Luminescence properties of violet-orange-red emitting SrCO$_3$:1% Eu$^{2+}$,x% Cr$^{3+}$ phosphors prepared by sol-gel technique

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Abstract. SrCO$_3$:1% Eu$^{2+}$,x% Cr$^{3+}$ powders were synthesized by sol-gel method at a low temperature below 80 °C. Metal nitrates were used as the source of metal ions and citric acid as a chelating agent. The mol% of Eu$^{2+}$ ions was kept constant at 1%, while the mol% of Cr$^{3+}$ ions were varied in between the range of 1 – 4% during synthesis. The annealed samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) spectroscopy. The XRD revealed that the annealed samples consist of pure orthorhombic SrCO$_3$. Varying the Cr$^{3+}$ concentrations does not affect the crystal structure of the phosphor. Morphology of the phosphor was influenced by varying the Cr$^{3+}$ concentrations. The PL results showed a strong emission peaks in the violet-orange-red regions of the spectrum. The emissions peaks at 430 and 616 nm are attributed to the Eu$^{2+}$ and Eu$^{3+}$ ions, respectively. The emission peak at 700 nm is attributed to the typical $^3$E$_2$ – $^3$A$_2$ transition from the cromophore Cr$^{3+}$ ion. Luminescence evolution from violet-orange-red to violet-red emission with an increase in Cr$^{3+}$ mol% is attributed to the energy transfer from Eu$^{2+}$ to Cr$^{3+}$.

1. Introduction

Nanomaterials with different morphologies have attracted great attention for their promising applications such as optical materials, effective catalyst, drug-delivery carriers [1-3], etc. SrCO$_3$ is one of nanomaterial widely used for the starting material in preparation of strontium compounds [4-6]. SrCO$_3$ is one of the important reagents used in firework, pigment, and electron manufacturing [7]. Similar to the inorganic oxides of the fourth main group of the periodic table, carbonates are expected to show excellent luminescence properties when doped with rare-earth ions [8]. Furthermore, carbonates have the advantages over the sulphites phosphors and these include stability, environmental friendly and they are cheap [8]. SrCO$_3$ doped with foreign atoms have been studied by many researchers around the world. For example, Folkerts et al. [9] have studied the luminescence properties of SrCO$_3$ singly doped with Pb$^{2+}$ and Eu$^{2+}$. On the other hand, the trivalent chromium ion (Cr$^{3+}$) is widely used as luminescent dopant as well as luminescent sensitizer in various hosts materials [10]. In addition, Cr$^{3+}$ ions have great potential applications in luminescent materials because it is cheap, produces deep color and bright luminescent [10]. Various methods have been reported on the preparation of SrCO$_3$ nanostructures including hydothermal [11] microwaves-assisted [12] microemulsion-mediated solvothermal methods [13] solid state reaction [14], co-precipitation method [15] and sol-gel [16]. In comparison with conventional techniques, sol-gel route is an effective technique for the synthesis of nano-phosphors materials. Sol-gel have several advantages such as good mixing of starting materials and relatively low reaction temperature resulting in more homogeneous products [16]. It is known that when incorporating different foreign atoms into the host lattice, the luminescent properties of phosphorescent material can be modified [17]. In this work, SrCO$_3$:1% Eu$^{2+}$,x% Cr$^{3+}$ nanophasor powders were synthesized via the sol-gel technique. The effects of varying the Cr$^{3+}$ mol%, while keeping the 1% Eu$^{2+}$ constant, were investigated. The main purpose is to develop the phosphor emitting a white light.
2. Experimental
The powders of SrCO$_3$:1% Eu$^{2+}$, x% Cr$^{3+}$ phosphors with different mol% of Cr$^{3+}$ were prepared by sol-gel process. The starting materials used were Sr(NO$_3$)$_2$, Al(NO$_3$)$_3$, Eu(NO$_3$)$_3$, Cr(NO$_3$)$_3$ and C$_6$H$_8$O$_7$ (citric acid) was used as a chelating agent. These materials were dissolved in deionized water and stirred constantly on the magnetic stirrer at a temperature below 80°C until gelation following the chemical reaction. After hydrolysis and condensation the prepared white gels were dried at 130°C in an oven. The dried gel was ground and subsequently annealed at 800°C. The crystal structure of the samples was characterized by powder X-ray diffraction (Bruker AXS Discover diffractometer) with CuKα (1.5418Å) radiation. The surface morphology of the phosphor powder was established using a Shimadzu Superscan ZU SSX-550 electron microscope (SEM). PL excitation and emission spectra were obtained by using Xenon lamp (Varian Carry eclipse fluorescence).

3. Results and discussion

3.1 Structure and morphology
Fig. 1. shows the diffractions peaks of the heat treated SrCO$_3$:1% Eu$^{2+}$, x% Cr$^{3+}$ powders at different mol% of Cr$^{3+}$ ions. The XRD pattern matches well with the peaks of SrCO$_3$ in JCPDS card no. 74-1491 [18]. The results suggest that varying the mol% of Cr$^{3+}$ ions does not affect the crystal structure of the phosphor. The grain sizes powders were estimated by using the Scherrer formula [19] using the most intense peak, and were found to be 71, 68, 75 and 70 nm for the 1%, 2%, 3% and 4% Cr$^{3+}$ co-doped, respectively. It is therefore concluded that the Cr$^{3+}$ ions hardly influences the particle size.

