Appendix 1
SYNOPSIS

OF THE THESIS TO BE SUBMITTED TO THE UNIVERSITY OF MUMBAI FOR
THE DEGREE OF DOCTORATE OF PHILOSOPHY IN SCIENCE (PHYSICS)

TITLE OF THE THESIS : SYNTHESIS AND CHARACTERISATION OF
DOPED LANTHANUM FLUORIDE
NANOPARTICLES AND MODIFICATION
OF THEIR SURFACE USING AMINO ACIDS

SUBJECT : PHYSICS

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MONTH & YEAR OF REGISTRATION : 04 May 2012

REGISTRATION NUMBER : 52/04 May 2012

DATE OF SYNOPSIS SUBMISSION : 23/03/2015

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SYNTHESIS AND CHARACTERISATION OF DOPED LANTHANUM FLUORIDE NANOPARTICLES AND MODIFICATION OF THEIR SURFACE USING AMINO ACIDS

The synopsis of the thesis entitled “Synthesis and Characterisation of Doped Lanthanum Fluoride Nanoparticles and Modification of their Surface using Amino Acids”, presents the studies on the synthesized nanocrystals. This work has been carried out independently by the candidate Singh Amit Tribhuwan under the guidance of Dr. Mahendra M Khandpekar, Associate Professor in Physics, Material Research Lab, Department of Physics, Birla College of Arts, Science, Commerce, Kalyan - 421304.

Advances in upconversion fluorescent nanomaterials has rare earth materials as frontrunners, among them the trivalent lanthanum ion (Ln³⁺) doped fluoride nanomaterials find varied applicability in different fields like photonic crystals [1], biological labeling [2], scintillators [3], optical amplifiers [4], drug and gene delivery [5] and light emitting diodes [6]. Furthermore hybrid nanoparticles containing organic inorganic dopants provide new avenue in nanoparticle particle application. The LaF₃ host matrix have low phonon energy (350 cm⁻¹) which minimizes the non radiative transitions and quenching of excited state of rare earth ions resulting in high quantum yield with longer life times. Lanthanum fluorides have been observed to have wide spectral window with large band gap which avoids self-absorption making them suitable for optoelectronic applications.

The surface modification of the rare earth (cerium and dysprosium) doped LaF₃ doped has been done by amino acids [7]. The ligands from the amino acids lead to polydentate chelation of rare earth doped LaF₃ nanoparticles and control the growth of the nanoparticles while reducing the aggregation of synthesized nanoparticles. Amino acid
have been found to possess strongly charged ligand molecules which forms a dense layer on the rare earth doped LaF$_3$ nanoparticles and stabilize the particles for longer time.

The structural and morphological characterization of the synthesized nanocrystals have been done by X-ray diffraction (XRD), Transmission Electron microscopy (TEM), Scanning Electron microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDAX) and Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AEP). The vibrational studies for confirming the presence of ligands on the surface of the nanoparticles have been done by Fourier Transform Infrared Spectra (FTIR) and FT-Raman Spectra. The optical studies have been done by Uv-Visible spectra, Photoluminescence Spectra and Non Linear Optical (NLO) measurements. The thermal studies to study the phase changes and decomposition of the synthesized nanocrystals have been done by TGA and DTA profiles. The electrical /dielectric characteristics of the synthesized nanocrystals have been reported in the thesis. The thesis comprises of six chapters and the contents of each chapter are presented in brief below.

**Chapter I Introduction**

This chapter gives general introduction to green synthesis [8-9], nucleation and growth, luminescence, inorganic and organic doping and theoretical aspect of lanthanum fluoride (LaF$_3$) nanocrystals. This chapter also gives the literature review of the research articles recently reported along with the scope of the present work.

