



STUDIES ROOM TEMPERATURE OPTICAL PROPERTIES OF $\text{LaF}_3: \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Sm}^{3+}$ NANOCRYSTALS BY MICROWAVE TECHNIQUE

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Abstract: Lanthanum fluoride ($\text{LaF}_3: \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Sm}^{3+}$) synthesized by water soluble $\text{LaCl}_3 + \text{CeCl}_3 + \text{PrCl}_3 + \text{SmCl}_3$ and NH_4F as starting materials in de-ionized water as solvent using microwave assisted technique. The structure of $\text{LaF}_3: \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Sm}^{3+}$ nanocrystals analyzed by XRD and TEM analysis is found to be in hexagonal structure and average crystalline particle size is 20 nm (JCPDS standard card (32-0483) of pure hexagonal LaF_3 crystals). The absorption edge in UV spectra is found at 250 nm corresponding to energy of 4.9eV. It further shows a wide transparent window lying between 200 nm - 800 nm. For $\text{LaF}_3: \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Sm}^{3+}$ nanocrystals emission of blue color (458 nm) has been observed with at an excitation wavelength of 254 nm. The measured relative second harmonic generation (SHG) efficiency of $\text{LaF}_3: \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Sm}^{3+}$ in de-ionized water with respect to KDP crystal is 0.186.

Index Terms: Microwave radiation, Hexagonal shape, X-ray diffraction, Luminescent, SHG

I. INTRODUCTION

LaF_3 is an ideal host material for various phosphors to its low phonon energy and the consequent minimal multi phonon relaxation of its excited states [1, 2]. Such rare earth nanophosphors appear in a rich variety of components used in semiconductor displays like Light Emitting Diode (LED) [3], up converters [4, 5], magnetic resonance imaging (MRI) [6], biological fluorescent labels [7], optical amplifiers, transparent glass, scintillators, photonic crystals [8].

LaF_3 in particular exhibits excellent photochemical stability, biocompatibility, and relatively low crystalline temperature. Currently research on nanophosphors is a dominant field in modern material chemistry. Particle size greatly influences luminescence properties of nanophosphors. Narrow emission lines are a remarkable characteristic of lanthanide luminescence. Several research papers attempt studies on photoluminescence properties of LaF_3 [9]. Jouda et al [10] study X-ray excited luminescence of solid LaF_3 and CeF_3 at various temperatures, Rodnyi et al [11] study such luminescence mechanisms in detail.

Lanthanide ions show emission in the near-UV, visible, near-infrared and infrared spectral regions. Lanthanide luminescence has been characterized by narrow emission lines. The absorption of lanthanide ions is typically weak due to the forbidden transitions. Lanthanide ions which emit visible light are Eu^{3+} (red color), Eu^{2+} (blue color), Tb^{3+} (green color), Sm^{3+} (orange color) and Tm^{3+} (blue color). Typical near-infrared emitting lanthanide ions are Nd^{3+} , Er^{3+} and Yb^{3+} [12].

In the past two decades, the use of microwave technique has attracted a considerable amount of attention, owing to its successful application in organic and inorganic synthesis of nanomaterial's, material sciences, polymer chemistry, nanotechnology, and biochemical processes. In many circumstances, the use of microwave dielectric heating as a non-classical energy source has been shown to dramatically reduce processing times, increase product yields, and enhance product purity or material properties compared to conventionally processed experiments and hence is favored here for synthesis of LaF_3 nanocrystals.

In the past several investigations have been carried out to study the optical properties of study $\text{LaF}_3: \text{Ce}^{3+}, \text{Tb}^{3+}$ [13-15] for their possible applications in optoelectronics devices. In present work the synthesized $\text{LaF}_3: \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Sm}^{3+}$ nanoparticles exhibit hexagonal shape with average particle size of a 20nm, blue (458nm) luminescent behavior has been observed with excitation wavelength of 357nm and 254nm respectively for the synthesized nanocrystals.

