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Research Paper

Mechanical evaluation of calcium-zirconium-silicate (baghdadite) obtained by a direct solid-state synthesis route

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ABSTRACT

$Ca_3ZrSi_2O_9$ (baghdadite) has become a major research focus within the biomaterial community due to its remarkable *in-vitro* and *in-vivo* bioactivity. Although baghdadite seems to exhibit interesting biological properties, as yet there has been no data published concerning its mechanical properties. This lack of knowledge hinders targeting this novel bioactive material towards potential applications. In this study we prepare dense $Ca_3ZrSi_2O_9$ bulk ceramics for the first time, allowing the evaluation of its mechanical properties including hardness, bending strength, Young's modulus, and fracture toughness. The preparation of baghdadite has been accomplished by a direct solid-state synthesis in combination with conventional sintering at 1350–1450 °C for 3 h. Our results show that samples sintered at 1400 °C exhibit the best mechanical properties, resulting in a bending strength, fracture toughness, and hardness of 98±16 MPa, 1.3±0.1 MPa $m^{0.5}$, and 7.9±0.2 GPa. With a comparable mechanical strength to hydroxyapatite, but with an increased fracture toughness by 30% and hardness by 13% baghdadite is highly suitable for potential applications in non-load bearing areas (*e.g.* coatings or filler materials).

1. Introduction

The restoration of bone defects is still a major challenge in both medicine and biomedical science, where finding the ideal bone substitute material is crucial. Calcium silicates ($CaSiO_3$ and Ca_2SiO_4) and calcium silicate based ceramics, have become a major research focus in the biomaterial community (De Aza et al., 2000; Gou and Chang, 2004; Gou et al., 2004; Zhong et al., 2011). It has been shown that these materials exhibit superior biological properties including bioactivity, resorbability, and enhanced cell interaction, compared to conventional calcium phosphates like hydroxyapatite (HAp) or β-tricalcium phosphate (β-TCP) (Ni et al., 2007). Thus these minerals are promising candidates as bone graft materials.

The incorporation of metal atoms (*i.e.* Mg, Zn, and Zr) into the crystal structure of calcium silicates further improved the biological performance of these materials. Resulting minerals,

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namely $CaMgSi_2O_6$ (diopside), $Ca_2ZnSi_2O_7$ (hardystonite) and $Ca_3ZrSi_2O_9$ (baghdadite), have already been tested *in-vitro* and *in-vivo*, and indicate significant improvement in comparison to simple calcium silicates (Luo et al., 2012; Ramaswamy et al., 2008a,b; Roohani-Esfahani et al., 2012; Wu et al., 2010; Zreiqat et al., 2010).

Among the different modified calcium silicates, baghdadite is of major interest and several research groups have determined its biological properties. Ramaswamy et al. investigated the *in-vitro* interaction of osteoblast and osteoclast cells on $Ca_3ZrSi_2O_9$ and $CaSiO_3$ materials. Results showed that cells on baghdadite ceramics exhibited an increased proliferation, and bone related gene expression compared to $CaSiO_3$ materials (Ramaswamy et al., 2008a). Promising *in-vivo* studies have been conducted by Roohani-Esfahani et al. who implanted $Ca_3ZrSi_2O_9$ and HAp/β-TCP scaffolds into the radius of rabbits. An excessive new bone formation was observed for baghdadite scaffolds as opposed to HAp/β-TCP (Roohani-Esfahani et al., 2012). Luo et al. implanted $Ca_3ZrSi_2O_9$, $CaMgSi_2O_6$ and β-TCP microbeads in the femur of rats and found similar results. The investigation of *in-vivo* osteogenesis after 2 and 4 weeks revealed an induction of more new bone formation and greater expression of type I collagen on baghdadite compared to diopside and β-TCP (Luo et al., 2012).

Different processing routes for the preparation of $Ca_3ZrSi_2O_9$ have been investigated. Baghdadite is primarily synthesized by a sol–gel route (Luo et al., 2012; Ramaswamy et al., 2008a; Roohani-Esfahani et al., 2012) which usually requires expensive precursor materials and only allows a relatively low yield. In contrast Lian et al. prepared $Ca_3ZrSi_2O_9$ coatings on Ti–6Al–4V implants *via* solid-state synthesis using SiO_2, $CaCO_3$, and ZrO_2, demonstrating the ability of this method to produce a pure product (Liang et al., 2010).