**Chapter II Synthesis and Characterisation Techniques**

The chapter reports the materials used, the wet chemical synthesis of the doped LaF$_3$ nanoparticles and the instruments used for their characterization. The glycine doped LaF$_3$:Ce has been synthesized using reagents LaCl$_3$.7H$_2$O (0.064mol,0.16637gm), CeCl$_3$.7H$_2$O (0.064mol,0.03570gm), Glycine HNH$_2$COOH (0.064mol,0.007206gm) and
NH₄F (0.576mol, 0.2133gm). Lanthanum chloride, Cerium chloride and Glycine collectively form one part of the solution and ammonium fluoride forms three part of the solution of the total composition giving 1:3 molar proportion[10]. The chemical reaction for the synthesis of one of the sample being

\[
\text{LaCl}_3\cdot 7\text{H}_2\text{O} + \text{CeCl}_3\cdot 7\text{H}_2\text{O} + \text{HNH}_3\text{COOH} + 3 \text{NH}_4\text{F} \rightarrow \\
\text{HCN(COOH)LaF}_3\cdot \text{Ce} + 4\text{NH}_3 + 16\text{H}_2\text{O} + 3\text{Cl}_2
\]

The solution has been prepared in a 100 ml beaker by taking 7 ml of lanthanum fluoride (LaCl₃·7H₂O) and mixing 1.5 ml of cerium chloride (CeCl₃·7H₂O) and 1.5 ml of glycine (HNH₃·COOH) and finally 10 ml of ammonium fluoride has been swiftly injected in the beaker by a syringe. The glycine doped LaF₃·Ce (GLFC) nanocrystals in the form of precipitate appear after few seconds of mixing. The precipitate has been dried in SHARP microwave oven (800W, 24L) for 30 minutes. The nanocrystals have been further washed in distilled water several times and subsequently dried in microwave oven.

The XRD analysis have been done using PANALYTICAL X’PERT PROMPD diffractometer model using CuKα radiation (λ =1.5405 Å) with scanning rate of 2° per min in the 2θ range from 0° to 80°. The Transmission Electron Microscopy has been done on PHILIPS (CM 200) transmission electron microscope having 0.24 nm resolution with operating voltage range from 20-200 kV. ZEISS ULTRA scanning electron microscope (SEM) instrument, with accelerating voltage (0.1 kv to 30 kv), beam current (100 nA), resolution (0.8 nm at 30 kV), magnification (10x to 1000kx) and image structure down to 10 nm sizes have been used to study morphology of synthesized nanocrystals. Quanta 200 FEG scanning electron microanalysis instrument have been used to obtain Energy Dispersive X-Ray (EDAX) spectra. ARCOS spectrometer has been used to detect Dysprosium in the samples by Inductively Coupled Plasma-Atomic Emission
Spectrometer (ICP-AES). The specification of the instrument used is, R.F. generator having maximum power 1.6 kW at 27.12 MHz with wavelength range from 130 nm to 770 nm and having resolution of 9 pico meter. The Perkin Elmer Instrument has been employed to record the FTIR spectrum in the wavenumber range of 450 cm\(^{-1}\) – 4000 cm\(^{-1}\). The FT-Raman spectrum has been obtained on Bruker RFS 27 Stand-alone FT-Raman Spectrometer in scan range of 50 cm\(^{-1}\)- 4000 cm\(^{-1}\) with resolution of 2 cm\(^{-1}\). Cary 5E spectrophotometer have been used to obtain ultra violet (UV) high-resolution absorption spectra. Luminescence Spectrometer (Perkin Elmer Corp) has been employed to obtain Fluorescence spectrum using a high energy pulsed Xenon source for excitation and FL Win Lab™ software. The thermogravimetric profile have been obtained on Perkin Elmer Diamond TG/DTA instrument with temperature range ambient to 1500°C, heating rate 0.01° C/min - 100° C/min, balance type horizontal differential type, atmosphere (air, inert gas, vacuum 10\(^{-2}\) torr) and purge gas flow rate 0 - 1000 ml/min. The nonlinear optical (NLO) response to assess the second harmonic generation efficiency of the samples have been done by using an Nd-YAG laser source (Quanta Ray, Spectra Physics, 1064 nm).

