Fluorescence properties of red-emitting SrYAl3O7: Eu3+ nanophosphor

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Abstract
Eu3+ activated SrYAl3O7:nanophosphor was prepared by the solution combustion synthesis using urea as a fuel. The prepared samples were characterized by powder x-ray diffraction pattern (XRD) and studied for their photoluminescence (PL) properties. The excitation spectrum is composed of charge-transfer (CT) of Eu–O and excitation lines of Eu3+ ions. The emission spectra with variable concentration of Eu3+ showed strong peaks at 593 and 612 nm. The optimal Eu3+ doping concentration was found to be 0.5mol% based on the concentration dependent emissionspectra. The results indicated that YSrAl3O7:Eu3+ might be a promising red phosphor for w-LEDs.

Keywords: SrYAl3O7; Solution combustion; Red-emitting nanophasor; photoluminescence; Eu3+.

1. Introduction
White light-emitting diode (w-LED) is recognized as a fourth generation illuminate lamp after incandescent lamps, fluorescent lamps, high-temperature tungsten filament lamps, and vapor discharge lamps. Due to its advantages in terms of energy saving, environmental friendliness, and long-lasting performance, LED is now known as the new lamp-house of the 21 century[1–3]. There are several ways to obtain white light emission. The most common method is to employ the yellow emitting YAG:Ce3+ phosphor and blue In GaN chips. However, such w-LEDs encounter low color rendering index (Ra < 80) and high color temperature (Tc > 7000 K) due to the scarcity of red emission[4,5]. To solve the problem, white LEDs have been fabricated by combining the near ultraviolet (n-UV) or UV LED with the red, green, and blue (RGB) tricolor phosphors. For example, white LEDs are composed of n-UV LED, Y2O2S:Eu3+ (red), ZnS:Cu+, Al3+ (green) and BaMgAl10O17:Eu2+ (blue). However the efficiency of Y2O2S:Eu3+ is less than that of green and blue phosphors, and it has the poor chemical stability under the high temperature[6]. Hence, it is a task to seek alternative red phosphor with high luminescent intensity and satisfactory chemical stability.

Recently, the ABC3O7compounds (A = Ca, Sr, Ba; B = La, Gd, Y; C = Al, Ga) have been studied due to their good stability, cheap raw materials, simple synthesis conditions and good photoluminescence properties. SrYAl3O7 was selected as a host material in this work. The compounds have melitite structure[7–9]. A fast and simple combustion method has been employed to synthesize CaYAl3O7:Ce3+, Tb3+[10], CaYAl3O7:Eu3+[11], Er3+/Yb3+ codoped CaYAl3O7[12], GdCaAl3O7: Eu3+[13] doped with variety of ns2 and rare earth activators. Eu3+ ion exhibits red fluorescence due to its 5D0 →7FJ (J = 1, 2, 3, 4) transitions and is an excellent activator for luminescent materials.

To the best of our knowledge, there is no report on the systemic study of SrYAl3O7:Eu3+ synthesized by solution combustion method. Hence, we prepared SrYAl3O7:Eu3+ nanophasors with different Eu3+doping concentration by solution combustion method and investigated their luminescent properties.

2. Experiments
SrYAl3O7:xEu3+ (x = 0.001, 0.002, 0.003, 0.005, 0.007 and 0.01) phosphors were prepared by a solution combustion method. In a typical preparation, stochiometric amounts of Sr(NO3)2, Y2O3, Al(NO3)3.9H2O, Eu2O3 and urea (CO(NH2)2) were taken. First oxides of yttrium and europium were dissolved in aqueous nitric acid. Then all nitrates and urea were mixed and dissolved in distilled water. A homogeneous solution was obtained after stirring vigorously for 20 minutes. The solution was transferred to a muffle furnace pre-heated and maintained at a temperature of 500 ± 20°C. After all the liquid had evaporated, the reagents decomposed and released large amounts of gases. A large amount of heat released (due to the exothermic nature of this process) resulted in a flame that decomposed the reagents further and released more gases. The flame lasted for about 60 seconds and the...
combustion process was completed within 5 minutes. The resulting powders were cooled down to room temperature and were ground gently using a pestle and mortar. The powders were heated at 900°C for 2 hours. This powder was then used for further characterization.

Phase and crystallinity of the prepared material were checked by a powder XRD pattern using PAN-analytical diffractometer with Cu Kα radiation (λ = 1.5405 Å) operating at 40 kV, 30mA in the 2θ range 10–80°. The photoluminescence excitation (PLE) and emission (PL) spectra of the samples were recorded using a SHIMADZU spectrofluorophotometer (RF-5301 PC). All the measurements were performed at room temperature.

3. Results and discussions

3.1 XRD phase analysis

Fig. 1. XRD pattern of prepared SrYAl₃O₇:0.005Eu³⁺ along with standard JCPDS file 49-0604.

Fig. 2. SEM images of SrYAl₃O₇:Eu³⁺ phosphor.

Fig. 1 shows the XRD patterns of prepared SrYAl₃O₇:0.005Eu³⁺ phosphor after calcination at 900°C for 2h along with the standard JCPDS file of SrYAl₃O₇ (JCPDS Card no. 49-0604). All the diffraction peaks of prepared sample are very well matched with standard JCPDS data. No diffraction peaks of any other phases or impurities are detected. Structural investigations indicate that they form tetragonal crystals with space group P42₁/m. The particle size is calculated using Scherrer’s formula and is found to be about 52 nm.

