

OPTICAL STUDIES IN ER DOPED NANOCRYSTALLINE CaF_2

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ABSTRACT Morphological features of co-precipitation synthesized Erbium doped Calcium fluoride nanoparticles show agglomeration and porous nature. Powder X-ray diffraction pattern of the nanoparticles confirm the cubic crystallinity. The crystallite size is found to be ~25 nm. The Fourier Infrared Transmission Spectroscopy confirm the purity of the synthesized samples. The optical absorption spectrum of as-prepared samples show a strong and prominent absorption with peak at ~333 nm besides three weak ones at ~413, 485 and 584 nm. Photoluminescence studies show a broad and prominent emission with peak at ~387 nm along with weak emissions at ~442, 460 and 517 nm when excited at 330 nm.

KEYWORDS : Nanoparticles, Co-precipitation, X-ray diffraction, Electron Microscopy, optical absorption, Photoluminescence

1. Introduction

With the development of nanoscience and nanotechnology more attention has been given to develop new routes to synthesize nanoscale materials with controllable size to achieve enhanced electronic, magnetic, optical and chemical properties. Luminescent nanomaterials doped with rare-earth ions attracted the scientific community due to their potential technological applications for displays, X-ray imaging, solid-state lasers and optical amplifiers [1, 2]. The fluoride nanomaterials form the subject of interest because of their wide range of potential applications based on their low energy phonons and high transparency when compared to other sulfides and metal oxides [3, 4]. Among the alkali fluoride compounds calcium fluoride (CaF_2) is an attractive material because of its high stability and non-hygroscopic behavior. Rare earth doped CaF_2 gained a renewed interest as a laser material. Literature reveals that CaF_2 nanoparticles are synthesized by different methods such as sol-gel method [5], solvothermal process [6], reverse micelle method [7], precipitation method [8] flame synthesis [9] etc. Co-precipitation method is a Simple and economical process for preparing nanoparticles and it offers the following advantages. In this method preparation of samples can be done rapidly. It is easy to obtain pure phase of nanoparticles with uniform size and morphology. Doped nanoparticles can be prepared easily with suitable composition at low temperature. This method provides various possibilities to modify the homogeneity and morphology of various nitrates, sulphates, chlorides and fluorides. Though extensive studies were carried out on the optical absorption and emission of single crystals of Er doped CaF_2 [10-13], reports on optical absorption and luminescence studies of nanocrystalline CaF_2 :Er are very limited. In the present work 2 mol% each Er doped CaF_2 nanocrystals are synthesized by co-precipitation method and characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier Transform Infra red spectroscopy (FTIR), Optical absorption and Photoluminescence (PL) techniques. The synthesized nanoparticles are of small crystallite size 25nm. The defects present in CaF_2 nanoparticles are identified by optical method. As the defects studies on nanoparticles are very limited, the present results gain significance. Further, the work focuses on optical absorption and photoluminescence of Er doped CaF_2 nanoparticles which are rarely reported. Thus, the present work gains novelty.

2. Experimental

The flow chart for the synthesis of Er doped nanocrystalline CaF_2 by co-precipitation method is shown in Figure 1. Stoichiometric quantity of erbium oxide (Er_2O_3) is taken in a 250ml conical flask and small quantity of nitric acid (HNO_3) was added in to it and stirred well. The mixture is evaporated slowly on a sand bath to convert the Er_2O_3 to erbium nitrate [$\text{Er}(\text{NO}_3)_3$]. Calcium chloride (CaCl_2) and ammonium fluoride (NH_4F) are added in to the conical flask in stoichiometric quantities and the mixture is dissolved in 100 ml of distilled water and stirred for 2 hours constantly. The resulting solution mixture is centrifuged for 10 minutes at 3000 rpm. The residue is washed thoroughly with ethanol and extracted on to a ceramic dish. The product is dried slowly on a sand bath maintained at about 100°C. The

XRD measurements of synthesized samples is carried out using a Philips X-pert PRO powder diffractometer with Cu-K_α radiation ($\lambda=1.54056\text{\AA}$) in the scan range 10-90°. The morphology of synthesized samples is studied using scanning electron microscopy by sputtering technique with gold as covering contrast material (JEOL JSM-840A). The FTIR spectrum is recorded using Nicolet Magna 550 spectrometer with KBr pellets in the range from 400 - 4000 cm^{-1} . The Optical absorption measurements of the samples is carried out in the wavelength range 200 to 900 nm using V-570 UV/VIS/NIR double beam spectrophotometer. The PL emission spectrum of the samples is recorded at room temperature using a spectrofluorometer (Jobin Yvon Fluorolog 3) equipped with a 450W Xenon lamp as the excitation source.

