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Eu^{3+} and Dy^{3+}-activated $LaAlO_3$ phosphor for solid-state lighting

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Abstract

Rare earth Eu^{3+} and Dy^{3+}-activated $LaAlO_3$ phosphor were prepared by wet chemical method. The prepared phosphors were characterized by, X-ray diffraction(XRD) for phase purity, scanning electron microscopy (SEM) for morphology and photoluminescence (PL) emission and excitation spectra. SEM analysis does not reveal the crystal structure; however, it shows that the prepared phosphor has irregular morphology with particle size in micron range. Under both 395 nm and 466 nm excitation, $LaAlO_3:Eu^{3+}$ phosphor shows emission at 593 nm and 614 nm. $LaAlO_3:Dy^{3+}$ phosphor shows emission at 484 nm and 575 nm when excited by wavelength of 351 nm. The synthesized phosphors have mercury-free excitation, and therefore, prepared phosphor might be applicable in environmental-friendly solid-state lighting.

1 Introduction

Currently, phosphor-converted white light-emitting diodes (w–LEDs) have been attracted worldwide attention as a new source for the solid-state lighting to next generation due to their special advantages such as long lifetimes, luminous efficiency, absence of mercury, low energy consumption, weak environmental impact, excellent chemical as well as physical stability, availability of final products in different sizes, and so on [1, 2]. A lot of studies have been investigating different luminescent materials to help the growth of suitable phosphors. Phosphors are also useful for producing white light when they are excited by blue or near-ultraviolet (NUV) lights (300–420 nm). It is very important to choose the right compound materials and assure they have outstanding physical and chemical stability for obtaining phosphors with highly proficient emissions [3, 4]. Lanthanides elements such as Tb^{3+}, Pr^{3+}, Eu^{3+}, Sm^{3+}, Dy^{3+}, La^{3+} etc. have been broadly used as luminescent centres in phosphor materials due to their intense transitions in d→f shell. Between these ions, dysprosium and europium is mostly used as a dopant and it has been used in phosphor materials for developing solid-state lighting [5–7]. Recently, there is developing interest in luminescence of trivalent rare earth ions such as tungstate, phosphates, borates, aluminates and molybdates; among which rare earth-doped aluminate are especially attractive due to their magnificent physical, chemical and thermal stability, high UV transparency and high-luminescence efficiency [8–14]. Research on the luminescence of a series of such compounds offers much valuable data for optical applications such as flat panel displays, high-density optical storage, temperature sensors, under sea communication, various fluorescent devices, colour display and visible solid-state lasers traffic signals, safety indicators on emergency appliances and less energy-consuming light sources. Oxide phosphors are non-toxic in nature due to this they are environmental friendly [15, 16]. Lanthanum aluminate is well known for its perovskite-like crystalline structure. Materials having these properties are applicable for various technological applications due to their special magnetic and electrical properties. Maczka et al. reported the $LaAlO_3$ phosphors doped with Eu^{3+} and Er^{3+} ions were synthesized by low temperature method and studied its optical properties [17]. Hernández et al. synthesized the $LaAlO_3$ phosphors doped with Eu^{3+} prepared by Modified Pechini (MP) method and studied its photoluminescence, thermoluminescence properties for ionizing radiation dosimeter [18]. Mao et al. developed $LaAlO_3$:Eu phosphor for white light emitting diode [19]. In addition, Eu^{3+}-doped $LaAlO_3$ nanosystems reported by Quiang et al. which is synthesized by

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a simple hydrothermal method [20]. Jin et al. successfully synthesized the $LaAlO_3:Eu^{3+}$ phosphors by coprecipitation moltan salt synthesis and found phosphor may be good candidate in color display [21]. It was our main interest to synthesize $LaAlO_3$ doped with rare earth ions prepared via low temperature initiated wet chemical process and investigating their photoluminescence properties for solid state lighting applications.

2 Experimental

The $LaAlO_3:Eu^{3+}$ and $LaAlO_3:Dy^{3+}$ phosphors were prepared using wet chemical method. For the synthesis of $LaAlO_3:Eu^{3+}$, analytical-grade reagents of Lanthanum nitrate ($LaN_3O_9{\cdot}6H_2O$), Aluminium nitrate ($Al(NO_3)_3{\cdot}9H_2O$) and Europium oxide (III) (Eu_2O_3) were used as starting materials.

