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PREPARATION AND CHARACTERIZATION OF CALCIUM FLUORIDE NANO PARTICLES FOR DENTAL APPLICATIONS

Mohammad S. Al-Ajely [*1], Kareema M. Ziadan [2], Rafed. M. Al-Bader [3]
[*1] Department of Chemistry, College of Education, University of Mosul, Mosul, Iraq
[2] Department of Physics, College of Science, University of Basrah, Basrah, Iraq
[3] College of Dentistry, University of Basrah, Basrah, Iraq

Abstract

The aim of the present study was to prepare a calcium fluoride (CaF2NP) Nano particle which is used in dental composites as dental filling compo glass type. CaF2 Nano powders were prepared using a Co-precipitation method using binary liquid. Crystal Structural characteristics and Elemental composition of (CaF2NP) Nanoparticles were predicted by X-ray diffraction (XRD), which showed crystalline peaks of this material. Elemental composition was obtained from EDX analysis. Morphology and diameters of the Nano fibers were studied by scanning electron Microscope (SEM). The size of the particles was also measured from SEM images about 58 ± 21 nm.

Keywords: Nano; Preparation; Characterization; Calcium Fluoride.

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1. Introduction

Due to the importance of Nanotechnology in improving the physical and mechanical properties of a dental restorative material it has received considerable attention of researchers in this field. Alkaline fluorides (CaF_2, LiF_2, and BaF_2) are dielectric in nature and are widely used in microelectronic and optoelectronic devices such as wide-gap insulating over layers, gate dielectrics, insulators and buffer layers semiconductor-on-insulator structure and more advanced three- dimensional devices [1]. CaF2NPs have a technological importance because of their potential applications including advanced phosphor, photonic [2], display monitors, imaging, and light amplification [3]. The extremely high laser damage threshold of Calcium Fluoride has made Calcium fluoride (CaF_2) is an attractive material due to its excellent properties: low refractive index, corrosion-resistance, thermal stability, and significant hardness, also cost effective and chemically stable, with good optical properties, and a deficiency of absorbance of visible light. Furthermore Low concentration of F in oral fluids derived from labile F reservoirs formed by the use of F dentifrices and rinses have been shown to have a profound effect on the progression of dental caries (1–3). However, the low calcium (Ca) concentration in the mouth provides a limited driving force for the CaF2 formation, and only very small amounts of CaF2-like deposits are formed after a conventional sodium fluoride (NaF) rinse [4]. It was found that the composite containing 20% CaF2 had a cumulative F release of 2.34 mmol/L at 10 weeks [5]. Other Resercher found that the initial F release rate was 2 g/(h cm2), and the sustained release-rate at 10 weeks was 0.29 g/(h cm2) [6].

There are several methods to the synthesis of CaF2NPs which successfully prepare Nano scale material with controllable size and shape such as sol–gel method [7-9], solvo thermal process [10-12], reverse micelle method [13, 14], different precipitation methods [15-20], liquid-phase synthesis method [21], and flame synthesis [22, 23]. Co-precipitation is simple an easier method to synthesize Nano CaF2 and it was used successfully to prepare Nano composites. Hydrothermal method is also a novel method to synthesize Nano particles of better quality [6, 17, 24, and 25].

The aim of this study was to synthesize CaF2 Nano particles which is more important in dentistry especially in recent years in which the efforts focused on its use in light cured filling and intern could be used as a labile F reservoir for developing potentially more effective F regimens and as an agent for use in the reduction of dentin permeability.

2. Materials and Methods

2.1. Materials

The starting materials used in the experiments were CaCl2 (≥99.0%) purchased from Merck, NH4F (≥95.0%) purchased from PRS Panreac (Barcelona Espana), and Ethanol (≥99.0%) From Fluka chemical company.

2.2. Preparation of Nano-Caf2 Powders

(CaF2NPs) Nanoparticles were prepared by co-precipitation method. CaCl2 (0.01 mol) was dissolved in 100 ml distal water taken in 250 ml conical flask. NH4F (0.02 mol) was added into the flask under vigorous stirring on a magnetic stirrer.

