

Synthesis and Luminescence Studies of Eu doped AlSrLaO₄ Phosphor

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Abstract:- AlSrLaO₄ phosphors were synthesized using standard solid state reaction [SSR] method with varying Eu molar concentration as 0.1, 0.2, 0.3, 0.4, 0.7, 1.0, 1.5, 2.0 and 2.5%. The mixture of reagents was ground together to obtain a homogeneous powder in acetone base. To prepare Aluminum Strontium Lanthanate (ASL) doped with various concentrations of Eu, consists of heating stoichiometric amounts of reactants at 1000°C for 2 h in a muffle furnace. The received powder being ground thoroughly using an agate mortar, to ensure the best homogeneity and reactivity, powder was transferred to alumina crucible, and then reheated in a muffle furnace at 1200°C for 4 hours. The phosphor materials were cooled to room temperature naturally. All samples were found out to be white who are studied for photoluminescence [PL]. Photoluminescence spectra were recorded at room temperature using Shimadzu-5301 Spectrofluorophotometer. The phosphors are characterized using XRD and SEM. The effect of doping of Eu in ASL on the PL emission/excitation was also studied. Eu shows all its primary allowed emissions hence it is concluded that this phosphor can be used in display devices.

Keywords: - Photoluminescence, X-ray diffraction [XRD], Scanning Electron Microscopy [SEM], AlSrLaO₄ [ASL], Solid State Reaction.

I. INTRODUCTION

The luminescence associated with Eu in different host lattices has found applications related to its near UV- blue to red light emission, which is important in the field of displays. The past few decades have seen a lot of work reported on the use of divalent/trivalent Europium as a dopant in phosphors as they have very good optical properties (in the blue to red regions) which make them as a part of many display devices. Among all the rare-earth ions, Eu³⁺ is the most extensively studied, owing to the simplicity of its spectra and stability in host led to use in commercial red phosphors. Many workers reported work on La, Al, Sr oxides as host materials and Eu³⁺ as dopant [1-6]. When the phosphor is prepared in reducing atmosphere getting the final phosphor is mostly in Eu²⁺ state however few percentages in Eu³⁺ also found [7-8]. Few display phosphors thermo luminescence also studied [10-12].

In the trivalent rare earth ions, the luminescence arises mainly due to transactions within the 4 f shell. The efficiency of emission depends on the number of electrons in the 4f shell. The Eu³⁺ ion has 6 electrons in the 4f shell, which can be excited in the 4f-5d excitation band [12-13]. The electron in the excited 4f⁷ - 5d state remains at the surface of the ion and comes under the strong influence of the crystal field resulting in the splitting of the excitation band. The excitation Spectra thus has multiple peaks. The excited ion in the 4f⁷ - 5D State decays stepwise from this state to the luminescent levels 5D4f₃ or 5d4f₄ by giving up phonons to the lattice [14-20]. Luminescence emission occurs from either of these states, with the ion returning to the ground state.

1.1 Solid State Diffusion Process

This reaction also called solid state reaction [SSR]. The chemical reactions in solid state can be initiated and accelerated by intimately mixing the reactants in fine powder form and by heating the mixture. Thus, the degree of dispersion and mixing of one reacting solid with another are important to the overall mechanism of solid-state reaction. Thus the overall solid state reaction is dependent upon the rate of diffusion of the two species. These two rates may or may not be the same. The rate of solid state reaction depends on the number of nuclei produced per unit volume. A nucleus is a point where the atoms or ions have reacted and begun formation of the product structure. Higher firing temperatures and longer firing times result in larger particles. Particle growth is rapid in the initial stage of firing, and slows down after a certain period of time.

