

Investigation of Crystallization and Microstructure of Na₂O-CaO-P₂O₅-SiO₂-Al₂O₃ Bio Glass Ceramic System

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ABSTRACT

The effects of Al₂O₃ on the crystallization behavior of glass compositions in the Na₂O-CaO-P₂O₅-SiO₂ system were investigated by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). In this system, thermal parameters of glasses were studied by DTA. The density of the glass ceramic samples was measured by Archimedes' method. It was found that the glass-ceramic containing 2.0 molar percent Al₂O₃ had desirable sintering behavior and reached to an acceptable density. Phase investigation and micro structural study were performed by XRD and SEM, respectively.

Keywords: Bio Glass-Ceramic; Alumina; Crystallization; Mechanical Behavior

1. Introduction

Bioglasses can be classified by chemical compositions which include SiO₂, CaO and P₂O₅, Na₂O, K₂O, MgO, Al₂O₃, CaF₂, B₂O₃ and other compositions as optional [1-4]. The main bioactive glasses, glass-ceramics and ceramics used clinically are bio glass in the system Na₂O-CaO-P₂O₅-SiO₂ hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂), tricalcium Phosphate Ca₃(PO₄)₂, HA/TCP of different phases, ceramics and glass-ceramics, A/W containing crystalline oxyfluoroapatite [(Ca₁₀(PO₄)₆O,F) and wollastonite (CaSiO₃) in MgO-CaO-SiO₂ glassy matrix [5,6]. Na₂O-CaO-P₂O₅-SiO₂ glass ceramic is a commercially available inorganic material, which has been used as bone replacement for more than 20 years [1]. This is the first bioactive glass developed by Hench *et al.* in 1969 [7]. They are excellent biomaterials because they are nontoxic, they match the composition of natural bone, and show excellent integration with bone in the framework of *in vitro* and *in vivo* studies. Unfortunately, the low toughness of bioactive glass has limited its use to non-load-bearing applications [8,9]. Crystallization of bioactive glasses may be the best way to improve their mechanical properties [8,10,11]. It has been reported [12] that some glass-ceramics in the Na₂O-CaO-P₂O₅-SiO₂ system, containing apatite and wollastonite phases, with good mechanical properties and the ability of forming tight chemical bonds with living bone can be produced

through sintering and subsequent crystallization of glass powders. The effect of compositional changes on the bioactivity [13] and the crystallization behavior of some glass-ceramics located in certain compositional regions of the system have also been investigated [14]. The addition of a network former oxide like Al₂O₃ reduces the glass dissolution compare to other bioactive glasses. This lower dissolution and the lower release in aluminum lead to the formation of the (Si, O, Al) layer. On the other hand, addition of network formers could significantly reduce the bioactivity of the material because the ability to form an apatite is reduced as the ionic field strength increases. This is not the case with 2.0 mol% of Al₂O₃, in our study there is the formation of a (Ca, P) rich layer [15]. The main objective of the present investigation is to study the effect of Na₂O replacement by P₂O₅ on the hardness of the above mentioned glass-ceramics. The effect of these composition changes on the crystallization behavior of these materials, in relation to their mechanical properties was also investigated.

2. Experimental

The glass of Na₂O-CaO-P₂O₅-SiO₂ was prepared by the melt quench technique. The glass compositions in the mol% are given in **Table 1**. The glass batches were prepared from reagent grade powders: calcium carbonate (CaCO₃, 100%), quartz (SiO₂, 99.9%) and sodium carbonate (Na₂CO₃, 99.98%), ((NH₄)₂HPO₄, 99.8%), Alumina (Al₂O₃, 99.9%). The amounts of oxides were

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Table 1. Nominal glass compositions (mol%).