The mixed solution was stirred for 4 h which is gradually transform the transparent reaction mixture into opaque white suspension. Then, centrifuged for 15 min at 5000 rpm and washed three times with ethanol, centrifugation to eliminate the residual chloride and the ammonium ions. Finally the solid product was extracted onto a ceramic dish and dried on a sand bath. The reactions of CaCl2 and NH4F solutions show in the following Eq:

$$CaCl_2 + 2NH_4F \rightarrow CaF_2 + 2NH_4Cl \quad (1)$$

2.3. Characterization

X-ray diffraction (XRD) measurements were performed on SIEMENS, D5000 (GERMANY) using Fe Kα radiation. The 2θ angular resolution was 0.02. The diffraction patterns were scanned slowly over the 2θ range 10~70, at a rate of 2º/min.

The crystallite size (D) of CaF2NPs was determined by the Scherrer equation [26]

$$D = \frac{\beta \lambda}{\cos\theta} \quad \ldots\ldots \quad (2)$$

Where λ is the wavelength of the incident X-ray (0.193604 nm), β Scherrer constant between 0.9 -1 depending on the particle morphology, in this experiment the average value of β = 0.94 was used giving for spherical crystals with cubic symmetry, θ is the diffraction angle and W is the full width at half maximum (FWHM in radian). Assuming spherical crystal, the diameter of the sphere (L) can be estimated [27]:

$$\langle L \rangle = \frac{4}{3} D \quad \ldots\ldots\ldots (3)$$

Where D crystallite size.

If the consideration is restricted to cubic crystal, the lattice planes spacing can be expressed as follows [28].

$$d = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \quad \ldots\ldots\ldots (4)$$

a_0 : lattice constant, here h, k, l are the miller indexes of the set lattice planes under consideration, we can write the quadratic form

$$\sin^2\theta = \frac{\lambda^2}{2a_0} \left((nh)^2 + (nk)^2 + (nl)^2\right) \quad \ldots\ldots\ldots (5)$$

Micromorphology of the obtained nanoparticles was observed by scanning electron microscopy (VEGA TESCAN – Czech)

The IR spectra were obtained by using Fourier transform infrared spectroscopy (FTIR, FTIR-8300, Shimadzu Co., Kyoto, Japan,) Spectra were obtained in the mid infrared region (400-4000 cm-1) with a resolution of 4 cm-1, averaging scans 32cm-1 per minute.

Multipoint BET (Brunauer-Emmett-Teller surface analysis is a technique for measuring specific surface area of the powders and porosity) surface area analyses were done (CHEMBET 3000 QUANTACHROME) with ultra-high purity nitrogen as the adsorbate gas and liquid nitrogen as the cryogen. The samples were dried in air overnight at 110 ºC before the measurement. The particle size of the primary crystals of glass was estimated from the BET surface area by calculating equivalent spherical diameter, or BET particle. The mean diameter obtained by applying the BET method, dBET is represented by [29, 30]

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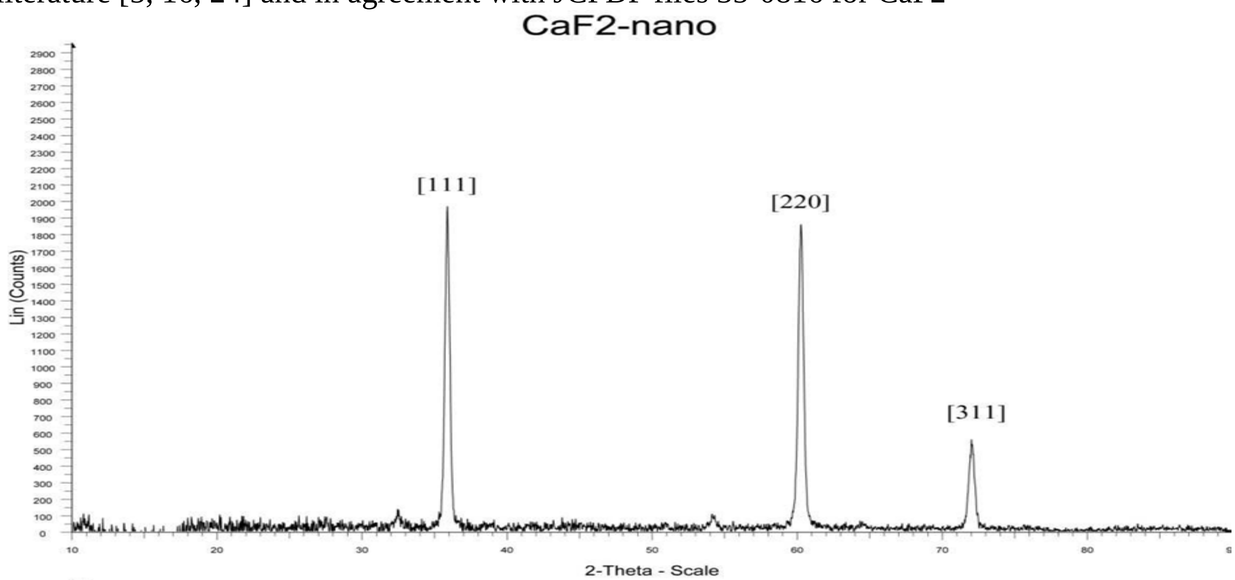
$$d_{BET} = \frac{6}{A_s \rho} \quad (6)$$

