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# A comparative study on the synthesis mechanism, bioactivity and mechanical properties of three silicate bioceramics

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In the present study three akermanite ($Ca_2MgSi_2O_7$), diopside ($CaMgSi_2O_6$) and baghdadite ($Ca_3ZrSi_2O_9$) applicable bioceramics were synthesized via a sol-gel based method. The combination of sol-gel method and the raw materials used in this study presents a new route for the synthesis of the mentioned bioceramics. By the use of thermal analysis, the mechanisms occurred during the synthesis of these bioceramics were investigated. The differences in the structural density and their relation with the degradation rate and mechanical properties of all three ceramics were studied. In vitro bioactivity and apatite formation mechanisms of the samples soaked in the simulated body fluid were considered. The results showed that baghdadite as a Zr-containing material has a more dense structure in comparison with the other ceramics, which leads to a lower degradation rate and also lower bioactivity. There were also main differences between akermanite and diopside as Mg-containing ceramics. Diopside showed a structure with lower porosity content compared to the akermanite samples which resulted in the lower degradation rate and higher compressive strength.



## 1. Introduction

A ceramic is introduced as an inorganic, nonmetallic solid material which is comprised of metal, nonmetal or metalloid atoms. The bonds in ceramics are primarily ionic and covalent [1]. Bioceramics as one of the most important branches of ceramic materials are biocompatible. Bioceramics are classified as the ceramic oxides, which are inert in the body, and the resorbable materials, which are eventually replaced by the body after they have assisted repair. Bioceramics are used in many types of medical procedures and typically used as rigid materials in surgical implants, though some bioceramics are flexible [2].

$CaSiO_3$ has shown great potential in bone re-generation. Although $CaSiO_3$ based ceramics have a bending strength close to the human cortical bone [3] and higher than the hydroxyapatite (HAp) based ceramics [4], not so well mechanical properties compromises their osseo-integration ability [5].

To the ability to find clinical applications, the mechanical properties of $CaSiO_3$ based ceramics should be improved. As a successful method to improve orthopedic application, one can refer to the incorporation of trace elements (bioinorganics) into the calcium silicate structures. The trace elements such as magnesium ($Mg^{2+}$), zinc ($Zn^{2+}$), titanium ($Ti^{4+}$) and zirconium ($Zr^{4+}$) have been incorporated in the Ca—Si structure [6]. Resulting minerals, namely $CaMgSi_2O_6$ (diopside), $Ca_2MgSi_2O_7$ (akermanite) 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 [7–10].

According to the previous researches, the incorporation of Zr ions into a calcium silicate structure leads to the synthesis of the baghdadite ceramic as an applicable material for bone tissue engineering which has no any toxic effects on osteoblasts [8]. Kulakov et al. reported that Zr implants have an excellent osseointegration and Zr-containing materials such as zirconia ceramics and coatings have a good potential to be introduced as bone implant materials [11]. Besides, baghdadite showed that can sustain bridging in large bone defects [9]. Moreover, baghdadite based coatings would increase the chemical stability of the samples [12]. Baghdadite also increased the tight bonding with the surface and had a good potential for in vitro HAp formation in SBF solution and in vivo bone formation [12].

It is well-known that glass-ceramics containing Si, Ca and Mg have a significant bioactivity and can be used for biomedical applications [13, 14]. These materials can also be closely bonded to the bone tissue when implanted in rabbits [15,16]. Akermanite ($Ca_2MgSi_2O_7$), as a Ca, Mg and Si-containing bioceramic, has received more attention due to its more controllable mechanical properties and degradation rate [17].

Diopside ($CaMgSi_2O_6$) as another raised bioceramic, shares some properties with $CaSiO_3$ and akermanite, except that its degradation rate is slightly slower than akermanite [18]. Like akermanite, diopside bulk ceramics have showed in vitro and in vivo potential [15]. Previous studies showed that diopside samples possess a significant bioactivity and excellent bending strength and fracture toughness [19,20].

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In the current work a comparison was conducted on the synthesis mechanisms, in vitro bioactivity, degradation rate, structural density and mechanical properties of three applicable bioceramics, i.e. akermanite, diopside and baghdadite.

## 2. Materials and methods

Sol–gel technique was used for synthesizing baghdadite powders from the tetraethyl orthosilicate ($(C_2H_5O)_4Si$, TEOS), Zirconium(IV) nitrate hexahydrate ($ZrO(NO_3)_2 \cdot 6H_2O$) and calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) as raw materials. The TEOS was mixed with ethanol and 2 M $HNO_3$ (mol ratio: TEOS/$H_2O$/$HNO_3$ = 1:8:0.16) and hydrolyzed for 45 min under stirring. In continue, $ZrO(NO_3)_2 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ were added into the mixture, and were stirred for 5 h at room temperature. Then, the obtained solution was maintained at a constant temperature 75 °C for 24 h and dried at 120 °C for 48 h to obtain the dry gel. The resultant gel was milled and sieved to 250-mesh, transferred into a corundum crucible and sintered at 1200 °C for 3 h. Finally, to ensure the preparation of nanoparticle powder, the resultant powder was milled by a planetary ball mill (NARYA MPM 4*250,Amin Asia Fanavar Pars, Iran) for 10 h (rotational speed of 250 rpm, ball/powder ratio of 5/1). Akermanite and diopside were also synthesized at stoichiometric conditions, according to the abovementioned method. The only difference was that magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) was used instead of $ZrO(NO_3)_2 \cdot 6H_2O$.

