



EFFECT OF PARTICLE SIZE AND EUROPIUM DOPING ON THE EMISSION CHARACTERISTICS OF THE Sr₂CeO₄ PHOSPHOR

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Abstract

The synthesis technique has been elaborated in paper by both the sol-gel and the solid-state reaction. The doping of the europium into the phosphor was done at the initial stage of the reaction using the Eu₂O₃. Successful Sol-gel synthesis of europium doped Sr₂CeO₄ phosphor. 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 57 nm. The photoluminescence of the obtained phosphors were studied. Comparison with solid state reaction revealed a marked difference in the emission characteristics from 580 nm-630 nm for the 0.5mol% doped europium sample. This may be due to the nano crystal size of the phosphor formed with sol-gel. Greater splitting of the ⁵D₀→⁷F₁, ⁵D₀→⁷F₂ when compared with solid state reaction and few additional lines were seen at 595nm and 611nm for the sol-gel prepared sample. Excellent tunability of phosphor observed when doped with various concentrations of Europium.

Keywords: Sol Gel Method, Phosphor, Emission, Particle Size.

4.1 Introduction

Doping of trivalent rare earths into the host can help and modify the emission characteristics of any phosphor. Doping forms an integral part of any material to be synthesized or the core area, be it semiconductors used in display or insulators like phosphor for the display industry [1]. Judicious use of the dopants enhances and sometimes changes the emission characteristics of the phosphor. Rare earth-based research has been the backbone of the display industry and still the 4fⁿ levels play significant role in enhancing and improving the industry with their charming and fascinating spectroscopic transitions [2]. The rare earth studied for the present case was europium as it gives a lot of information about the host along with other useful information like environment of the host. This rare earth element is the most studied and forms an integral part of many display devices, its transitions are very simple and give valuable information on the host environment. This rare earth element can be doped in two forms viz divalent and trivalent; it requires inert or reducing atmosphere to get into the divalent state. The europium in divalent state has transitions from the 4f⁶ 5d¹ to lower state whereas for the trivalent state it is generally from the ⁵D₀, ⁵D₁ to the ground state at ⁷F_J (where J = 0, 1, 2, 3, 4). Our interest in this work was to monitor and study trivalent Europium, and to see what information it provides about the host in which it has been incorporated. The line emission makes it more appealing to study this rare earth. Till date there are only few reports which have mentioned the doping of tri and tetravalent rare earth ions into the host (Sr₂CeO₄), the efficient mechanism of the emission among them is studied. But there are still no reports of doping by sol-gel synthesis into the host, efficient energy transfer between the host and the guest and their interpretation are still few [3-11].

In this paper, a new modified solid state reaction method was used to synthesize Sr₂CeO₄:Eu³⁺ phosphor. This process perfectly combines the merits of solid-state reaction processing and a high-temperature combustion process. This synthesis has the advantages of inexpensive precursors, convenient process control, and large mass production. The Sr₂CeO₄:Eu³⁺ phosphor was synthesized at a high temperature of 1200°C. The structure, and photoluminescence, study of Sr₂CeO₄:Eu³⁺ phosphor is investigated in detail.

Synthesis and Characterization

The Sr₂CeO₄ 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. The starting materials were Strontium Carbonate SrCO₃, Cerium Oxide CeO₂, Europium Oxide Eu₂O₃ 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 °C at the rate 300 °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 sample was characterized using XRD, The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The X-rays were produced using a sealed tube and the wavelength of X-ray was 0.154 nm (Cu K-alpha). The photoluminescence (PL) emission and excitation spectra were recorded at room temperature by use of a Shimadzu RF-5301 PC spectrofluorophotometer. The excitation source was a xenon lamp. The CIE coordinates (x, y) of prepared materials was calculated with color calculator version2, software from Radiant Imaging.

Result and Discussion

X-ray diffraction studies

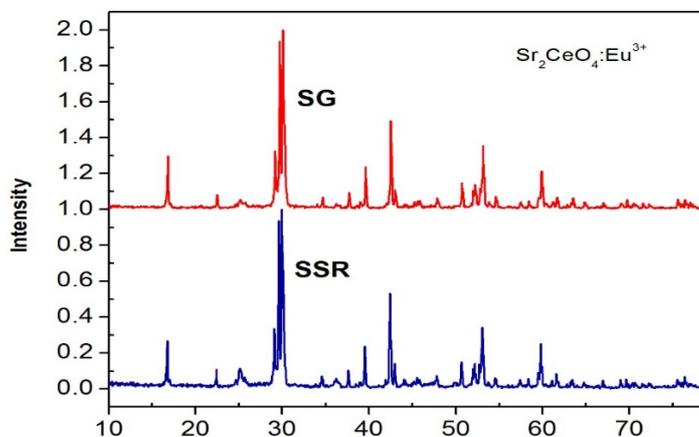


Fig. 1 X-ray diffraction pattern of the europium doped Sr_2CeO_4 synthesized with sol-gel and solid-state reaction Method.

The figure-1 shows the powder X-ray diffraction pattern of the synthesized phosphor sample. The result shows that the phase of the material is almost pure with traces of SrCeO_3 present in it a bit. The average crystallite size was calculated using the Scherrer formula

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where k = Constant (0.9), λ = Wavelength of the x-ray (0.154 nm in the present case), β = full width at half-maxima (FWHM), θ = Bragg angle of the XRD peak.

