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CaF_2 nanoparticles: Synthesis and characterization

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ABSTRACT

The aim of the present study was to prepare nano-sized calcium fluoride (CaF_2). Calcium fluoride nanoparticles were synthesized by $CaCl_2.6H_2O$ and ammonium fluoride. Nanoparticles were synthesized by co-precipitation method. The synthesized nanocrystals were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM). The crystallite size estimated using Scherer's formula was found to be in the range of 20–30nm for nanocrystals synthesized by this method. The morphological features as studied using SEM revealed that the nanoparticles were agglomerated, crispy with porous.

Keywords: *Synthesis; Characterization; Nanoparticles; Calcium fluoride.*

INTRODUCTION

The synthesis of inorganic nano- and micro materials with well-defined and controllable morphologies has stimulated considerable attention, because it is well known that the properties of the materials closely interrelate with geometrical factors such as morphology, dimensionality, and the size [1–5]. It has been well-established that alkali earth metal (AEM) fluorides MF_2, where M = Ca, Sr or Ba, should be very attractive host crystals for some applications. These applications may Ba as Ln and transition metal laser activators since they possess a broad optical transparency region, moderate Raman gain coefficients, relatively small linear and non-linear refractive indices, and rather flat curvature of the refractive index dispersion over a wide wavelength range in the near IR. Under such unique optical properties and rather reasonable physical characteristics one may expect high peak laser action. That is why these single AEM fluorides doped by some rare-earth (RE) trivalent ions appeared objects of intensive investigations from the very beginning of the last decade of 20th century. The ambitious purpose was to establish whether these materials were suitable for use as effective laser-pumped amplifier media [6]. Furthermore Calcium fluoride (CaF_2) and "CaF_2-like" materials are of significant interest in dentistry due to their roles as labile fluoride (F) reservoirs in cavities prevention.

Low concentration of F used in oral fluids derived as F reservoirs formed by the use of F dentifrices and rinses, have been shown to have a profound effect on the progression of dental cavities [7–9]. However reports on synthesis of fluoride nanoparticles are limited. CaF_2 nanoparticles were synthesized by different methods such as sol–gel method [10–15], solvothermal process [16,17], reverse micelle method [18,19], different precipitation methods [20–23], and flame synthesis [24]. In the present work CaF_2 nanoparticles are prepared by co-precipitation method and are characterized by XRD, SEM, IR techniques.

EXPERIMENTAL

Material and methods

Calcium fluoride, ethanol and ammonium fluoride were purchased from Merck Company. The XRD measurements of synthesized samples were carried out using a Philips X-pert PRO powder diffractometer with Cu-Kα radiation (λ = 1.54060 Å) in the scan range 0-100°. The morphology of synthesized sample was studied using scanning electron microscopy (Philips-XL30) by a sputtering technique with gold as covering contrast material. The IR spectra were recorded using Bruker spectrometer with KBr pellets in the range from 400 to 4000 cm^{-1}.

Synthesis of nanoparticles

Calcium chloride hexahydrate ($CaCl_2.6H_2O$), ammonium fluoride (NH_4F) were prepared in ethanol for synthesis of CaF_2 nanoparticles by co-precipitation method. $CaCl_2$ (0.01 mol) was a dissolved in 50 ml ethanol taken in 250 ml conical flask. NH_4F (0.02 mol) was added into the flask under vigorous stirring on a magnetic stirrer. The mixed solution was stirred for 3 h to gradually transform the transparent reaction mixture into opaque white suspension. Then, the mixture was centrifuged for 15 min at 4000 rpm and washed three times with water via centrifugation to eliminate the residual chloride and the ammonium ions. Finally the solid product was extracted and then kept in a desiccator over P_2O_5.

RESULTS AND DISCUSSION

Powder X-ray diffraction (XRD)

The XRD patterns of CaF_2 nanoparticles is shown in Figure 1, and all of the diffraction peaks can be readily indexed to a pure cubic phase (space group: Fm3m (225)) [25], which are in agreement with the standard values for cubic CaF_2 (JCPDS Card no. 87 - 0971). The XRD results indicate that the products we obtained were CaF_2 nanoparticles. The XRD pattern presents broad peaks revealing the small crystallite size of the synthesized samples. The nanoparticles size was calculated from the full width at half maximum (FWHM) technique using Scherer's formula D= Kλ/ (β cos θ) 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 nanoparticles size obtained in the range 20–30 nm.

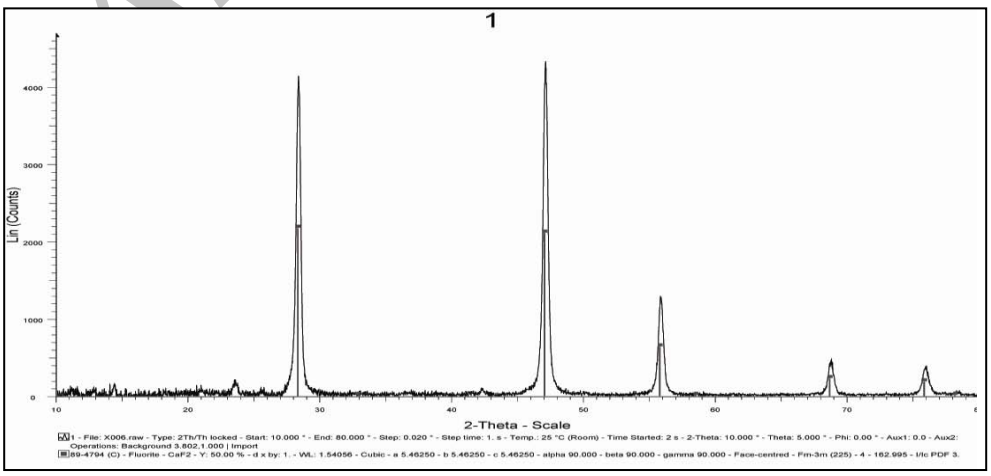

Fig. 1. X-ray diffraction spectrum of CaF2 nanoparticles

Scanning electron microscopy (SEM)

The SEM images are shown in Figure 2. 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 prepared products were agglomerated from few microns to a few tens of microns, fluffy and porous.

