

Thermal analysis and luminescent properties of Sr_2CeO_4 blue phosphor

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ABSTRACT

In this paper we report Strontium Cerium Oxide (Sr_2CeO_4) blue phosphor was synthesized via solid state reaction method using strontium carbonate SrCO_3 and cerium oxide CeO_2 as raw materials. The samples were characterized by Thermo analytical techniques (TG, DTA, DTG and DSC) in nitrogen atmosphere, Fourier transformation infrared (FTIR) spectroscopy, and Photoluminescence at room temperature. Thermal analysis indicates that Sr_2CeO_4 phosphor can be prepared at temperature higher than 1100 °C. In excitation spectra two excitation peaks were located at 262 and 399 nm respectively. The emission spectrum was a broad band peaking at 470 nm, which was suitable for the doping of rare earth ions. The color co-ordinates for the pure Sr_2CeO_4 were $x = 0.1918$ and $y = 0.2483$. This material has potential for applications in the field of emission devices. Copyright © 2013 VBRI press.

Keywords: Solid state reaction; TG; DTA; FTIR; DTG; photoluminescence; X-ray diffraction.



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Introduction

Recently various phosphor materials have been actively investigated to improve their luminescent properties and to meet the development of display and luminescence devices [1]. Red emitting phosphors $Y_2O_3:Eu^{3+}$ and green emitting phosphor $Y_3Al_5O_{12}:Ce^{3+}$ have found many applications. However, conventional blue emitting rare earth or transition metal activated sulphides cannot adapt to new applications due to intrinsic problems such as their chemical instability and sensitivity to moisture. Thus the blue luminescent materials with sufficient efficiency and chemical stability have been persistently pursued [2-3]. Compared with organic materials and sulfide phosphors, oxide-based phosphors have the advantages: stable crystalline structure and physical and chemical stability. Therefore oxide based phosphors, especially rare earth based oxides, are attracting more and more attention [4]. Metal oxides with photoluminescence property, especially rare earth based composite materials have been of interest with respect to possible applications. However, it is more difficult to find a suitable blue phosphor because wide band gap is required, and the naked eye sensitivity is quite low in the blue special region. Recently, much attention has been paid to the preparation of blue phosphors using different chemical and physical methods [5]. Among them, a novel blue luminescence compound Sr_2CeO_4 was successfully identified using combinatorial Material synthesis by electron beam evaporation with multiple targets moving masks, which was reported by Danielson et al. [6,7] synthesized a new rare-earth luminescent material Sr_2CeO_4 , possessing one-dimensional chain structure of edge-sharing CeO_6 octahedron separated by Sr atoms, studied its optical properties, and determined that the emission of Sr_2CeO_4 displays a broad band with a peak position at 475 nm, which can be ascribed to the charge-transfer transition $Ce^{4+}-O^{2-}$. Since, then lots of scientists have taken great interest in studying the structure and luminescent properties of this novel material [6-12]. Sankar and Rao [13] reported a PL study on pure and Eu^{3+} doped compounds synthesized by conventional solid state reaction and the photoluminescence of Sr_2CeO_4 have proved as a good candidate for the blue oxide-based phosphors.

In this paper, we report here blue phosphor Sr_2CeO_4 was synthesized using solid state reaction method in air atmosphere. The samples were characterized by Thermo analytical techniques (TG, DTA, DTG and DSC), Fourier transformation infrared (FTIR) spectroscopy, and Photoluminescence at room temperature. The Chromatic coordinates (x,y) of prepared materials was calculated with color calculator version2, software from Radiant Imaging. Photoluminescence properties show that the phosphors have potential application for solid-state lighting purpose.

