



Eu³⁺ ACTIVATED LiAlPO₄Cl NOVEL RED HALOPHOSPHATE PHOSPHOR

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Abstract

Eu³⁺ activated LiAlPO₄Cl phosphors prepared by combustion synthesis and the completion of the synthesis was confirmed by XRD (X-ray diffraction) patterns. The surface morphology studied by scanning electron microscopy (SEM) and photoluminescence (PL) properties has been reported in this paper. The Eu³⁺ PL emission spectrum was observed at 594 nm (orange) and 614 nm (red) regions, the spectrum due to ⁵D₀-⁷F₁ and ⁵D₀-⁷F₂ transitions at mercury free excitation, respectively. The CIE chromaticity coordinate of LiAlPO₄Cl:Eu³⁺ phosphor excited at 394 nm is (x ≈ 0.6774, y ≈ 0.3223). Its considerable emission intensity under 394 nm excitations makes it possible candidate materials as red component of tricolour luminescence materials and for near ultra violet light emitting diode (n-UVLED) phosphors.

Keywords: Luminescence, X-ray diffraction, SEM, CIE & Phosphate

1. Introduction

White light generation through GaN-based light-emitting diodes (LEDs) has a number of advantages over the existing incandescent and halogen lamps in terms of power efficiency, reliability, and long lifetime [1]. Innovative structures and designs of the device have led to dramatic improvements of the performance in LED technology, groundbreaking performance records are being reported constantly [2]. Europium ion is widely used as luminescent centre in lots of phosphors for the exhibited

characteristic red emission mainly corresponded to its ⁵D₀→⁷F₂ transition [3,4]. Phosphates doped with some trivalent europium ion have excellent efficiencies and appropriate absorption bands. A great deal of work has been done on Eu³⁺ activation of these hosts. Akojwar et.al., have synthesized KAlPO₄Cl:F:Eu³⁺ phosphor via a facile combustion method and reported its optical properties [5,6]. These studies mostly concentrated on the choice of the host materials and the luminescent central ions. Phosphate compounds can provide many crystal field environments imposed on emission centres. Moreover, phosphate phosphors doped with rare earth ions have excellent thermal and charge stabilization [7,8] and also phosphate compounds are known to be multifunctional materials. In particular, orthophosphates have been extensively investigated, due to their structural diversity. This makes them suitable as hosts to accommodate active rare earth ions. The phosphate family symbolizes possibly one of the most attractive kinds of novel inorganic material, largely owing to the ability of the tetrahedral (PO₄)³⁻ group to bond with other structural units. Recently, Shinde et.al. Reported several phosphate phosphors for lamp applications [9–11]. Therefore, Eu³⁺ doped in phosphates compounds has excellent luminescence.

In this article, LiAlPO₄Cl was selected as the host material. After doping Eu³⁺ into LiAlPO₄Cl, the effect of the dopant on the luminescence properties was investigated, i.e. the emission and excitation spectra. The intensities of the excitation and emission bands

of the prepared phosphors are enhanced with Eu^{3+} doping.

II. Experimental:

2.1 Synthesis:

The Eu-doped LiAlPO_4Cl phosphate phosphors were synthesized by the facile combustion method. The starting material were taken as Lithium Nitrate (LiNO_3), aluminium nitrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], di-ammonium hydrogen phosphate [$(\text{NH}_4)_2\text{HPO}_4$], Ammonium chloride (NH_4Cl), Europium nitrate was prepared by dissolving europium oxide [Eu_2O_3] in nitric acid. All the reagents were of analytical grade from Merck with 99.99% purity were used without further purification. The correct amount of each excess urea [$\text{CO}(\text{NH}_2)_2$] were injected into the precursor solution or these compositions. The amount of 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 a maximum. After stirring for about 20 min, precursor solution was transferred to a furnace preheated 750°C .

2.2 Measurements:-

Several complementary methods were used to characterize the prepared phosphors. The prepared host lattice was characterized for its phase purity and crystallinity by X-ray powder diffraction (XRD), using a PAN-analytical diffractometer (Cu-K α radiation) at a scanning step of 0.01° , continue time of 20 s and in the 2θ range $10-70^\circ$; The photoluminescence measurements of excitation and emission were recorded on a Shimadzu RF5301PC spectrofluorophotometer. The same amount of sample (2g) was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. All the measurements were conducted at room temperature.

