

Sol-Gel Synthesis of $\text{SiO}_2\text{-CaO-Na}_2\text{O-P}_2\text{O}_5$ Bioactive Glass Ceramic from Sodium Metasilicate

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ABSTRACT

Bioactive glass ceramic with $\text{SiO}_2\text{-Ca}_2\text{O-Na}_2\text{O-P}_2\text{O}_5$ composition was prepared by the sol-gel method using sodium metasilicate (Na_2SiO_3) as silica source. The monolith obtained was sintered at 1000°C for 2 hours after which X-ray diffraction (XRD) analysis showed presence of combeite ($\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$) as the crystalline phase. *In vitro* bioactivity test conducted on the material using simulated body fluid (SBF) showed the formation of carbonated hydroxyapatite on its surface. The material during the SBF test was observed to transform from a mechanically strong crystalline phase $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$ to an amorphous phase after incubation for 14 days indicating that the material was biodegradable. Scanning electron microscopy (SEM) was used to investigate the surface morphology, while Fourier transform infrared (FTIR) spectroscopy facilitated the confirmation of hydroxyapatite (HA) formation. The monolith material obtained may be a good candidate for application in tissue engineering scaffolds.

Keywords: Bioactive Glass; Sol-Gel; Crystalline; Sodium Metasilicate; Hydroxyapatite

1. Introduction

Despite the significant risks, autograft and allograft treatments for bone loss have achieved varying degrees of success in restoring form and function. While donor site morbidity is a common side effect of autograft [1], complications associated with allografts include disease transmission [2] and the possibility of compromised materials from the sterilization process. Another drawback for both is the limited supply of these materials. Consequently, as life expectancy increases there is also the growing and urgent need for an attractive alternative to bone grafts in form of a biocompatible osteoconductive synthetic scaffolds able to withstand mechanical loading [3], as a paradigm from replacement to regeneration [4].

Silica-based glasses with their interesting properties [5] have been explored for use as alternative second generation bone defects and soft tissue treatment biomaterials due to their biocompatibility [6]. For example, dissolution products from bioactive glasses up-regulate expression of genes that control osteogenesis [7,8], which explains their higher rate of bone formation in comparison to other inorganic ceramics such as hydroxyapatite [9].

The melt method is the traditional approach to produce bioactive glasses from mixtures of carbonates and phos-

phates at high temperatures before quenching to form a glass. Inclusion of Na_2O or K_2O offers reduced melting temperature [10] and increased solubility advantages of the materials in aqueous media thereby facilitating host tissue-material interaction, [8,11-14]. Furthermore, it is envisioned that inclusion of Na_2O will facilitate crystallization of certain sodium calcium silicate phases, such as $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$ [15] which ultimately will improve their mechanical properties. This approach however, often leads to chemically heterogeneous materials with incipient crystallization and some degree of possible contamination from chemicals used, during the cooling or grinding procedures [16].

A viable alternative is the sol-gel method with several advantages in comparison to the melt and solidification route showing higher purity and homogeneity, and a wider range of compositions [17,18]. In this regards synthesis of sodium-containing quaternary $\text{SiO}_2\text{-CaO-Na}_2\text{O-P}_2\text{O}_5$ bioactive glasses are well documented [16,19] based on alkoxysilanes, such as tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS) as precursors. However, alkoxides are hazardous and expensive [20-23] and are therefore not suitable for large-scale production. Our objective in this work is to prepare sodium containing quaternary bioactive glass-ceramic material using sodium metasilicate as cheap silica source.

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2. Materials and Experimental Procedures

2.1. Materials

The chemicals used for synthesizing the bioactive glass were: sodium metasilicate, Na₂SiO₃ with composition SiO₂ 24.9, Na₂O 20.9 and H₂O 54.2 wt% (obtained locally), nitric acid (Fluka, Germany), phosphorus pentoxide (BDH Laboratory, 98%) and calcium nitrate tetrahydrate (LOBA, 98%).

2.2. Experimental Procedures

Bioactive glass having the composition (mol%); 50SiO₂:25Na₂O:21CaO:4P₂O₅ was synthesized through the sol-gel process from sodium metasilicate, Na₂SiO₃ according to the following procedure. The Na₂SiO₃ (5.0 g) was stirred in a beaker using a magnetic stirrer in deionised water (15.0 ml) followed by addition of ethanol (2.5 ml) to give a clear solution. To the stirred mixture was added 2M HNO₃ dropwise, stirring was continued further for 1 hour to allow complete hydrolysis. P₂O₅ (0.5 g) and Ca(NO₃)₂·4H₂O (4.1 g) were added in sequence under constant stirring. Each reagent was allowed 45 minutes to react before adding the next reagent, finally the mixture was stirred for 1 hour after the last addition. The resulting gel was aged at room temperature for 5 days, dried at 60°C for 72 hours to give the monolith. The monolith was further heat treated as follows; 200°C (40 hours), 600°C (5 hours), 800°C (3 hours) and 1000°C (2 hours).