X-ray diffraction analysis (XRD, Bruker, D8 advance, Germany) was utilized for identifying the phases of the obtained ceramic samples (Cu-Kα, Ni filtered radiation (=1.5406°A)). Fourier transform infrared (FTIR) spectroscopy (IR Affinity- 1, Shimadzu) was used for the examination of the functional groups in the bioceramic samples. A Hitachi S-3400N scanning electron microscope (SEM) was employed for recording the samples images at the accelerating voltage of 20 kV. Inductive coupled plasma atomic emission spectroscopy (ICP-AES; Zaies 110394c) tested the Ca, Si, … ions concentrations in the SBF solution after soaking. The shape and size of prepared akermanite samples were visualized by means of transmission electron microscopy (TEM, Hyundai, 100 keV). Thermogravimetry (TG), and differential thermal analysis (DTA) measurements were performed with a simultaneous thermal analyzer (SDTQ-600/Thermo Star of TA).

Simulated Body Fluid (SBF) test, a method that is well recognized to characterize the in vitro bioactivity of ceramic materials, consists in their immersion in an aqueous SBF solution which simulates the properties of human plasma for certain period and verifies the formation of the HA layer on the surface of the samples [21]. Simulated body fluid is prepared in laboratory with the ionic concentration nearly similar to human blood plasma [22], according to procedure proposed by Kokubo (Kokubo method) [23]. The appropriate quantities of reagents comprised of NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $Na_2SO_4$, and tris buffer are dissolved in 1 l of double distilled water so as to have ionic concentration of various inorganic ions similar to those of the human blood plasma [22].

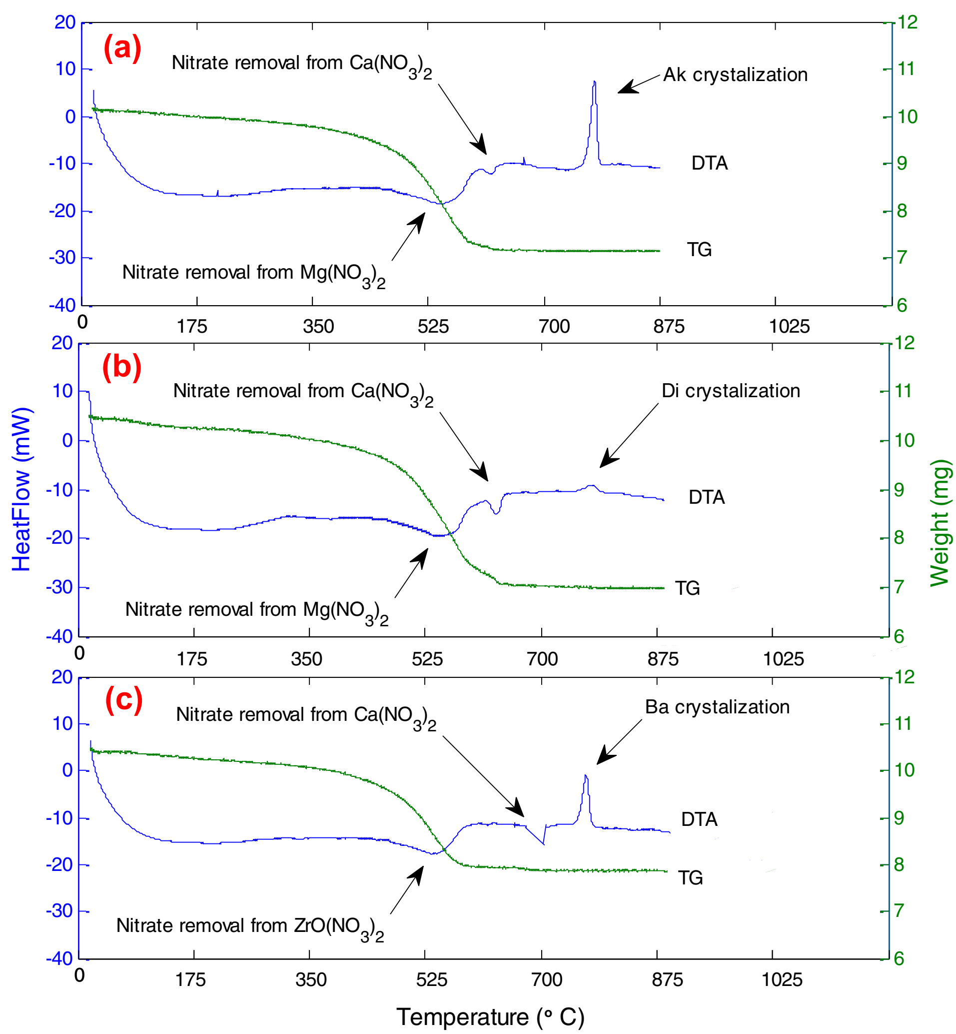


**Fig. 1.** Thermal analysis of a) akermanite (Ak), b) diopside (Di), and c) baghdadite (Ba) bioceramics.