

Akermanite Nanoparticles (AMN) as a novel bio-ceramic nano powder by sol-gel method: synthesis and characterization

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ABSTRACT: Natural Akermanite (NAM) has been successfully prepared by a modified sol-gel method. Optimization in calcination temperature and mechanical ball milling resulted in a pure and nano-sized powder which characterized by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infrared Spectroscopy (FT-IR). Calcium nitrate, magnesium nitrate, Tetra Ethil Ortho Silicate (TEOS) and all other solvent and chemicals were analytical grade from Sigma Chemical (Tc. Litch, MO, USA). A magnesia mechanical ball mill (Jaha science, Ben, Germany) has been used to ensure the smallest particle sizes of the ceramic powder. The morphology of (AM) nanoparticles was examined by Scanning Electron Microscopy (SEM, Zaiex JSM-8500, Switzerland). In this research, pure natural Akermanite (PNAM) powders were successfully obtained via a simple sol-gel method followed by calcination at 1250°C. Mechanical grinding in a ceramic ball mill for 7 hours resulted in (AM) nanoparticles in the range of about 32-55 nm. Our study suggests that nano akermanite (NAM) might be a potential candidate by itself as a nano bio-ceramic filling powder or in combination with other biomaterials as a composite scaffold in bone tissue regeneration.

Keywords: *Akermanite; Nanoparticle; Nano powder; Novel bio-ceramic; Sol-gel*

INTRODUCTION

Nano technology has a great potential to improve ultimate biomaterials used for tissue engineering. Engineering systems for controlled release of biological nano molecules and supplementing scaffolds with inorganic nanoparticles improve tissue function by means of mimicking the natural external cell matrix (ECM). Many attempts in the field of engineering novel nano biomaterials played a key role in the recapitulation of the basic building blocks of native microenvironment of the cells for replacing tissue deficiencies like bone

losses from trauma or diseases (Sun, *et al.*, 2008). Upon this, the approach of incorporating inorganic nanoparticle into the matrix will progress rapidly. Although various inorganic nanomaterials have been used to replace damaged bones (Sun, *et al.*, 2008, Moffat, *et al.*, 2008, Kumar and Mohammad, 2011, Laurant, *et al.*, 2011, Pouponeau, *et al.*, 2011, Kratz, 2007, Wacker, *et al.*, 2011, Longley, *et al.*, 2003, Pinedo and Peters, 1988, Alter, *et al.*, 2006, Alter, *et al.*, 2006, Wigmore, *et al.*, 2010, Fadeian, *et al.*, 2015, Gheisari, *et al.*, 2010)

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but silicate biomaterials such as bio-glass, CaSiO_3 and Ca-Si-M ($M = \text{Mg, Zn, Ti, Zr}$) ceramics have a significant characteristic of the ability to release Si ions at a concentration that stimulates osteoblast growth and differentiation suggesting their application for bone tissue regeneration (Fadeian, *et al.*, 2015). The superiority of these ceramics in bone tissue regeneration compares to hydroxyapatite and other ceramic scaffolds have been reported and among them akermanite (AM) with the chemical formula of $(\text{Ca}_2\text{MgSi}_2\text{O}_7)$ both in powder or bulk form possesses slower degradation rate and efficiently has the ability of in vitro apatite formation and in vivo bone regeneration (Kumar and Mohammad, 2011). Akermanite ($\text{Ca}_2\text{Mg}[\text{Si}_2\text{O}_7]$) is a melilite mineral of the sorosilicate group, containing calcium, magnesium, silicon, and oxygen. It is a product of contact metamorphism of siliceous limestones and dolostones, and rocks of sanidinite facies. Sanidinite facies represent the highest conditions of temperature of contact metamorphism and are characterized by the absence of hydrous minerals. It has a density of 2.944 g/cm^3 . Akermanite ranks a 5 or 6 on the Mohs scale of mineral hardness, and can be found grey, green, brown, or colorless. It has a white streak and a vitreous or resinous luster. Akermanite (AM) powders and dense ceramics have been shown to be bioactive material for bone regenerations in biomaterial science. Wu and Chung proved the quite better cell growth on (AM) disks compare to the other members of $\text{CaO-SiO}_2\text{-MgO}$ systems like bredigite and baghdadite as a result of the reduction in their degradation rates (Kumar and Mohammad, 2011). Moreover, this ceramic is higher in mechanical properties when it is synthesized in a dense bulk format. Excellent mechanical stability, high bioactivity properties and appropriate cell biocompatibility features due to slow degradation rate made the (AM) ceramic a hot point of concern among bio-materialists. In addition, various powder preparation methods have been reported such as solid state reaction, sol-gel, co precipitation and spray pyrolysis technique (Moffat, *et al.*, 2008, Kumar and Mohammad, 2011, Laurant, *et al.*, 2011, Pouponeau, *et al.*, 2011, Kratz, 2007, Wacker, *et al.*, 2011, Longley, *et al.*, 2003, Pinedo and Peters, 1988, Alter, *et al.*, 2006, Alter, *et al.*, 2006, Wigmore, *et al.*, 2010, Fadeian, *et al.*, 2015). Among them sol-gel technique was chosen