2.3. Methods of Characterization

The sintered specimen was analysed by X-ray diffraction (XRD, Mini Diffractometer MD-10) before and after immersion in SBF using CuK α radiation source operated at 40 kV and 40 mA. The diffraction patterns were obtained in the 2 θ range from 10° - 75°. The surface morphology of the material before and after incubation in SBF was assessed by SEM (EVO/MA10) at an accelerating voltage of 15 kV. Fourier transform infrared (FTIR, Perkin Elmer Spectrum X) spectroscopy employing KBr pellets operating in a reflectance mode with a 4 cm⁻¹ resolution was used to monitor the types of bonds present in the glass network before and after immersion in SBF.

2.4. Evaluation of Bone Bonding Ability in Simulated Body Fluid (SBF)

The ability of the material to bond to host bone involves the formation of a carbonated HA layer on the surface of the material, either when implanted or placed in contact with biological fluids [6,23]. This was assessed *in vitro* in SBF by monitoring the formation of HA on the monolith surface using standard procedure [24]. Solution of analytical grade reagents; NaCl, KCl, K₂HPO₄, MgCl₂, CaCl₂ and Na₂SO₄ of ion concentrations (**Table 1**) were

prepared in deionised water and buffered to pH 7.4 at 37 °C with tris (hydroxymethyl) aminomethane and hydrochloric acid (HCl). The dimension of the monolith sample was 10 × 10 × 10 mm which was soaked in an SBF containing flask and kept in an incubator for 14 days. The sample was removed from the incubator and rinsed gently in 100% ethanol, then deionised water, and finally left to dry at ambient temperature in a dessicator. The dried sample was investigated with XRD, SEM and FTIR.

3. Results and Discussion

3.1. Morphology of the Sintered Bioactive Glass

The porous microstructures SEM images of the quarterary bioactive glass are illustrated in **Figures 1(a)-(b)** at two different magnifications. The cross-section of the sample is coarse and consists of interconnected pores (with average diameter ~3 μ m). The presence of small pores and less sidestep surfaces on the sample suggests a crystalline and less residual glass phase. The effect of sintering shows thicker pore struts observed at a higher magnification in **Figure 1(b)** indicating a nearly fully densified material under the sintering condition (1000°C for 2 hours).

3.2. XRD Analysis of the Sintered Bioactive Glass

XRD pattern of the bioactive glass sintered at 1000°C for 2 hours is shown in **Figure 2**. Both angular location and intensity of the peaks was of good match to the standard PDF #22.1455 by indicating formation of the crystalline phase of Na₂Ca₂Si₃O₉. Similar phase has been previously identified [25,26]. The extensive densification and fine crystallinity of Na₂Ca₂Si₃O₉ confers on the scaffold good mechanical property [27].

3.3. Biocompatibility Analysis in SBF

The XRD diffraction investigation of the bioglass after immersion in SBF for 14 days is shown in **Figure 3**. New peaks can be observed at 2 θ 29° and 32° assigned to (211) and (320) apatite reflections according to the standard JCPDS (09-0432). There is also an intense apatite

Table 1. Ion concentration of SBF in comparison with human plasma [24].

Fluid/Ions	Ion Concentrations (mM)						
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	HCO ₃ ⁻	HPO ₄ ²⁻
SBF	142	5	1.5	2.5	148.8	4.2	1
Blood plasma	142	5	1.5	2.5	103	27	1

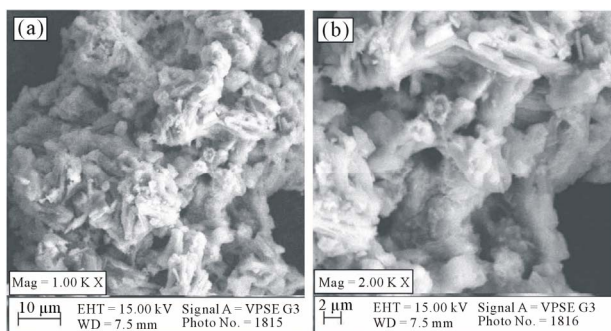


Figure 1. SEM micrographs of the bioactive glass sintered at 1000°C for 2 hour at different magnifications.

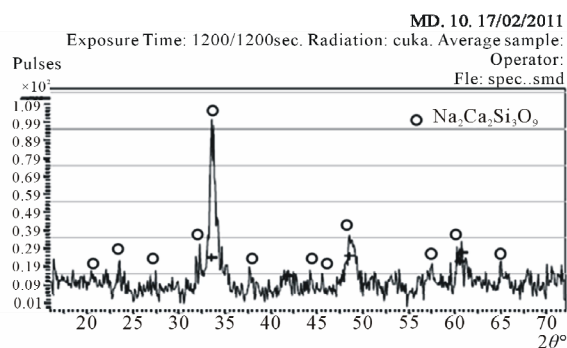


Figure 2. XRD pattern of the bioactive glass sintered at 1000°C for 2 hours showing major peaks of Na₂Ca₂Si₃O₉.

