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LaPO$_4$:Tb^{3+} NANOPHOSPHOR: LOW TEMPERATURE SOLUTION COMBUSTION ROUTE AND PHOTOLUMINESCENCE PROPERTIES

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ABSTRACT :

Terbium III doped LaPO$_4$ *has been prepared using low temperature solution combustion route with metal nitrates as precursors and urea as a fuel. The X-ray diffraction (XRD) revealed the single phase monoclinic structure of* LaPO$_4$*. The crystallite size by Scherrer formula is found to be 42 nm. The nanorod structure was confirmed by transmission electron microscopy (TEM). The phosphor exhibited bright green emission upon excitation of 278 nm ultra violet (UV) light. The characteristics photoluminescence peaks between 425 nm to 650 nm are attributed to* $^5D_4 \rightarrow {}^7F_J$ $(J = 6, 5, 4, 3)$ *transitions of* Tb^{3+} *ions respectively. Thus the present phosphor can be used as a green emitting phosphor in tricolor lamps and display devices.*

KEYWORDS : *Nanophosphor, Lanthanum Orthophosphate; green emission; Nanorods* .

1. INTRODUCTION

Particles at nanoscale have been intensively studied over the last two decades because they reveal interesting and useful properties like luminescence, biocompatibility, targeted drug delivery and other optoelectronic properties [1-6]. The luminescent nanomaterials form a group of special interest wherein inorganic host materials like aluminate, borate, phosphate, silicate and vanadate are doped with lanthanides [7, 8]. They have high temperature resistance and they can form a stable colloidal solution which is the desired feature for biocompatible materials. They have less possibility of degradation over a long period of time [9].

Tb^{3+} doped inorganic phosphors have been widely used as green color emitting phosphors because of their intense $^5D_4 \rightarrow {}^7F_5$ emission in green spectral region [10-13]. LaPO$_4$:Ln^{3+} have attracted lots of attraction due to their unique photoluminescence properties [14, 15] which is prerequisite for lighting and display applications. LaPO$_4$:Tb^{3+} has been synthesized by various methods like co-precipitation [16], hydrothermal [17-19], Microwave assisted method [20]. In this work, solution combustion method is used for synthesizing LaPO$_4$:Tb^{3+}nanophosphor, which is a promising material for optical devices like tricolor lamps, displays like plasma panel displays, white light emitting diodes (WLED) etc. The morphology and photoluminescence properties of the prepared samples are studied.

2. EXPERIMENTAL

Solution combustion synthesis is a self-propagating, effective and low cost method for the production of very fine agglomerated multi component oxide ceramic powders without intermediate decomposition and/or calcinations steps [21-24]. It has been reported in our previous work that nanophosphors or metal-oxide nanoparticles can be produced by combustion synthesis technique [7, 8, 15]. The advantages of combustion synthesis method such as inexpensive sources, easy to set-up equipment and a facile process to produce the nanoscale materials led to use this method for reported work.

The aqueous solutions of corresponding metal nitrates (oxidizers) and the organic fuel urea (reducer), predetermined in stoichiometric ratio, were heated slowly in a preheated furnace maintained at 500 ± 10°C to evaporate water until rapid combustion occurs. The mixture ignited and a self-sustaining fast combustion reaction produced fine crystalline oxide powders. The formation of nanoparticles with no subsequent particle growth was the result of the explosive nature of the combustion reaction. Ultimately, by adjusting the fuel-to-oxidizer ratio, the reaction temperature is maintained and thus, the particle size is controlled [25]. In this work the nanophosphor $LaPO_4:Tb^{3+}$ is synthesized as per the following chemical reaction

$(1-x)\ La(NO_3)_3.6H_2O + NH_4H_2PO_4 + 5(NH_2)_2CO + xTb(NO_3)_3.5H_2O \rightarrow (1-x)\ LaPO_4:xTb^{3+}$
$(x= 0.01, 0.03, 0.05)$.

The prepared samples were subjected to the X-Ray Diffraction (XRD) analysis on Rigaku Miniflex X-ray Diffractometer operating at 40 kV, 30 mA with scan speed of 2.000 deg./min and with Cu Kα radiation (λ = 1.5405 Å). The photoluminescence properties of the phosphor (excitation and emission) were measured using Hitachi F-7000 fluorescence spectrophotometer at room temperature. The morphology and particle size of the sample was determined for Transmission Electron Microscopy (TEM) on Philips CM 200 TEM machine operated at a voltage of 200 kV and having resolution of 0.23nm.

