Retrospection of polymer capped LaPO₄: Eu³⁺ luminescent nano phosphor for ingenious solid state lighting

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Abstract
In the present work, the optical properties of LaPO₄:Eu³⁺ luminescent nano phosphors passivated with different capping agents have been probed in depth. Nano particles of Lanthanum orthophosphate nano phosphor were successfully synthesized employing wet chemical synthesis route. The structural properties were investigated through XRD, SEM and TEM whereas the optical properties were explored using photo luminescent characterizations along with afterglow studies. The PL emission intensity peaks were observed at 588nm, 593 nm, 613 nm and 621 nm corresponding to ⁵D₀-⁷F₁ and ⁵D₀-⁷F₂ spectroscopic transitions and are supposed to emit orange-red energy spectrum. With the help of diffuse reflectance spectroscopy, the optical band gaps of differently capped phosphors were calculated employing Kubelka Munk equations.

Introduction
Nanophosphors are supposed to have a significant potential for future generation optoelectronics and sensing devices [1–3]. As lanthanide doped nano phosphors are a consequence of 4f electronic configuration, their chemical peculiarities make them favorable for better performance luminescent devices [4, 5]. As a host LaPO₄ possesses high quantum efficiency and therefore when it is doped with suitable rare earth activator, it shows an improved radiative transition rate attributed to change in dipole field [6]. Since rare earth Europium ion offers symmetry sensitive emission because of non-degenerate ground state ⁷F₀ and non-overlapping ⁴S+1L multiplets; it is most preferred as a dopant. It shows the characteristic intense red emission without splitting into sub-levels due to its crystal field [7]. It has been observed that photoluminence efficiency of nano phosphors is comparatively lower than that of bulk phosphors because of the presence of non-radiative decay channels on the surface of nano particles. Hence, the research is channelized towards the control of surface morphology of nano particles by passivation of their defect states with the support of suitable organic capping agents so that the luminescence yield and photo physical properties of nano phosphors can be raised. The organic capping molecules bind the nanoparticles against aggregation and thus stabilize them. When the particle size is controlled, energy band gap of nano phosphor increases because of shifting of the absorption edge towards the higher energy side [8, 9]. Nevertheless, bulk phosphors of LaPO₄ doped with lanthanides have remarkable luminescent intensity, they are restricted for wide practical applications because of their non-uniform sizes and ungoverned properties. In bulk phosphors as the particle size is large, the light excitation is unable to strike the core region of the phosphor since its size remains unmatched with the light wavelength and hence a large portion of phosphor goes unutilized [10, 11]. Therefore, nano scale phosphate phosphors have been synthesized in order to control and match their size with the wavelength of light and explore them for practical applications like white light generation (white LEDs) and nano thermometry [12].

The variation in synthesis and temperature are reported to have profound effect on morphology and luminescent properties of nanomaterials. Varying synthesis period and annealing temperature indirectly affects crystallinity and geometry around dopant ions in inorganic phosphor [13]. Phosphors synthesized by wet chemical method exhibit better morphology and strong emission characteristics in visible range in comparison
to conventional solid state reaction method [14]. When capping agents acting as surfactants are added in the prepared chemical solution, they tend to minimize the surface tension of the solution. Also, they obstruct grain growth so that aggregation formation is prevented which subsequently leads towards improved morphology and optical properties [15, 16]. In the present manuscript, lanthanum orthophosphate nano phosphor doped with Europium and capped individually with three different capping agents has been explored. Polystyrene, Mercaptoethanol and SHMP in the role of capping agents arrest the free growth of phosphor particles in the reaction and prevent agglomeration and particle coarsening. The co-ordination bonds between polymer ligand, which is defined as an ion or molecule that binds to a central metal atom to form a complex and central rare earth lanthanide activator Eu$^{3+}$ are formed by the ligands electron donating pairs. When light photons are incident on the host LaPO$_4$, the ligand electrons of the capping polymers get excited from their fundamental state. The ligand binds the lanthanide ion tightly and shields the lanthanide ion from quenching effects of undesired impurities present in the host. When the lowest energy level of the ligand in the coordination compound is approximate or above the resonant energy of the activator ion, then according to G. A Crosby et al the ligand energy is transferred to energy levels associated with the rare earth 4f orbital. Eventually, the activator ion expresses luminescence and then relaxes to its fundamental state with a multitude of well separated emission peaks [17]. Since the luminescent emissions are in the visible spectrum, stokes shift of capped polymer lanthanide chelate is large which facilitates accurate emission measurements. In addition, the luminescence lifetime is long as the coordination complex does not suffer from self-quenching. In the reported manuscript, structural and optical properties are studied and compared based on characterization evidences.