3. Results and discussion:

3.1. XRD of $\text{LiAlPO}_4\text{Cl}:\text{Eu}^{3+}$ phosphor powders:

Fig. 1 gives the XRD patterns of LiAlPO_4Cl material. However, the obtained diffraction peaks of all compounds do not match any data in the JCPDS base after careful comparison with the reported compounds for the obtained phase;

it is carefully observed that there are no peaks of raw materials. It is found that the main phase does not agree to any JCPDS available. Different temperatures do not result in new other phase except the unknown main phase. Consequently, we speculate that the obtained unknown phase is likely to be a new phase. With respect to this point, a further study is still being carried on.

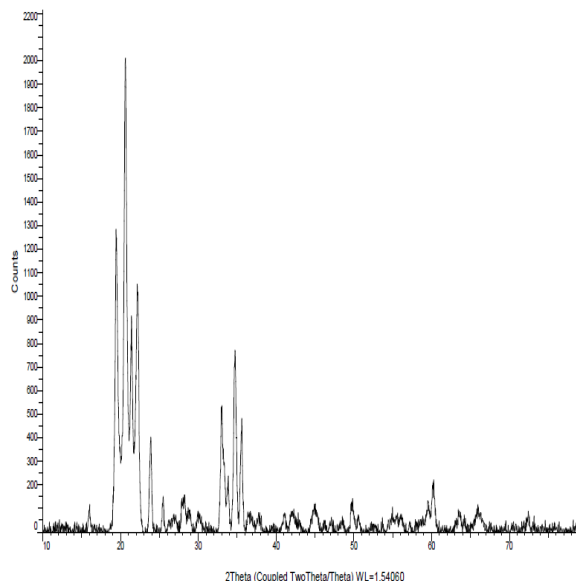


Fig. 1 X-ray diffraction (XRD) patterns of $\text{LiAlPO}_4\text{Cl}:\text{Eu}$

3.2. SEM of $\text{LiAlPO}_4\text{Cl}:\text{Eu}^{3+}$ phosphor powders:

Characterization of particles, surface morphology and size for nano crystals is done routinely using scanning electron microscope. The main advantage of SEM is that they can be used to study the morphology of prepared particles and composites. Fig.2 shows the SEM pattern of $\text{LiAlPO}_4\text{Cl}:\text{Eu}^{3+}$ phosphors prepared at 750°C . It is clearly seen that the grains prepared by combustion method are irregular in shape with particles size of about $1-5\mu\text{m}$. This shows that the combustion reactions of the mixtures took place well. The particles possess foamy like morphology formed from highly agglomerated crystallites. Hence it is suitable for solid state lighting (coating purpose). [12]

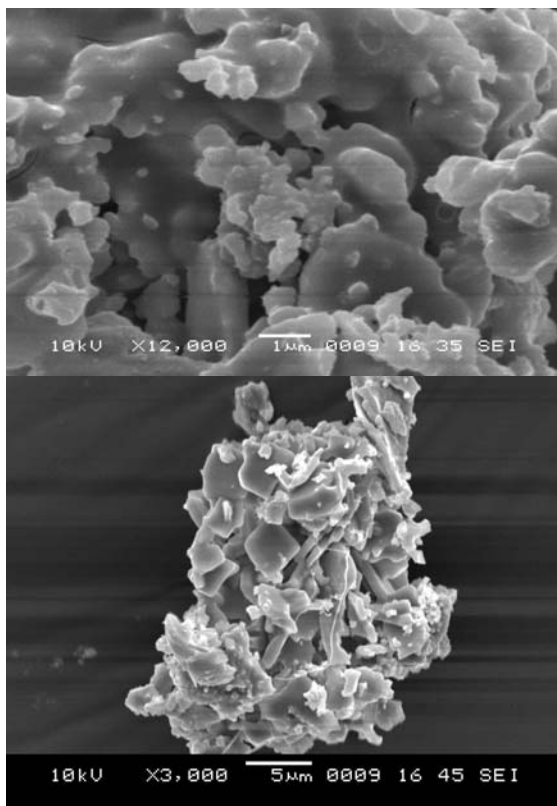


Fig. 2 SEM image of LiAlPO₄Cl:Eu phosphor at different magnifications.