II. SYNTHESIS OF LaF_3 NANOCRYSTALS

Synthesis of $\text{LaF}_3: \text{Ce}^{3+}, \text{Pr}^{3+}$ and Sm^{3+} has done following an aqueous route and use a microwave heating at low power range. The method is simple and cost effective. Water soluble $\text{LaCl}_3 + \text{CeCl}_3 + \text{PrCl}_3 + \text{SmCl}_3$ (1unit) and NH_4F (3 units) were mixed to obtain a solution in 1:3 molar proportion [16]. A 10 ml of the homogenous mixture prepared (de ionized water) in a 100 ml beaker using 0.064mol of $\text{LaCl}_3 + \text{CeCl}_3 + \text{PrCl}_3 + \text{SmCl}_3$, allowed 10 ml solution of 0.768mol NH_4F to drip into this solution uniformly through a funnel attached with a stopper to facilitate control of dripping. White crystalline precipitate of $\text{LaF}_3: \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Sm}^{3+}$ appeared instantly. Initial appearance of white precipitate indicated formation of LaF_3 . Placed the whole set-up inside a conventional microwave oven set at low power range (in on-off mode set at 30sec) for around 30 min. This low power range setting largely helped us to avoid spilling of the

solution. A white crystalline precipitate identified as doped LaF₃ nanocrystals appears almost instantly and settled down to the bottom of the beaker. After subsequent drying at room temperature for about 1 hour, the powder was stored in sealed tubes for characterization.

III. CHARACTERIZATION

Powder X-ray diffraction (XRD) measurements have been performed using a PANALYTICAL X'PERT PROMPD diffractometer model using CuK α radiation $\lambda = 1.5405$ A.U with a scanning rate of 2^o per min in the 2 θ range from 0^o to 80^o. Transmission electron microscope (TEM) analysis has been carried out for different magnification by PHILIPS (CM 200) 0.24 nm resolution, operating at 200kV. The UV-visible spectrum of the samples was recorded in the spectral range of 200nm – 800nm using a double beam (Perkin Elmer Corp.) spectrophotometer. The fluorescence spectrum was measured on LS 45 luminescence spectrometer (Perkin Elmer Corp.) using a high energy pulsed Xenon source for excitation and FL Win Lab software. NLO studies for the measurements of SHG efficiency are obtained through the crystalline powder sample by using Kurtz and Perry technique.

IV. RESULT AND DISCUSSION

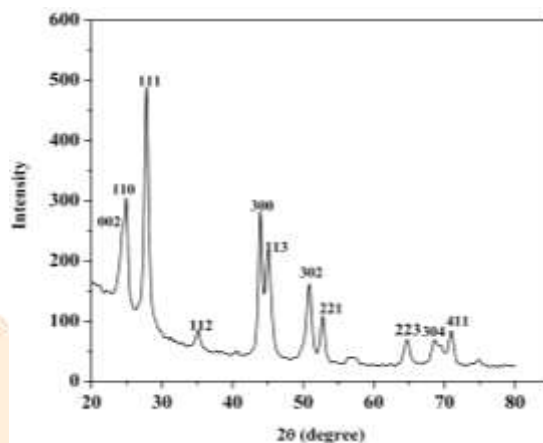


Figure1. X-ray diffraction pattern of LaF₃: Ce³⁺, Pr³⁺ and Sm³⁺ nanocrystals

XRD pattern obtained from the LaF₃: Ce³⁺, Pr³⁺, and Sm³⁺ nanocrystals is shown in Figure 1. The results of the XRD are in good agreement with the hexagonal LaF₃ structure as described in the reports LaF₃ (JCPDS card No. 32-0483) [17]. The average crystallite size estimated from the Scherrer equation, $D = 0.90\lambda / \beta \cos\theta$, where D is the average crystallite size, λ is the x-ray wavelength (0.15405 nm), θ and β are the diffraction angle and full width at half maximum of an observed peak, respectively. The strongest peak (111) at $2\theta = 27.84^\circ$ for LaF₃: Ce³⁺, Pr³⁺, Sm³⁺ samples have been used to calculate the average crystallite size (D) of the nanocrystals [18, 19]. The average crystallite size of LaF₃: Ce³⁺, Pr³⁺, Sm³⁺ nanoparticles is 20 nm, which is in agreement with the TEM results. The XRD pattern of the LaF₃: Ce³⁺, Pr³⁺, Sm³⁺ nanocrystals is nearly close to that of LaF₃: Ce³⁺, Tb³⁺ [20]. This indicates that Ce³⁺, Pr³⁺ and Sm³⁺ are doped into the LaF₃ crystal lattice. The ionic radii of Ce³⁺ (1.034 Å), Pr³⁺ (1.01 Å) and Sm³⁺ (0.96 Å) are very close to that of La³⁺ (1.061 Å); therefore Ce³⁺, Pr³⁺, Sm³⁺ can easily substitute for La³⁺ ions in LaF₃ crystals. The standard formula used for the determination of cell parameters for hexagonal structure is given below:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + l^2}{a^2} \right) + \frac{l^2}{c^2} \quad (1)$$

