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Formation of Nanparticles and Red Floursecenceinleucine Capped Cerium Fluoride Nanoparticles

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Abstract:
Fluorides of rare earth metal have been investigated thoroughly in the past due to the potential they hold for a variety of optical applications. However, presence of low luminescence and poor water solubility limit the use of these in bio-medical applications. Among the various materials, CeF_3 nanostructures are found to have hollow inner cavities, which have attracted attention of scientific community. Cerium fluoride was synthesised by co-precipitation method in the presence of the Leucineas a ligand. Analytical grade salt of Cerium(III) chloride heptahydrate and Ammonium Fluoride were used as raw materials with assay of 99.9%.The X- ray diffraction pattern indicates hexagonal crystal structure (JCPDS card no. 70-0002). TEM measurements show assorted sized nanocrystals of hexagonal geometry with average particle size of nearly14 nm. The UV profile shows multiple absorption edges below 328 nm indicating quantum dot nature of the synthesised nano crystals. The PL emission wavelength lying at 331nm corresponding to 5d to 4f transition of $Ce^{+3}$and is in close agreement with UV counterpart. The synthesised nanocrystals are found to show red fluorescence around 628nm.

Keywords: *Cerium fluoride, Leucine, luminescence*

1. Introduction

Rare earth compound nanocrystals with controllable shape and size have been extensively studied recently for their potential applications in display devices, laser materials, catalysis and biological near infrared (NIR) probes. Among various rare earth compound nanocrystals, the nanoparticles of Cerium fluoride (CeF_3) is the most frequently studied and used one, which is arepresentative nanoparticles with well-controlled shape and structure, suitable as potential scintillators, a good solid lubricant, in biological fluorescence labeling, and so on. By addition of suitable ligands luminescent properties of cerium fluoride can be improved. The ligands modify surface of these molecules rendering them as water soluble.It has also been noted that coating CeF_3 with organic ligand, the distance between the luminescent lanthanide ions increases whereas that between surface quenchers decreases thereby reducing the non-radioactive pathways. Among various rare earth fluorides, CeF_3 nanostructures shows fullerene-like structure (IF)with hollow cavities,which has attracted increasing attention because of its novel applied value [2]. Recent interest in Cerium fluoride is as a highly radiation-resistive, high density and fast response host material inscintillation detectors [3]. The present work is focused on the development of water soluble Cerium fluoride nanoparticles modified with amino acid – Leucine. This paper reports the detailed synthesis and characterization of Leucinemodified CeF_3 nanoparticles.

2. Synthesis

The nanoparticles of cerium fluoride were prepared by a co-precipitation method. To Synthesize Leucine modified CeF_3 was carried out in two steps. First, by mixingCerium(III) chloride heptahydrate ($CeCl_3.7H_2O$, 99.9%) andAmmonium Fluoride(NH_4F, 99.9%) in molar ratio 1:3 in de-ionized water. Mixture of 7 ml of $CeCl_3.7H_2O$ (2.384 g, 0.064 mol) and 3ml of$C_6H_{13}NO_2$(0.4197gm, 0.064mol) was taken in a beaker. In the second step 10 ml NH_4F(1.066g, 0.192mol) prepared in de-ionized water wasswiftly injected into the mixture. Due care was taken to avoid contamination of any kind. White precipitate appeared instantly and was found to settle at the bottom. The final mixture was subjected to microwave heatingat 800 W for 1 hr with on-off mode having a time interval of 30 sec. The final product was then washed twice with water and finally with methanol. The precipitate was dried at room temperature for 1hour, sealed and stored for characterization.