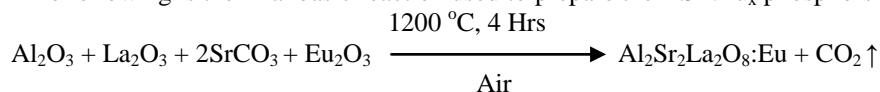
1.2 Why Solid State Reaction Method

- It is better to prevent waste than to treat or clean up waste after it has been created.
- SSR method output gases are mostly CO₂, H₂O and NH₄ etc., can be stabilized in atmosphere [15].
- Atom Economy is defined as synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Less Hazardous Chemical Syntheses wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment. Chemical reactions should be designed to affect their desired function while minimizing their toxicity which is nothing but designing safer chemicals
- If possible, synthetic methods should be conducted at ambient temperature and pressure.
- In SSR most of the above conditions are satisfied except the temperature. Therefore SSR can be called green chemistry route

II. EXPERIMENTAL

Aluminum oxide, Strontium carbonate, Lanthanum oxide were taken as raw materials for the host and the molar ratio of rare earth Europium oxide taken as activator ion which is doped in host at different concentrations. All the chemicals were purchased from National Chemicals, Baroda, of assay 99.9%. The base materials and activator were mixed and ground thoroughly using agate mortar and pestle prior to this all the materials are weighed as per the required quantities. Acetone is added to get uniform mixing of the oxides while grinding using agate mortar and pestle for 30 minutes. AlSrLaO₄ Phosphor is synthesized using standard solid state reaction with varying Eu (0.1, 0.2, 0.3, 0.4, 0.7, 1.0, 1.5, 2.0 and 2.5%) molar concentration. To prepare Aluminum Strontium Lanthanate (ASL) doped with various concentrations of Eu, consists of heating stoichiometric amounts of reactants at 1000 °C for 2 hours in a muffle furnace. The received powder being ground thoroughly using an agate mortar, to ensure the best homogeneity and reactivity, powder was transferred to alumina crucible, and then reheated in a muffle furnace at 1200 °C for 4 hours. The phosphor materials were cooled to room temperature naturally.

The following is the final basic reaction used to prepare the ASL:Eu_x phosphors



2.1 General flow chart of phosphor synthesis

Refinement of Raw Materials (Matrix, Activator, Flux) → Blending, Ball mill (large scale) Mortar and pestle (Laboratory scale) → Synthesis (firing 1200°C for 2-4 hours) → Coarse Crushing → Final Product → Milling and Sieving → Characterization → Applications [16]

2.2 Characterization techniques

Photoluminescence spectra were recorded at room temperature using Shimadzu-5301 Spectrofluorophotometer and the phosphor is excited with 254, 268 and 278nm excitations. Due to high emission intensity of the present phosphor the sample holder is redesigned as follows: Shimadzu-5301 Spectrofluorophotometer supplied sample holder diameter: 25mm. We made 15, 10, 8, 5mm dia sample holders so as to record the PL within the range of the machine (1015units). In the present study 8mm diameter sample holder was used. The phosphors were characterized using XRD and SEM.

III. RESULTS AND DISCUSSIONS

3.1 Photoluminescence study

The excitation and emissions of the Eu(1.5%) Doped AlSrLaO₄ Phosphor is presented in Fig.1 with 254, 268 and 278nm excitations. The excitation of the Eu doped AlSrLaO₄ phosphor material with 254, 268 and 278 nm wavelengths generates sharp PL emissions at 468, 514, 529, 535, 541, 555, 582, 589, 598, 615 and 627nm among the emissions 627nm is strong. It is interesting to note when the phosphor is excited with 278nm the emission intensity increased by 400% when compared with 254nm excitation. It is also observed from the figure, three peaks at 555, 589 and 615 nm are with less intensity. All the emissions are allowed transitions of Eu³⁺. The peaks at 588 and 595nm corresponding to orange red color are derived from the allowed magnetic dipole transition (⁵D₀→⁷F₁), whose intensity is barely affected by the crystal environments surrounding Eu³⁺. The peaks at 615 and 627nm corresponding to red color are generated from the forced electric dipole transition (⁵D₀→⁷F₂), whose intensity is hyper-sensitive to crystal fields. Here, Eu³⁺ ion is allowed to occupy a site without an inversion center [17-22].

