Rare-Earth Ion (Eu$^{3+}$ And Dy$^{3+}$) Substituted SrAl$_2$O$_4$ Phosphor: A Study of Structural And Luminescence Properties

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Abstract. In this work, we report the synthesis and characterization of rare-earth doped strontium aluminate phosphors of the formula Sr$_{0.95}$Eu$_{0.05}$-xDy$_x$Al$_2$O$_4$ [$x = 0.05, 0.025$]. These aluminate phosphor prepared by chemical combustion method and were characterized for structural studies using X-ray diffraction and Raman techniques. XRD spectral studies of the samples under observation reveal the crystallization of these compounds into single monoclinic phase exhibiting space group P21/n. The monoclinic phase formation was witnessed from the fingerprint mode of vibration in Raman inelastic spectra. The PL studies of these phosphors convey the emission in blue region by Dy$^{3+}$ doped SrAl$_2$O$_4$, whereas emission by Eu$^{3+}$ and Eu$^{3+}$/Dy$^{3+}$ doped lies in the orange-red region.

Keywords: Phosphors; Structure; Raman Scattering; Photoluminescence.

INTRODUCTION

The materials with the ability of absorbing energy from UV or sunlight and then release it slowly in the dark are called the long afterglow or persistent phosphors [1, 2]. Rare earth elements doped inorganic phosphors doped display a broad emission band from blue to red region. This feature makes them fascinating and suitable for a variety of industrial applications. Among various technologically important applications, the worth mentioning are fluorescent lamps, plasma display panels, color display, X-ray imaging and radiation dosimetry [3]. While synthesis, this long afterglow luminescence by a phosphor is influenced by a variety of factors likewise the type of activator, amount of dopants, the conditions for the sample synthesis, host lattice structure before recording the luminescence spectrum, the emission wavelength, its intensity and duration. For a phosphor to perform the best for the desired application, it is indispensable to optimize these factors. Rare earth activator substituted strontium aluminate (SrAl$_2$O$_4$) have gained attention researchers for their ubiquitous features like high brightness and long-persistent. Theses phosphors glow for hours after the irradiation source is removed. Additionally, these phosphors are proved to be safer, chemically stable, inert and hazardous radiation free (radioactive radiations) in comparison to other traditional phosphors [4].

The luminescence of Eu$^{3+}$ doped SrAl$_2$O$_4$ is well known for its fascinating features. The persistence of the luminescence of SrAl$_2$O$_4$:Eu$^{3+}$ is subject to modification from application point of view. The luminescence is usually enhanced via substituting Sr-site in SrAl$_2$O$_4$ by other rare earth elements in addition of Eu$^{3+}$[5]. The phosphors based on SrAl$_2$O$_4$ were synthesized exploiting various techniques among which the most used methods are: sol–gel [7], co-precipitation [6], and solid state reaction [2]. However, in the current report, the SrAl$_2$O$_4$: Eu$^{3+}$, Dy$^{3+}$ phosphors, we selected solution-combustion synthesis technique. In comparison to these conventional methods, synthesis via solution-combustion method is time and energy saving, facile and safe [8].
This work throws light on the synthesis, structure and luminescence nature of Sr_{0.95}Eu_{0.05-x}Dy_xAl_2O_4 \ [x = 0.05, 0.025] phosphors. The as-synthesized phosphors were subjected for structural studies using XRD and Raman experiments. To study the luminescence properties, PL spectroscopic technique was exploited.

EXPERIMENTATION

The rare-earth substituted SrAl_2O_4 polycrystalline aluminate phosphors of the formula Sr_{0.95}Eu_{0.05-x}Dy_xAl_2O_4 \ [x = 0.05, 0.025] phosphors were synthesized by conventional, facile, energy/time saving, safe, fast and accurate solution combustion method. To synthesize Sr_{0.95}Eu_{0.05-x}Dy_xAl_2O_4 \ [x = 0.05, 0.025] aluminate phosphors, the starting raw materials used were Strontium nitrate \ [\text{Sr} (\text{NO}_3)_2], \ aluminum nitrate \ [\text{Al} (\text{NO}_3)_2\cdot\text{H}_2\text{O}], \ and \ oxides \ of \ europium \ \text{Eu}_2\text{O}_3, \ dysprosium \ \text{Dy}_2\text{O}_3. \ Also, \ the \ urea \ \text{CO}(\text{NH}_2)_2 \ was \ used \ as \ a \ fuel \ agent. \ To \ convert \ the \ Eu_2\text{O}_3 \ and \ Dy_2\text{O}_3 oxides into nitrates, we dissolved in them separately in 2ml of concentrated HNO_3. \ The \ calculated \ and \ carefully weighed \ starting \ materials \ were \ ground \ using \ mortar-pestle \ in \ the \ presence \ of \ urea \ \text{[CO}(\text{NH}_2)_2] \ till \ a \ paste \ like \ material \ is \ formed. \ The \ paste \ was \ transferred \ into \ a \ crucible \ and \ was \ subjected \ to \ a \ temperature \ of 600 ^\circ \text{C}. \ AT \ this \ temperature, \ the \ solution \ catches \ fire \ due \ to \ fuel \ (urea) \ and \ we \ obtained \ a \ white \ foam \ (ash) \ within \ seconds \ of \ time duration. \ Grinding \ the \ ashes \ of \ the \ solution \ results \ in \ the \ formation \ of \ fine \ powder. \ We \ annealed \ the \ final \ fine \ powder 1050 \text{C} \ to \ remove \ the \ impurities \ for \ luminescence \ properties. 