**Experimental details**

Lanthanum orthophosphate phosphor was successfully prepared through wet chemical method using Polystyrene, SHMP and Mercaptoethanol as capping agents respectively. It is well recognized that wet chemical process provides excellent chemical compatibility of the final product. In this method, stoichiometric ratio of initial raw materials, Lanthanum (III) Nitrate La (NO$_3$)$_3$ (Merck, 99% pure AR grade), Ammonium dihydrogen phosphate (NH$_4$)$_2$H$_2$PO$_4$ (Merck, 99% pure GR grade) and 0.5 mole percent Europium (III) oxide Eu$_2$O$_3$ (Merck) were dissolved in double ionized distilled water and stirred vigorously in separate beakers till constituents dissolved completely. All the separate solutions were then mixed together in a final beaker and respective capping agent was added drop wise to ensure homogeneity of the precursor solution followed by constant stirring. The solution was put on stirrer at 100 °C till the evaporation of volatile constituents. Then it was kept still and allowed to cool at room temperature for the formation of white precipitate. The precipitate was centrifuged at 1200 rpm, washed with methanol, filtered and then was dried at room temperature for twenty four hours. Ultimately, the dried precipitate was annealed at 1000 °C in a muffle furnace for three hours in air atmosphere to get the final product.

The structural properties of synthesized nano-phosphor were studied through x-ray diffraction meter (Brukers Pan Analytical X-pert Pro XRD). Grain size and surface morphology were observed on Scanning Electron Microscopy (JEOL 6380 A) and Transmission Electron Microscopy (JEOL JEM 2100). Optical excitation and emission properties were identified on luminescence spectrometer (Shimadzu RF 5301 PC) with 150 W xenon lamp as the excitation source. Lifetime calculations were recorded on M/s Edinburgh Instruments Spectrofluorometer UK, model F900. The nature of chemical bonds present in the compound was verified from Perkin Elmer Fourier Transform Infra Red Spectrometer in the range 4000 cm$^{-1}$–450 cm$^{-1}$.

**Results and discussion**

**Structural investigations**

Figures 1(a)–(c) show the well resolved and indexed XRD patterns for the capped LaPO$_4$ nano crystallites capped with Mercaptoethanol (ME), sodium hexametaphosphate (SHMP) and polystyrene (PS). The graphs were recorded at room temperature on Pan Analytical X’Pert Pro x-ray diffractometer with Cu K$\alpha$ rotating anode source having generator settings as 40 kV and 40 mA along with scanning step size of 0.0170. The maximum intensity peaks obtained at two theta values of 21°, 26°, 28°, 30° and 45° were identified to originate from (101), (200), (120), (012) and (212) h k l planes of LaPO$_4$ respectively. The reciprocal lattice corresponds to monazite (monoclinic) system with precise lattice parameters (a = 6.83 Å, b = 7.06 Å, c = 6.50 Å) consistent with the space group P21/n. The obtained parameters were found in good agreement with the standard ICDD 32 #0493. Using Scherrer formula, the mean crystallite size was estimated 63.46 nm for LaPO$_4$ capped with PS, 63.85 nm for LaPO$_4$ capped with ME and 68.25 nm for LaPO$_4$ capped with SHMP. The variation in average crystallite size may be attributed to crystal distortion due to confinement basically caused by capping. The nature and magnitude of intra molecular bonding is also considered to be decisive in determining the average crystallite size.
Because of long reaction time during wet chemical synthesis process all the compounds have achieved an approximate percent crystallinity of 69 percent. The percent crystallinity is calculated by dividing the total area of crystalline peaks by the total area under the diffraction curve. On comparing the experimental lattice constants with the values given in ICDD32\#0493, hardly any traces of impurity phases could be detected. The XRD results thus validate the formation of pure phase of distinct capped LaPO₄:Eu³⁺ under heat annealing treatment of 1000 °C for three hours.