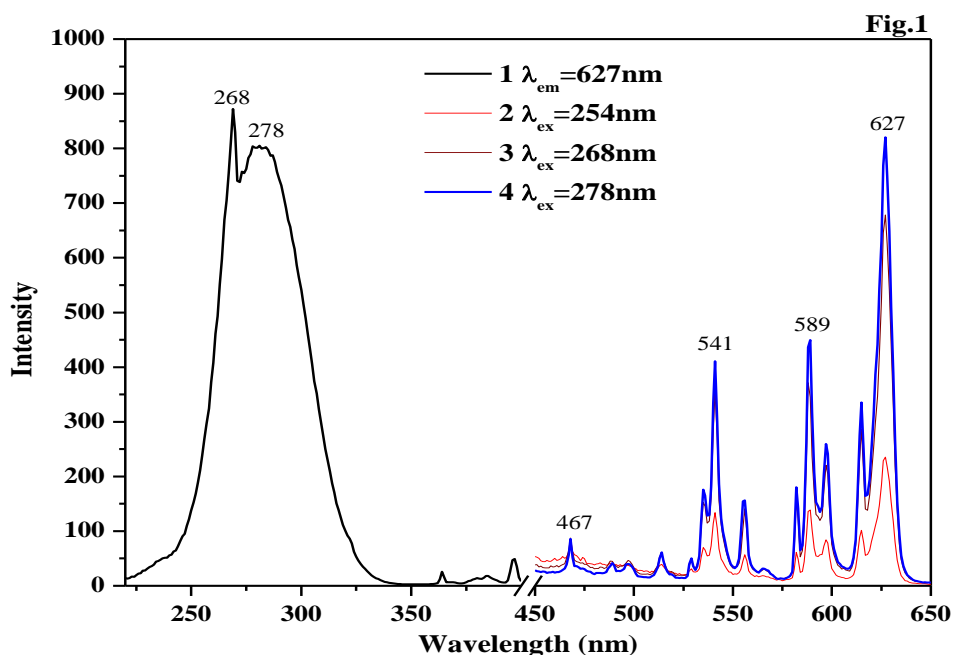


Fig.1 PL Excitation and Emission spectra of AlSrLaO₄: Eu(1.5%) phosphor under different excitations

Compared with $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$, the intensities of $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ were suppressed greatly. The emission intensity ratio of $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ gives a measure of the degree of distortion from the inversion symmetry of the local environment surrounding the Eu³⁺ ions in the matrix [17, 19, 23, 24]. The materials present is very attractive luminescent properties for the generation of green-red band. There are in fact multiple emission lines at each of these due to the crystal field splitting of the ground state of the emitting ions. As the Eu concentration increases the PL intensity also increases and quenching occurs after 1.5% Eu in the host ASL.

Fig.2 represents various PL emissions of 0.1 to 2.5 % Eu doped AlSrLaO₄ excited with 278nm. Fig. 3 is the variation of Eu concentration in ASL and behaviour of subsequent PL emissions when excited with 278nm. Table.1 contains various emission peak intensities of Eu doped AlSrLaO₄ under different excitations presented for better comparison and understanding.