to obtain pure and homogeneous (AM) with no extraneous phase. However, to the best of our knowledge, in none of the previous studies that focused on (AM) powder or bulk scaffolds preparation and characterization, interests has been taken to the preparation of this exceptionally advantageous bio-ceramic in nano-size powder format. Keeping the above points in view, this study was aimed to report the chemical synthesis and characterization of the sol-gel prepared bone-like powder of (AM) in a nanostructure type. When we consider replacing bone deficiencies with a synthetic material, it is necessary to mimic natural bone nanostructure as much as possible. In this study, we have focused on developing a substitute for biological apatite in a submicron level considering the advantage of high surface area owing to the nanostructure dimensions.

EXPERIMENTAL

Materials and Methods

In this research Calcium nitrate, magnesium nitrate, Tetra Ethil Ortho Silicate (TEOS) and all other solvent and chemicals were analytical grade from Sigma Chemical (Tc. Litch, MO, USA). A magnesia mechanical ball mill (Jaha science, Ben, Germany) has been used to ensure the smallest particle sizes of the ceramic powder. The morphology of (AM) nanoparticles was examined by Scanning Electron Microscopy (SEM, Zaies JSM-8500, Switzerland). The nanopowders were mounted onto sample studs and coated with gold using a sputter-coater (Eiko IB4, Switzerland) for 5 min. The microscope was operated at 15 kV to visualize the sample. The phase composition and structure of prepared samples were examined by X-ray powder diffraction (XRD). A Philips X'PERTMPD X-ray diffractometer (XRD) with Cu K α radiation at a scan rate of $0.002^\circ/\text{min}$ was used for the crystallographic structural analysis of the sample.

Transmission electron microscopy (TEM, JOLE JSMI-5600FG field emission transmission electron microscope) was used to determine the particle size of sol-gel prepared (AM) powders. Sample preparation has been done by obtaining a suspension from ultra sonification of the powder in ethanol on a foil

surface followed by dropping on a copper grid and finally dried to capture the images by means of TEM. A TRAMPKIN FT-IR-560 + spectrometer were used to record IR spectra using KBr Pellets. FT-IR spectra of the catalysts were recorded by FT-IR spectrophotometer in the range of 200-1800 cm^{-1} with a resolution of 6 cm^{-1} by mixing the sample with KBr.

Preparation of Natural Akermanite Nano Powder (NAMNP)

The (AM) ceramic was prepared via a modified sol-gel method. Briefly we dissolved a same molar ratio of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in an absolute ethanol and stirred vigorously for 30 minutes in 100°C to dissolve these precursors in the solvent. TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$) was added to the homogeneous solution and slowly stirred to transform to a wet gel. Drying in an oven at 120°C for 36 hours resulted in a dried powder which was grounded in a hand-mortar, then calcined at 750°C for 3 h and 1250°C for further 36 hours. Finally it was ball-milled in a zirconia mechanical ball mill for 7 hours to supply akermanite nanopowder (AMN).

