Journal of Alloys and Compounds 489 (2010) 592–595

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Synthesis and characterization of CaF_2 nanocrystals

C. Pandurangappa [a], B.N. Lakshminarasappa [b,*], B.M. Nagabhushana [c]

[a] Department of Physics, RNS Institute of Technology, Channasandra, Bangalore 560061, India
[b] Department of Physics, Jnanabharathi Campus, Bangalore University, Bangalore 560056, India
[c] Department of Chemistry, M.S. Ramaiah Institute of Technology, Bangalore 560054, India

ARTICLE INFO

Article history:
Received 24 August 2009
Received in revised form
17 September 2009
Accepted 19 September 2009
Available online 25 September 2009

Keywords:
Precipitation
Crystal structure
Point defects
Luminescence
Scanning electron microscopy (SEM)
X-ray diffraction

ABSTRACT

Calcium fluoride nanocrystals (CaF_2) were synthesized by two different techniques namely co-precipitation and hydrothermal. The synthesized nanocrystals were characterized by powder X-ray diffraction (PXRD), Fourier transform infrared red spectroscopy (FTIR), scanning electron microscopy (SEM), optical absorption and photoluminescence (PL). The crystallite size estimated using Scherer's formula was found to be in the range 30–35 nm for nanocrystals synthesized by co-precipitation method where as in case of hydrothermally synthesized nanocrystals it is in the range 20–28 nm which is less compared to those obtained by co-precipitation method. The morphological features as studied using SEM revealed that the nanocrystals are agglomerated, crispy with porous. The SEM images of hydrothermally synthesized nanocrystals showed less agglomeration than those obtained by co-precipitation method and the images confirm the formation of nanoparticles. The optical absorption spectrum showed a strong absorption band peaked at 244 nm for nanocrystals synthesized by co-precipitation method and it is 218 nm peak in case of hydrothermally synthesized ones. The PL emission spectrum showed two prominent emission bands peaked at 330 and 600 nm when excited at 218 nm.

1. Introduction

Change in physical and chemical properties of materials on nanoscale have resulted important applications and have received considerable attention in various fields [1,2]. They exhibit novel electronic, magnetic, optical, chemical and mechanical properties that cannot be obtained in their bulk counter parts. Nanomaterials captivate the materials world with the promising applications in science and technology. There is large academic interest in nanocrystalline systems due to high surface to volume ratio and quantum confinement of electronic states. Luminescent materials based on rare-earth ions attracted the scientific community due to their potential technological applications for displays, X-ray imaging, solid-state lasers and optical amplifiers [3,4]. Nanoparticles of fluorides have low phonon frequencies and high ionicity that lead to less absorption and high transparency over a wide optical region [170–780 nm]. The fluoride nanomaterials form the subject of interest because of their wide range of potential applications based on their low energy phonons and high activity that lead to less absolute fundamental absorption with respect to other sulfides and metal oxides [5]. Alkaline fluorides are dielectric in nature and are widely used in microelectronic and optoelectronic devices, such as wide-gap insulating overlayers, gate dielectrics, insulators and buffer layers semiconductor-on-insulator structure and more advanced three-dimensional devices [6]. With the development of nanomaterials, inorganic nanoscale fluorides are going to play an essential role in various applications based on their unique optical, electrical and magnetic properties.

Among the alkali fluoride compounds, CaF_2 is an attractive material because of its high stability and non-hygroscopic behavior. Recently CaF_2 gained a renewed interest as a laser material when doped with rare-earth material [7,8]. With the development of nanoscience and nanotechnology, more attention has been attracted to develop new synthetic pathways towards nanoscale materials. It is known that, many synthetic methods have been developed successfully to prepare nanoscale materials with controllable size and shape. Nanoparticles of different chemical compositions, shapes and size distributions have been prepared by different methods such as chemical vapor deposition, gas-phase condensation, reverse micelle method, sol–gel method, hydrothermal method, micro-emulsion techniques. These methods have been widely investigated first for the production of luminescent semiconductor nanoparticles [9,10]. However reports on synthesis of fluoride nanoparticles are limited. CaF_2 nanoparticles were synthesized by different methods such as sol–gel method [11–16], solvothermal process [17,18], reverse micelle method [19,20], different precipitation methods [21–24], and flame synthesis [25]. Chemical co-precipitation is a simple method to synthesize

* Corresponding author. Tel.: +91 9448116281 (Mobile).
E-mail address: bnlnarasappa@rediffmail.com (B.N. Lakshminarasappa).