The crystal structure and phase formation of Sr_{0.95}Eu_{0.05-x}Dy_xAl_2O_4 \ [x = 0.05, 0.025] phosphors were investigated by X-ray diffraction characterization technique. The diffraction spectra was recorded over the angular range 20 (10°-80°) using Bruker D8 Advance X-ray diffractometer with CuKα1 (1.5406Å) radiation with a step size of 0.02°. Raman characterization was carried out using Micro Raman System from JobinYvon Horiba LABRAM-HR visible (400-1100 nm) with excitation source as Argon (488 nm). To record the photoluminescence spectra, Edinburgh Instrument FLS920-s fluorescence spectrometer was used. All the characterizations were carried out at room temperature.

RESULTS AND DISCUSSIONS

The solution combustion technique synthesized Sr_{0.95}Eu_{0.05-x}Dy_xAl_2O_4 \ [x = 0.05, 0.025] phosphors materials were investigated for structural confirmation and phase formation using XRD characterization. The XRD spectra of these aluminate phosphors is displayed as Figure 1: From the analysis of the diffractionograms of the as synthesized phosphor aluminate samples, all the samples were found to have crystallized into the monoclinic structure with space group P21/n. Furthermore, it is evident from the Figure 1 that all the diffractionograms are similar in appearance. This infers that samples are single phase in nature and no trace of other phase is present in the phosphor aluminate samples under investigation. Even the intensity of reflection peaks do hardly alter. The absence of deviation in the reflection peaks and same intensity can be attributed to same ionic radii of the host Sr^{2+} -Site [1.22Å] and those of guest ions viz Eu^{3+} [0.950Å] and Dy^{3+} [1.11Å][11].

Also the intense characteristic reflection peaks witness the crystalline nature of the samples whereas the broadness (FWHM) of these characteristic peaks is indicative of the lower average crystallite size. The average crystallite size of the samples under investigation were determined from the classical Debye-Scherer formula viz. $D = k \lambda / \beta \cos \theta$ where $D$ is thickness, $\lambda$ is wave length of X-ray used (1.5406 Å), $k$ is a constant (shape factor ≈ 0.9), $\theta$ is the angle of diffraction, $\beta$ is the FWHM of the characteristic peak. The estimated average particle size were observed to be 56nm, 49 nm and 61 nm for Eu^{3+}, Eu^{3+}/Dy^{3+} and Dy^{3+} doped SrAl_2O_4 aluminate phosphor materials respectively.

To understand in depth the doping effect on the structure of Sr_{0.95}Eu_{0.05-x}Dy_xAl_2O_4 \ [x = 0.05, 0.025] phosphors materials, Raman inelastic scattering study is an indispensable characterization. Exploiting this ubiquitous tool, we investigate the lattice vibrational modes to get clear information about the lattice structure. We recorded the spectral data of Sr_{0.95}Eu_{0.05-x}Dy_xAl_2O_4 \ [x = 0.05, 0.025] phosphors materials in the wavenumber range of 50cm^{-1} – 750cm^{-1} represented by the Figure 2. From the plots, it is clear that all the samples under investigation display similarly appearing spectrum which confirms that the Sr_{0.95}Eu_{0.05-x}Dy_xAl_2O_4 \ [x = 0.05, 0.025] phosphors materials exhibit homogeneity with same lattice structure. As revealed from the literature, by first approximation, modes of vibration appearing above 600cm^{-1} are attributed to the Al–O stretching vibrations whereas the vibration modes below 250cm^{-1} are attributed to the tetrahedral vibrations or tilts. The available literature further reveals that the modes of vibration in the region of 250cm^{-1} - 6000cm^{-1} are almost impossible to assign. However, in our Raman study of Sr_{0.95}Eu_{0.05-x}Dy_xAl_2O_4 \ [x = 0.05, 0.025] phosphor materials, only one intense reflection peak is observed in the
intermediate region. By analogy with other compounds, the intense mode of vibration appearing in the intermediate region at 465 cm$^{-1}$ is ascribed to the bending vibration of the O–Al–O bond associated with [AlO$_4$]$^{5-}$ tetrahedra [12,13]. This mode of vibration is useful to understand the electron-phonon interactions. Thus intermediate region of the Raman spectra of Sr$_{0.95}$Eu$_{0.05}$–$x$Dy$_x$Al$_2$O$_4$ [$x = 0.05, 0.025$] phosphors materials is the most important region for structural confirmation.

