# Photoluminescence properties of $Dy^{3+}$-doped LaOF nanophosphor for white LED applications

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**The present study involves the synthesis of a series of $Dy^{3+}$ (1–11 mol%) doped LaOF nanophosphor prepared by solution combustion method using Aloe Vera gel as fuel. The samples were characterized by powder X-ray diffraction and scanning electron microscopy. The average crystallite size was estimated from Debye–Scherer's and Williamson–Hall plots and the values were found to be in the 25–40 nm range. The effect of $Dy^{3+}$ ions on luminescence characteristics of LaOF was studied and the results discussed. The CIE diagram clearly indicated that the entire co-ordinates were well coated in the white region and as a result it was quite useful for fabrication of white-light-emitting diodes.**

**Keywords:** Lanthanum oxyfluoride, nanophosphor, PXRD, SEM, synthesis.

IN the past few years, white-light-emitting diodes (WLEDs) have drawn much attention due to their superior properties such as high efficiency, energy consumption, reliability, safety, long operational lifetime and environmental friendliness[1]. Rare earth-doped oxyfluorides have been widely used in high performance luminescent devices, magnets, catalysts and other functional materials based on electronic, optical and chemical characteristics arising from their $4f$ electron[2]. Among the rare earth compounds, more attention has been paid to $Dy^{3+}$ ions because of its potential practical applications in electro luminescent displays, plasma display panels, field emission mercury-free lamps, etc.[3]. The $Dy^{3+}$ ion with $^4f_9$ electronic configuration generally shows two dominant emission bands at 483 ($^4F_{9/2} \rightarrow {}^6H_{15/2}$, blue) and 574 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$, yellow)[4,5]. It has been observed that the host material plays an important role on the luminescence properties of rare earth ions. Among the hosts, lanthanum oxyfluoride (LaOF) has been widely studied due to its various advantages such as favourable thermal and chemical stability, ability to generate strong fluorescence in different emission wavelengths and long lasting characteristics[6]. A variety of methods have been used to synthesize LaOF-based phosphor, such as sol–gel techniques, hydrothermal methods and solid state reactions[7–11]. Combustion synthesis is a novel wet chemical route because reaction can be completed in short time, it is energy saving and mainly the rapid decomposition of rare earth ions occurs in the presence of an organic fuel.

In the present study, $Dy^{3+}$ (1–11 mol%) doped LaOF nanoparticles were synthesized by solution combustion method using Aloe Vera (AV) gel as a fuel. The final product was well characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), etc. The luminescence properties were well studied for their possible application in WLEDs.

LaOF : $Dy^{3+}$ (1–11 mol%) nanophosphors were synthesized by solution combustion technique using AV gel. Lanthanum nitrate $La(NO_3)_3 \cdot 6H_2O$ (99.9%, Sigma Aldrich, USA), dysprosium nitrate $Dy(NO_3) \cdot 2H_2O$ (Sigma Aldrich, USA), ammonium fluoride $NH_4F$ and AV gel were dissolved in double distilled water, taken in a cylindrical Pyrex dish. The cylindrical Pyrex dish was then introduced into a pre-heated muffle furnace maintained at 500°C. The reaction was initiated and a flame appeared on the surface of the foam and proceeded rapidly throughout the entire volume, and a white powder was obtained. The entire combustion process was over in less than ~8 min. Further the sample was calcined at 700°C for 1 h. The final product was ground into a fine powder by agate and mortar.

The crystalline nature of the powder sample was characterized by powered X-ray diffraction (PXRD) using X-ray diffractometer (Shimadzu, Tumakuru, India) (operating at 50 kV and 20 mA by means of $CuK_\alpha$ (1.541 Å) radiation with a nickel filter at a scan rate of 2° $min^{-1}$). The surface morphology of the product was examined by Hitachi table top (SEM). Photoluminescence studies were carried out using Horiba spectrofluorometer (model fluorolog-3) at room temperature using 450 W xenon as excitation source. Fluor Essence™ software was used for spectral analysis. All the measurements were carried out at room temperature.

