Development of Phosphor for applications in solid state lighting

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Abstract: Strontium aluminate phosphor doped with \( \text{Eu}^{2+} \) was synthesized by solid state reaction at high temperature. Photoluminescence (PL) excitation spectra showed a broad peak at 340 nm extending well up to 450 nm. PL emission peaks at 505 nm. The developed phosphor also exhibits green afterglow. Time resolved decay of PL showed two fluorescence lifetimes on the order of 9 \( \mu s \) and 90 \( \mu s \) in the initial part of decay, in addition to a much longer phosphorescence lifetime. Suitability of such a phosphor for phosphor – converted LED (pc-LED) is discussed.

Keywords: Photoluminescence; phosphor; Time resolved decay; lifetime, pc-LED

Introduction
Solid state lighting have a very bright future in various lighting applications because of their high energy efficiency and cost effectiveness compared to incandescent bulbs. A very effective way to produce white light from UV/blue LED is by coating on LED suitable phosphors excitable by LED light, so that white light is produced either by mixing of basic colours or complementary colours. For such phosphor converted LED (pc-LED) producing white light, suitable phosphor materials are being developed. Available white LEDs have low colour reproducibility as they are mostly based on combination of a blue LED and a yellow emitting phosphor. Such white LEDs lack green and red part of the white spectrum. In the present study, our aim was to search a green emitting phosphor excitable by LED light. In addition, our aim was also to develop chemically and thermally stable phosphors free of toxic elements e.g., Cd, S, Cl etc. and environmental hazards. Alkaline earth aluminates doped with rare earth ions were observed to be efficient light emitters \([1,2]\) and found many applications as long afterglow phosphors. Such phosphors are non toxic and can be synthesized and produced in laboratory and industry. The present work explores the suitability of Europium doped strontium aluminate phosphors as light converters for pc-LED.

Experiments

Sample Preparation: Srontium Aluminate was prepared from stoichiometric proportions of \( \text{SrCO}_3, \text{Al}_2\text{O}_3 \). Percentage of dopant Eu was 0.01% and was added as \( \text{Eu}_2\text{O}_3 \). Additional flux of Boric acid and carbon was added. This was done since small percentage of Boric acid has been observed to enhance PL characteristics and carbon would add to creating reducing atmosphere due to formation of \( \text{CO}_2 \) at high temperature. All the components were thoroughly grind and mixed. The mixture was fired in a furnace at 1250 \( ^\circ \text{C} \) in reduced atmosphere (Nitrogen) for 140 minutes and allowed to cool slowly.

Characterization

Sample was ground to a fine powder and powder X-ray diffraction was taken with a Bruker's X-ray diffractometer with \( \text{CuK}_{\alpha} \) (1.54 \( \AA \)) radiation and is shown in Fig.1. All the peaks could be indexed to monoclinic \( \text{SrAl}_2\text{O}_4 \) phase \([3]\). Grain size calculated from Scherrer formula is about 100 nm.

Photoluminescence (PL): Photoluminescence (PL) spectra were recorded using a double monochromator based Perkin Elmer LS55 Fluorescence spectrometer with a Xe lamp source. PL excitation spectra were broad ranging from 250 to 450 nm with two peaks at 340 and 420 nm. PL emission spectra were recorded at both the excitation wavelengths.

Figure 1. XRD of \( \text{SrAl}_2\text{O}_4: \text{Eu}^{2+} \) sample prepared by high temperature solid state reaction.

Figure 2. PL excitation and emission spectra of \( \text{SrAl}_2\text{O}_4: \text{Eu}^{2+} \) sample.
though emission at 340 nm excitation was brighter than 420 nm excitation.

**Time Resolved Decay of Photoluminescence:** Time resolved decay of PL was measured with FLSP920 Phosphorescence lifetime spectrometer (Edinburgh Instruments, UK) using a μs Xe flash lamp. The sample was excited at 340 nm and time resolved PL decay at 505 nm is shown in Fig.3. The decay curve exhibits an initial growth and then decay, which could be fitted into a biexponential. The two fluorescence life times obtained are 9 μs and 90 μs in the initial part of decay, in addition to a much longer phosphorescence lifetime. The sample also exhibited a green afterglow after removal of the excitation light.

![Figure 3. Time resolved decay of PL emission of SrAl$_2$O$_4$: Eu$^{2+}$ sample at peak emission wavelength.](image)

**Discussion**

For alkaline earth aluminates doped with rare earth ions, PL arises due to electronic transitions in the rare earth ion. Among the rare earth ions, Eu$^{2+}$ has been extensively studied in different host crystals. In Eu$^{2+}$, electronic transition 4f$^7 \leftrightarrow 4f^65d^1$ is responsible for luminescence. It can be seen from Fig. 2 that Eu$^{2+}$ ion in host SrAl$_2$O$_4$ lattice produces broad excitation spectra. 4f $\rightarrow$ 5d transitions are electric dipole allowed optical transition and correspond to strong optical absorption. During excitation, 4f electron get transferred to the 5d orbital, which is split into a number of levels due to crystal field. Since the crystal field splitting varies considerably depending upon the host crystal, the spectral position of the excitation band would also change. In our case the excitation spectra is broad with two peaks at 340 and 420 nm. The emission bands do not always depend upon the 5d level splitting and 4f $\rightarrow$ 5d de-exications. Considering the ionic radii of Eu$^{2+}$ (1.09 Å) and Sr$^{2+}$ (1.12 Å) in SrAl$_2$O$_4$ lattice, Eu$^{2+}$ ions can substitute in Sr$^{2+}$ sites. Due to atomic coordination and strong crystal field splitting, 5d orbital splitting is high and lowest sublevel is shifted to lower energy. The emission occurs between lowest 4f$^5$5d$^1 \rightarrow$ 4f$^7$ levels. Hence the PL emission occurs at longer wavelength peaking at 505 nm.

The lifetime of the PL emission obtained is 9 μs and 90 μs, which is relatively long for an allowed transition. Multiplicity of the excited state 4f$^6$5d$^1$ is either 6 or 8. The sextet portion of the excited state contributes to spin forbidden transition [4]. In case of forbidden transitions, lifetimes could be longer than expected from allowed transition.

The excitation spectra of the developed SrAl$_2$O$_4$: Eu$^{2+}$ phosphor covers the wavelength range of commercially available UV, violet and blue LEDs. The emission is in the green and hence the developed phosphor has the potential to be used in phosphor converted LED as a primary colour emitter.

**Conclusions**

Development of SrAl$_2$O$_4$: Eu$^{2+}$ phosphor and study of its PL characteristics show that the phosphor has a wideband excitation spectra covering wavelength range of available UV, violet and blue LEDs. The developed phosphor emits in green and hence could provide one of the three primary colour components in phosphor converted LED producing white light. Such phosphors are easy to synthesize, free of toxic materials in production, use and disposals. Hence such phosphors are promising for solid state lighting applications.

**References**

3. *JPCDS* Card No.34-0379