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STRUCTURAL AND OPTICAL PROPERTIES OF Ce^{3+} DOPED $LaPO_4$ PHOSPHOR

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ABSTRACT:
The present paper reports the economical synthesis, structural and Photoluminescence (PL) characterization of the $LaPO_4$ phosphor incorporated with Ce^{3+} at different concentration i.e. 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mole %. The phosphor was synthesized using the simple and economical wet chemical co-precipitation technique. The prepared powder samples were characterized by X-ray Diffraction (XRD), Fourier Transformation Infra-Red (FTIR) spectroscopy and Scanning Electron Microscopy (SEM) to know the crystalline structure and morphology. The crystalline size of Ce^{3+} doped $LaPO_4$ was calculated using the Debye-Scherer equation and found to be around 70nm. The Infrared spectra for the prepared sample was recorded in the range between 500 and 4500 per cm on a Fourier transform spectrometer. The Photoluminescence (PL) excitation spectra were recorded at 255 nm monitoring at 545nm. The PL emission of $LaPO_4$ doped with Ce^{3+} (at 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mol% concentration) was recorded for excitation wavelength of 255 nm. The intense PL emission peaks are found at 545, 589 and 594 nm along with small peaks not recorded here. The prepared samples have many applications in display and lighting devices.

Keywords: - Wet Chemical, $LaPO_4$, RE ions, XRD, FTIR, SEM, Photoluminescence [PL].

INTRODUCTION :

Recently, considerable effort has been taken in synthesizing inorganic nanomaterials as they are commercially demanded. It has been focused for controlled shapes and size of a material due to their unique physical nature and properties and having important applications in manufacturing nanoscale display, sensing and optoelectronic devices [1-5]. Phosphors are broadly used in display panels and lighting devices. The shape and size of the phosphor is one of the crucial parameters to use them for various applications. Sphere-shaped phosphor particle can enhance the optical and geometrical structure of Phosphor layers. The particle size of a phosphor affects the amount of phosphor particles required to produce an ideal coating for a particular application. Therefore, considerable efforts in research have been directed toward the techniques to prepare nanoscale materials with specific morphology [6-9].

In recent times, nanoscale $LaPO_4$ doped with rare earth (RE) ions, have been extensively studied due to their importance in the fields of optical display panels, integrated optical systems, sensitive devices, plasma display panels, opto-electronic devices etc. The useful applications of rare earth compound particularly lanthanum phosphate doped with inorganic materials have been touched in broad way. Even though much progress has been made in the preparation such materials, it is challenging to synthesize them economically. The phosphors like $LaPO_4$ doped with lanthanide (Ln) has found to be good commercial phosphor for various applications. These phosphors have been actively investigated to improve their luminescent properties as well as to meet the development of different display panels and

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devices. $LaPO_4$ doped with rare earth ions developed an important class of phosphor due to their some interesting characteristics such as good chemical stability, high luminescence efficiency and flexibility in emission of coloures with different activist. $LaPO_4$:Ln material has been studied by researchers prepared by different methods like solution phase routes, solid state reaction, sol-gel, water oil micro emulsion, ultrasonification, hydrothermal, and mechanochemical method etc [10-15]. It has been tried to lower the reaction time, temperature and to obtain high-quality $LaPO_4$ based nanoparticles. But production of $LaPO_4$ with nanoscale size and uniform morphology still remains a challenge. It seems that the best solution to control powder morphology with low cost is the synthesis by wet chemical co-precipitation technique [16-21]. Here simple wet chemical co-precipitation technique have been adopted to prepare $LaPO_4$ and $LaPO_4$:Ce with different concentrations with good morphology and fine crystal structures. In this paper the photoluminescence (PL) of the $LaPO_4$:Ce phosphor with different concentration have been reported.

SAMPLE SYNTHESIS:

The entire chemical purchased were of AR grade and used without further purification. $LaPO_4$ phosphor doped with different concentration of Ce (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mol %) have been prepared using wet chemical co-precipitation method. Lanthanum oxide (La_2O_3) was used as a host material. Ammonium dihydrogen phosphate and Citric acid monohydrate were used as precipitating agent and catalyst respectively. Cerium oxide (Ce_2O_3) was used as a dopant and PEG4000 as a surfactant. 1 gm of La_2O_3 and Ce_2O_3 in stoichiometric ratio was dissolved completely in HNO_3. It was heated repeatedly till evaporation and 2.45 gm citric acid and 50 ml of deionized water was added and stirred hard for 1 hr. The solution of $NH_4.H_2PO_4$ with PEG in water was added and solution was heated at 120 °C constant temperature for 100minutes. Then it was kept still and allowed to cool at room temperature which forms the white ppt. It was centrifuged, washed and dried at room temperature. The prepared phosphor samples were characterized by X-ray diffraction, FTIR, SEM. The Photoluminescence (PL) emission and excitation spectra were measured by Spectrofluorophotometer.