An appropriate amounts of Lanthanum nitrate, Aluminium nitrate powders were taken in beaker, dissolved in distilled water and stirred it until the solution becomes transparent. The Europium oxide was converted into nitrate by dissolving it in appropriate amount of dilute HNO_3, and then added this solution in beaker. The solution was then kept on magnetic stirrer maintained at 80 °C for 10 h. The final product was using funnel and filter paper, dried and grinded in mortar pastel to get fine powder. Finally, the fine powder was annealed at 800 °C for 3 h which was then used for further characterization. Similar procedure was applied for $LaAlO_3:Dy^{3+}$ phosphor. The basic chemical reaction is given as follows

$$\begin{aligned} &\mathrm{Al(NO_3)_3 \cdot 9H_2O + LaN_3O_9 \cdot 6H_2O} \\ &\quad \rightarrow \mathrm{LaAlO_3 + 6NH_3 + 6H_2O + 12O_2} \end{aligned}$$

3 Results and discussion

3.1 X-ray diffraction pattern of $LaAlO_3$ phosphor

The XRD pattern of the $LaAlO_3$ powder sample annealed at 800 °C is shown in Fig. 1. XRD is well matched with the standard JCPDS file no. 820478. All the peaks in the XRD pattern is in accordance with JCPDS file no. 820478, which indicates that the prepared phosphor has fully turned into $LaAlO_3$ phase.

3.2 Morphology of $LaAlO_3$ phosphors

The surface morphology of pure $LaAlO_3$ phosphors prepared via a wet chemical method is shown in Fig. 2. It is clearly evident that, the powders show highly porous structure, agglomeration of several crystals with an irregular

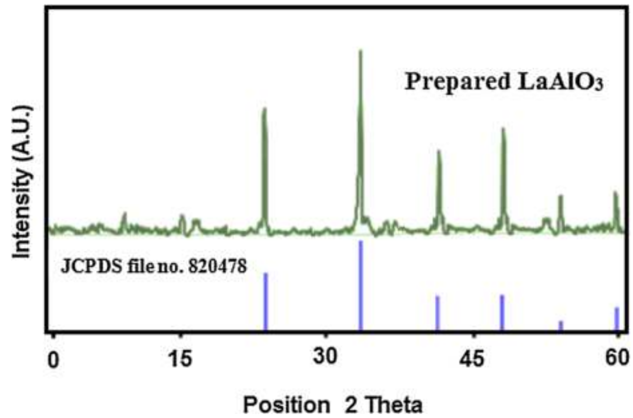

Fig. 1 XRD pattern of $LaAlO_3$ phosphor

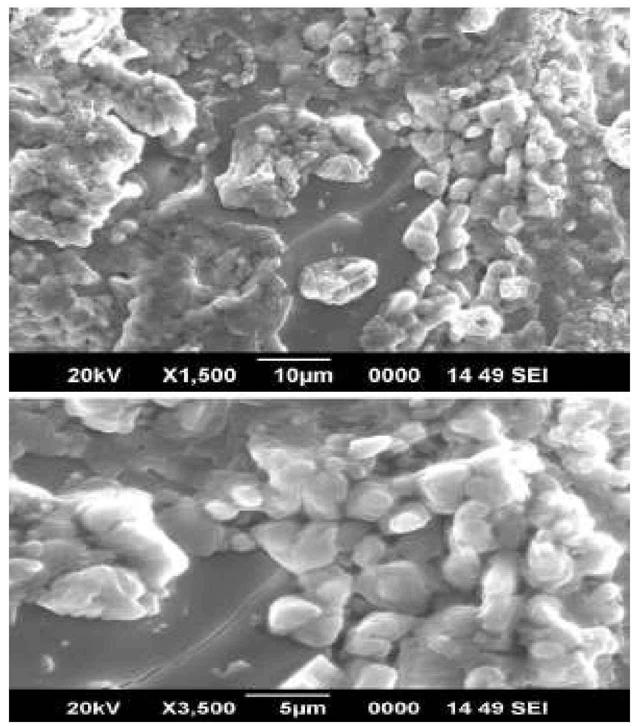

Fig. 2 SEM micrographs of $LaAlO_3$ phosphor

morphology, large voids and shapes. The particle size can be seen in micro-meter range. This type of morphology is due to the escape of a large volume of gas during wet chemical process. The SEM image at two different magnifications shows that crystallites have no uniform shapes and sizes.

