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A cost effective synthesis of white light emitting Dy^{3+} doped La_2O_3 nanophosphor

KonsamReenabati Deviand S.Dorendrajit Singh
Department of Physics, Manipur University, Canchipur, Manipur-795003,
Corresponding author: dorendrajit@yahoo.co.in

Abstract

Lanthanum oxide (La_2O_3) is a semiconductor material having a low phonon energy of about 400cm^{-1} which makes it a viable candidate as host matrix that can be efficiently probed with rare earth ions. In this work, Dy^{3+} doped La_2O_3 nanocrystalline powder has been synthesized by a very cost effective simple precipitation method. X-ray diffraction (XRD) pattern confirmed the hexagonal phase of sample. Further, energy dispersive analysis of x-rays (EDAX) and photoluminescence (PL)were performed to characterize the sample. Photoluminescence analysis of the sample includes excitation, emission and CIE co-ordinate determination of the sample. Emission peaks of Dy^{3+} were observed at 486 nm and 575 nm corresponding to $^4F_{9/2}$-$^6H_{15/2}$ and $^4F_{9/2}$-$^6H_{13/2}$.The co-ordinates of the sample are very close to that of standard white color (0.33, 0.33).

Keywords: Hexagonal; Semiconductor; WLEDS

1. INTRODUCTION

Over the past few years, rare earth sesquioxides like La_2O_3, Lu_2O_3, Y_2O_3, Gd_2O_3 etc. are known to be excellent optical host materials for lanthanide active ions because, they are transparent to visible and infrared light. Research in the field of nanoscale rare earth doped luminescent material are part of quickly advancing nanoscience and nanotechnology [1]. Compared to other RE host materials, low cost La_2O_3 has many industrial and technological applications such as solid state lasers, luminescent lamps, flat displays, optical fibre communication systems, and other photonic devices [1, 2].

Lanthanum oxide,La_2O_3 has a low phonon energy of about 400 cm^{-1} which makes it a viable candidate as a host matrix that can efficiently been probed with fluorescent rare earth ions[4]. Trivalent europium (Eu^{3+}) activated phosphors have been extensively investigated due to their application as red phosphors [1]. It has been previously introduced in several materials, including La_2O_3 using different synthesis techniques such as calcination methods , solution combustion synthesis, [5-7],conventional hydrothermal [8] and microwave hydrothermal methods [9]. However,so far, the photoluminescence characteristics of nanocrystalline La_2O_3:Dy^{3+} phosphor have not been observed. Keeping this in mind, the present work is dedicated to the production of white light emiting La_2O_3:Dy^{3+} nanocrystal through a very cost effective chemical precipitation route.

2. EXPERIMENTAL

Lanthanum(III) nitrate (99.99%, Aldrich) and Dysprosium (III) chloride (99.9%, Aldrich) were used as starting materials without further purification. The reagents were dissolved in distilled water and stirred for 10-15 minutes. 0.4M of NaOH was added to the solution and stirred for 1 hour and the precipitate were collected by continuous washing with distilled water and acetone. The precipitate so obtained were dried,,ground and annealed at 800^0C for 2 hours. XRD data of the samples were recorded in X'PertPANalytical diffractometer at 40kV and 30mA. Wavelength of the x-ray used is 1.54Å (CuKα). Percentages of elements present in the sample were quantified by EDAX (AMETEK) attached to scanningelectron microscope, SEM (Quanta250) at 20 kV. Photoluminescence (PL) emissions were recorded on F-7000 Fluorescence and Spectrometer (HITACHI).

3 .RESULT AND DISCUSSION

3.1. XRD studies:

Fig.1 shows the XRD patterns of La_2O_3 and La_2O_3:Dy^{3+}(1at.%) samples. X'pertHighScore's search and match analysis shows the presence of hexagonal phase (ICDD ref.code :00-002-0688) for both undoped sample and doped sample. Introduction of the dopant Dy^{3+} to the host does not alter the crystal structure of the system. The crystallite sizes were calculated using Scherrer formula $t= 0.9\lambda/\beta\cos\Theta$ where λ is the wavelength of the X-ray, 0.9 is shape factor, β is full width at half maximum (FWHM) and Θ is Bragg angle. The average crystallite sizes were found to be in the range of 40-42 nm .

