

Photoluminescence Properties of LaF₃:Ce Nanoparticles Embedded in Polyacrylamide

Thiruvallankadu Krishnamoorthy Srinivasan^{1*}, Balasubramaniam Venkatraman¹, Durairaj Ponraju², Akhilesh Kumar Arora³

¹Radiological Safety and Environment Group, Indira Gandhi Centre for Atomic Research, Kalpakkam, India

²Physical Chemistry Section, Reactor Engineering Group, Indira Gandhi Centre for Atomic Research, Kalpakkam, India

³Condensed Matter Physics Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, India

Email: *tkrsri@igcar.gov.in

Received August 1, 2012; revised August 29, 2012; accepted September 6, 2012

ABSTRACT

Oleic acid coated LaF₃:Ce nanoparticles were synthesized and embedded in polyacrylamide through a two-step procedure. In the first step nanoparticles were synthesized by adopting co-precipitation technique and in the second step, nanoparticles were embedded in polyacrylamide (PAM) hydro-gel through the solution route. Nanoparticles were characterized for their crystal structure, particle size, organic coating and photoluminescence behavior using X-ray diffraction, SEM, TEM, FTIR and photoluminescence spectroscopy. Size of nanoparticles was estimated using the Scherrer formula. Polymer nano composite (PNC) material was synthesized with two different weight percent of the nano powder viz 1.634% (termed as NG1) and 0.1664% (termed as NG2). The nanoparticle-polymer composite exhibits emissions at 308 and 370 nm. A comparison of the emission spectrum of LaF₃:Ce nano-powder pellet with that of the composite suggests a suppression of emission from the PAM host in the composite.

Keywords: Lanthanum Fluoride Cerium; Polyacrylamide; Oleic Acid; Photoluminescence; Nanocomposite

1. Introduction

In the quest for new optical materials, polymer nanocomposites (PNC) are currently being explored. Luminescent PNC materials are inexpensive and can be synthesized in different shapes and sizes. These materials find applications in sensing high energy X- and gamma radiation. In this context rare-earth doped nanophosphor with sizes <100 nm in transparent polymer composites have been studied. In order to protect the nanophosphor material from the host environment and to achieve better dispersibility in the monomer, these are coated with organic materials such as oleic acid. These nanoparticles possess unique chemical and optical features such as low toxicity, characteristic narrow emission, and excellent photo stability [1].

Cerium doped Lanthanum halides display desirable high light yields with fast decay component. Inorganic as well as organic surfactant capped LaF₃:Ce have been extensively studied [2-6]. Considerable interest is shown in surface modification of luminescent nanoparticle with functional groups, which increases possibility of uniform embedding in different transparent polymer hosts [7-9]. The methods involve synthesizing nanoparticles first and

then blend into the required matrices through intimate mixing of nanoparticles with monomer solution and subsequent immobilization through polymerization. In this work, we report the synthesis and embedding of oleic acid coated LaF₃:Ce nanoparticles in polyacrylamide host medium. The photoluminescent characteristics of the synthesized polymer nanocomposite are presented.

2. Experimental Details

LaF₃:Ce embedded polyacrylamide (PAM) disc was made in two steps. LaF₃:Ce was synthesized by co-precipitation technique. First, oleic acid coated nano cerium doped lanthanum fluoride was synthesized as ref [10]. Next, the powder was embedded inside PAM disc using a slightly different procedure that reported in [11]. A solution containing 8 g of acrylamide in 10 g of deionized water was prepared. LaF₃:Ce embedded discs were synthesized using the acrylamide solution with two different nano-powder concentration of 16.6 and 1.75 mg/ml. The mixtures were thoroughly stirred for 30 minutes and placed in an ultrasonic water bath for 20 minutes for the gas bubbles, if any, to escape. Then the mixture was polymerized in the gamma chamber (GC 5000) containing 4.8 TBq activity of Cobalt-60 radioisotope and irradiated for four minutes to a gamma dose of 221 Gy. The po-

*Corresponding author.

lymerized samples were taken dried in a vacuum oven at 90°C for 4 h. The discs were circular in shape with 2 cm diameter and 1 cm thickness. The weight percent of the nano powder in the polymer composites were 1.634% (termed as NG1) and 0.1664% (termed as NG2) respectively. The NG1 disc was little opaque while NG2 disc was a completely transparent. Similarly another pure polyacrylamide disc without LaF₃:Ce (blank-PAM) was prepared for comparing the optical behavior.