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doi:10.1016/j.jallcom.2009.09.118

fluoride nanocompounds. Also hydrothermal method is a novel method to synthesize nanoparticles of better quality. In the present work CaF_2 nanocrystals are synthesized by both co-precipitation and hydrothermal methods and are characterized by XRD, SEM, IR, optical absorption and PL techniques.

2. Experimental

2.1. Synthesis

Analar grade Calcium chloride ($CaCl_2$), Ammonium fluoride (NH_4F) and Ethanol were procured from Sigma–Aldrich Company. In co-precipitation method synthesis of CaF_2 nanocrystals, 0.01 mol $CaCl_2$ was a dissolved in 100 ml distilled water taken in 250 ml conical flask. 0.02 mol NH_4F was added into the flask under vigorous stirring on a magnetic stirrer. The mixed solution was stirred for 2 h to transform the transparent reaction mixture into opaque white suspension gradually. Then, the mixture was centrifuged for 10 min at 5000 rpm and washed three times with ethanol via centrifugation to remove the residual chloride and the ammonium ions. Finally the solid product was extracted onto a ceramic dish and dried on a sand bath.

For hydrothermal synthesis CaF_2 nanocrystals, 0.01 mol $CaCl_2$ was a dissolved in 25 ml distilled water taken in 100 ml conical flask. 0.02 mol NH_4F was added into the flask and the mixture was stirred till it transformed into opaque white suspension solution. The solution was transferred in to a 30 ml autoclave and kept in an oven at 160 °C for 24 h. Then the autoclave was taken out of the oven and was cooled to room temperature naturally in air. A white product was deposited at the bottom of the autoclave. This product was obtained by centrifuging the mixture for 10 min at 5000 rpm and washing three times with ethanol via centrifugation. The final product was extracted onto a ceramic dish and dried on a sand bath.

2.2. Characterization

The XRD measurements of synthesized samples were carried out using a Philips X-pert PRO powder diffractometer with Cu Kα radiation (λ = 1.54056 Å) in the scan range 10–90°. The morphology of synthesized sample was studied using scanning electron microscopy (JEOL JSM-840A) by a sputtering technique with gold as covering contrast material. The IR spectra were recorded using Nicolet Magna 550 spectrometer with KBr pellets in the range from 400 to 4000 cm^{-1}. The Optical absorption measurements of the samples were carried out in the wavelength range 200–900 nm using V-570 UV/VIS/NIR double beam spectrophotometer by dispersing the synthesized samples in liquid paraffin (nuzol). The PL emission spectra of the samples were recorded at room temperature by exciting the samples at 218 nm using a spectrofluorometer (Hitachi F-4010) equipped with a 450 W Xenon lamp as the excitation source.

3. Results and discussion

3.1. Powder X-ray diffraction (XRD)

Fig. 1 shows the powder X-ray diffraction patterns (XRD) of as synthesized CaF_2 nanoparticles by co-precipitaion and hydrothermal methods respectively. All the obtained XRD peaks are indexed in to CaF_2 cubic phase of the fluorite type structure with space group Fm3m [26]. The pattern was compared with JCPDS Card no. 87-0971. The XRD pattern was found to match exactly with those reported in the literature [11,12]. The XRD patterns confirm the cubic crystallinity of synthesized nanoparticles. The displayed peaks correspond to ⟨*h k l*⟩ values of (1 1 1), (2 2 0), (3 1 1), (4 0 0), (3 1 1) and (4 2 2). Using the ⟨*h k l*⟩ values of different peaks, the lattice constant (a) of the sample was calculated. The average value of lattice constant was found to be $a = 5.42$ Å which is in good agreement with literature value $a = 5.4355$ Å (JCPDF 772096) [21]. The XRD pattern presents broad peaks revealing the small crystallite size of the synthesized samples. The crystalline size was calculated from the full width at half maximum (FWHM) technique using Scherer's formula $D = K\lambda/(\beta \cos\theta)$ where K is the constant (0.99), λ is the wavelength of Cu Kα (1.54 Å) line, β is the FWHM and θ is the diffraction angle. The crystalline size of nanoparticles synthesized by co-precipitation method was found to be in the range 30–35 nm, whereas the hydrothermally synthesized one was found to have less particle size in the range 20–28 nm. This indicated that the agglomeration of particles was less in hydrothermal method.

