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Preparation Characterization Optical and Photoluminescence Studies of Gamma Rayed Erbium Doped Nanocrystalline CaF_2

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Abstract

Erbium doped Calcium fluoride (CaF2) nanoparticles are synthesized by co- precipitation method. Preliminary characterizations of the samples are carried out using PXRD, SEM and FTIR. The nanoparticles are irradiated with γ-rays and optical absorption and Photoluminescence measurements are made on the irradiated samples. From the study of Optical Absorption (OA) spectra various color centers responsible for the absorption are identified. Photoluminescence (PL) spectrum exhibited emission peaks at ~387, 442, 460 and 517 nm. The mechanisms of OA and PL of the observed samples are discussed in detail.

Keywords:* *Nanocrystals; Optical absorption; Photoluminescence; Lattice defects; Color centers

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. 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. Among the alkali fluoride compounds, Calcium Fluoride (CaF_2) is an attractive material because of its high stability and non-hygroscopic behavior. CaF_2 has wide band gap (12eV) material with a large-scale transparency [1].

Therefore, color center formation is possible just by irradiating CaF_2 by ionizing radiations such as gamma rays. CaF_2 nanoparticles were synthesized by different methods such as sol-gel, solvothermal, reverse micelle, hydrothermal,Precipitation, flame synthesis etc.

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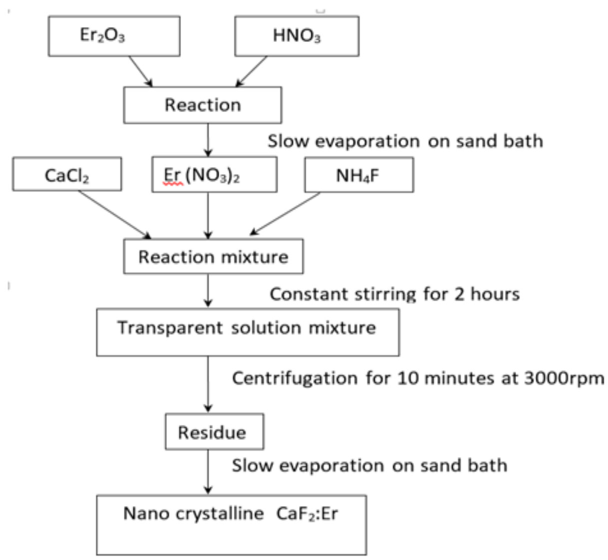
Literature Review

In the present study 2mol% Erbium (Er) doped CaF_2 Nano crystals are synthesized by co-precipitation method and are characterized by XRD, FTIR, SEM, Optical absorption and PL techniques [2].

FIG.1. **Flow chart for the synthesis of Erbiuum doped CaF_2 nanoparticles by co-precipitation method**.

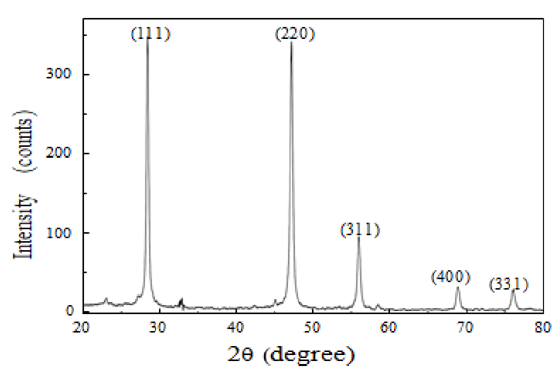


The resulting solution mixture was centrifuged for 10 minutes at 3000 rpm. The residue was washed thoroughly with ethanol and extracted on to a ceramic dish. The morphology of synthesized samples was studied using scanning electron microscopy (JEOL JSM-840A) by a sputtering technique with gold as covering contrast material. The FTIR spectra were recorded using Nicolet Magna 550 spectrometer with KBr pellets in the range from 400 - 4000 cm^{-1}. The samples are exposed to 5 KGy x-rays. The Optical absorption measurements of the samples was carried out in the wavelength range 200 to 900 nm using V-570 UV/VIS/NIR double beam spectrophotometer. The PL emission spectra of the samples was recorded at room temperature using a spectrofluoremeter (Jobin Yvon Fluorolog 3) equipped with a 450 W Xenon lamp as the excitation source [3-7].