Experimental

Materials and synthesis

Sr_2CeO_4 blue phosphor was synthesized by the solid state reaction method. Strontium Carbonate $SrCO_3$, and Cerium Oxide CeO_2 , of 99.5 % purity were used as starting materials to prepare Sr_2CeO_4 phosphor. A Stoichiometric mixture of these powders was thoroughly homogenized in

agate mortar for 1hr. and then transferred to alumina crucibles. The homogenized mixture was heated in air at 1200 °C for 4h in a muffle furnace with heating rate of 300 °C/hr. Finally cool down to room temperature by furnace shut off. All samples were prepared by same technique.

The synthesis route for solid state reaction method is very easy and does not require expensive as well as sophisticated equipments. The major advantage of solid state reaction method is, the final production solid form is structurally pure with the desired properties depending on the final sintering temperatures. This method is environment friendly and no toxic or unwanted waste is produced after the solid state reaction is complete. In this process the powders produced from solid state reaction is very fine as well as the cross contamination is very less. This method is also convenient for large scale production on industrial scale.

Characterizations

Thermo gravimetric analysis (TG, DTA, DTG, and DSC) of precursor of Sr_2CeO_4 was carried out in nitrogen atmosphere in 30–1200 °C temperature range using a Perkin Elmer, Diamond TG/DTA instrument. The initial mass of sample taken for recording the TG/DTA curves was 64.778 mg and hold for 1.0 min at 30 °C, and then heating rate was maintained at 10 °C/min. The phase composition and phase structure were characterized by X-ray diffractograms (XRD) using an automated Rigaku Miniflex X-ray diffractometer (D Max III VC, Japan). The FTIR spectra of Sr_2CeO_4 were recorded on SHIMADZU IRAffinity-1 spectrophotometer with KBr pellet method over the wave number range 400–4,000 cm^{-1} . The photoluminescence excitation and emission spectra were measured by Spectrofluorophotometer (SHIMADZU, RF – 5301 PC) equipped with a 150 W Xenon lamp as excitation source. All the spectra were recorded at room temperature. The emission and excitation spectra of Sr_2CeO_4 phosphor were recorded for excitation at 263 nm and 362 nm, and for emission at 468 nm.

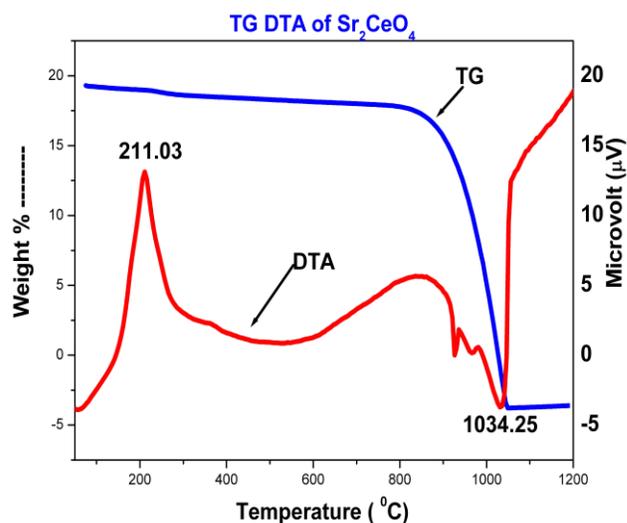


Fig. 1. TG, DTA curves of Sr_2CeO_4 .

Results and discussion

Thermogravimetric analysis

Fig. 1 shows simultaneous TG, and DTA curves of the precursor prepared by solid state reaction method. Initial Weight loss of about 0.037% in TG curve in the range of temperature 200 °C to 500 °C arises due to solid to solid phase transition at the starting of reaction between SrCO₃ and CeO₂. The Weight loss of about 18.365 % occurs through the broad range 565.43 °C to 1032.25 °C due to accompanied by release of 2CO₂ it is in good agreement with the calculated value 18.82 %. The step inflection point in this stage occurs at 1032.25 °C and onset temperature is 940.71 °C. After this stage TG curve did not show an appreciable mass change in the temperature range of 1032-1200 °C, the precursor is thermally stable in this range and the stable residual weight 80.52% corresponds to Sr₂CeO₄ (calculated value 81.15%). It indicate that the phosphor formation reaction is over by 1032.25 °C.