3.2 SEM

For surface morphology and particle size, SEM was used (Fig. 2). Here the prepared sample shows good morphology and connectivity with grain with some defects and agglomerates formation, when sample was prepared by combustion synthesis technique. The particles are nano crystalline.

3.3 Photoluminescence properties

Fig. 3 exhibits the excitation spectrum of the SrYAl₃O₇:0.005Eu³⁺ samples. The excitation spectrum is obtained by monitoring 612 nm emission, which corresponds to the ⁵D₀→⁷F₂ transition of Eu³⁺. It can be observed that the excitation spectrum composed of a broad band ranging from 220 nm to 270 nm with a maximum at 251 nm and some small peaks at the longer wavelength region. The wide band at about 251 nm was attributed due to the charge transfer band (CTB) between Eu³⁺ and the neighboring O²⁻. A group of small peaks in the longer wavelength region due to the f-f transitions within Eu³⁺ ⁴f⁶ configuration [14].

Fig. 4 illustrates the emission spectra of SrYAl₃O₇:xEu³⁺ (x=0.001, 0.002, 0.003, 0.005, 0.007 and 0.01 moles) phosphors under 251 nm excitation. The emission spectra consist of emission lines from the ⁵D₀ excited state to ⁷Fₗ ground state of Eu³⁺ i.e. ⁵D₀→⁷F₁ (581 nm), ⁵D₀→⁷F₂ (589 and 594 nm), ⁵D₀→⁷F₃ (612 nm), ⁵D₀→⁷F₄ (653 nm) and ⁵D₀→⁷F₅ (712 nm), respectively [15, 16]. Out of these, the peaks at 594 nm and 612 nm are most prominent. The line shape of the emission does not change with the variation of Eu³⁺ concentration because most of the valence electrons of trivalent rare-earth elements are shielded by 5s and 5p outer electrons. According to the Judd -Ofelt theory, the electric dipole transition ⁵D₀→⁷F₂ is hypersensitive, and the emission intensity is strongly influenced by ligand ions in the crystals. If Eu³⁺ occupies an inversion symmetry site, a dominant reddish orange emission will be obtained according to the magnetic transition ⁵D₀→⁷F₁. Conversely, an electric dipole transition ⁵D₀→⁷F₂ will predominate in the emission spectra. Therefore, the intensity ratio of ⁵D₀→⁷F₂ to ⁵D₀→⁷F₁ is usually regarded as a measure of
site symmetry around the Eu$^{3+}$ ions. In our case, the red

![Excitation spectrum of SrYAl$_3$O$_7$:0.005Eu$^{3+}$ phosphor under the emission at 612 nm.](image)

emission ($^5$D$_0$→$^7$F$_2$) is stronger than the orange emission ($^5$D$_0$→$^7$F$_1$), indicating that Eu$^{3+}$ is located in a non-centro-symmetric position in the SrYAl$_3$O$_7$. The lack of an inversion center around the Eu$^{3+}$ ions can provide high color purity and bright red phosphors.

The inset of Fig. 4 shows relation between the relative intensity of $^5$D$_0$→$^7$F$_2$ transition and concentration of Eu$^{3+}$. As shown in the inset, with the increase of doping concentration, the emission intensity increased and reached maximum when doping concentration was $x = 0.005$ mole. Then the emission intensity decreased due to concentration quenching [17]. In this study, the electric dipole transition ($^5$D$_0$→$^7$F$_2$) is dominant as compared to magnetic dipole transition ($^5$D$_0$→$^7$F$_1$).

Fig. 5. Energy level diagram for PL transition of Eu$^{3+}$ ions.

![Energy level diagram for PL transition of Eu$^{3+}$ ions.](image)

3.3 CIE analysis

The International Commission on Illumination (CIE) chromaticity coordinates of SrYAl$_3$O$_7$:Eu$^{3+}$ phosphors are calculated based on the corresponding PL spectra and are represented in Fig. 6. Consequently, the CIE values are calculated to (0.670, 0.321), which is close to the standard red chromaticity of Nation Television Standard Committee (NTSC) (x = 0.67, y = 0.33). The CIE chromaticity coordinates for these phosphors are located in the red region. Thus, YSrAl$_3$O$_7$:0.005Eu$^{3+}$ can be used for white LEDs.

![Chromaticity diagram of YSrAl$_3$O$_7$:0.005Eu$^{3+}$.](image)

4. Conclusion

Eu$^{3+}$ doped YSrAl$_3$O$_7$ nanophosphor was successfully prepared by solution combustion route using urea as a fuel. The samples synthesized by combustion synthesis techniques show nano crystalline behavior. Surface morphology was determined...
by SEM and it shows good connectivity with grains including some agglomerates and defect in the prepared phosphor. The show a strong red emission at about 612 nm, owing to 5D0 → 7F2 transition of Eu3+. The optimal doping concentration is about 0.5 mol%. The CIE coordinate of SrYAl3O7:Eu3+ phosphor is calculated. The prepared nanophosphor can be used as a red phosphor for w-LEDs.

References