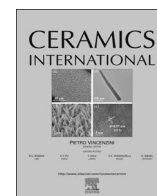




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# In vitro degradation and apatite-formation of ZnO–CaO–SiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub> glass–ceramics by substitution of zinc for calcium

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## ABSTRACT

A series of CaSiO<sub>3</sub>–Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub>-based glass–ceramics of the type ZnO–CaO–SiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub> were successfully obtained by the partial substitution of calcium with zinc. The effect of zinc addition on structure, dissolution behavior and apatite-forming ability of the resultant glass–ceramics was comprehensively investigated by X-ray diffraction (XRD), thermogravimetric and differential scanning calorimetry (TG/DSC), and scanning electron microscopy coupled to an energy dispersive X-Ray spectrometer (EDS). The data revealed that the zinc addition favored the generation of Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub> and induced the formation of ZnSiO<sub>4</sub> and SiO<sub>2</sub> phases. In addition, the excessive content of these compounds led to the attendant loss in the dissolution rate and apatite-forming ability, indicating that the incorporation of zinc into CaSiO<sub>3</sub> is a promising route to regulate the dissolution and apatite formation of CaSiO<sub>3</sub>–Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub>-based bioceramics.

## 1. Introduction

Recently, bioceramics have attracted a wide range of research interest because of their ready diversification, ease of processing, excellent biocompatibility and bioactivity. For example, silicate bioceramics such as wollastonite (CaSiO<sub>3</sub>) [1–3], strontium silicate (SrSiO<sub>3</sub>) [4] and akermanite (Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>) [5] show excellent biocompatibility, bioactivity and mechanical property. Moreover, it has also been shown that CaSiO<sub>3</sub> is capable of stimulating bone formation, and that Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> could enhance bone regeneration [6,7]. Therefore, silicate bioceramics are viewed as potential biomaterial for application in bone repair and regeneration.

However, CaSiO<sub>3</sub> bioceramics suffers from high dissolution rate resulting in reduced mechanical strength. In addition, the high dissolution rate also increases the pH of the surrounding fluids, which in turn can seriously affect osseointegration between implants and natural bone [8,9]. Thus, how to effectively regulate the dissolution rate of CaSiO<sub>3</sub> becomes the focus of this study.

For dissolution rate modification, the chemical method of doping ions into CaSiO<sub>3</sub> is considered as an effective approach. Zinc (Zn) is one of the most important trace elements in the body, in small amounts, it is essential for realization of metabolic process and will stimulate the mineralization and formation of natural bone [10,11]. Moreover, Zn plays an important role in human immune system, and has been considered as an effective antibacterial agent [12,13]. However, in

excess, Zn becomes harmful and toxic to organisms, the maximum allowable value for zinc in the aquatic environment is 5 mg/L proposed by Ministry of Health of Brazil [10,14]. Therefore, zinc-containing CaSiO<sub>3</sub> are promising biomaterials with potential applications in hard tissue replacement. In this work, a series of quaternary ceramics by the gradual doping of ZnO into CaO–SiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub> system were carried out and the influence of zinc addition on the structure, dissolution rate and apatite-forming ability of obtained CaSiO<sub>3</sub>-based glass–ceramics was systematically investigated.

## 2. Experimental details

### 2.1. Preparation of glass and glass–ceramics

The new series of sol–gel-derived glasses are represented by the general formulation,  $x\text{ZnO}-(38-x)\text{CaO}-58\text{SiO}_2-4\text{P}_2\text{O}_5$  (mol.%), and are listed in Table 1. Briefly, the glasses were prepared by hydrolysis and polycondensation of tetraethyl orthosilicate (TEOS), triethyl phosphate (TEP), calcium nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) and zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) in deionized water (mole of H<sub>2</sub>O/mole of (TEOS + TEP) = 10) with stoichiometric amounts. HNO<sub>3</sub> (2 N) was used to catalyze the hydrolysis of TEOS and TEP, using a molecular ratio of HNO<sub>3</sub>/(TEOS + TEP) = 0.05. After the addition of each reactant, the solution was stirred for 1 h, and the resultant solution was cast into a polyethylene container and sealed at room temperature when gel

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**Table 1**  
Compositions of  $x\text{ZnO}-(38-x)\text{CaO}-58\text{SiO}_2-4\text{P}_2\text{O}_5$  glass-ceramics.