Differential thermal analysis

The exothermic at temperature 211.03^o C is occurs due to the phase change in starting of reaction between SrCO₃ and CeO₂. The endothermic peak at 1034^o C in DTA curve corresponds to the Weight loss due to the release of 2CO₂.

Derivative thermogravimetric analysis

The curve DTG shown in **Fig. 2(a)** the sharp endothermic peak at 980^o C is attributed due to the loss of CO₂. This endothermic peak observed in the DTG curve indicates the reaction starts at 965 °C and inflection occurs at 1061 °C. The peak observed in the DTG curve corresponding to the weight loss in the TG curve. Beyond the temperature 1100^o C, the reaction proceed and finally a stable residue Sr₂CeO₄. No further Weight loss is found, suggesting that the Sr₂CeO₄ can be prepared at higher than 1100^o C. Following chemical reaction is expected to occur during the decomposition stage,

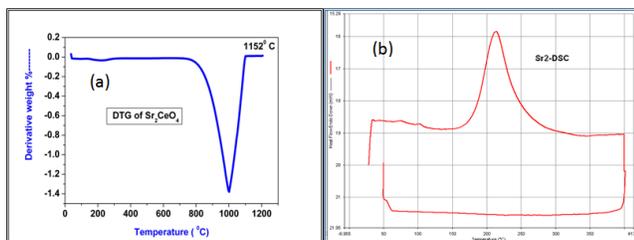
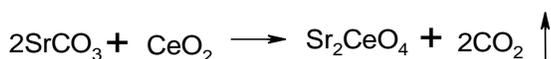


Fig. 2. (a) DTG and (b) DSC curves of Sr₂CeO₄.

Differential scanning calorimetry

The DSC curve for Sr₂CeO₄ prepared by solid state reaction method is shown in **Fig. 2(b)**. The exothermic peak observed at 215 °C due to the phase change in starting of reaction between SrCO₃ and CeO₂. Since the instrument cannot go beyond 400 °C, complete endothermic could not be recorded.

Structural properties

The structure and phase purity of the synthesized Sr₂CeO₄ phosphor was investigated by X-Ray Diffraction Method. Results are shown in **Fig. 3** and all diffraction peaks can be well indexed based on the JCPDS data card No. 50-0115.

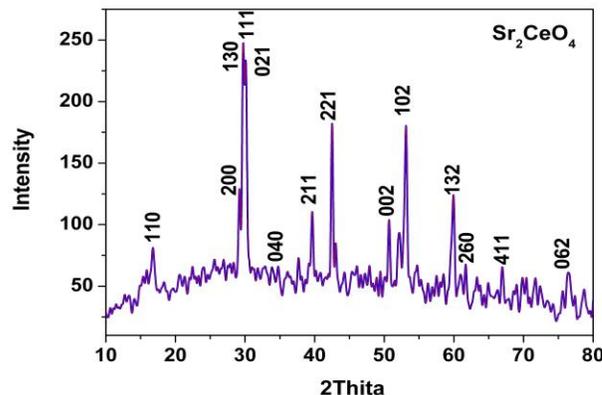


Fig. 3. XRD pattern of Sr₂CeO₄.

All diffraction patterns were obtained using Cu K α radiation ($\lambda = 1.54051 \text{ \AA}$), at 30 kV and 15 mA. Measurements were made from $2\theta = 10^\circ$ to 80° with steps of 0.02° . The crystallite size of powders samples were calculated from X-ray peak broadening of the diffraction using Scherer's formula. The calculated average crystallite size of the Sr₂CeO₄ phosphor is 22 nm. The XRD patterns of the powders revealed that the structure of Sr₂CeO₄ is orthorhombic having lattice parameters $a = 6.1200 \text{ \AA}$, $b = 10.3600 \text{ \AA}$, $c = 3.5900 \text{ \AA}$ and cell volume $V = 227.62 \text{ (\AA}^3)$, which agrees with the findings of previous research work of Danielson et al [5, 7], Sankar et al [13].

