



# Investigation of thermoluminescence and electron-vibrational interaction parameters in SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphors

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## ABSTRACT

Combustion synthesis method was employed for the synthesis of green-emitting monoclinic SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphors. The phase-purity of the prepared phosphors were examined using X-ray diffraction (XRD). The prepared phosphors exhibited green light emission with the peak centred at 510 nm, under 350 nm UV excitation. The excitation and emission spectra were analysed and the parameters of electron-vibrational interaction (EVI), such as the Huang–Rhys factor, effective phonon energy and zero-phonon line position were estimated using the spectrum fitting method. Thermoluminescence (TL) behaviour of the as-prepared phosphors were analysed for UV and <sup>137</sup>Cs γ-ray source irradiation. TL glow curves for UV-irradiated SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphors were analysed.

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## 1. Introduction

Rare-earth doped phosphors have already marked their significance enchanted with remarkable developments in modern lighting, radiation detection, medical applications, solar energy utilization, etc [1–4]. In recent years, however, researchers witnessed an ever-increasing popularity of persistent luminescence wherein the phosphor materials can absorb energy in the form of light, store the energy, and then release it as visible light [1,5,6]. The demand for advanced persistent luminescence phosphors is on a rise due to their exceptional characteristics required in a wide range of applications such as luminescent paint, luminescent plastic, luminescent ceramic, thermal sensors, decoration, emergency signs, image storage, utilization of solar energy, etc. A large number of persistent luminescence phosphors with different color emissions have been reported till date [7]. There has been rapid commercialization of many persistent luminescence phosphors, such as blue (CaAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>/Nd<sup>3+</sup>, SrMgSi<sub>2</sub>O<sub>6</sub>:Eu<sup>2+</sup>/Dy<sup>3+</sup>) [8,9], green (SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>/Dy<sup>3+</sup>, MgAl<sub>2</sub>O<sub>4</sub>:Mn<sup>2+</sup>) [10,11], red (CaS:Eu<sup>2+</sup>/Tm<sup>3+</sup>/Ce<sup>3+</sup>, Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>2+</sup>/Mg<sup>2+</sup>/Ti<sup>4+</sup>, Zn(Ga<sub>1-x</sub>Al<sub>x</sub>)<sub>2</sub>O<sub>4</sub>:Cr<sup>3+</sup>/Bi) [12–14], yellow (Ca<sub>2</sub>BO<sub>3</sub>Cl:Eu<sup>2+</sup>/Dy<sup>3+</sup>, Ca<sub>6</sub>BaP<sub>4</sub>O<sub>17</sub>:Eu<sup>2+</sup>/Ho<sup>3+</sup>) [1,15], pink (La<sub>3</sub>GaGe<sub>5</sub>O<sub>16</sub>:Pr<sup>3+</sup>) [16], etc. Among these, the popularity of SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>/Dy<sup>3+</sup> phosphors have surged to a new extent leading to immense research on its versatile properties [10,17,18].

The alkaline earth aluminate, SrAl<sub>2</sub>O<sub>4</sub> is one of the most

imperative persistent luminescent materials. Their high initial luminescent intensity and low-dimensional long afterglow property makes strontium aluminate phosphors an ideal substance to be widely used in many fields such as the dial plate of glow watch, warning signs, escape routine, airport, buildings and various kinds of ceramic materials, as well as in textiles, etc. and it may lead to future nanoscale display devices [19–21]. Strontium aluminate phosphors replaced the existing sulphide phosphors (ZnS) that were chemically unstable due to their nature of absorbing moisture from the surrounding environment to form sulphates, resulting in the destruction of the sulphide lattice and degrading their persistence properties [22]. During the late 1960s, lanthanide doped strontium aluminates such as SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup> were prepared and shown to be highly efficient phosphors [23]. In the mid-1990s, strontium aluminates were further explored by Matsuzawa et al. as a viable persistence phosphor [24]. They prepared these new phosphors by doping the strontium aluminate matrix with Dy<sup>3+</sup> and Eu<sup>2+</sup> to form SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>, which exhibited strong emission centred at 520 nm along with superior phosphorescence compared to SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup> and the sulphide based phosphors. Strontium aluminate phosphors have drawn massive attention due to their stable nature, high quantum yield, and wide range of excitation in the UV region of the electromagnetic spectrum, as well as chemically and biologically inert nature [25–27].

SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphors have emerged as one of the most promising elastico-mechanoluminescent material also [28,29]. SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphors have attracted vast attention due to its high mechanoluminescence (ML) intensity, variation of ML intensity with temperature, increase in ML intensity

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with change in activator ion and also due to its appropriateness for applications such as impact sensors, fracture sensor, damage sensor, sensor for stress indicators, etc. Elastico-mechanoluminescence was observed in  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$  phosphors for the first time by Akiyama et al. in 1998 [30]. The ML intensity in this phosphor was so intense that it was clearly visible in day light and they reported that the ML intensity recorded for this phosphor was 500 times greater than that observed in sugar crystals [31]. In the present context, investigation of photoluminescence and thermoluminescence properties of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$  phosphors is primarily targeted. The novelty of the work presented here is mainly the determination of EVI parameters of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$  phosphors. These parameters are vital for understanding the luminescence mechanisms taking place in the phosphor and the influence of electron-vibrational coupling on the photoluminescence spectra [32]. The broadness of the spectra and the thermal stability of the phosphor are dependent on the electron-phonon vibrations.

Here, combustion synthesis method was employed to prepare  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ , phosphors with different concentration of  $\text{Dy}^{3+}$ .  $\text{H}_3\text{BO}_3$  was used as flux and urea was used as fuel. The phosphors were characterized by X-ray diffraction (XRD) to determine the phase purity and structure of the as-prepared phosphors. Photoluminescence (PL), thermoluminescence (TL) properties and electron-vibrational interaction (EVI) of the as-prepared  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$  phosphors were briefly examined.

## 2. Experimental

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$  phosphors were prepared by using stoichiometric amounts of strontium nitrate [ $\text{Sr}(\text{NO}_3)_2$  (99.90%)], aluminium nitrate [ $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99.90%)], boric acid ( $\text{H}_3\text{BO}_3$ ) and urea [ $\text{NH}_2\text{CONH}_2$  (99.99%)] as raw materials. To prepare  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$  phosphor, stoichiometric composition of the metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valences of the components, which serve as the numerical coefficients so that the equivalence ratio is unity and the heat liberated during combustion is at its maximum. The precursors were dissolved in deionized distilled water in separate beakers. We introduced 2% europium oxide [ $\text{Eu}_2\text{O}_3$  (99.99%)] as activators and 2%  $\text{Dy}_2\text{O}_3$  as co-activator in the solution. Before introducing these rare-earth oxide dopants, they were converted into nitrate form. For this purpose, we have dissolved desired amount of  $\text{Eu}_2\text{O}_3$  in few drops of conc. Nitric acid in a test-tube and then kept it in oven for heating at 100 °C for 10 min [33]. The rare-earth solution was then diluted with deionized distilled water. Similarly,  $\text{Dy}_2\text{O}_3$  was also converted into nitrate form. Boric acid [ $\text{H}_3\text{BO}_3$  (99.90%)] was used as flux while urea ( $\text{NH}_2\text{CONH}_2$ ) was used as fuel. All the precursors, including the rare earth dopants in the form of nitrates, were introduced in a single glass beaker and mixed well. The solution was kept for stirring and heating at 100 °C. After evaporation of sufficient amount of water-content, the solution was then transferred into the crucible with comparatively larger volume and was placed in a furnace already maintained at 600 °C temperature. Initially, the solution underwent dehydration, followed by decomposition releasing large amounts of gases (oxides of carbon, nitrogen, and ammonia). Soon the reagent spontaneously ignited and combusted to produce foamy and voluminous ash. The combustion flame lasted for several seconds. Then the crucible was taken out of the furnace and kept in the open to allow cooling. Upon cooling, a fluffy form of material was acquired, which was then crushed into fine powder. The whole process lasted for not more than 5 min. In order to assure complete conversion of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  ions, the as-prepared phosphors were annealed at 600 °C for 4 h in a reducing

atmosphere. The prepared phosphors were reduced in an activated charcoal environment. Two more similar samples with 2% europium oxide and different concentrations of  $\text{Dy}_2\text{O}_3$  (4% and 6%) were also prepared.