3.3. Photoluminescence of LiAlPO₄Cl:Eu³⁺ phosphor powders:

Figures 3(a) and 3(b) show the excitation and emission spectra of LiAlPO₄Cl:Eu³⁺ phosphor, respectively. Two excitation bands are observed at 380 and 394 nm; both caused by the f–f transitions and observed at a narrow peak with a maximum intensity at 394 nm (see Figure 3(a)). Under the excitation of 394 nm, the phosphor of LiAlPO₄Cl:Eu³⁺ has two sharp orange/red-emission bands at 594 and 614 nm, as shown in Figure 3(b). Among these two emission bands, the 594 nm is main line corresponding to the magnetic dipole transition $^5D_0 \rightarrow ^7F_1$ of Eu³⁺ which is less prominent, whereas other corresponds to the electric dipole transition $^5D_0 \rightarrow ^7F_2$ of Eu³⁺ ion. These two peaks are obtained due to the splitting of Eu³⁺ ion emission. The PL intensity ratio of the transitions $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$, $R = I_2/I_1$, is a good way to detect the symmetry of crystal field environment around Eu³⁺ ion [12]. A low symmetry leads to a high value of ($R > 1$), the opposite will lead to a low value ($1 > R > 0$). In this work, the R value of LiAl_{1-x}PO₄Cl:Eu_x³⁺ ($x=0.5$ mol %) phosphor is 1.4229, which strongly indicates that Eu³⁺ ions occupy the sites with no inversion symmetry [13]. The emission

intensity of the dominant peak located at 613 nm increases with the increasing of Eu³⁺ ion concentration and reaches the maximum when the molar fraction is 0.5mol%, then it decreases because of the concentration quenching shown in fig3(c). The multiphoton relaxation derived from the vibration of phosphate groups. These phosphate groups can bridge the gaps between the lowest 5D_0 level of Eu³⁺ and the higher energy levels (5D_1 , 5D_2) effectively so there is no emission from the higher energy levels of Eu³⁺ ion can be detected. Figure 3(d). Represents the schematic energy levels of the Eu³⁺ ion showing the states involved in the luminescence process and the transition probabilities. The high contribution of the orange $^5D_0 \rightarrow ^7F_1$ emissions and the low intensity of the red $^5D_0 \rightarrow ^7F_2$ emission result in high colour purities adequate for solid state lighting applications. The luminescent properties of Eu³⁺ ion in the crystalline LiAlPO₄Cl phosphor are in good agreement with those obtained through other processes, indicating that Eu³⁺ ions have been effectively doped into the host lattice of LiAlPO₄Cl. In the present case, the low contributions of the red $^5D_0 \rightarrow ^7F_2$ emissions and the high intensity of the orange $^5D_0 \rightarrow ^7F_1$ emission result in high colour purities that are adequate for solid state lighting applications.

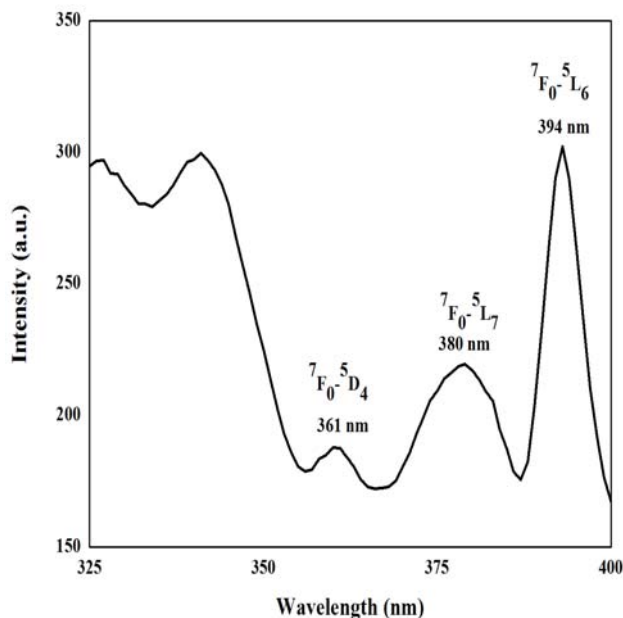


Fig 3(a) Excitation spectrum of LiAlPO₄Cl:Eu³⁺ phosphor ($\lambda_{\text{emi}} = 614$ nm)

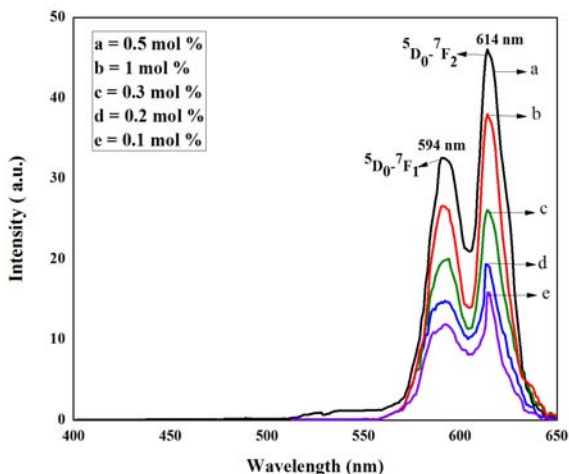


Fig3 (b) Emission spectra of LiAlPO₄Cl:Eu³⁺ (a = 614nm at λ_{exc} = 394 nm)

