

Synthesis and luminescence study of Eu³⁺ doped Lanthanum Aluminate phosphor

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Abstract:-LaAlO₃:Eu³⁺ phosphor was prepared by modified solid state reaction method at a high temperature of 1250° C in air atmosphere, which is most suitable for large-scale production. Photoluminescence curves were studied. Intense peaks at 594 nm and 619 nm were obtained. Thermoluminescence (TL) glow curve of the phosphor with different concentrations was recorded with heating rate 6.7°C/s. The intensity of glow curve was studied with variation in UV exposure time. Evaluation of kinetic parameter such as activation energy, order of kinetics and frequency factor was studied by using Chen's peak shape method.

Keywords: LaAlO₃, Synthesis, Photoluminescennce, Thermoluminescence, Europium.

I. INTRODUCTION:

Rare-earth doped Lanthanum Aluminate phosphors are promising materials for color light emission. The molten salt method, the combustion method, the sucrose method, and the coprecipitation technique are the best methods for preparing LaAlO₃ phosphors with small particle size and high surface area by low temperature synthesis. LaAlO₃ usually has a rhombohedral structure. It has good dielectric properties and, hence, is regarded as an attractive alternative to SiO₂ in microelectronic devices. LaAlO₃ phosphors have excellent chemical and thermal stability, mechanical durability, and exploitable optical and electronic properties, leading to a wide range of potential applications. LaAlO₃ phosphors doped with rare-earth ions have luminescence properties and can, hence, be used in optical display systems. This paper photoluminescence presents the and thermoluminescence studies of Eu³⁺ doped LaAlO₃ phosphor [1].

II. EXPERIMENTAL:

The Eu³⁺ activated LaAlO₃phosphor was prepared via high temperature modified solid state reaction.The mixture of reagents was ground together to obtain a

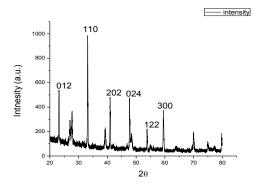
homogeneous powder. After being ground thoroughly in stoichiometric ratios by using an agate mortar by dry grinding for nearly 45 minutes, to ensure the best homogeneity and reactivity, powder was transferred to alumina crucible, and then heated in a muffle furnace at 1250 °C for 2 hr.

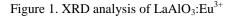
The sample was characterized using photoluminescence (PL), thermoluminescence (TL), and XRD. The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The X-rays were produced using a sealed tube and the wavelength of Xray was 0.154 nm (Cu K-alpha). The X-rays were detected using a fast counting detector based on Silicon strip technology (Bruker LynxEye detector). The photoluminescence (PL) emission and excitation spectra were recorded at room temperature by use of a Shimadzu RF-5301 PC spectrofluorophotometer. The excitation source was a xenon lamp. Thermally stimulated luminescence glow curves were recorded at room temperature by using TLD reader I1009 supplied by Nucleonix Sys.Pvt.Ltd. Hyderabad. The obtained phosphor under the TL examination is given UV radiation using 254nm UV source [5-9].

III. RESULT AND DISCUSSION:

XRD Analysis:

The X-raydiffraction patternsofLaAlO³:Eu³⁺ are shown in Fig.1. According to XRD analysis(Fig.1), the LaAlO₃ obtained crystallizes in a purerhombohedral perov skite structure (JCPDSno.01-082-0478) with spacegroup R-3c (No.167), with unitcell dimensions a=5.37Å and c=13.10Å. So all diffraction peaks in these XRD pattern scould be attributed to the rhombohedral perovskite crystal structure of LaAlO³ which confirm that the doping concentration does not influence the crystalline phase formation. The particles size of LaAlO₃ calculated from the Scherrer formula is about 56nm.





Photoluminescence study:

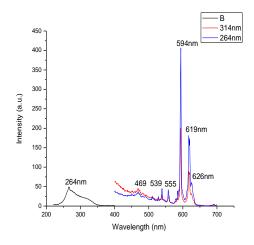


Figure 2. Photoluminescence excitation and emission spectra of LaAlO₃: Eu (1.5 mol %) with the variation of excitation wavelength

Figure 2 is the excitation and emission spectra of LaAlO₃: Eu excitation monitored at 612nm the following excitations are found 264nm, 314nm having the intensities are 65 and 90. The excitation spectra of LaAlO₃: Euphosphor recorded by monitoring the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺ at 612nm. In excitation spectra a broad peak at 264nm observed which are originating from the ${}^{7}F_{0} \rightarrow {}^{5}D_{4}$ (264 nm) and ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ (314 nm). The maximum intensity of the absorption spectrum was determined to be at 254, 264 and 314 nm. The excitation spectrum contains an intense broad band with a maximum at 264 nm (figure 2) arising from the charge transfer band (CTB) between Eu³⁺ and the neighbouring O²⁻ and a group of lines in the longer wavelength region due to the f-f transitions within Eu³⁺ 4f⁶ configuration. The prominent excitation band observed at 364nm (NUV) due to the transition of Eu^{3+} $({}^{7}F_{0} \rightarrow {}^{5}L_{6})$ and this clearly indicates that LaAlO₃: Euphosphors are effectively excited by near ultraviolet light emitting diodes (NUV-LEDs). All the PL emission intensities for different excitations are presented in Table.1 for better understanding.