FT-IR spectrometry

The synthesized Sr₂CeO₄ by solid state reaction method have been subjected to Fourier transform infrared studies, which are used to analyze qualitatively the presence of functional group in the powder. The FTIR spectrums of powders were recorded using IR affinity-1 made by Shimadzu FTIR Spectrometer by KBr pellet technique. The FTIR spectrum of the Sr₂CeO₄ is shown in **Fig. 4**.

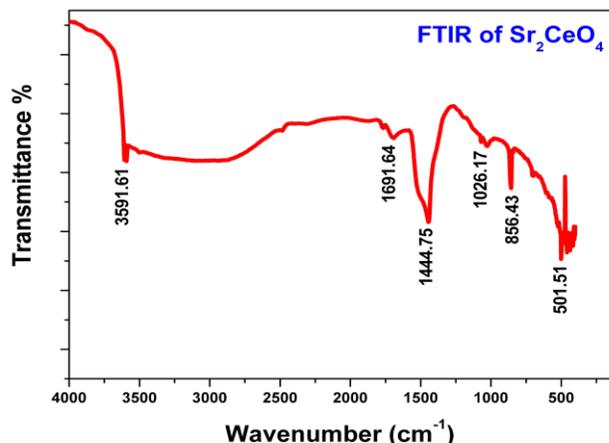


Fig. 4. FTIR of Sr₂CeO₄.

The peaks at 3700 cm^{-1} are assigned to water molecules that may be present due to absorption of moisture or impurities, usually present in KBr respectively. The absorption peaks at 1691.64 , 1444.75 , 1026 , 856.43 , and 501.51469 cm^{-1} were assigned to stretching characteristics of SrCO_3 [2]. The absorption peak between $600\text{--}300\text{ cm}^{-1}$ is assigned to the metal oxide frequency band. The peak 459 cm^{-1} is assigned to the Ce \square O vibration of octahedra CeO_6 [17].

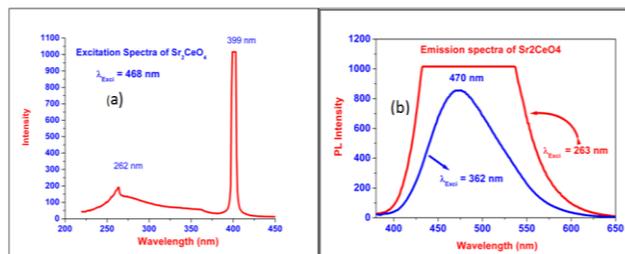


Fig. 5. (a) Excitation spectra (b) Emission spectra of Sr_2CeO_4 .

Photoluminescence properties

The excitation spectrum recorded for the Sr_2CeO_4 phosphor at room temperature displays a broad band with two peaks, one in the range $226\text{--}375\text{ nm}$ and the other at around $390\text{--}410\text{ nm}$ as shown in fig. **Fig. 5 (a)**. The excitation spectrum of Sr_2CeO_4 shows a broad band with two peaks around 262 and 399 nm , and the latter stronger than former. These two excitation peaks may be related to different Ce^{4+} - O^{2-} distances in the lattice. This broad band could be assigned to the transition $t_{1g} \rightarrow f$, where f is the lowest excited charge transfer state of the Ce^{4+} ion and t_{1g} is the molecular orbital of the surrounding ligand in six fold oxygen co-ordination. This broad band is the charge transfer (CT) band of the Ce^{4+} ions in this lattice with 262 nm to check for its suitability for applications. In addition, efficient excitation with radiation of wavelengths in the range $390\text{--}410\text{ nm}$ is also possible, [13].