Sample NO.	P ₂ O ₅	CaO	SiO ₂	Na ₂ O	Al ₂ O ₃
G0	6	24.5	45	24.5	0
G1	6	24.5	45	24.0	0.5
G2	6	24.5	45	23.5	1.0
G3	6	24.5	45	22.5	2.0

weighed by using digital electronic balance. The chemicals were then mixed in a pestle mortar. The mixed powder of these samples were placed in recrystallized alumina crucible and melted in an electrically heated furnace. The powder of the samples were initially kept at 1000°C for 1 hour for calcination to occur and release of water from the starting materials then they were reheated at 1550°C and kept at this temperature for half an hour in order to achieve the homogeneity. Melted glasses were poured into cold water and, after grinding they were remelted. After the second melting a portion of the melt was poured into water to obtain frit and milled up frit to obtain a powder glass with particle size smaller than 30 μm. Particle size distributions of glass powders were characterized by a laser particle size analyzer Fritsch analyses 22. Glass powders with 0.2 wt% carboxy methyl cellulose (CMC) water solution (based on dried frit weight) were uniaxially pressed at 30 MPa and were shaped in a 20 mm cylindrical die. The obtained compacts were then sintered in an electric laboratory furnace at their crystallization temperature for 3 hour. For firing the samples a constant heating rate of 7°C/min and a soaking time of 1 hour were used and then the furnace was allowed to cool down. The soaking time was 3 hour. The hardness was measured by Rockwell (switzerland model ROC 190). The densities of the resulting glass ceramics were measured via Archimedes's method.

2.1. Thermal Measurements

The thermal behavior of glasses was monitored by DTA scans which were carried out using a simultaneous thermal analyzer (Polymer Laboratories STA-1640). Platinum containers were used for both the glass and the reference samples in air static atmosphere. The DTA equipment was calibrated periodically using Na₂SO₄ as a standard at the same conditions used for the samples measurements. The data were recorded and analysed in a computer interfaced with the DTA equipment. The error in the determination of the maximum position is due primarily to the accuracy of the DTA, which is ±2°C.

2.2. X-Ray Diffraction (XRD) and Microscopic Examinations

In order to determine the crystallisation products, the

heat-treated samples were subjected to XRD analysis (Siemens, D-500) using Cu (Kα) radiation at 40 kV and 20mA setting and in 2θ range from 5° to 70°. Information concerning the mechanism of crystallisation and the microstructure of the glass ceramic materials were obtained by a SEM (VEGA-TESCAN), on superficially polished gold-coated specimens. Energy dispersion X-ray spectroscopy, EDS, was used to identify the chemical composition of the different phases in the samples.

3. Results

3.1. Differential Thermal Analysis (DTA)

Typical DTA of the samples crystallized at the heating rate of 10°C/min are shown in **Figure 1**, and **Table 2**, for different bio glasses samples. The results revealed that the crystallization temperature increased with increasing Al₂O₃. When aluminium ion substituted for sodium ions the bonds are formed with the strong covalent Al-O bond than Na-O because of the electronegativity of aluminium is higher than sodium. The increasing of crystallization temperature with increasing of Al₂O₃ content related due to the stronger bonding in to the glass structure.

3.2. Density

Results presented in **Figure 2** show that the density increases with increasing Al₂O₃ in the glass. Samples have been sintered at their crystallization temperature. This is due to presence of Al₂O₃ provide more density than Na₂O. This indicates that replacement of Na⁺ ion by Al³⁺ ion increase the density of glass. With comparison of density

