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Research Article

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Synthesis and Characterization of Red Emitting Sr₂CeO₄: Eu³⁺ Nano Phosphors

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ABSTRACT

The phosphors Sr_2CeO_4 : Eu^{3+} was successfully synthesized by solid state reaction method. The X-Ray diffraction (XRD) profile confirms the orthorhombic structure of Eu3+ doped Sr2CeO4 nano phosphors. The efficiency of the prepared phosphors was analyzed by means of its emission spectral profiles. We also observed a rich red emission from the prepared phosphors under Ultra- Violet (UV) source. Such luminescent powders are expected to be applied as red phosphors in display devices applications. In addition, Scanning electron Microscopy (SEM), Fourier-Transformation IR spectroscopy (FTIR), and Raman Spectrum were also used to study the synthesized phosphors.

Keywords: Photoluminescence, FTIR solid state reaction method, XRD, SEM, Phosphor.

INTRODUCTION

In recent decades, the luminescent properties of trivalent europium have attracted much attention because of its potential use as a dopent, since it can emit red fluorescence with high luminescence efficiency under UV light excitation. [1]. The blue emitting phosphor, Sr2CeO4 which has been discovered by Danielson et. al. [2] Sr_2CeO_4 consist of infinite edge-shearing CeO₆ octahedra chains separated by Sr atoms. In CT transitions, an electron is transferred from an external ligand to the 4fⁿ shell of the RE ion. However such a transition involves a considerable reorganization of the charge density distribution around the metal ion along with transfer of electrons. Some states that arise at such a transition are stable and can relax to the ground state with photon emission (CT Luminescence) [1-7]. The luminescence originates from a ligand-to metal Ce⁴⁺ charge transfer [5]. The broad emission band is suitable for the doping of rare earth ions in pursuing new luminescent materials. The blue phosphors are very few and if a suitable blue phosphor. The rare earth materials exhibit excellent sharp- emission luminescence properties with suitable sensitization and effectively used in designing of white light emitting materials. In this paper, the formation process, micro-structure and luminescent properties of the synthesized Sr_2CeO_4 and Sr_2CeO_4 :Eu³⁺ were investigated.

EXPERIMENTAL SECTION

Eu3+ doped Sr2CeO4 phosphors were prepared by conventional solid state reaction method. The starting materials were; Strontium Carbonate SrCO₃, Cerium Oxide CeO₂, and Europium Oxide Eu₂O₃ supplied by National Chemicals, Baroda, (Gujarat State) of 99.5 % purity. The starting materials were taken in Stoichiometric proportions were thoroughly homogenized in agate mortar for 45 min and then transferred to alumina crucibles for heat treatment in air in muffle furnace. The compounds were subjected to heat treatment at 1050° - 1150° C for 40 -

50 h with three intermediate grindings and heating, and finally cooled to room temperature by furnace shut off. All samples were prepared by same technique.

The powder X- ray diffractograms (XRDs) of the compounds were recorded using an automated Rigaku Miniflex Xray difractometer (D Max III VC, Japan). The observed (hkl) reflections and their intensities were compared with the calculated ones generated using the computer program POWD (an Interactive Powder Diffraction Data Inerpretation and Indexing Program, Version 2.2). The Scanning Electron Micrographs (SEMs) of the samles were obtained using a Leica Stereoscan 440 model fitted with an E5000 Polaron coating unit (rating 10kV, 25 pA beam current) The FTIR spectrums were recorded on SHIMADZU IR Affinity-1 model transmission spectrometer with KBr pellet method over the range 400- 4000 cm⁻¹. Raman spectra were carried out by Renishaw Invia Raman Microscope. The photoluminescence excitation and emission spectra were recorded at room temperature using Spectrofluorophotometer (SHIMADZU, RF – 5301 PC) equipped with a 150 W Xenon lamp as excitation source

RESULTS AND DISCUSSION

The structure and phase purity of the Sr_2CeO_4 phosphor and Sr_2CeO_4 doped Europium with different concentration synthesized by solid state reaction method was investigated by X-Ray Diffraction Method. Results are shown in Fig. 1. All diffraction patterns were obtained using Cu K α radiation ($\lambda = 1.54051$ A°), at 30 kV and 15 mA. The 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 equation

$D = 0.9\lambda / \beta$. Cos θ

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($\lambda = 1.54051 \text{ A}^\circ$), and θ the diffraction peak angle.



Figure 1 XRD Pattern of Sr₂CeO₄ and Sr2CeO4: Eu³⁺

The calculated average crystallite size of the Sr_2CeO_4 phosphor is 22 nm. When Europium doped with Sr_2CeO_4 the crystallite size is 48 nm. The computer program POWD (an Interactive Powder Diffraction Data Interpretation and Indexing Program, Version 2.2) was used to calculate hkl and d values and lattice parameters. The XRD patterns of the powders revealed that the structure of Sr_2CeO_4 is Orthorhombic, which are very close to the reported values JCPDS card (50-0115). Except this no other phase exists in the XRD spectra, indicating the formation of the final product

The FTIR spectrums of powders were recorded using IR affinity-1 made by Shimadzu FTIR Spectrometer by KBr pellet technique. Fig.2 represent FTIR spectrum of Sr_2CeO_4 and $Sr_{2-x}Eu_xCeO_4$. From spectrum it is observed that the peak at 3591 cm-1 is assigned to H_2O .