Where as is the specific surface area (m2/g) and ρ is the theoretical density of the phase (g/cm3), Density measurements were performed on each sintered specimen using the pycnometric method [31]

3. Results and Dissection

Figure (1) shows X-ray diffraction patterns of CaF2NPs powder. All the XRD peaks are indexed in to CaF2 cubic phase of the fluorite type structure with space group Fm3m. The XRD pattern was found to match exactly with those reported in the literature [32]. All characteristic diffraction peaks at 2θ 35.819º (111), 60.264º (220), 72.044º (311), which are in good agreement with the standard values for the bulk cubic CaF2 (JCPDS 87-0791). The calculated d values (lattice plane spacing) for the crystal planes (111) and (220) were respectively 3.14785°A and 1.92834°A, shown in Table 1, which were close to the standard values: 3.153°A for (111) and 1.93°A for (220), respectively [25].

The XRD patterns confirm the cubic crystallinity of the synthesized Nano particles. Using the (h k l) values of (1 1 1), (2 2 0) and (3 1 1) of different peaks, the lattice constant (a) of the samples were calculated. The average value of lattice constant was found to be a = 5.45682 ± 0.000204Å which is in good agreement with literature value a = 5.46250 Å (JCPDS 87-0791). The XRD pattern presents broad peaks revealing the small crystallite size of the synthesized samples. The Nano particles size was calculated using technique which uses Scherer's formula equation 2. The crystal size of CaF2NPs obtained in the range 27.915 ± 3.99 nm. The results match well with literature [5, 16, 24] and in agreement with JCPDF files 35-0816 for CaF2



CaF2-nano- File:X643.RAW-type 2Th/Th locked- start: 10.000º - End: 90.000º - step: 0.020- step time: 1. S – Temp.: 25ºC (Room)-time start: 2S- 2Theta: 10.000º - theta: 35.000º- Phi: 0.00º- Aux1: Operations: smoth 0.044 | Background 56.234, 1.000| Import.

Figure 1: X-ray diffraction of CaF2NPs powder

Table 1: The particle size analyses of a CaF2NPs

2 θ degree	Miller index (hkl)	d value (Å)	crystalline size D (nm)	dimeter <L> (nm)	lattice constant a0 (Å)
35.819	(111)	**3.14785**	25.459	33.946	0.545483
60.264	(220)	**1.92834**	26.571	35.428	0.545673
72.044	(311)	**1.64516**	25.497	33.996	0.54589

The morphology and diameters of the CaF2NPs show in figure 2. SEM image. The size of the particles was also measured by using the NIH Image program and the mean size of particles was 58 ± 21 nm calculated from approximately 100 Nano particles. The SEM picture shows that CaF2NPs 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. This result is close to what were a study reached such as Nandiyanto el at [21], Nakhaei [19] and Shahtahmassebi el at. [20].

