



Study of Luminescence Properties of Strontium Cerium Oxide Phosphor activated Dy³⁺ for yellow emitting light

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Abstract - In this paper Sr₂CeO₄: 1.0% Dy³⁺ phosphor was synthesized by high temperature Modified solid state diffusion method and its luminescence properties were studied. The starting materials, Strontium Carbonate SrCO₃, Cerium Oxide CeO₂, and Dysprosium oxide Dy₂O₃ of 99.5 % purity were used to prepare phosphor. The samples were characterized by XRD, FESEM, and Photoluminescence excitation and emission. The X-Ray diffraction patterns reveal the crystallite size of powder. The samples were excited with 256 nm for the 1200°C prepared sample. The emission spectra shows broad band peaking at 547 nm for the excitation wavelength 254. Color co-ordinates of Sr₂CeO₄: 1.0% Dy³⁺ are $x = 0.47$ and $y = 0.53$, which color is located in the yellow region.

Keywords: Photoluminescence, XRD, FTIR, CIE coordinates, Phosphor

1. INTRODUCTION

Phosphor based on oxide matrices are smart host materials for the development of advanced phosphors due to their simplicity of synthesis and stability. The search for blue phosphor has been growing due to their applicability in many fields, such as field emission displays (FEDs), cathode ray tubes (CRTs), projection televisions (PTVs), fluorescent tubes, and X-ray tubes [1, 2]. In recent times various phosphor materials have been actively investigated to develop their luminescent properties and to meet the development of different display and luminescence devices [3-5]. However, oxide-based phosphors are more stable and environment friendly compared to organic materials and sulfides. Therefore, metal oxides with photoluminescence property, especially rare earth based composite materials, have been of interest with respect to possible applications. Although, it is more difficult to find a suitable blue phosphor because wider band gap is required, and the naked eye sensitivity is quite low in the blue spectral region [6]. A moment ago much attention has been paid to the preparation of blue phosphors using different chemical and physical methods. Among them a novel blue luminescence compound Sr₂CeO₄ was identified using combinatorial material synthesis by electron beam evaporation with multiple targets and moving

mask, which reported in 1998 using combinatorial technique by Danielson et al. [7, 8]. The structure of Sr₂CeO₄ is highly anisotropic and is an unusual phosphor in that, it contains one-dimensional chain fig. 1 shows the crystal structure of Sr₂CeO₄. The structure of Sr₂CeO₄ phosphor has been investigated and the orthorhombic crystal structure was suggested by Danielson et al. [8]. If blue phosphor Sr₂CeO₄ doped with trivalent rare earth europium and samarium it emits in the red region of the visible spectra [9-17]. In this paper the prepared samples were characterized by XRD, FESEM and PL (excitation and emission spectra) and emission spectra are converted into CIE coordinates.

2. MATERIALS AND METHOD

For the preparation of strontium cerium oxide doped dysprosium Sr₂CeO₄: Dy³⁺ phosphor, solid state diffusion method was used, Strontium Carbonate SrCO₃, Cerium Oxide CeO₂ and Dysprosium oxide Dy₂O₃ of 99.5 % purity were used as starting materials. Stoichiometric amounts of these starting materials were thoroughly mixed and ground with acetone in an agate mortar and pestle for one hour and then put into an alumina crucible. Then, those mixtures were dried at 55 °C for 3h, heated in air at 250 °C for 1h, and later sintered at 1200 °C for 4h with an intermediate grinding. Finally furnace cool down to room temperature, by furnace shut down.

