Preparation and Photoluminescence Study of Eu2+ doped SrAl4O7 and Sr3Al32O51

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Abstract

Up to now, strontium aluminate SrAl4O7 (SA2) could be synthesized by solidification from the high temperature liquid state, a spray dried amorphous precursor etc. In this paper Combustion synthesis was used for preparation of SrAl4O7 and Sr3Al32O51 compound. Combustion synthesis furnishes a quick method for preparing these phosphors. Further, Eu2+ luminescence in these hosts is studied. X-ray diffraction (XRD) results confirmed the formation of single-phase compounds. The photoluminescence spectrum of SrAl4O7:Eu2+ gives a broad band emission at 508 nm corresponding to 4f65d1 → 4f6 (8S7/2) transition upon excitation of 342 nm and Sr3Al32O51:Eu2+ shows emission at 450 nm for excitation at 325 nm. This paper reports results on the luminescence of Eu2+ in strontium aluminate.

Keyword: Photoluminescence, Combustion synthesis, rare earth activator, aluminate

Introduction

Double oxides containing Strontium and Aluminium doped with rare-earth metal ions, exhibit excellent properties such as high quantum efficiency, long persistence of phosphorescence and good stability [1, 2]. In recent years, many reports are there on strontium aluminate phosphors doped with rare earth ions such as Sr2Al6O11:Eu2+, Sr4Al10O25:Eu2+[1, 3, 4], SrAl2O4:Eu2+,Dy3+[5], SrAl2O19:Eu2+, Sr3Al2O6:Eu2+ etc. These are known as efficient green and blue emitters and for their long persistent properties. Nanocrystalline SrAl2O4:Ce2+, Pr3+, Tb3+ [6] phosphor has been also reported with rare earth dopant effect on the optical properties of this phosphor. Among them, SrAl4O7 could only be obtained by solidification of the melt [7, 8, 9, 10] while it was not formed by solid state reaction between aluminium hydroxide and strontium carbonate at 1400 or 1550°C [10]. Lindop et al. [11] synthesized SrAl4O7 single crystal by Czochralski technique and reported the structural data. Capron and Douy [12] studied the
synthesis of SrAl$_4$O$_7$ from a spray-dried amorphous precursor. They found that slow heating, annealing or grinding the powder could produce pure SrAl$_4$O$_7$. Moreover they concluded that SrAl$_4$O$_7$ was metastable between temperature ~ 1100°C and a temperature close to its melting point (~ 1800°C). Yebin Xu et al. [13] synthesize single-phase SrAl$_4$O$_7$ powder via citric acid precursor route and to determine its stability as a function of time and temperature. SrAl$_4$O$_7$ have monoclinic structure. It belongs to C2/c space group with lattice constants $a=13.0389$, $b=9.0113$, $c=5.5358$ [14]. More study on combustion synthesis and photoluminescence characterization of SrAl$_4$O$_7$ was not found and it is also seen that there are not many studies on Sr$_3$Al$_{32}$O$_{51}$ host and also no literature was found on the luminescence of Eu$^{2+}$ in Sr$_3$Al$_{32}$O$_{51}$ host. Eu$^{2+}$ luminescence in these hosts is studied. These phosphors have been prepared by combustion synthesis. The results are reported and discussed in this paper.

**Experimental**

SrAl$_4$O$_7$ and Sr$_3$Al$_{32}$O$_{51}$ powders doped with Eu$^{2+}$ rare earth activator was prepared by combustion synthesis which involves heating of metal nitrate and aluminium nitrate in stoichiometric proportions with fuels such as urea at temperature around 500°C. Stoichiometric amounts of strontium nitrate (Sr(NO$_3$)$_2$), aluminium nitrate (Al(NO$_3$)$_3$. 9H$_2$O) and activator (Eu$_2$O$_3$) (i.e. in nitrate form) were thoroughly mixed with urea. SrAl$_4$O$_7$: Urea was in the ratio1:4:11.66. Due to the presence of large crystallization water in aluminium nitrate, a thick paste was formed. A china dish containing the paste was inserted in a furnace preheated to 500°C in ambient air. No reducing atmosphere was provided. Within minutes the paste foamed and a flame was produced which lasted for several seconds. The china dish was immediately removed from the furnace. After few minutes when it was cooled, it was crushed to get fine white powder. The compounds so prepared were identified using XRD techniques.