**SEM morphology**

The surface morphology of the product was examined by scanning electron microscopy (SEM, JEOL 6380A). Figure 2 exhibits the SEM micrographs of LaPO₄: Eu³⁺ capped with SHMP, ME and PS. The SEM images of LaPO₄: Eu³⁺ capped with different capping agents are found in close resemblance with each other. The micrographs explore the formation of uniform and nearly spherical ball like microspheres with a slight
coarsened surface. The evolution of low intensity coarsened surface is because of passivation of majority surface defects. However, the reason for the formation of spherical phosphors with a regular shape may be attributed to homogenous precipitation during synthesis with suitable amount of capping agent. Also during reaction process, the van der Waals interactions between organic capping agents and inorganic host have promoted the formation of spherical morphology. However, evolution of nano sized particles can be well appreciated through reverse Ostwald ripening mechanism \cite{18, 19}. Corresponding to this theory, nano particles are assumed to be negatively charged \cite{20, 21}. As nanoparticles are electrically charged, they possess an electrostatic energy which is inversely proportional to the radius of the particle. Since electrostatic energy rises up with decrease in particle size, it prevents the nanoparticles from shrinking away completely and the charged nanoparticles do not coagulate with each other.

**TEM characterization**

Figures 3(A)–(C) explores TEM micrographs of LaPO₄:Eu³⁺ capped with PS, ME and SHMP respectively. The micrographs (A), (B) and (C) clearly reveals the formation of lanthanum phosphate nano particles with nearly spherical to slightly ellipsoidal particles with a size range of 66nm to 69 nm. The SAED pattern for LaPO₄:Eu³⁺ capped with PS has spotty annular sharp diffraction rings validating the crystalline nature of phosphor particles. The ring pattern satisfies the Bragg’s condition and is successfully indexed in terms of monazite phase of LaPO₄ consistent with the phase obtained in XRD. The HR-TEM image reveals a complete crystallite surface in which the distance between adjacent lattice fringes has been calculated to be 0.47nm corresponding to (011) plane of LaPO₄ crystallite. Thus, enhanced PL intensity is attributed to better crystalline phase and absence of large vacancies between the crystallites as seen in bright field images of TEM morphology.

