Journal of Non-Crystalline Solids 449 (2016) 75–82

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Sol-gel derived vitroceramic materials for biomedical applications

Georgeta Voicu, Vladimir-Lucian Ene, Daniel-Florin Sava, Vasile-Adrian Surdu, Cristina Busuioc *

University POLITEHNICA of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Gh. Polizu Street, RO-011061, Bucharest, Romania

A R T I C L E I N F O

Article history:
Received 22 February 2016
Received in revised form 15 July 2016
Accepted 16 July 2016
Available online 20 July 2016

Keywords:
Biomaterials
Glass-ceramics
Sol-gel
Simulated body fluid
Fluorapatite

A B S T R A C T

Starting from SiO_2–CaO–P_2O_5–ZnO–CaF_2 oxide system, vitroceramic materials were obtained by employing the sol-gel approach, followed by thermal treatment in order to provide, in a controlled manner, the nucleation and growth of crystalline phases in the parent glassy matrix. Thermal analysis, X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, transmission electron microscopy, selected area electron diffraction and Fourier transformed infrared spectroscopy were employed for the characterization of the resulting samples. The sintered vitroceramics present calcium silicates as crystallized nano-domains and a porosity that decreases with the enhancement of the processing temperature. The assessment of the biological properties was carried out *in vitro* by simulated body fluid immersion for 14 days, associated with a detailed analysis of the apatitic layer formed on the surface.

1. Introduction

The research in the field of materials with biological application continues to be a hot topic since it is directly and strongly connected with people's health, in a continuous attempt to improve the quality of life for the healthy individuals and also to relieve the suffering for the diseased ones. Although a huge amount of money has been invested in the last decades as respects to solving medical issues with global impact, great developments can still be made, while addressing the economic, environmental and ethical demands. Moreover, the increased frequency of bone diseases has propelled the field of regenerative medicine in general and tissue engineering in particular in the attention of many research groups from Materials Science. In this context, the future belongs to the systematic and interdisciplinary approaches which transcend the financial interests and public prejudices and focus on the most important factors involved in the optimisation of the biological performances of materials: chemical composition, processing technology and microstructural features [1].

Since the first report of Hench's glass in the late 60′s (Bioglass®), the first bioactive glass comprising Na_2O, CaO, SiO_2 and P_2O_5 [2,3], many other systems have been proposed for the developing of biomaterials able to promote bone bonding in the physiological environment [4]. However, there is an increasing need for bone replacement and regeneration materials with superior properties in terms of chemical, mechanical and biological behaviour.

Glass-ceramics or vitroceramics represent an important family of polycrystalline materials obtained after applying a controlled procedure of crystallization (nucleation and growth) on a glass matrix. Regarding the bioactive exponents of this category, most of them are based on compositions similar with those of Bioglass®, but with reduced contents of alkali oxides [1]. The advantages that immediately emerge when it comes to glass-ceramics are the potential of producing complex shapes due to the accentuated machinability [5,6], the achievement of higher mechanical characteristics as a consequence of the accurate tuning of the microstructure through the applied thermal treatments [7,8], as well as the enhancement of the biological response by controlling the composition of the crystalline and glassy phases [9]. Their bioactivity can be assessed by measuring the bone formation rate on the substitute material surface, process that will lead to strong bonding to living tissue. Furthermore, vitroceramic materials are promising candidates for the development of multiple applications in the field of medicine, from hard tissue scaffolds [10–12] to coatings for biomedical implants [13,14].

One of the most extensively studied glass-ceramic dedicated to bone replacement and regeneration is that which contains oxyfluorapatite and wollastonite as main crystalline phases (Cerabone®) and vitreous phase in MgO–CaO–SiO_2 system [15]. It has been successfully used in bulk, granular and porous forms mainly in spinal surgery [1]. Abbasi et al. [8] reported the modification of dental ceramic powder with sol-gel derived bioglass in order to provide apatite layer formation on the surface of the resulting mixtures and subsequently prolong the lifetime of the fixed dental prosthesis. As well, few researchers [7,16] demonstrated that sol-gel prepared glasses are promising reinforcing additive for the improvement of the mechanical and biological properties of melt-quenching bioglasses. Another research group proposed bioactive glass-ceramics obtained by wet chemical methods, having as main crystalline phase either miserite [5] or wollastonite [6], both systems showing chemical durability, high strength and excellent machinability, properties required for non-metallic one-pieced dental implant

* Corresponding author.
E-mail address: cristina.busuioc@upb.ro (C. Busuioc).

http://dx.doi.org/10.1016/j.jnoncrysol.2016.07.021

Table 1
Molar composition of the vitroceramic materials.

SiO_2	CaO	P_2O_5	ZnO	CaF_2
(mol%)				
35.4	56.0	1.0	7.2	0.4

applications. ElBatal et al. [17] prepared glass-ceramics with lithium disilicate as main crystalline phase by the melting-annealing route and concluded that their chemical durability is excellent to all studied leaching media, being recommended for dental applications, while Diba et al. [9] demonstrated the superior mechanical properties of Mg containing silicate ceramics and glass-ceramics, which become thereby noteworthy candidates for various biomedical applications. Mollazadeh et al. [18] fabricated biocompatible fluorapatite-mullite glass-ceramics by the classical approach and verified the effect of thermo-cycling process duration on the strength and micro-hardness properties. Kumar et al. [19] choose the mechano-chemical synthesis for the obtaining of leucite based glass-ceramic, which was further integrated in a bioactive dental veneering composite. Baino et al. [20] focused on the development of a three-layer system comprising a ceramic substrate, a glass derived trabecular coating and a glass-ceramic interlayer that joins the other two elements together for use in prosthetic applications.

