# Structure, optical bandgap and luminescence studies of $SrAl_2O_4$: $Eu^{3+}$, $Dy^{3+}$ aluminate phosphor

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**Abstract**: This report throws light on the preparation by solution combustion method of europium and dysprosium ($Eu^{3+}$, $Dy^{3+}$) doped strontium aluminate phosphor generally represented as ($SrAl_2O_4$: $Eu^{3+}$, $Dy^{3+}$). The phosphor was characterized for structural studies exploiting X-ray diffraction (XRD) and Fourier transform infer-red (FTIR), scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX) techniques. To study the optical properties, we employed UV-Vis spectroscopy and Photoluminescence studies. The analysis of X-ray diffraction technique infer that the sample is single phased and has found to have crystalized into the monoclinic phase (P 21 /n). The lattice parameters calculated were *a*= 8.4470 Å, *b* = 8.8160 Å and *c* = 5.1630Å which confirms sample formation. The average crystallite size calculated using classical Scherer formula was found ≈ 39 nm. The Fourier Transform Infra-red (FTIR) spectra analysis witnessed sample formation via the appearance of signature absorption bands in the data. The UV-Vis spectral study reveals the synthesized phosphor is a wide band gap material and the of the order of 4.47eV. The photoluminescence study revealed the three glow peaks using excitation wave length $\lambda_{ex}$ = 393nm, two corresponding to $Eu^{3+}$ and one corresponding to $Dy^{3+}$. The peaks are intense and lie in the visible range.

**Keywords:** Structure; Morphology, Bandgap, Phosphors.

## 1 Introduction

From device application point of view, rare earth alkaline earth aluminate phosphorescent materials are potential and have attracted the interest of researchers. The well-known phosphor materials based ZnS - have been extensively studied and exploited in many display applications. The only demerit of these sulphide phosphors is their short durability by virtue of its unstability to moisture or carbon dioxide impurities. The alkaline earth aluminates based on $REAl_2O_4$ [*RE* = Sr, Ba, Mg] are chemically stable and hence in the modern day luminescence devices, they are used as excellent matrix materials for better luminescence [1].

The luminescence can occur from the ultraviolet to the red region of the electromagnetic spectrum and strongly relies on the nature of host lattice. The photoluminescence of $REAl_2O_4$ (*RE* = Ca, Sr, Ba) based phosphor aluminates show luminescence with a very long lifetime [2, 3]. A considerable attention for potential applications is given to the long-afterglow characteristic of alkaline earth aluminate phosphors. The various fields such as luminous paint, safety indicators on emergency devices, electronic instrument dial pads, lighting apparatus and switches, automobile dials and panels, writing and printing inks, plasma display phosphors, etc. exploit these materials [4, 5].

Various techniques have been found to synthesize the alkali-earth aluminate family phosphor materials. The excellent luminescent property exhibiting phosphors include blue emitting $CaAl_2O_4$ ($Eu^{2+}$, $Nd^{3+}$) phosphor, green $SrAl_2O_4$ ($Eu^{2+}$, $Dy^{3+}$) phosphor and $BaAl_2O_4$ ($Eu^{2+}$, $Dy^{3+}$). Through the creation of exceptionally dense trapping levels, the doping of $Dy^{3+}$ ions in the matrix of $SrAl_2O_4$: Eu enhances the luminescence property [6]. For long-afterglow characteristics, $SrAl_2O_4$ phosphor doped with Eu and Dy is technologically an indispensable material [7]. For the preparation of the long afterglow phosphors, the solid-state reactions was mainly used. This method led to a large grain size more than 10μm in routine. The luminescence properties of these long-lasting phosphors are greatly affected by the grain size as the emitting centre is affected by the surrounding lattice environment. These properties are enhanced enormously in the nanoscale grain size range, which may include the peak shift either in the excitation or the emission spectrum [8, 9].

In the current study, nanocrystalline powder of $SrAl_2O_4$:$Eu^{3+}$, $Dy^{3+}$ phosphor were prepared by a solution combustion method. The phosphor sample was studied for the structural and optical properties. The discussion motivates for the phosphor preparation in the nanoscale range.

## 2 Experimentation

### 2.1 Synthesis

The polycrystalline $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ aluminate phosphor was synthesized by solution combustion method. For the synthesis of $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ aluminate phosphor, the raw materials were Strontium nitrate [$Sr(NO_3)_2$], aluminium nitrate [$Al(NO_3).H_2O$], and oxides like europium oxide [$Eu_2O_3$], and dysprosium oxide [$Dy_2O_3$] and Urea [$CO(NH_2)_2$]. The $Eu_2O_3$ and $Dy_2O_3$ oxides were dissolved in 2ml of concentrated $HNO_3$ to convert them into nitrates. The starting materials with stoichiometric amounts were mixed with urea and ground using mortar-pestle till a paste of the mixture was obtained. The paste was calcined at 610 °C after transferring it to the crucible. The solution catches fire due to fuel (urea) within

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seconds and a white foam (ash) is formed. The ashes of the solution was turned into fine powder via severe grinding. To remove the impurities for better emission, the final product was annealed at 1050 °C.