Pxrd SEM and Ftir

The Powder X-Ray Diffraction patterns (PXRD) of Er doped CaF_2 is shown in Figure 2. The PXRD confirmed the cubic crystallinity of synthesized nanoparticles. The obtained peaks are indexed in to cubic phase of the fluorite type structure with space group Fm^3 m. The pattern was compared with JCPDS Card no. 87-0971.

FIG.2. **Powder XRD spectrum of Er doped nanocrystalline CaF_2.**



The average value of lattice constant obtained was 0.5464 nm. The crystalline size calculated using Scherrer's formula was found to be about 30 nm. The SEM pictures of Er doped CaF_2 shown in Figure 3 revealed that the nanoparticles are porous and agglomerated with polycrystalline nanoparticles. The nanoparticles are spherical and homogeneously distributed and found to have voids and agglomerated from few microns to a few tens of microns, fluffy and porous. Figure 4 shows FTIR spectrum of Er doped CaF_2. There are two strong IR absorption bands at ~3419 and 1555 cm^{-1} which are characteristic of H-O-H bending of the H2O molecules revealing the presence hydroxyl groups in the as-prepared sample. The fundamental frequency at ~ 364 cm^{-1} arises due to hindered rotations of the hydroxyl ions. The first-order vibrational overtone of O-H (3419 cm^{-1}) is strongly in resonant with the I13/2→4I15/2 transition of Er3+ ions. The band at ~2360 cm^{-1} is due to KBr pellets used for recording FTIR spectrum [8].

FIG.3. **SEM pictures of Er doped nanocrystalline CaF_2.**

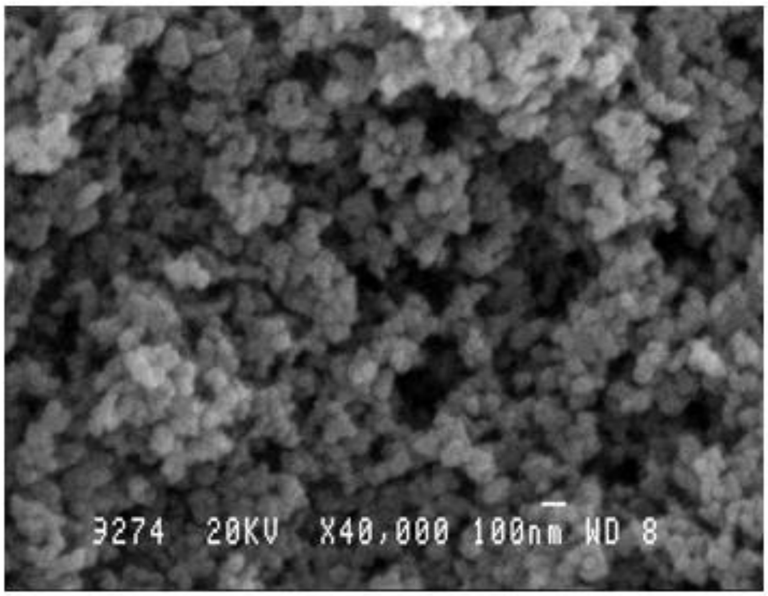
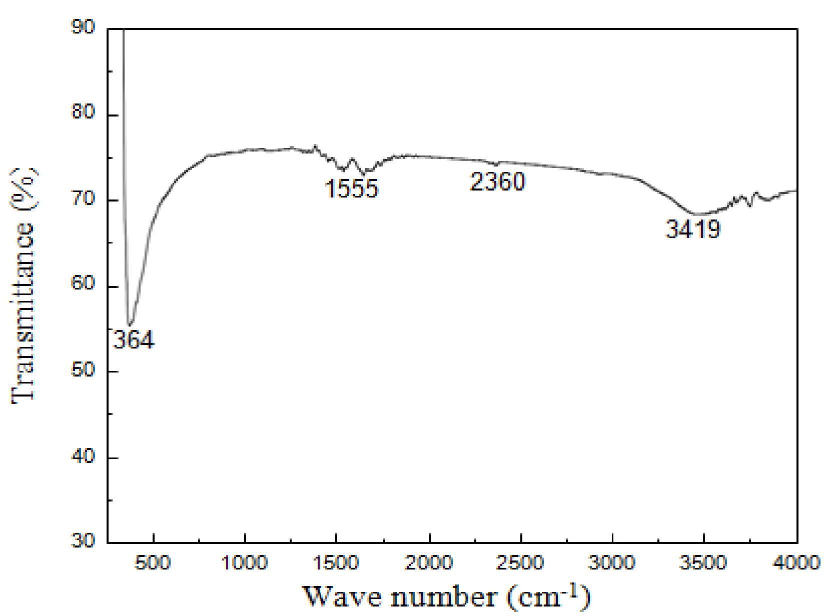


