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RESEARCH ARTICLE - PHYSICS

Synthesis and Characterization of Diopside Nanoparticles for Drug Delivery by sol-gel

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Abstract

Diopside ($CaMgSi_2O_6$), a calcium magnesium silicate mineral, is of significant interest for its potential applications in ceramics, bioceramics, and glass-ceramics due to its excellent thermal and mechanical properties. This study explores the synthesis of diopside powders using the sol-gel method, a versatile chemical process that offers precise control over composition and homogeneity at the molecular level. The sol-gel process involves hydrolysis and polycondensation of metal alkoxides in an aqueous or alcoholic solution, followed by drying and calcination to achieve the desired crystalline phase. In this work, calcium nitrate ($Ca(NO_3)_2{\cdot}4H_2O$), magnesium nitrate ($Mg(NO_3)_2{\cdot}6H_2O$), and tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$) were used as precursors for Ca, Mg, and Si, respectively. The preparation began with dissolving the metal nitrates in deionized water, followed by the addition of TEOS under continuous stirring to form a clear sol. The sol was then aged, dried, and calcined at various temperatures to determine the optimal conditions for diopside formation.

Characterization techniques such as - Thermal gravimetric analysis (TGA) Differential thermal analysis(DTA),X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) were employed to analyze the phase composition, microstructure, and chemical bonding of the synthesized powders scanning electron microscopy (SEM),. The results indicated that a pure diopside phase was successfully obtained at a calcination temperature of around 900°C, with the powders exhibiting a fine and uniform microstructure.

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Keywords: sol-gel, calcined, drug delivery, mesopours

1- Introduction

Due to the urgent need in the field of bone tissue engineering and the fact that the bio ceramic material is characterized by its high biological activity and the ability to be degraded controlled by stimulants, and most importantly, biocompatibility, the calcium magnesium silicate material was chosen [1][2]. Some of these bioactive medical materials belong to the sio2-cao-system. mg is diopside. Diopside has the ability to develop into the crystalline phase in bioactive glass ceramics with interesting bone-bonding properties, which causes the formation of hydroxytite in vitro[3][4] and stimulates bone cells to proliferate in vivo [1][2] .There are multiple methods for producing diopside, including the sol-gel method [2], which relies on wet chemistry and goes through several stages from solution then gel to the calcination stage [5][6]. In the beginning, the raw materials are mixed with solvents, which include salts or alkoxides, until a homogeneous and stable solution is obtained. After that,

hydrolysis and gelation processes take place [1], then it turns into a transparent gel, and then it is heated to form the white powder [7][8]. This is one of the most important features. Sol-gel is to control surface morphology and strong adhesion during deposition and to obtain homogeneous compounds at low temperatures[8][9]. Powders can be sintered when treated with a high thermal method[9][10] .It was found that diopside, which was manufactured by the sol-gel method followed by calcination at high temperatures at 950°C, consists of particles with sizes ranging from 22 to 32 nanometers. Research has shown that doping silica with different types of oxides containing Ti, Zr, Zn, Cu, and Sr is An advanced and developing field. [10][11][12][13][14] It has been proven that combining diopside powders with other materials in composite scaffolds gives biomaterials such as diopside (PCL)[14][15], and these oxides have a catalytic ability to form flat apatite, which resembles bone.

The susceptibility to biodegradation increases when exposed to a biomimetic substance for several days. In the case of diopside, it was found that apatite crystals increase with the soaking time from 9 to 28 days [16][2]. The significant increase in the content of calcium and magnesium ions in the simulated body fluid solution after immersion for 28 days provides contact with living bone and high biodegradability. IN order to develop bone tissue substitutes and fillers for bone defects and have significant calcium and magnesium potential, a diopside system was designed in the form of a heat-treated ceramic powder to understand the effects of increased calcium content in diopside. Diopside has biological activity in the form of a chemical reaction with the surrounding bone through the biological intermediate layer of apatite[1] , where the hydroxyapatite layer is deposited on the glass surface placed in the liquid of the simulated body.The hydroxyapatite layer (apatite is a biologically active surface layer) is when a chemical reaction occurs between the biologically active materials used gradually to form this layer, which can chemically bond with the bone. This is considered the basic step for stable and rapid bone integration [2][17].