### 2.2 Characterizations

The $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ aluminate phosphor was examined for crystal structure and phase formation by X-ray diffraction characterization over the angular range 2θ (10°-80°) using Bruker D8 Advance X-ray diffractometer with CuK$\alpha$1 (1.5406Å) radiation. The instrument Frontier-Perkin-Elmer FTIR SP 10 STD was exploited to record FTIR spectrum to investigate the finger print region (400–1400cm1) as well as the functional group region (1400–4000cm-1) of $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ phosphor by mixing the sample with potassium bromide (KBr). Scanning electron micrographs and energy dispersive spectrum analysis of X-ray diffraction was obtained using SEM instrument model JEOL JSM-5600 with a resolution of 3.5 nm, magnification power of x 18-300000 kV (in 136 steps), acceleration voltage of 0.5-30 kV (53 steps) and energy dispersive spectrometer, model INCA Oxford. For optical bandgap study of the sample under investigation, we employed UV–vis spectrometer (Perkin Elmer, Lambda 950 - USA). Edinburgh Instrument FLS920-s fluorescence spectrometer was used to record the photoluminescence spectra. All the characterizations were carried out at room temperature.

## 3 Results and Discussions

The $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ phosphor was synthesized by chemical combustion successfully. For structural studies, the phosphor was characterized by XRD diffraction technique. For oxide formation, FTIR characterization technique was used, SEM/EAX characterization was carried out for morphological, microstructural and compositional studies and PL characterization for luminescence studies. The XRD data collected in the angular range of $10^o$ – $80^o$ is displayed in Figure 1.

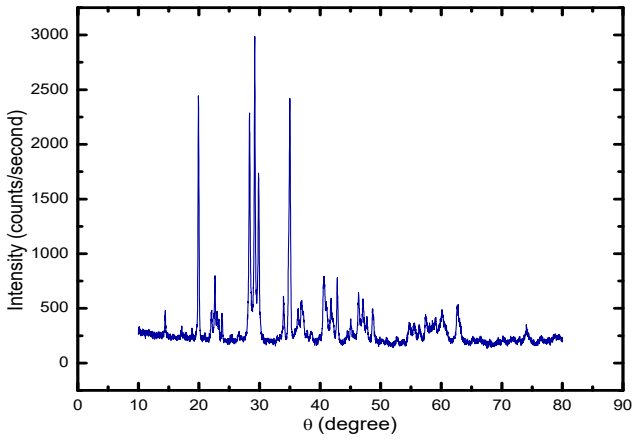


**Fig. 1:** XRD spectrum of $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ phosphor

The analysis revealed the sample is single phase in nature and has acquired monoclinic structure with space group P 21/n. The intenseness of the characterization peak convey the sample to be crystalline e in nature whereas the broadness of the peaks witness the sample exhibits lower average crystallite size. The average crystallite size was calculated using classical Debye-Scherer formula, $t = k\lambda / \beta\cos\theta$ and average particle size was estimated to 39 nm. The lattice parameters were calculated to be and the density was found to be $\varrho \approx 2.853$ g/cm$^3$and volume = 383.7974 Å$^3$.

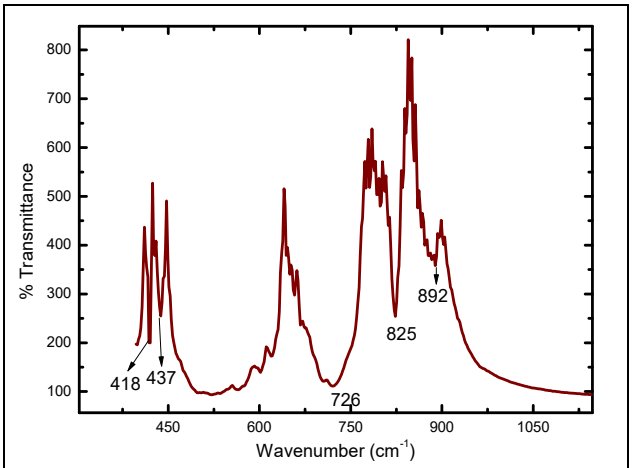


**Fig. 2:** FTIR spectrum of $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ phosphor in 200cm$^{-1}$ to 1100 cm$^{-1}$ range.