Notation	Composition (mol.%)					
	ZnO	CaO	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>		
$x = 0$	0		38		58	4
$x = 5$	5		33		58	4
$x = 10$	10		28		58	4
$x = 20$	20		18		58	4

formation occurred. The gel was heated at 60 °C for 3 d in a constant temperature water bath, and dried. The dried gel was ball milled and sieved to particles of size 38–74 μm. Subsequently, fractions of 0.5 g of powder were compacted at 200 MPa isostatic pressure at room temperature to obtain disks of 10 mm in diameter and 2 mm in height. The powders and disks were sintered at 1200 °C for 2 h with a heating rate of 3 °C/min.

## 2.2. Sample characterization

Thermogravimetric and differential scanning calorimetry (TG/DSC) measurements were performed on dried gels using a NETZSCH STA449C (Germany) simultaneous thermal analyzer at a heating rate of 20 °C/min. X-ray powder diffraction (XRD) data were measured on a Bruker D8 Advance X-ray diffractometer (Germany) equipped with a CuK<sub>α</sub> radiation at a scan speed of 2°/min. The morphology of samples surface was characterized by scanning electron microscopy (SEM) using a ZEISS Sigma 500 system (Germany) with energy dispersive X-ray spectroscopy (EDS). The as-sintered disks were polished and etched with HF solution (10% V/V) for 60 s. For the SEM study, the samples were gold plated.

## 2.3. Degradation tests

Pre-weighed disks of glass-ceramics were vertically soaked in a Tris-HCl buffer solution (pH 7.4 ± 0.1) with a surface area-to-volume ratio of 0.1 cm<sup>-1</sup> at 37 °C for several days up to 28 d. Three specimens of each sample were simultaneously soaked and the buffer solution was replaced every 2 d. After soaking for the set time, disks were washed with deionized water and ethanol successively, and dried thoroughly. The dried disks were then weighed to an accuracy of 0.1 mg using an electronic analytical balance, and the relative mass loss percentage was determined. In addition, elemental analysis of the solution at different reaction times was performed on clear liquid by inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent 720, USA).

## 2.4. In vitro assays

Powdered samples were used to appraise the apatite-forming ability of the glass-ceramics. The powders were soaked in a solution of simulated body fluid (SBF) at 37 °C following a method described by Kokubo and Takadama [15]. The ionic concentration of SBF solution was nearly equal to those of human blood plasma. During immersion, the SBF solution was replaced every 2 days. After soaking, the powders were filtered, rinsed with water, and dried.

## 3. Results

TG/DSC curves of dried gels of the four different formulations of  $x\text{ZnO}-(38-x)\text{CaO}-58\text{SiO}_2-4\text{P}_2\text{O}_5$  (where  $x = 0, 5, 10$  or  $20$ ) are shown in Fig. 1. For all cases, two pronounced mass loss steps are observed in TG curves. The first one occurs between 50 °C and 156–225 °C, and it accompanies with a mass loss of 18–34%, which can be attributed to the removal of residual water and ethanol. The second mass loss is terminated at 524–569 °C, and the mass loss corresponds to the

removal of free metal nitrates. Subsequently, no significant mass loss is observed with the temperature increasing. In addition, the accompanying DSC curves show glass transition ( $T_g$ ) in the range of 838–865 °C, and two sharp exothermic peaks ( $T_{p1}$  and  $T_{p2}$ ) associated with the glass crystallization. Table 2 lists the values of thermal parameters measured for all dried gels. It is revealed that the value of  $T_g$  increases gradually with the increase in the amount of doped ZnO except for the sample containing most ZnO. The temperature of the first crystallization peak ( $T_{p1}$ ) decreases monotonically with increase in ZnO content for all the samples. And the second crystallization peaks ( $T_{p2}$ ) varies with ZnO content albeit in a much narrower temperature range of 14 °C.