3.3 Photoluminescence properties of $LaAlO_3:Eu^{3+}$ phosphor

The luminescence emission shows the characteristic peaks associated with the trivalent Europium ion's inter-electronic energy level transitions. Figure 3 shows the excitation

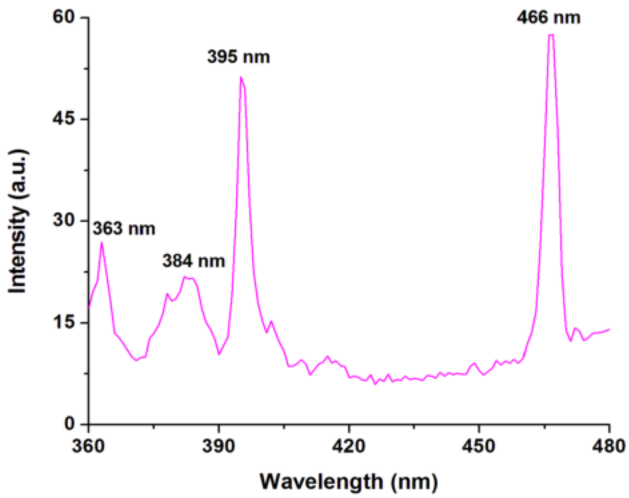

Fig. 3 Excitation spectrum of $LaAlO_3:Eu^{3+}$ phosphor ($\lambda_{em,}=614$ nm)

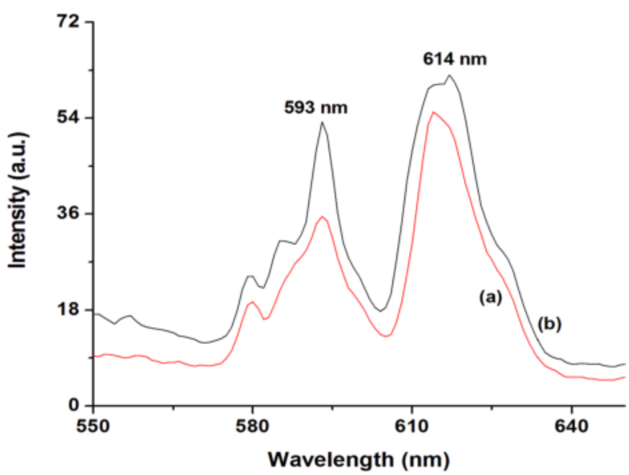

Fig. 4 Emission spectrum of $LaAlO_3:Eu^{3+}$ phosphor, where a $\lambda_{ex,}=395$ nm, b $\lambda_{ex}=466$ nm

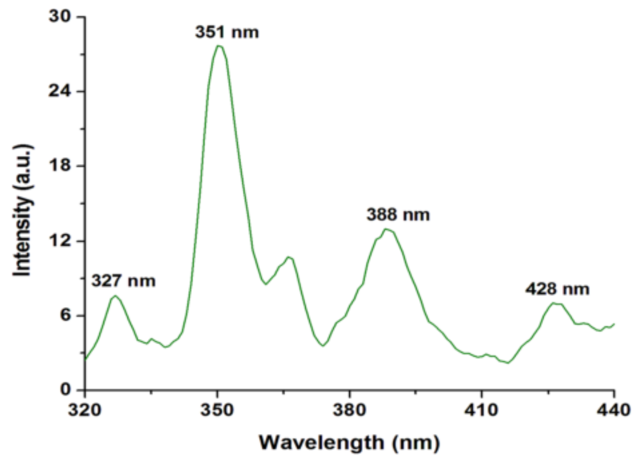

Fig. 5 Excitation spectrum of $LaAlO_3:Dy^{3+}$ phosphor ($\lambda_{em,}=484$ nm)

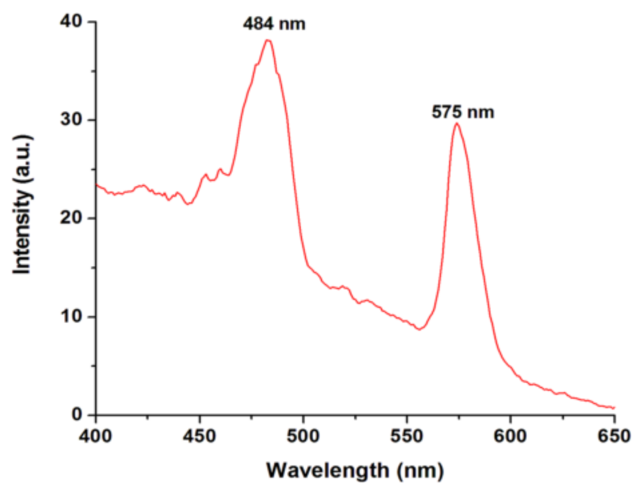

Fig. 6 Excitation spectrum of $LaAlO_3:Dy^{3+}$ phosphor ($\lambda_{ex,}=351$ nm)