HIOKI 3532 LCR HITESTER (50 Hz -5 MHz) has been used to study the dielectric constant and dielectric loss as a function of frequency. The measurement of electrical resistivity has been carried with the IV setup consisting of regulated D.C power supply and a digital Pico ammeter (DPM 111) from Scientific Equipment.

**Chapter III Structural and Morphological Studies**

In this chapter the XRD analysis ,TEM images, SEM images SAED Pattern , EDAX and ICP-AES analysis of the synthesized nanoparticles have been presented .The lattice plane spacing for hexagonal systems has been calculated using the formula \((1/d^2) = (4/3)\)
(h^2+hk+k^2) (1/a^2) + (l^2/c^2). The observed and calculated interplanar lattice spacing 'd' for glycine doped LaF₃:Ce (GLFC) for (111) plane has been obtained as 3.211 Å and 3.235 Å respectively. The cell parameters confirms the hexagonal crystal phase structure of bulk LaF₃ with JCPDS card no [32-0483] having lattice parameters a = b = 7.187 Å and c = 7.350 Å and α = β = 90⁰, γ = 120⁰ along with the space group P6₃c1(165) [11]. The Debye-Scherrer formula D = (0.90 λ / β cosθ) gives the average particle size for the synthesized nanoparticle with full width half maximum (FWHM) of 0.3656⁰ at the strongest peak corresponding to 2θ = 27.75⁰ with Cu Kα radiation wavelength 1.5406 Å as 22 nm. Similarly the particle sizes have been calculated for the other samples and have been found in the range of 12 nm to 22 nm. The average particle size have been in nanoscale dimension, which has been confirmed by broadening of diffraction peaks and it also minimizes coherent scattering i.e., Rayleigh’s scattering. The low intensity peaks in the diffraction pattern can be attributed to reflections from ligands present on the surface of the synthesized nanoparticles.

The TEM image of the as prepared (GLFC) nanocrystals shows the particles have been well separated with mostly hexagonal morphology. The SEM image of the (GLFC) nanocrystals shows globular agglomeration with assorted sizes. The agglomeration observed confirms the bonding due to the functional groups of amino acid dopant confirming the surface modification of synthesized nanocrystals. The selected area electron diffraction (SAED) pattern of (GLFC) nanocrystals shows strong diffraction rings, which confirms the crystallinity of the nanocrystals formed and also ascertains that the hexagonal structure of the LaF₃ has been retained after the doping. The EDAX analyses of the (GLFC) nanocrystals show traces of lanthanide, cerium, fluorine, carbon, nitrogen and chlorine along with other impurities. The chlorine impurities can be
removed by further washing of the samples. The lattice parameters, average particle size and unit cell volume for different synthesized nanocrystals have been listed in the table 1.

**Table 1.** Lattice Parameters of Synthesized Nanoparticles.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Sample</th>
<th>a = b (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>D nm</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Glycine@LaF₃:Ce</td>
<td>7.173</td>
<td>7.212</td>
<td>1.005</td>
<td>15.55</td>
<td>321.3</td>
</tr>
<tr>
<td>2</td>
<td>Alanine@LaF₃:Ce</td>
<td>7.181</td>
<td>7.188</td>
<td>1.009</td>
<td>22.39</td>
<td>320.9</td>
</tr>
<tr>
<td>3</td>
<td>Tyrosine@LaF₃:Ce</td>
<td>7.248</td>
<td>7.287</td>
<td>1.005</td>
<td>19.95</td>
<td>331.5</td>
</tr>
<tr>
<td>4</td>
<td>Glutamine@LaF₃:Ce</td>
<td>7.128</td>
<td>7.373</td>
<td>1.034</td>
<td>12.38</td>
<td>324.4</td>
</tr>
<tr>
<td>5</td>
<td>Cysteine@LaF₃:Ce</td>
<td>7.447</td>
<td>7.160</td>
<td>0.961</td>
<td>17.30</td>
<td>330.7</td>
</tr>
<tr>
<td>6</td>
<td>Glycine@LaF₃:Dy</td>
<td>7.370</td>
<td>7.167</td>
<td>0.972</td>
<td>16.60</td>
<td>327.9</td>
</tr>
<tr>
<td>7</td>
<td>Alanine@LaF₃:Dy</td>
<td>7.112</td>
<td>7.340</td>
<td>1.320</td>
<td>21.61</td>
<td>321.6</td>
</tr>
<tr>
<td>8</td>
<td>Tyrosine@LaF₃:Dy</td>
<td>7.408</td>
<td>7.166</td>
<td>0.967</td>
<td>22.89</td>
<td>329.4</td>
</tr>
<tr>
<td>9</td>
<td>Glutamine@LaF₃:Dy</td>
<td>7.177</td>
<td>7.182</td>
<td>1.006</td>
<td>15.01</td>
<td>320.4</td>
</tr>
<tr>
<td>10</td>
<td>Cysteine@LaF₃:Dy</td>
<td>7.182</td>
<td>7.264</td>
<td>1.014</td>
<td>14.31</td>
<td>324.5</td>
</tr>
</tbody>
</table>

