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Synthesis and Characterization of CaF_2 NPs with Co-precipitation and Hydrothermal Methods

Nakhaei omolfajr[1,2]*, Shahtahmassebi Nasser[1,2], Rezaeeroknabadi Mahmood[1] and Ahmad Kompany[1]

[1]Department of physics, Ferdowsi University of Mashhad, Iran
[2]Nanotechnology research center of Ferdowsi University, Iran

Abstract

We used $CaCl_2$ and NH_4F from Merck Company for synthesis CaF_2 NPs. We synthesized CaF_2 Nanoparticales (NPs) using Co-precipitation and hydrothermal method successfully. The synthesized NPs were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), UV-Vis spectroscopy and Photoluminescence (PL) techniques. The XRD results indicated the formation of CaF_2 NPs with Cubic phase and the crystallite size is estimated using Scherrer's formula to be in the range 20–27nm for the powders prepared by co-precipitation and 20–31nm for hydrothermal methods, respectively. TEM images revealed the grains have almost spherical shape. Optical absorption spectrum shows a strong absorption edge at about 300nm.

Keywords: Nanoparticle; Co-precipitation; Hydrothermal; Photoluminescence (PL); Scherrer's formula

Introduction

Changes in physical and chemical properties of Nanomaterials have resulted important applications and have received considerable attention in various fields [1]. CaF_2 NPs is a kind of alkali halides with wide band gap (12ev) [2]. It has been extensively studied in recent years. It has high stability, non-hygroscopic, high refractive-index and homogeneity behavior. CaF_2 NPs have a technological importance because of their potential applications including advanced phosphor, photonic [3], display monitors, imaging, and light amplification [4]. The extremely high laser damage threshold of Calcium Fluoride has made it the material of choice for use in Excimer laser (an Excimer laser is a form of ultraviolet laser which is commonly used in the production of microelectronic devices, semiconductor integrated circuits or "chips", eye surgery, and micromachining) [5]. The most important quality features of Calcium Fluoride include excellent UV transmittance [6-9]. On the other hand the photoluminescence properties of this material when doped with some rare earth ion, made it more important [10], also its uses in tribology as an additive of lubricating [11]. Furthermore, Calcium Fluoride has become very interesting as an ultraviolet optical material for integrated circuit lithography in beam delivery [7]. The liquid-phase methods, with the advantages of simple operation, controllable granularity, and the nanoscale powders materials have high-surface activity. The liquid-phase methods include Co-precipitation [11], hydrothermal [1] (high temperature hydrolysis), Sol-gel and (colloidal chemistry) [12] and radiation chemical synthesis [13]. So, in this work we synthesized CaF_2 NPs with Co-precipitation and hydrothermal method.

Experimental

Synthesis

In Co-precipitation method for preparing of CaF_2 NPs, 0.01mol $CaCl_2$ was dissolved in 100ml distilled water, then 0.02mol of NH_4F was added into the besher under vigorous stirring by a magnetic stirrer. The mixed solution was stirred for 2hours to transform gradually the mixture into opaque white suspension. Then, the mixture was centrifuged for 10min at 3000rpm and washed five times with Ethanol via centrifugation to remove the residual chloride and the ammonium ions.

In Hydrothermal method 0.01mol of $CaCl_2$ was a dissolved in 25ml distilled water, then 0.02mol NH_4F was added into the besher and the mixture was stirred till it transformed into opaque white suspension solution. The solution was transferred in to an oven at 160°C for 24 hours. The mixture dried in an oven and the white powder was deposited at the bottom of the dish, then the powder was centrifuged for 10min at 3000rpm and washed five times with Ethanol; finally the solid product was extracted onto a ceramic dish and dried at room temperature.

Characterization of powder

The typical XRD spectra of the samples were obtained using X Ray Diffraction (Cu K_α line λ=0.15406nm). The SEM and TEM were used to observe the size and morphology of the samples. For optical studies, the absorption spectra of the NPs were obtained by UV-Vis spectrophotometer (UVD 2950), and the PL studies were carried out using (Ls 45) Fluorescence spectrometer. FTIR spectrums were carried out using FTIR spectrometer (Shimadzu 4300).

