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# White light emitting lanthanum aluminate nanophosphor: Near ultra violet excited photoluminescence and photometric characteristics

T. Manohar[a], S.C. Prashantha[a,*], H.P. Nagaswarupa[a], Ramachandra Naik[b], H. Nagabhushana[c,*], K.S. Anantharaju[d], K.R. Vishnu Mahesh[d], H.B. Premkumar[e]

[a] Research Center, Department of Science, East West Institute of Technology, VTU, Bengaluru 560091, India
[b] Department of Physics, New Horizon College of Engineering, Bengaluru 560103, India
[c] Prof. C.N.R. Rao Center for Advanced Materials, Tumkur University, Tumkur 572103, India
[d] Department of Chemistry, Dayananda Sagar College of Engineering, Bengaluru 560078, India
[e] Department of Physics, Dayanand Sagar Academy of Technology and Management, Bengaluru 560082, India

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ABSTRACT

$LaAlO_3:Dy^{3+}$ (1–11 mol%) nanophosphors (NPs) were synthesized using solution combustion route and the final product was well characterized. The bandgap energy ($E_g$) was estimated using diffuse reflection data and the value was found to be in the range 5.70 – 5.90 eV. Upon ~ 353 nm [$^6H_{15/2} \rightarrow {}^6P_{5/2}$] excitation, a characteristic emissions peaks of $Dy^{3+}$ ions were recorded at ~ 480, 576 and 673 nm and ascribed to transitions from $^4F_{9/2}$ to $^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$ respectively. Judd–Ofelt parameters ($\Omega_2$, $\Omega_4$ and $\Omega_6$), transition probabilities ($A_T$), quantum efficiency ($\eta$), luminescence lifetime ($\tau_{rad}$), branching ratio ($\beta$), color chromaticity coordinates (CIE) and correlated color temperature (CCT) values were estimated from the emission spectra and discussed in detail. The estimated branching ratio was found to be ~75%, as a result the phosphor may be potentially useful for display device applications. Further, the optimized $LaAlO_3:Dy^{3+}$ (5 mol%) nanophosphor can be effectively used in the white light emitting diodes (WLEDs) under NUV excitation.

## 1. Introduction

Recently perovskite ($ABO_3$) structure materials play an important role in modern electronics and/or photonics, as they exhibit low coefficient of thermal expansion, good lattice coordinating, negligible loss at microwave frequencies, relatively high dielectric constant (~25), low leakage current density, good chemical stability etc. [1–5]. Among $ABO_3$ structure materials, lanthanum aluminate ($LaAlO_3$) is considered as a potential candidate for replacement in Si-based electronic devices [6–8]. In addition to this, it can be widely used as buffer layer or substrate for growth of high-temperature superconducting thin films, ferroelectric thin films and visible–blind UV photodetectors [9–12]. Due to its wide bandgap energy (5.6 eV), $LaAlO_3$ is an efficient host for doping with various rare earth (RE) and transition metal ions. Also the maximal phonon energy is relatively low (~ 742 $cm^{-1}$) which reduces the probability of nonradiative transitions [13–17]. By proper adjusting the composition, method of preparation and selective doping with RE ions the luminescence efficiency of the phosphors can be enhanced which in turn is useful in fabricating stable efficient and eco-friendly white light emitting diodes [18–20].

As one of the activator ions used in phosphors, $Dy^{3+}$ ions have been investigated thoroughly in many hosts like aluminates, oxides, phosphates, molybdates, silicates, etc. $Dy^{3+}$ ions show two foremost bands in the emission spectrum; one at yellow and another one at blue region and these two colours were prominent in obtaining WLED's. The emission at yellow is due to the hypersensitive transitions of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and the blue emission corresponds to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition. Therefore, $LaAlO_3$ host doped with $Dy^{3+}$ ions may find potential applications in WLEDs, security ink, bar codes, imaging, display devices, laser sources, environmental monitoring, etc. [6,21–24]. $LaAlO_3$ has a rhombohedral crystal structure with hexagonal space group *R-3c* stable at 300 K and above 800 K cubic crystal structure (space group *Pm-3m*) is achieved [2,25,26].

