Journal of Non-Crystalline Solids 491 (2018) 98–105

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Substitutions of zinc in mesoporous silicate-based glasses and their physicochemical and biological properties

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ARTICLE INFO

Keywords:
Bioactive glasses
Zinc
Degradability
Bioactivity
Sol–gel
Biomedical applications

ABSTRACT

Mesoporous bioactive silicate-based glasses in the system of (38-x)CaO–xZnO–58SiO_2– 4P_2O_5 (mol.%), where x varies between 0 and 20, have been prepared by the sol–gel method. The influence of zinc addition on glass physicochemical properties, degradability and apatite- formation ability was comprehensively investigated. The nitrogen adsorption/desorption results confirmed the glasses mesoporous structure. The degradability of glass was studied in *Tris*–HCl, the addition of zinc would lead to a decrease. Furthermore, the glass apatite-formation ability was assessed by immersion of samples in simulated body fluid (SBF) solution for up to 7 days. The changes in glass surface morphology and composition were detected using X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and fourier transform infrared spectroscopy (FTIR). It was observed that the apatite precipitation rate slowed down with the increase of zinc, suggesting that the incorporation of zinc could be a promising route to regulate the dissolution and apatite formation of silicate-based glasses.

1. Introduction

Nowdays, bioactive glasses (BGs) are considered as high potential biomaterials using for orthopedic applications and bone tissue regeneration [1–3]. The significant characteristics of BGs is high bioactivity, osteoconduction and osteoinduction. The *in vivo* tests have proven that these materials are able to bond to bone directly [4,5]. In addition, the dissolved ions from BGs have been shown to be effective in stimulating osteoblast proliferation [6,7] and enhancing angiogenesis [8]. Thus, various new types of BGs are developed and the doping of BGs with meaningful trace elements is increasingly considered.

Zinc is one abundant and widely distributed trace element in the human body, and its biological functions have been well researched. It is indicated that zinc has a strong effect on the synthesis and activation of numerous enzymes, and results in a positive effect on stimulating DNA and RNA replication [9]. Also, zinc closely associates with human bone growth, development and maintenance by promoting osteoblast cells proliferation and enhancing ALP activity [10]. So far, the incorporation of zinc into BGs has been conducted, the researches indicate that zinc-doped BGs present well biocompatibility and possess a good antimicrobial activity to *Staphylococcus aureus* [11–13]. However, given the controversial role of zinc on the BGs *in vitro* bioactivity, *i.e.* inactive [14] and/or inhibitory effect [15], more research related to the structure, physicochemical and biological properties of zinc-doped BGs has become essential.

As we known, the sol–gel method is a potential technique for making hybrid materials. The synthesis process involves the transition of a system from a mostly colloidal liquid into a solid, that is, the transformation of the "sol" to "gel", and it allows the easy synthesis of glasses and ceramics, even doped with various ions [16,17]. In the light of above-mentioned facts, BGs in CaO–ZnO–SiO_2–P_2O_5 system were synthesized by sol–gel method, where calcium oxide was equimolar substituted by zinc oxide. The influence of zinc-incorporation on the glass microstructure, dissolution behaviour and bioactivity was researched, and a better understanding about the relationships between microstructure and physicochemical properties of Zinc-doped BGs was investigated.

2. Experimental

2.1. Design and synthesis of glasses

A series of glasses with compositions of (38-x)CaO–xZnO–58SiO_2–4P_2O_5 (mol.%), where x varies 0, 5, 10 and 20 was synthesized by sol–gel method. According to its respective ZnO content, the glass sample was respectively noted as Zn-0, Zn-5, Zn-10

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https://doi.org/10.1016/j.jnoncrysol.2018.04.002
Received 28 February 2018; Received in revised form 31 March 2018; Accepted 2 April 2018
0022-3093/