We tried to elucidate on the photoluminescence of the Sr$_{0.95}$Eu$_{0.05}$–$x$Dy$_x$Al$_2$O$_4$ [$x = 0.0, 0.05, 0.025$] aluminate phosphors. For this purpose, we recorded room temperature excitation and emission spectra of the as synthesized phosphor materials. The excitation spectra of these phosphors are given in Figure 3 and the radiation of excitation with wavelength of 394 nm was employed. In the excitation spectrum for substitution of Eu$^{3+}$ and Eu$^{3+}$/Dy$^{3+}$ in the
matrix of SrAl$_2$O$_4$, the broad band between 300nm – 400nm is attributed to f-f transition of Eu$^{3+}$ called intra-configurational transitions. The strong and sharp peak appearing at 396 nm results from transition $^5F_0$ to $^5L_6$ in Eu$^{3+}$. The prepared SrAl$_2$O$_4$: Eu$^{3+}$ phosphor can be excited by near UV (NUV) at about 394 nm effectively. So, it can match well with UV and NUV-LED, showing a great potential for practical applications.

The excitation spectrum of SrAl$_2$O$_4$: Dy$^{3+}$ shows strong excited peak at 356 nm ascribed to the transitions from the ground state to excitation states in the $^4I_{9/2}$ configuration of Dy$^{3+}$. However in the high energy region, it is difficult to assign due to overcrowded and somewhat overlapped levels of 4f configuration of Dy$^{3+}$. The transitions involved in blue has been identified as $^4F_{9/2}$-$^4I_{15/2}$[1]. In the excitation spectra for Eu$^{3+}$ and Eu$^{3+}$/Dy$^{3+}$ doped SrAl$_2$O$_4$, the glow peak appearing about 700nm is assigned to the transition $^5D_0$ - $^7F_4$[1,2].

The emission spectra of Sr$_{0.95}$Eu$_{0.05}$Dy$_{0.05}$O$_2$ [x = 0.0, 0.05, 0.025] aluminate phosphors was recorded in the range of 400–750 nm displayed as Figure 4. Under the 394 nm excitation, the emission spectrum of synthesized phosphors was composed of a sharp emission line at 592nm, corresponding to transitions from the excited states $^7F_0$ to $^7F_1$ transition of Eu$^{3+}$, and the transition hardly varies with the crystal field strength [3,4]. The orange emission at about 590 nm belongs to the magnetic dipole $^5D_0$ to $^7F_1$ transition of Eu$^{3+}$, while the peak appearing at 470nm is attributed to $^5D_0$ - $^7F_2$[5-8]. In the emission spectra the glow peaks observed about 430nm and 470 nm are attributed $^5F_{0}$-$^7D_{1}$ and $^7F_{0}$-$^5D_{2}$ transitions respectively. For Dy$^{3+}$, the peak appearing at 470nm is attribute of $^4F_{9/2}$-$^4I_{15/2}$ (blue)[9, 10]

In conclusion, we successfully synthesized Sr$_{0.95}$Eu$_{0.05}$Dy$_{0.05}$O$_2$ [x = 0.0, 0.05, 0.025] aluminate phosphors by solution combustion method. The monoclinic phase acquired was confirmed from XRD and Raman data analysis. The desire luminescence was established exploiting Photoluminescence (PL) data study. It was found that Sr$_{0.95}$Eu$_0.05$Al$_2$O$_4$ and Sr$_{0.95}$Eu$_0.025$Dy$_0.025$Al$_2$O$_4$ emit in orange-red region while as Sr$_{0.95}$Dy$_{0.05}$Al$_2$O$_4$ show emissivity in the blue region.

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