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Structural and Optical Properties of Samarium Doped Sr_2CeO_4 via Solid State Reaction Method.

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ABSTRACT

Strontium cerium oxide Sr_2CeO_4 doped Sm^{3+} phosphor was synthesized by solid state reaction method at temperature 1200^0 C for 4h. The powder samples were characterized by X-ray diffraction (XRD), Raman spectra, Fourier Transform infrared spectra (FTIR), Scanning Electron microscope (ESM), Energy dispersive spectra (EDS), and photoluminescence. The X-Ray diffraction pattern reveals the crystallite size and the structure is orthorhombic. Photoluminescence excitation and emission spectra of $Sr_2Ce\ O_4$: xSm^{3+} ($0.5 \leq x \leq 1.5$) are recorded at room temperature. The color co-ordinates for the $Sr_2Ce\ O_4$: 1.0 mol % Sm^{3+} were x =0 .6687 and y = 0.3311.This phosphor has a good potential for applications in display devices.

INTRODUCTION

The Rare earth materials have attracted much attention for their impressive applications in artificial light, X-ray medical radiography, lamps and display devices [1, 2]. The discovery and development of new phosphor materials is of great importance for the advance of flat panel display and illumination technology. Compared with organic materials and sulfide phosphors, oxide-based phosphors have the advantage: stable crystalline structure and high physical and chemical stability. Therefore, oxide-based phosphors, especially rare earth-based oxide phosphor are attracting more and more attention [3,4,5]. It has been found that the luminescence materials with low-dimensional structures generally exhibit special luminescence properties [6, 7]. Sr_2CeO_4 consists of infinite edge-sharing CeO6 octahedra chains separated by Sr atoms. Luminescence originates from a ligand to metal Ce^{4+} charge transfer. The broad emission band of Sr_2CeO_4 blue phosphor 471 nm is suitable for the doping of rare earth ions in pursuing new luminescent materials. The rare earth materials exhibit excellent sharp- emission luminescence properties with suitable sensitization and effectively used in designing of white light emitting materials [6,7,8,9]. In this paper, the formation process, micro-structure and luminescent properties of the synthesized Sr_2CeO_4: xSm^{3+} ($0.5 \leq x \leq 1.5$) were investigated.

MATERIALS AND METHODS

The starting materials were Strontium Carbonate $SrCO_3$, Cerium Oxide CeO_2, and Samarium Oxide Sm_2O_3 of 99.9 % purity. These materials were taken in Stoichiometric proportions of Sr: Ce as 2:1. $SrCO_3$ and CeO_2 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.

The structural studies were carried out by X- ray diffraction technique in reflection mode with filtered Cu Kα radiation (λ = 1.54051 A^0 with Rigaku, D Max III VC, Japan. Raman spectra were recorded on Renishow Invia Raman microscope. 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 spectra was recorded at room temperature using Spectrofluorophotometer (SHIMADZU, RF – 5301 PC) using Xenon lamp as excitation source.

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RESULTS AND DISCUSSION

The typical X-ray diffraction pattern of the resultant Sr_2CeO_4:xSm^{3+} ($0.5 \leq x \leq 1.5$) phosphors prepared via the solid state reaction method are shown in fig. 1. The patterns of the samples ($0.5 \leq x \leq 1.5$) were well consistent with the data indicated in JCPDS card No. 50-0115 [2] and structure of Sr_2CeO_4 phosphor is orthorhombic. The calculated average crystallite size of the Sr_2CeO_4 phosphor is 22 nm [7]. When Samarium doped with Sr_2CeO_4 the crystallite size is increases which is shown in table1.

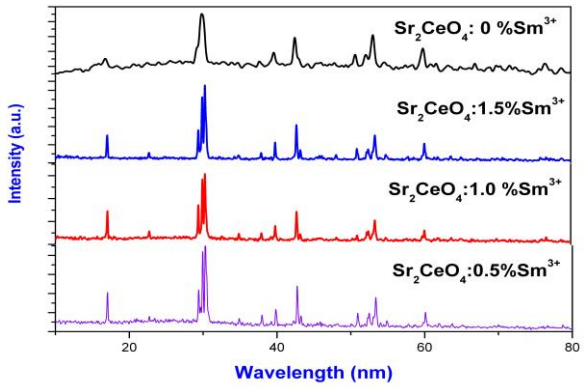

Figure 1: XRD Pattern of Sr_2CeO_4: Sm^{3+}

Phosphors	Crystallite size
Sr_2CeO_4: 0% Sm^{3+}	22nm
Sr_2CeO_4: 0.5% Sm^{3+}	35 nm
Sr_2CeO_4: 1.0% Sm^{3+}	46 nm
Sr_2CeO_4: 1.5% Sm^{3+}	50 nm