1.2

Characterization Techniques

In the present work, an effort has been made to characterize phosphor prepared via modified solid state diffusion method. The prepared phosphor was characterized by different techniques. The structural studies were carried out by X-ray diffraction technique in reflection mode with filtered Cu K α radiation ($\lambda = 1.54051 \text{ \AA}$) with Rigaku, D Max III VC, Japan. The FTIR spectra were recorded on SHIMADZU IR Affinity-1 model transmission spectrometer with KBr pellet method over the range 400- 4000 cm^{-1} . The surface morphology of $\text{Sr}_2\text{CeO}_4: 1.0\% \text{ Dy}^{3+}$ was carried out by Scanning Electron Microscopy (SEM) using Hitachi S4800 model. The samples for FESEM studies were coated with a layer of gold to prevent charging of the specimen. The photoluminescence excitation and emission spectra were recorded at room temperature using Spectrofluorophotometer (SHIMADZU, RF – 5301 PC) equipped with Xenon lamp as excitation source. The CIE coordinates (x, y) of prepared materials was calculated with color calculator version2, software from Radiant Imaging.

3. RESULTS AND DISCUSSION**3.1 X-Ray powder diffraction analysis (XRD)**

The structural property of $\text{Sr}_2\text{CeO}_4: \text{Dy}^{3+}$, synthesized by solid state method was investigated by X-Ray Diffraction Method. X-ray powder diffraction (XRD) data of $\text{Sr}_2\text{CeO}_4: \text{Dy}^{3+}$ phosphor were collected at room temperature. All diffraction pattern were obtained using Cu K α radiation ($\lambda = 1.54051 \text{ \AA}$). The current in the X-ray tube was 15 mA and the voltage was 30 kV. The regular resolution in 2θ scan was 0.02° over a 2θ range of 10° - 80° . The mixture of SrCO_3 and CeO_2 powder were calcined at different calcinations temperature to investigate the evaluation of crystalline phases. The corresponding XRD patterns for the resultant powders are shown in fig. 1.

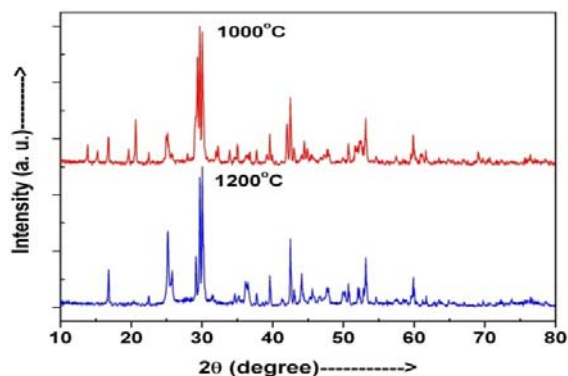


Fig. 1 XRD patterns of $\text{Sr}_2\text{CeO}_4: \text{Dy}^{3+}$ for 1000 °C and 1200 °C temperatures

The powder showed weak crystalline phases of SrCO_3 , Dy_2O_3 and CeO_2 at 1000 °C with increasing calcinations temperature from 1000 °C to 1200 °C, the diffraction peaks of SrCO_3 , Dy_2O_3 and CeO_2 become much sharper. When the mixture was calcined at 1200 °C for 4h, $\text{Sr}_2\text{CeO}_4: \text{Dy}^{3+}$ a single phase with the orthorhombic symmetry appeared, which was in good agreement with the reported data (JCPDS 50-0115) [7]. The crystallite size of particle of prepared powders samples were calculated from X-ray peak broadening of the diffraction using Scherer's equation

$$d = 0.9\lambda / \beta \cdot \cos\theta$$

Where, d is the crystallite size in nm, β the full width at half maximum (FWHM) of XRD lines. λ the radiation wavelength of X-ray ($\lambda = 1.54051 \text{ \AA}$), and θ the diffraction peak angle. The calculated average crystallite size of particles of $\text{Sr}_2\text{CeO}_4: 1.0\% \text{ Dy}^{3+}$ phosphor is 48 nm

3.2 Field Emission Scanning Electron Microscopy (FESEM)

The particle morphology of the synthesized sample was observed by FESEM and typical morphological image is represented in fig.2. Samples $\text{Sr}_2\text{CeO}_4: 1.0\% \text{ Dy}^{3+}$ revealed a very porous structure and particles possess foamy like morphology formed from agglomerated crystalline. The size of sample prepared at 1200 °C is in the range 40 to 140 nm. The particles were connected with each other through necking; they could be easily crushed to obtain separate particles. Most particles showed rounded surfaces.