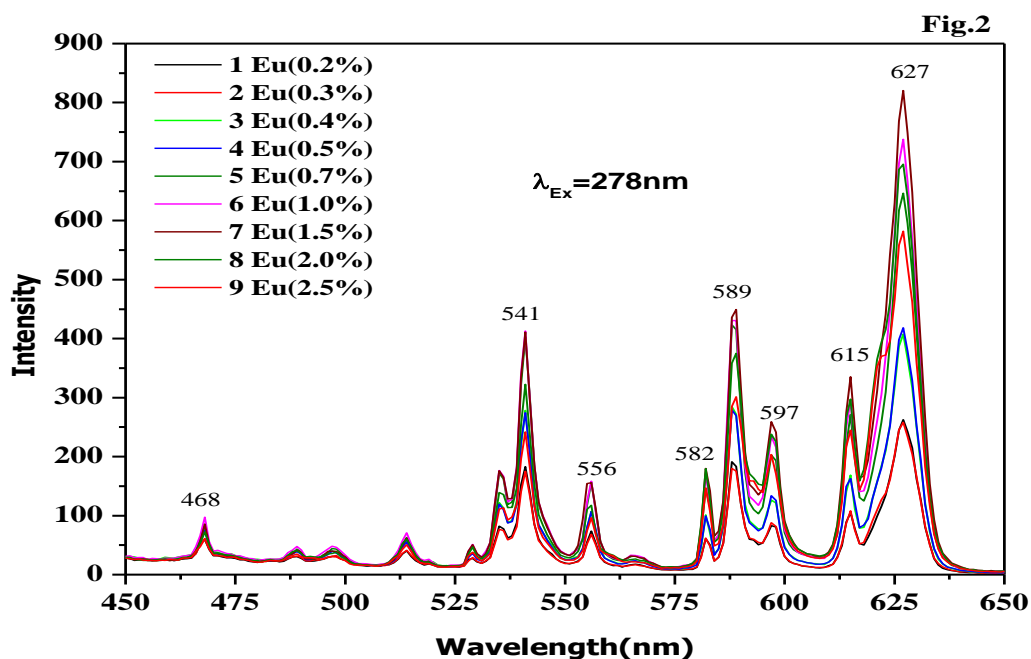


Fig.2 PL Emission spectra of AlSrLaO₄: Eu (0.1 to 2.5%) under 278nm excitation

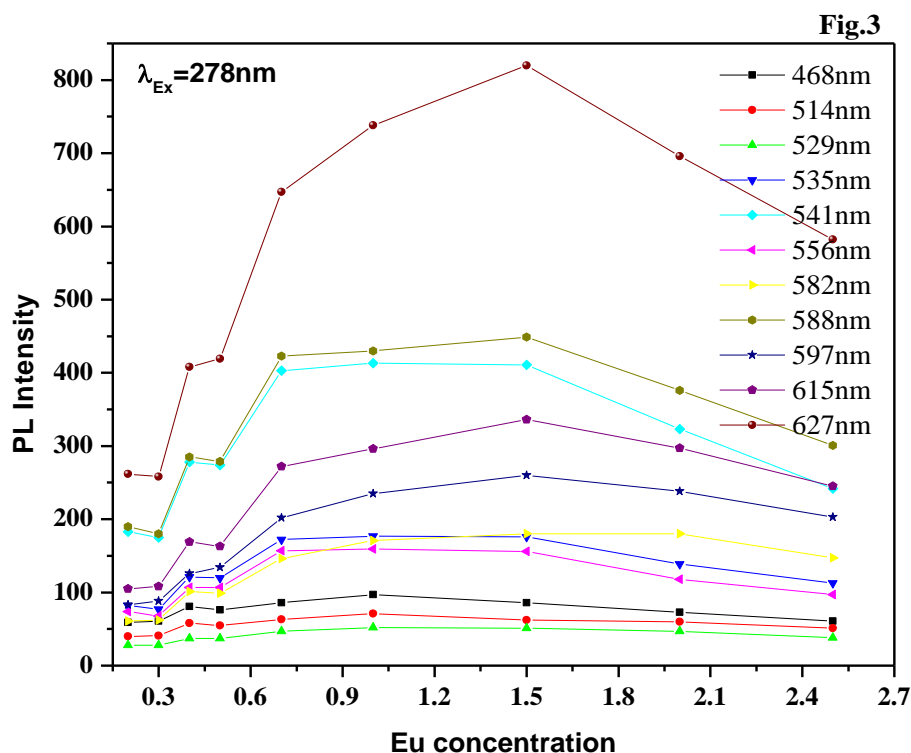


Fig. 3 The variation of Eu concentration in ASL and behaviour of subsequent PL emissions when excited with 278nm

Table 1 Emission peak intensities under different excitations

Phosphor	λ_{ex} nm	Emission peak Intensities							
		468	541	556	582	589	597	615	627
Al ₂ Sr ₂ La ₂ O ₈ : Eu(1.5%)	254	73	134	56	61	137	84	101	235
	268	88	357	140	156	372	220	287	679
	278	86	411	156	180	449	260	336	820

