Characterization and evaluation of copper-doped akermanite ceramic

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Abstract. The aim of this study is to investigate the influence of copper (Cu²⁺) on structural and mechanical properties of akermanite ceramic synthesized via high-energy wet planetary ball-milling route. Based on structural analysis, partial substitution of copper ions did not affect the phase stability of host akermanite. Moreover, Cu²⁺ suppressed the grain growth, thus considerably improved the sinterability and mechanical properties of akermanite ceramic. Vickers microhardness values of doped samples increased five- or six-times compared to that of pure akermanite at 1200°C. Our study indicated that the Cu²⁺-doped akermanite ceramic could potentially be used as an alternative material for bone replacement in biomedical applications.

1. Introduction

Silicate bioceramics, such as wollastonite (CaSiO₃), diopside (CaMgSi₂O₆), akermanite (Ca₂MgSi₂O₅), bredigite (Ca₃MgSi₃O₈) and merwinite (Ca₃MgSi₃O₈) have been developed in the past ten years. It has been shown bioceramics containing CaO and SiO₂ possess bone-like apatite-forming ability and exhibit good bioactivity for bone implant materials [1].

An alkaline earth silicate-based compound of akermanite (Ca₂MgSi₂O₅), a member of CaO-MgO-SiO₂-based bioceramics, belongs to a tetragonal crystal system, space group P-42m and Z = 2 [2]. Akermanite has garnered considerable interest in biomedical applications due to its dual angiogenesis/ostegenesis stimulation, controllable biodegradability, cytocompatibility, as well as in vitro bioactivity [3]. Additionally, akermanite possessed superior mechanical properties to those of stoichiometric hydroxyapatite (HA), beta-tricalcium phosphate (β-TCP) and bioglass [4]. Previously, Wu and co-workers prepared akermanite ceramics at 1370°C for 6 h. They reported that akermanite ceramics induced apatite formation after 10 days of immersion in stimulated body fluid (SBF) [5], which reflects the substrate is suitable in enhancing bone formation both in vitro and in vivo [1]. Even though akermanite retains both excellent in vitro and cell biological behaviours, its low fracture toughness limited its use in load-bearing tissue regeneration [6]. So far, the improvement is still a need.

Copper (Cu²⁺), an essential inorganic ion in human body, is of interest due to its participation in blood vessel formation (angiogenesis) [7]. Sufficient copper level supports bone growth, but prevents osteoporosis [8]. Earlier researchers demonstrated that the combination of Cu²⁺ and Si⁴⁺ ions resulted in stronger stimulatory effects of human umbilical vein endothelial cells (HUVECs) on vascularization in comparison to pure CaSiO₃ bioceramics [9]. In addition, Željko R et al. highlighted that Cu²⁺ could improve the mechanical properties of calcium phosphate-based bioceramics synthesized hydrothermally [10]. Therefore, the synergetic effects of Cu²⁺ and akermanite ceramics might be an interesting approach to achieve better mechanical characteristics than intrinsic counterparts for bone repair and regeneration applications.
Previously, calcium silicate-based materials were prepared through four main methods such as chemical precipitation, sol-gel, hydrothermal and mechanical activation methods [1]. In our work, high-energy mechanical activation route was applied as a processing technique for nano-structured powders preparation due to its simplicity of experiment, low production cost and rapid synthesis of the product [11].

To the authors’ best knowledge, no study has been reported on the physical and mechanical properties of pure and Cu$^{2+}$-doped akermanite ceramic for bone tissue engineering applications. Hereby, akermanite is doped with different Cu$^{2+}$ contents (2.5, 3.5 and 4.5 mol%) through high-energy planetary ball milling. Phase analysis, morphology and physico-mechanical properties were compared between Cu$^{2+}$-doped akermanite and akermanite ceramics alone.