![X-ray patterns of SrCO$_3$:1% Eu$^{2+}$, x% Cr$^{3+}$ phosphors.](image)

3.2 SEM
The morphologies of the phosphor powders are shown in Fig. 2. Fig 2(a) shows the mixture of the small spherical particle dispersed over the surface and agglomerated granular particles with grain boundaries. In Fig. 2(b), there are small spherical particles agglomerates. Fig. 2(c), shows a smooth surfaces, which suggests a good adhesion of particle-to-particle interaction with holes or pores morphology. It is suggested that the pores are formed by the degassing during annealing process [8]. As the mol% of Cr$^{3+}$ is increased to maximum, (see Fig. 2(d)) the degree of particles agglomeration is high with the mixture of the smooth surfaces and pores. Thus, the increase in the mol% of Cr$^{3+}$ influences the morphology of the phosphor.
Fig. 2. SEM images of SrCO$_3$:1% Eu$^{2+}$, X% Cr$^{3+}$ phosphors for various mol% of Cr$^{3+}$ (a) SrCO$_3$:1% Eu$^{2+}$, 1% Cr$^{3+}$, (b) SrCO$_3$:1% Eu$^{2+}$, 2% Cr$^{3+}$, (c) SrCO$_3$:1% Eu$^{2+}$, 3% Cr$^{3+}$ and (f) SrCO$_3$:1% Eu$^{2+}$, 4% Cr$^{3+}$, respectively. Field of view 0.05 nm.

3.3 Photoluminescence characteristics

Fig. 3(a) shows the PL excitation spectra when monitored the red emission at 700 nm. It was observed that the main peaks of excitation are at 240 and 350 nm. The broad absorption band with maximum at 240 nm is attributed to the charge transfer (CT) state of Eu$^{3+}$ - O$^2-$ or the host absorption. The 350 nm absorption corresponds to the transition from the lowest sublevel of the 5d states to the $^2F_{7/2}$ multiplets of the 4f configuration in Cr$^{3+}$ [20]. In the study of Sr$_4$Al$_{14}$O$_{25}$, Zong et al. [21] reported that at the range of 200 – 400 nm, UV light can excite only Eu$^{2+}$ not Cr$^{3+}$ since Cr$^{3+}$ excitation consists of the $^4A_2$ – $^4T_2$ absorption at 420 nm and $^4A_2$ – $^4T_1$ absorption at 570 nm [21]. Thus, the strong red emission at 700 nm should be the results of energy transfer from Eu$^{2+}$ to Cr$^{3+}$ in the SrCO$_3$ phosphor.

The emission spectra of SrCO$_3$:1% Eu$^{2+}$, X% Cr$^{3+}$ powders is shown in Fig. 3(b). The position of the peaks at 430 and 700 nm in the emission spectra shows no change, regardless of Cr$^{3+}$ ions doped mol% [22]. The emission at 430 nm is due to 5d-4f transitions of Eu$^{2+}$ ions in the host [23], while the emission at 616 nm is attributed to Eu$^{3+}$ due to the oxidising of Eu$^{2+}$ to Eu$^{3+}$ [23]. The emission peak at 700 nm is attributed to the typical $^5(E_{7} - ^5A_{2})$ from the cromophore (Cr$^{3+}$ ion) transitions [10]. It can be seen that only SrCO$_3$:1% Eu$^{2+}$, 1% Cr$^{3+}$ has three emissions peaks suggesting that Eu$^{3+}$ can oxidize to Eu$^{3+}$ at this Cr$^{3+}$ mol% [14]. Above 1% Cr$^{3+}$, only two emissions peaks are observed at 430 and 700 nm. No any emission peaks of Eu$^{3+}$ were observed in the emission spectra for Cr$^{3+}$ concentrations above 1%, indicating that Eu$^{3+}$ ions in these samples were completely reduced to Eu$^{2+}$. It is clear from Fig. 3(b) that emission intensity at 450 nm was sharply reduced by further addition of Cr$^{3+}$ ions. The energy transfer from Eu$^{2+}$ to Cr$^{3+}$ is confirmed by the decrease of the peak intensity, while the Cr$^{3+}$ peaks intensity is significantly enhanced. A well-known concentration quenching phenomena [10] is also observed as the mol% of Cr$^{3+}$ is increased further. The maximum intensity as a function of Cr$^{3+}$ mol% is shown in Fig. 3(c), which suggests that the optimum concentration is at 2.3% Cr$^{3+}$.
Fig. 3(a) PL excitation spectra of annealed SrCO$_3$:1%Eu$^{2+}$, x%Cr$^{3+}$ (λ$_{em}$ = 700 nm) (b) PL emission spectra (λ$_{ex}$ = 350 nm) of annealed SrCO$_3$:1%Eu$^{2+}$, x%Cr$^{3+}$ phosphors (c) Variation in the intensity as a function of the Cr$^{3+}$ ion concentration.

4. Conclusion
The SrCO$_3$:1% Eu$^{2+}$, x% Cr$^{3+}$ powders were successfully synthesized by sol-gel processing technique. The XRD revealed that the annealed samples consist of pure orthorhombic SrCO$_3$. Varying the mol% of Cr$^{3+}$ does not affect the crystal structure but influences the crystallites sizes of the phosphor. SEM results revealed that the Cr$^{3+}$ affects the nanophosphor morphology. PL results suggest that co-doping at 1% Cr$^{3+}$, Eu$^{2+}$ oxidized to Eu$^{3+}$. It also showed that co-doping above 1% Cr$^{3+}$ results in the luminescence evolution from violet-orange-red to violet-red emission due to energy transfer from Eu$^{2+}$ to Cr$^{3+}$ and suppression of Eu$^{3+}$. It can be interesting task to post anneal the same samples at temperature above 900 °C.

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References