Results and Discussion

Structural studies

Powder X-ray diffraction (XRD): Figure 1 (a) and (b) show the powder X-ray diffraction patterns the synthesized CaF_2 NPs by co-precipitation and hydrothermal methods. All the obtained XRD peaks are indexed in to CaF_2 cubic phase of the fluorite type structure with space group Fm3m. Using the (hkl) values of different peaks, the lattice constant (a) of the samples were obtained. The average value of lattice

***Corresponding author:** Omolfajr Nakhaei, Master of Science student of Solid State Physics, Ferdowsi University of Mashhad, Iran, Tel: +98-9155620899; E-mail: Fa.nakhaei@stu.um.ac.ir

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constant were found to be a=5.42 for both samples, which are in good agreement with literature value a=5.4355 [14]. The crystallite size estimated using Scherrer's formula; Scherrer's formula is [15]

$$d = K\lambda / \beta \cos\theta$$

Where k is a constant which is taken to be 1 for cubic CaF_2, the wavelength of X-rays used (0.15406nm), β the full width at half maximum (FWHM) and θ is the angle of diffraction. The particles size calculated 20–27nm for co-precipitation and 20-31nm for hydrothermal method.

Morphological studies

Transmission Electron Microscopy (TEM): Figure 2(a) and (b) show the TEM photograph of CaF_2 powders and their histogram. The TEM images reveal that the powder is crystalline and the average size of NPs synthesized by co-precipitation is less than NPs synthesized by hydrothermal method. Histogram plots show the average sizes of NPs are 53.7nm and 75nm for co-precipitation and hydrothermal method, respectively. The shape of particles synthesized via co-precipitation method is almost spherical, and agglomerated with rather same size.

Scanning Electron Microscopy (SEM): Figure 3(a) and (b) show the SEM photographs of as prepared CaF_2 NPs by co-precipitation and hydrothermal methods respectively. The Figure 3(a) reveals that the

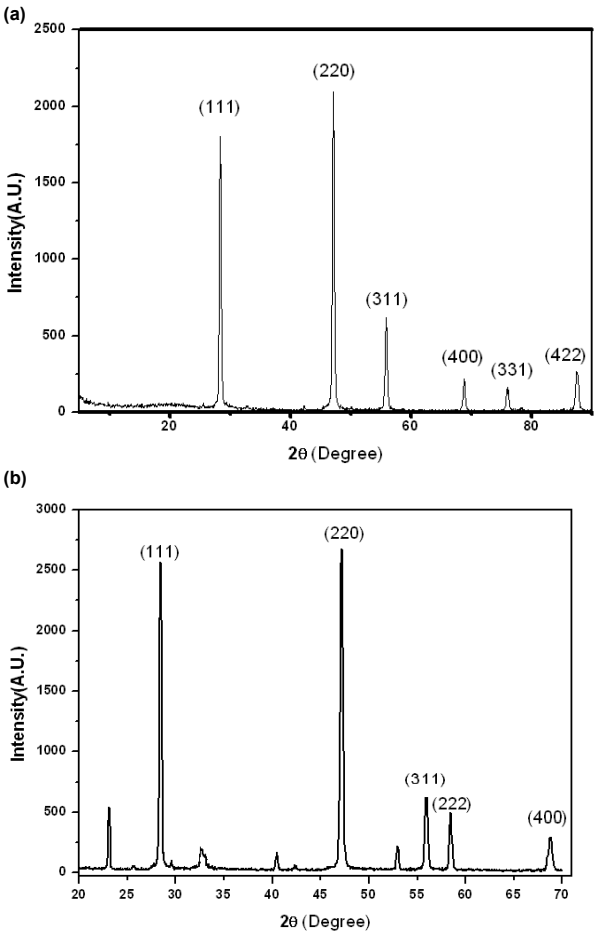

Figure 1: X-ray diffraction spectra of CaF_2 NPs synthesized by (a) co-precipitation method and (b) hydrothermal method.

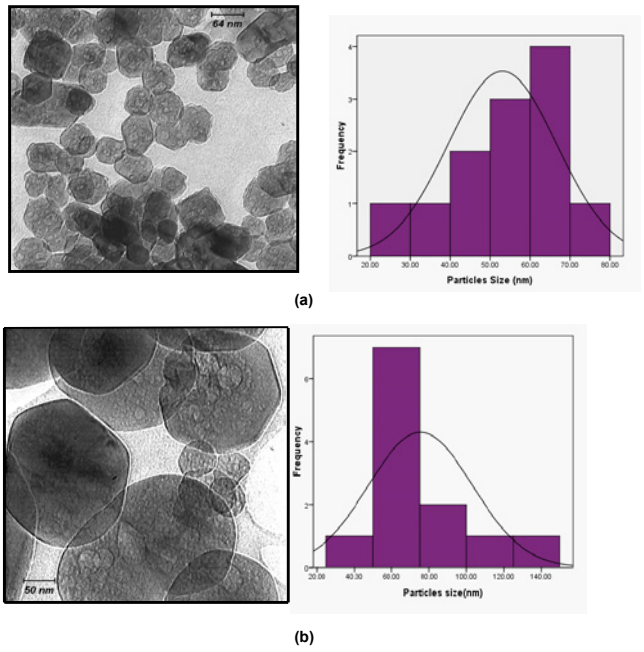

Figure 2: TEM image of CaF_2 NPs synthesized by (a) co-precipitation method and its histogram (b) hydrothermal method and its histogram.