Where (h k l) are the Miller indices corresponding to XRD peaks, 'a' and 'c' are hexagonal cell parameters, d is the spacing distance. Figure 2 shows the transmission electron microscopy (TEM) images of LaF₃:Ce³⁺, Pr³⁺, Sm³⁺ nanocrystals that the particles are well separated from each other; the nanocrystals have a hexagonal disk like shape with an average particle size of 20 nm. Figure 3 shows the selected area electron diffraction (SAED) pattern, three strong diffraction rings are observed. From the measurement of d-spacing for the XRD pattern, the rings are assigned in the following Miller indices (0 0 2), (1 1 1) and (3 0 0) respectively starting from the center which is in close agreement with the hexagonal LaF₃ structure [21, 22]. The average size of the nanocrystals is close to that obtained by XRD analysis. This shows that the original structure of LaF₃ may be retained even after the modification.

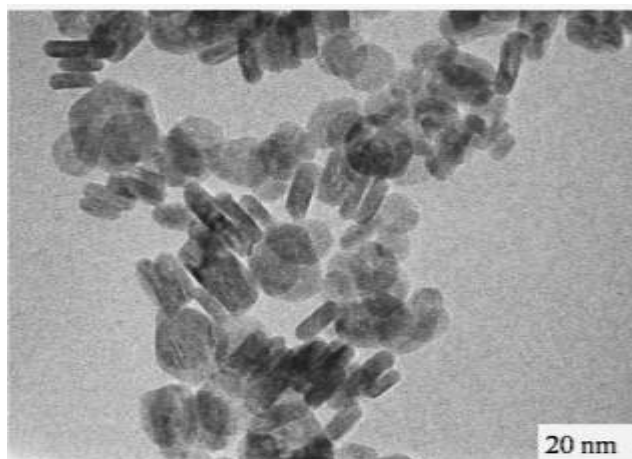


Figure2. TEM image of Ce³⁺, Pr³⁺ and Sm³⁺ doped LaF₃ nanocrystals

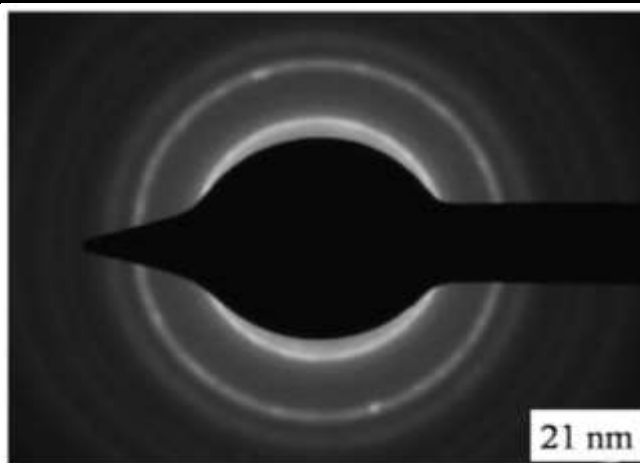


Figure3. Selected area electron diffraction (SAED) pattern image of $\text{LaF}_3: \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Sm}^{3+}$ nanocrystals

To obtain UV spectrum of $\text{LaF}_3: \text{Ce}^{3+}, \text{Pr}^{3+}$ and Sm^{3+} nanocrystals were dissolved in de-ionized water. This solution was used for UV-VIS analysis, which indicates an absorption edge at edge at 264 nm and 235 nm in the UV region, (calculated using the relation $E = hc/\lambda$) with corresponding energy gap of 4.6eV and 5.2eV as shown in Figure 4. A wide transparent window is present between 200nm - 800nm suggesting its use in optoelectronics devices.

