Synthesis and Characterization of Akermanite by Mechanical Milling and Subsequent Heat Treatment

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Abstract. In this study, nano-structured akermanite was synthesized by mechanical milling and mixing using calcium oxide, magnesium oxide, cobalt oxide and silicon dioxide in a planetary ball milling with the speed of 500 rpm for 3 h. The milled powder was pelletized and sintered at 1200°C subsequently were characterized by X-ray diffraction (XRD), transmission Fourier transform spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM) confirming FESEM a dense sintered akermanite. The diametral tensile strength (DTS) value of akermanite was found to be 5.71 MPa, which was in the range of human cancellous bone i.e. 1.5-38 MPa. Finally, akermanite induced obvious apatite formation on the surface after 7 days of soaking. All the results postulated that the akermanite ceramics might be potentially used as bone repair biomaterials for non-load bearing applications.

1. Introduction

Bone damages mostly due to disease such as osteoporosis or accident have been a significant challenge in the field of biomedical science. Bone graft substitutes including autograft and allograft possess some drawbacks such as bone availability for transplantation, potential disease transmission, and immunogenic response, respectively [1]. Scientists have been making effort to develop bioceramic and bone filler or substitute material, particularly with bioactive fixation capability to the bone tissue through hydroxyapatite layer formation [2].

Calcium (Ca), magnesium (Mg) and silicone (Si) are also known as important elements in the human body which plays a vital role in the bone formation process and their deficiency can result in severe disorders. Calcium is abundantly found in the bone and tooth tissues [3]. Magnesium is important in the regulation of bone tissue growth and repair while silicon plays a vital role in skeletal development [4]. Calcium silicate-based biomaterials (CaSiO$_3$, CS) have shown excellent in vitro bioactivity mainly due to the release of Ca and Si ions into the surrounding environment [5]. However, their major drawback is the high dissolution rate which leads to high pH value [6] which is detrimental to cells [7].
One way to control the dissolution rate of these biomaterials is to incorporate another trace element such as magnesium (Mg), zinc (Zn), zirconium (Zr), titanium (Ti) etc. [6]. Akermanite is calcium magnesium silicate-based biomaterials (Ca$_2$MgSi$_2$O$_7$) which is formed by the incorporation of magnesium into the calcium silicate ceramics. One of the methods to synthesize akermanite is mechanical activation [8] which is known as one of the important methods to synthesize bioceramic nanopowders [8]. The major objective of the present study is to synthesize akermanite ceramics by high-speed planetary milling and evaluate the in vitro bioactivity and mechanical properties for bone and dental applications.

2. Experimental study

2.1 Synthesis of akermanite powders

Akermanite nanopowder was synthesized using a wet high-energy and high-speed planetary ball milling. Briefly, calcium oxide (CaO, Merck, 98%), magnesium oxide (MgO, Merck, 98%), silicon dioxide (SiO$_2$, Sigma-Aldrich, 99.9%), were weighed based on the stoichiometric ratio of akermanite and then were ball milled for 3 h in the planetary ball milling (PM 400-Reutcher) using zirconia vial and 37 zirconia balls. The ball to powder weight ratio was 10:1, while the powder to deionized water ratio was 3:1. The speed of vial was set at 500 rpm. Wet milling was adopted for higher efficiency and avoiding any dead zone. After milling, the mixture was dried in oven for 24 h at 100°C. Then, the dried powder was ground using agate mortar pestle and sieved through 200 µm. Finally, sieved powders were pressed into pellets using uniaxial hydraulic press (24T Laboratory hydraulic Press, MTI Cooperation) with the dimension of 13 mm (diameter) under the pressure of 200 MPa. The pellets were then sintered 1200°C for 4 h with a heating rate of 5°C/min.