2- Materials and method

In this study, due to the possibility of mesoporous in diopaside nanoparticles, the Venice TB Method Mislay pattern was used to synthesize diopaside nanoparticles. In the. In this study of non-ionic coupelian surfactant P 123 with polyethylene polyethylene Oxide –polypropylene oxide -polyethylene oxide (PEO20 , PPO 70 , PEO 20) p 123 (as a pattern Misley used such as tetra ethyl urto silicate) Si(OC3H2)4(TEOS) as a source of silicate, for Calcium nitrate tetrahydrate Ca(NO3)2.4H2O ،as a source of calcium and of the Magnesium nitrate hexahydrate Mg(NO3)2.6H2O was used as a source of magnesium for synthesis of CaMgSi2O6 nanoparticles

3 -Sample synthesis steps

The amount of 30 moles of distilled water with 3.036 grams of P 123 and 120 ml of hydrochloric acid (HCL).They were mixed in a water bath at a temperature of 36O using a magnetic stirrer for 2 hours until a clear solution was obtained.

In the synthesis, the acid HNO3 without HCL was used, and for comparison, the X-ray diffraction of those samples was also used. They are submitted under the title D-1

2- To the solution containing micelles prepared during mixing, 4.817 grams of ، Ca(NO3)2.4H2O , 5.3 grams Mg(NO3)2.6H2O and 9.04 ml of (TEOS) with molar ratio Si: Ca :Mg=2:1:1 (additional figure) 3-

2) and stirred for 24 hours at the previous temperature in a water bath until a milky tuber was obtained.

3- To separate the sediment, the milky solution obtained from the previous step in 15 ml Falcons

They were poured and centrifuged for 10 minutes at a speed of 700 rpm after draining the solution inside Falcons put the remaining substance inside the container.

4- To dry the material obtained from the previous step, white precipitate for 12 hours at temperature110 degrees Celsius was placed inside the oven .

5- The obtained dry powder to remove mold, nitrate and form the desired structure inside the oven for 3 Clock set at 9 degrees per minute at different temperatures (1000, 800, 700, 600 degrees Celsius) were calcined .

6- Finally, the calcined powder was crushed by a mortar and prepared for the necessary NM analyzes.

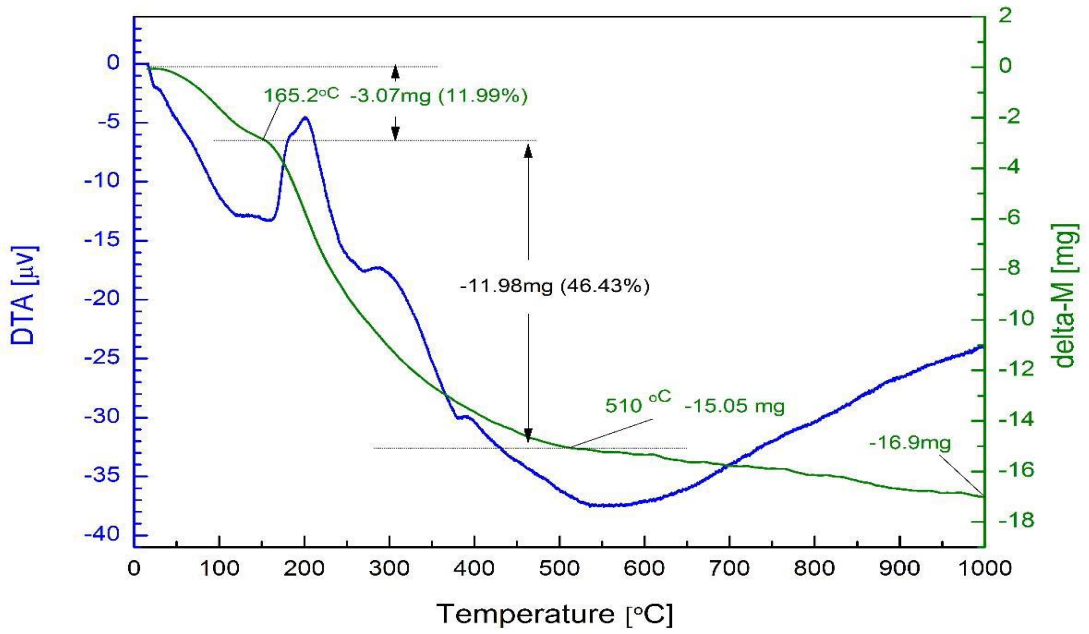
4-Results and Discussion

Using the sol-gel method is an easy method that relies mainly on heat in most of its stages. High temperatures or sintering help in losing amounts of water and some nitrates, which leave gaps in their place, or mesoporous ones, which give the diopside compound a spongy appearance to work as a drug delivery. The manufactured material was examined to ensure its conformation and suitability as a drug delivery. Thermal gravimetric analysis (TGA), Differential thermal analysis(DTA)

X-ray, Fourier transform infrared spectroscopy (FTIR , and surface morphology testing devices were used- Field emission scanning electron microscope (FE- SEM), and the results were satisfactory, as shown in the following paragraphs.

1- Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) is the measurement of the mass change according to changes in temperature and travel time. This method of reducing or increasing mass



Fig(1) DTA and TGA The mass decreases with increasing temperature

caused by cleaning, oxidation or loss of volatile substances (such as moisture) Fig(1) shows information such as Changes in the composition , thermal stability and structural transitions of seeds are deduced In order to determine the minimum calcination temperature necessary for the formation of calcium magnesium silicate macrostructure And such diopside crystal structure, thermal age weight analysis with a rate of 9 degrees Celsius per minute (from room temperature up to 1000 degrees Celsius, during the environmental journey using the device available in Sanan University (LINSEIS L70/2171) such differential thermal analysis (DTA), which measures It plots the temperature difference between the investigated and reference samples as a function of temperature, while both They are heated with the same thermal program In the new TGA analysis (Delta-M (Fig. 1), we see two significant weight reductions, the first time from room temperature up to a temperature of about 165 degrees Celsius, where the weight loss in this area is equal to 3.07 mg. (11.99% of the initial weight of the test specimen had a weight of 25.8 mg) which is related to evaporation Water is an endothermic process according to DTA, the second region is from 165 degrees Celsius to It is about 510 degrees Celsius, and the weight loss in this area is equal to 11.98 mg (46.43%) It is, that the number of significant weight loss was due to the departure of micellar pattern, so it can be done It was concluded that the empty space of the pattern has formed a cavity and the mass reduction in this area is related to evaporation Nitrate is in the precursors Thermogravimetry Analysis

2- Differential thermal analysis(DTA)

According to the DTA model in the second area of mass reduction, we first see an exothermic process that is related to organic substances (breakdown of the organic layers of the surfactant and its purification) and the formation of phases It is intermediate, then the process of complete evaporation of the model and such nitrates becomes endothermic processes are and occur in almost the same temperature range, after the temperature of 510 degrees Celsius, the rate of decrease .The mass decreases very slowly (1.85 mg to 1000°C), the total weight loss is not equal. with 16.9 mg (65.5%) from a temperature of about 600 degrees, we can see the exothermic process, which is related to It can be diopside crystal growth, but it does not have a sharp peak. According to the material mentioned above, the first calcination temperature of 600 °C was chosen, because with Paying attention to the results of thermal analysis, it is predicted that at this temperature, the grain will be completely pure and the mold will be removed and we have achieved a mesoporous structure, higher calcination temperatures of 1000, 800, 700 degrees Celsius were also selected to investigate the formation of the diopside crystal structure at a suitable calcination

temperature. It should be determined that the effect of calcination temperature on the appearance and physical properties also investigated TGA and DTA spectra of the synthesized samples before the purification process as shown Fig(1)

