Development of nitride phosphors for phosphor converted white LED

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Abstract: *For phosphor converted LED producing white light, suitable phosphor materials have to be developed which would absorb blue LED light and emit predominantly yellow and also some red to produce a sun like spectrum. Development of such down conversion inorganic phosphors has been a major R&D activity in the field of solid-state lighting and displays. Nitride phosphors have been promising materials; in addition they are non-toxic and free of environmental hazards. Eu^{2+} Doped ternary nitride phosphor $Sr_2Si_5N_8$ has been prepared by the Carbothermal reduction and Nitridation method. Photoluminescence (PL) spectra of the sample show that the sample can be excited by blue light (480) to emit in the red (emission peak at 650nm). The results indicate that such phosphors are excitable by commercial blue LED and can be used as potential candidate for the phosphor converted white LED.*

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

Introduction

A lighting revolution is sweeping all over the world and is stealthily coming in and improving our everyday life. In comparison with incandescent and fluorescent lamps, the InGaN-based white light emitting diodes (LEDs) have many advantages in energy efficiency, long lifetime, compactness, environment friendliness and designable features. Excitingly, the efficiency of white LED lightning has already exceeded that of the incandescent lamps and now is competitive with fluorescent lamps [1]. Without doubt, the white LED is setting foot in the lighting industry and greatly challenges the conventional lighting. In the solid-state lighting innovation, the wavelength conversion phosphor materials play a crucial role as they once did in fluorescent lamps. In Phosphor converted–LED (pc-LED), white LED system can be realized by several approaches: first, a combination of an InGaN-based blue LED chip with a yellow phosphor (e.g., YAG:Ce^{3+} based materials); second a blue LED chip combined with a green (~530nm) and a red emitting (>600nm) phosphor instead of single yellow emitting phosphor [2,3]. The two phosphors absorb the blue light from the InGaN chip and convert it into green and red light and then by colour mixing the white light is generated. Among the various phosphors, the red emitting phosphors are the most urgent ones to be improved. Recently, the invention of a new class of red emitting nitride phosphors $M_2Si_5N_8$: Eu^{2+} (M=Ca, Sr, Ba) has triggered a renewal of interest in the field of pc-LED[4]. In the past several years, synthesis of such phosphors was rare due to the scarcity of appropriate synthesis methods. The reason is ascribed to the inert property of Si_3N_4 even at high temperature, as well as the oxygen and moisture sensitivity of alkaline earth metals and nitride as starting materials.

Experiments

Sample Preparation

In the present work, $(Sr_{1-x}Eu_x)_2Si_5N_8$ compound has been synthesized by employing the corbothermal reduction and nitridation (CRN) method [1] Stoichmetric amounts of $SrCO_3$, Si_3N_4, Eu_2O_3 and fine graphite powder were mixed thoroughly and pressed in to a graphite crucible positioned in a furnace under flowing N_2 gas at 1200^{o}C for two hours and gradually cooled to room temperature.

Characterization

Fired sample was ground to a fine powder and powder X-ray diffraction was taken with a Brucker-AXS D8 advance Diffractometer (with DIFFRAC plus software) using CuK_α (1.54 Å) at 55 kV tube voltages and 11mA tube current. XRD pattern is shown in Fig.1. In addition to the $(Sr_{1-x}Eu_x)_2Si_5N_8$ phase, mixed phase signal is also seen which may be due to incomplete annealing process.

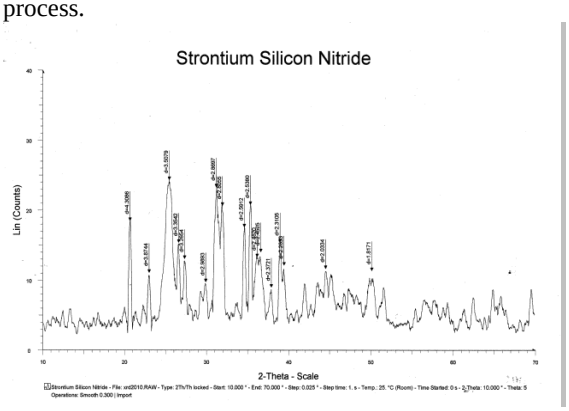

Figure 1. XRD of $(Sr_{1-x}Eu_x)_2Si_5N_8$: Eu^{2+} sample

Microstructure

SEM micrograph of the synthesized sample is shown in Fig.2

Photoluminescence (PL*)*

Photoluminescence (PL) spectra were recorded using a double monochromator based Perkin Elmer LS55 fluorescence spectrometer with Xenon flash lamp as the source of excitation. With a filter at 515 nm, the emission spectrum was recorded in the range 520-700 nm. PL excitation and emission spectra of strontium silicon nitride is shown in figure 3. Excitation spectra peak was at 480 nm and this wavelength was chosen as fixed wavelength for recording emission. Emission spectra peak was at 650 nm in the red part of the spectrum.