**Photo luminescent investigations**

PL spectra reveals the spectroscopic properties of Eu³⁺ doped lanthanum orthophosphate nanophosphor. The photoluminescent excitation spectra for Eu³⁺ doped LaPO₄ capped with ME, SHMP and PS are plotted in figures 4(a)–(c) The broad band at 265 nm in the ultraviolet region of electromagnetic spectrum is referred as ligand to metal charge transfer band between Eu³⁺ and the surrounding oxygen anions. The charge transfer band is highly intense since the transition is allowed by Laporte’s selection rule. The broad nature of transition is a characteristic of electron transfer to the neighboring anions of 4f orbital. The excitation graph exhibits several
peaks between the spectral ranges of 300 nm to 400 nm. These peaks are attributed to distinctive absorption bands of Eu$^{3+}$ corresponding to direct excitation from the ground state to the excited state of europium f electrons. The strongest excitation peak positioned at 295 nm is associated to $^7F_0 \rightarrow ^{5}D_0$ transition of Eu$^{3+}$ [22]. In figures 5(a)–(c), the emission spectra demonstrate several sharp and well resolved emission peaks associated with europium ions which are ascribed to radiative relaxation from $^5D_0-^7F_1$ magnetic dipole transitions. The intensity of $^5D_0-^7F_1$ transition is assumed to be influenced by spectroscopic J mixing. The intensity peaks observed at 593 nm, 613 nm and 621 nm corresponds to $^5D_0-^7F_2$ electric dipole transitions that are found sensitive to changes in ligand environment. When Eu$^{3+}$ ion is inserted into the ligand surrounding then $(2J + 1)$ degenerate J mixing level gets split into Stark sub-levels because of ligand field effect. Since LaPO$_4$ has a monazite crystal structure, it offers a crystal site with C$_1$ space group for both La$^{3+}$ and Eu$^{3+}$ which poses a low inversion symmetry [23]. Because of identical charge, the substitution of La$^{3+}$ with Eu$^{3+}$ does not cause significant lattice distortion. Since Eu$^{3+}$ occupies an inversion symmetry site in the crystal lattice, orange red emission due to magnetic dipole transition $^5D_0-^7F_1$ around 593 nm is the dominant transition. PL spectra reveals that emission peak in LaPO$_4$ capped with PS (Polystyrene) is more intensive because of comparatively reduced particle size. As the particle size reduces, the edge of valence band shifts downwards. Consequently, the emitted photon releases high energy PL emission. Also, in LaPO$_4$ capped with PS, the organic part dissociates and gets involved in ligand formation with La ions. The strong ligand formation helps in passivating defects along with unsaturated bond density implicating in better luminescence output. Nevertheless, in LaPO$_4$ capped with SHMP and MS, the low emission intensity is attributed to the formation of rather dense organic inorganic chelating network during synthesis reaction. Dense cross linking network is supposed to interrupt with the colloidal nature of the coordination complex formed which eventually results in low luminescence yield.

**FTIR analysis**

FTIR analysis has been carried out in order to validate the phosphate functional group in the samples. Figure 6 represents the FTIR spectra of LaPO$_4$; Eu$^{3+}$ capped with PS, ME and SHMP. The FTIR bands are characteristic
of vibrations of $\text{PO}_4^{3-}$ phosphate group. $\text{LaPO}_4$ has $C_1$ symmetry with ($v_3$ and $v_4$) vibration regions in the monazite structure. The $v_3$ vibration corresponds to phosphate $P$–$O$ stretching. The $v_4$ vibration corresponds to $O$–$P$–$O$ bending mode. Bands present at 538 cm$^{-1}$, 553 cm$^{-1}$ and 614 cm$^{-1}$ are the characteristic peaks of monazite phase and are clearly observed in the $v_4$ region of $\text{PO}_4^{3-}$ group. The characteristic bands at 871 cm$^{-1}$, 984 cm$^{-1}$ and 1282 cm$^{-1}$ belong to anti symmetric $v_3$ region. The vibrational spectra present a conclusive evidence for monazite phase formation in lanthanum phosphate. Peaks at 1643 cm$^{-1}$, 2178 cm$^{-1}$, 2343 cm$^{-1}$, 3023 cm$^{-1}$ and 3515 cm$^{-1}$ may be attributed to presence of water vapor in the form of stretching vibrations of OH bands absorbed by KBr during testing.

**Diffuse reflectance spectra and calculation of band gap**

Diffuse reflectance spectra of $\text{LaPO}_4:\text{Eu}^{3+}$ capped with SHMP, PS and ME phosphors have been plotted in figure 7, so as to calculate the optical band gap. Figure reveals strong absorption edge in the range 250 nm to 300 nm corresponding to the band gap ($E_g$) of respective nanophospor. The spectra were recorded at room temperature in the range of 0 to 800 nm wavelengths. The absorption spectra reciprocate the absorption transitions from the ground state to the excited state of $\text{Eu}^{3+}$ activator ion. From the diffuse reflectance graphs, the optical band gap of nano phosphor was determined employing Kubelka- Munk equation. The Kubelka Munk function is given as [24]