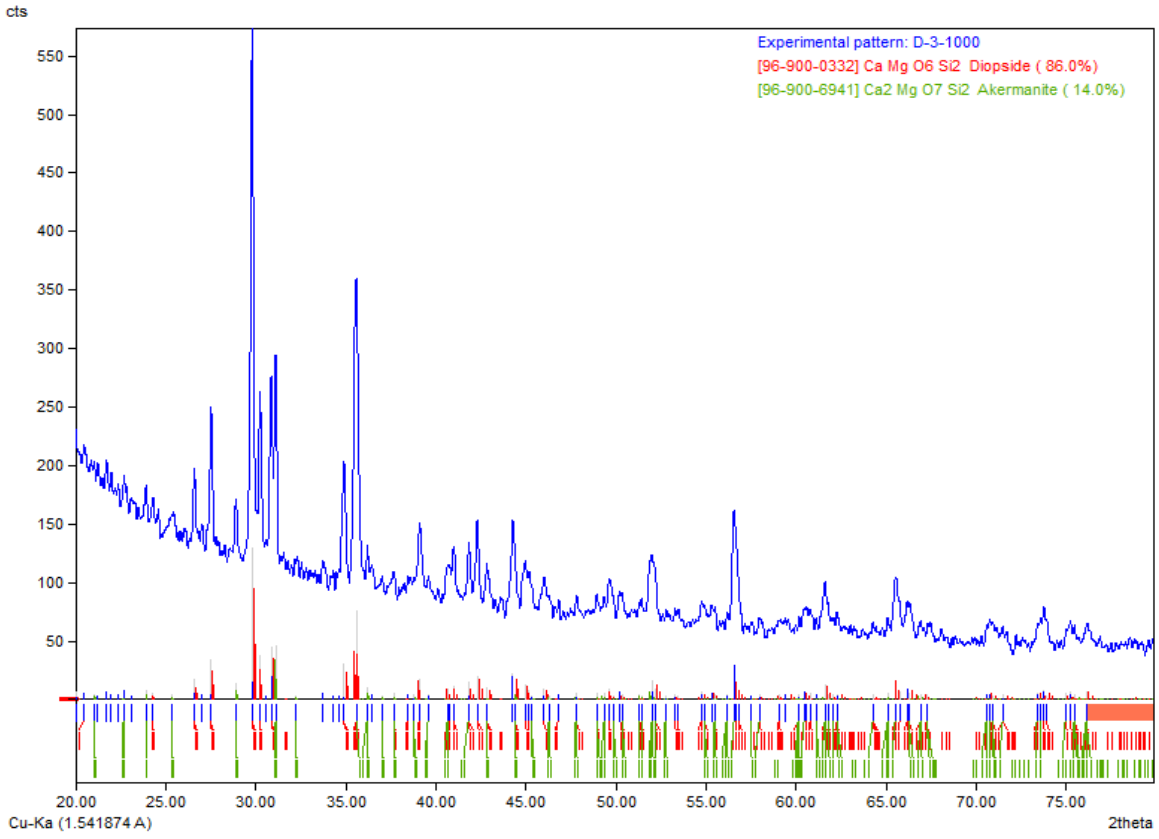
3- X-ray diffraction analysis (XRD)

The use of X-ray diffraction is a long and widely used method in investigating the structural properties of crystals. This method uses X-ray diffraction to check the characteristics of the new material, including determining the parameters related to the structure crystalline, lattice constant, phase determination, size of crystals, stress and defects in the lattice are used X-ray. At When the ray falls at an angle θ, the ray hits the crystal plates. A diffraction pattern is formed and the following Bragg relation can be applied:

$2\ dhklSin\ \theta = n\lambda$ (1)

In this relation, $dhkl$ is the distance between parallel plates, n is the diffraction order, θ is the diffraction angle, and λ is the wavelength of the X-ray. It is used XRD analysis in this research using X-ray diffractometer with copper target and wavelength λ= 1.5406 Angstrom available in the central laboratory of Ferdowsi University of Mashhad and in the range 20-80° = 2θ has been measured.

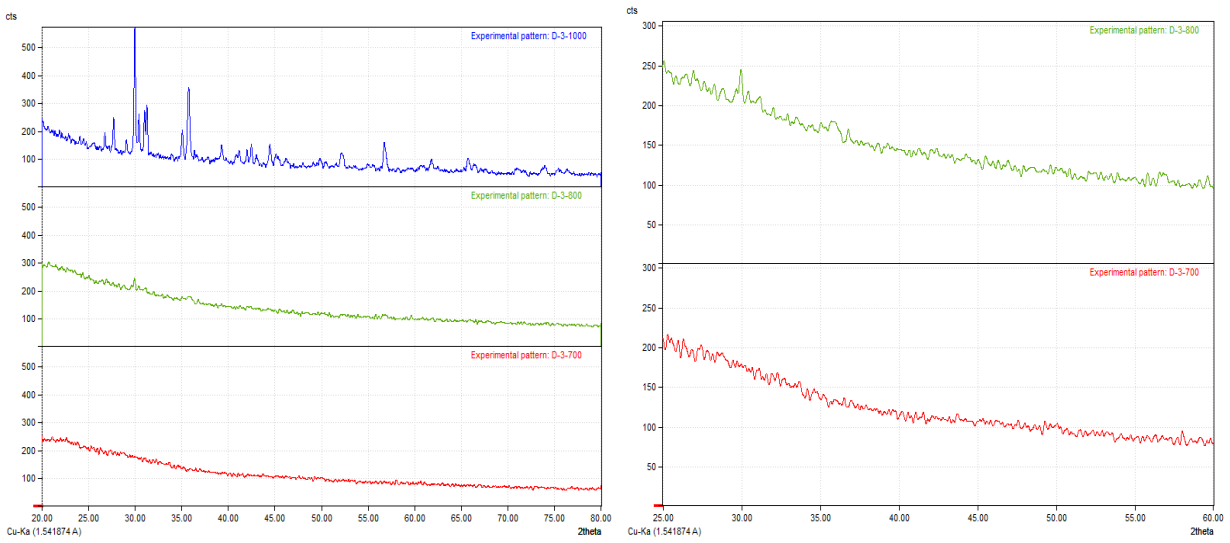
Synthesized with HCL that has been calcined at the previous temperature (D-3-1000), see Fig (2-a). It is possible that the peak related to the meronite structure has been removed, so only 14% of the akermanite structure is identified and the rest (86%) is the diopside structure. It should be noted that most of the peaks of these two structures are the reason for the closeness of the object structure and formula of these two materials is the main difference in their diffractions. The structure is in the intensity of the peaks and the synthesized samples (D-3) are almost single phase. That the most important common peak is at the angle of 23.31°., which is the highest for the structure of akermanite .It has the intensity of other peaks, but it is more intensity for the diopside structure, and the highest intensity is related to the peak It is located at an angle of 29.92 °. The intensity changes of the mentioned peaks can be seen in two figures (2-a) and (observed (2-b).



