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Structural and photoluminescent analysis in Judd-Ofelt framework of color tunable $SrGd_{2(1-x)}Eu_{2x}Al_2O_7$ nanophosphor for white light emitting materials

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ABSTRACT

Eu^{3+} doped $SrGd_2Al_2O_7$ nanophosphor was synthesized for the first time via very economic urea assisted solution combustion approach. X-ray diffraction studies reveal that single phased $SrGd_{2(1-x)}Eu_{2x}Al_2O_7$ nanophosphor is developed with a heat treatment of 3 h at 1300 °C crystallize in tetragonal lattice with I4/*mmm*(139) space group. TEM (transmission electron microscopy) analysis confirms the nano scaling of the phosphor with semi spherical shaped crystallites in 40–65 nm range. Photoluminescent spectral analysis infers that these nanophosphors can be excited by NUV light yielding emission with color tunability. These nanophosphor exhibits maximum luminescent properties at 10 mol% optimal concentration. The refractive index of the host was calculated to be 2.1532. Schematic energy transfer mechanism and Judd-Ofelt intensity parameters of the nanophosphors are also examined. Concentration dependent luminescent behaviour can be indexed to tune chromaticity from blue to red region reflecting the possibility of practical application of this nano-crystalline phosphor for single phased white LEDs excited with NUV light.

1. Introduction

Advances in the field of nanotechnology sets new vistas in the ongoing research on rare earth doped luminescent nanomaterials. The research community is strongly allured towards this fascinating regime accounting their vital applications in display fields like plasma display panel (PDP) or flat displays panel (FDP), field emission display, solid state lighting system especially white light emitting diodes [1,2]. In the light of intercontinental environmental concerns regarding controlled energy consumption and weather vitiation, solid state lighting (SSL) has emerged as a indispensable replacement of traditional incandescent and fluorescent lamps for lighting [3–5]. Holding this, the phosphor converted white light emitting diodes (pc-WLEDs) are widely explored owing to their remarkable merits like low power consumption, high color rendering index (CRI), durability, stability and color temperature tunability [6–10]. This in turn can be manufactured by applying a coat of red-blue-green (RGB) phosphor over a near ultraviolet excited (NUV) LED chip. This is more efficient route then the fabrication of WLEDs by combining a blue GaN LED chip with yellow phosphor yielding a low color rendering index as well as low chromatic stability.

Furthermore, the nanoscaling of these phosphors imparts larger surface to volume ratio, diminished internal scattering as well as non-radiative phenomenon yielding greater luminous efficacy with enhanced optoelectronic properties when applied over the WLEDs [6]. Among the various oxide based host matrices like fluorides, sulphides, tungustates, molybdates and silicates, the aluminates specially the ternary aluminate oxide based host matrix are widely explored realising their far-more stability over sulphides or other hosts and ecologically friendliness [11,12]. These ternary aluminate oxide based lattices assisted with rare earth doping are also gathering wide attention on grounds of their stable crystallographic, optical and electronic properties. In particular these are associated with broadened absorption and emission spectra with high dopant concentration, marks these as an efficient host matrix for laser technology. Moreover, $SrGd_2Al_2O_7$ is claimed to be worthy host material for its higher thermal stability and crystallinity. $SrGd_2Al_2O_7$ is found to have phase prototype $Si_3Ti_2O_7$ as reported by Ruddlesden and Popper [13]. In $SrGd_2Al_2O_7$; Sr ions occupy twelve fold coordinative sites while Gd occupies nine fold coordinative sites as explained by Fava et al. [14].

Luminescence of the rare earth doped nanophosphors arises as the emission transition originating from the intervening 4*f* electrons which are highly shielded from the chemical surrounding [15–18]. As a consequence, a line like spectra originated on irradiance irrespective of the crystal field around it when doped in suitable host matrix [19]. Amid

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the class of rare earth ions, europium is extensively used as a dopant for various host matrices owing to its capability to function as red emission centre in divalent and trivalent oxidised states (Eu^{2+} and Eu^{3+}). Eu^{3+} ion shows characteristic emission transitions arising from $^5D_0 \rightarrow {}^4F_j$ (j = 0–4) in the red region of visible spectrum. By choosing an appropriate Eu doped host matrix, color tuning from blue to red through white region (emission from different ^5D_j levels; where j = 0, 1, 2) at particular dopant concentration can be achieved yielding white emission [20].