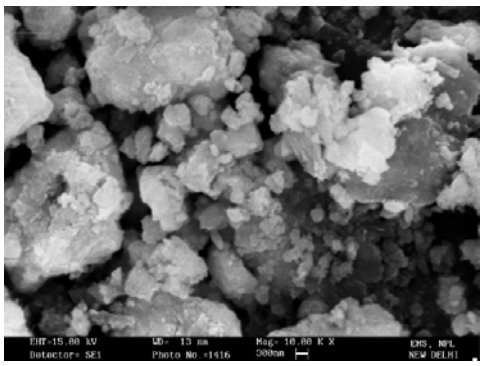

Figure 2. Micrograph of $(Sr_{1-x}Eu_x)_2Si_5N_8$: Eu^{2+} sample

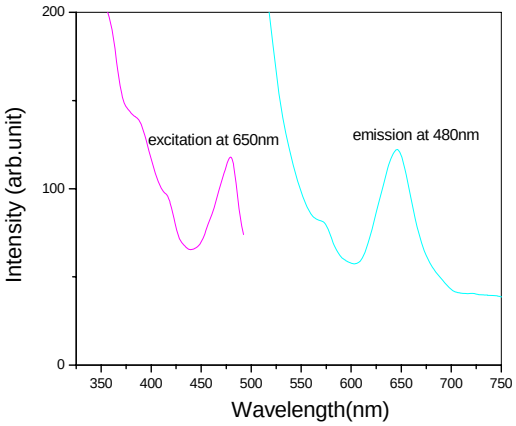

Figure 3. PL excitation and emission spectra of $(Sr_{1-x}Eu_x)_2Si_5N_8$: Eu^{2+} sample

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 peak excitation wavelength and time resolved PL decay at peak emission wavelength is shown in Fig.4. The decay curve could be fitted into a biexponential. The two fluorescence life times obtained are 7.5 μs (relative percentage 39%) and 83.5 μs (relative percentage 61%).

Result and discussion

For the synthesized nitride phosphor doped with rare earth Europium ion, PL arises due to electronic transitions in the rare earth ion. In Eu^{2+}, electronic transition $4f^7 \leftrightarrow 4f^6 5d^1$ is responsible for luminescence. In the Strontium silicon nitride host crystal, the emission from Eu^{2+} ion produces emission spectra with peak at 650 nm. Compared to other host crystals, in this nitride phosphor emission occurs at longer wavelength. The change is excitation and emission wavelength pertaining

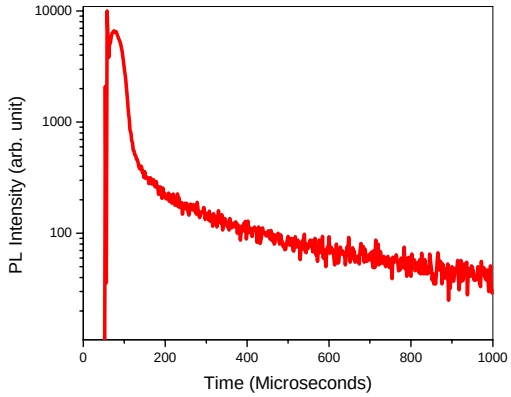

Figure 4. Time resolved decay of PL emission of $(Sr_{1-x}Eu_x)_2Si_5N_8$: Eu^{2+} sample at peak emission wavelength.

to the same rare earth impurity in different hosts could be explained based on varied crystal field splitting. Considering the ionic radii of Eu^{2+} (1.09 Å) and Sr^{2+} (1.12 Å) in $(Sr_{1-x}Eu_x)_2Si_5N_8$ lattice, Eu^{2+} ions can substitute in Sr^{2+} sites.

The lifetime of the PL emission obtained are 7.5 μs and 83.5 μs which is relatively long for an allowed transition and could be related to the spin forbidden character of the sextet portion of excited state. The excitation spectra of the developed $(Sr_{1-x}Eu_x)_2Si_5N_8$ phosphor covers the wavelength range of commercially available blue LEDs. The developed nitride phosphor emits in the red and hence the developed phosphor has the potential to be used in phosphor converted LED as a primary colour emitter in 3 band pc-LED or red spectrum enhancer in yellow phosphor converted white LED.

Conclusion

The red phosphor $Sr_2Si_5N_8$: Eu^{2+} was prepared by the CRN method. The powder sample doped with Eu^{2+} ion at the optimized concentration of 2 at % (substitutional at Sr^{2+} site) was efficiently excited by blue light of wavelength 480 nm to emit in the red at 650 nm. The results show that this red phosphor can be used for phosphor converted white LEDs.

References

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