Table 1: Showing Crystallite size for different concentration

As doping concentration increases from 0 to 1.5 %, the crystallinity of Sr_2CeO_4: xSm^{3+} ($0.5 \leq x \leq 1.5$) phosphor was decrease slightly with the increase in doping amount of Sm^{3+}. Samarium ions were doped to substitute strontium ions in the host lattice of Sr_2CeO_4 due to the similar ionic radius and electric charge. However the difference of ionic radius of Sr^{2+} (For 6-coordination, ionic radius of Sm3+ (0.0958 nm) was smaller than that of Sr^{2+} (0.118 nm), would lead to destroy the crystal structure of Sr_2CeO_4, resulting in the formation of SrCeO3 and decrease in crystallinity of Sr_2CeO_4.

In order to study the morphology of the Sr_2CeO_4: Sm^{3+}, SEM analysis was carried out. Figure 2 a) shows the SEM photograph of Sr_2CeO_4: Sm^{3+} powder prepared via the solid state reaction method heating at 1200 ^{0}C for 4h. From the results it is clear that the particles of Sr_2CeO_4: 1 mol % Sm^{3+} is in irregular shape and loosely agglomerated. EDS was performed to further confirm the composition of the obtained products. Figure 2 b) indicates that the product is composed of Sr, Ce, O, and Sm with an approximate molar ratio of 1.99:1:4:0.01, which is in good agreement with those of the feed.

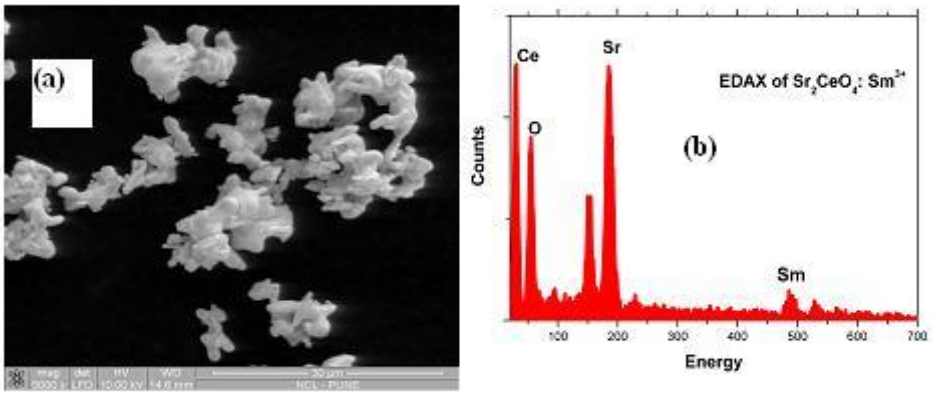

Figure 2: a) SEM of Sr_2CeO_4: $Sm^{3+}$and b) EDS of Sr_2CeO_4: Sm^{3+}

The synthesized Sr_2CeO_4: x mol % Sm3+ ($0.5 \leq x \leq 1.5$) prepared by solid state reaction method has 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 Sr_2CeO_4 is shown in Fig. 3. The peaks at 2316 cm^{-1} are assigned to water molecules that may be present due to

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absorption of moisture. usually present in KBr respectively. The absorption peaks at 1444, 1072, and 486 cm^{-1} were assigned to stretching characteristics of $SrCO_3$ [4].

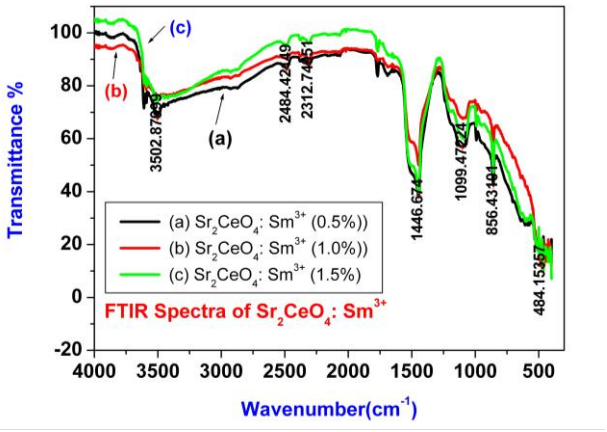

Figure 3: FTIR spectra of Sr_2CeO_4: Sm^{3+}

Raman spectroscopy is very useful tool to determine the phase and structure of multioxide system [6]. The figure 4 shows room temperature Raman spectra of Sr_2CeO_4: x mol % Sm^{3+} ($0.5 \leq x \leq 1.5$) sample calcineted at 1200 ^{0}C temperature for 4h. The Raman band at 557 cm^{-1} is assigned to symmetric stretching mode of $SrCO_3$ which coincide well with the IR features. The band at 553 cm^{-1} is attributed to antisymmetric bending vibration. Two strong Raman bands at 286 and 385 cm^{-1} are detected, which can be attributed to the stretching modes of the Ce-O_2 and Ce-O_1 of CeO_6 octahedra in Sr_2CeO_4 respectively. So the contribution of Ce-O_2 bonds increases corresponding with Ce-O_1 bonds to induce the charge transfer [5], which related to the luminescence of this material.