3.2. Scanning electron microscopy (SEM)

Fig. 2(a) and (b) shows the SEM photographs of as prepared CaF_2 powders by co-precipitation and hydrothermal methods respec-

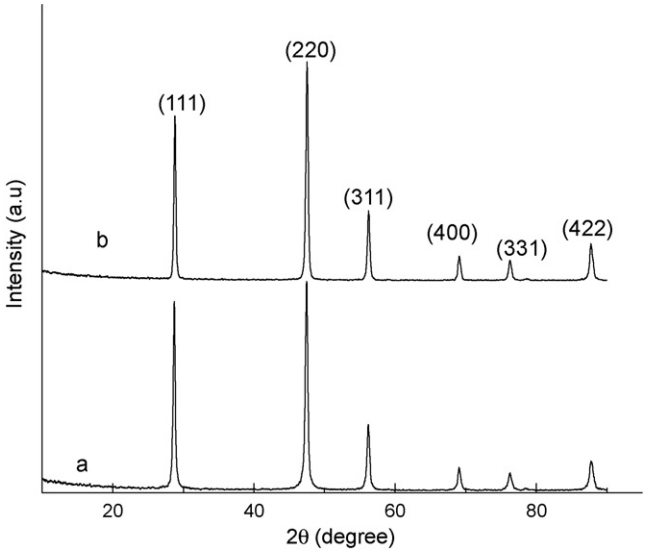

Fig. 1. X-ray diffraction spectrum of CaF_2 nanocrystals synthesized by (a) co-precipitation method and (b) hydrothermal method.

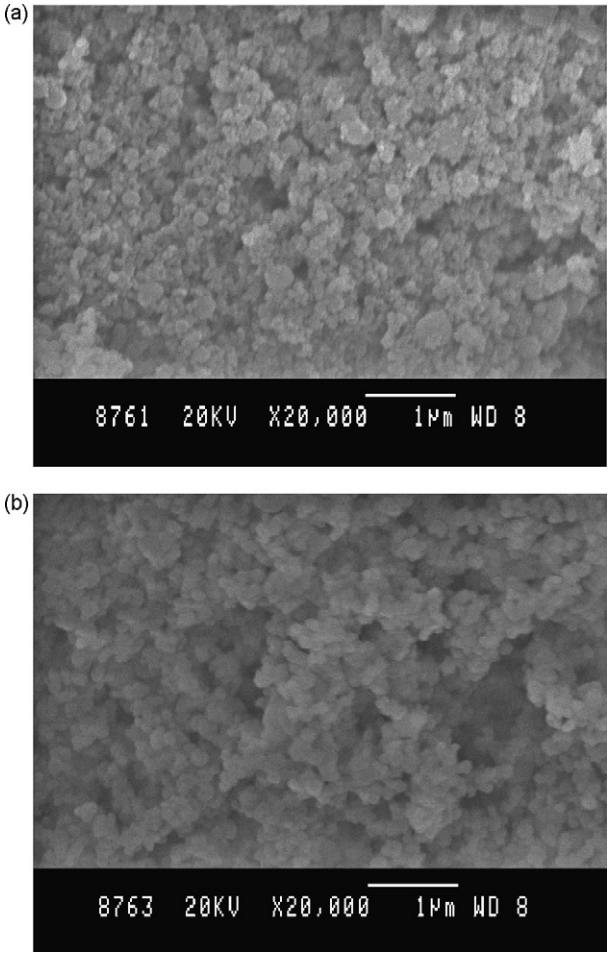

Fig. 2. SEM of CaF_2 nanoparticles synthesized by (a) co-precipitation method and (b) hydrothermal method.