3.2 XRD study

Fig.4 shows XRD reflections of AlSrLaO₄: Eu(1.5%) phosphor, synthesized via SSR. All the reflection peaks can be completely indexed, basing on the JCPDS card No. 81-0744, to a pure tetragonal phase of with space group I4/mmm (139). Unwanted impurities were not observed from XRD. The strong and sharp peaks indicate that highly crystallized and structurally ordered at long-range. The average crystallite size had been estimated by the Scherrer's equation using the full width at half maximum (FWHM) for the intense peak (1 0 3). The average crystallite size was calculated using the Debye-Scherrer formula given in the literature, i.e., $d = k/\beta$, Where k is constant (0.9), λ is the wavelength of the x-rays used (0.154 nm in the present case), β is the full width at half maxima (FWHM), θ is the Bragg angle of the XRD peak. The calculated average crystal size of the phosphor sample is calculated by measuring the full width at half maxima was found to be around 54nm for Eu (1.5mol %) doped AlSrLaO₄ Phosphor.

3.3 SEM study

Fig.5 is SEM image of ASL:Eu(1.5%). From SEM micrograph it is seen irregular, granular shaped, agglomerated and different sized particles are seen. The particulates having an average basal diameter of ~450nm and a length of ~0.700nm are seen. Agglomerations of particulates are also seen this may be due to SSR however by adding flux this problem can overcome.