2.2 Characterization of akermanite powders

The phase composition, lattice parameter and crystallite size of synthesized akermanite powders were determined using X-ray diffraction (XRD, Bruker Advanced X-ray Solution D8, XRD) through CuKα radiation (λ=0.154 nm at 20 kV and 30 mA). The diffraction angles (2θ) between 10° and 90° was scanned with a step size of 0.05° and a count time of 1.25 s per step. In order to determine the phase compositions, the patterns were matched to the International Center for Diffraction Data (ICDD) reference files. The crystallite size of akermanite powders was further calculated from XRD patterns using modified Scherrer equation (Eq.1) [9]:

\[
\ln \beta = \ln k \lambda / D + \ln 1 / \cos \theta
\]

where \( \beta \) (in Rad) is the diffraction peak width at half maximum intensity (FWHM), \( \theta \) is the Bragg diffraction angle(°), \( D \) crystallite size (nm), \( \lambda \) the wavelength of the radiation (0.15406 nm), and \( k \) is Scherrer constant which is usually 0.9. The sum of the absolute error values (i.e. \( \pm \Delta \ln \beta \))^2 is decreased by using modified Scherrer equation which yields a single line in which, the line intercept is \( \ln k \lambda / D \).

To investigate the crystallographic lattice parameters, Rietveld refinement was also employed using X’Pert software.

Functional groups of akermanite powders were evaluated by transmission Fourier transform infrared spectroscopy (FTIR, PerkinElmer, USA). The spectrum was recorded in the region of 400-4000 cm$^{-1}$ with a resolution of 2 cm$^{-1}$.

In order to evaluate the morphology and elemental composition, the sintered pellets were coated with a layer of gold (Au) by sputtering (EMITECH K450X, England) and the morphology and microstructure of samples were observed on a field emission scanning electron microscopy (FESEM, ZEISS, Germany) equipped with energy dispersive spectroscopy (EDS) with a voltage of 10 kV.
2.3 Shrinkage, porosity, and density

The linear shrinkage (length) of akermanite was calculated based on the following equation:

\[
\text{Linear shrinkage (\%) } = \frac{(L_g - L_s)}{L_g} \times 100
\]

(2)

Where \(L_g\) is the bulk length before sintering (green sample) and \(L_s\) is the bulk length after sintering (sintered samples), respectively. In addition, the density and porosity of akermanite were calculated based on ASTM B962-17 [10] and using the Archimedes method as follows:

\[
D (\%) = \frac{W_1}{(W_1 - W_3)} \times 100
\]

(3)

\[
P (\%) = \frac{(W_2 - W_1)}{(W_2 - W_3)} \times 100
\]

(4)

Where \(D\) is the bulk density, \(W_1\) is the weight of dry pellet in air, \(W_2\) is the weight of pellet after saturation in water, and \(W_3\) is the weight of samples suspended in water.

2.4 Mechanical properties

For mechanical evaluation of akermanite, the diametral compression test (DTS) was performed on the sintered compacted pellet of 13 mm through universal experimental instrument (INSTRON 3367) with the speed rate of 1 mm/min. The tensile strength of the pellets parallel to the applied force is calculated as follows [11]:

\[
\sigma_{\text{tensile}} = \frac{2P}{\pi dh}
\]

(5)

In equation 5, the \(d\) is diameter (mm), \(h\) is thickness (mm) of sample and \(P\) is the applied force (N).

2.5 In vitro bioactivity evaluation of akermanite powders

The in vitro bioactivity of akermanite was evaluated by soaking the samples in simulated body fluid (SBF) solution as described by Kokubo [12]. The sintered pellets were soaked in 25 ml of SBF solution (pH=7.4) at 37°C for 1, 7, 14, 21 and 28 days. After soaking, the samples were rinsed with deionized water and dried at 100°C for 24 h and the apatite formation on the surface was evaluated by FESEM analysis.

3. Results and discussion

In the present study, akermanite was successfully synthesized by mechanical milling and mixing for 3 h and subsequent heat treatment at 1200°C. The XRD patterns of powders sintered at 1200°C in Fig 1 (a) revealed characteristic peaks of akermanite (ICCD No#035-0592) with a small amount of diopside [13]. Furthermore, according to the modified Scherrer equation (Eq.1), Rietveld refinement, phase composition, crystallite size (nm), grain size (nm) and lattice parameters \(a\), \(b\) and \(c\) were estimated (Table 1). The crystal structure of akermanite is tetragonal with the space group of \(P4_21m\) in which, the lattice parameters are \(a=b\) and \(c\).