a

In Figure (2-b) the diffraction pattern of three calcined at temperatures of 700°C, 800 °C and 1000 degrees Celsius. From the diffraction pattern of 700 degrees, it can be deduced that the calcined grains at this temperature It is completely without structure and no crystalline structure has yet grown. In 800 degrees Celsius at the location of the main peak of the diopside structure (29.92 °C) and about 36 °C Hill-like peaks are formed, which indicates the beginning of crystal growth to diopside

structure at temperature Annealing is 800 degrees Celsius. In the figure (4) the mentioned twins are more recent and you can see It is possible that in 700, these two peaks are not formed at all Shape



b c

Figure (2) a-X-ray diffraction (D-3) in 1000 °C b-X-ray diffraction in 1000,600 and 700 °C c-X-ray diffraction in 600°C and 700 . °C

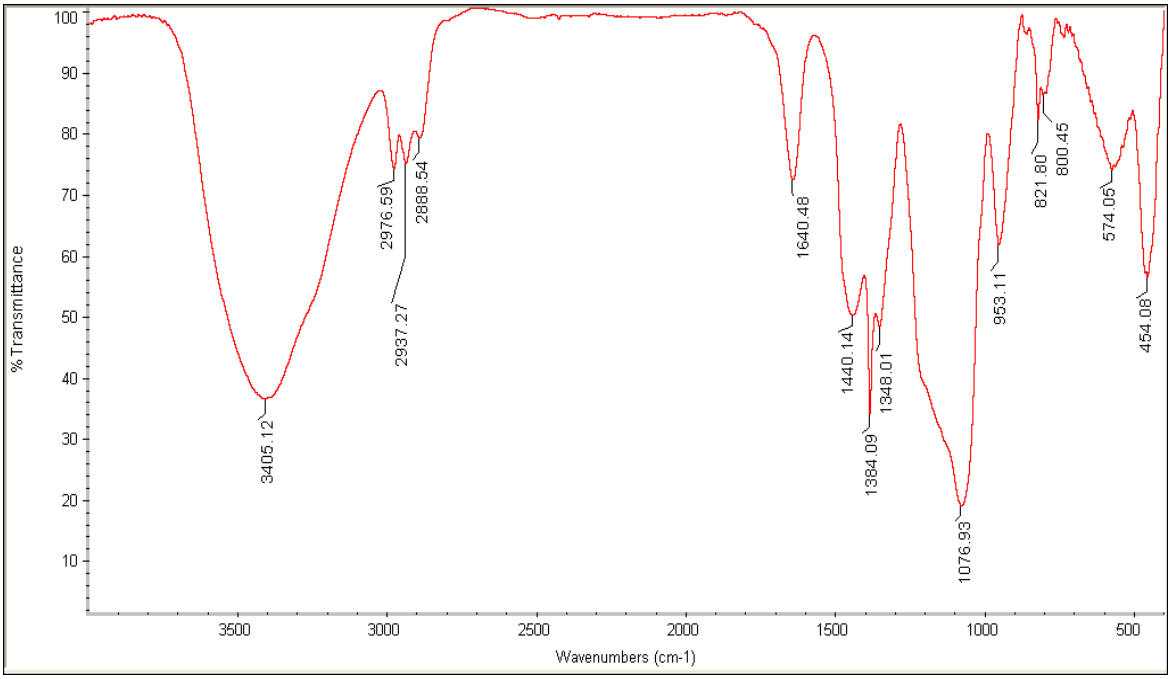
Scherer's formula cleared in equation (2) it was used to calculate the average size of the crystals in the synthesized samples .

$$D=k\lambda\beta cos\theta \qquad (2)$$ [17][18]