RESULTS AND DISCUSSION

Preparing micron size akermanite (AM) by means of sol-gel method has been previously reported (Alter, *et al.*, 2006, Wigmore, *et al.*, 2010) but here some modifications in the post-treatments of the as-prepared ceramic including thermal treatments and mechani-

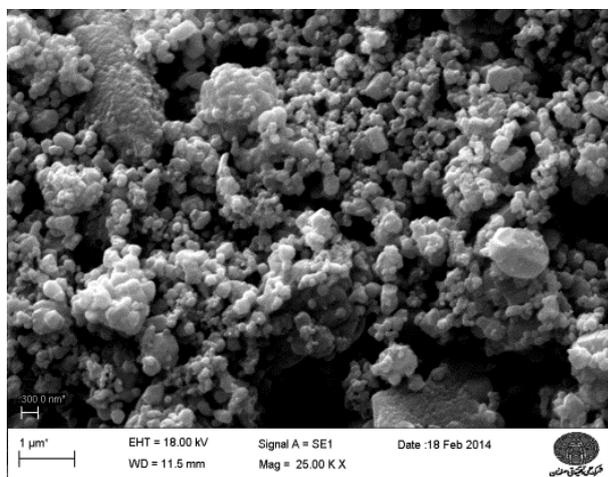


Fig. 1. SEM micrograph of Akermanite (AM) nano powders

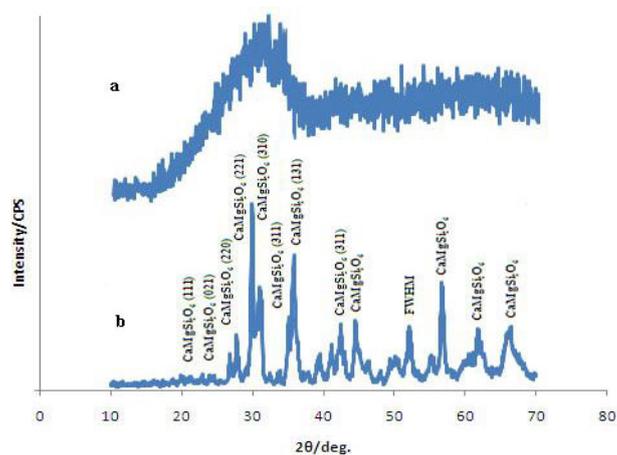


Fig. 2. XRD Pattern of akermanite powders calcined at different temperatures of 850°C (A) and 1250°C (B)

cal manipulations resulted in a pure akermanite nano powder with particle sizes in the range of 30-45 nm. The (AM) grain size and surface morphology of the particles are shown in Fig. 1, indicating that particles agglomerated as a result of high surface energy. So, it is obvious that the dimensions of agglomerated grains are in nano scale.

Fig. 2 show the XRD patterns of the akermanite nano powders prepared via the sol-gel method and calcined at different temperatures. Calcination at 750°C resulted in no characteristic peak (Fig. 2). Critical calcination temperature of 1250°C was obviously ideal to obtain pure (AM) with no impurity of other ceramics. It yielded strong (AM) peaks at about 212° , 202° , 313° , 103° , 221° , which indicates that the dominant resultant of the process is (AM) (Fig. 3). However, in the sample calcined at temperatures below 1250°C , akermanite, and in higher temperatures, bredigite was detectable. Furthermore, it is possible to estimate the

