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Synthesis and luminescent performance of $LaPO_4$: Dy nanophosphor

D. M. Pimpalshende[1], S. J. Dhoble[2]*

[1]*Department of Physics, Dr. Ambedkar College, Chandrapur (M. S.), India*
[2]*Department of Physics, RTM Nagpur University, Nagpur 440033, India*

*Corresponding author. E-mail: sjdhoble@rediffmail.com

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ABSTRACT

Nowadays the research on synthesis of inorganic luminescent material with proper dimensions and morphologies has attracted great attention. Inorganic luminescent materials like $LaPO_4$ have found many practical applications in the field of electroluminescent devices, integrated optics, biological labels, modern lighting and display fields. We have prepared Dysprosium (Dy) doped $LaPO_4$ nanoparticles at relatively low temperature in polyethylene glycol (PEG) medium by wet chemical method. Dy^{3+} is doped in $LaPO_4$ at various atomic concentrations (1, 2, 5 and 10 at %). All the samples have been characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), photoluminescence (PL) and thermoluminescence (TL) techniques. XRD study reveals the monoclinic structure of prepared nanoparticles. Unit cell volume is found to be decrease linearly with increasing Dy^{3+}concentration indicating homogeneous substitution of La^{3+} ions in $LaPO_4$ by Dy^{3+}. From the FTIR study it is found that the band at 1044 cm^{-1} assigned to the phosphate group PO_4^{3-} in the region of υ_3 anti-symmetric stretching of P-O band. The PL spectrum shows emission band at about 435 nm is observed due to the transision of Dy^{3+} ions corresponding to wavelength in the blue color region. The glow curve of $LaPO_4$: Dy phosphor obeys second order kinetics. Copyright © 2014 VBRI press.

Keywords: Wet-chemical synthesis; XRD; PL; TL; TEM; $LaPO_4$.

Dewrao M. Pimpalshende passed B.Sc. in 1990 and obtained Masters Degree in Physics in the year 1992 from Nagpur University, Nagpur (M.S.), India. Since Sept. 1993, he is working as an Assistant Professor in Department of Physics, Dr Ambedkar College of Arts, Commerce and Science, Chandrapur (M.S.) India. He obtained M. Phil. Degree in Physics in 2008 and presently working as research student for Ph. D. degree at Department of Physics, R.T.M. Nagpur University, Nagpur, India. His research area is synthesis and characterization of organic and inorganic nano materials for lighting applications. There are some National and international research papers published in the refereed journal. He is Member of Intrenational Association of Advanced Materials (IAAM) and life member of Luminescence Society of India (LSI).

S. J. Dhoble obtained M.Sc. degree in Physics from Rani Durgavati University, Jabalpur, India in 1988. He obtained his Ph.D. degree in 1992 on Solid State Physics from Nagpur University. Dr. S. J. Dhoble is presently working as an Associate Professor in Department of Physics, R.T.M. Nagpur University. During his research carrier, he is involved in the synthesis and characterization of solid state lighting nanomaterials as well as development of radiation dosimetry phosphors using thermo-luminescence, mechano-luminescence and lyo-luminescence techniques. Dr. Dhoble published several research papers in International reviewed journals on solid-state lighting, LEDs, radiation dosimetry and laser materials. He is an executive member of Luminescence Society of India.