When excited with the radiation of wavelength 262 nm , Sr_2CeO_4 emits a broad band in the blue region which extends from $380\text{--}600\text{ nm}$ with peak around 470 nm as shown in **Fig. 5(b)**. This is good agreement with the result of Danielson et al. [5] and R. sankar et al. [13], and the broad band can be assigned to the $f \rightarrow t_{1g}$ transition of Ce^{4+} . In present work, the spectrum broad band from $350\text{--}650\text{ nm}$, which is broader than reported by yong dong Jiang [10]. The emission spectrum of Sr_2CeO_4 observed with 362 nm excitation, similar to that observed with 262 nm excitation, the only difference is the appearance of a weak intensity at same peak.

CIE Coordinates

Most lighting specifications refer to colour in terms of the 1931 CIE chromatic colour coordinates which recognize that the human visual system uses three primary colours: red, green, and blue. In general, the colour of any light source can be represented on the (x, y) coordinate in this colour space. The colour purity was compared to the 1931 CIE Standard Source C (illuminant Cs ($0.3101, 0.3162$)).

The dominant wavelength is the single monochromatic wavelength that appears to have the same colour as the light source. The dominant wavelength can be determined by drawing a straight line from one of the CIE white illuminants (Cs ($0.3101, 0.3162$)), through the (x, y) coordinates to be measured, until the line intersects the outer locus of points along the spectral edge of the 1931 CIE chromatic diagram [14-16].

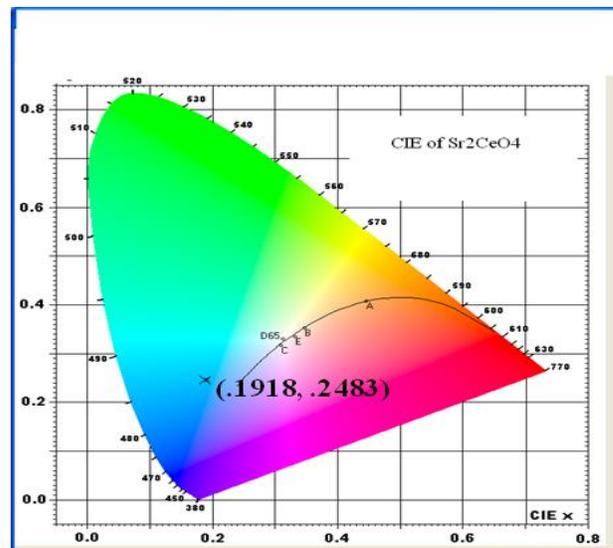


Fig. 6. CIE co-ordinates of Sr_2CeO_4 depicted on 1931 chart.

The color co-ordinates for the pure Sr_2CeO_4 were $x = 0.1918$ and $y = 0.2483$ as shown in **Fig. 6** this does not match with the co-ordinates reported by Danielson et al. ($x=0.20, y=0.30$) [6] and those of Jiang et al. ($x=0.19, y=0.26$), [10]. This phosphor having color tunability from blue to white light and this phosphor has an application in the lighting system.

Conclusion

Strontium Cerium Oxide Sr_2CeO_4 was successfully synthesized by solid state reaction method. The XRD patterns of the powders revealed that the structure of Sr_2CeO_4 is orthorhombic, Thermal analysis indicates that Sr_2CeO_4 can be prepared at temperature higher than $1100\text{ }^\circ\text{C}$. The emission spectra of Sr_2CeO_4 phosphor was observed under excitation 262 and 320 nm , phosphor shows broad emission from $350\text{--}650\text{ nm}$ peaking at 470 nm . The color co-ordinates for the pure Sr_2CeO_4 were $x = 0.1918$ and $y = 0.2483$. Solid state reaction method proved to be very promising for the controlled preparation of this blue phosphor material, with an even better CIE chromacity index than reported previously. The result shows this phosphor has potential application in the field of emission devices.

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