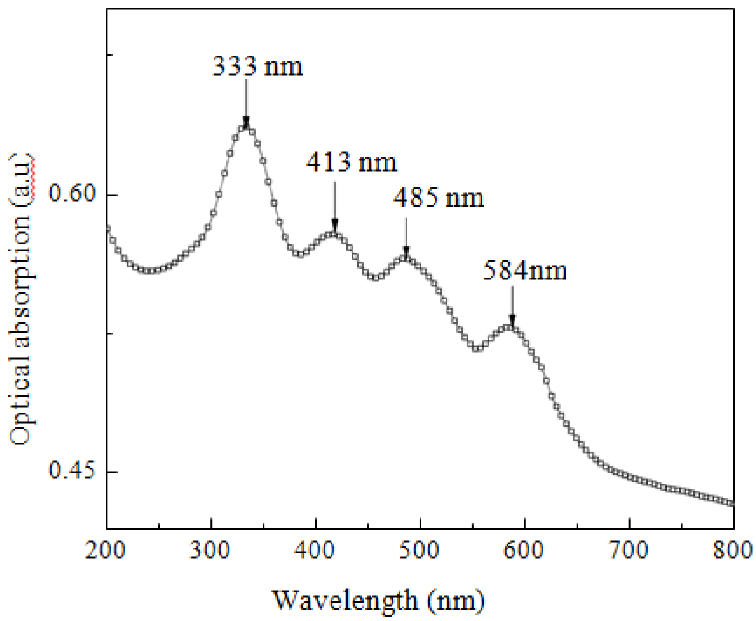
FIG.4. **FTIR Spectra of Er doped nanocrystalline CaF_2.**



Optical absorption studies

Optical Absorption (OA) spectrum of irradiated Er doped nanocrystalline CaF_2 samples is given in Figure 5. It shows a series of absorption peaks with a prominent and strong one at ~333 nm and three weak ones at 413, 485 and 584 nm. Generally, when an impurity ion substitutes for host ion of different charge in an ionic crystal, compensation is accomplished by the incorporation of the lattice vacancies, interstitial host ions, another species of impurity ion in interstitial or substitutional sites or a combination thereof. The extra positive charge of the trivalent Erbium ions in CaF_2 crystals is compensated by interstitial fluoride ions (F-). It is established that crystalline CaF_2 is sensitive to gamma-rays to form color centers. They form various color-centers at room temperature due to gamma irradiation. Major sources of absorption in CaF_2 crystals are F and F-aggregate centers created by irradiation. Irradiation produces free electrons. These electrons when get trapped at negative ion vacancies form F-centers. The F- center is a fluoride ion vacancy binding one electron. The electronic structure of the F-center has shown that the ground state of the 1s wave function of the F-center is restricted to the anion vacancy. The F-center absorption correspond to an electronic excitation from 1s state to 2p state [9-12].