Fourier transform infrared spectrum (FTIR)

Although the synthesized CaF_2 was a white powder, its purity was further examined by means of FT-IR spectrometry. The peak at 443 cm^{-1} in the FT-IR spectrum in Figure 3 was assigned to the Ca–F stretching vibration of CaF_2. The spectrum shows strong IR absorption bands at ~3423 cm^{-1} which is characteristic of H–O–H bending of the H_2O molecules revealing the presence hydroxyl groups in the as prepared sample [26, 27].

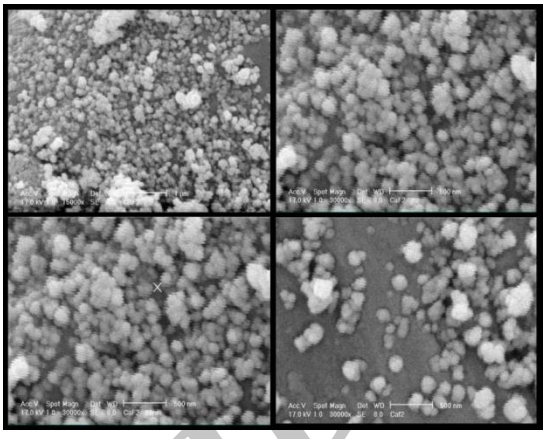

Fig. 2. SEM images of CaF_2 nanoparticles synthesized by co-precipitation method

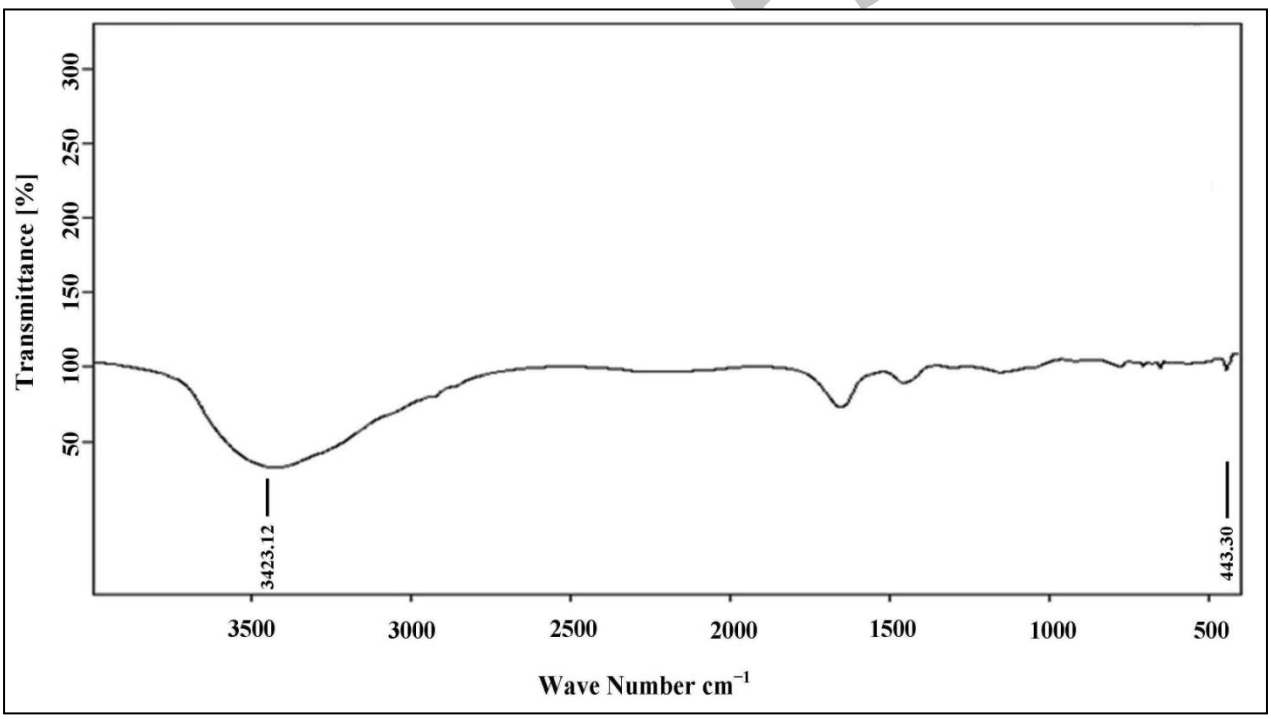

Fig. 3. FT-IR spectrum of CaF_2 nanoparticles

CONCLUSION

In conclusion, the current report describes the synthesis of pure phase CaF_2 nanoparticles in uniform diameter of ~20 nm by co-precipitation method and characterized by XRD, SEM, IR, and optical absorption. It is noteworthy that the co-precipitation method is effective for obtained pure phase nanomaterials with controllable size, uniform morphology and shape. This method has several advantages such as: wide range of achievable compositions, lower processing temperature, easier composition control, and better chemical homogeneity of the product. Resulting nanocrystals have been characterized using spectroscopy data. The nano-CaF_2 can be used as an effective anticaries agent in increasing the labile F concentration in oral fluid and thus enhance the tooth remineralization. It can also be very useful in the treatment for the reduction of dentin permeability. Also fluorides are well known for their antimicrobial activity, The CaF_2 nanoparticles can be used as an antimicrobial compound in various cases.

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