Optical absorption and Photoluminescence studies in Gamma-irradiated nanocrystalline CaF$_2$

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Abstract
Calcium fluoride (CaF$_2$) nanoparticles were synthesized by co-precipitation method and characterized by powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM). Also, optical absorption (OA) and photoluminescence (PL) studies on gamma irradiated (γ-rayed) CaF$_2$ nanoparticles were carried out. The XRD patterns confirmed the cubic crystallinity of the samples and the particle size was found to be ~25 nm. The purity of the synthesized nanoparticles was confirmed by FTIR spectrum. The morphological features studied using SEM revealed the agglomerated and porous nature of nanoparticles. γ-rayed CaF$_2$ nanoparticles showed a prominent absorption with a peak at ~360 nm besides three weak but well separated absorptions at ~ 267, 442 and 510 nm. The various defect centers responsible for the absorption peaks were identified. The PL studies of samples showed strong emissions at ~396 nm and 425 nm. The observed PL emissions are attributed to defects created in nanocrystalline CaF$_2$.

Keywords: Synthesis; Nanoparticles; Scanning electron microscopy; Optical absorption; Photoluminescence

Introduction
The strong interest in nanotechnology stems from the concept that structures may be designed and built that exhibit superior electrical, mechanical, chemical or optical properties compared to the materials we know today. Some of the key issues in using nanoscale materials include the location, distribution of trapping centers, electron–phonon interactions and the potential for energy transfer to a luminescent center in a nanostructure. Many of the preparation methods of nanoparticles can be modified to create nanostructured films and nanocomposites, although some types of nanostructures require completely novel approaches [1-5].

Fluorides have attractive structural and optical characteristics. One of the fluorides with wide band gap and large scale transparency is Calcium fluoride (CaF$_2$). It is well established that when CaF$_2$ crystals are irradiated with high energetic radiations such as Gamma, X-ray, electron beam, ion beam they generate defects and give rise to color centers. These centers can be identified from various experimental techniques like OA, PL and TL. Literature reveals that irradiation effects on nanocrystalline CaF$_2$ are limited. The defects studies in CaF$_2$ nanocrystals are rare. Hence, the aim of the present work is to irradiate synthesized and characterized (XRD, FTIR, SEM) CaF$_2$ nanoparticles by γ-rays and to study the defects created by OA and PL techniques.

Experimental
Calcium chloride (CaCl$_2$) and ammonium fluoride (NH$_4$F) were added into the conical flask in stoichiometric quantities and the mixture was dissolved in 100 ml distilled water. The mixture was stirred constantly for 2 hours using a magnetic stirrer. The transparent reaction mixture transformed into opaque white suspension gradually. The stirred solution was centrifuged for 10 minutes at 5000 rpm and a white residue was obtained. The residue was washed thoroughly with ethanol and the product was extracted on to a ceramic dish and dried slowly on a sand bath.

The structure of the synthesized samples was confirmed by XRD measurements using Philips X-pert PRO powder diffractometer with Cu-K$_{α}$ radiation ($λ=1.54056Å$) in the scan range 10-90° at a low speed of ~1° /minute. The morphology of synthesized samples was studied using scanning electron microscope (JEOL JSM-5500) by sputtering with gold as covering contrast material. The FTIR spectrum was recorded using Nicolet Magna 550 spectrometer with KBr pellets in the range 400 - 4000 cm$^{-1}$. The samples were exposed to γ-rays from a Co$^{60}$ source with an activity 3.89 Kgy/hr for doses in the range 0.0324–15.56 Kgy. The Optical absorption measurements of the γ-rayed samples were carried out in the wavelength range 200-900 nm using V-570 UV/VIS/NIR double beam spectrophotometer by dispersing the samples in liquid paraffin (nuzol). The PL emission spectra of the γ-rayed samples was recorded at room temperature using a Fluorolog 3 Jobin Yvon spectroflurometer (FL3-11) equipped with a 450W Xenon lamp as the excitation source.

Results and Discussion
PXRD, SEM and FTIR
Figure 1 shows the PXRD pattern of nanocrystalline CaF$_2$. The pattern reveals cubic phase of the fluorite type structure ([JCPDS Card no. 87-0971] [6]). The displayed peaks correspond to $<h k l>$ values (1 1 1), (2 2 0), (3 1 1), (4 0 0), (3 1 1) and (4 2 2). The results match well with literature [7, 8]. Using the $<h k l>$ values the lattice constant (a) of the sample was calculated. The average value of lattice constant was found to be a=5.454Å which is in good agreement with literature value a= 5.4355Å [9]. The XRD pattern presents broad peaks revealing the small crystallite size of the synthesized samples. The crystallite size was calculated from the full width at half maximum (FWHM) technique.