3.2.EDAX studies:

Fig. 2 represents the EDAX spectrum obtained from the La_2O_3:Dy^{3+} (1 at. %) sample. The spectrum shows the presence of carbon (C), oxygen (O), lanthanum (La) and dysprosium (Dy) in the sample. The percentage of La and Dy present in the sample, calculated from EDAX, ZAF Quantification, are observed to be 98.8% and 1.2% respectively. This clearly indicates the concentration of Dy^{3+} introduced in the host La_2O_3 is in agreement with the

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data from EDAX observation. It is to be noted that presence of C in the spectra, is due to carbon-coated tape used in recording the spectra [10,11].

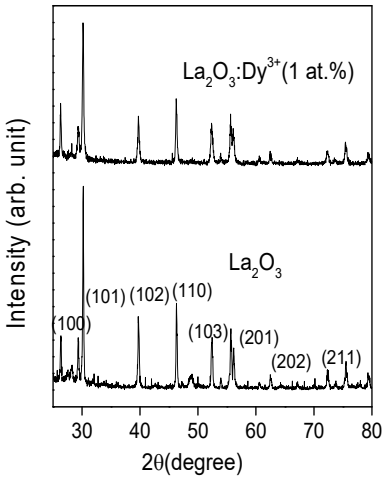


Fig. 1: XRD pattern of undoped and 1 at.% Dy^{3+} doped La_2O_3 samples

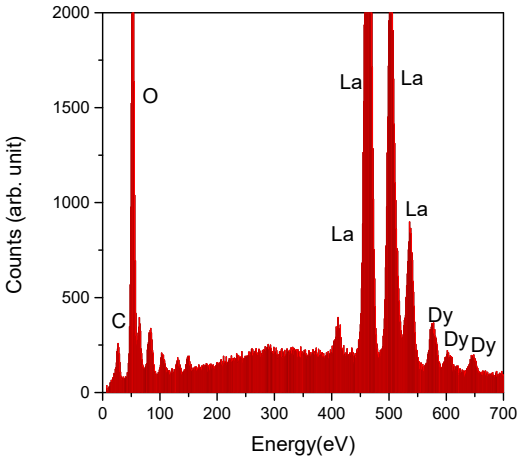
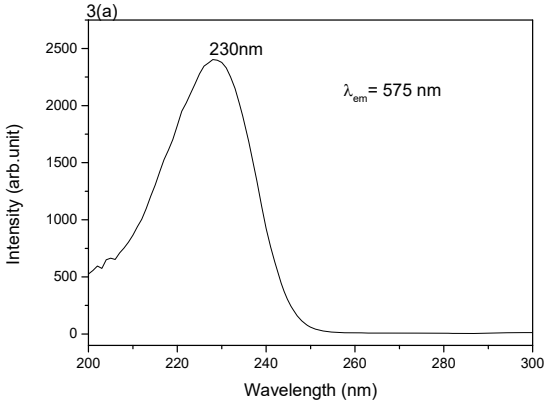


Fig.2: EDAX spectra of 1at.% doped sample

3.3.Photoluminescence(PL) studies:

Photoluminescence excitation and emission spectra of the hexagonal La_2O_3:Dy^{3+} are shown in Fig.3(a) and (b). On monitoring the emission at 575 nm corresponding to structurally sensitive, $^4F_{9/2}$-$^6H_{13/2}$,electric dipole transition of Dy^{3+},the excitation spectrum shows strong peak at 230 nm Fig.3(a). This peak corresponds to O2- and Dy3+ charge transfer state.Upon the excitation at this charge transfer state(CTS), two intense peaks at 486 nm and 574 nm are observed .The peak at 486 nm is attributed tomagnetic dipole transition $^4F_{9/2}$-$^6H_{15/2}$ of Dy^{3+}.On the other hand, the peak at 575 nm is attributed to structurally sensitive electric dipole transition ,$^4F9/2$-$^6H_{13/2}$ of Dy^{3+}.