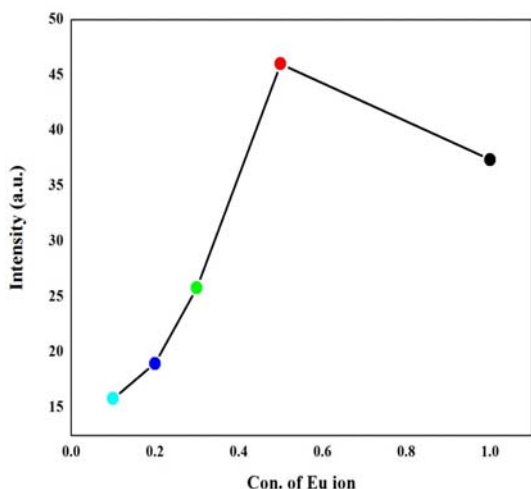


Fig.3(c) maximum PL intensity of LiAlPO₄Cl:Eu³⁺ with varying concentration

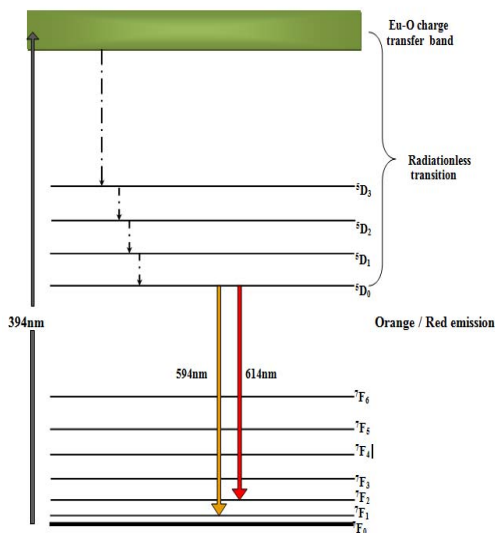


Fig 3(d) Energy level diagram of Eu³⁺

3.4. Chromatic Properties:-

Most lighting specifications refer to colour in terms of the 1931 CIE chromatic colour coordinates, which recognizes that the human visual system uses three primary colours: red, green, and blue [14,15]. The chromatic coordinates (x, y), were calculated using the colour calculator program radiant imaging [16]. The coordinates of the Eu³⁺ doped LiAlPO₄Cl phosphors of red colour (x ≈ 0.6774, y ≈ 0.3223) are show in Figure 4. The location of the colour coordinates of the LiAlPO₄Cl phosphate based phosphor powder doped with Eu³⁺ on the CIE chromaticity diagram, presented in Figure 4, indicates that the colour properties of the phosphor powder prepared by combustion method are approaching those required for field emission displays.

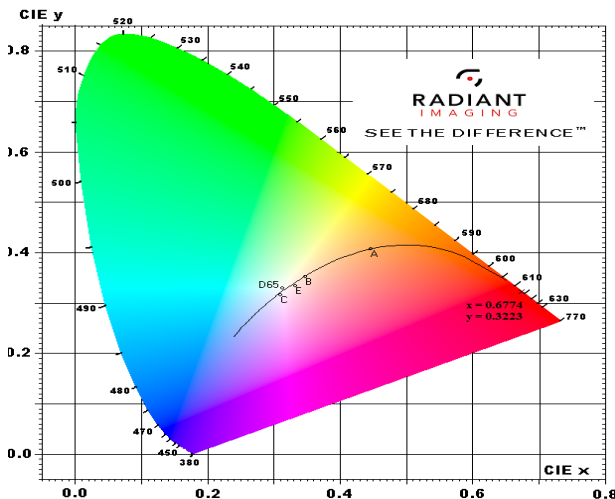


Figure 4. CIE coordinates of LiAlPO₄Cl:Eu³⁺ phosphor

4. Conclusions:

In the present work, the phosphors LiAlPO₄Cl doped with Eu³⁺ ions have been synthesized by a combustion method. The prepared phosphors confirmed by X-ray diffraction (XRD) pattern. The phosphors exhibit an intense orange emission with the strongest emission peak at around 614 nm. The strongest excitation peak is located at 394 nm in the near UV light region. The PL intensity increases under the excitation of NUV light with increasing concentration. Strong concentration quenching of Eu³⁺ emission was observed when the Eu³⁺ doping level exceeds 0.5 mol%. The above observations hint at the promising application of Eu³⁺ doped LiAlPO₄Cl phosphors in production of warm white light for NUV-LEDs.

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