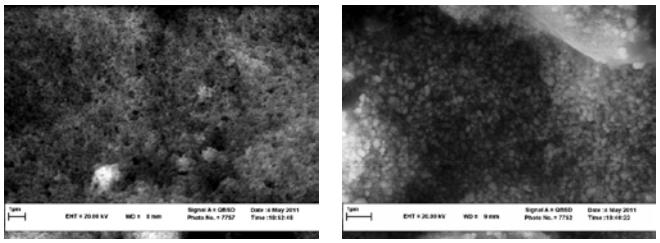

Figure 3: SEM image of CaF_2 NPs synthesized by (a) co-precipitation method and (b) hydrothermal method.

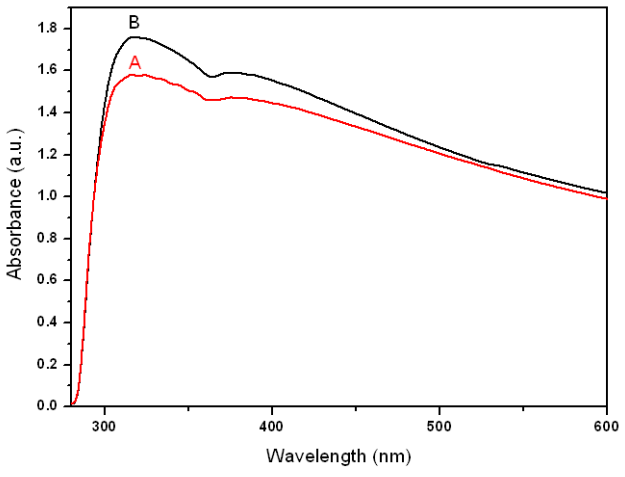

Figure 4: Optical absorption spectrum of CaF_2 NPs synthesized by (a) hydrothermal method and (b) Co-precipitation method.

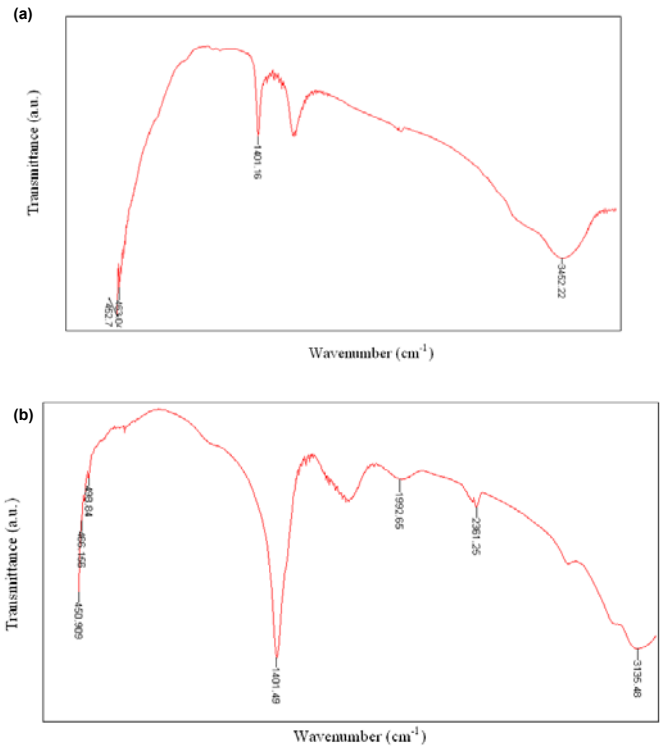

Figure 5: FTIR spectrum of CaF_2 NPs synthesized by (a) Co-precipitation method and (b) hydrothermal method.

powder was porous and there are some perturbances on the surface, suggesting that they were formed during the precipitation process.

Optical studies

Optical absorption: UV-Vis spectroscopy CaF_2 NPs are shown in Figure 4. The spectrum shows a strong absorption band at 314 nm in UV range for co-precipitation and 317 nm for hydrothermal method. Smaller size NPs (~20–27 nm) are found to have high surface to volume ratio. This causes the increase of defects distribution on the surface of NPs. Thus the low particle size NPs exhibit strong absorption. Hence, the co-precipitation synthesized NPs in the present study exhibit strong absorption because of their smaller size.