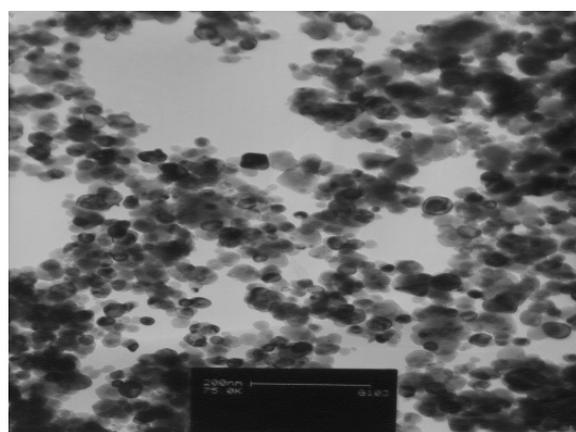


Fig. 3. TEM micrograph of akermanite nanoparticles

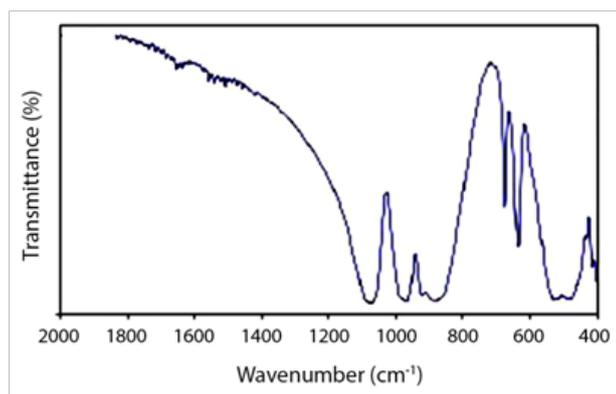


Fig. 4. FT-IR spectrum of the Akermanite (AM) nanoparticles

crystallite size (x_s) in a direction perpendicular to the crystallographic plane of XRD reflection (Gheisari, *et al.*, 2010, Gheisari, *et al.*, 2015). Sharper and isolated diffraction peaks such as $2\theta = 56.575$ were chosen for calculation of the crystallite size. Based on the Modified Scherrer formula ($L = K\lambda/\beta \cdot \cos\theta$), FWHM is the full width at half maximum for the chosen diffraction peaks in rad (in this case FWHM is equal to 0.0033662) and λ is the wavelength of X-ray beam for Cu K α radiation ($\lambda = 1/542$ nm). Accordingly, the average crystallite size of 36.153 was calculated. None of the other chosen peaks for estimation of crystallite size exceeded the result of 37 nm.

Fig. 3 presents the TEM micrograph of the 1250°C heat-treated (AM) and taken images enables the detailed observation of the morphological properties of particles. It shows the spherical border of a non-agglomerated mono disperse particle and particle size of 45 nm.

In the FT-IR spectra of the (AM) bands (Fig. 4) in the 400–2000 cm^{-1} spectral range in the region 850 cm^{-1} can be attributed to the bending vibrations, and bands in the region 750–1000 cm^{-1} which are attributed to the stretching vibrations of the silicate structure. They are ascribed to the Si–O symmetric stretching of bridging & non-bridging oxygen atoms, Si–O–Si symmetric stretching, and Si–O–Si asymmetric stretching. Our results are in agreement with previous studies (Karamian, *et al.*, 2015, Ghorbanian, *et al.*, 2010).

CONCLUSIONS

In this research, pure natural Akermanite (PNAM)

powders were successfully obtained via a simple sol-gel method followed by calcination at 1250°C. Mechanical grinding in a ceramic ball mill for 7 hours resulted in (AM) nanoparticles in the range of about 32–55 nm. Conventional micron-size (AM) had been previously investigated by many researchers but it is obviously different from bone mineral in aspect of mimicking the mineral resorption process. Bone crystals of hydroxyapatite are in nano-size dimensions and possess very large surface area. In contrast micron-size particles with lower surface area lack the potency of homogeneous absorption by osteoclasts and miss the unique advantage of nanotechnology for bioactivity and resorb ability. Our study suggests that nano akermanite (NAM) might be a potential candidate by itself as a nano bio-ceramic filling powder or in combination with other biomaterials as a composite scaffold in bone tissue regeneration.

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