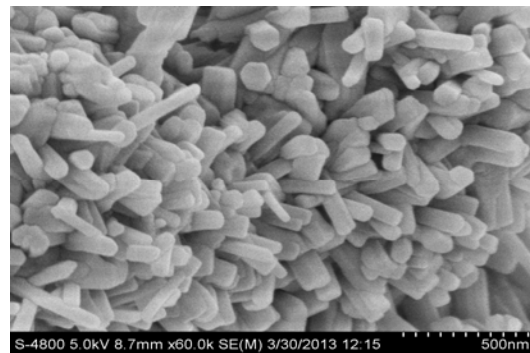


Fig. 2 FESEM image of $\text{Sr}_2\text{CeO}_4: \text{Dy}^{3+}$ phosphor

3.3 FTIR spectra

The FTIR spectra of the $\text{Sr}_2\text{CeO}_4: 1.0\% \text{ Dy}^{3+}$ is shown in Fig. 3

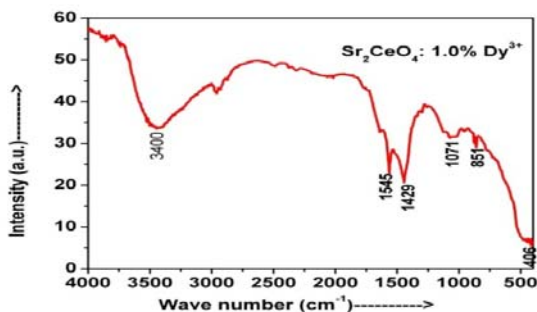


Fig.3 FTIR Spectrum of Sr₂CeO₄: 1.0% Dy³⁺

The peaks at 3400 cm⁻¹ are assigned to water molecules that may be present due to absorption of moisture and is assigned to the hydrogen bonding in water and impurities, usually present in KBr respectively. The absorption peaks at 1545, 1429, 1071, 851 and 406 cm⁻¹ were assigned to stretching characteristics of SrCO₃.

3.4 Photoluminescence properties

The samples was excited with different wavelengths From 240nm to 360nm for the 1200°C prepared sample, the interesting result that we can observe from the graph is that the peak position does not change much with the excitation wavelength. Another interesting feature of these emission curves is that when the excitation wavelength was kept at 256 nm the peak was very broad. The shape of the emission curve was same at all the wavelengths. Such type of broad excitation can be useful for many applications. Correlation of these with the excitation curves can lead to useful information on the nature and the origin of the luminescence.

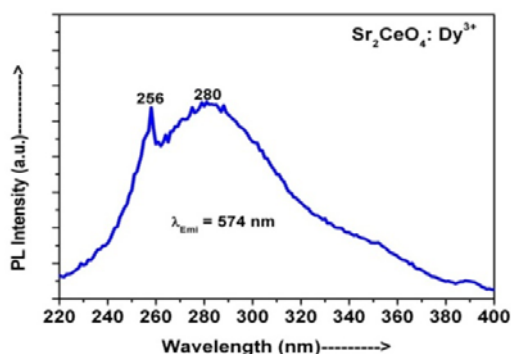


Fig. 4 PL Excitation spectrum of Sr₂CeO₄: Dy³⁺

The excitation spectra for all the samples are shown in fig.4 monitored with 574 nm of the Dy³⁺ ion and the 469nm of the Sr₂CeO₄ host. The excitation spectrum has a strong absorption band with a maximum at 258nm (sharp peak) and a broad band at around 280nm (when monitored with 574nm). This is in accordingly the results of the excitation spectra of the host due to the two different bond

lengths in the Ce-O. When monitored with 574 nm wavelength, the peak is at 256nm and then it falls steeply, whereas it has additional peak at around ~ 280nm.