The Figure 2 depicts the Fourier transform Infra-red spectra recorded in the wavenumber range of 400cm$^{-1}$-4000 cm$^{-1}$. In the current study, as the higher order absorption bands are absent, only the range of 400-1100 cm$^{-1}$ is displayed in. There are many absorption peaks in the region of 400–900 cm$^{-1}$, which are ascribed to the monoclinic crystal structure of $SrAl_2O_4$.The bands on the range 350-1000 cm$^{-1}$ can all be assigned to infra-red active vibration modes of $SrAl_2O_4$ phosphor and associated with the vibrations of Al = O, Sr = O and Sr – O - Al bonds The band at 418 cm$^{-1}$ is due to a symmetric bond of O-Al-O, while the anti-symmetric stretching bands range from 588-845 cm$^{-1}$ is due to the Sr-O vibrations, implying that the band at 826 cm$^{-1}$ is likely representing SrO. The bands below 1000 cm$^{-1}$ are typically inherent active IR vibration modes of the strontium aluminate. The absorption band at 630 cm$^{-1}$, 726 cm$^{-1}$, 825 cm$^{-1}$, 892 cm$^{-1}$ are anti-symmetric stretching bands of Sr-O vibrations in $SrAl_2O_4$ [11,12].

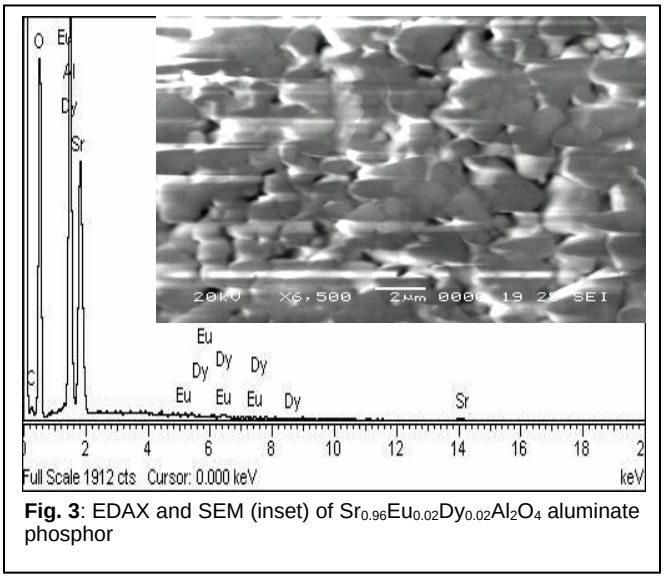


**Fig. 3**: EDAX and SEM (inset) of $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ aluminate phosphor

The $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ phosphor was examined for microstructural and morphological studies using the scanning electron microscopy (SEM). The SEM image of $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ phosphor is shown as the inset of the Figure 3. The close observation of the micrograph reveals the heavy growth of the grains attributed to the high temperature firing of the material. The large grain size in the micrograph is attributed to the diffusion (mass transport) mechanism easily facilitated by the high temperature firing. The grain size was calculated using the ImagJ software and the range of size lies between 1.5 μm - 2 μm.

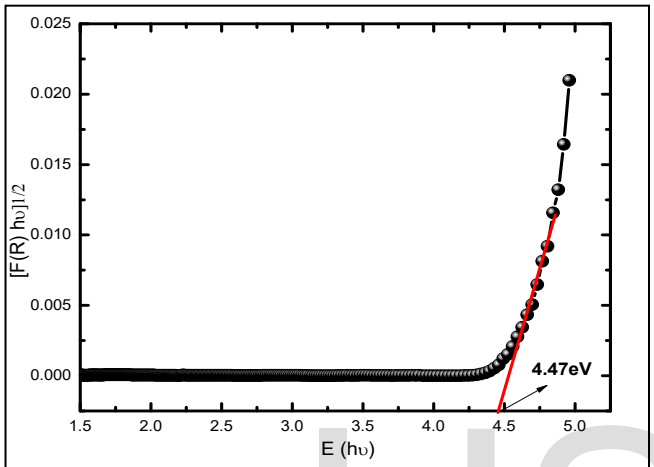


**Fig. 4:** UV-Vis spectrum of $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ aluminate phosphor for energy bandgap determination.

Further, we investigated the elemental composition of the phosphor under investigation. The EDAX spectrum displayed in the Figure 3. The general observation of the EDAX spectrum reveals that all the integral elements of the sample are present. Further, within the experimental limits, no foreign element is observed. In addition, the intense energy peaks reveals the presence of the elements as per their concentration.