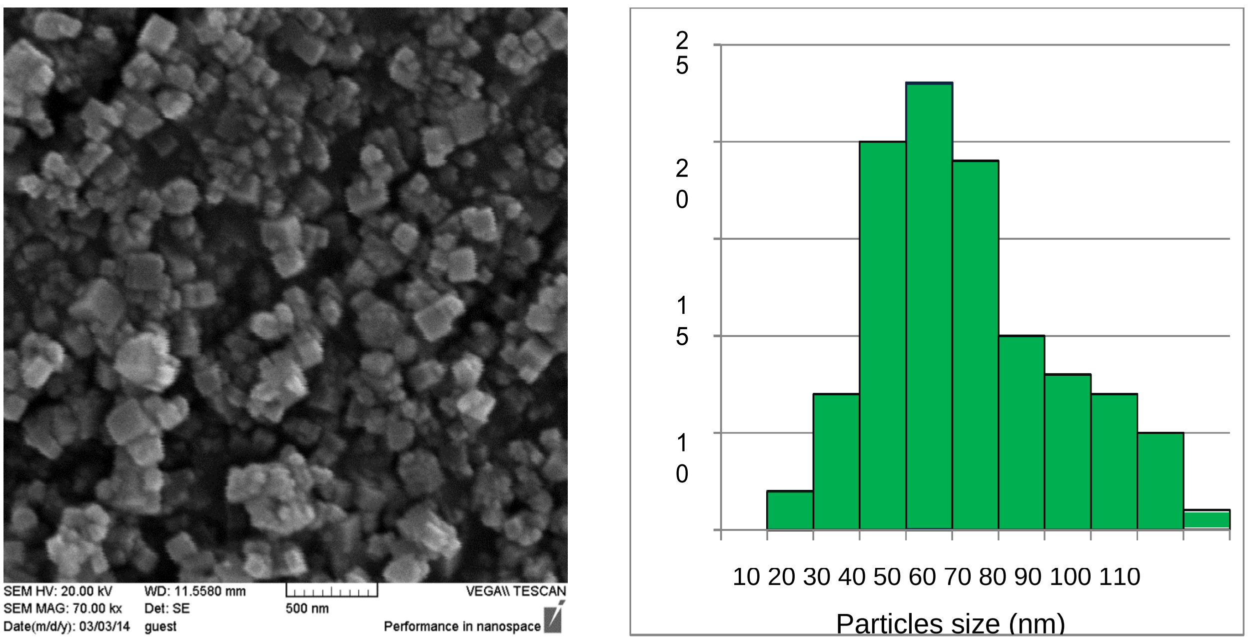


Figure 2: The morphology and diameters of CaF2 NPs measured by SEM

FTIR absorption was measured in order to show that the Oxygen bonds exist in the samples. The IR Spectrum of Nano crystals synthesized by co-precipitation method is shown in Figure 3. A Strong IR absorption bands at 450 cm-1 and 3452 cm-1 receptively belonging to Ca – F, H – O.

FTIR spectrum was also used to check the purity of the synthesized powder. Figure 3 shows the FTIR spectrum of the synthesized CaF2NPs. This spectrum showed two strong IR absorption bands at ~3400 and 1550 cm-1. They are characteristic of H–O–H stretching and bending of the H–O group. This finding reveals the presence of water molecules within the crystal structure of the prepared sample [16].

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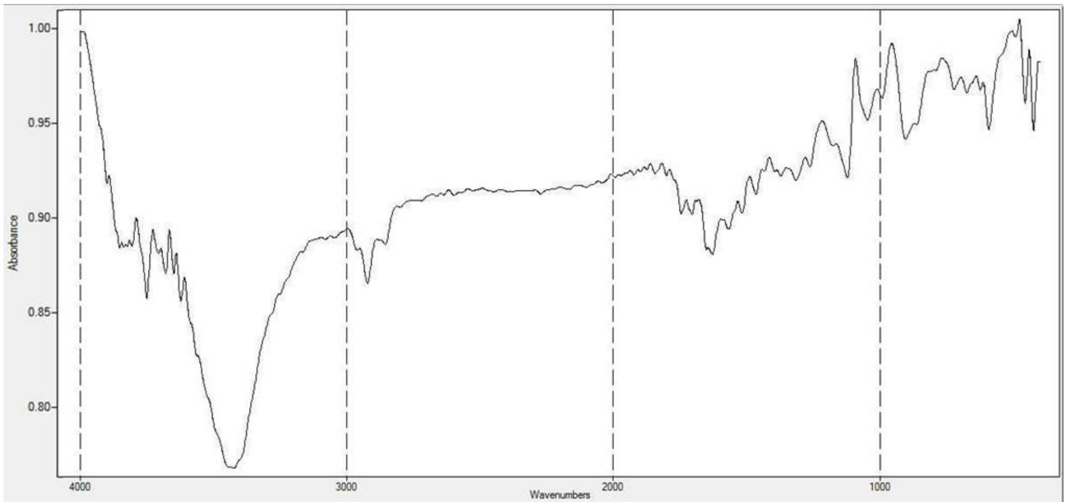

Figure 3: FTIR of CaF2 NPs

Figure 4 shows the EDX spectra of CaF2NPs, For Elemental composition obtained from EDX analysis, confirming peaks corresponding to the calcium and fluoride. The ratio of element was shown in Table 2.