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S}$$

where R represents the diffuse reflectance of the sample, $K$ serves as the absorption coefficient and $S$ stands for scattering coefficient. The direct band gap ($E_g$) and linear absorption coefficient are related by well known Tauc relation:
where $\alpha$ is the absorption coefficient, $h\nu$ is light energy and $c$ is constant. Equation (2) is modified by substitution of equation (1) and is ultimately given as

$$[F(R)h\nu]^2 = A(h\nu - E_g)$$

Figure 8 represents the graph of $[F(R)h\nu]^2$ as a function of photon energy $h\nu$. The optical band gap values were determined by extrapolating the linear fitted regions in the graph. The point of the photon energy axis, at which the extrapolated line meets with the $h\nu$ value, corresponds to the direct optical band gap of phosphor. Consequently, LaPO$_4$:Eu$^{3+}$ capped with PS has optical band gap 4.42 eV whereas LaPO$_4$:Eu$^{3+}$ capped with SHMP and ME have band gap values as 3.93 eV and 3.63 eV respectively. According to the described experimental characterization on bulk LaPO$_4$, the band gap energy between 5.11 eV to 8.21 eV has been observed [25–28] which are quite more than the band gap values reported in the manuscript. This phenomenon is generally referred as band gap narrowing and is strongly associated with change in strength of LaPO$_4$ crystalline potential. Along with doping when capping agents are introduced in the host, the impurity bands broaden and merges with the bottom of the conduction band, eventually decreasing the band gap of the material [29].

**CIE chromaticity diagram**

Color of synthesized nano phosphor host material is represented through color co-ordinates. The luminescent color of lanthanum phosphate nano phosphor excited under 395 nm has been experimentally characterized by CIE (Commission International de l’Eclairage) 1931 chromaticity diagram. Emission spectra of Eu$^{3+}$ doped lanthanum phosphate phosphor was converted to CIE 1931 with the aid of photo luminescent (PL) data values and interactive CIE software (CIE color co-ordinate calculator). Figure 9 explores $(x,y)$ coordinates that are disclosed inside the chromaticity zone representing saturated orange-red spectrum color $(x = 0.58, y = 0.40)$. The chromaticity co-ordinates are in good agreement with PL emission intensity results and are approaching those values for potent red phosphor component required for generation of warm white lighting and field emission displays.

**Conclusions**

The experimental results confirm the formation of LaPO$_4$:Eu$^{3+}$ phosphor nano particles capped with PS, ME and SHMP through wet chemical synthesis. Eu$^{3+}$ ions have shown to greatly influence the intensity of absorption and emission bands because of partially filled 4f$^0$ electron shell that possess large number of probable energy states. XRD spectra justified the formation of pure crystalline monazite phase of lanthanum phosphate nano phosphor with an average crystallite size of approximate 68nm. SEM images explore the spherical morphology of synthesized moieties with a slight coarsened surface due to large surface defect passivation by suitable capping agents. HRTEM analysis approved the formation of lanthanum orthophosphate in nano crystalline regime having distinct grain boundaries with particle size in between 66 nm–69 nm and is consistent
with XRD findings. FTIR exhibits strong absorption bands around 538 cm\(^{-1}\), 984 cm\(^{-1}\) and 1282 cm\(^{-1}\) verifying the presence of phosphate functional group. It was found that polystyrene capped nano particles consisted of high density crystallites leading to higher luminescence efficiency as compared to lanthanum phosphate capped with other capping agents. In LaPO\(_4\):Eu\(^{3+}\) nano phosphor, variation in luminescent intensity was recorded due to incorporation of different capping agents. However, because of strong ligand formation between capping agent, host and activator the surface defects were almost passivated and unsaturated dangling bonds were nearly removed resulting in better luminescent output. Thus, the reported work demonstrates that synthesis of inorganic orthophosphate phosphor nano particles capped with appropriate organic capping agents which can prove to be a promising opportunity for obtaining better quality LEDs.

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