2. Material and methods

2.1. Sample preparation

The akermanite and Cu-doped akermanite powders were synthesized via high-energy mechanical activation route. Briefly, the reagents calcium oxide (reagent grade, Sigma-Aldrich, USA), magnesium oxide (99%, Alfa Aesar, USA), silicon dioxide (99%, Sigma-Aldrich, USA), and copper (II) oxide (99%, Sigma-Aldrich, USA) were milled according to stoichiometric compositions of Ca$_2$Cu$_x$MgSi$_2$O$_7$, (where $x = 0, 0.25, 0.35, 0.45$) in a planetary ball mill (PM 100, Retsch GmbH, Germany) for 4 h at ambient conditions. The rotational speed of main disc was set at 500 rpm. The ball-to-powder weight ratio used was 10:1. Deionized water was used as suspension media. Afterwards, the resultant powders were uniaxially pressed at 150 MPa in an evacuable metal die into 13 mm diameter discs. Consequently, sintering was performed at 1200°C for 3 h in ambient air.

2.2. Material characterization

The structural analysis was conducted using X-ray diffractometer (XRD; D2 Phaser, Bruker AXS Inc., USA) fitted with Cu–K$_\alpha$ radiation ($\lambda = 0.154$ nm) in a scan range of $20^\circ \leq 2\theta \leq 60^\circ$, with an integration time 1.25 sec/0.02$^\circ$ step. The crystallite size was estimated using the Scherrer’s formula.

Morphological observation was conducted on the gold-coated akermanite ceramics using Field Effect Scanning Electron Microscope (FESEM; Gemini Zeiss Supra™ 35 VP, Germany). The average grain size of samples was evaluated using an image analysis software (ImageJ 1.51k, USA).

For diameter shrinkage evaluation, dimensions of ceramic bodies before and after sintering were measured with the use of a digital vernier calliper (Mitutoyo 500-197-30 AOS Absolute, Japan). Then, the shrinkage values were calculated using the equation reported by Hana N et al. [12].

Relative density of the pellets was determined in accordance with ASTM B962-17 by applying Archimedes’ relations [13].

Vickers hardness ($H_v$) was assessed on polished sintered pellets in accordance with ASTM (E-384) procedure [14] applying a digital Vickers microhardness tester (FV-810, Future-Tech Corp., Japan) with 5 kilograms-force (kgf) load and a dwelling time of 10 secs. Fracture toughness ($K_{IC}$) was estimated by using Avans and Charles’ relation [15].

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K_{IC} = 0.0824 \frac{F}{C^{3/2}} ,
\]

where, $F$ is the applied load (N), and $C$ is radial crack length (m) measured from the center point of the indented area.

3. Results and discussion

3.1. Structural analysis

XRD patterns of pure and Cu$^{2+}$-doped akermanite are illustrated in Figure 1. The resultant diffraction peaks of Ca$_2$Cu$_x$MgSi$_2$O$_7$ were well matched with akermanite standard pattern (ICDD: 35-592). As an analogue with akermanite in component, a minor presence of diopside (CaMgSi$_2$O$_6$; ICDD: 41-1370), a bioactive phase, was also detected.

Cu$^{2+}$ doped in akermanite structure slightly altered the lattice parameters, which may be induced by lattice distortion. As evidenced by the enlarged spectra between 25° and 35°, Cu$^{2+}$-doping somewhat
engendered an insignificant shift of diffraction peaks towards the higher angles in term of dopant content. This attributed to the partial substitution of Cu\(^{2+}\) into Ca\(^{2+}\) site of akermanite host. Herein, the explanation for site occupancy of Cu\(^{2+}\) in akermanite structure could be made as follows.