The structural characterization was carried out using X-ray diffraction measurements using a Shimadzu (XRD-6000) diffractometer equipped with a CuK_α (1.5406 Å) X-ray source. The micrographs of as prepared samples were obtained using field emission scanning electron microscope [FESEM, ZEISS]. TEM [JEOL 2000 EX II], FTIR spectra were recorded using HORIZON MB3000 ABB spectrophotometer in order to check the surface organic coating and the spectrum was measured in transmission mode using KBr disc. In order to prepare the TEM specimen, the powder was ultra-sonicated in methanol medium and one drop of the suspension was loaded on to carbon coated grids. This was dried under a lamp for over 12 hours and loaded into the specimen carousel of the JEOL 2000 EX II TEM operated at 200 kV. Electron diffraction, diffraction contrast and phase contrast imaging was also carried out. Photoluminescence (PL) measurements on the discs were carried out using a SHIMADZU spectrophotometer [Fluorolog-RF-5301PC] in the range of 200 - 400 nm at 1.5 nm slit widths and in high sensitivity mode.

3. Results and Discussion

Figure 1 shows the XRD pattern of oleic acid coated nanoparticles. The peak positions and intensities agree well with the data reported in the JCPDS standard card (32-0483) for pure hexagonal LaF₃:Ce particles. The large width of the diffraction peaks is an indication of the nanosize of the particles. The structure was determined to be hexagonal with $a = 7.1889$ and $c = 7.3231$ Å. The sizes of the nanoparticles were calculated from the XRD data based on the Debye-Scherrer formula. The results showed that the oleic-coated nanoparticle size was 11 nm.

Figure 2(a) shows the FESEM micrograph of Ce-doped LaF₃ nanoparticles synthesized at 70°C. The particles were of spherical and slightly oblong in shape with the diameter ranging between 8 and 36 nm. However some agglomeration of particles leading to bigger particle sizes was also observed. The modified approach of Feng Wang *et al.* [3] yielded primary particles of smaller size. **Figure 2(b)** shows the size distribution of the particles. The 60 and 85 nm particles are essentially aggregates and don't correspond to the individual particles. It is clear that majority of particles were between 8 and 11

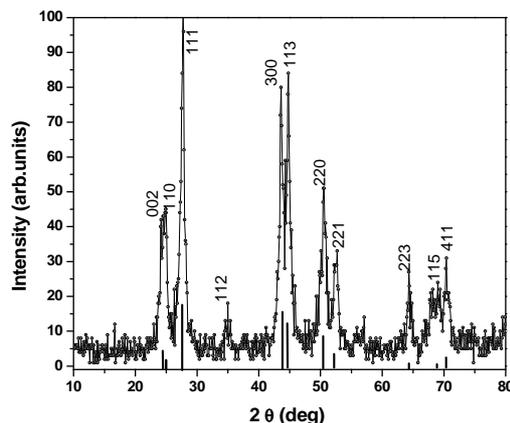
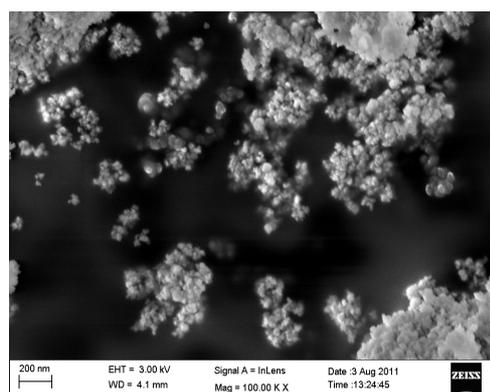
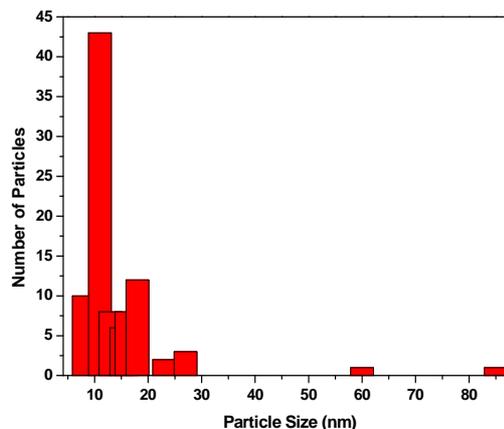


Figure 1. XRD pattern of LaF₃:Ce nanoparticles. The reported reference pattern is also shown for comparison (JCPDS card No. 32-0483).



