

Research article

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StudyofCo-doping on Luminescent Properties of Strontium Cerium Oxide phosphor

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ABSTRACT

Luminescence properties and colorimetric study of Sr_2CeO_4 doped 0.5% Gd³⁺, x% Eu³⁺ was investigated in this paper. The phosphors Sr_2CeO_4 doped europium and gadolinium were successfully synthesized by solid state diffusion method. X-Ray diffraction (XRD) profile confirms the orthorhombic nature of Eu³⁺ and 0.5% Gd³⁺ doped Sr_2CeO_4 phosphors. In addition, scanning electron Microscopy (SEM), Fourier- Transformation IR spectroscopy (FTIR), was also used to study the synthesized phosphors. From emission spectra the CIE coordinates (x, y) of x% Eu³⁺ and 0.5 %Gd³⁺ doped Sr_2CeO_4 phosphors was calculated and compared. It is clear that with increasing Eu³⁺ ion concentration, the color tone changes from blue (Sr_2CeO_4 : 0.0 % Gd³⁺, 0.0 % Eu³⁺), through bluish white (Sr_2CeO_4 : 1.0 % Gd³⁺1.0 % Eu³⁺) and lastly to orange red (Sr_2CeO_4 : 1.0 % Gd³⁺, 2.0 % Eu³⁺). This phosphor having color tenability this phosphor has an important candidate of the lighting system.

KEYWORDS: Photoluminescence, FTIR, CIE, Phosphor.

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INTRODUCTION

During past decades, to a great extent concentration has been paid to rare earth doped ceramics for developing novel optical devices such as solid state laser, fiber amplifiers, displays etc. Among the rare earth ions, the Eu^{3+} ions is usually adopted as a red emitting center because of its intrinsic characteristics that $Eu^{3+}(_4f^6)$ ions can emit pure red light with high efficiency and can be efficiently excited by ultraviolet rays or cathode rays. Rare earth ions are widely employed in the development of luminescent materials for exhibiting monochromatic emission colors due to their intrinsic optical properties. Therefore it is very significant to know the optical transitions of the 4f levels of the rare earth ions involved¹⁻³. 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 Sr_2CeO_4 by combinatorial chemistry method in 1998 by Danielson. Sr₂CeO₄ consist of infinite edge-shearing CeO₆ octahedral chains separated by Sr atoms. The luminescence originates from a ligand-to metal Ce⁴⁺ charge transfer⁴⁻⁸. 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 Sr_2CeO_4 doped with trivalent rare earths europium and samarium emit in the red region of the visible spectra⁹⁻¹¹. 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 bulbs¹²⁻¹⁷.

In present paper report the preparation and spectroscopic study of Sr_2CeO_4 : x Eu³⁺, 0.5 % Gd³⁺. Phosphors were synthesized via Modified solid state Diffusion method. The CIE coordinates (x, y) of prepared materials was calculated with color calculator version2, software from Radiant Imaging.

MATERIAL AND METHODS

The Sr_2CeO_4 samples are prepared using standard solid state reaction by doping Eu in the host material with change of concentrations as 0.1, 0.5, 1.0, 1.5, and 2.0 mole % respectively by keeping Gd^{3+} constant at 0.5 mole%. The starting materials were Strontium Carbonate SrCO₃, Cerium Oxide CeO₂, Europium Oxide Èu₂O₃ and Gadolinium Oxide Gd₂O₃ of 99.9 % purity. These materials were taken in Stoichiometric proportions of Sr: Ce as 2:1. SrCO₃ and CeO₂ with rare earth were weighed in molecular stoichiometry. These all materials were ground in an agate mortar and pestle, grinded thoroughly to get fine powder. This powder was taken in alumina crucible. After closing the cover,

the crucible was loaded in furnace and heated to the temperature $1200 \, {}^{0}C$ at the rate $300 \, {}^{0}C$ /hr. The samples were kept at the set temperature for four hours then cooled down naturally. All samples were prepared by same technique.

CHARACTERIZATION

The structural studies of Sr_2CeO_4 : 0.5%Gd³⁺, xEu³⁺were carried out by X- ray diffraction technique in reflection mode with filtered Cu K α radiation ($\lambda = 1.54051$ A⁰ with Rigaku, D Max III VC, Japan. The surface morphology of Sr₂CeO₄ and Sr₂CeO₄: Sm³⁺ was carried out by Field Emission Scanning Electron Microscopy (FESEM) with JEOL- JSM – 520. The FTIR spectrums were recorded on SHIMADZU IR Affinity-1 model transmission spectrometer with KBr pellet method over the range 400- 4000 cm⁻¹. The photoluminescence excitation and emission spectra was recorded at room temperature using Spectrofluorophotometer (SHIMADZU, RF – 5301 PC) using Xenon lamp as excitation source. The CIE coordinates (x, y) of prepared materials was calculated with color calculator version2, software from Radiant Imaging.

RESULTS AND DISCUSSION

X-ray powder diffraction (XRD) of Sr_2CeO_4 : 0.5%Gd³⁺, 0.5% Eu³⁺phosphor was carried out at room temperature. Fig.1 shows X-ray powder diffraction (XRD) pattern of Sr_2CeO_4 : 0.5%Gd³⁺, 0.5% Eu³⁺phosphor.