In recent years, solution combustion method has been widely used due to its simple, inexpensive, eco-friendly with a homogeneous product and smaller sized particles [27,28]. The present paper describes the low-temperature combustion synthesis and characterization of $LaAlO_3:Dy^{3+}$ NPs using Oxalyl di-hydrazide (ODH) as a fuel. The effect of $Dy^{3+}$ concentration on photoluminescence (PL) studies was investigated in detail from the point of view of their possible usage in display device applications.

* Corresponding authors.
*E-mail addresses:* scphysics@gmail.com (S.C. Prashantha), bhushanvlc@gmail.com (H. Nagabhushana).

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## 2. Experimental

### 2.1. Sample preparation

In a typical synthesis, the composition of 1 mol% $Dy^{3+}$ ions in $LaAlO_3$ was prepared by taking 3.217 g of lanthanum nitrate [$La(NO_3)_3{\cdot}6H_2O$ (99.9% purity) Sigma Aldrich], 0.035 g dysprosium nitrate [$Dy(NO_3)_3$ (99.9% purity) Himedia], 2.13 g of aluminum nitrate [$Al(NO_3)_3{\cdot}9H_2O$ (99.9% purity) Sigma Aldrich] were used as oxidizers (O) and 3.54 g of laboratory made Oxalyl di-hydrazide ODH [$C_2H_6N_4O_2$] was used as fuel (F). All the chemicals were taken without further purification and calculated stoichiometrically. The detailed synthesis procedure for the combustion synthesis was described elsewhere [13]. Similar procedure was used for other compositions (3, 5, 7, 9 and 11 mol%) of Dy in $LaAlO_3$. The chemical reaction used for the synthesis may be written as:

$$10\ La(NO_3)_3 + 10\ Dy(NO_3)_3 + 10\ Al(NO_3)_3 + 48\ C_2H_6N_4O_2 = 10\ LaAlO_3{:}\ Dy + 144\ H_2O + 141\ N_2 + 96\ CO_2 \quad (1)$$

### 2.2. Characterization

The phase formation of the obtained product was analyzed by using Powder x-ray diffraction (PXRD) [(Shimadzu) operating at 50 kV and 20 mA] using $CuK_\alpha$ (1.541 Å) radiation with a nickel filter at a scan rate of ~ $2^o$ $min^{-1}$. The stretching and bonding vibration were analyzed using Fourier Transform Infrared (FTIR) Spectroscopy in Perkin Elmer FTIR spectrophotometer (Spectrum-1000). The surface morphology of the product was examined by Hitachi table top Scanning Electron Microscopy (SEM) (Model TM 3000) (accelerating voltage up to 20 kV using Tungsten filament). The particle size was obtained by means of Transmission Electron Microscopy (TEM) on a JEOL, JEM-2100 (accelerating voltage up to 200 kV, $LaB_6$ filament). The diffuse reflectance (DR) spectral studies of the samples were performed in the range 200–800 nm using Shimadzu UV–vis spectrophotometer model 2600. Photoluminescence studies were carried out using Horiba, (model Fluorolog-3) spectrofluorometer at room temperature (RT) using 450 W Xenon lamp as an excitation source and Fluor Essence™ software was used for spectral acquisition.

## 3. Results and discussion

Fig. 1 shows the PXRD patterns of asformed and calcined (at 800 °C for 3 h) $LaAlO_3{:}Dy^{3+}$ (1–11 mol%). The product exhibits pure rhombohedral crystalline structure (JCPDS File No. 31-22 with space group: R-3c) [13,15]. It was observed that the pure phase obtained in the present