In order to identify the products of the crystallization processes, specimens were heated up and kept at its respective crystallization temperature for 2 h. Fig. 2 represents typical XRD patterns for specimens containing 0 and 10 mol% ZnO. It is revealed that the first exothermic peak for specimen without ZnO can be attributed to the wollastonite ( $\beta\text{-Ca}(\text{SiO}_3)$ ) crystallization, whereas the second one represents the crystallization of pseudowollastonite ( $\text{Ca}_3(\text{Si}_3\text{O}_9)$ ). In the case of specimen containing ZnO, the crystallization peaks have overlapped. The first exothermic peak is due to the crystallization of  $\beta\text{-Ca}(\text{SiO}_3)$  and hardystonite ( $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ ), and the second one can be attributed to the pseudowollastonite ( $\text{Ca}_3(\text{Si}_3\text{O}_9)$ ) and cristobalite ( $\text{SiO}_2$ ). So, in this work, the same sintering temperature of 1200 °C was employed, which was well enough for the samples crystallization. In addition, the corresponding XRD patterns of sintered samples are also given in Fig. 3. The data reveal that on zinc addition, the diffraction peaks of  $\text{Ca}_3(\text{Si}_3\text{O}_9)$  and  $\beta\text{-Ca}(\text{SiO}_3)$  calcium silicate phases disappear gradually, whereas new peaks of  $\text{Ca}_2\text{ZnSi}_2\text{O}_7$  and  $\text{SiO}_2$  begin to appear. Besides,  $\text{ZnSiO}_4$  crystal phase is also discovered. From these results, it is suggested that the addition of Zn disfavors the formation of silicon and calcium rich phases (calcium silicate). In other words, Zn competes with Ca, and induces phase separation [16]. Moreover, the addition of Zn also promotes the formation of zinc and silicate rich phases (hardystonite and zinc silicate) and a silica polymorph phase (cristobalite).

Fig. 4 shows the SEM surface micrographs for all sintered samples, and the EDS analysis confirms the presence of Si, Ca, P species introduced during the sol-gel process. Moreover, the emergence of ZnL peak at low energy supports the addition of zinc. Since the disks were obtained by cold isostatic processing, the surface micrographs of the prepared samples exhibit a certain amount of porosity. The glass-ceramics containing 0, 5 and 10 mol% ZnO content show tiny spherical crystallites indicating homogeneous crystallization behavior as shown in Fig. 4(a, b and c). With even more zinc content, columnar crystals accompanied with homogeneous spherical crystallites are observed, as shown in Fig. 4(d). And the corresponding chemical composition analysis indicates a relatively high content of Si and O in columnar crystals, which can be taken as evidence for the presence of cristobalite. On the other hand, the spherical crystallites are found to be Ca-Si-Zn-rich phases, and the presence of F is due to the etched solution of HF.

Mass losses measured after soaking in Tris-HCl solution for glass-ceramics disks are represented in Fig. 5. After 4 weeks of soaking, the final mass loss of samples with increasing zinc content was 18.3%, 13.9%, 8.4% and 5.3%, respectively. On the other hand, the mass loss rises with the increase in soaking time for all samples, and the sample containing more zinc content shows significantly lower degradation rate.

In order to gain a better insight into the dissolution process, the changes of ions concentrations in Tris-HCl solution as a function of soaking time were monitored. As shown in Fig. 6, the variation trends of Si and Ca concentrations are similar. A continuous increment as soaking time is found, and the Si and Ca concentrations are definitely higher for specimen containing non ZnO than for ZnO containing specimens. This means that, during the soaking process, the release of Si and Ca ions from glass-ceramics was carried out, and the reason might be attributed to the exchange of  $\text{Ca}^{2+}$  with proton or hydrate

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