spectra of $LaAlO_3:Eu^{3+}$ phosphor. The excitation spectrum consists of series of peaks located at 363 nm, 384 nm, 395 nm and 466 nm. When $LaAlO_3:Eu^{3+}$ phosphor is excited at 395 nm and 466 nm; corresponding emission spectrum is shown in Fig. 4. Emission spectrum consists of two characteristics peaks located at 593 nm and 614 nm. The emission band of Eu^{3+} ions in $LaAlO_3$ shows the emission at 593 nm (orange) and 614 nm (red). The emission peaks observed at 593 nm and 614 nm corresponds to the magnetic dipole ($^5D_0 \rightarrow {}^7F_1$) and electric dipole ($^5D_0 \rightarrow {}^7F_2$) transitions, respectively [22, 23]. As it can be seen, the highest intensity was found to be stronger in magnetic dipole transition than that of the electric dipole transition. It implies that Eu^{3+} has a symmetric environment, which means that more Eu^{3+} ions seized the La^{3+} lattice sites and lesser Eu^{3+} ions seized the grain boundary or defect lattice. The larger excitation wavelength has no effect on the peak position, however, peak intensity found to be considerably increased.

3.4 Photoluminescence properties of $LaAlO_3:Dy^{3+}$ phosphor

Figure 5 shows the excitation spectra of $LaAlO_3:Dy^{3+}$ phosphor monitored at 484 nm emission wavelength. Excitation spectrum consists of series of lines peaking at 327 nm, 351 nm, 388 nm and 428 nm. Strongest excitation peak observed at 351 nm. The luminescence emission shows the characteristic peaks associated with the trivalent Dy ion's inter-electronic energy-level transitions. Figure 6 shows the PL emission spectra of $LaAlO_3:Dy^{3+}$ phosphor. The emission band of Dy^{3+} ions in $LaAlO_3$ shows the emission at 484 nm (blue) and 575 nm (yellow).The peaks at 484 nm and 575 nm correspond to magnetic dipole transitions

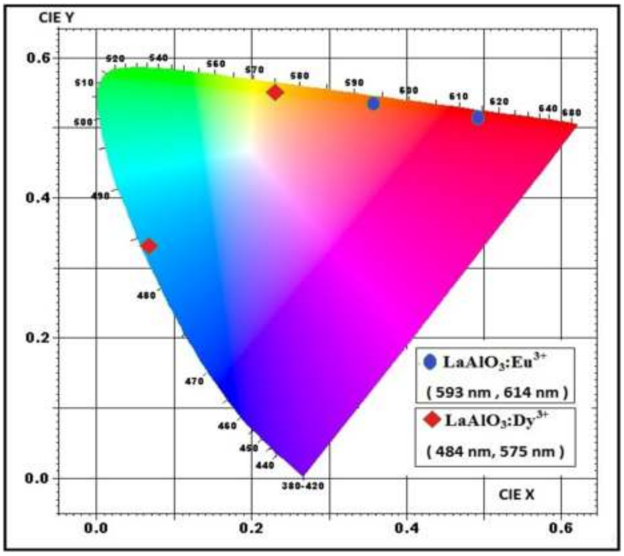

Fig. 7 CIE chromatic diagram of $LaAlO_3$:Eu^{3+} and $LaAlO_3$:Dy^{3+} phosphors

$^4F_{9/2} \rightarrow {}^6H_{15/2}$ and electric dipole transitions $^4F_{9/2} \rightarrow {}^6H_{13/2}$ of Dy^{3+}, respectively [24–26].

3.5 Chromatic properties of $LaAlO_3$:Eu^{3+} and $LaAlO_3$:Dy^{3+} phosphors

Figure 7 shows CIE chromatic diagram of $LaAlO_3$:Eu^{3+} and $LaAlO_3$:Dy^{3+} phosphors. The CIE color coordinates of the $LaAlO_3$:Eu^{3+} phosphors of wavelength 593 nm is ($X=0.592$, $Y=0.407$) and of wavelength 614 nm is ($X=0.677$, $Y=0.322$). The CIE color coordinates of the $LaAlO_3$:Dy^{3+} phosphor of wavelength 484 is ($X=0.073$, $Y=0.185$) and of wavelength 575 is ($X=0.478$, $Y=0.520$). All the color co-ordinates are situated at the edge of chromaticity diagram indicating high color purity [5, 27].

4 Conclusions

Rare earth Dy^{3+} and Eu^{3+}-activated $LaAlO_3$ phosphors were prepared by wet chemical method. X-ray diffraction pattern confirms the phase purity of $LaAlO_3$ phosphor. SEM morphology shows porous irregular agglomerated structures with particle size in micro-meter range. $LaAlO_3$:Eu^{3+} phosphor gives emission at 593 nm and 614 nm upon excitation with 395 nm and 466 nm. $LaAlO_3$:Dy^{3+} phosphor exhibit emission at 484 nm and 575 nm under excitation of 351 nm. The calculated color coordinates are situated at the edge indicating high-color purity. Both the excitations are mercury-free excitation, therefore, prepared phosphor might be applicable in solid-state lighting.

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