Upconversion luminescence in Eu$^{3+}$ activated SrAl$_{12}$O$_{19}$ nanophosphor

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The synthesis and optical properties of Eu$^{3+}$ in SrAl$_{12}$O$_{19}$ nanophosphor have been studied. All the phosphors were prepared by combustion synthesis and characterized by XRD, EDS, TGA, DTA, particle size analyzer and photoluminescence measurements are carried out. The XRD characterization shows the formation of hexagonal crystalline SrAl$_{12}$O$_{19}$ matched with the JCPDS file no. 00-026-0976. SEM and EDS show the formation of nanophosphor and the presence of aluminium, strontium, europium and oxygen. Luminescent characterization shows the emission at 580 nm (yellow) in the visible region by the 858 nm infrared excitation. These results indicate that the Eu doped material is a promising yellow colour fluorescence powder used in colour display or yellow-LED light device using LASER diode as an excitation source.

Keywords: Upconversion, SEM, TGA, Luminescence, Nanophosphor

1 Introduction
In the past two decades, frequency upconversion of infrared light to visible light has been extensively investigated in trivalent rare earth (RE) ion-doped materials for a wide range of application, such as three-dimension volumetric display$^{1,2}$, all-solid-state compact laser devices operating in the blue–green region$^3$, optical data storage$^4$, infrared quantum counter detectors$^5$ and fluorescent labels for sensitive detection of biomolecules$^5,7$. Up to present, the upconversion fluorescence of Tm$^{3+}$ and Ho$^{3+}$ ions in many kinds of materials have been reported$^{8-11}$. The upconversion spectroscopy of Eu$^{3+}$ doped SrAl$_{12}$O$_{19}$ has been investigated.

2 Experimental Details
The SrAl$_{12}$O$_{19}$:Eu material was prepared by a combustion method with urea as fuel. The starting AR grade materials (99.99% purity) taken are strontium nitrate [Zn(NO$_3$)$_2$·6H$_2$O], aluminium nitrate [Al(NO$_3$)$_3$·9H$_2$O], europium nitrate [Eu(NO$_3$)$_3$], urea (NH$_2$CONH$_2$). In the present investigation, materials were prepared according to the chemical formula Sr$_{1-x}$Al$_{12}$O$_{19}$:Eu$_x$ (where $x = 0.01-0.03$). The XRD technique was used in order to identify the product and check their crystallinity. The phase composition and phase structure were characterized by X-ray diffraction (XRD) pattern using a PAN-analytical diffractometer with Cu Kα radiation ($λ=1.5405$ Å) operating at 40 KV, 30 mA.

Thermogravimetric analysis (TG/DTA) was used in order to record the sintering reactions. TG and DTA curves were obtained on the prepared sample using Perkin Elmer Diamond TG/DTA instrument. The sample was heated in the temperature range 10-900°C with constant rate of 10°C/min, in an atmosphere of argon.

The morphology and the composition of the products were examined by scanning electron microscopy (SEM, JED-2300) equipped with an energy-dispersive spectrometry (EDS). Energy dispersive spectrometry (EDS) attached to the JEOL 2300 was used to determine the composition of the products. The photoluminescence properties of the phosphor (excitation and emission) were measured using a Shimadzu RF5301PC Spectroflurophotometer at room temperature.

3 Results and Discussion

3.1 Structural property
The formation of crystalline phases in the samples prepared by the combustion method was confirmed by powder XRD measurements. Fig. 1 shows the XRD pattern of Eu doped SrAl$_{12}$O$_{19}$ phosphor. The small
amount of doped rare earth ions has virtually no effect on phase structures. The observed pattern was found to match with the standard data of the compound SrAl$_{12}$O$_{19}$ (JCPDS, 00-026-0976). The XRD data indicate hexagonal phase for SrAl$_{12}$O$_{19}$.

The excited states for upconversion can be populated by several well-known mechanisms: (1) excited state absorption (ESA), (2) energy transfer (ET), and (3) photon avalanche. REs include both the lanthanides (atomic numbers 57-71) and the actinides (atomic numbers 89-103) and are not so rare as their name implies. Szabadvary$^{12}$ has written an in-depth review on the 200+ year history and separation of REs. REs have unique luminescent properties and are considered to be non-toxic$^{13}$ making them ideal for a number of modern day commercial applications.

Research and applications using lanthanides have dominated over actinides. One reason for this is that lanthanides have luminescent properties covering the ultraviolet (UV), visible and NIR wavelengths which have been exploited in many applications including lasers, fibre amplifiers and phosphors (as used in fluorescent lighting and cathode-ray tubes). Lanthanides are particularly common in their ionised trivalent state, henceforth, denoted as RE$^{3+}$, and are commonly investigated for their luminescent properties. Literature covering the spectroscopic studies of RE$^{3+}$ ions is mostly technical and aimed predominantly at inorganic chemists who have a detailed understanding of quantum chemistry. The recent developments of RE$^{3+}$ ions to commercial applications have resulted in a number of engineering and introductory texts being written bridging the gap between the inorganic chemistry of RE$^{3+}$ spectroscopy and the larger multidisciplinary scientific community.

Figure 2 shows the emission spectra of SrAl$_{12}$O$_{19}$ Eu excited by 858 nm wavelength. It is observed from the graph by exciting 858 nm wavelength SrAl$_{12}$O$_{19}$ Eu shows the emission at 578 nm in yellow region of the spectrum. The upconversion emission is observed by the energy transfer between ions. In this process, the energy is transferred from impurity (non-luminescent) ions or energy transfer process between different luminescent ions for example crosses relaxation. The electron has been excited (directly or by UC) to the 858nm photon. The excited electron could decay from $^7F_1$ state to $^5D_0$ state which observed in the 578 nm emission. The maximum intensity is observed for the 3mol % of Eu ion doping in SrAl$_{12}$O$_{19}$.

The thermal decomposition of SrAl$_{12}$O$_{19}$ Eu phosphor prepared by combustion synthesis is shown in Fig. 3. The DTA analysis reveals only one significant thermal effect- endothermic peak at around 40°C, which is associated with the decomposition of physically adsorbed molecular water. The TGA analysis shows that this thermal effect is accompanied...
by weight loss. From the graph of Fig. 3, it can be observed that there is no recrystallization of dispersed SrAl\textsubscript{12}O\textsubscript{19} phosphor seen up to a temperature of 900°C as lack of any noticeable exothermic effects. The DTA curve of the sample indicates that the SrAl\textsubscript{12}O\textsubscript{19}:Eu phosphor is stable compound up to a temperature of 900°C. Hence, the nano-phosphor prepared by the combustion technique is thermally stable and not decomposing over a usable temperature range.

In order to study the morphology structure of phosphor prepared by combustion synthesis, scanning electron microscopy has been carried out. The morphology and chemical composition of SrAl\textsubscript{12}O\textsubscript{19}:Eu nanophosphors were characterized by scanning electron microscopy and EDS (Fig. 4). In case of combustion synthesis, instantaneous and in-situ very high temperature combined with release of large volume of volatiles from liquid mixture is likely to result in the production of nano particles. The calcined phosphor particles have an irregular morphology, ranging in size from 0.1 to 5 µm. The energy-dispersive X-ray spectroscopy (EDS) of the nano-phosphor shown in Fig. 4, confirmed that the nano-phosphors were composed of barium, aluminium, oxygen, and europium is present in sample.

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References