Although the biological properties of baghdadite have been extensively investigated, a comprehensive mechanical characterization does not exist. Thus it is highly important to bridge this gap and provide mechanical characteristics of this bioceramic in order to define its potential fields of application.

In this study, dense and high purity $Ca_3ZrSi_2O_9$ (baghdadite) samples were prepared *via* an easy and versatile solid-state reaction and related structural, mechanical, and biological properties were studied.

2. Materials and methods

2.1. $Ca_3ZrSi_2O_9$ synthesis

The synthesis of $Ca_3ZrSi_2O_9$ *via* a solid-state sintering route was achieved by mixing CaO (Sigma Aldrich, 12047, lot. SZBC2430V), ZrO_2 (Absco Materials, NZ-911, lot. 090509), and SiO_2 (Fiber Optics, SiO2P015-01, lot. 110205-01) powders. For this a molar ratio of 3:1:2 for CaO, ZrO_2, and SiO_2 is required. As volatile compounds like organics and water are released from the starting materials during sintering, the determination of these amounts is important to ensure the correct molar ratio at the elevated synthesis temperature. The quantity of these compounds was measured *via* thermogravimetric analysis (TGA) (STA 503, Bähr Thermoanalyse GmbH) up to 800 °C. For SiO_2, CaO, and ZrO_2 the mass losses were determined with ≈11%, ≈3.0%, and ≈0.5% respectively. Taking these weight losses into account, gave the correct initial weights of the starting materials. The mixed powders (500 mL poly ethylene bottle) were then dispersed in 150 mL acetone (technical grade, VWR) and homogenized for 24 h using a ball mill (UR400, Germatec GmbH) and 300 g of Al_2O_3 milling balls (Germatec GmbH). After homogenization the suspension was dried at room temperature. Further acetone removal was achieved by heating on a heating plate for 6 h. Disc shaped green bodies were uniaxially dry pressed at ~4 MPa and sintered (HT 04/17, Nabertherm) at three different temperatures: 1350 °C, 1400 °C, and 1450 °C. To remove water and any possible organic residues, green bodies were heated from 0 to 500 °C at 1 K/min, afterwards the samples were sintered up to 1350 °C, 1400 °C, or 1450 °C using 2 K/min (dwell time of 3 h) and cooled down at room temperature with 2 K/min.

2.2. Crystal phase analysis

X-ray diffraction characterization was conducted with a Philips PW1800 Bragg–Brentano powder diffractometer using Cu-K_α radiation ($\lambda = 1.5418$ Å). Diffractograms were detected from 10 to 50° with a stepscan of 0.03° and a dwelling time of 2 s. Powder Diffraction Files (PDF) from the International Centre of Diffraction Data (ICDD) were used to identify the crystal phases.

2.3. Simulated body fluid (SBF) bioactivity

The ability of apatite formation, which is an *in-vitro* indicator for bioactivity (Kokubo and Takadama, 2006), was determined on $Ca_3ZrSi_2O_9$ materials *via* immersion into simulated body fluid (SBF). Disc shaped samples were pressed and sintered at 1400 °C for 3 h. Cleaning of the samples prior to testing included 5 min of sonification in isopropyl alcohol and 3 h heating at 200 °C. After cleaning, the samples were mounted inside 50 mL Falcon™ Tubes, hung using a clip and a nylon string and contact with the bottom or side walls was prevented. The SBF solution was prepared according to the standard ISO 23317 (International Standards Organization, 2012) and the composition was equal to the conventional SBF media as in Oyane et al. (2003). Apart from the original recipe we substituted $K_2HPO_4 \cdot 3H_2O$ with K_2HPO_4 and adjusted its concentration. SBF composition is given in Table 1.

$Ca_3ZrSi_2O_9$ discs were immersed in 42 mL SBF solution and stored for 3 and 7 days at 37 °C, respectively. The measurements were performed in triplicates. The discs were afterwards rinsed with double deionized water (Synergy systems, Millipore corp.) and dried at room temperature. Apatite formation on the sample surface was investigated by scanning electron microscopy (SEM) (Supra™ 40, Carl Zeiss AG) after sputtering a gold layer on the samples.

2.4. Microstructure and grain length analysis

Sintered baghdadite samples were ground with SiC grinding paper (down to P1200) and polished with diamond pastes (down to 1 μm). Afterwards the samples were thermally etched at 50 °C below sintering temperature for 10 min in a tube furnace (VFT7, Vecstar Ltd.). SEM analysis was performed to investigate the