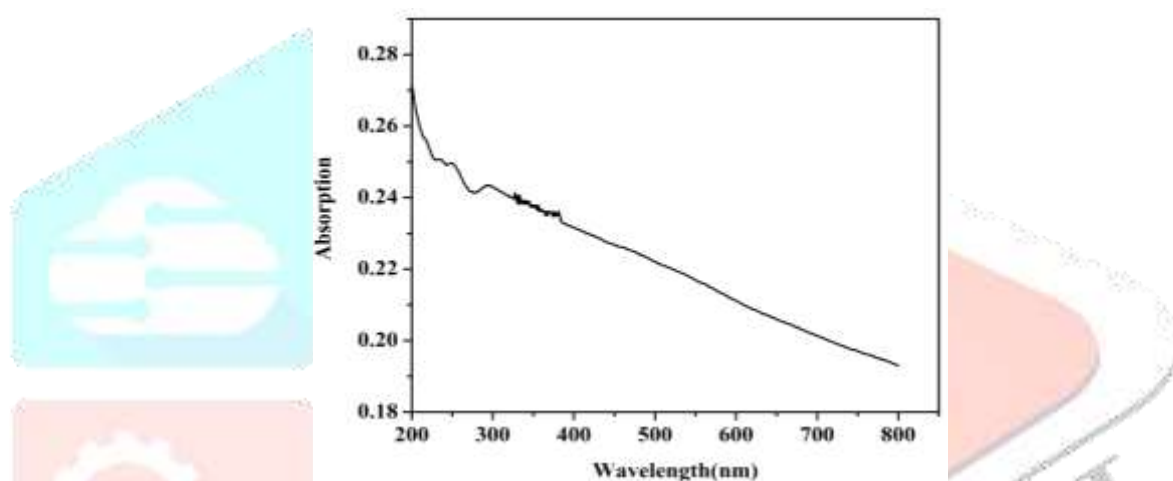


Figure4. UV-VIS absorption spectra of doped $\text{Ce}^{3+}, \text{Pr}^{3+}, \text{Sm}^{3+}$ LaF_3 nanocrystals

Figure 5 shows the emission spectra of synthesized $\text{LaF}_3: \text{Ce}^{3+}, \text{Pr}^{3+}$ and Sm^{3+} nanocrystals. The excitation spectra are obtained by monitoring (254 nm) the $4f-5d$ or ${}^2F_{5/2} \rightarrow 5D$ transition of Ce^{3+} ions. The broadband emission is located at 458 nm due to the electronic transitions from $5d$ to $4f$ state of Ce^{3+} ions [23, 24]. The sharp emission peaks originate from the $4f5d-4f^2$ transitions of Pr^{3+} ions ${}^3H_4 \rightarrow {}^3P_2$ (458 nm), ${}^3H_4 \rightarrow {}^3P_0$ (495 nm), ${}^3H_4 \rightarrow {}^1D_2$ (608 nm) transitions. The quenching of Ce^{3+} emissions and the enhancement of Pr^{3+} emissions is strong evidence of efficient energy transfer from Ce^{3+} to Pr^{3+} and Pr^{3+} to Sm^{3+} . The peaks at 315nm, 458nm and 499nm correspond to ${}^6H_{5/2} \rightarrow {}^4P_{5/2}$, ${}^6H_{5/2} \rightarrow {}^4I_{9/2}$, ${}^6H_{5/2} \rightarrow {}^4G_{7/2}$ transitions, for Sm^{3+} ions due to the $4f5d-4f^3$ transitions. The emission spectrum is mainly located in the region corresponding to blue color. Here, the doping Ce^{3+} ions act as sensitizers, and the doping $\text{Pr}^{3+}, \text{Sm}^{3+}$ can be considered as the luminescent centers.