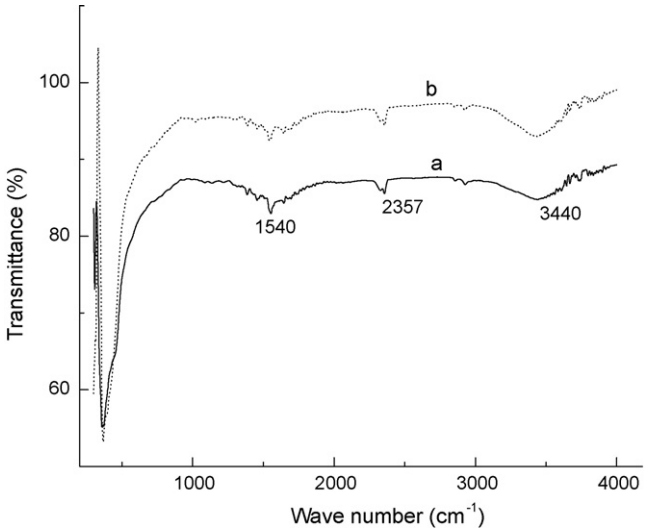

Fig. 3. FTIR spectrum of CaF_2 nanoparticles synthesized by (a) co-precipitation method and (b) hydrothermal method.

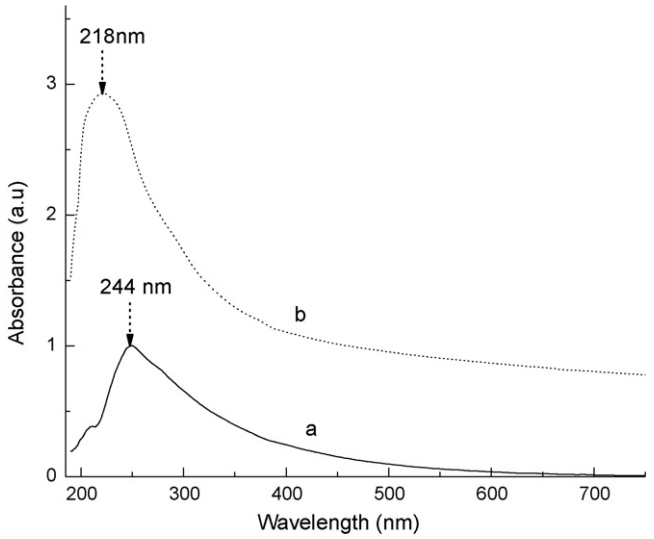

Fig. 4. Optical absorption spectrum of CaF_2 nanocrystals synthesized by (a) co-precipitation method and (b) hydrothermal method.

tively. The SEM results reveal that the powder was porous and agglomerated with polycrystalline nanoparticles. The larger particles exhibited numerous spherical perturbances on the surface, suggesting that they were formed during the precipitation process through fusion of the much smaller particles. The as prepared products were agglomerated from few microns to a few tens of microns, fluffy and porous. By comparing the SEM pictures of the samples prepared by the two methods it was found that, hydrothermally synthesized CaF_2 nanoparticles were smaller size and less agglomerated.

3.3. Fourier transform infrared spectrum (FTIR)

FTIR absorption was measured in order to check the purity of the synthesized powder. Similar spectra were observed for nanocrystals synthesized by both co-precipitation and hydrothermal methods and are shown in Fig. 3. The spectrum shows two strong IR absorption bands at ~3400 and 1550 cm^{-1} which are characteristic of H–O–H bending of the H_2O molecules revealing the presence hydroxyl groups in the as prepared sample [13,27]. The fundamental frequency at ~364 cm^{-1} arises due to hindered rotations of the hydroxyl ions [28]. The band at ~2357 cm^{-1} is due to KBr pellets used for recording FTIR spectrum.

