrix.

Emission wavelength (nm)	Transition	Energy (cm^{-1})
467	$^5\text{D}_2 \rightarrow ^7\text{F}_0$	21459
491	$^5\text{D}_2 \rightarrow ^7\text{F}_2$	20408
511	$^5\text{D}_2 \rightarrow ^7\text{F}_3$	19646
538	$^5\text{D}_1 \rightarrow ^7\text{F}_1$	18726
557	$^5\text{D}_1 \rightarrow ^7\text{F}_2$	18018
587	$^5\text{D}_0 \rightarrow ^7\text{F}_1$	17123
617	$^5\text{D}_0 \rightarrow ^7\text{F}_2$	16207

sharp peaks, which are overlapped on broad peak originating from Ce ion, peaking at 467, 491, 511, 538, 557, 587 and 617 nm are observed. Further, it is observed that the peak broadness is increased (i.e. 467, 538 and 617 nm of blue, green and red peaks). These above-mentioned unusual luminescent properties are due to the low vibration energy of Sr_2CeO_4 host-lattice and different energy transfer process from host to activator. Furthermore, the high efficiency of the energy transfer allows us to expect that the Sr_2CeO_4 crystal structure could make the basis for the creation of luminescence materials that are effective

in different spectral ranges. This effect is similar to the results described by others on Eu^{3+} -activated Sr_2CeO_4 phosphor synthesized by different routes. The three main emission bands, i.e. blue, green and red (467, 538 and 617 nm) are combined to generate white emission observed by naked eyes. The CIE chromaticity coordinates $x = 0.33$ and $y = 0.33$ of the phosphors indicate the white emission (point A in figure 6) under 350 nm (nUV chip) excitation.

3.3 $\text{Sr}_2\text{CeO}_4:\text{Eu}^{2+}$ phosphor luminescent properties

Figure 4 shows the excitation spectrum of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{2+}$ phosphor fired at 1100 °C for 2 h under reductive atmosphere. The excitation spectrum was obtained under 470 nm monitoring wavelength. The excitation spectrum exhibits a broad band ranging from 250 to 400 nm. The strong absorption at 350 nm can be attributed to the transitions from the 4f_7 ($^8S_{7/2}$) ground state to the $^4f_6^5d_1$ excited state of the Eu^{2+} ions. The broadness of the excitation spectrum means that the phosphors can be well excited by nUV light from 350 to 380 nm, matching well with the emission bands of the nUV LED chips.

Figure 5 shows the emission spectra of Eu^{2+} ion in Sr_2CeO_4 phosphor under 350 nm excitation wavelength. In detail, it shows intense broad sharp emission bands peaked from 467 to 620 nm. The sharp peaks depicted in the spectra are from the transitions $^5D_2 \rightarrow ^7F_{0,2,3}$, $^5D_1 \rightarrow ^7F_{1,2}$ and from $^5D_0 \rightarrow ^7F_{1,2}$. The emission bands are ascribed to the energy of transitions (involving d , p or s orbital) is very sensitive to the crystal field splitting induced by Sr_2CeO_4 host matrix (Arunachalam Laxmanan 2007). The results in figures 5 and 6 clearly showed us that the Eu^{2+} -activated Sr_2CeO_4 phosphor will emit a white light (RGB) upon the nUV excitation. These two

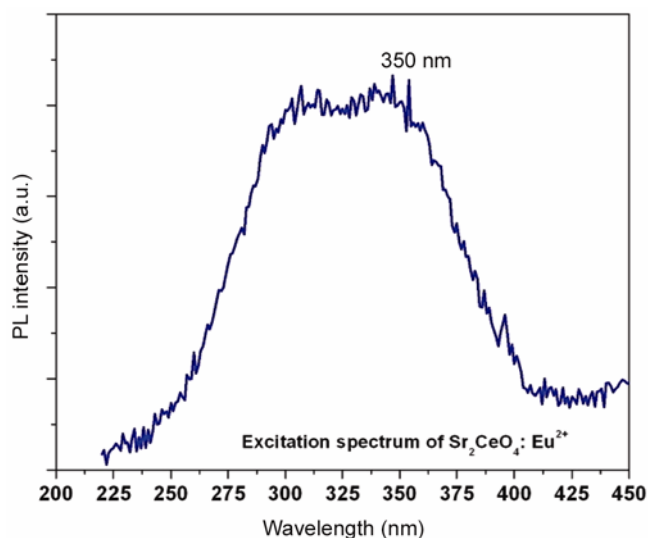


Figure 4. Excitation spectrum of Eu^{2+} -activated Sr_2CeO_4 phosphor monitored under 470 nm wavelength.

phosphors show great application potential as candidate phosphors for white LEDs pumped by a nUV chip, and our method is better to elaborate these phosphors.