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Received January 04, 2011; Accepted February 19, 2011; Published February 23, 2011

DOI: 10.4172/2157-7439.1000108
using Scherer’s formula \( D = \frac{K\lambda}{\beta \cos \theta} \) where \( K \) is the constant (0.99), \( \lambda \) is the wavelength of Cu-Kα (1.54 Å) line, \( \beta \) is the FWHM and \( \theta \) is the diffraction angle. The average crystallite size of nanoparticles was found to be ~25 nm. It is observed that the PXRD pattern of 500°C heat treated samples was similar to that of as prepared one but with slight increase in intensity. This indicates that 300°C heat treatment does not reveal any structural changes in the nanocrystalline \( \text{CaF}_2 \). However, the crystallite size was found to be increased to 32 nm. Thus heat treatment of the synthesized samples causes agglomeration of nanoparticles.

The SEM picture of as prepared nanocrystalline \( \text{CaF}_2 \) is shown in Figure 2. The SEM results reveal the morphology of the synthesized nanoparticles. The as prepared nanopowder is agglomerated with polycrystalline nanoparticles. The agglomeration ranged from few microns to a few tens of microns. The SEM picture shows that \( \text{CaF}_2 \) nanoparticles have many voids and are fluffy and porous. The larger particles exhibited numerous spherical perturbances on the surface, suggesting that they were formed during the precipitation process through fusion of the smaller particles.

FTIR spectrum was measured to check the purity of the synthesized powder. Figure 3 shows the FTIR spectrum of as prepared \( \text{CaF}_2 \) nanoparticles. The spectrum shows two strong IR absorption bands at ~3400 and 1550 cm\(^{-1}\). They are characteristic of H-O-H bending of the \( \text{H}_2\text{O} \) molecules. This reveals the presence hydroxyl groups in the as prepared sample [10]. The fundamental frequency at ~364 cm\(^{-1}\) arises due to hindered rotations of the hydroxyl ions [11]. The band at ~2357 cm\(^{-1}\) is due to KBr pellets used for recording FTIR spectrum. The FTIR pattern of 500°C heat treated samples showed decrease in the absorption of each band. The decrease in absorption of the ~3419 and 1555 cm\(^{-1}\) bands on heating could be attributed to the release of water molecules trapped inside the solid matrix.

**Optical absorption studies**

The optical absorption spectrum of pristine and \( \gamma \)-rayed pure \( \text{CaF}_2 \) nanocrystals is shown in Figure 4. The pristine sample showed a weak absorption band at ~370 nm. The \( \gamma \)-rayed \( \text{CaF}_2 \) nanocrystals showed a prominent absorption at ~360 nm besides three weak ones at ~267, 442 and 510 nm. The optical absorption increased marginally with increase in \( \gamma \)-dose, but the peak positions were unaltered with increase in \( \gamma \)-dose. The origin of the absorption bands 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 [12]. Also, surfaces of nanoparticles are well known to comprise of several defects.
defects such as H centers. The H center is a F
in calcium fluoride is accompanied by the formation of fluorine-rich
resulting in the fluorine vacancies. Some fluorine may occupy interstitial
attributed to F-center generated during γ-irradiation.

Impurities, method of preparation and other varying factors. Based on
16]. Considerable deviations in the coloration spectra are reported for
fundamental absorption at 375 nm and it is attributed to F-center [14-
F-centres. Literature reveals that irradiated CaF
electrons which when get trapped at negative ion vacancies form the
resulting in absorption of light by
such as Schottky or Frenkel which result in absorption of light by
under 360 nm excitation.
Figure 5: Photoluminescence spectrum of γ-rayed pure nanocrystalline CaF
under 265 nm excitation.

It is well established that when CaF
single crystals are γ-rayed F-centers are formed at room temperature. The F-center consists of
an electron trapped at fluorine vacancy. -irradiation produces free
electrons which when get trapped at negative ion vacancies form the
F-centres. Literature reveals that irradiated CaF
exhibit the
structural change. Optical absorption and Photoluminescence studies in Gamma-irradiated nanocrystalline
CaF
are the self-
trapped exciton (STE), F and F-aggregate centers created by irradiation. It is well established that irradiation of CaF
leads to the formation of F and F-aggregate centers in it. F-center has an absorption peak in the range 360-380 nm. When the sample containing F-centers is excited with UV light, due to electronic transitions in the sample, emission of light takes place and the energy absorbed by the defects gets released in the form of photons leading to PL emission. The PL emission at 396 nm is attributed to F-center formed during γ-irradiation [17]. X. Zhang et al. observed similar emission at ~400 nm in nanocrystalline CaF
and attributed them to the presence of electronic centers [13].

Under γ-irradiation STE are typically formed when a free electron is
localized at a self-trapped hole. The resulting excitations can decay
radioactively yielding a distinctive luminescence [20]. Many F–H center pairs produced by STE decay are promptly destroyed by recombination. The PL emission peak at 425 nm is attributed to surface defects like STE [21].

Conclusions
CaF
nanoparticles were synthesized successfully by co-precipitation
method and the average particle size was found to be in the range 25
nm. The as prepared samples were agglomerated fluffy, porous and contain small traces water molecules. Heat treatment resulted in the release of water molecules and increase in particle size without any structural change. Optical absorption and Photoluminescence studies revealed the presence of number of defect centers in the γ-irradiated CaF
nanoparticles.

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