3. Elemental/Structural Analysis

3.1. XRD Studies

As XRD analysis gives the information about phase, size, cell parameters and space groups.In present work Powder X-ray diffraction (XRD) analyses were performed with Cu-Kα irradiation (λ= 1.5444A^o) over the range of 20^o -80^o. The diffraction pattern of sample shows hexagonal phase with space group p3c. The lattice parameters are found to be in accordance with JCPDS Card No 70-0002. The strong and sharp diffraction peaks confirm the high crystallinity. The cell parameter is in good agreement with value a= b= 7.046 A. U and c= 7.2713 A.U. [4]. X-Ray diffraction profile with assigned planes for the sample is shown below in figure 1a. The average particle size (D_{hkl}) of the sample was estimated from the full width at half maximum (FWHM) of the (002), (110) and (111) diffraction peaks of the powderusing Debye- Scherrer equation and is found to be 8.21 nm.

Generally, the broadening of the diffraction peaks contains both strain and particle size. The effective strain (ε) has been calculated using Williamson –Hall equation through the graph of βcosθ verse sinθ in figure 1b. The slope estimate ε as 0.0418. Y-intercept of the graphis used to determine D_{hkl} as 14 nm. Additionally, the cell volume (*Vcell*) was calculated through $V_{cell}= (\sqrt{3}/2)\, a^2c$, which is found to be 312.6Å^3[5].

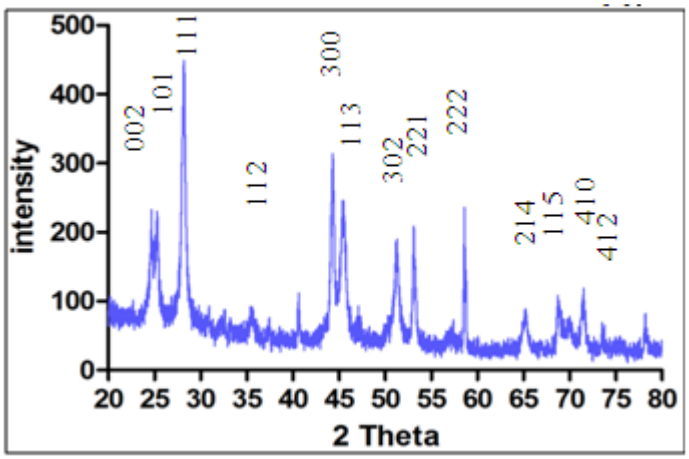

Figure 1a: XRD pattern of Leucine modified CeF_3 nano crystals

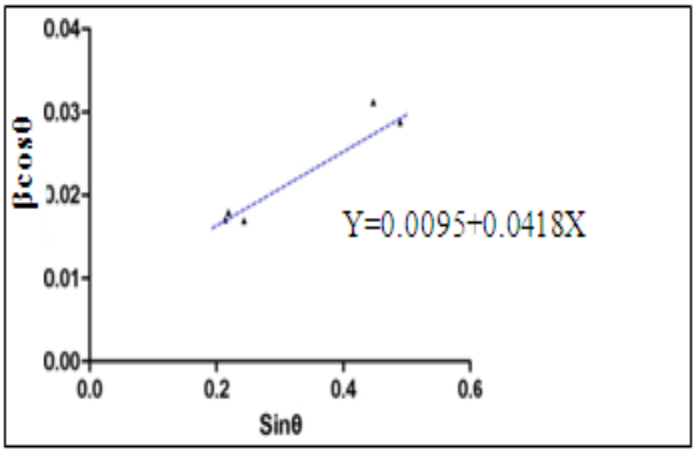

Figure 1b: Williamson –Hall equation [βcosθ verse sinθ]

3.2. Tem Studies

To ascertain the exact morphology of nanocrystals TEM was used. Near hexagonal, broad discs with assorted morphology can be seen in the TEM image (Fig 2a). The TEM image shows formation of nanodiscs with multi-morphologies with incidences of particles interlocked together. The magnified TEM image indicates that one or a few cavities exist in each particle of the CeF_3 obtained using NH_4F as the fluoride source. The average particle size is found to be 21.66 nm.Which is in near agreement with those obtained using Williamson –Hall equation. The variation in particle size may be due to interlocking. Corresponding SAED patterns (inset) of fig 2 (b) shows presence of three prominent concentric rings corresponding to crystal planes (110), (111) and (113). The other faint rings may be attributed to (302),(221),(222) and (412) planes. All these planes remain verified in the XRD analysis.