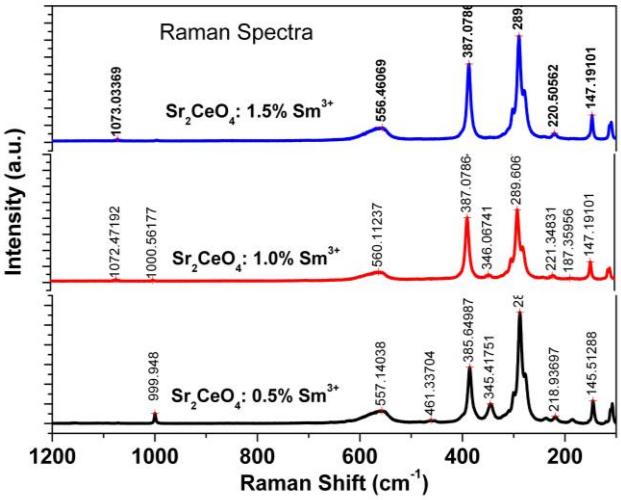

Figure 4: Raman Spectrum of Sr_2CeO_4: Sm^{3+}

Luminescent Properties

The excitation spectra of solid state reaction derived Sr_2CeO_4: xSm^{3+} ($0.5 \leq x \leq 1.5$) calcinated at 1200 ^{0}C for 4h, as shown in figure 5. The excitation spectra is broad spectra from 220 to 400 nm and centered located at 356 nm. The broad band could be assigned to the legend to-metal charge transfer from O^{2-} to Ce^{4+}.

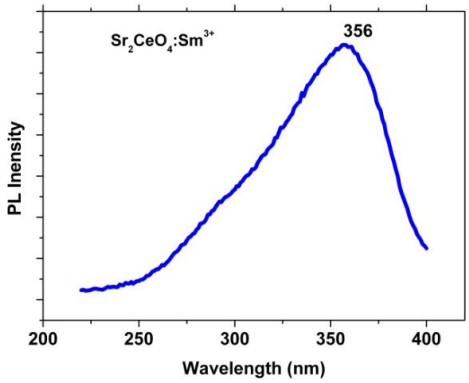

Figure 5: Excitation spectra of Sr_2CeO_4: Sm^{3+}

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The emission bands in figure 6 can be attributed into two groups corresponding to different transition of Sm^{3+} [6]. The emission peak at 568 nm corresponds to $^4G_{5/2} \rightarrow {}^6H_{5/2}$, transition, 611nm corresponds to $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition and the transition 653 nm corresponds to $^4G_{5/2} \rightarrow {}^6H_{9/2}$, the strongest emission peak located at 611 nm showing prominent and red light is due to the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ magnetic dipole transition of Sm^{3+}.