Introduction

In the last decade of years, lanthanide phosphates ($LnPO_4$) have attracted much attention due to their novel promising applications in several fields of science and technology. Thus, many papers have been recently published dealing with the use of these materials in biological imaging. Other proposed applications include their use in plasma display panels **[1-5]**. Among the different $LnPO_4$ systems, lanthanum phosphate ($LaPO_4$) is perhaps the most studied one, in particular, its monoclinic polymorph (monazite). This material has been suggested as a good candidate for the immobilization of radioactive waste elements **[6]**, as well as protective coating for ceramics **[7]**. Besides, it is one of the most commonly employed host matrices for the preparation of lanthanide-based phosphors. The fluorescent materials with tuned emission in the visible region and promising applications as bio-labels are obtained when monazite nanoparticles are doped with some lanthanide (Ln) cations such as Eu, Ce, Tb or Dy **[1]**. Lanthanum phosphate ($LaPO_4$) possesses the properties like low solubility in water, very high thermal stability and high refractive index **[8, 9]**. Because of these properties it has got importance for the production of display lamps and sensors. Dysprosium (Dy) doped $LaPO_4$ materials have potential applications in fluorescent lamp, optoelectronics and telecommunication **[10]**. Different methods can be used for the synthesis of lanthanide phosphate like solid state reaction, combustion, sol-gel, hydrothermal, precipitation, micro-emulsion, etc. **[11-15]**. We have prepared $LaPO_4$ and Dy^{3+} doped $LaPO_4$ nanoparticles at relatively low temperature (120 °C) in polyethylene glycol (PEG) medium by wet chemical method. The prepared sample was analyzed by XRD, TEM, FTIR, TL and PL measurement.

Experimental

Lanthanum oxide (La_2O_3 *Himedia*) was used as a host material. Ammonium dihydrogen phosphate ($NH_4.H_2PO_4$) and Citric acid monohydrate (*Merck*) were used as precipitating agent and catalyst respectively. Dysprosium oxide (Dy_2O_3 *s. d. fine)* was used as a dopant and PEG-4000 (*LoBa Chem*) as a surfactant. All chemicals (from *Mumbai, India)* were of analytical reagent (AR) grade and used without further purification. 1 gm of La_2O_3 and Dy_2O_3 in stoichiometric ratio was dissolved completely in 3 ml of HNO_3. It was heated repeatedly by adding deionized water 2-3 times till evaporation. Then 2.45 gm citric acid and 50 ml of deionized water was added and stirred hard for 1 h using magnetic stirrer. The solution of 0.67 gm $NH_4.H_2PO_4$ with 3 gm PEG in 50 ml of water was added to the stirred solution which turns milky. The prepared solution was heated at 120 °C constant temperature for 1½ h. Then it was kept still and allowed to cool at room temperature which forms the white precipitate. It was centrifuged at 12000 rpm, washed with water & methanol 2-3 times and dried at room temperature. For doping at different concentration of Dy^{3+} in host material similar procedure was adapted. The crystallinity as well as phase purity of pure and Dy doped $LaPO_4$ samples were examined on a XPERT-PRO diffractometer using nickel filtered Cu-Kα radiation (λ = 0.15405 nm) at UGC-DAE, CSR, Indore. The Scherrer's relation: $t = (0.9\lambda / \beta \cos\theta)$, where λ the wavelength of X-ray and β is the half maximum line width (FWHM) was used to calculate the average crystallite size (t). The JEOL-JEM 2010 transmission electron microscope TEM was used for the morphological study. Hitachi F-4500 spectrometer was used for the photoluminescence (PL) characteristics of Dy^{3+} doped $LaPO_4$. For FTIR spectra, Perkin Elmer (Bruker) IR spectrometer was used. NUCLEONIX-TL1009I was used for the TL characteristics. All the measurements were carried out at same atmosphere.

Results and discussions

XRD analysis

The X-ray diffraction patterns of as-prepared samples of 1, 2, 5 and 10 at % Dy^{3+} doped $LaPO_4$ in powder form along with pure $LaPO_4$ is as shown in **Fig. 1**. All the peaks of XRD are in well agreement with reported $LaPO_4$ (JCPDS file No. 32-0493). It can be seen from the pattern that all the samples exhibit the characteristic diffractions of crystalline monoclinic $LaPO_4$, which well indexed to a monoclinic lattice of pure $LaPO_4$. No traces of impurity phases related with the doped components are observed in the XRD patterns, revealing the high purity of the as-prepared nanoparticles. The average crystallite size of 17 nm is calculated for pure $LaPO_4$ using Debye-Scherrer relation. Unit cell volume is found to be decrease linearly with increasing Dy^{3+} concentration indicating homogeneous substitution of La^{3+} ions in $LaPO_4$ by Dy^{3+}. The crystallite sizes are found to be decrease to 10 nm with increasing the Dy^{3+} concentration **[10, 16]**.