FIG.5. **Optical absorption spectrum of Er doped nanocrystalline CaF_2.**



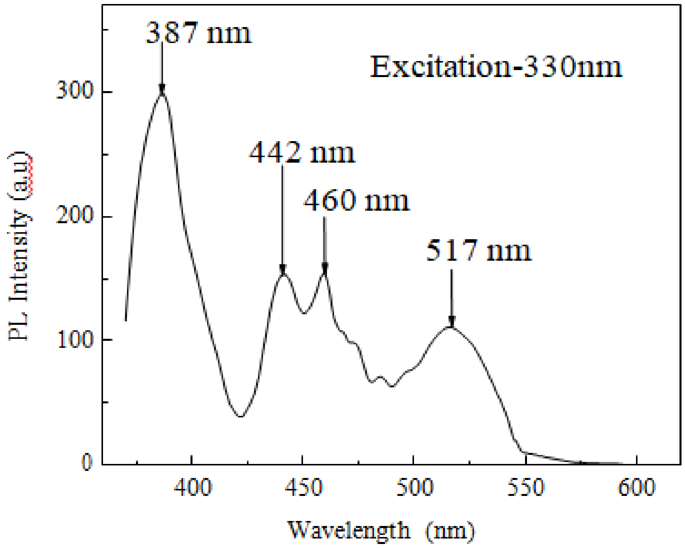
The present absorption spectra resemble the absorption spectrum of CaF_2 crystals. The absorption peak at 333 nm may be attributed to Vk center. The 413 and 485 nm absorption peaks in Er doped samples may be assigned to perturbed Vk and M centers respectively. These are due to transition from the ground state 4I15/2 to the excited states 4G11/2 and 4F5/2 respectively

The absorption at ~584 nm may be due to formation of CA colloids.

Photoluminescence studies

Photoluminescence (PL) is used to identify specific defects and their relative concentration. PL is able to detect the defects which overlap in absorption spectrum. The PL emission spectrum of -irradiated Er doped CaF_2 nanoparticles is as shown in Figure 6. There are several peaks lying from the near UV to the near infrared region, characteristic of the Er ion electronic transitions. The gamma rayed CaF_2 nanoparticles were excited under 330 nm. The corresponding PL emission spectrum showed peaks at ~387, 442, 460 and 517 nm. In irradiated Er doped CaF_2 nanocrystals erbium can be in trivalent (Er3+) state. As already mentioned, irradiation of CaF_2 forms F and F-aggregate centers in it. When the sample containing F-center is. Excited with UV light (to record the emission), due to electronic transitions in the sample the energy absorbed by the defects gets released in the form of photons leading to PL emission [13].

FIG.6. **Photoluminescence spectrum of Er doped nanocrystalline CaF_2.**



The PL spectra greatly depend on the nature of the dopants, their concentration and location in the host lattice. Based on these facts the PL emissions could be attributed to different electronic transitions as a result of irradiation. The PL emission at 387 nm is attributed to 4G9/2 →4I15/2 transitions of Er3+ ions. Similarly 442 nm, 460 and 517nm emissions are attributed to 2G9/2→ 4I15/2, 4F9/2 → 6H15/2 and 2H11/2→ 4I15/2 transitions respectively.

Conclusions

Er doping of CaF_2 nanoparticles was successfully prepared by co-precipitation method. The nanocrystalline CaF_2: Er was characterized by XRD, SEM, FTIR, Optical absorption and PL. PXRD showed that the average particle size of CaF_2: Er is about 30 nm. The morphological features studied using SEM showed that the as-prepared samples were agglomerated from few microns to a few tens of microns, fluffy and porous. The presence of hydroxyl groups in the Sample is revealed by the FTIR spectrum. Optical absorption showed that radiation creates F-aggregate centers in Er doped nanocrystalline CaF_2. PL studies revealed various transitions responsible for emission in rayed nanocrystalline CaF_2: Er.

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