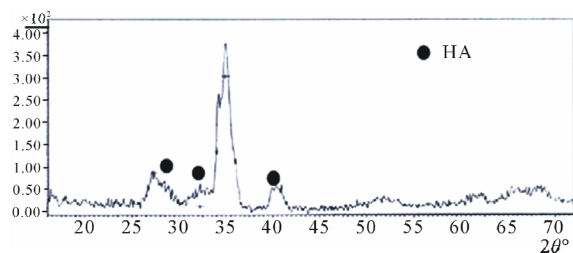


Figure 3. XRD analysis of the sintered bioactive glass after soaking in SBF for 14 days.

peak at 2040°. Analysis of the SEM in **Figure 4** shows evidence of an almost complete transition from Na₂Ca₂Si₃O₉ to an amorphous phase after soaking for 14 days [28], while the presence of Na₂Ca₂Si₃O₉ decreases the kinetics of apatite formation without inhibiting the growth of an apatite layer on the surfaces. It has been reported [27] that 28 days in SBF transforms Na₂Ca₂Si₃O₉ completely into possibly an amorphous calcium phosphate phase [5,29] ensuring biodegradability of the scaffold.

Figures 4(a) and (b) shows the surface morphology of the glass-ceramic specimen after incubation in SBF for 14 days. When compared for instance to the neat and SBF un-soaked sample (**Figure 1(b)**), there is evidence of more rounding and finer grains on the larger grains in **Figure 4(b)**. This pattern is typical of HA precipitated in SBF, populating the surface of the glass-ceramics, **Fig-**

ures 4(a) and (b).

3.4. FTIR Analysis of the Bioactive Glass

The FTIR spectroscopy analysis of the neat and SBF soaked samples are shown in **Figures 5(a) and (b)** respectively. In **Figure 5(a)**, the peak at 729 cm⁻¹ is assigned to the symmetric Si-O-Si stretching vibration in SiO₄⁴⁻, typical of crystalline silicates. The 477 cm⁻¹ peak is assigned to Si-O-Si bending vibration which is attributed to normal vibration modes of Si-O in the SiO₄⁴⁻ group indicating the presence of amorphous silicate [28]. The peak at 612 cm⁻¹ can be attributed to the crystalline phase which corroborates the XRD result thereby suggesting the presence of crystalline phosphates [30].

The intensity of the Si-O-Si bending vibration attributed to normal vibration modes of Si-O decreased from 477 cm⁻¹ to 465 cm⁻¹ after soaking for 14 days in SBF. Furthermore, a new absorption band due to bending mode of PO₄³⁻ group and attributed to the formation of HA is seen at 575 cm⁻¹ [31]. A very broad OH absorption band from 2500 - 3700 cm⁻¹ and a weak water absorbed band around 1650 cm⁻¹ appeared in the spectrum. The bands at 1420 and 1550 cm⁻¹ were considered for the absorption of carbonate group (ν₃). The peak around 900 to 1300 cm⁻¹ were mainly attributed to the phosphate absorptions [16,32].

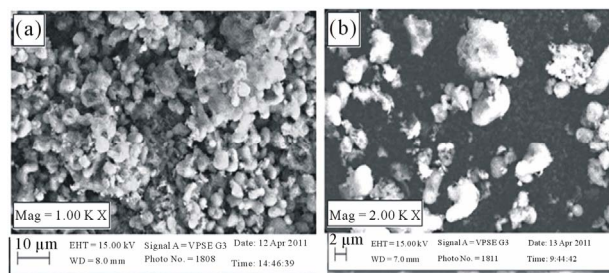


Figure 4. SEM micrographs showing the growth of hydroxyapatite on the surface of the glass-ceramic after incubation in SBF for 14 days at different magnifications.

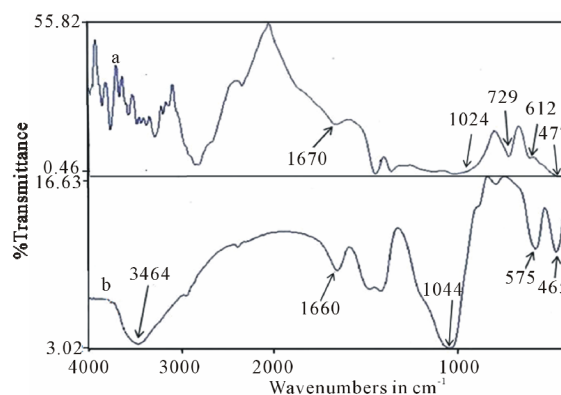


Figure 5. FTIR spectra of the bioactive glass, (a) before and (b) after soaking in SBF for 14 days.

4. Conclusion

SiO₂-CaO-Na₂O-P₂O₅-based glass-ceramics was synthesized through the sol-gel process using sodium metasilicate as a silica precursor. The material was sintered at 1000°C for 2 hours resulting in the formation of the sodium calcium silicate crystal Na₂Ca₂Si₃O₉. The growth of carbonated hydroxyapatite on the material after it was soaked in SBF for 14 days and transformation of the crystalline Na₂Ca₂Si₃O₉ into almost complete amorphous phase of calcium phosphate showed that the material was highly biocompatible and biodegradable. We therefore envision that sodium metasilicate may be a low cost precursor for sol-gel synthesis of sodium containing quaternary bioactive glass-ceramic materials.

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