Figure 1 XRD Pattern of Sr₂CeO₄: 0.5%Gd³⁺, 0.5%Eu³⁺

The calculated average crystallite size of the particles of Sr_2CeO_4 : 0.5%Gd³⁺, 0.5%Eu³⁺phosphor is 31 nm. The computer program POWD (an interactive Powder diffraction Data Interpretation and Indexing Program, Version 2.2) was used to calculated hkl and d values were found to be in good agreement with the JCPDS data card No. 50-0115.

Figure 2 shows FESEM image of Sr_2CeO_4 : 0.5%Gd³⁺, 0.5% Eu³⁺ phosphor. It shows irregular shape like morphology. The particles are agglomerated.



Figure 2 FESEM Photograph of Sr₂CeO₄: 0.5% Gd³⁺, 0.5% Eu³⁺

The FTIR spectra of Sr_2CeO_4 : 0.5%Gd³⁺, 0.5%Eu³⁺ phosphor was recorded on SHIMANDZU IRAffinity-1 model transmission spectrophotometer with KBr pallet method over the wave number range 400-4000 cm⁻¹ at Instrumentation lab, M. J. College, Jalgaon.



Figure 3 FTIR of Sr₂CeO₄: 0.5% Gd³⁺, 0.5% Eu³⁺

From Figure 3 it is observed that the prominent IR bands are located around 3424, 2957, 1577, 1440, 1080, 855and 425 cm⁻¹. The bands around 3403 2957, 1577 and 1440 are due to water molecules that may be incorporated in to the samples during preparation of samples for IR measurements. The IR bands around 1080 and 855cm⁻¹ due to the coordination of metal with oxygen atom, which produce vibrations along the chemical bond and are due to metal – oxygen bond (Ce – O) stretching¹⁷.



Figure 4 PL excitation spectrum of Sr₂CeO₄: Gd³⁺, Eu³⁺

Figure 4 shows the Photoluminescence excitation spectrum of Sr_2CeO_4 : Gd,Eu, emission wavelength at 467 nm. The excitation spectrum of Sr_2CeO_4 shows a broad band with two peaks around 254 nm. This broad 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 co-ordination.

Figure 5 shows the PL emission spectra of Sr_2CeO_4 : 0.5% Gd^{3+} , x%Eu³⁺ with 330 nm excited wavelength. When the Sr_2CeO_4 : 0.5% Gd^{3+} , x%Eu³⁺ with 330 nm excited the PL emissions are same in the case of 254nm excitation except reduction of its intensity by 15%.





On comparison PL emission of sample Sr_2CeO_4 : 0.5% Gd³⁺, 0.1% Eu³⁺ with 330 nm excitation with the same samples under 254nm excitation, all the emitted wavelengths were decreased in all samples.



Figure 6 CIE Chromaticity diagram of Sr₂CeO₄: 0.5% Gd³⁺, 1.5%Eu³⁺ at λ_{Exc} = 330 nm

The CIE chromaticity coordinates for the Sr_2CeO_4 : 0.5 %Gd³⁺, 1.5% Eu³⁺ phosphor excited at 330 nm are summarized in table 1. The CIE coordinates of Sr_2CeO_4 : 0.5 %Gd³⁺, 1.5% Eu³⁺ phosphor excited at 330 nm are x = 0.28 and y = 0.27 as shown in figure 5.30, from CIE 1931 diagram it is in the bluish blue color region.

Table 1CIE chromaticity coordinates of Sr₂CeO₄: 0.5 %Gd, x %Eu

Phosphor	Excitation (nm)	Strong Emission (nm)	(x,y) Coordinate	CCT (K)	Color region
Sr_2CeO_4 : 0.5 % Gd^{3+} , 1.5 % Eu^{3+}	330	616	(0.28, 0.27)	11904	Bluish White

CONCLUSION

- Sr_2CeO_4 doped with $Eu^{3+}(0.1\%, 0.5\%, 1.0\%, 1.5\%$ and 2.0%) and co-doping 0.5% Gd^{3+} phosphor was successfully synthesized.
- From XRD pattern the structure is orthorhombic and the average crystallite size of particles of Sr₂CeO₄: 0.5%Gd³⁺, 0.5%Eu³⁺ is 31 nm.
- The PL emission in of Sr₂CeO₄: 0.5%Gd³⁺, 1.0 %Eu³⁺sample shows maximum intensity for well resolved peak of 586nm.
- Phosphor Sr₂CeO₄: 0.5%Gd³⁺, 1.5 %Eu³⁺sample shows maximum intensity for well resolved peak of 616nm.
- ButSr₂CeO₄: 0.5%Gd³⁺, 2.0%Eu³⁺doped sample shows decrease of all the well resolved emitted peaks expect 589 and 616nm in comparison with Sr₂CeO₄: 0.5%Gd³⁺, 1.5%Eu³⁺phosphor.

- The reduction of intensity is high for wavelengths of 467,491,511nm, intermediate to wavelengths of 538, 586 nm, less to the wavelength 586nm, but the intensity of peak having wavelength 616 nm was abruptly increases with the doping of Europium in Sr_2CeO_4 phosphor.
- The CIE coordinates of Sr_2CeO_4 : 0.5 %Gd³⁺, 1.5% Eu³⁺ phosphor excited at 330 nm are x = 0.28 and y = 0.27, from CIE 1931 diagram it is in the bluish blue color region.

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