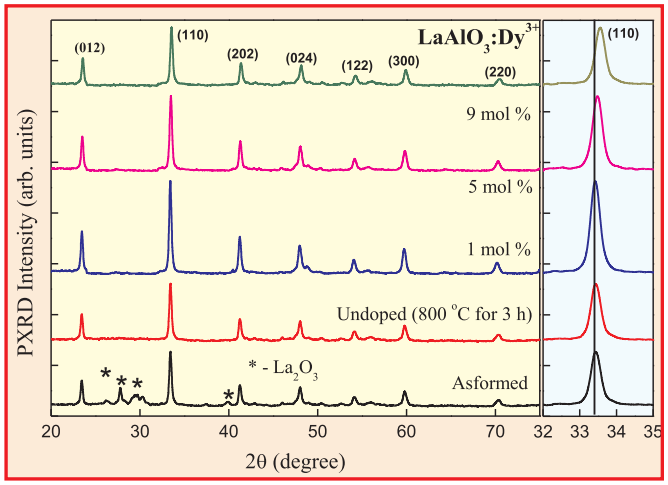


**Fig. 1.** PXRD patterns of un-doped and $Dy^{3+}$ (1–9 mol%) doped $LaAlO_3$.

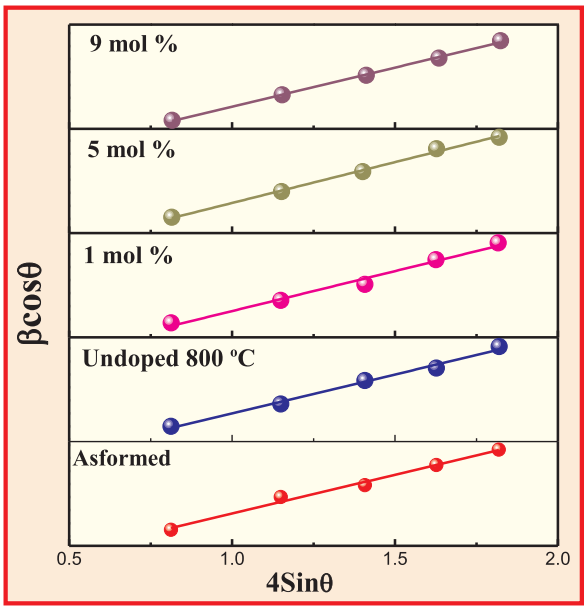


**Fig. 2.** W-H plots of un-doped and $Dy^{3+}$ (1–9 mol%) doped $LaAlO_3$.

studies (800 °C for 3 h) was much lesser than that of solid state reaction technique (1700 °C for 20 h) [29,30]. When $Dy^{3+}$ ions were doped in the $LaAlO_3$ host, it causes expansion of the unit cell volume in host matrix resulting in tensile stress, micro strain and shifting of PXRD peaks towards higher angle side. The average crystallite size (D) was estimated from Scherrer's formula [31] and was found to be ~ 25 nm.

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (2)$$

Further, strain present in the $LaAlO_3{:}Dy^{3+}$ nanophosphor was calculated by the following relations (W-H plots) (Fig. 2).

$$\beta\cos\theta = \frac{0.9\lambda}{D} + 4\varepsilon\sin\theta \quad (3)$$

$$D = \frac{0.9\lambda}{\beta\cos\theta - 4\varepsilon\sin\theta} \quad (4)$$

where, K; constant, λ; wavelength of X-rays and β; full width at half maximum (FWHM) and ε; the strain associated with the sample [32].

Fig. 2 shows the graph between '4 sinθ' along x-axis and 'β cosθ' along y-axis, in accordance with Eq. (3), which represents a straight line (of the form y = mx + C), where βcosθ as y, 4sinθ as x, ε as slope and (0.9λ)/D as intercept. The slope of the line gives the strain (ε) and intercept of this line on y-axis gives the crystallite size (D). From Eq. (4), it was clear that the crystallite size (D) increases with increase in strain (ε) and the similar results were obtained by W-H plots and the obtained values were tabulated in Table 1. It was clear from the table that a small variation in crystallite size values was due to the fact that in Scherrer's formula strain component was assumed to be zero and observed broadening of diffraction peak was considered as a result of reducing crystallite size [33,34].

**Table 1**
Estimated crystallite size and strain values of $LaAlO_3{:}Dy^{3+}$ nanophosphors.

| $Dy^{3+}$ (mol%) | Crystallite size 'D' (nm) | | Strain ($\times 10^{-4}$) |
|---|---|---|---|
| | [Scherrer's] | [W-H Plot] | |
| As formed | 25 | 36 | 13 |
| Calcined (800 °C) | 24 | 53 | 25 |
| 1 | 26 | 50 | 22 |
| 5 | 24 | 62 | 28 |
| 9 | 25 | 51 | 22 |