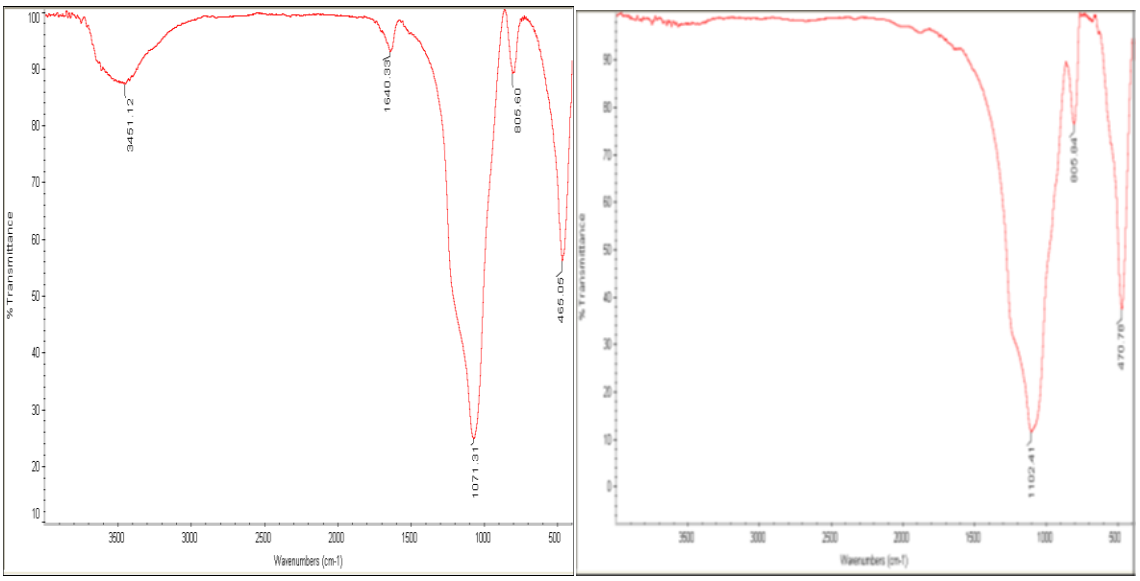
In this formula, β is the average width at half maximum height (in radians), θ is the Bragg angle, D is the size of the crystals, and k is a constant that is approximately equal to 0.94. Can be Using Scherer's formula and the average width at half maximum height of the main peak of the diopside structure for 800°C and 1000°C, crystal size 51.4 nm and 62.4 nm respectively. The increase in crystal size was calculated and the result was from 800°C to 1000°C. This is due to the growth of the physical crystal, which is also evident in the diffraction patterns given [18][19]

4- Fourier transform infrared spectroscopy (FTIR)

Infrared spectrum based on absorption of infrared radiation and examination of vibrational transitions of molecules and polyions. This method is usually used to identify organic compounds, the interaction of infrared radiation. It causes the bond vibration in its molecules and is a suitable method for identifying groups factor and molecular structure Traxyl spectrum in the infrared region for synthesized seeds using the FTRI spectrometer (model AVATAR 370 made by Thermo Nicolet Company (available in the laboratory of the Faculty of Science Ferdowsi University was prepared in the wavelength range of 1-cm 400-4000 .The FTIR spectrum of the synthesized samples before the calcination process (Fig 5), includes two large absorption bands in .The ranges are cm^{-1}1640 and cm^{-1}3400, which respectively correspond to the absorption vibrations of molecules Water and the stretching vibrations of -OH groups, which are calcined at 600 degrees Celsius, these bands are greatly reduced and completely removed at 800 degrees Celsius, Fig (4) . This is due to the complete evaporation of the water in the seeds, such absorption bands between cm^{-1}2850 to cm^{-1}3000 and cm^{-1}1348 band belong to stretching vibrations of -C-H bonds and the absorption band is in the range cm^{-1}1440 belongs to 2CH- and 3CH- vibration vibrations [17]. These four mentioned bands are due to 123 P polymer micelles in the structure of the nanotubes are before the calcination process, which in the FTIR spectrum The calcined samples at the first calcination temperature (600°C) have completely removed these bands, which An indicator of the complete removal of the mycelial pattern from seedlings due to the heating process at 600 degrees Celsius From the result of TGA analysis, we expect that the mold will be completely removed from the temperature of 600 degrees Celsius. It has been fulfilled and it is waiting for this sample to be completely mesoporous. The absorption valley in the low wavelength range of cm^{-1}400 to cm^{-1}550 indicates the formation of bonds O-Ca-O and O-Mg-O and the absorption bands cm^{-1}805 and cm^{-1}1071[18] also belong to vibrations stretching Si-O-Si, which is a confirmation of the formation of bonds in diopside bischel phase and the formation The structure is according to the formula of its object, Figure 3-12-b and C