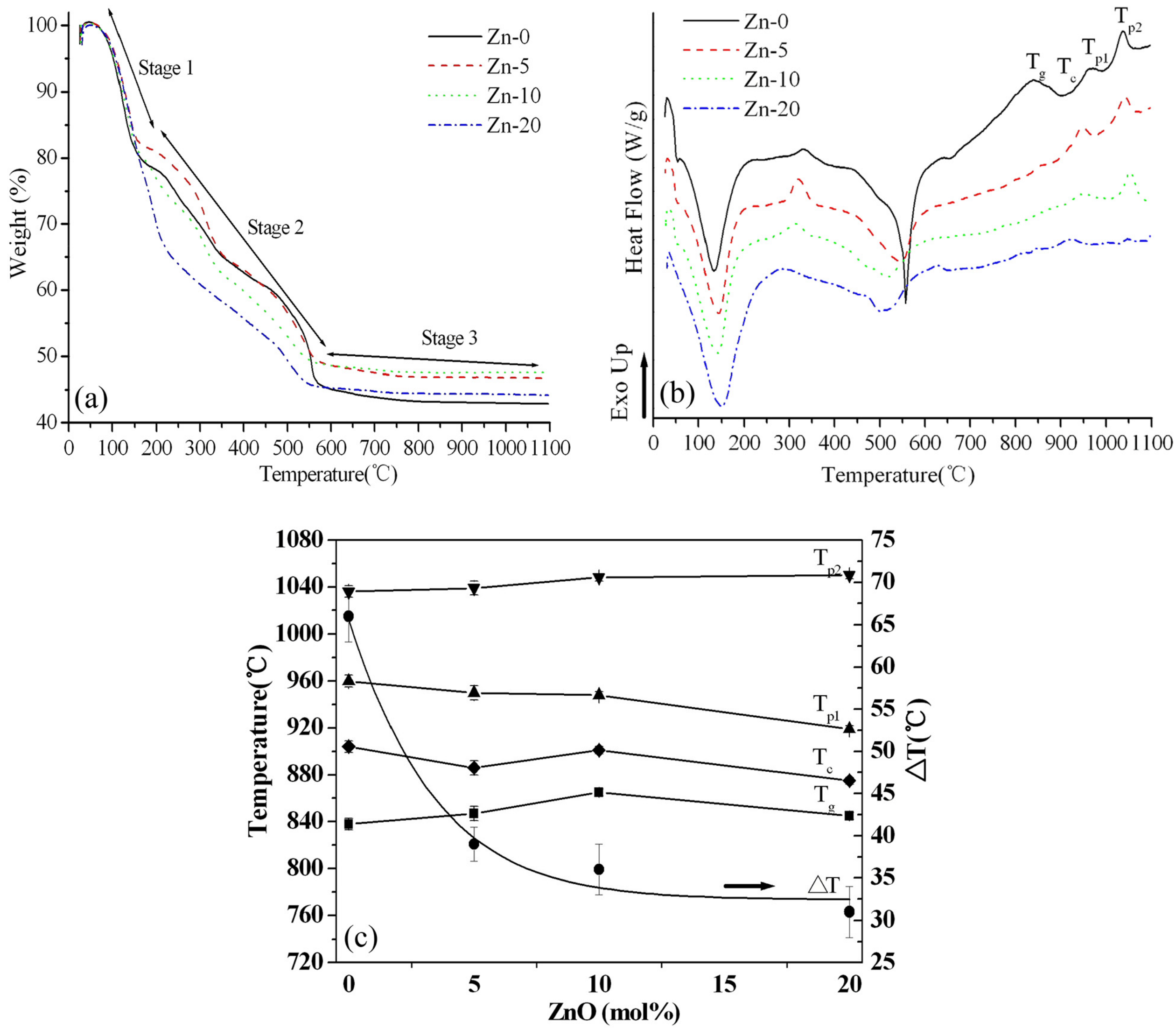

Fig. 1. TG (a) and DSC (b) curves of the dried gels; (c) influence of ZnO content on the glass thermal parameters as obtained from DSC data.

and Zn-20. Briefly, with continuous stirring, raw materials such as $Si(OC_2H_5)_4$ (TEOS), $(C_2H_5O)_3PO$ (TEP), $Ca(NO_3)_2{\cdot}4H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ (if necessary) was added into deionized water in turn, and 1 M HNO_3 solution was used as the catalyzer. The mixed sol was stored in polyethylene bottles and sealed at room temperature until the gel was accomplished. After that, the formed gel was placed in a constant temperature water bath at 60 °C, followed by drying and ball milling to gain the powders with the average diameter of 38 to 74 μm. Finally, compacted discs were obtained at 200 MPa isostatic pressure and heated at 700 °C for 2 h.

2.2. Sample characterization

Thermogravimetric and differential scanning calorimetry (TG/DSC) analysis was carried out by using a NETZSCH STA449C simultaneous thermal analyzer system with a heating rate of 20 °C/min. The surface area and pore structure information were measured by a Micromeritics Tristar 3000 pore analyzer. X-ray diffraction (XRD) was analyzed with a Bruker D8 Advance X-ray diffractometer equipped Cu K_α radiation with a scan speed of 2°/min and a step size of 0.02°. Fourier transform infrared spectroscopy (FTIR) was conducted on a Bruker Optics VERTEX-70 FTIR spectrometer using KBr pellets in the range of 400 to 4000 cm^{-1} with a transmission mode. The resolution used was 4 cm^{-1} and the number of scans was 32. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) in ZEISS Sigma 500 system was utilized, and before tests samples were coated with a film of gold.

2.3. In vitro assays

The *in vitro* bioactivity of glasses was investigated by soaking them in simulated body fluid (SBF) solution at 37 ± 0.5 °C, according to the protocl described by Kokubo et al. [18]. During soaking, 0.10 g of glass powders in 100 ml of SBF solution was utilized and the SBF solution was periodically refreshed every 2 days. When the set time arrived, glass powders were removed, rinsed and dried at room temperature. Then, the sample was evaluated by means of XRD, FTIR and SEM-EDS.

2.4. Degradation tests

The glass degradation tests were carried out by soaking glass discs in fresh *Tris*–HCl solution with a pH value of 7.4 ± 0.1 at 37 °C for the longest 4 weeks. When the set soaking time arrived, the glass discs were washed and dried completely. Then, the sample weight loss was expressed as the percentage of the initial weight, and the measurements were performed in duplicate. In addition, solution element analysis at