(a)



(b)

Figure 2. (a) FESEM micrograph image of LaF₃:Ce nanoparticles; (b) The size distribution plot of FESEM micrograph image of LaF₃:Ce nanoparticles.

nm sizes. In order to know with what sizes the particles have formed, a size distribution plot was arrived at by analyzing the obtained SEM micrograph using the Image J software. As the particle sizes are small, more weight % can be incorporated in the polymer retaining the opti-

cal transparency.

Figure 3 shows the high resolution TEM image of as synthesized Oleic acid coated $\text{LaF}_3\text{:Ce}$ nanoparticles. The coating thickness was found to be around 3.5 nm. It can be seen that the nanoparticles have a certain degree of agglomeration.

Figure 4 shows the FT-IR spectra of both pure oleic acid (curve a) and oleic acid coated $\text{LaF}_3\text{:Ce}$ nanoparticles (curve b). In curve a&b, the two band at 2922 and 2856 cm^{-1} are corresponds to CH_2 asymmetric and symmetric stretching vibrational frequency respectively [12]. A weak band at 3011 cm^{-1} indicates the presence of unsaturated alkene ($=\text{C-H}$) group. In curve (b) presence of CH_2 stretching vibrational peak reveals the presence of organic surfactant on surface of $\text{LaF}_3\text{:Ce}$ nano particle. In curve (a) strong peak at 1708 cm^{-1} attributed to stretching vibration of C=O group. When compared to curve (a) in curve (b) the reduction peak intensity of 1708 cm^{-1} C=O stretching vibration and appearance of two new absorption peaks at 1582 and 1546 cm^{-1} are due to carboxylate formation on the nano $\text{LaF}_3\text{:Ce}$ surface, which are attributed to the characteristic of the asymmetric (COO^-) stretch and the symmetric (COO^-) stretch [13]. The disappearance of C=O stretching vibration and presence of two COO^- stretching confirms that Oleic acid is not physically adsorbed on the surface of $\text{LaF}_3\text{:Ce}$ nano particle, its coordinated through carboxylate group with nano particle. These results confirm that Oleic acid molecules were chemisorbed on nano $\text{LaF}_3\text{:Ce}$ particles.

Figure 5 shows the excitation and emission spectrum of the 5 mole % Ce-doped LaF_3 nanoparticle pellet. The excitation spectrum was recorded for the sample by scanning the excitation wavelength from 200 nm to 280 nm, while the emission monochromator was fixed at 306 nm with spectral bandpass at 1.5 nm. The excitation peak was found to be at 251 nm (curve a), which closely agrees with the position of lower energy levels in the 4f to 5d (4.96 eV) configuration of cerium. The emission spectrum was acquired by exiting the pellet at 251 nm wavelength in the region between 265 nm to 400 nm with the same spectral band pass. The broad emission

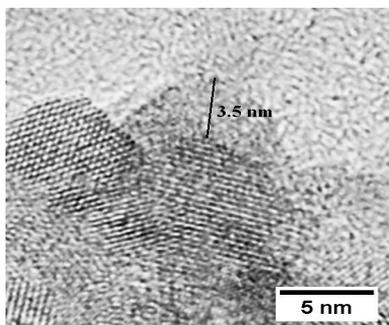


Figure 3. HR-TEM image of the oleic acid coated $\text{LaF}_3\text{:Ce}$ nanoparticles.