**Chapter IV- Vibrational and Thermal studies**

In this chapter the results for FTIR and FT RAMAN studies of the synthesized samples have been discussed. The band assignments in the mid infrared region extending from 4000 cm⁻¹ to 500 cm⁻¹ have been obtained by FT-IR [12-13] spectra and band assignments below 500 cm⁻¹ in the far infra-red region have been given studied by FT-Raman spectra [14-15]. The band assignment for glycine doped LaF₃:Ce (GLFC) nanoparticles have been given in the table 2.
Table 2. Wavenumber Assignments of Glycine doped LaF$_3$:Ce Nanoparticles.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Sr. No</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3455.55</td>
<td>ν$_{OH}$ (H$<em>2$O)$</em>{(as)}$</td>
<td>5</td>
<td>2316.66</td>
<td>C-H stretch</td>
</tr>
<tr>
<td>2</td>
<td>2916.67</td>
<td>C-H alkyl group</td>
<td>6</td>
<td>1628.04</td>
<td>H$_2$O bending</td>
</tr>
<tr>
<td>3</td>
<td>2833.33</td>
<td>C-H alkyl group</td>
<td>7</td>
<td>1566.66</td>
<td>δ$_{s}$(NH$_3^+$)</td>
</tr>
<tr>
<td>4</td>
<td>2364.20</td>
<td>C-H stretch</td>
<td>8</td>
<td>1416.66</td>
<td>δ(CH$_2$)</td>
</tr>
</tbody>
</table>

The chelation of polydentate ligands lead in formation of a stable coordination compound NHC(COOH)LaF$_3$:Ce. The coordination compound thus formed has carboxyl group (COOH) and a nitrile group (HCN) as attachment along with other functional groups like C-H alkyl group, δ(CH$_2$), etc. The wave numbers of organic attachment for the different samples have been tabulated in the chapter. The FT-Raman spectra of the samples synthesized amino acid doped LaF$_3$:Ce and LaF$_3$:Dy nanocrystals shows torsional motion of lattice due to electron phonon interaction corresponding to $A_{1g}$ phonon mode and fundamental $E_g$ phonon mode.

The phase changes and the thermal stability of the synthesized (GLFC) nanocrystals have been studied by TGA/DTA profile by heating the nanocrystals samples from 50$^\circ$C to 920.0$^\circ$C at 15$^\circ$C per minute [16-17]. The TGA profile shows weight loss in three stages, first below the temperature of 150$^\circ$C which has been due to loss of residual water molecules on the nanocrystals surface, second sharp weight loss of 50.54% has been observed between 200$^\circ$C to 300$^\circ$C of which can be attributed to removal of OH$^-$, NH$_4$F and NH$_4$Cl from the particle surface thus confirming the modification of the surface of the synthesized nanocrystals by functional groups from glycine and third between 340$^\circ$C to 400$^\circ$C of 4.46%, indicating the crystalline nature of nanocrystals formed. Finally
beyond the temperature of 600°C the weight loss indicates decomposition of lanthanides structure of the synthesized nanocrystals. The DTA profiles shows the endothermic peak at the 244.4 °C with onset temperature at 194.6 °C indicating the decomposition of the functional group on the surface of the synthesized nanocrystals which has been corroborated with TGA profile. The exothermic peak at 550 °C indicates crystallization of the nanocrystals and beyond this temperature the decline in the DTA graph has been ascribed to decomposition of lanthanides. The structural stability from the XRD and TEM measurements has been reconfirmed with the thermal stability from TGA/DTA analysis. Similarly the TGA/DTA of the other samples have been reported and discussed in this chapter.