Synthesis of single phased phosphor with nano scaling can be achieved in a very economic way via ecologically suitable solution combustion process. The phosphors produced this way are of high chemical purity, homogeneity, better crystallinity and well within nano dimension having narrow size distribution [21]. Herein, we are reporting the synthesis and luminescent behaviour of Eu^{3+} doped $SrGd_2Al_2O_7$ nanophosphors in Judd-Ofelt framework synthesized through a facile urea assisted solution combustion approach. However to the best of authors knowledge, no reports have been found in literature regarding solution combustion synthesis of trivalent Eu doped $SrGd_2Al_2O_7$. Judd-Ofelt intensity parameters of the nanoscaled phosphor have also been investigated in the present work. PL spectra as well as color co-ordinates advocates the applicability of $SrGd_{1.94}Eu_{0.06}Al_2O_7$ and $SrGd_{1.8}Eu_{0.2}Al_2O_7$ nanophosphors for single phased WLEDs and NUV excited tricolor based phosphor converted white LEDs, respectively.

2. Experimental

2.1. Material and synthesis

A series of $SrGd_{2(1-x)}Eu_{2x}Al_2O_7$ (x = 0.5–15 mol%) nanophosphors were synthesized by urea assisted solution combustion approach involving high purity nitrates such as $Sr(NO_3)_2$, $Gd(NO_3)_3{\cdot}6H_2O$, $Eu(NO_3)_3{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}6H_2O$. The ingredient materials were stoichiometrically mixed with calculated amount of the organic fuel urea in minimum amount of deionized water in a 250 mL capacity beaker until homogenous solution was obtained. By taking into account of total oxidizing or reducing valencies in the balanced reaction the molar ratio of urea was calculated [22]. Urea acts as a fuel for the propellant reaction which in turn gets oxidised by nitrate ions and allows growth of stoichiometrically precised oxide with uniformity. The beaker was then referred into the preheated furnace maintained at 500 °C for few minutes. The process begins with dehydration and foaming accompanied by decomposition generating flammable gases which burn with flame yielding desired solid. The product was then taken out of furnace, allowed to cool at room temperature, grounded to powdered form and sintered at different temperatures.

2.2. Materials characterization

The structural aspect of $SrGd_{2(1-x)}Eu_{2x}Al_2O_7$ (x = 0.5–15 mol%) nanophosphors as prepared and sintered at different temperatures was analysed using high resolution Rigaku Ultima-IV X-ray powder diffractometer powered with Cu Kα1 radiation at 40 kV voltage and 40 mA tube current setting. XRD profile was collected within 2θ range 10–80° with scan rate 2° min^{-1}. The morphological aspect was analysed using Technai-G^2 transmission electron microscope (TEM) in addition to confirm grain size as calculated by X-ray diffraction analysis. The photoluminescent excitation or emission spectra and decay curves of the nanophosphors were analysed by using Hitachi F-7000 fluorescence spectrophotometer assembled with Xe-lamp at scanning rate 1200 nm min^{-1}, 400 V PMT voltage set up and keeping excitation and emission slit width 2.5 nm. Judd-Ofelt analysis as well as chromaticity color coordinates was also examined. All the studies were examined at room temperature and atmospheric condition.