a



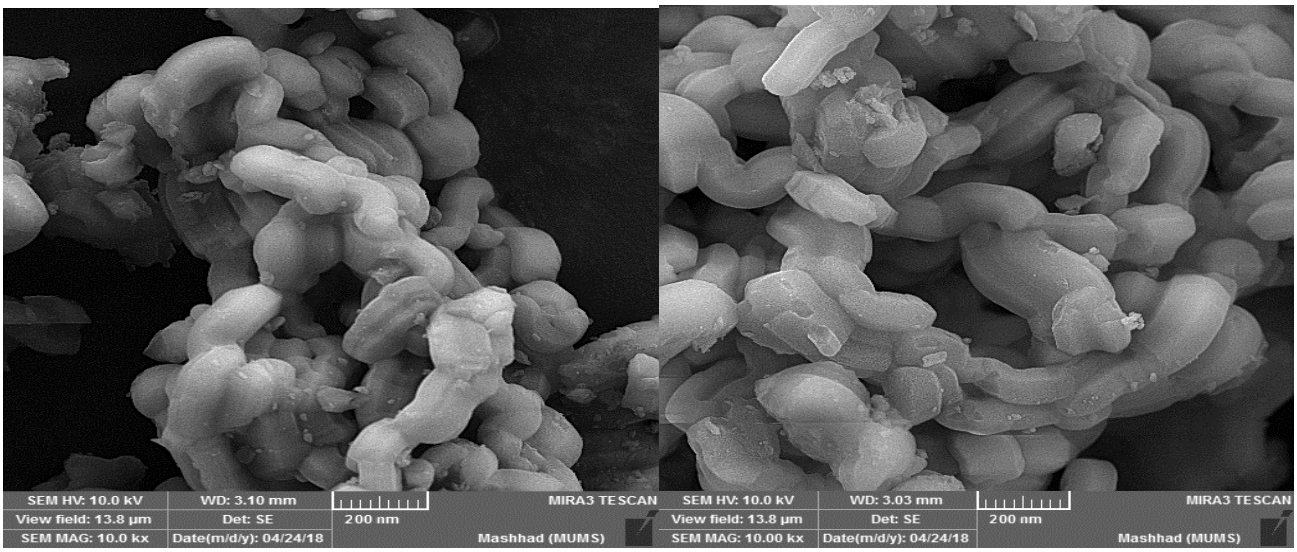
b c

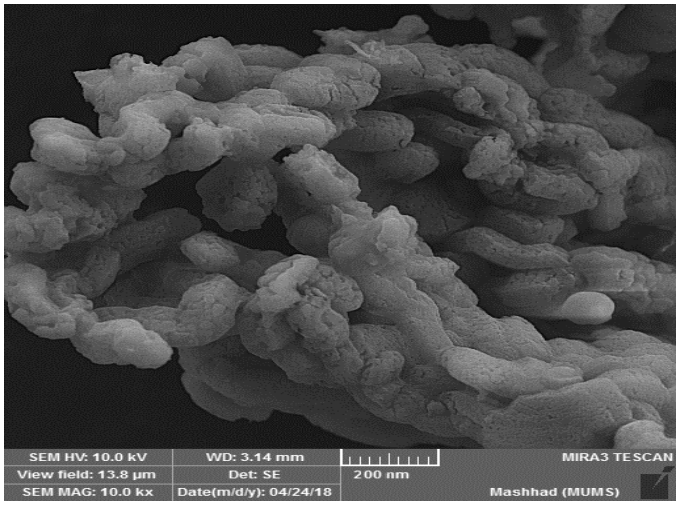
Figure (3) FTIR spectro for, a- before calcinate, b-in 600 °C, C- in 800°C .