These spectra show that the NPs synthesized with co-precipitation method is more pure than the sample prepared with hydrothermal method.

Photoluminescence spectrum (PL): The PL emission spectrum of the CaF_2 NPs synthesized by co-precipitation and hydrothermal routs were shown in Figure 6 (a) and (b). The PL spectrum shows a series of emission peaks at ~ 382 and 768nm when the sample was excited at 394.4 nm for co-precipitation method, and shows a series of emission peaks at ~ 394 and 790 nm when the sample was excited at 392.2nm for hydrothermal method. It is well known that the surface defects like Schottky and Frenkel exist in the lattice structure of alkali halides at different temperatures. These kinds of vacancies present on the surface of NPs cause PL emissions to occur at different wavelengths [1].

Fourier Transform Infrared spectrum (FTIR): FTIR absorption was measured in order to show the bonds exist in the samples. Spectra were observed for nanocrystals synthesized by both co-precipitation and hydrothermal methods and are shown in Figure 5(a) and (b).

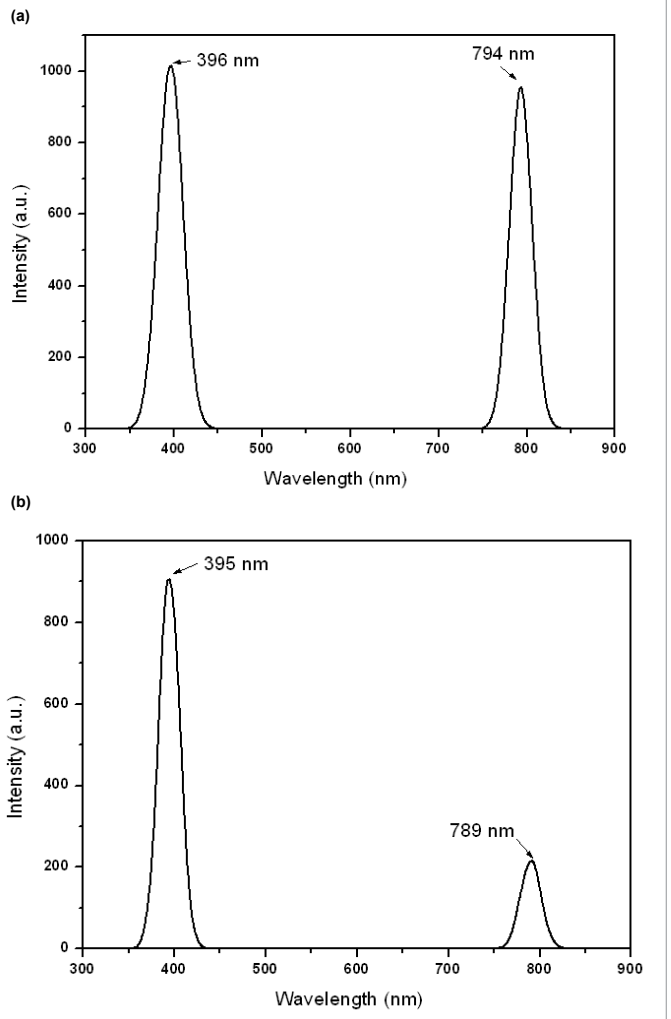

Figure 6: PL spectrum of CaF_2 NPs synthesized (a) by Co-precipitation method and (b) by hydrothermal method.

Figure 5(a) shows strong IR absorption bands at 450(cm^{-1}), 1400 (cm^{-1}), 3452(cm^{-1}) receptively belonging to Ca-F, N-O and H-O bonds. Figure 5(b) shows the frequency in 450(cm^{-1}), 1400(cm^{-1}), 1900(cm^{-1}), 2361(cm^{-1}), 3125(cm^{-1}) respectively belonging to Ca-F, N-O, C-O, N-H and O-H bonds.

Conclusions

CaF_2 NPs were prepared successfully by two different methods, and were characterized by XRD, TEM, SEM, UV-Vis spectroscopy techniques and PL spectrum. The XRD, TEM and characterization showed that the obtained NPs are single phased with homogeneous chemical composition that agree with Lihua Zhou et al. [16] work. The purity and the absorbance intensity are better in the samples synthesized via co-precipitation method. TEM images revealed that the size of NPs is smaller prepared by co-precipitation method. The PL spectrum shows two main picks, due to the transition of electrons between two levels, and emitting photons, which makes the application of CaF_2 NPs for fabricating optical and laser devices [17].

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