3. Results and Discussion

3.1 Structure and Morphology

The powder X-ray diffraction patterns (PXRD) of as-prepared Er doped CaF_2 nanoparticles are shown in Figure 2. The pattern confirmed the cubic crystallinity of synthesized nanoparticles. The obtained peaks are indexed in to cubic phase of the fluorite type structure (JCPDS Card no. (35-0816) [14]. The average value of lattice constant is found to be 5.492Å which is relatively more than that of undoped CaF_2 (5.4355Å, JCPDF 772096) [15]. This is due to the fact that when the trivalent Er^{3+} ion substitute a Ca^{2+} ion, charge compensating F ions enter the fluorite (CaF_2) structure in interstitial cubic sites and the electronic repulsion between F ions leads to a net increase of the lattice parameter. The broad XRD peaks reveal small crystallite size of the synthesized samples. The crystallite size is calculated by full width at half maximum (FWHM) technique using Scherrer's formula $D=K\lambda/(\beta\cos\theta)$ where K is the constant (0.99), λ is the wavelength of $\text{Cu-K}\alpha$ (1.54Å) line, β is the FWHM and θ is the diffraction angle. The average crystallite size of Er doped CaF_2 sample is found to be ~25 nm. The XRD patterns of heat treated (500°C) samples show narrow peaks with relatively high intensity. The average crystallite size of heat treated samples is found to be ~35 nm. This indicates the increase in particle size due to heating. The SEM results (Figure 3) reveal that the synthesized powder is porous and agglomerated with polycrystalline nanoparticles. The as prepared products contain voids. The particles are agglomerated from few microns to a few tens of microns, fluffy and porous. The SEM of the heat treated samples show larger particles than the as prepared one and indicated the agglomeration of the nanoparticles. Figure 4 shows the FTIR spectrum of as synthesized Er doped CaF_2 . Two strong IR absorption bands are observed at ~3400 and 1550 cm^{-1} . These are characteristic of H-O-H bending of the H_2O molecules [16] and reveal the presence hydroxyl groups in the as prepared sample.

3.2 Optical Spectra

The Optical absorption spectrum of Er doped CaF_2 nanocrystals is shown in Figure 5. It consists of a prominent absorption peak at ~333 nm besides three weak but well separated ones at ~413, 485 and 584 nm. The absorption peaks indicate the presence of several defects in the nanocrystalline CaF_2 . The origine of these absorption peaks can be

explained in the following way. It is well established that nanoscale materials have large surface to volume ratio. This results in the formation of voids on the surface as well inside the agglomerated nanoparticles. Such voids can cause fundamental absorption in the UV wavelength range. Also, surfaces of nanoparticles are well known to comprise of several defects such as dangling bonds, regions of disorder and adsorption of impurity species. Such defects are known to result in optical absorption by nanocrystals [17]. It is well known that the surface defects like Schottky and Frenkel exist at all temperatures. Such defects cause optical absorption in the UV range. Thus the 333 nm absorption peak in the present study may be attributed to defects such as schottky and frenkel. Also, there are vacancies created due to the absence of fluorine atoms in the lattice structure of nanocrystalline CaF₂ [18]. This kind of vacancies present on the surface of nanoparticles cause absorption in the visible wavelength range. Smaller size nanoparticles are found to have high surface to volume ratio. This results in increase of defects distribution on the surface of nanomaterials. Thus the low particle size nanomaterials exhibit strong and broad absorption bands. Hence, the absorption peak at 413 nm may be attributed to vacancies on the surfaces of nanoparticles.

During the formation of nanoparticles there will be diffusion of fluorine in the lattice. Also, the fluorine vacancies get aggregated centered at nanoparticle locations. The formation of fluorine vacancies in calcium fluoride is accompanied by the formation of fluorine-rich defects. Also, when an impurity ion of different charge substitutes a host ion in an ionic crystal, charge compensation is usually accomplished by the incorporation of interstitial host ions or other species of impurity ions in interstitial or substitutional sites. In Er doped CaF₂ lattice Er³⁺ ions substitute for host ion of different charge and the charge compensation is done by the interstitial host ions. The extra positive charge of the Er³⁺ ions in CaF₂ crystals is compensated by interstitial fluoride ions (F⁻). Some fluorine may occupy interstitial sites as neutral atoms or molecules. Electron transfer from metallic calcium to these interstitial fluorine defects ionizes Ca to Ca²⁺ and restores the fluorite lattice. The absorption at 485 nm may be attributed to fluoride ions at the interstitial positions. The 584 nm peak is characteristic of the transition from the ground state (⁴I_{15/2}) to excited state (⁴S_{3/2}) of Er³⁺ ions [19].