On doping dysprosium we found that the visible emission from the nano-crystal was predominantly yellow, from the ⁴F_{9/2}→⁶H_{13/2} transition, centered at approximately 574nm. This visible transition of dysprosium in the yellow region makes it an important material for technological applications, which require yellow light as emission. The visible spectra also consist of lines in the blue-green region at around 480 nm and 490 nm. These may be assigned to the transitions from ⁴F_{9/2}→⁴H_{15/2}. Similar results were also observed for the Eu³⁺ which had a dominant ⁵D₀→⁷F₂ transition, which is also a hypersensitive transition. No other higher transitions of Dysprosium were observed in the red and near IR region even at different mol % of doping. The photoluminescence spectra show that it can be used to tune the emission color with different mol % of the Dysprosium.

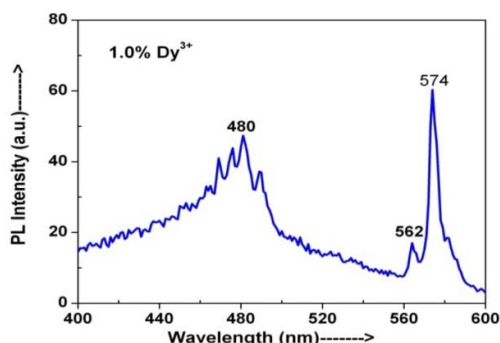


Fig. 5 PL emission spectra of Sr₂CeO₄: Dy³⁺

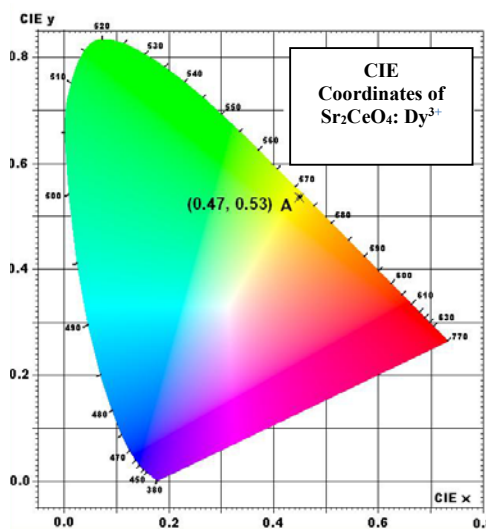


Fig. 6 CIE co-ordinates of Sr₂CeO₄: Dy³⁺ depicted on 1931 chart

The CIE coordinates for the Photoluminescence spectra of the doped Dy^{3+} Sr_2CeO_4 was calculated by spectrophotometric method using the spectral energy distribution, then calculating the color coordinates x and y [14]. The CIE coordinates for Sr_2CeO_4 : 1.0 % Dy^{3+} (0.47, 0.53) for excitation wavelength 254 nm as shown in table 1. The values of the CIE clearly suggest that on doping the host with Dy^{3+} , the yellow light emission can be achieved from a single host compound rather than the mixing of other phosphors. This property of the synthesized phosphor makes it suitable and predicts its use in various display devices.

Table 1 CIE coordinates for Sr_2CeO_4 : 1.0 % Dy^{3+}

Phosphor	Excitation (nm)	Strong Emission (nm)	(x, y) Coordinate	Color region
Sr_2CeO_4 : 1.0 % Dy^{3+}	254	574	(0.47, 0.53)	Yellow

CONCLUSIONS

From the above studies the following conclusions are drawn:

Sr_2CeO_4 : 1.0% Dy^{3+} blue phosphor successfully prepared by Modified Solid state diffusion method

From XRD it is confirmed that the product is in single phase.

Powder samples of Sr_2CeO_4 : 1.0% Dy^{3+} prepared by the modified solid state diffusion technique exhibits high homogeneity, more uniformity and nano crystalline size (~23 nm).

XRD pattern shows very sharp peaks having high intensity, unit cell parameter values and d values match very well with the JCPDS data and the structure of Sr_2CeO_4 : 1.0% Dy^{3+} is orthorhombic, as conformed by XRD.

FESEM photograph shows thick rod like morphology with loosely agglomerated.

The color co-ordinates for Sr_2CeO_4 : 1.0% Dy^{3+} were $x = 0.47$ and $y = 0.53$. From this the present phosphor has potential for the application for display devices.

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