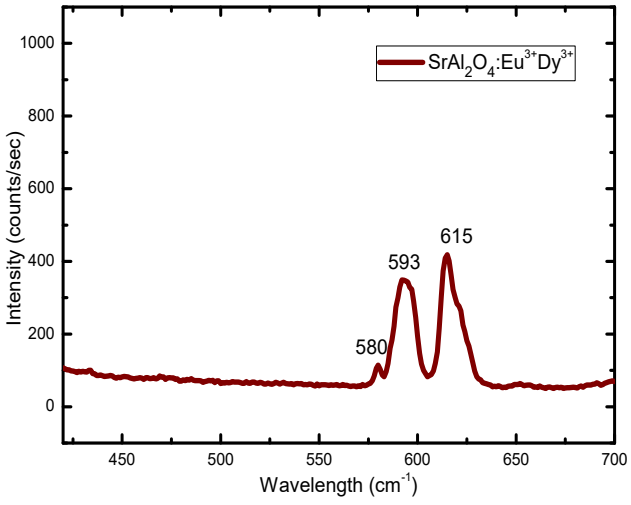


**Fig. 5:** Emission spectra of $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ phosphor.

The band gap estimation is important characterization of a material. For this purpose, the Diffuse Reflectance spectroscope (DRS) is a simple and powerful spectroscopic tool. The UV-visible absorption spectra of Eu, $Dy^{3+}$ doped $SrAl_2O_4$ phosphor is measured using a diffuse reflection spectroscopy. The band gap was estimated by plotting the square of the Kubelka-Munk-function F $(R)^2$ against energy, where R is reflectance [13]. For the plot, the best fit was obtained by plotting $[h\upsilon F(R)]^n$ against hυ for n = 1/2, displayed in Figure 4. An extrapolated straight line along the sharp edge of the curve intercepts the energy axis at a point which gives the estimation of the band gap and the value of optical band gap in the current case is 4.47eV [14].

The emission spectrum of $SrAl_2O_4$: $Eu^{3+}$, $Dy^{3+}$ phosphor synthesized via solution combustion method with excitation wavelength 393nm is depicted in Figure 5. The presence of a sharp emission peak at 615 nm, a characteristic feature of $Eu^{3+}$ emission due to the $^5D_0 \rightarrow {}^7F_2$ transition, indicates the presence of $Eu^{3+}$ ions. Also the photoluminescence spectrum of the phosphor with the $Dy^{3+}$ activator ion was detected near 580 nm. The peak at 580nm corresponds to $Dy^{3+}$ and attributes to the transition between $^4F_{9/2} \rightarrow {}^6F_{13/2}$energy levels [12, 15].

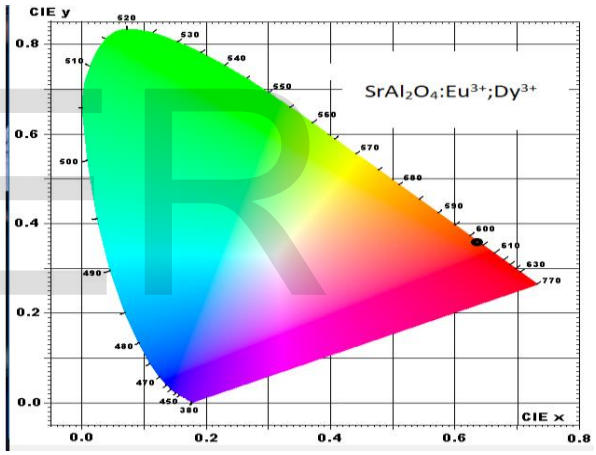


**Fig. 6:** Chromatograph for CIE coordinate determination for $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ phosphor

The CIE coordinates for the photoluminescence emission spectra data of $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ aluminate phosphor was calcconvulated using CIE 931. The CIE (Commission International de I'Eclairage) co-ordinates for $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ aluminate phosphor were found to be $x$ = 0.634 and $y$ = 0.363. The CIE chromatic diagram of $Sr_{0.96}Eu_{0.02}Dy_{0.02}Al_2O_4$ aluminate phosphor excited at wavelength 393 nm is shown in Figure 6. The value of CIE coordinates corresponds to red region.

## 4 Conclusion

In conclusion, the phosphor $SrAl_2O_4$: $Eu^{3+}$, $Dy^{3+}$ was successfully prepared via solution combustion method. The type of phase and crystal structure was verified from XRD data revealing sample to be single phase of monoclinic structure having space group P 21/n. The oxide formation was examined via FTIR technique also. Optical bandgap study revealed the sam-

ple to be wide bandgap material with $E_g$ = 4.7 eV. The PL emission spectra displayed characteristic glow peaks corresponding to $Eu^{3+}$ and $Dy^{3+}$ in the visible range.

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