 Table 1.PL emission intensities for different excitations

S. No.	Sample Name	λ_{exe}	λ_{emi}	Intensity		
1.	LaAlO ₃ : Eu (1.5%)	264	468, 539, 555, 594, 619, 626	33, 45, 45, 410, 185, 65		

Table 2 excitation spectra: for excitation wavelength 612 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$).

S.No.	λ_{exe}	Transitions		
1.	264nm	$^{7}F_{0} \rightarrow ^{5}D_{4}$		
2.	314nm	$^{7}F_{0}\rightarrow ^{5}L_{6}$		

Table 3 emission spectra: for excitation wavelength264 and 364 nm

S. No.	λ_{emi}	Transitions			
1	594nm	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$			
2	619nm	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$			
3	626nm	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$			

By exciting the CTB at 264 nm yields the emission spectrum which are shown in Fig.2, which is composed of ${}^{5}D_{0}-{}^{7}F_{J}(J=1, 2, and 4, as labelled in the figure)$ emission lines of Eu^{3+} . In general, when the Eu^{3+} ion is located at crystallographic site without inversion symmetry, its hypersensitive forced electric-dipole transition ${}^{5}D_{0}-{}^{7}F_{2}$ red emission dominates in the emission spectrum. If the Eu³⁺ site possesses an inversion centre, ${}^{5}D_{0}-{}^{7}F_{1}$ orange emission is dominant [2]. The distinct emission lines lying between 450-650 nm are observed due to transitions from excited 5D_0 to the ${}^{7}F_{J}$ (J=0-3) levels of Eu³⁺ ions. The origin of these transitions (electric dipole or magnetic dipole) from emitting levels to terminating levels depend upon the location of Eu^{3+} ion in LaAlO₃ lattice and the type of transition is determined by selection rule [3]. The most intense peak in the vicinity of 594nm is ascribed to the magnetic dipole transition of ${}^{5}D_{0}$ and ${}^{7}F_{1}$ levels. The weak emission at 619 and 626nm corresponds to the hypersensitive transition between the ${}^{5}D_{0}$ and ${}^{7}F_{2}$ levels due to forced electric dipole transition mechanism (Figure 2).

Emission spectrum consists of emission peaks in the range of 450–650 nm, which result from ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J=1, 2) transitions of Eu³⁺ ion, respectively. For an excitation wavelength of 314nm, the emission spectrum of LaAlO₃: Euconsists of sharp emission lines at 594nm,

619 nm and 626nm. The emission at 594nm originates from the allowed magnetic dipole (MD) transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ which is having highest intensity. The peaks observed at 619 and 626 nm are due to the electric dipole ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition has the half the intensity when compared to highest emission intensity peak which is 594nm. The ratio of 594nm peak intensity to 619 and 626 nm peaks are half. This result is interesting when compared with the earlier work where the 594:612:626nm peak intensities are nearly same [4]. Both magnetic dipole transition and electric dipole transition transitions are shown in the emission spectra. If the magnetic dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ having the highest intensity then Eu^{3+} ions in host lattice occupies an inversion centre. If the emission intensity of magnetic dipole transition was lower than that of electric dipole transition, which indicates that Eu³⁺ ions occupied without an inversion symmetric centres in the host. The increasing concentrations of Eu³⁺ ions have no change on the peak position of emission spectra. The results indicate that LaAlO₃: Euphosphors can be selected as a potential candidate for LED application (Ex.314) as well as for FL and CFL (Ex.264).

Thermoluminescence

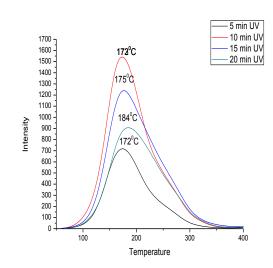


Figure 3. LaAlO₃:Eu (1.5%) variation with UV exposure time

Thermoluminescence glow curve of Eu^{3+} doped LaAlO₃ phosphor was recorded using TLD reader with heating rate 6.7°C. The phosphor was given UV exposure for different time period and variation in the intensity of TL glow curve was recorded. The highest intensity peak is obtained for UV exposure time of 10 minutes and further increase in exposure time results in decrease in intensity of glow curve. The kinetic parameters such as activation energy, shape factor, frequency factor etc for the glow curve are calculated using peak shape method. Second order kinetics is observed for the glow curves.

UV Mi n	HTR	T ₁ (°C)	T _m (°C)	T2 (°C)	τ	δ	ω	μ=δ/ ω	Activation Energy	Frequency Factor	Frequenc y Factor	Lifetime of charge in the trap (\u03c6)
5	6.7	139	172	225	33.00	53.00	86.00	0.62	0.62	0.62	4.8 x 10 ⁷	548.11
10	6.7	138	173	226	35.00	53.00	88.00	0.60	0.61	0.64	9.1 x 10 ⁷	542.48
15	6.7	140	175	245	35.00	70.00	105.00	0.67	0.50	0.54	3.2 x 10 ⁶	354.92
20	6.7	144	184	254	40.00	70.00	110.00	0.64	0.50	0.59	2.2 x 10 ⁷	434.59

IV. CONCLUSION:

Photoluminescence studies of Eu^{3+} doped LaAlO₃ phosphor shows that peaks in red region of visible spectra are obtained i.e. 594nm and 614nm. The intensity of peaks increases with increase in concentration of Eu^{3+} ion concentration. But no change in the position of peaks is observed for different concentration. Hence, LaAlO₃: Eu^{3+} can be selected as a potential candidate for display devices like LED etc.

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