3.4 CIE coordinates

Figure 6 shows the CIE coordinates of both the phosphors under nUV excitation, which are calculated using the spectral energy distribution (1931 chart).

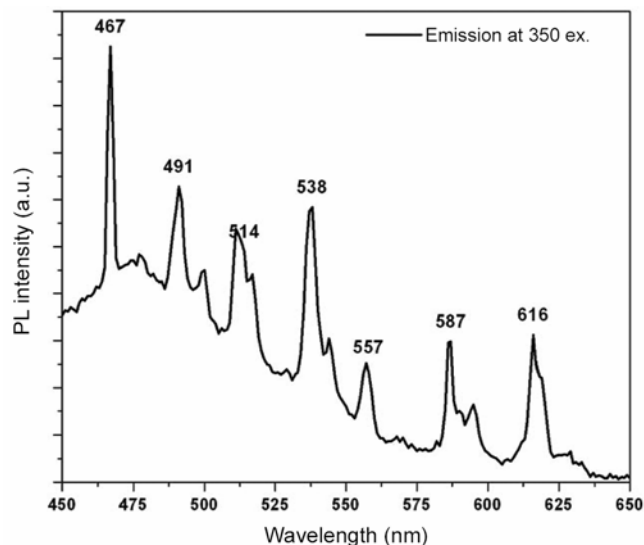


Figure 5. Emission spectrum of Eu^{2+} -activated Sr_2CeO_4 phosphor under 350 nm excitation wavelength.

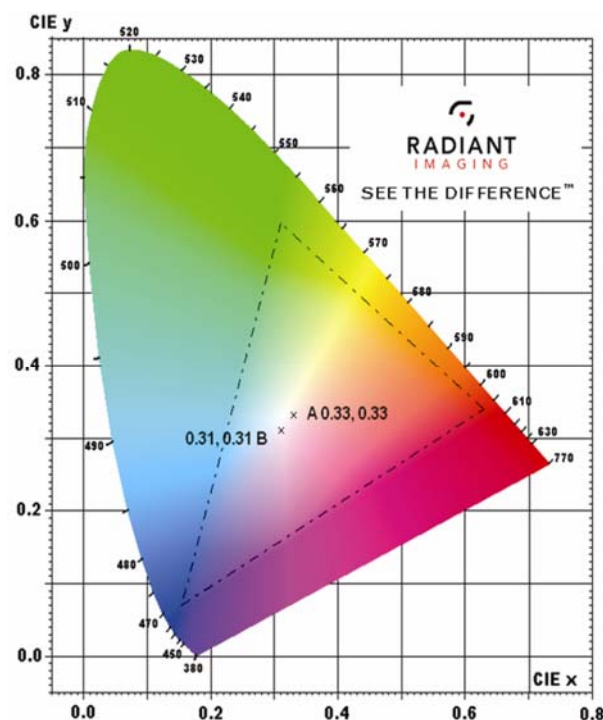


Figure 6. CIE diagram 1931 chart.

The CIE coordinates of the $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ (1 mol%) sample are $x = 0.33$ and $y = 0.33$ (point A in figure 6) phosphor emitting white light under the excitation of 350 nm, respectively. The CIE coordinates of the $\text{Sr}_2\text{CeO}_4:\text{Eu}^{2+}$ (1 mol%) sample are $x = 0.31$, $y = 0.31$ (point B in figure 6) phosphor is also emitting white light under 350 nm excitation. From the CIE 1931 chart, the 1 mol% doped both phosphors can be utilized for many applications. These single host lattices emitting white light under UV and nUV excitations is an interesting phenomenon. Hence, these phosphors are multifunctional phosphors, which one can use according to the need.

4. Conclusions

In the blue emitting luminescent material, Sr_2CeO_4 , both the absorption and the emission processes originate from optical transitions between the $4f \leftrightarrow 5d$ levels of the Eu ion. The results in figures 3 and 5 clearly showed us that the Eu^{3+} - and Eu^{2+} -activated Sr_2CeO_4 (single host) phosphors emitting white light (by combining blue, green and red emissions) has potential applications not only in the fields of lamps and display devices under 280 nm excitation, but also in the field of LEDs under nUV (350 nm) excitation. CIE 1931 chart clearly shows that $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ (1 mol%) phosphor sample emitting perfect white emission under 350 nm (nUV chip) excitation can be used for LED applications.

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