**Chapter V – Optical and Electrical Studies**

The UV-visible spectrum, photoluminescence (PL) spectrum and the electrical studies of the synthesized nanocrystals have been discussed in this chapter. The synthesised nanocrystals have been observed to show multiple absorption edges in the range of 3.402 eV to 5.781 eV, which indicates artificial atom like structure of the nanocrystals [18]. The wide transparent window between 400 nm to 800 nm suggests the potential application of nanoparticles in optoelectronic devices.

The PL studies show 4f→5d transitions of the synthesized nanocrystals. The Dieke diagram shows Ce³⁺ consist of two multiplets of the 4f ground state ²F⁵/₂ and ²F⁷/₂, due to spin orbit splitting, with the transition being attributed from lowest 5d level to the multiplets of the 4f ground state [19-20]. The excitation peak has been at 616 nm and the emission peak has been at 338 nm which shows the up conversion nature of the (GLFC) nanocrystals prepared. Thus the upconversion nature of synthesized nanocrystals makes it suitable for bio imaging and biotagging. The sharp chromaticity of the glycine doped
LaF$_3$: Ce (GLFC) nanoparticles can be attributed to disorder on the surface of the nanoparticles, which can be corroborated to the replacement of lanthanum ions with rare earth ions in the lattice and decrease in its surface area. The Kurtz Perry techniques have been employed to study second harmonic generation (SHG) property of the nanocrystals [21]. The synthesized nanocrystals have not shown any significant efficiency as compared to KDP crystals.

The variations of dielectric constant and dielectric loss with frequency have been discussed in this chapter. The resistivity and conductivity of the samples synthesized have been in the range of $1.10 \times 10^2$ $\Omega$-cm to $475.45 \times 10^2$ $\Omega$-cm and $2.103 \times 10^{-3}$ S cm$^{-1}$ to $9.049 \times 10^{-3}$ S cm$^{-1}$ respectively.

Chapter VI – Conclusions and Scope for Future Work

The conclusions obtained from the present studies have been included in this chapter. The amino acid doped LaF$_3$:Ce and LaF$_3$:Dy nanocrystals have been synthesized by wet chemical method with subsequent irradiation by microwave for reducing agglomeration. The nanocrystals synthesized have been largely hexagonal in shape with average particle size ranging from 12 nm to 22 nm. The XRD studies have confirmed the single phase formation of the nanocrystals. The SAED pattern confirms the crystallinity of the synthesized nanocrystals. The presence of the organic and inorganic elements have been confirmed by the EDAX studies and ICP-AES measurements. The presence of fundamental vibrations corresponding to organic attachments has been confirmed by FTIR studies. The electron phonon interactions in far IR region below 500 cm$^{-1}$ have been observed in the FT-RAMAN analysis. The wide transparency window suggests the application of the synthesized nanoparticles to optoelectronic devices. The PL studies indicate the upconversion nature of the synthesized nanocrystals which make it suitable
for application in biological labeling. The TGA/DTA studies indicate the phase change, thermal decomposition and also confirm the crystallinity of the obtained nanocrystals. The synthesized nanoparticles have been observed to show no efficiency as compared to KDP crystals. Ionic conductivity of the synthesized nanocrystals has been of the order of $10^{-3}$ S cm$^{-1}$.

The scope of future work and the list of papers presented and published have been added at the end of this chapter.

The references used in the present study have been included at the end of every chapter.

References