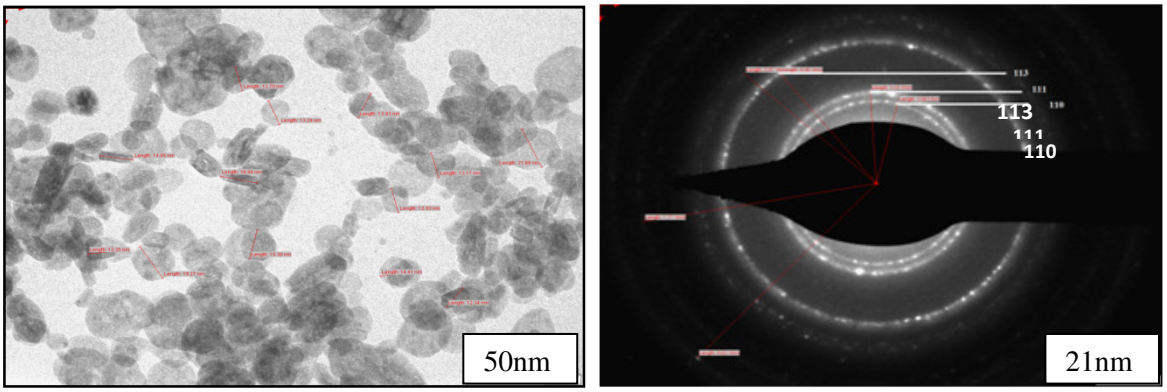

Figure 2: (a) TEM and (b) SAED pattern of Leucine modified CeF_3nanocrystals

3.3. UV-VIS Studies

The UV-visible spectrum of the Leucine doped CeF_3 nanoparticles have been shown in figure 3. Below 328nm, multiple absorption edges can be noticed indicating quantum dot nature [6] of the synthesized nanoparticles. Figure 3a shows the UV-Vis absorption spectrum of the CeF_3 nanoparticles. An absorption peak is obvious at 253 nm and can be ascribed to the 4f→5d transition of Ce3+ ions.In order to calculate the value of the optical band gap, Tauc et al. [1] proposed the following expression for different transitions:

$$\alpha h\upsilon = B\,(h\upsilon - E_g^{opt})^r$$

Where hυ is the photon energy, B is the absorption constant,E_g^{opt} is the optical band gap, and r is a number that dependson the type of transition: r=1/2 for direct allowed transition,r =2 for indirect allowed transition.Furthermore, α is the absorption coefficient derivedfrom the Beer-Lambert law:

$$\alpha = 2.303A/t$$

Where A is the measured absorbance and t is the thicknessof the sample. The band gap was estimated at 4.9 eV by extrapolatingto zero a linear fit to a plot of (αhυ) ½ against hυ (Fig. 3b) The second part of the UV-Visible spectrashows wide transparent window beyond 400 nm and up to 800 nm suggesting its use in optoelectronic devices.