A silicate compound akermanite (Ca\(_2\)MgSi\(_2\)O\(_7\)), belonging to \(X_2T^{(1)}T^{(2)}_2O_7\) melilite family of minerals with tetragonal crystal symmetry. The akermanite structure was reported to possess three independent cation sites (\(X = Ca^{2+}\), \(T^{(1)} = Mg^{2+}\), \(T^{(2)} = Si^{4+}\)). The Ca\(^{2+}\) ion is coordinated by six or eight neighbouring oxygen (O\(^{-2}\)) ions. Mg\(^{2+}\) and Si\(^{4+}\) ions were documented to occupy in the tetragonal sites [16]. Considering the effective ionic radii (\(r\)) and charge balance of the cations corresponding to coordination number (CN), the ionic radius of Cu\(^{2+}\) (\(r = 0.73\) Å, CN = 6) is close to that of Ca\(^{2+}\) (\(r = 1.00\) Å, CN = 6) rather than Mg\(^{2+}\) (\(r = 0.57\) Å, CN = 4) and Si\(^{4+}\) (\(r = 0.26\) Å, CN = 4). Therefore, from a crystallographic viewpoint, it could be predicted that the accommodation of Cu\(^{2+}\) ions in Ca\(^{2+}\) sites of Ca\(_2\)MgSi\(_2\)O\(_7\) host is more possible than the Mg\(^{2+}\) and Si\(^{4+}\) sites.

Adopting Scherrer’s relation, the crystallite size was then estimated from the (111), (021), (121), (130), (122), and (132) planes of akermanite. The crystallite size was decreased from 53.981 to 52.524, 51.075 and 49.321 nm in terms of dopant content. The unit cell volume (\(V_{cell} = a^2 \times c\)) were decreased from 307.374 cm\(^3\) to 307.320, 307.254, 307.175 cm\(^3\) for AK, 2.5Cu-AK, 3.5Cu-AK and 4.5Cu-Ak respectively, proving lattice contraction [17]. Any additional phase formation was not detected in the profiles, clearly proving the structural stability with doping. Notably, the increase in monoclinic phase with further increase in Cu\(^{2+}\) dopant was expected.

![Figure 1. XRD patterns of Ca\(_2\),Cu\(_x\)MgSi\(_2\)O\(_7\) samples: (a) 20° to 60°, and (b) partial magnification from 25° to 35°.](image)

3.2. Morphological and physical evaluations

Figure 2 compares the grain growth behaviour of outermost and fractured surfaces of pure and Cu\(^{2+}\)-doped samples at 1200°C. As observed from microstructural analyses, the different amounts of Cu\(^{2+}\) dopant had a direct effect on the grain growth. The grains were in irregular geometry. The grains grew slowly and the average granule size range (1.05 \(\mu\)m -1.37 \(\mu\)m) remained a non-significant difference. A possible explanation of this result is that the introduction of smaller Cu\(^{2+}\) ions imposed an effective restriction on grain growth of Ca\(_2\)MgSi\(_2\)O\(_7\) by reducing the movement of grain boundaries during sintering.

Further fracture studies signified that the grains were fractured in transgranular and intergranular modes, especially with large fraction of transgranular after doping. It could be assumed that smaller Cu\(^{2+}\) ions substituted into akermanite structure reinforced the grain boundary strength leading to a transgranular-prominent fracture. Consequently, this fracture mode restricted crack propagation [18].
In addition, the physical study revealed that dopant changed the density of sintered samples (Table 1). Diameter shrinkage and relative density of ceramics remarkably increased after doping. The shrinkage increased from 15.34% to 26.61% as well as relative density rose from 62.67% to 94.25% with Cu²⁺ content. This result indicated that copper accelerated sinterability of akermanite ceramics. Therefore, the current results were well consistent with the hypothesis that the densification rate was influenced by the radii of ions doped; i.e., the smaller the ionic radii, the better the densification rate [19]. Hence, our study highlighted that Cu²⁺ affects the solid-state reactions and lowered the required densification temperature of akermanite ceramics. From an economic standpoint, this property is useful for less time- and energy- consumption reduction in producing engineering ceramics.

