

Fluorescence properties of red-emitting SrYAl₃O₇: Eu³⁺ nanophosphor

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Abstract

 Eu^{3+} activated SrYAl₃O₇nanophosphor 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 Eu^{3+} ions. The emission spectra with variable concentration of Eu^{3+} showed strong peaks at 593 and 612 nm.The optimal Eu^{3+} doping concentration was found to be 0.5mol% based on the concentration dependent emissionspectra. The results indicated that YSrAl₃O₇: Eu^{3+} might be a promising red phosphor for w-LEDs.

*Keywords: SrYAl*₃*O*₇*; Solution combustion; Red-emittingnanophosphor; photoluminescence; Eu*³⁺*.*

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⁺ $Al^{3+} \\$ (red), ZnS:Cu⁺, (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 intensityand satisfactory chemical stability.

Recently, the ABC₃O₇compounds (A = Ca, Sr, Ba; B = La, Gd, Y; C = Al, Ga) have been studieddue 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 ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1, 2, 3, 4) transitions and is an excellent activator for luminescent materials.

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

2. Experiments

 $SrYAl_{3}O_{7}:xEu^{3+}$ (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 $Sr(NO_3)_2$, Y_2O_3 , $Al(NO_3)_3.9H_2O$, Eu_2O_3 and urea $(CO(NH_2)_2)$ were taken. First oxides of vttrium 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 stirringvigorously for 20 minutes. The solution was transferred to a muffle furnace pre-heated and maintained at a temperature of $500 \pm 20^{\circ}$ C. After all the liquid had evaporated, the reagentsdecomposed and released large amounts of gases. A large amount of heat released (due to theexothermic nature of this process) resulted in a flame that decomposed the reagents furtherand released more gases. The flame lasted for about 60 seconds and the



combustion process was completed within 5 minutes. The resulting powders were cooled downto 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 K α radiation ($\lambda = 1.5405$ A°) operating at 40 kV, 30mA in the 2 θ 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.

Results and discussions 1 XRD phase analysis





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

Fig.1shows 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 P42₁m. The particle size is calculated using

Scherror'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 goodmorphology and connectivity with grain with some defects andagglomerates formation, when sample was prepared by combustion synthesis technique. The particles are nano crystalline.

3.3 Photoluminescence properties

Fig. 3exhibits the excitation spectrum of the SrYAl₃O₇:0.005Eu³⁺ samples. The excitation spectrum is obtained by monitoring 612 nm emission, which corresponds to the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺. It can be observed thatthe 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 Eu³⁺ f-f transitions within the 4f⁶configuration[14].

Fig. 4illustrates 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 ${}^{5}D_{0}$ excited state to ${}^{7}F_{J}$ ground state of Eu³⁺ i.e. ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ (581 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (589 and 594 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (612 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ (653 nm) and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ (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 $^{5}D_{0} \rightarrow ^{7}F_{2}$ electric dipole transition 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 ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$. Conversely, an electric dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ will predominate in the emission spectra. Therefore, the intensity ratio of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ to ${}^{5}D_{0} \rightarrow 7F_{1}$ is usually regarded as a measure of



site symmetry around the Eu^{3+} ions. In our case, the red



Fig. 3 Excitation spectrum of $SrYAl_3O_7:0.005Eu^{3+}$ phosphor under the emission at 612 nm.



Fig.4.Emission spectra of SrYAl₃O₇:xEu³⁺ phosphor under the excitation at 251 nm. The inset shows dependence of emission intensity on Eu³⁺ doping concentration. (X= 0.001, 0.002, 0.003, 0.005, 0.007, and 0.01).

emission $({}^{5}D_{0} \rightarrow {}^{7}F_{2})$ is stronger than the orange emission $({}^{5}D_{0} \rightarrow {}^{7}F_{1})$, indicating that Eu^{3+} is located in a non-centro-symmetric position in the SrYAl₃O₇. The lack of an inversion center around the Eu^{3+} ions can provide high color purity and bright red phosphors.

The inset of Fig. 4shows relation between the relative intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition and concentration of Eu³⁺. 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 intensity emission decreased due to concentration quenching [17]. In this study, the electric dipole transition(${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) is dominant as compared



Fig. 5.Energy level diagram for PL transition of Eu3+ions.

to magnetic dipole transition $({}^{5}D_{0} \rightarrow {}^{7}F_{1})$. Fig. 5 shows energy level diagram for PL transition of Eu ${}^{3+}$ ions.

3.3CIE analysis

The International Commission on Illumination (CIE) chromaticity coordinates of SrYAl₃O₇:Eu³⁺ 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 redchromaticity 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, YSrAl₃O₇:0.005Eu³⁺can be usedfor white LEDs.



Fig.6. Chromaticity diagram of YSrAl₃O₇:0.005Eu³⁺.

4. Conclusion

Eu³⁺ doped YSrAl₃O₇ nanophosphor was successfully prepared by solution combustion route using urea as a fuel. The samplesynthesized by combustion synthesis techniques shows 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 ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ 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.

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