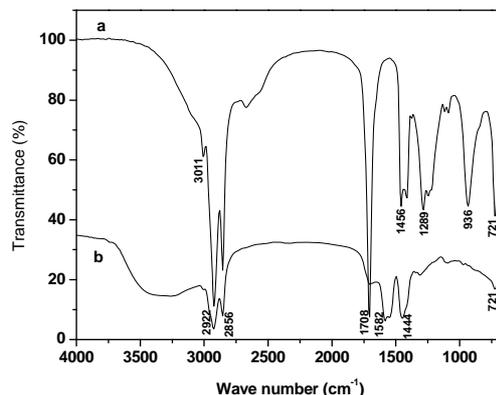


Figure 4. FTIR spectrum of (a) oleic acid and (b) oleic acid coated $\text{LaF}_3\text{:Ce}$ nano-powder.

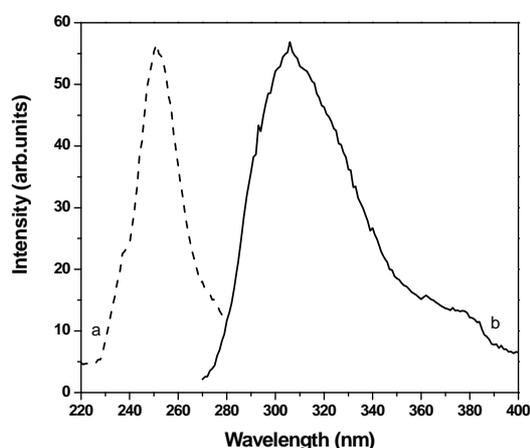


Figure 5. PL excitation and emission spectra of oleic acid coated 5 mole % Ce^{3+} -doped LaF_3 nanoparticle pellets (a) Excitation ($E_m = 306$ nm); (b) Emission ($E_x = 251$ nm).

peak found at 306 nm (curve b) can be ascribed to 5d to 4f transitions revealing the nature of Ce^{3+} emission [14]. One can see that the emission from the pellet is intense. The presence of hydrocarbon chains on the surface might quench the output light intensity by radiation less energy transfers.

Figure 6 shows the excitation and emission spectra of the blank-PAM, $\text{LaF}_3\text{:Ce}$ embedded PAM-NG1 and NG2 discs. The spectra of blank-PAM and nanocomposite materials were recorded in the region 220 - 400 nm. Curves a and b respectively correspond to the excitation and emission of blank-PAM disc. The emission peak at 370 nm corresponds to the 253 nm absorption of blank-PAM. Curves c (NG2), e (NG1) and d (NG2), f (NG1) respectively correspond to the excitation and emission spectra of doped-PAM discs. One can see that the emission spectra of the composite exhibit two peaks, one at 308 nm and the other at 370 nm. The spectral positions slightly shift towards the blue region as compared to that of pure $\text{LaF}_3\text{:Ce}$ nano-powder pellet. It is important to point out that the 253 nm excitation of the nano

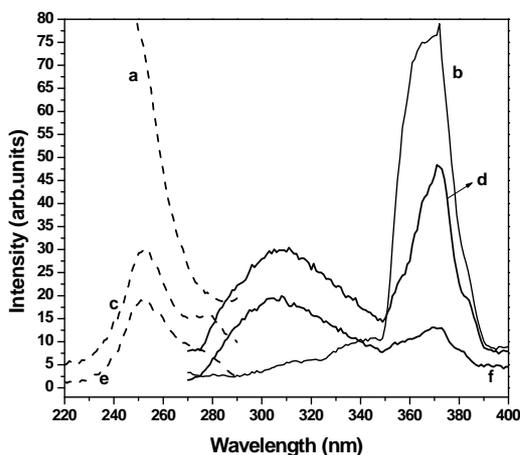


Figure 6. Excitation and emission spectra of blank PAM and $\text{LaF}_3:\text{Ce}^{3+}$ embedded PAM discs. (a) Blank PAM excitation ($E_m = 370$ nm); (b) Blank PAM emission ($E_x = 253$ nm); (c) and (e) NG2 and NG1 excitation ($E_m = 308$ nm); (d) and (f) NG2 and NG1 emission ($E_x = 253$ nm).