![FESEM micrographs](image)

**Figure 2.** FESEM micrographs of outermost and fractured surfaces: (a, e) AK, (b, f) 2.5Cu-AK, (c, g) 3.5Cu-AK, and (d, h) 4.5Cu-AK ceramics at 1200°C.

**Table 1.** Physical properties of akermanite ceramics

| Sample     | Diameter shrinkage (%) | Relative density (%) | Grain size (µm) |
|------------|------------------------|---------------------|-----------------|
| AK         | 15.34                  | 62.67               | 1.05            |
| 2.5Cu-AK   | 25.25                  | 95.28               | 1.26            |
| 3.5Cu-AK   | 26.63                  | 98.07               | 1.27            |
| 4.5Cu-AK   | 26.62                  | 97.12               | 1.37            |

3.3. Mechanical evaluations

Hardness and fracture toughness are the important parameters required for the prediction of the mechanical performance of brittle materials for bone implant applications.

The SEM images of resultant impressions are shown in Figure 3 (a-d). As observed from the micrographs, the doped specimens definitely possessed higher densification and toughness than pure ones. The cracking feature around Vickers indentations was surface radial cracks. The indentation depth and size on AK was obviously deeper and larger than that of doped samples. As seen in Table 1, HV improved from 0.76 GPa to 5.48 GPa, 6.172 GPa and 6.06 GPa for AK, 2.5Cu-AK, 3.5Cu-AK, and 4.5Cu-AK, respectively. As seen, the enhanced in HV values were obtained in denser doped samples. This could be explained that since HV technique is a surface technique, the HV of ceramics mainly depends on the microstructure (i.e., surface porosity) of ceramics [20]. The resultant values were higher than that of hydroxyapatite (1.35 GPa) [21] and human cancellous bone (0.35 GPa) [22] in comparison. A slight reduced HV in 4.5Cu-AK was assumed to be its microstructure tended towards a combination of crystalline and glassy phases, indicating the margin of Cu²⁺ content.

In a similar trend with HV, fracture toughness (KIC) increased from 0.75 to 2.06, 2.37, and 2.30 MPa.m⁰.⁵ for AK, 2.5Cu-AK, 3.5Cu-AK and 4.5Cu-AK, respectively. These KIC values were higher than the previously reported data of pure akermanite (0.35 MPa.m⁰.⁵) [22], wollastonite (0.67 MPa.m⁰.⁵) [23],
HA (0.70 MPa.m$^{1/2}$) and β-TCP (0.46 MPa.m$^{1/2}$) [24]. The percentage increment in $H_V$ was up to 174% (2.5Cu-AK), 216% (3.5Cu-AK), 206% (4.5Cu-AK) in current work, as well as 114% (AK), 11% (wollastonite), 7% (HA), and 63% (β-TCP) compared to the previous works. Thus, densification of akermanite ceramic has a direct effect on its microhardness and fracture toughness as well as agreed well with the earlier microstructural study provided (Figure 2).

Figure 3. Typical microhardness indented areas at 1200°C: (a) AK, (b) 2.5Cu-AK, (c) 3.5Cu-AK, and (d) 4.5Cu-AK ceramics.

4. Conclusions
A range of Cu$^{2+}$-doped akermanite ceramics have been successfully prepared through high-energy milling and mixing method, with subsequent sintering at 1200°C. According to the structural analysis, akermanite phase was not disrupted by Cu$^{2+}$ doping. The development of materials with reduced densifying sintering temperature could be beneficial for less time- and energy-consumption. Moreover, this reduced temperature due to Cu$^{2+}$ additive could be advantageous for suppressing grain growth, accompanying the effective improved sinterability (i.e., diameter shrinkage and relative density) and mechanical properties (i.e., Vickers hardness and fracture toughness). Therefore, the optimized Cu$^{2+}$ ion-modified akermanite ceramic can meet the requirements for bone replacement materials in biomedical applications. For future studies, the doping effects of Cu$^{2+}$ ions on the biological properties of akermanite ceramics will be conducted.

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