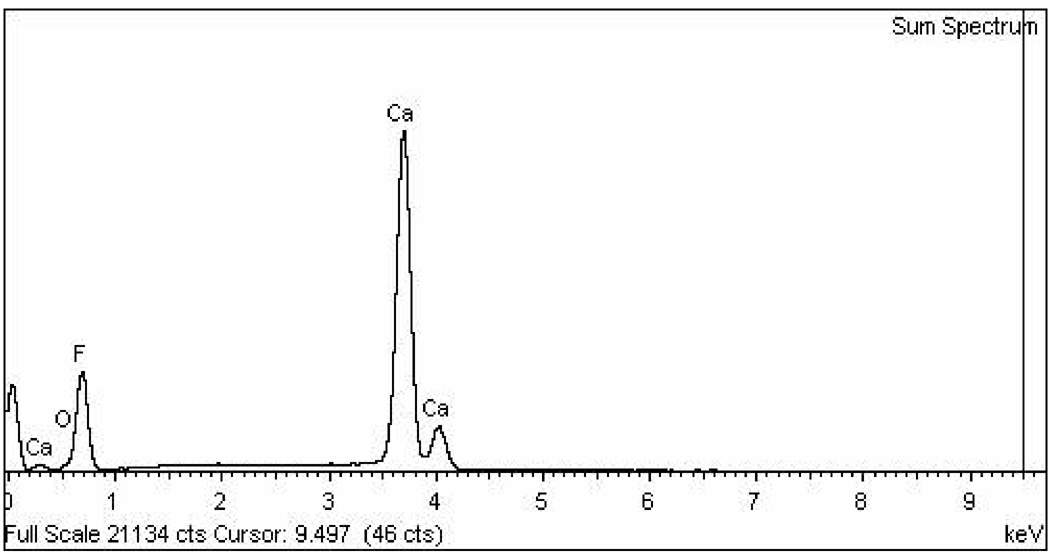

Figure 4: The EDX spectra of CaF2NPs

Table 2: Elemental composition (mass %) of CaF2 NPs

Sample	**ratio**	**O**	**F**	**Ca**
CaF_2 NP	Weight%	2.69	61.62	35.69
	Atomic%	4.33	74.38	21.30

One of the benefits of the mode of analysis is that it enables the power density distribution by pyecnomtric methods, the density was found 3.041± 0.006 g/cm3 and the theoretical density is 3.18g/cm3. The particle size of the primary crystals of CaF2NPs was estimated from the BET surface area by calculating equivalent spherical diameter, BET measurements of the CaF2NPs

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gave a specific surface area found 25.279 m2/g. This corresponded to a particle size of ~ 70 nm assuming a density of 3.18 g/cm3 and a spherical particle shape for the CaF2NPs, from the fundamental equation 6. This results were similar to those obtained by Pandurangappa [16] and Xu [24] which are35 and 56nm respectively. The Properties of CaF2NPs were tabulated in Table 3.

So CaF2NPs was prepared successfully by co-precipitation method; this suggests that the CaF2NPs could be a good agent for use in the reduction of dentin permeability furthermore It was successfully used in compo glass filling which is light cured type and will be published in next paper.

Table 3: Properties of CaF2NPs

d_{XRD}	27.91547nm
Density	3.041 g/cm^3
BET specific surface area,	25.279 m^2/g
SEM average particle size (d_{SEm})	58 nm
BET equivalent spherical particle size(d_{BET})	70 nm

4. Conclusions and Recommendations

In the present work the Nano particle of CaF2NPs have been successfully produced and applied in compo glass filling (our unpublished work) using the co-precipitation method.

The XRD data of these nanoparticles shows high crystallinity with lattice constant, in which (a) equal 5.45682 ± 0.000204Å. The Nano particles size of CaF2NPs obtained from Scherer's formula was within the range of 27.915 ± 3.99 nm, From SEM images it was found between 40.49 nm and 92.35 nm.

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*Corresponding author.
E-mail address: mohamadalajelee@ yahoo.com