Out of the numerous wet chemistry techniques, the sol-gel method is very common due to the capability of easily obtaining homogenous powders with controlled morphology, while significantly reducing the processing temperatures [5,6,14,21–23]. Therefore, in this work, we report on the synthesis of vitroceramic materials starting from SiO_2–CaO–P_2O_5–ZnO–CaF_2 system and using the sol-gel route, followed by a detailed characterization of the samples both before and after soaking in simulated body fluid for 14 days. The novelty of our work consists in the wet-chemistry approach of a new compositional domain, which has the ability to generate the formation of a fluorapatite based coating with particular morphology by simulated body fluid immersion.

2. Experimental

2.1. Materials

The vitroceramic materials were obtained by using the sol-gel technique, a wet chemistry method which enables the synthesis of complex oxide materials with good control in terms of stoechiometry, homogeneity and morphology. In this context, a composition with four types of oxides and an alkaline-earth metal fluoride was chosen, each of them playing a specific role. Thus, SiO_2 is the network former; CaO is the network modifier, also having an important contribution in apatite formation; P_2O_5 gives bioresorbability to the final material, phosphorus ions being as well constituents of the physiological fluids; ZnO increases the surface area, thereby providing more nucleation centres for apatite, slows the glass-ceramic dissolution, enhances phosphorus incorporation and acts as radio-opacifier; CaF_2 favours the densification process [24] and influences the biological response. Based on our research experience, the composition presented in Table 1, from SiO_2–CaO–P_2O_5–ZnO–CaF_2 system, was selected.

Tetraethyl orthosilicate (TEOS, $Si(OC_4H_9)_4$, >98%, Fluka), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, >99%, Sigma-Aldrich), triethyl phosphate (TEP, $PO(OC_2H_5)_3$, >99.8%, Sigma-Aldrich), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, >98%, Riedel-de-Häen) and calcium fluoride (CaF_2, >99.9%, Sigma-Aldrich) were used as starting materials.

2.2. Vitroceramic materials preparation

Briefly, the amounts of precursors were calculated according to the selected oxide composition (Table 1). TEOS and TEP were hydrolysed

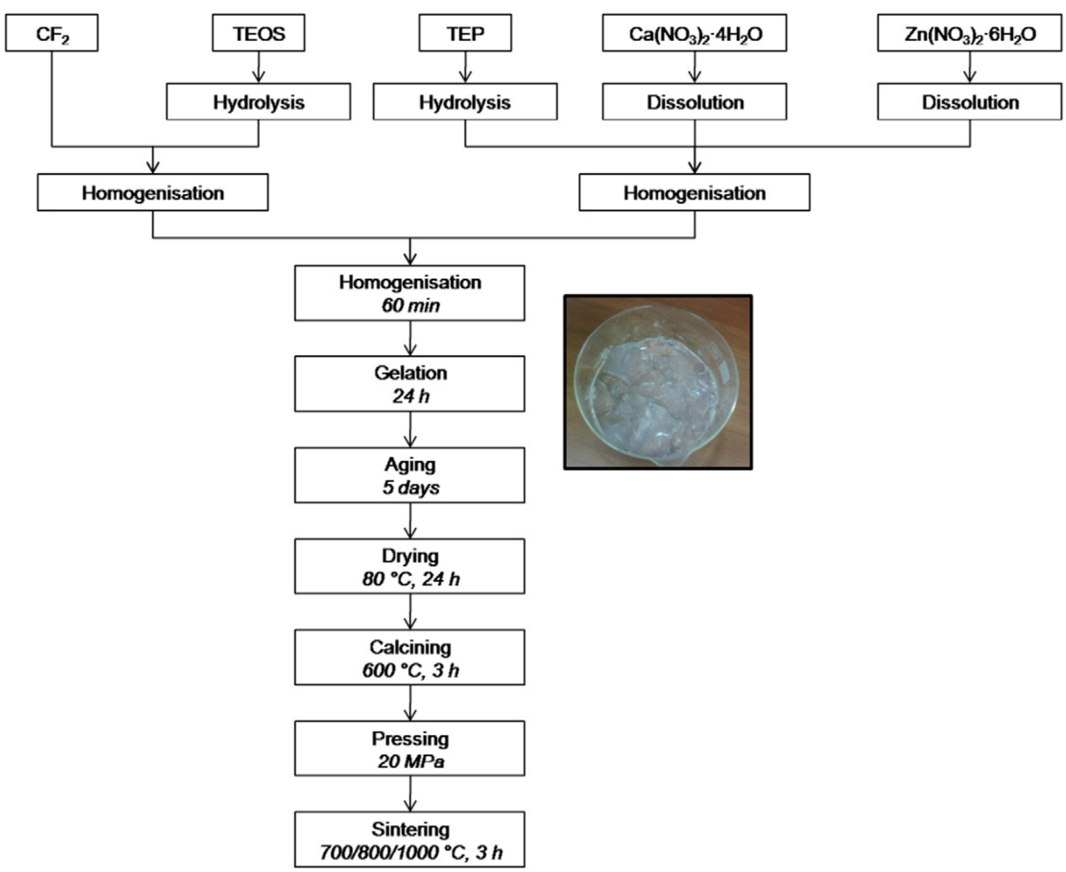

Fig. 1. Schematic representation of the synthesis procedure.