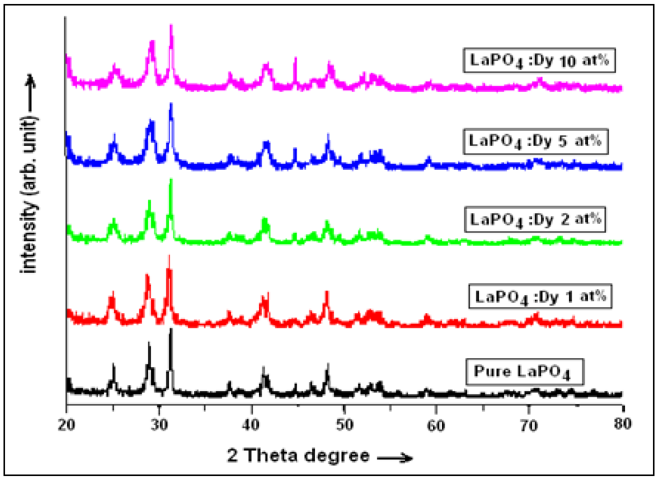

Fig. 1. XRD pattern of pure $LaPO_4$ and Dy^{3+} doped $LaPO_4$.

TEM morphology

The TEM micrograph of Dy^{3+} doped $LaPO_4$ phosphor is as shown in **Fig. 2**. From the micrograph it can be seen clearly that the structure of synthesized phosphor have the shape of cuboids. The length is about three times the width and the sectional area is nearly10 nm x 10 nm. The average size of particles is around 17 nm. Incorporation of Dy^{3+} in the host $LaPO_4$ reveals the reduction of the size particles to about 10 nm. The result of TEM confirms the crystalline structure of Dy^{3+} doped $LaPO_4$ phosphor. This morphological structure of nano size of phosphors can be used for coating purpose in various display units.

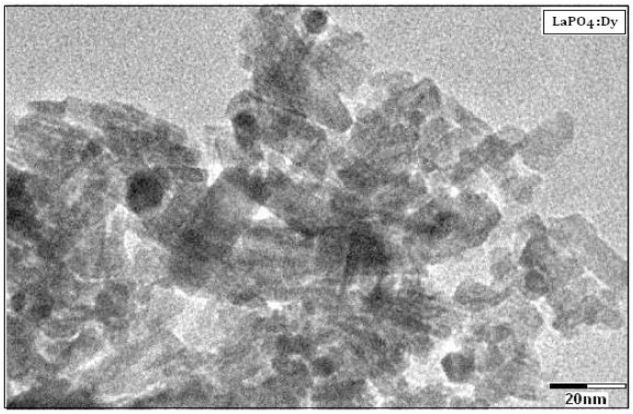

Fig. 2. TEM micrograph of Dy^{3+} doped $LaPO_4$ phosphor

FTIR study

The Perkin Elmer (Bruker) IR spectrometer was used to record the FTIR spectra of pure $LaPO_4$ between the range of wave number 3800 to 600 cm^{-1}which is shown in **Fig. 3**. The spectrum shows the characteristic band assigned to the phosphate PO_4^{3-} group. The band centered at 1054 cm^{-1} is assigned to the υ_3 anti-symmetric stretching of P-O band. The bands at the wave number 620 cm^{-1} and 692 cm^{-1} are related to the υ_4 region of vibration of PO_4^{3-} groups. Therefore the band exhibits the characteristics of vibration of phosphate groups PO_4^{3-} in $LaPO_4$. The peaks at 1695, 1760, 1791 as well as 3739 cm^{-1} are observed due to the bending stretch vibration of O-H group of capping agent PEG, which is near to standard stretching value 3650 cm^{-1} of O-H group. The twisting, wagging, rocking, stretching vibration due to presence of CH_2 group from PEG is observed at 2174, 2313, 2887, 3005 cm^{-1} respectively. Most of the peaks are found missing in the spectrum $LaPO_4$:Dy as that in the case of $LaPO_4$ due the doping of Dy^{3+} ion. But large band is observed in the region of υ_3 anti-symmetric stretching of P-O band at 1044 cm^{-1} assigned to the phosphate group PO_4^{3-}. The two bands located at 600 cm^{-1} and 673 cm^{-1} are assigned to the υ_4 region of vibration of PO_4^{3-} groups **[17, 18]**.