Figure 6 shows the PL emission spectrum of the Er doped CaF₂ nanoparticles due to 330 nm excitation. A broad and prominent emission with peak at ~387 nm along with weak emissions at ~442, 460 and 517 nm were observed. It is well known that the PL spectra greatly depend on the nature of the charge compensating ions and on their location in the host lattice. Also, the nature of the luminescence centers depends on the host lattice, the rare earth concentrations and the thermal treatment of the samples. Because of the charge compensation effects, the lattice of CaF₂:Er³⁺ is a slightly distorted. The observed PL emissions are unambiguously attributed to various possible transitions of Er³⁺ ions in the following way. The peak at 387 nm is due to ⁴G_{11/2} ⁴I_{15/2} transitions of Er³⁺ ions. The weak emissions at 442 and 460 nm are assigned to ⁴F_{3/2} ⁴I_{15/2} and ⁴F_{5/2} ⁴I_{15/2} transitions of Er³⁺ ions respectively [20]. The emission at 517 nm may be attributed to ²H_{11/2} ⁴I_{15/2} transition of Er³⁺ ions.

4. Conclusions

Co-precipitation synthesized Er doped CaF₂ nanoparticles are of size ~25 nm. The morphological features show that nanoparticles are agglomerated from few microns to a few tens of microns, fluffy and porous. Heat treatment increased the particle size by 10 nm and removed the hydroxyl groups in the as-prepared sample. The optical absorption spectrum revealed the presence of intrinsic defects in the as prepared samples. PL spectra show various transitions of Er³⁺ ions.

Figure 1. Flow chart for the synthesis of Er doped CaF₂ nanoparticles by co-precipitation method

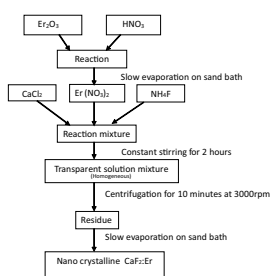


Figure 2. Powder XRD spectrum of Er doped nanocrystalline CaF₂

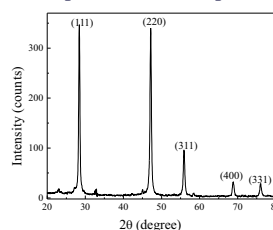


Figure 3. SEM pictures of Er doped nanocrystalline CaF₂

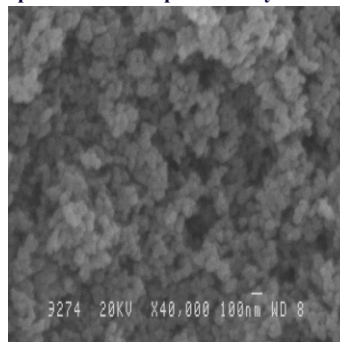


Figure 4. FTIR Spectra of Er doped nanocrystalline CaF₂

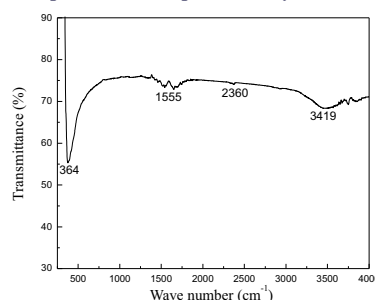


Figure 5. Optical absorption spectrum of Er doped nanocrystalline CaF₂

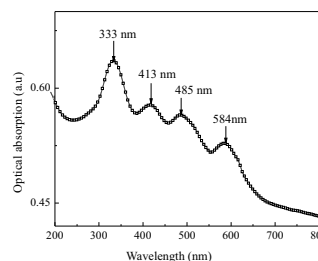
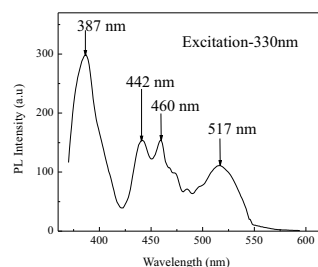


Figure 6. Photoluminescence spectrum of Er doped nanocrystalline CaF₂



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