Figure 1 *a* shows the PXRD patterns obtained of various $Dy^{3+}$ (1–11 mol%) doped LaOF. All the diffraction peaks in the pattern can be well indexed to tetragonal phase and matched with JCPDS card no. 89-5168. Further, the strong and sharp diffraction peaks indicate good crystallinity of LaOF nanoparticles. Also, no impurity peaks were observed in the XRD pattern, indicating high purity of the product. The average crystallite size ($D$) was estimated using Scherer's formula $D = K\lambda/(\beta \cos\theta)$ (where $K$, constant; $\lambda$, wavelength of X-rays and $\theta$, FWHM)[12]. The crystallite size was found to be in the range of 20–25 nm. Further, the strain present in the

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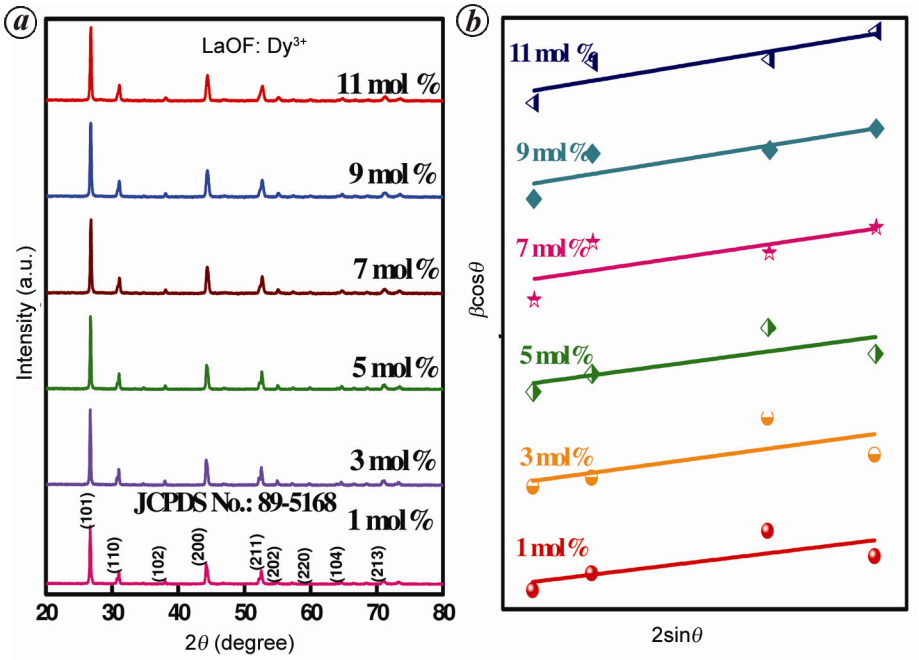


**Figure 1.** (*a*) PXRD pattern and (*b*) W–H plot of LaOF : $Dy^{3+}$ (1–11 mol%).

LaOF : $Dy^{3+}$ (1–11 mol%) nanoparticles were also calculated using the relation

$$\beta\cos\theta = 0.9\lambda D + 4\varepsilon\sin\theta, \quad (1)$$

where $\varepsilon$ is the strain associated with the nanoparticles. The above equation represents a straight line between $4\sin\theta$ ($x$-axis) and $\beta\cos\theta$ ($y$-axis) (Figure 1 *b*). The slope of the line gives the strain and intercept of this line on $y$-axis gives grain size ($D$). The crystallite size was found to be in the range of 25–40 nm.

Figure 2 shows the SEM micrographs of $Dy^{3+}$ doped (3 mol%) LaOF nanophosphor. The micrographs show porous structure with agglomerated particles. Further, the dopant concentration does not influence the morphology of the sample.

Figure 3 *a* shows the photoluminescence excitation (PLE) spectrum of LaOF : $Dy^{3+}$ nanophosphor monitoring the emission at 580 nm. The spectrum consists of excitation peaks at 350, 364, 385 and 425 nm and that correspond to the electron transitions of $Dy^{3+}$ from the ground state $^6H_{15/2}$ to higher levels $^4I1_{5/2}$, $^4F_{9/2}$, $^4I1_{3/2}$ and $^4F_{11/2}$ respectively[13]. Figure 3 *b* shows the emission spectra of LaOF phosphors doped with different $Dy^{3+}$ ion concentrations excited under 394 nm near UV light. The spectra indicate that the emission spectrum essentially consists of three intense and sharp lines ranging from 450 to 700 nm. The characteristic emission takes place from $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (485 nm), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (575 nm) and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (636 nm) and recorded in all the doped samples. The blue emission corresponds to the magnetic dipole transition and the yellow emission belongs to the hypersensitive (forced electric dipole) transition with the selection rule $\Delta J = 2$ (ref. 14). It was observed that PL intensity increases up to 3 mol% $Dy^{3+}$ ions and beyond this, the intensity decreases due to concentration quenching. Concentration quenching may occur due to two reasons: (i) the distance between the ions shortens and the interaction of the ions becomes stronger, thus producing energy transfer interaction; (ii) it may be due to cross-relaxation[13,14].