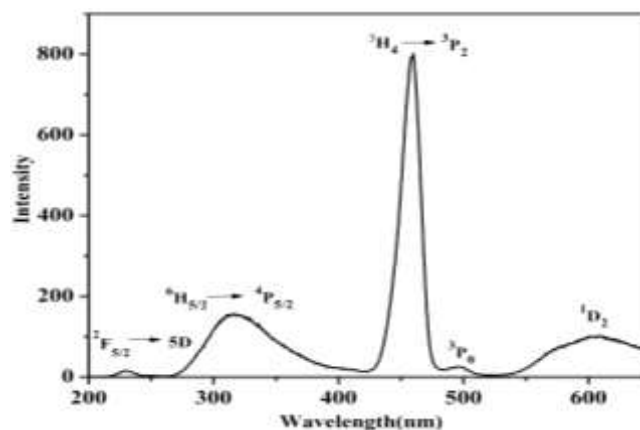


Figure5. Excitation ($\lambda_{em} = 458$ nm) and Emission ($\lambda_{ex} = 254$ nm) spectra of $\text{LaF}_3: \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Sm}^{3+}$ nanocrystals

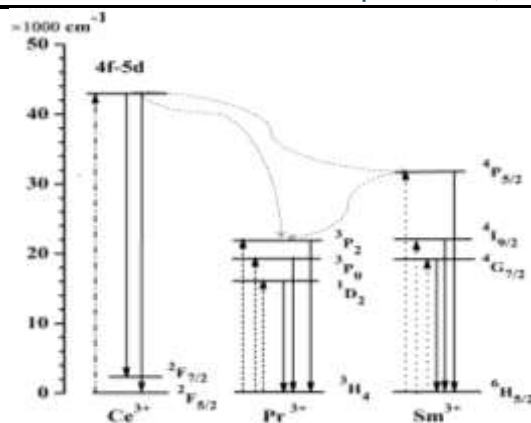


Figure6. Energy level scheme of LaF₃: Ce³⁺, Pr³⁺, Sm³⁺ nanocrystals

Figure 6 shows the energy level diagram for the doped LaF₃: Ce³⁺, Pr³⁺ and Sm³⁺ nanocrystals. It is well known that the luminescence spectrum of trivalent lanthanide ions in crystals comes mainly from two types of electronic transitions: 4f–4f transition and 5d–4f transition. The excited electronic configuration of Ce³⁺ is ⁵D₁. The 5d electron has a strong interaction with the neighboring anion ligands in the compounds and results in broadband emissions. The 4f orbital is shielded from the surroundings by the filled 5s² and 5p⁶ orbital. Therefore, the influence of the host lattice on the optical transitions within the 4fⁿ configuration is small [25, 26].

The nonlinear optical property of LaF₃:Ce³⁺, Pr³⁺, Sm³⁺ in de-ionized water was tested by passing the output of Nd: YAG Quanta ray laser emitting 1064 nm, generating about 6mJ / pulse through the samples. SHG is a key technology as frequency doublers of laser light. The SHG efficiency of LaF₃:Ce³⁺, Pr³⁺, Sm³⁺ nanocrystals were determined in de-ionized water by modified Kurtz and Perry technique [27]. Crystalline powder of Potassium dihydrogen phosphate (KDP) taken as the reference material. The measured relative SHG efficiency of LaF₃:Ce³⁺, Pr³⁺, Sm³⁺ in de-ionized water with respect to KDP crystal is 0.186.

V. CONCLUSION

LaF₃ nanocrystals successfully have been synthesized using LaCl₃ + CeCl₃ + PrCl₃ + SmCl₃ and NH₄F in deionized water. Elongated & assorted size hexagonal geometry of LaF₃ nanocrystals has been observed. XRD and TEM studies indicate that the average particle size is 20 nm. The absorption edge in UV spectra is found at 250 nm corresponding to energy of 4.9eV. It further shows a wide transparent window lying between 200 nm-800 nm. For LaF₃:Ce³⁺, Pr³⁺, Sm³⁺ nanocrystals emission of blue color (458 nm) has been observed with at an excitation wavelength of 254 nm. The SHG property was tested by using Nd: YAG laser. The second harmonic efficiency of LaF₃:Ce³⁺, Pr³⁺, Sm³⁺ nanocrystals is found to be 0.186 in deionized water using KDP as standard material.

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