X-ray diffraction patterns were recorded on Philips PANalytical X’Pert Pro diffractometer. Photoluminescence (PL) characteristics were studied using a Hitachi F-4000 Spectrofluorimeter, at room temperature, using 1.5 nm spectral slit width in the range of 200-700nm.

**Results and Discussion**

In order to determine the phase purity, chemical nature and homogeneity of the phosphors, X-ray diffraction (XRD) measurements were carried out. Fig. 2(a) shows a comparison of stick pattern obtained for SrAl$_4$O$_7$ powder prepared by combustion synthesis and the corresponding pattern obtained from data file ICDD 30-1276. An excellent match is observed. From this comparison, it was found that the prominent phase formed is SrAl$_4$O$_7$. 
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Similarly Figure 2(b) shows a comparison of stick pattern obtained for Sr\textsubscript{3}Al\textsubscript{32}O\textsubscript{51} powder prepared by combustion synthesis and the corresponding pattern obtained from data file ICDD 44-0024. It was found an excellent match with the standard data.

![Flow chart for Combustion process](image)

Figure 1 Flow chart for Combustion process

Rare-Earth Activator

Eu\textsuperscript{3+}: Europium can act as an activator in two forms, viz. Eu\textsuperscript{2+} and Eu\textsuperscript{3+}. Eu\textsuperscript{2+} and Eu\textsuperscript{3+} can be identified from the characteristics PL they exhibit. Eu\textsuperscript{2+} emission arises from the lowest band of 4f\textsuperscript{6}5d\textsuperscript{1} configuration to \textsuperscript{8}S\textsubscript{7/2} state of 4f\textsuperscript{7} configuration.

![Comparison of stick pattern obtained for SrAl\textsubscript{4}O\textsubscript{7} with ICDD 30-1276](image)
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Fig. 2(b):- Comparison of stick pattern obtained for Sr$_3\text{Al}_3\text{O}_{51}$ with ICDD 44-0024.

The excitation arises from the transition from $^8S_{7/2}$ state of 4f$^7$ configuration to the states belonging to the 4f$^6$5d$^1$ configuration. Due to the allowed nature of the transition, PL is intense. Spectral positions of these bands vary a great deal from lattice to lattice. f-f transitions of Eu$^{3+}$, on the other hand, are forbidden and Eu$^{3+}$ PL is in general weak, unless there is excitation by charge transfer or energy transfer from a sensitizer. In general, narrow emission bands may be observed at about 570, 590, 610, 650 and 700 nm corresponding to transitions $^5D_0 \rightarrow ^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, $^7F_4$, respectively. Eu$^{3+}$ emission usually occurs from $^5D_0 \rightarrow ^7F_1$ transitions.

Fig. 3(a) shows PL spectra for Sr$\text{Al}_4\text{O}_7$:Eu$^{2+}$ (1mol%). A strong emission is observed around 463 nm and 508 nm (curve a). The excitation maximum is located around 340 nm and 342 nm (curve b & c).

![Fig. 3(a): Typical photoluminescence spectra of Sr$\text{Al}_4\text{O}_7$ doped with Eu$^{2+}$](image)

a) Sr$\text{Al}_4\text{O}_7$ emission for $\lambda_{\text{ex}} = 340$ nm & 342 nm.

b) Sr$\text{Al}_4\text{O}_7$ excitation for $\lambda_{\text{em}} = 508$ nm.

c) Sr$\text{Al}_4\text{O}_7$ excitation for $\lambda_{\text{em}} = 463$ nm.
Fig. 3(b) shows the PL emission (curve a) and excitation (curve b) spectra of Sr$_3$Al$_{32}$O$_{51}$ doped with Eu$^{3+}$ in which the emission found is 450 nm for excitation of 325 nm. The results illustrate that all of them are broad band spectra. There is no special emission of Eu$^{3+}$ in the spectra, which indicated that Eu$^{3+}$ ions have been reduced as Eu$^{2+}$ completely, in the matrices crystal lattice.

![Photoluminescence of Eu$^{2+}$ in Sr$_3$Al$_{32}$O$_{51}$.](image)

**Conclusion**

Alkaline earth strontium aluminates viz. SrAl$_4$O$_7$:Eu$^{2+}$ and Sr$_3$Al$_{32}$O$_{51}$:Eu$^{2+}$ phosphors were prepared by combustion synthesis. Appreciable luminescence has been observed.

**References**