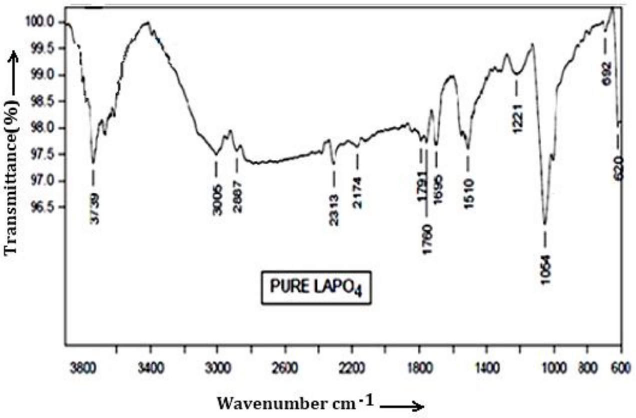

Fig. 3. FTIR spectrograph of $LaPO_4$ phosphor.

Photoluminescence characterization

The PL excitation and emission at different concentration (1, 2, 5 and 10 at %) of $LaPO_4$:Dy are as shown in **Fig. 4** and **Fig. 5** respectively. From the emission spectra of $LaPO_4$:Dy , the broad emission band is observed at 435 nm with small shoulder at 472 nm corresponding to emission of blue colour when moniterd at excitation wavelength 253 nm. The corresponding emission band is observed due to the $4f_{9/2} \rightarrow 5d_{15/2}$ transition of Dy^{3+} ions **[19-21]**. Figure 5 shows the broad band emission is the characteristic of the allowed d–f transition of Dy^{3+} ions. The nanostruture of synthesized $LaPO_4$:Dy phosphors and favarable emission in the deep blue region will make it one of the best candidate as a blue phosphor for SSL technology.

Thermoluminescence characterization

The optoelectronic properties of luminescent materials depend upon defects in crystal, chemical composition and doping of impurities. The study of thermoluminescence (TL) is very useful for determination of trapping parameter like activation energy, frequency factor, and relaxation time of a luminescent and photo conducting materials. For the estimation of the activation energy and other parameter, most of the methods used are based on the electron kinetics.

Fig. 6 shows the thermoluminescence glow curve of $LaPO_4$:Dy doped at 2 % and obtained at a heating rate of 5 °C/sec with 1 mg of phosphor. The TL glow curves shows single glow peak as only one type of traps is being activated.

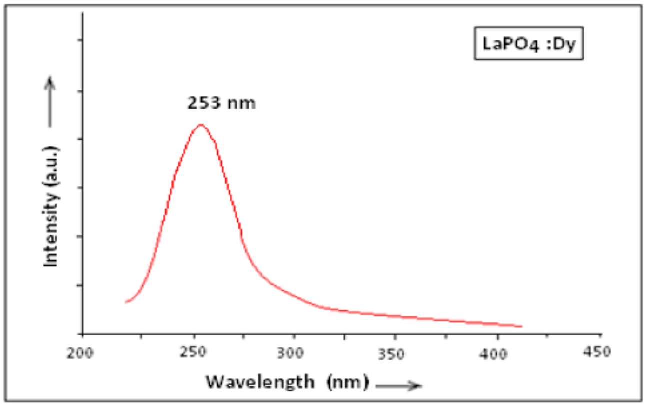

Fig. 4. Excitation spectrum of $LaPO_4$:Dy.