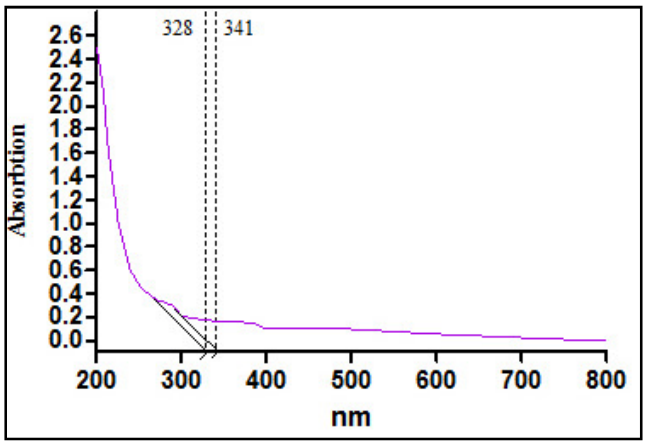

Figure 3a: U-V profile modified CeF_3

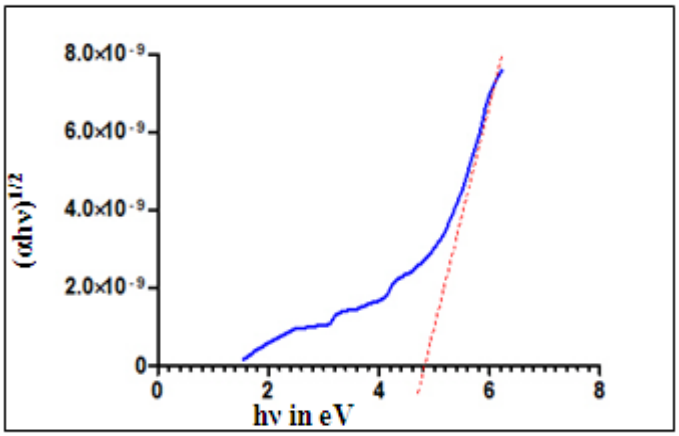

Figure 3b: A plot of (αhυ) ½ against hυ U-V profile modified CeF_3

3.4. PL Spectra

The photoluminescence spectrum of the synthesized nano particles has been shown in figure 4. Previous studies show that cerium ion absorbs one photon at 630 nm (1.97 eV) and is excited to the 5d level., thereafter it relaxes to ground state by emission at 335 nm (3.71 eV) [7]. Thus under excitation, modified CeF_3 nano particle emits light with peak at 328 nm due to 5d-4f transition. From figure 5 it is clear that the excitation peak at 628 nm (with emission peak is at 328 nm) and is due to up conversion nature of the sample prepared.

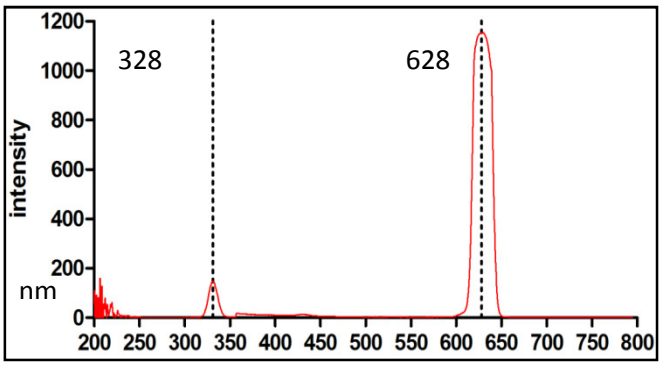

Figure 4(a): PL spectra of Leucine @ CeF3 nanoparticles

4. Conclusion

Water soluble CeF_3 nanodiscs capped with aminoacid- leucine have been conveniently synthesised by co-precipitation at room temperature. Microwave irradiation has been employed to get the final end product. Broad peaks in the powder X-ray diffraction profileindicates the existence of nano particles and are in agreement with the standard JCPDS card no. 70-0002. The average particle size by Debye- Scherrer is found to be 8.1nm and using Williamson –Hall equation it is estimated as 14 nm. The nature of slope of the graph (β cos θ verse sin θ) further indicates tensile strain. The TEM images shows formation of nanodiscs of assorted sizes with average particle size of 21.66 nm. The SAED pattern shows three prominent rings (111), (113), (110) along with others. UV profile shows presence of quantum dots below 300nm. The excitation peak between 328 nm to 341nm is in good agreement with the PL spectra where the peak lies nearly in the same range. An energy band gap of 4.9 eV is found from the graph of $(\alpha h\nu)^{1/2}$ verse hν. The PL spectra show the emissionof red colour fluorescence corresponding to peak at 628 nm.

5. References

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