The resultant CIE coordinates were estimated by utilizing the PL emission spectrum. It was observed that the CIE coordinates were located well within the white region (not shown in the figure) which clearly indicated that the phosphors could be used for WLEDs and solid state lighting devices. Correlated colour temperature (CCT) also can be estimated by Planckian locus, and it is used to define the colour temperature of a light source. CCT was obtained by transforming the ($x$, $y$) coordinates of the light source to ($U'$, $V'$) by using eqs (2) and (3), and by determining the temperature of the closest point of Planckian locus to the light source on the ($U'$, $V'$) uniform chromaticity diagram[15,16]

$$U' = 4x - 2x + 12y + 3, \quad (2)$$

$$V' = 9y - 2x + 12y + 3. \quad (3)$$

The estimated CCT was found to be ~5092 K which was almost equal to 5000 K using $U' = 0.3138$ and $V' = 0.5532$. Hence, this phosphor was highly useful for the production of artificial white light in white LEDs and in solid state display applications.

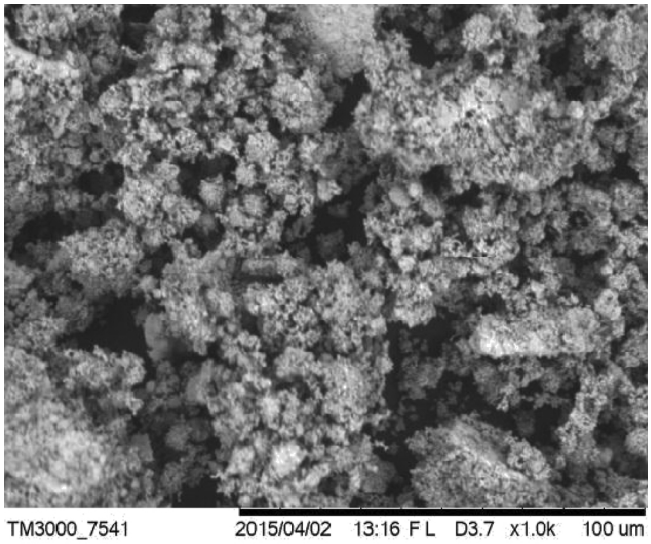


**Figure 2.** SEM image of LaOF : $Dy^{3+}$ (3 mol%).

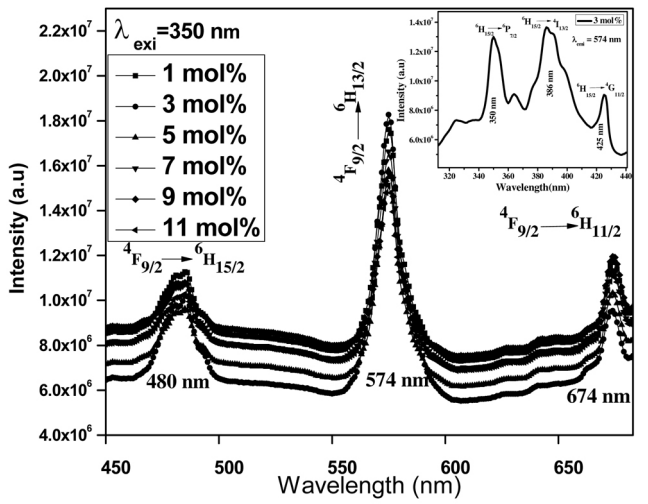


**Figure 3.** Emission spectrum of LaOF : $Dy^{3+}$ (1–11 mol%). (Inset) excitation spectra of LaOF : $Dy^{3+}$(3 mol%).

LaOF : $Dy^{3+}$ (1–11 mol%) nanophosphors were prepared by solution combustion method. The PXRD patterns showed tetragonal structure and the crystallite size was observed to be ~20–25 nm. In the present study, $Dy^{3+}$ (1–11 mol%) doped LaOF phosphor showed white emission and 3 mol% Dy doped sample showed superior PL intensity. Further, the phosphor showed excellent CIE chromaticity co-ordinates (*x*, *y*), as a result it was quite useful for display applications.

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Received 18 September 2015; revised accepted 26 April 2017

doi: 10.18520/cs/v113/i06/1139-1141