The X-ray diffraction (XRD) pattern of the prepared phosphor was recorded in the  $2\theta$  range 10° to 60° using a PANalytical 3kW X'pert X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The Photoluminescence (PL) spectra were recorded by Perkin-Elmer LS 45 Fluorescence Spectrometer using xenon lamp as the excitation source. Thermoluminescence (TL) measurements for this phosphor were recorded with the help of Nucleonix 1009I TL reader, at a heating rate of 5 °C/s. The TL glow curves for the phosphor were recorded for both UV exposure as well as Cs-137 exposure.

## 3. Results and discussions

### 3.1. Crystal structure and morphology

Fig. 1 represents the XRD pattern of the as-synthesized  $\text{SrAl}_2\text{O}_4:0.02\text{Eu}^{2+}$ ,  $0.04\text{Dy}^{3+}$  phosphor. The diffraction pattern depicted intense peaks, thereby, giving a strong indication that the prepared phosphor has high degree of crystallinity. The obtained XRD pattern matches well with the standard JCPDS Data No. 74-0794. Pure monoclinic phase of  $\text{SrAl}_2\text{O}_4$  with a space group  $\text{P}2_1$  was observed and no other impurity phases were detected. The obtained XRD pattern confirms the existence of a predominant monoclinic  $\text{SrAl}_2\text{O}_4$  phase which was determined through Reference Intensity Ratio (RIR) method using the ICDD PDF 00-024-1187 and JCPDS No. 74-0794 files. It is to be noted that small amounts of dopant rare-earth ions ( $\text{Eu}^{2+}$  and  $\text{Dy}^{3+}$ ) do not produce significant effect on the basic crystal structure of  $\text{SrAl}_2\text{O}_4$ . The principal peaks were identified as the (011),  $(2\bar{1}1)$ , (220), (211) and (031) planes that characterize the crystalline  $\text{SrAl}_2\text{O}_4$  structure. The dopant concentrations were decided keeping in mind that the Unit cell parameters must not change. It is reported that concentration of upto 30 mol%  $\text{Eu}^{2+}$  ions do not change the lattice parameters of the  $\text{SrAl}_2\text{O}_4$  unit cell. Still, contrary to the expectation, small shift is observed in the XRD peaks of  $\text{SrAl}_2\text{O}_4:0.02\text{Eu}^{2+}$ ,  $0.04\text{Dy}^{3+}$  phosphor [34]. It is also mentioned that the intensity of  $\text{Eu}^{2+}$  ions increase upto 2.5 mol% and beyond this limit concentration quenching is bound to occur.

$\text{SrAl}_2\text{O}_4$  is related to  $\text{AB}_2\text{O}_4$  spinel structure and crystallizes in a

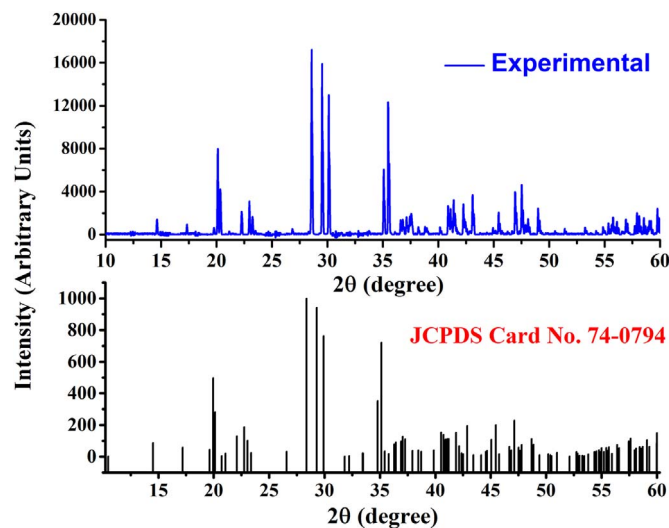


Fig. 1. XRD pattern of  $\text{SrAl}_2\text{O}_4:0.02\text{Eu}^{2+}$ ,  $0.04\text{Dy}^{3+}$  phosphor.

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