3. RESULTS AND DISCUSSION

3.1 Structural and Morphological properties

3.1.1 X-Ray Diffraction analysis

The XRD patterns are well matched with standard International Centre for Diffraction Data (ICDD) file no. 01-084-0600 of $LaPO_4$ as shown in Figure 1(Inset).

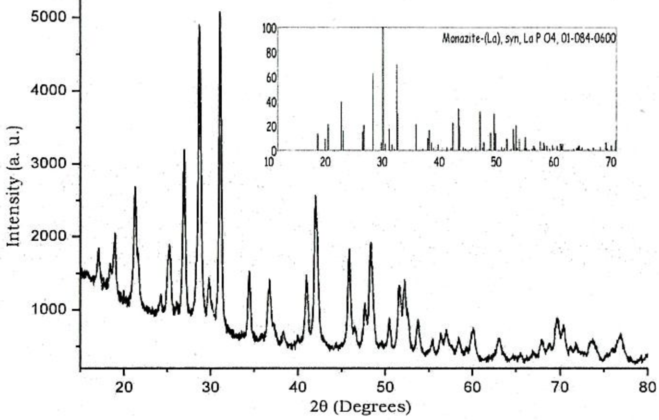

Figure 1: X-Ray Diffraction pattern for $LaPO_4$ [Inset-ICDD file of $LaPO_4$]

$LaPO_4$ has a single pure phase with a monoclinic monazite crystal structure, whose lattice constants are *a* = 6.84 A°, *b* =7.07 A° and *c* = 6.45 A°, and inter planar angles are $\alpha = \gamma = 90°$ and $\beta = 103.85°$. As the Tb^{3+} ionic radius (r=1.12Å, CN=9) is closest to that of La^{3+} (r=1.17Å, CN=6), it is believed that the La^{3+} sites are replaced by Tb^{3+} in this lattice. The crystallite size calculated by Scherrer formula was found to be nearly equal to 42 nm [26-28].

3.1.2 TEM analysis

TEM micrograph revealed the shape of the particles as nanorods [Figure 2(a) (b) (c)] with average width in the range 30-50 nm. The Selected Area Electron Diffraction (SAED) pattern [Figure 2(d)] showed the concentric rings of the crystalline planes corresponding to diffraction peaks shown in XRD pattern.

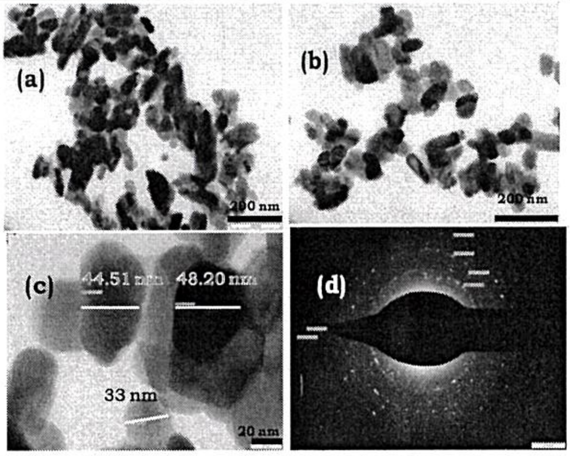

Figure 2: (a) (b) (c) TEM images and (d) SAED pattern of $LaPO_4$: Tb^{3+}

3.2 Photoluminescence properties

The photoluminescence excitation (PLE) spectra [Figure 3 (a)] showed a broad band peaking at 220 nm and 278 nm that is attributed to the charge-transfer band (CTB) which is the result of transferring the electrons in the neighboring anions to a 4*f* orbital, leading to f → f emissions [29]. The excitation lines between 300 nm – 400 nm correspond to the direct excitation from the terbium ground state to the higher excited states of the terbium f-electrons. This is attributed to the fact that the 4f electrons in RE^{3+} ions are effectively shielded from surrounding crystal fields because of the filled outer shells of $5s^2$ and $5p^6$ electrons. Two types of electronic states with different characteristics are shown by the rare earth ions. They are the $4fn\text{-}5d^1$ states and the charge transfer states. In the first case one of the 4*f* electrons is transferred to a 5d orbital and in second case electrons in the neighboring anions are transferred to a 4*f* orbital. Both cases show strong optical absorption [30, 31].