The density and porosity of akermanite were obtained 63.73% and 35.59%, respectively (Table.2). Besides, the linear shrinkage was nearly 17.30% after sintering at 1200°C. The FTIR spectra of sintered akermanite are shown in Fig 1(b). As observed, the bending vibration of 3439 cm\(^{-1}\) indicated the presence of OH group [14] and the vibration at 1637 cm\(^{-1}\) is related to bending vibration of H\(_2\)O molecules [15]. The bending vibrations at 511 cm\(^{-1}\) could be ascribed to O-Ca-O. In addition, the bending vibration at 573 cm\(^{-1}\) could be assigned to the O-Mg-O. In addition, vibrations at 641 and 684 cm\(^{-1}\) revealed Si-O-Si bonding. Also, the vibration at 1021 cm\(^{-1}\) was related to the symmetric stretching of Si-O-Si [8]. Finally, stretching Si-O bonding revealed vibrations at 848, 981 and 923 cm\(^{-1}\), respectively.
The FESEM micrograph of akermanite before and after immersion in SBF solution are depicted in Fig.2 (a, b). It appeared that akermanite possess uniformly distributed grain microstructure. However, akermanite did not clearly reveal the grain boundaries. In addition, after soaking in SBF for 7 days, an obvious apatite layer was formed on the surface indicating excellent in vitro bioactivity of akermanite. The pH value of the solution after 28 days of soaking reached to 7.69-7.72 which is in the range of human biological value compared to CaSiO$_3$ which was reported as 8.8 [16] revealing the chemical stability of akermanite (see Fig.2(c)).

The DTS value of akermanite was 5.71 MPa which is higher than conventional ceramics such as hydroxyapatite (HA) and beta-tricalcium phosphate (β-TCP) as summarized in Table.2, reflecting stronger bioceramics has been developed although with a higher porosity and lower bulk density. This suggests that silicate bioceramic has potentially good future for bone grafting materials.

![Figure 1. (a) XRD and (b) FTIR of akermanite and sintered at 1200°C](image)

![Figure 2. FESEM images of akermanite sintered at 1200°C (a) before and (b) after soaking in SBF solution for 7 days (10x magnification) and (c) The change of pH values in SBF after soaking of akermanite at different period of time](image)

**Table 1.** The grain size, lattice parameters, and crystallite size of akermanite

| Material    | Grain size (µm) | $a$(Å) | $b$(Å) | $c$(Å) | β(°) | Crystallite size(nm) |
|-------------|-----------------|--------|--------|--------|------|----------------------|
| Akermanite  | 0.93±0.25       | 7.837  | 7.837  | 5.011  | 90   | 45.69                |
Table 2. A comparison of mechanical properties of cortical and cancellous bone, hydroxyapatite (HA), akermanite (In this study)

| Material                  | DTS (MPa) | Relative density (%) | Porosity (%) | Reference   |
|---------------------------|-----------|----------------------|--------------|-------------|
| Cortical bone             | 50-150    | 87-95                | 5-13         | [17]        |
| Cancellous bone           | 1.5-38    | 0.05-0.7             | 30-90        | [18]        |
| Calcium silicate cement   | 2.57      | -                    | -            | [19]        |
| Hydroxyapatite            | 4         | 65-95                | 19.4-2.8     | [20]        |
| β-TCP                    | 3.82,2.85 | 85.9,91.2             | -            | [21]        |
| Akermanite                | 5.71      | 63.73                | 35.59        | This study  |

4. Conclusion

In this study, nano-structured akermanite was successfully synthesized by mechanical milling and mixing and subsequent sintering. The crystallite size of akermanite under 3 h ball milling time and subsequent heat treatment at 1200°C was 45.69 nm. The XRD and FTIR analyses demonstrated the formation of akermanite ceramics. Furthermore, the diametral tensile strength of akermanite was in the range of human cancellous bone suggesting that they might be used for bone tissue repair under non-load bearing application. Finally, akermanite revealed obvious apatite-forming ability after soaking in SBF solution for 7 days of soaking as demonstrated by FESEM analysis.

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