RESULTS AND DISCUSSION:

The prepared samples were characterized by X-ray diffraction to identify the crystalline structure and phase purity of the phosphor. The photoluminescence (PL) emission and excitation spectra were measured by Spectrofluorophotometer. The Perkin Elmer IR spectrometer was used to record the FTIR spectra. The particle morphology of the phosphor was characterized by SEM.

XRD Analysis: The X-ray diffraction patterns of $LaPO_4$ doped with Ce^{3+} at 2mol % in powder form is as shown in *Fig. 1.* The main intense peak in XRD pattern was found around at $2\theta=28.5^0$ along with other less intense peaks at $2\theta=21.2^0$, 26.8^0 and 31.1^0 corresponds to the monoclinic system of crystal structure of $LaPO_4$. The intense lines of XRD pattern are at Miller indices (101), (200), (120) and (012).

All the peaks of XRD are in good agreement with reported XRD pattern of $LaPO_4$ (JCPDS file No. 35-0731). This shows that the product is monazite $LaPO_4$ with monoclinic structure which is well indexed to a monoclinic lattice of pure $LaPO_4$. No traces of impurity phases related to the doped material are observed in the XRD pattern which indicates the high purity of the prepared nanoparticles. The sharp lines of diffraction indicates the crystalline structure of a prepared sample. The crystallite size (D) of powder sample was calculated by using Debye Scherer formula $D= 0.9\ \lambda\ /\ \beta\cos\theta$. Here β

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represents FWHM of intense XRD lines, λ = Wavelength of the X-rays (1.54 AU), θ = Braggs angle of the XRD peak.. The average crystallite size recorded for pure $LaPO_4$ is 60 nm and found to be increased to 70 nm with doping of Ce^{3+} at 2mol %.

SEM Study: Scanning electron microscopy (SEM) image of $LaPO_4$ doped with Ce^{3+} at 2mol % is recorded as shown in *Fig. 2*. The SEM image indicate that the particles appear in irregular shape and agglomerated having average particle size of about 1 micron.

FTIR Spectroscopy: The Perkin Elmer IR spectrometer was used to record the FTIR spectra of Ce^{3+} doped $LaPO_4$ in the range of wave number 4500 to 500 cm^{-1}which is shown in *Fig. 3*. The spectrum shows the characteristic band assigned to the phosphate PO_4^{3-} group. The main absorption around 3609 are assumed H-O-H stretching followed by other bonds of C-H bending, C-O stretching and CO-OH stretching. CO-OH and H-O-H stretching are due to absorbed CO_2 from atmosphere and deionized used in a reaction. The twisting, wagging, rocking, stretching vibration due to presence of CH_2 group from PEG is observed at 2015, 1909 cm^{-1} respectively. Most of the peaks are found missing in the spectrum $LaPO_4$:Ce as that in the case of $LaPO_4$ due the doping of Ce^{3+} ion.

Photoluminescence Study: The PL emission spectra of $LaPO_4$:Ce at different concentration (at 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mol %) recorded at excitation wavelength of 255 nm are as shown in *Fig. 4*. From the emission spectra of $LaPO_4$:Ce, it is observed that the intense PL peaks are at 545, 589 and 594 nm along with small peaks not recorded here. The emission line in the green region lying at 545 nm is due to the transition $^5d_4 \rightarrow {}^7f_6$, in yellow region at 589 nm due to $^5d_4 \rightarrow {}^7f_4$ and 594 nm due to $^5d_4 \rightarrow {}^7f_5$. As the concentration of Ce^{3+} mol % increases in $LaPO_4$: Ce; peak intensity at wavelength 545nm increases up to 2.0 mol % of Ce^{3+}. And for further increasing in the Ce^{3+} doping concentration, peak intensity gradually decreases. This reveals that the quenching effect started and quenching is at 2mol % of Ce^{3+} ions in $LaPO_4$:Ce is observed. The other major peaks at 589nm and 594nm peaks intensity found to be gradually decreases as Ce^{3+} concentration increases up to 3.0 mol%. It is clearly detected that the PL emission intensity of 545nm, 589nm and 594nm peaks is affected with respect to the doping concentration. The nanostruture of synthesized $LaPO_4$: Ce phosphors and favorable emission in the visible region will make it one of the best phosphor for SSL technology.