3.4. Optical absorption

The optical absorption spectra of the CaF_2 nanocrystals synthesized by co-precipitation and hydrothermal methods are shown in Fig. 4. The nanocrystals obtained by co-precipitation showed a strong absorption band at ~244 nm while the hydrothermally synthesized nanocrystals showed similar absorption at ~218 nm. The two optical absorption bands at 244 and 218 nm observed in hydrothermal and co-precipitation methods appear to be the characteristic absorption bands of CaF_2. The origin of these 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 [17]. Also, surfaces of nanoparticles are well known to comprise of several defects such as dangling bonds, regions of disorder and adsorption of impurity species which result in optical absorption of nanocrystals. Thus the absorption band in the wavelength range 218–248 nm in the present study may be attributed to surface defects in nano-CaF_2. Similar absorption bands were reported recently in CaF_2 nanoparticles synthesized by solvothemal method [18].

Smaller size nanoparticles (~10–20 nm) 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 hydrothermally synthesized nanocrystals in the present study exhibit strong absorption.

3.5. Photoluminescence (PL)

The PL emission spectra of the CaF_2 nanoparticles synthesized by co-precipitation and hydrothermal methods are shown in Fig. 5. The PL spectra show a series of emission bands peaked at ~328, 407, 470, 513 and 605 nm when the samples were excited at 218 nm. It is well known that the surface defects like Schottky and Frenkel exist in the lattice structure of alkali halides at all temperatures. These kinds of vacancies present on the surface of nanoparticles causes PL emissions at different wavelengths.

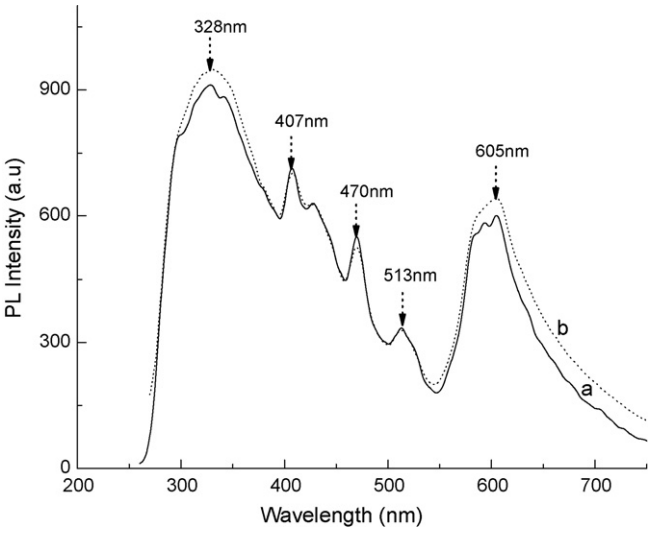

Fig. 5. Photoluminescence spectrum of CaF_2 nanocrystals synthesized by (a) co-precipitation method and (b) hydrothermal method.

Also, the formation of oxygen impurity vacancy in the nanocrystalline lattice during the synthesis leads to PL emissions. In both co-precipitaion and hydrothermal methods the final product was obtained by the slow evaporation of the precipitate. During this process oxygen may enter into the crystalline lattice and replace the fluorine molecule resulting oxygen impurity and a fluorine ion vacancy (impurity vacancy). The observed PL emission may be attributed to one or more of the above intrinsic defects [29] in the lattice of CaF_2.

4. Conclusions

CaF_2 nanocrystals were prepared successfully by co-precipitation and hydrothermal methods and characterized by XRD, SEM, IR, optical absorption and PL. The hydrothermally synthesized crystals were found to have less particle size than the one obtained by co-precipitation method. The agglomeration of particles was less in hydrothermally synthesized nanocrystals. The presence of surface defects in the as prepared samples were revealed by broad optical absorption bands in the wavelength range ~218–248 nm. The series of PL emission bands indicated the presence of intrinsic defects in both co-precipitation and hydrothermally synthesized CaF_2 nanocrystals.

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