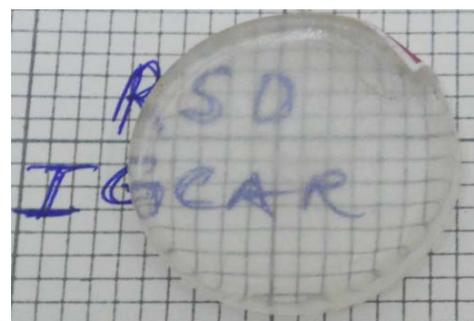
composite gives much lower intensity of the 370 nm emission compared to that of blank-PAM. This suggests that doping the PAM matrix by the nanoparticles causes suppression of the photoluminescent emission from the polymer host. The 370 nm PL emission of the host matrix is further suppressed when the doping concentration is increased (curve f). Thus the present results suggest that only the nano-particles are selectively excited while the host excitation is transferred to the nanoparticles. This property may be useful where interference from the host is to be avoided. Lower intensity of the 308 nm emission from the nanocomposite disc NG1 might be due to larger opacity. This suggests that low-doped NG2 translucent composites can be used as efficient intrinsic PL emission materials with reduced interference from the host. **Figures 7(a)** and **(b)** show the photographs of the synthesized PAM discs. It is clear that NG2 disc is translucent and NG1 disc is little opaque.

4. Conclusion

$\text{LaF}_3:\text{Ce}$ embedded in polyacrylamide discs were synthesized by a simple two step procedure. The particle size was estimated to be of 11 nm from XRD analysis. The FESEM micrograph confirmed that the particle sizes were distributed between 11 and 85 nm. FTIR spectra confirmed the presence of hydrocarbon chains surrounding the nano particles. TEM image analysis confirmed the presence of 3.5 nm thickness coating. The photoluminescent study confirmed the presence of the nanophosphor in the organic matrix. Although $\text{LaF}_3:\text{Ce}$ nanoparticles and PAM exhibit characteristic PL emission at 308 and 370 nm respectively, both these materials have excitation peaks at 253 nm. The nanocomposite is found to have reduced emission from the host matrix as com-



(a)



(b)

Figure 7. Photographs of polymer nanocomposite discs (a) NG1, (b) NG2.

pared to pure PAM disc, suggesting selective excitation of the nanoparticles and suppression of the PL from the matrix.

5. Acknowledgements

The authors thank S. C. Chetal, Director IGCAR for his support and encouragement. The authors also thank H. Krishnan for the help in synthesis and Dr. B. S. Panigrahi for the help during PL measurements. The authors also thank S. Kalavathi for the help rendered during XRD measurements and Dr. M. Kamarudin during the FESEM measurements. The authors also thank Dr. Mohandas, Dr. Diwakar and Chanchal Gosh for their help in TEM measurements and analysis. The authors also thank Dr. V. Meenakshisundaram and Dr. M. T. Jose for their useful discussions and support.

REFERENCES

- [1] M.-Y. Xie, L. Yu, H. He and X.-F. Yu, "Synthesis of Highly Fluorescent $\text{LaF}_3:\text{Ln}^{3+}/\text{LaF}_3$ Core/Shell Nanoparticles by a Surfactant-Free Aqueous Solution Route," *Journal of Solid State Chemistry*, Vol. 182, No. 3, 2009, pp. 597-601. doi:10.1016/j.jssc.2008.12.011
- [2] S. S. Mou, M. J. Islam and A. B. M. Ismail, "Photoluminescence Properties of LaF_3 -Coated Porous Silicon," *Materials Sciences and Applications*, Vol. 2, No. 6, 2011, pp. 649-653.
- [3] F. Wang, Y. Zhang, X. P. Fan and M. Q. Wang, "Facile