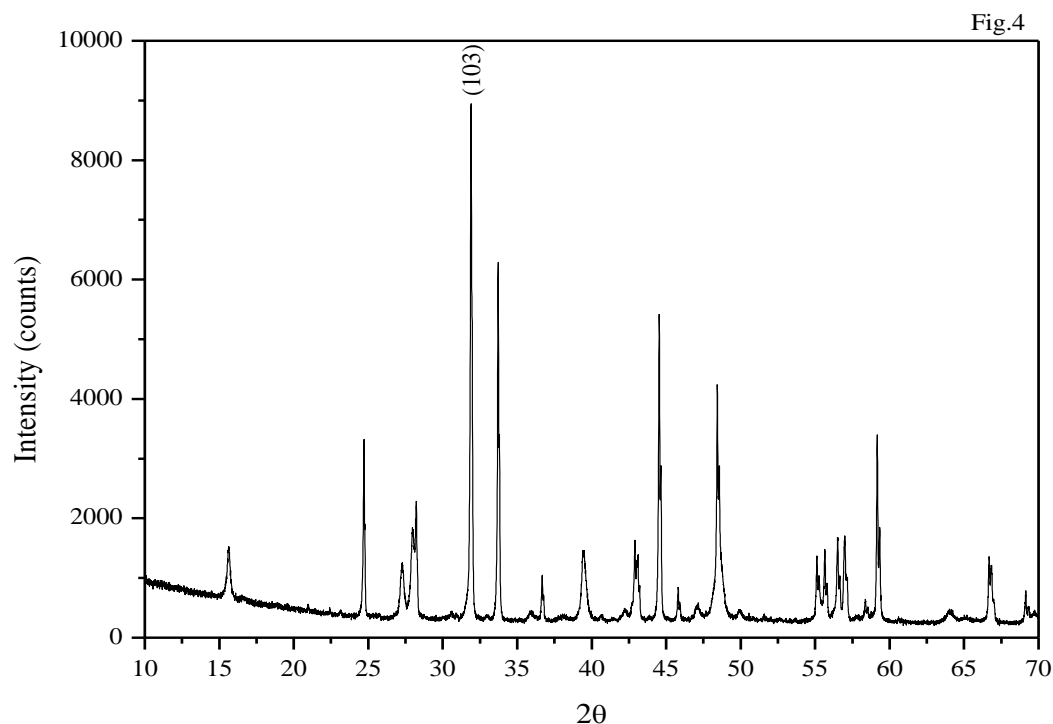


Fig.4 XRD pattern of 1.5% Eu doped AlSrLaO₄ phosphor

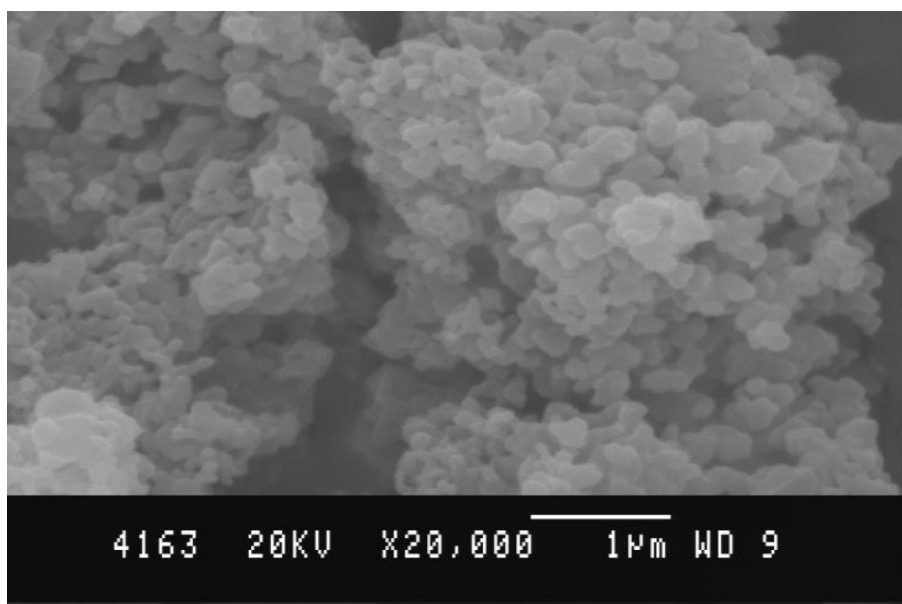


Fig.5 SEM image of 1.5% Eu doped AlSrLaO₄ phosphor

IV. CONCLUSIONS

By the SSR method a batch of samples based on the ASL was synthesized, and doped with Eu³⁺ ion. From the excitation as the excitation wavelength increases the emission peak wavelengths increased gradually. As the Eu concentration varies from 0.1 – 2.5 mol% the emission intensity increases up to 1.5 mol% and then decreases concludes that concentration quenching is observed. In the selected range of wt % of starting reactants, Eu-doped ASL and a mixture of them were produced and verified by X-rays diffraction. On the other hand, for samples particularly including Eu-doped ASL, PL associated to distinct electronic transitions of Eu³⁺ was detected. Some of those electronic transitions present sharp and narrow emissions, and their number is augmented when the Eu content in the samples is larger in ASL. In this way, it has been proved that ASL is an efficient host matrix for the Eu³⁺ ion. Finally, it is also concluded that that the following Eu³⁺ emissions are obtained from ASL host and the transitions are assigned to the allowed ones.

1. 468nm emitted peak is due to $^5D_2 \rightarrow ^7F_0$ transition of Europium and with energy 2.657 eV.
2. 515nm emitted peak is due to $^5D_2 \rightarrow ^7F_3$ transition of Europium and with energy 2.429 eV.
3. 545nm emitted peak is due to $^5D_4 \rightarrow ^7F_6$ transition of Terbium and energy 2.228 eV.
4. 588nm emitted peak is due to $^5D_0 \rightarrow ^7F_1$ transition of Europium and is due to magnetic dipole. with energy 2.118 eV
5. 615nm emitted peak is due to $^5D_0 \rightarrow ^7F_2$ transition of Europium and is due to electric dipole with energy 2.015 eV and is due to electric dipole.
6. 627nm emitted peak is due to $^5D_0 \rightarrow ^7F_3$ transition of Europium and is due to electric dipole with energy 1.985 eV and is due to electric dipole.

The emission peaks observed in AlSrLaO₄: Eu when excited with 278nm at 468(Blue), 514, 528, 541, 544, 548(green), 582, 588(Yellow), 615(orange) and 627nm (red) are observed. The obtained results on AlSrLaO₄: Eu is suitable for white light source using UV light as the primary excitation.

ACKNOWLEDGMENTS

One of the authors (K.Suresh) is grateful to University Grants Commission (UGC) for sanctioning the minor research project (MRP)

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