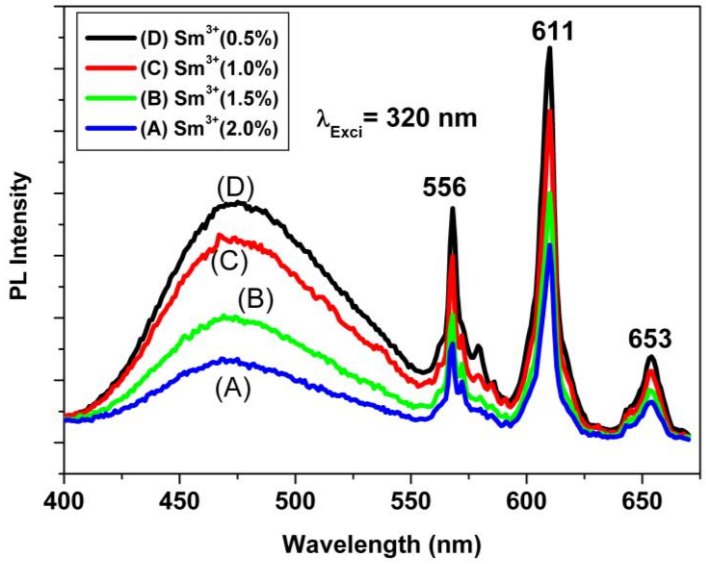

Figure 6: Emission spectra of Sr_2CeO_4: Sm^{3+}

To study the effect of trivalent samarium doping and to see the effect of the same on the emission characteristics of the host, photoluminescence spectra were recorded at room temperature for the Sr_2CeO_4: xSm^{3+} (x= 0.5%, 1%, 1.5%) as shown in figure 2 Under excitation with 320 nm wavelength the emission spectra shows the broad Ce^{4+}–O^{2-} charge transfer band in the blue region superimposed with the Sm^{3+} emission lines in the yellow and red region. These spectral features are characteristic of intra-configurationally f-f transitions of the RE ions. Because tetravalent cerium in Sr_2CeO_4 has no 4f electrons, emissions are due to the presence of Sm^{3+} having five 4f electrons. But on increasing the samarium concentration the sharp lines of the samarium emission appear prominently and the Ce^{4+}–O^{2-} CT transitions of the host decreases relatively. The narrow lines are assigned to the transitions from the between $^4G_{5/2}$ excited state to the lower ^6H_J (J = 5/2, 7/2 and 9/2) energy levels of the ground multiplets of Sm^{3+}. According to the selection rules [15] magnetic dipole transitions that obey J = 0 and ±1 (J = total angular momentum) are allowed for Sm^{3+} in a site with inversion symmetry. The emission spectra for the Sr_2CeO_4 sample were peaking at the 469nm but when doped with samarium, the emission spectra are dominated by the red $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition centered at 611nm. Additional emission were observed at the 568 and 653nm ascribed to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transitions, respectively.

The emission spectra shows broad Ce^{4+}–O^{2-} CT emission band in the blue-green region superimposed with the Sm^{3+} emission lines in the yellow and orange-red regions. It is further observed from the emission spectra of Sr_2CeO_4: xSm (0.5 to 2%), that as the samarium concentration increases, the photoluminescence intensity at 468nm goes on decreasing but the intensity at 568nm and 611nm shows an increase for Samarium (0.5mol%) concentrations.

CIE Co-ordinates

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. 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 (*C*s (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 [12,13,14].

The colour co-ordinates for the pure Sr_2CeO_4 were x = 0.1515 and y = 0.1674 and Sm, doped Sr_2CeO_4 phosphors were x=0.6687 and y=0.3311. Figure 7 illustrates the CIE chromaticity diagram for the emissions of pure and Sm^{3+}, (1.0mol %) doped Sr_2CeO_4. This phosphor having colour tenability from blue to white light and has potential for application in the lighting system.

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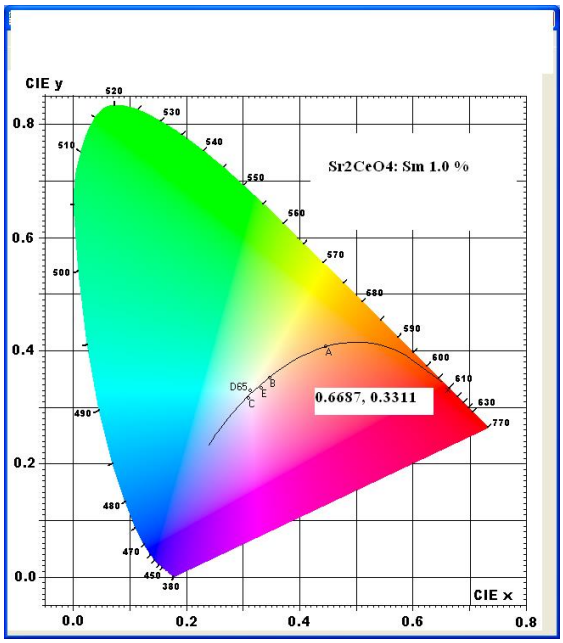

Figure 7: CIE co-ordinates for Sr_2CeO_4: Sm^{3+}

CONCLUSION

Sr_2CeO_4: xSm^{3+} (x = 0.5, 1.0, 2%), was successfully synthesized by solid state reaction method. The XRD study confirms that the Sm3+ doped Sr_2CeO_4 compound has orthorhombic structure at room temperature. The EDS studies confirm the formation of Sr_2CeO_4: Sm^{3+}. The average crystallite size of the trivalent Samarium doped with Sr_2CeO_4 the crystallite size is 68 nm. The emission peaks at 568nm corresponds to $^4G_{5/2} \rightarrow {}^6H_{5/2}$, 611nm corresponds to $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and the transition 653nm corresponds to $^4G_{5/2} \rightarrow {}^6H_{9/2}$, the strongest emission peak located at 611 nm showing prominent and red light is due to the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition of Sm^{3+}. The color co-ordinates for Sr_2CeO_4: 1.0 mol % Sm^{3+} were x = 0.6687 and y = 0.3311. Solid state reaction method proved to be very promising for the controlled preparation of 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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