- Synthesis of Water-Soluble LaF₃:Ln³⁺ Nanoparticles,” *Journal of Materials Chemistry*, Vol. 16, No. 11, 2006, pp. 1031-1034. [doi:10.1039/b518262j](https://doi.org/10.1039/b518262j)
- [4] J. Stouwdam and F. van Veggel, “Near-Infrared Emission of Redispersible Er³⁺, Nd³⁺, and Ho³⁺ Doped LaF₃ Nanoparticles,” *Nano Letters*, Vol. 2, No. 7, 2002, pp. 733-737. [doi:10.1021/nl025562q](https://doi.org/10.1021/nl025562q)
- [5] G. S. Yi and G. M. Chow, “Colloidal LaF₃: Yb, Er, LaF₃: Yb, Ho and LaF₃: Yb, Tm Nanocrystals with Multicolor up Conversion Fluorescence,” *Journal of Materials Chemistry*, Vol. 15, No. 41, 2005, pp. 4460-4464. [doi:10.1039/b508240d](https://doi.org/10.1039/b508240d)
- [6] T. Kezuka, M. Konishi, T. Isobe and M. Senna, “Preparation and Properties of Nanocrystalline ZnS: Mn-Polymer Composite Silms,” *Journal of Luminescence*, Vol. 87, No. 89, 2000, pp. 418-420. [doi:10.1016/S0022-2313\(99\)00438-X](https://doi.org/10.1016/S0022-2313(99)00438-X)
- [7] A. Klausch, H. Althues, C. Schrage, P. Simon, A. Szatkowski, M. Bredol, D. Adame and S. Kaskel, “Preparation of Luminescent ZnS:Cu Nanoparticles for the Functionalization of Transparent Acrylate Polymers,” *Journal of Luminescence*, Vol. 130, No. 4, 2010, pp. 692-697. [doi:10.1016/j.jlumin.2009.11.021](https://doi.org/10.1016/j.jlumin.2009.11.021)
- [8] V. Kalima, I. Vartiainen, T. Saastamoinen, M. Suvanto, M. Kuittinen and T. T. Pakkanen, “UV-Curable ZnS/Polymer Nanocomposite for Replication of Micron and Submicron Features,” *Optical Materials*, Vol. 31, No. 10, 2009, pp. 1540-1546. [doi:10.1016/j.optmat.2009.03.003](https://doi.org/10.1016/j.optmat.2009.03.003)
- [9] Y. Chen, X. Ji, Q. Sun, S. Jiang and B. Jiang, “A Novel Route for the Preparation of CdS Nanocrystal—Poly (Acrylic Acid) Composites Using γ -Radiation,” *Journal of Non-Crystalline Solids*, Vol. 311, No. 3, 2002, pp. 314-317. [doi:10.1016/S0022-3093\(02\)01854-9](https://doi.org/10.1016/S0022-3093(02)01854-9)
- [10] T. K. Srinivasan, B. Venkatraman, D. Ponraju, M. Kamarudin and A. K. Arora, “Synthesis and Characterization of Surface Modified LaF₃:Ce Nano Particles,” *International Conference on Nanoscience, Engineering and Technology (ICONSET)*, Chennai, 28-30 November 2011, pp. 528-531. [doi:10.1109/ICONSET.2011.6168023](https://doi.org/10.1109/ICONSET.2011.6168023)
- [11] N. Pewda, L. Mihut, I. Baltog, T. Velula and V. Teodorescu, “Optical Properties of Low-Dimensional PbI₂ Particles Embedded in Polyacrylamide Matrix,” *Journal of Optoelectronics and Advanced Materials*, Vol. 8, No. 3, 2006, pp. 909-913.
- [12] N. Q. Wu, L. Fu, M. Su, M. Aslam, K. C. Wong and V. P. Dravid, “Interaction of Fatty Acid Monolayers,” *Nano Letters*, Vol. 4, No. 2, 2004, pp. 383-386.
- [13] J. S. Wang, J. Hu, D. H. Tang, X. H. Liu and Z. Zhen, “Oleic Acid Modified LaF₃: Er, Yb Nanocrystals and Their Polymer Hybrid Materials for Potential Optical-Amplification Applications,” *Journal of Materials Chemistry*, Vol. 17, No. 16, 2007, pp.1597-1601. [doi:10.1039/b617754a](https://doi.org/10.1039/b617754a)
- [14] P. Dorenbos, “5D-Level Energies of Ce³⁺ and the Crystalline Environment. I. Fluoride Compounds,” *Physical Review B*, Vol. 62, No. 23, 2000, pp. 15640-15649. [doi:10.1103/PhysRevB.62.15640](https://doi.org/10.1103/PhysRevB.62.15640)