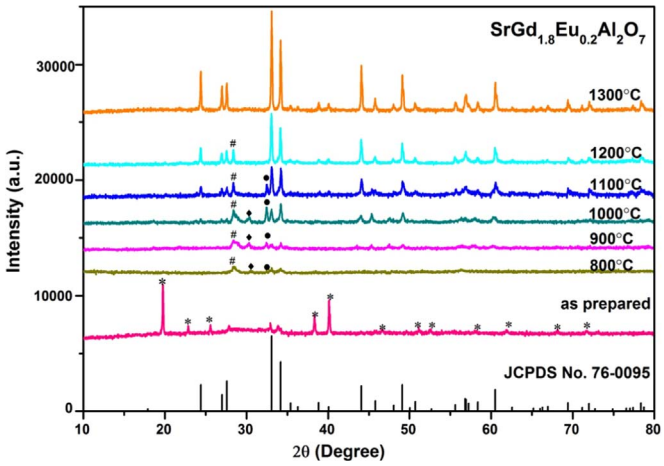

Fig. 1. XRD profile of $SrGd_{1.8}Eu_{0.2}Al_2O_7$ nano-crystalline phosphor along with standard data of $SrGd_2Al_2O_7$ (JCPDS Card No.: 76-0095 showing effect of sintering temperature.

3. Results and discussion

3.1. Crystal structure

The phase purity of the solution combustion synthesized $SrGd_{2(1-x)}Eu_{2x}Al_2O_7$ nano-crystalline phosphor was checked by assessing X-ray diffraction scanning. Different sintering temperatures accompanying different time set up were exploited to devise the maximum purity of the synthesized nanophosphor. The XRD framework of $SrGd_{1.8}Eu_{0.2}Al_2O_7$ as prepared and sintered at different temperatures accompanying the reference data JCPDS card No. 76-0095 is depicted in Fig. 1. The as prepared sample displays a very poor $SrGd_2Al_2O_7$ phase purity with the preponderance of unreacted $Sr(NO_3)_2$ phase as impurity marked by * (JCPDS card No. 76-1375). After sintering the sample at 800 °C for 3 h in the muffle furnace, $Sr(NO_3)_2$ phase reacted completely and the sample shows beginning of $SrGd_2Al_2O_7$ phase beside impurity phases of $SrAl_2O_4$, $SrGd_2O_4$ and Gd_2O_3 (JCPDS card No. 74-0749, 19-0889 and 43-1015) marked as #, ♦ and • positioned at 28.38, 30.40 and 32.46°, respectively. Similarly, at 900 °C and 1000 °C sintering temperature also the presence of these three unrequisite phases are seen in the spectra although with advancing sintering temperature the $SrGd_2Al_2O_7$ phase strengthen in intensity. The $SrGd_2O_4$ phase get diminish in the spectra sintered at 1100 °C however, the other two impurity phases persist in the spectra. At 1200 °C sintering temperature the spectra shows efficient phase purity of $SrGd_2Al_2O_7$ phase with solely impurity phase as $SrAl_2O_4$. Again sintering at 1300 °C for 3 h, all the unrequisite phases get removed from the spectrum and a single pure crystalline phase of $SrGd_2Al_2O_7$ is obtained. $SrGd_2Al_2O_7$ crystallize in tetragonal crystal structure with body centered lattice. The tetragonal host lattice is found to have lattice parameters a = 3.706 Å and c = 19.796 Å with I4/*mmm* (139) space grouping. In body centered tetragonal lattice of $SrGd_{1.8}Eu_{0.2}Al_2O_7$, The divalent Sr ion reside in twelve fold coordinative environment whereas, Gd/Eu ion occupies sites with nine coordination no. [14]. The XRD profile of $SrGd_{1.8}Eu_{0.2}Al_2O_7$ completely resemble with the reference data (JCPDS card No. 76-0095) making clear that the trivalent Eu ion get satisfactorily embedded in the host lattice. It is argued that the Eu^{3+} ion is expected to replace Gd^{3+} in the host lattice because of comparable ionic radii of both the ion (1.01 Å and 1.00 Å, respectively). Furthermore, the similar valence of both the ions makes it suitable for easy substitution in the host lattice avoiding any kind of charge compensation issue.

The increasing concentration of Eu^{3+} ion in $SrGd_{2(1-x)}Eu_{2x}Al_2O_7$ nano-crystalline phosphor is not found to have any remarkable effect on the crystal structure of the nanophosphor. The XRD profile of $SrGd_{2(1-$