CONCLUSIONS:

$LaPO_4$:Ce phosphor with different concentration was successfully synthesized by using wet chemical co-precipitation method at low temperature. The main intense peak in XRD pattern was found around at $2\theta=28.5^0$ along with other less intense peaks at $2\theta=21.2^0$, 26.8^0 and 31.1^0 corresponds to the monoclinic system of crystal structure of $LaPO_4$. From the XRD study it conforms the formation of phosphor is mostly in single phase and the average crystallite size for $LaPO_4$: Ce(2.0mol%) phosphors is 70 nm. The photoluminescence study shows that the emissions of 545 nm are due to transition $^5d_4 \rightarrow {}^7f_6$, 589 nm due to $^5d_4 \rightarrow {}^7f_4$ and 594 nm due to $^5d_4 \rightarrow {}^7f_5$. The PL intensity is very high; hence the $LaPO_4$:Ce phosphors are applicable in various types of lamp and display devices. The method of synthesis used here is easy and economical, hence can be potentially applied for the synthesis of other high quality rare earth ions doped phosphate phosphor.

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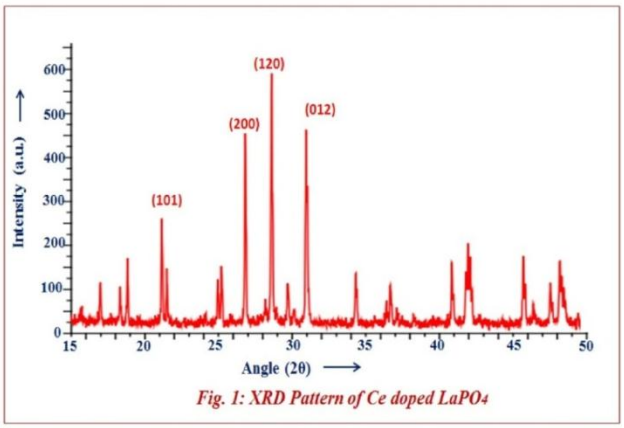

Fig. 1: XRD Pattern of Ce doped $LaPO_4$

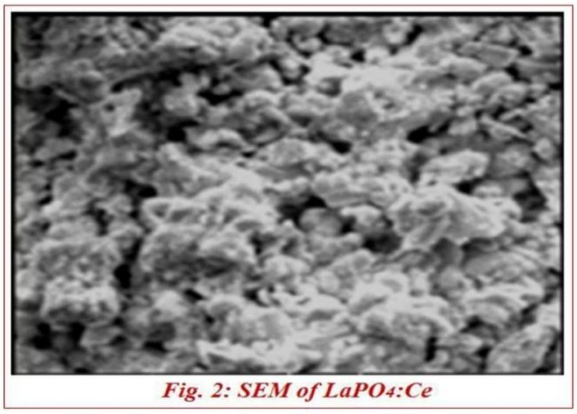

Fig. 2: SEM of $LaPO_4$:Ce

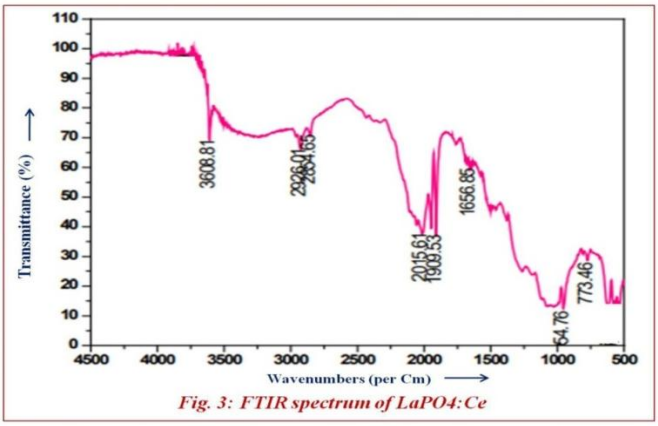

Fig. 3: FTIR spectrum of $LaPO_4$:Ce

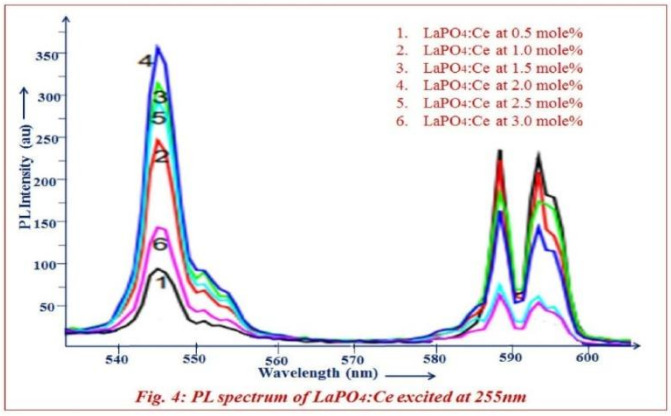

Fig. 4: PL spectrum of $LaPO_4$:Ce excited at 255nm

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