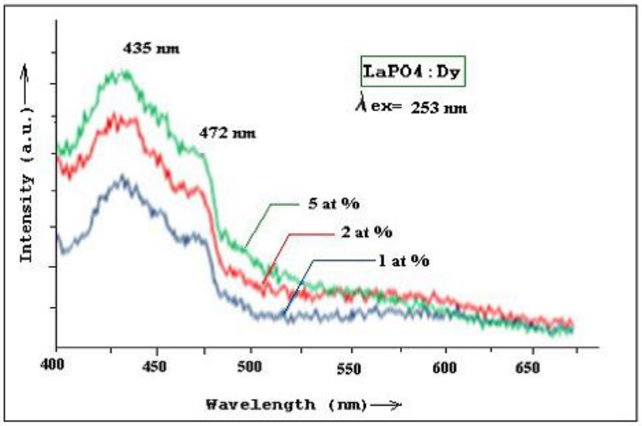

Fig. 5. Excitation spectrum of $LaPO_4$:Dy.

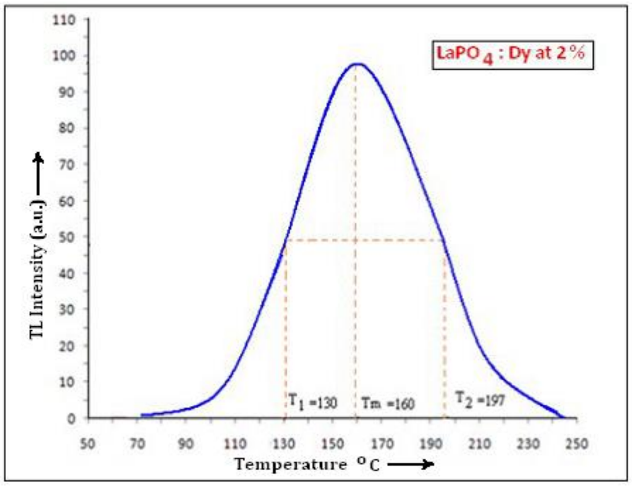

Fig. 6: TL glow curve of Dy^{3+} doped $LaPO_4$

TL glow curve can be analyzed with many methods. Here the Ilich method and Chen formula is used to determine the trap parameters. The shape or geometrical properties of the peak is considered to analyzing a TL glow curve in order to ascertain the kinetic parameters **[22, 23]**.

The activation energy was calculated by the

(1) Ilich method using the formula

$$E= k.(T_c)^2 / (T_c-T_0) \qquad \text{………(1)}$$

Where, k is Boltzmann constant.

(2) Chen's equations,

$$E_\alpha = C_\alpha (kT_m{}^2/\alpha) - b_\alpha(2kT_m) \qquad \text{………(2)}$$

Where, α is τ, δ or ω and C_α, b_α are given by

$C_\tau = 1.51 + 3 (\mu- 0.42)$ and $b_\tau = 1.58 + 4.2(\mu- 0.42)$
$C_\delta = 0.976 + 7.3 (\mu- 0.42)$ and $b_\delta = 0$
$C_\omega = 2.52 + 10.2 (\mu- 0.42)$ and $b_\omega = 1$

The value of μ is 0.42 for first order and 0.52 for second order kinetics.

The activation energy are found to be 0.79 eV calculated by equation 1and by using equation 2 for the second order, the activation energy are found to be E= 0.78 eV, $E\tau$= 0.81 eV, E_δ = 0.76eV and E_ω = 0.78 eV. All these values are in good agreement.

Conclusion

Simple wet chemical method based on homogeneous precipitation used for synthesis of monoclinic $LaPO_4$. The nano particles of size about 15 nm have been successfully synthesized by this process at low temperature. The emission band shows the standard emission wavelength range for the blue phosphor. Simple structure of TL glow curve is found in a Dy^{3+} doped $LaPO_4$ which obeys second order kinetics. The trapping parameters of glow peak have been calculated by Chen's formula. Demand of the dosimetric phosphors with simple and sharp glow curves can be fulfilled by this material and moreover it is eco-friendly. Thus these phosphors give potential application to improve the SSL technology due to their special properties.

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