5- Field emission scanning electron microscope (FE- SEM)

Using the FE-SEM device available in Bo Ali Research Institute, FE-SEM analysis of nanoparticles. Calcined at temperatures of 800, 600 and 1000 degrees Celsius were taken in FE-SEM . Fig (4 a,b,c) and Fig (5 a,b, c) represent the -FE-SEM images of all samples at 200nm and 500nm images zoon rate respectively. From these figs it can be seen that the particles

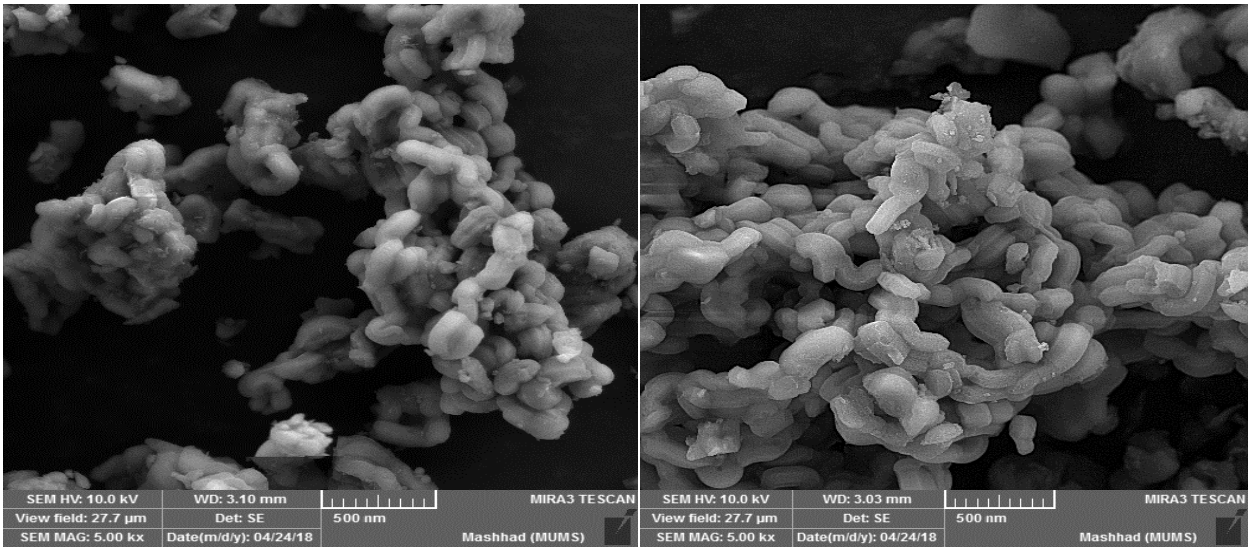
size is about 100nm, calcination temperature has become coarser and the surface of nanoparticles has also become rougher. Tow figures in different gage[19] [19] .



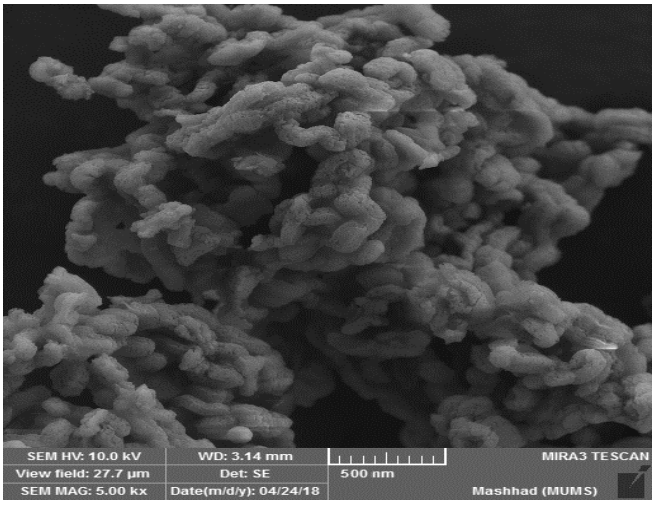


C

Figure (4) FE-SEM electron microscope images of calcined diopside nanoparticles at temperatures a) 600°C b) 800°C c) 1000 degrees Celsius, at 200nm image zoom rate .



a b



C

Figure (5) FE-SEM electron microscope images of calcined diopside nanoparticles temperatures a -600, b- 800, c- 1000 degrees Celsius, at 500nm image zoom rate .

5-Conclusions

This study demonstrated that the sol-gel method is an effective approach for synthesizing high-purity diopside. This technique offers precise control over the composition and particle size, along with relatively low processing temperatures. The pure diopside phase was successfully achieved at a calcination temperature of approximately 900°C, highlighting the potential of this method for various industrial applications.

[1]The prepared powders exhibited a pure crystalline structure and uniform microstructure, making them suitable for use in ceramics, bioceramics, and glass-ceramics applications. The use of the sol-gel method also allows for the tuning of the final material properties, enhancing design flexibility and contributing to the development of advanced high-performance materials.

Thus, this study establishes the sol-gel method as a promising technique for the production of diopside, applicable in a wide range of industrial and medical fields.

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