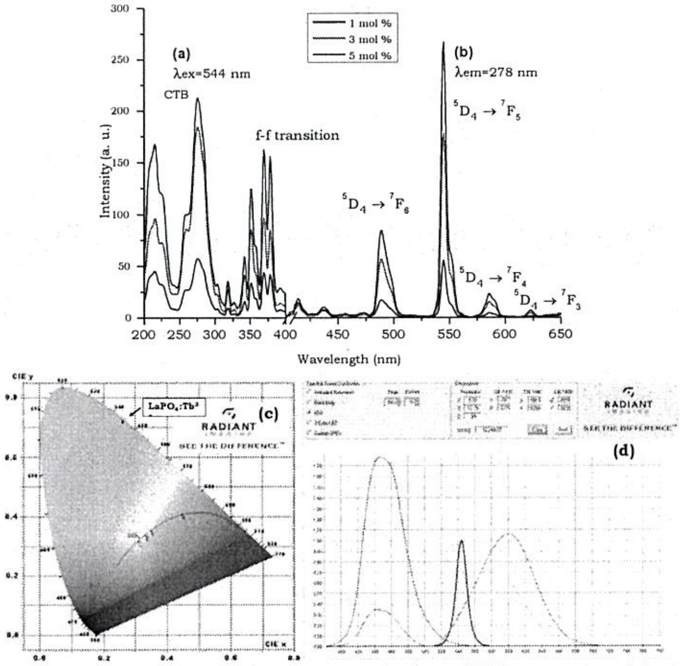

Figure 3: Photoluminescence (a) excitation (PLE), (b) emission (PL) spectra, (c) color chromaticity graph and (d) Spectral power distribution graph of $LaPO_4$: Tb^{3+} (5 mol %)

The emission spectra [Figure 3(b)] consist of the typical sharp line emissions ranging from 425 to 650 nm originated from the $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3) transitions of Tb^{3+} ions. The intensity of 543 nm peak which is attributed to $^5D_4 \rightarrow {}^7F_5$ is remarkably high. The optimum concentration was found to be 5 mol % of Tb^{3+}ions.The transitions attributed to $^5D_4 \rightarrow {}^7F_6$ corresponding to blue light emission (488 nm) has less intensity than the transition attributed to $^5D_4 \rightarrow {}^7F_5$ (543 nm). The other two transitions corresponding to $^5D_4 \rightarrow {}^7F_4$ (586 nm) and $^5D_4 \rightarrow {}^7F_3$ (622 nm) have weak emission. The color chromaticity values calculated using Radiant imaging color calculator 2.0 software [32] for reported phosphor were found to be (0.2577, 0.7276) that are close to Commission Internationale de'Eclairage (CIE) color coordinates of green color [Figure 3(c)]. This indicates the feasibility of the reported phosphor as a green light emitting phosphor for 278 nm excited tricolor lamps and display devices. Figure 3(d) showed spectral power distribution graph of reported phosphor considering its feasibility for LED lamp application. As the excitation spectra showed that this phosphor can be excited at 395 nm, the spectral distribution graph is plotted by considering narrow emission peak of Full Width at Half Maximum (FWHM) 15 nm at 543 nm. It is slightly shifted from the ideal peak of 556 nm green color emitting LED.

4. CONCLUSIONS

$LaPO_4:Tb^{3+}$ nanophosphor powder was successfully prepared by low temperature facile combustion synthesis method. The prepared $LaPO_4$ powder crystallizes in a single-phase monoclinic structure with a rod shape particle approximately 30 nm - 50 nm in width. The maximum intensity was found for 5 mol % of Tb^{3+}. The photoluminescence emission spectrum shows bright green color showing maximum peak at 543 nm which is characteristics transition $^5D_4 \rightarrow {}^7F_5$ of Tb^{3+}. The color chromaticity co-ordinates for this phosphor are calculated as (0.2577, 0.7276). Thus, reported phosphor can be used as a green color emitting phosphor in optical devices like 254 nm excited tricolor lamps and 395 nm excited white light emitting diodes (WLED) lamps.

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