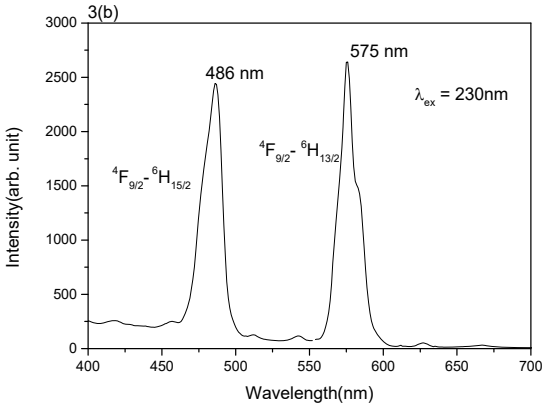


Fig. 3 (a) excitation spectra and (b)emission spectra of Dy^{3+} (1 at.%) doped La_2O_3 sample

Asymmetriy ratio also called the relative intensity of the electric (E) and magnetic (M) dipole transition, strongly depend on the local symmetry of Dy^{3+}. The asymmetry ratio of doped sample is found to be 1.01, which indicates high symmetry of the sample.

3.4. CIE chromaticity:

The Commission Internationale de l'e´clairage (CIE) co-ordinate is calculated in order to evaluate the phosphors' performance. The CIE co-odinate is found to be (0.32,0.34),which is close to that of the ideal whight light (0.33,0.33).

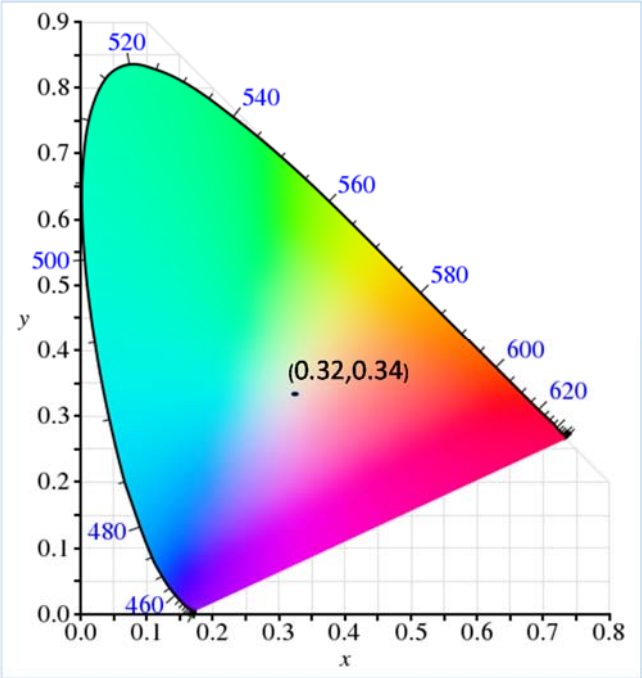


Fig. 4.CIE color co-ordinate for of Dy^{3+}(1 at.%) doped La_2O_3 sample.

4. CONCLUSION

White light emitting nanocrystalline $La_2O_3:Dy^{3+}$ phosphor was synthesized by a very cost effective simple precipitation route. Introduction of the dopant Dy^{3+} to the host does not alter the crystal structure of the system.Average crystallite sizes were found to be in the range of 40-42 nm.Characterizations of the samples were done effectively by XRD, EDAX and PL studies. PL emission shows two intense peaks at 486 nm and 575 nm upon excitation at charge transfer state, 230 nm. The CIE co-ordinate of the doped sample is found to be (0.32,0.34),which is closed to that of the ideal white light (0.33,0.33). This nanosized hexagonal phase $La_2O_3:Dy^{3+}$ may be a promising phosphor for white light applications.

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