The specimen might have absorbed moisture from the atmosphere. The absorption peaks at 1691, 1452, 1026 and 856cm^{-1} due to legand formation were assigned to stretching characteristics of SrCO₃. The FTIR spectra clearly indicate that the functional group of pure Sr₂CeO₄ and Sr₂CeO₄: Eu³⁺ is not altered by addition of Europium.

Raman spectra were used as a complement of FTIR spectra for studying phase and structure of Sr_2CeO_4 . There was some distinct differences observed from Raman spectra of fig 3. The Raman shift at 292 cm-1 is relatively to F_{2g} band of CèO₂ with fluorite type structure. The shift at 482, 562, 631 and 661 cm-1 is assigned to the vibration of Ce- O_1 , and the shift at 289, 383 and 439 cm-1 may be ascribed to the stretching mode of Ce- O_2 . With increasing temperature, the change of polarizability of Ce – O_2 is bigger than that of Ce- O_1 , which can be conform from the corresponding Raman intensity. The shift at 1003 cm⁻¹ is assigned to symmetric stretching mode of SrCO₃. The shift at 839 cm-1 is attributed to antisymmetric bending vibration. So the contribution of Ce- O_2 bonds increases comparing with Ce – O_1 bond to induce the charge transfer [5-11].

Fig4 (a) Shows the SEM Micrograph of pure Sr_2CeO_4 of particles prepared by solid state reaction method stained at $1200^{\circ}C$ for four hrs



Figure 4 (a) SEM image of Sr2CeO4



Figure 4(b) SEM Image of Sr2CeO4: Eu3+

Fig. 4 (b) shows SEM micrograph of particles of Sr_2CeO_4 : Eu (1.0%) prepared by same method stained at 1200^{0} C for four hrs, The SEM studies revealed the polycrystalline nature of Sr_2CeO_4 consisting of particles irregular shape and size. While at low magnification the particles appear agglomerated, at high enough magnification, the nature of the individual crystallite is clearly evident. The excitation spectrum of Sr_2CeO_4 is shown in Fig. 5(a). The spectrum displays a broad band with two peaks around 263 nm and 362 nm, and the latter is stronger than the former. These two excitation peaks may be related to different Ce^{4+} . O^{2-} distances in the lattice [2]. The excitation spectrum of Sr_2CeO_4 : Eu³⁺ shows two peaks around 248 nm and 360 nm and former stronger than the latter shown in Fig.5 (b). The emission spectra for pure Sr_2CeO_4 when excitation wavelength is 262 nm the emission peak is at 471 nm shows broad band due to $f \rightarrow t_{1g}$ transition of Ce^{4+} . The emission in perfect blue region with very good intensity shown in fig.6.this results are match with reported literature.



Figure 5 Excitation spectra of Sr2CeO4



Fig. 7 represents the emission spectra of Sr_2 -xEu_xCeO₄ phospors with doping concentration of 1 to 2.0 %.. The blue emission band at 471 nm is attributed to the Ce⁴⁺ - O²⁻ charge transfer transition in Sr2CeO4 host. After doping 1 % Eu³⁺, the phosphors shows white emission due to the overlap of host blue emission band and Eu³⁺ intra ₄F⁶ lines.





The emission spectra of Eu^{3+} contain not only the characteristics transition lines from the lowest excited ${}^{5}D_{0}$ level but also those from higher energy levels (${}^{5}D_{1}$ and ${}^{5}D_{2}$). The emission spectra of Sr2CeO4: xEu^{3+} consist of the characteristic lines of Eu^{3+} corresponding to transitions from the excited ${}^{5}D_{0}$ levels; ${}^{5}D_{2} \rightarrow {}^{7}F_{0}$, ${}^{5}D_{2} \rightarrow {}^{7}F_{2}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{2} \rightarrow {}^{7}F_{3}$, ${}^{5}D_{1} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{1} \rightarrow {}^{7}F_{2}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, and ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ located at 466, 491, 511, 537, 557, 585, 616, and 630 respectively. As Eu^{3+} concentration increases the relative intensity of both ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions at 587 nm and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 616 nm increased. Thus it is suggested that most of Eu^{3+} ions are located in a site without inversion symmetry. At Eu^{3+} (2%) phosphors have a red emission red emission intensity of transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ${}^{7}F_{2}$ was strongest due to the dominance of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition. No wavelength shift or peak at a new site is observed at high Eu^{3+} concentrations



CONCLUSION

 Sr_2CeO_4 : Eu^{3+} phosphor was successfully prepared by solid state reaction method at $1200^{\circ}C$ temperature. , The XRD patterns of Sr_2CeO_4 and Sr_2CeO_4 : Eu^{3+} shows the formation of majority of compound in single phase. The average crystallite size of the Sr_2CeO_4 phosphor is 22 nm. When trivalent Europium doped with Sr_2CeO_4 the crystallite size is 35 nm. The emission of pure Sr_2CeO_4 phosphor was observed at 471 nm which is blue emission, this conform the formation of nano blue phosphor. Sr_2CeO_4 : Eu^{3+} 2% phosphor have a red emission spectra pattern due to the dominance of ${}^5D_0 \rightarrow {}^7F_2$ transition. No wavelength shift or peak at a new site is observed at high Eu^{3+} concentrations. This phosphor can be useful in many lamps and display devices.

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