The crystallinity of the compound as revealed by the XRD pattern, increased on raising the calcining temperature. This was also observed by Shikao Shi et al. [8]. From the analysis of the XRD pattern, it was understood that the introduction of activator Eu^{3+} did not influence the crystal structure of the phosphor matrix. The calculated average crystal size of the sample calculated by measuring the full width half maxima was found to be of about 40 nm for europium 1 mole % doped sample.

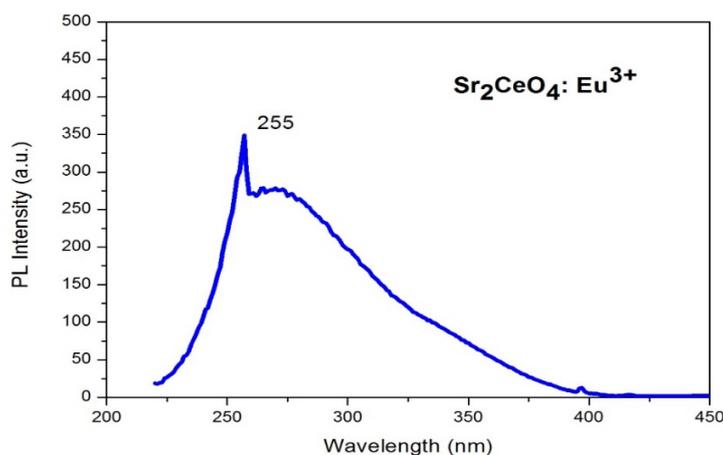


Fig. 2. Excitation spectrum of $\text{Sr}_2\text{CeO}_4: \text{Eu}^{3+}$

The emission spectra for europium doped show transitions starting from 467nm to 656nm. The interesting feature of these spectra is the appearance of europium transition from ${}^5\text{D}_2 \rightarrow {}^7\text{F}_0$ (467nm) which is very rare, since the general oxide host have higher photon energy and thus a non radiative loss from a higher 5D state due to multi phonon relaxation. There are few transitions which are magnetic dipole (MD) like ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_1 \rightarrow {}^7\text{F}_0$ and ${}^5\text{D}_2 \rightarrow {}^7\text{F}_0$ rest all of the transitions that appear are the electric dipole (ED).



We observe that the intensity of the sol-gel synthesized phosphor is quite high as compared to that of the solid-state reaction samples when monitored with 615nm. Whereas, the figure left shows the effect of nano size and the macro size particles. The excitation spectra of the sol-gel synthesized phosphor shows the peak at 254 nm and a hump at around 280 nm, the excitation spectra of the solid-state reaction synthesized samples shows the peak at 254 nm but a shift of hump in the red region is observed when monitored wavelength was 595nm. This peak (hump) shift indicates that as the particle size increases, as already elucidated from the X-ray diffraction pattern, from nano to few micro the excitation of the phosphor shows red shift.

Comparison between sol-gel and the solid-state reaction sample for europium 0.5mole % has been shown in fig. 3. There is a remarkable difference in the emission spectra of the sol-gel and solid-state reaction technique, the spectra is almost similar at all the wavelengths except at the 580-630nm. The most important difference is the generation of the high intensity 595nm peak and with small hump at 611nm for the sol-gel sample which is not seen in the solid-state reaction sample. These are due to splitting of ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ transition levels which are not observed in the solid-state reaction specimen. This shows that the crystal field splits the levels (7F_1 and 7F_2), further; this splitting may be correlated to the small crystal size of the sol-gel prepared sample, the smaller size facilitates the crystal field to split further

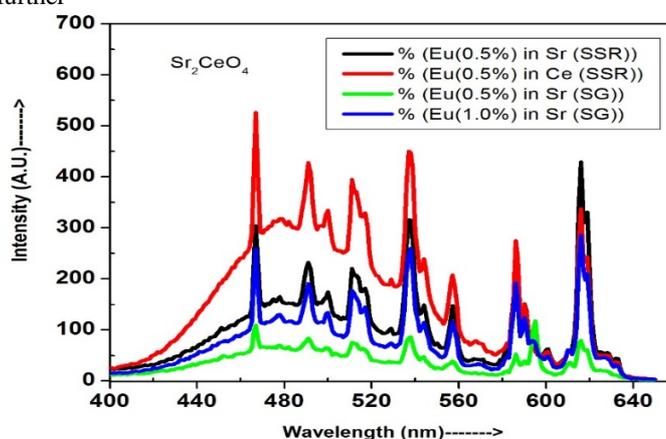


Fig. 3. Emission spectra of $Sr_2CeO_4: Eu^{3+}$ by both method

Conclusion

- Successfully synthesized Sol-gel and solid-state reaction method of europium doped Sr_2CeO_4 phosphor.
- Doping of europium at various concentrations and the study of effective mechanism of energy transfer.
- A very rare europium emission observed at 467nm, the transition being ${}^5D_2 \rightarrow {}^7F_0$ at room temperature photoluminescence measurements.
- Comparison with solid state reaction revealed a marked difference in the emission characteristics from 580nm- 630nm for the 0.5 mol % doped europium sample. This may be due to the nano crystal size (~57nm) of the phosphor formed with sol-gel.
- Greater splitting of the ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$ when compared with solid state reaction and few additional lines were seen at 595nm and 611nm for the sol-gel prepared sample.
- Excellent tunability of phosphor observed when doped with various concentrations of Europium.

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