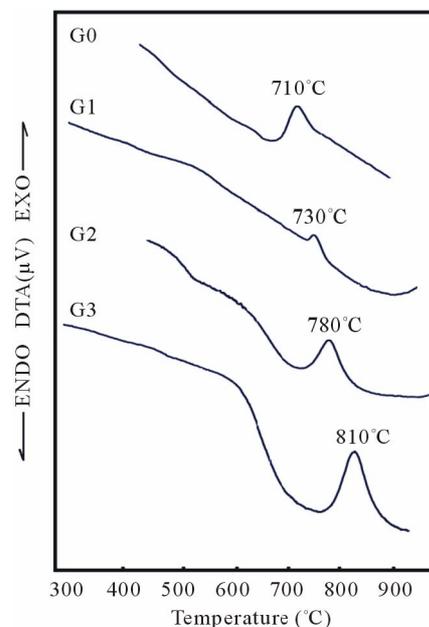
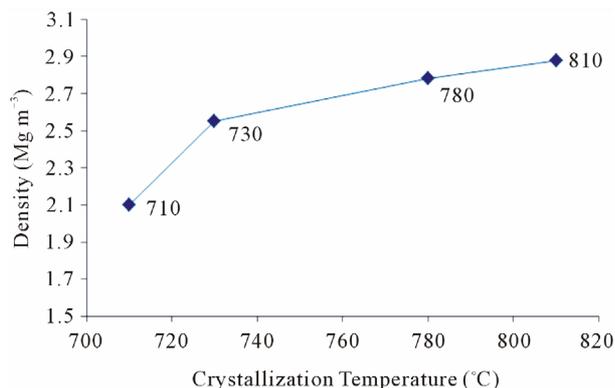


Figure 1. Variation crystallization temperature with increases of Al₂O₃ content of bioglass samples.

Table 2. Crystallization peak temperatures of bioglass samples with increase of Al₂O₃.

Samples	T _c (°C)
G0	710
G1	730
G2	780
G3	810

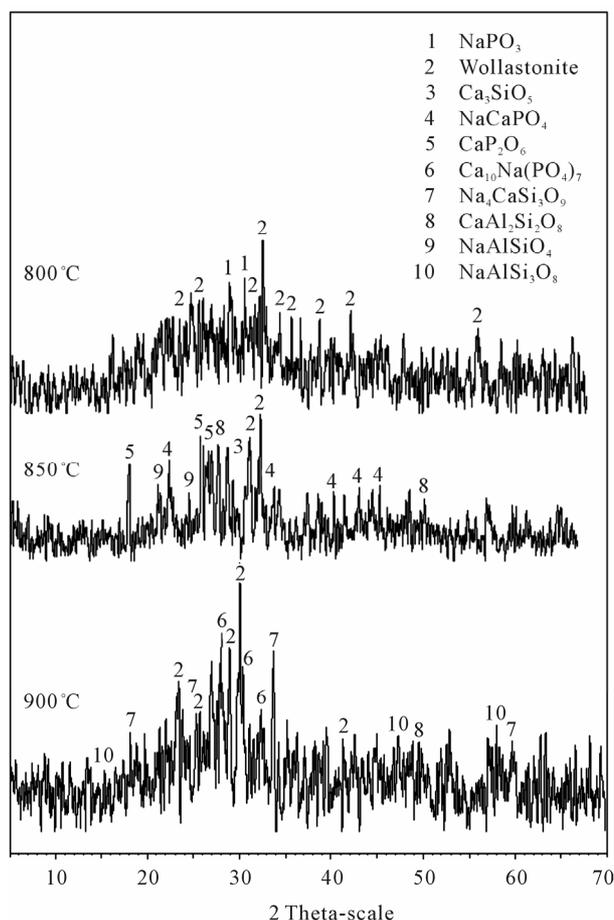
**Figure 2. Variation of density with increase of Al₂O₃ content of bioglass samples.**

results and crystallization peak temperature of each glass, it can be concluded that sample G3 reaches to maximum densification.

3.3. X-Ray Diffraction Results for Bio Glass-Ceramics

Phase formation study of G3 sample sintered at 800°C, 850°C and 900°C was carried out by XRD. The XRD patterns of this composition with various sintering temperature are shown in **Figure 3**. It can be seen that all sintered temperatures have amorphous phase coexist with some crystal phases. The X-ray diffraction analysis of G3, sintered at 800°C (**Table 3, Figure 3**), showed that wollastonite-CaSiO₃ was crystallized as a major phase together with Sodium Phosphate NaPO₃.

Increasing sintering temperature up to 850°C cause that the peaks of the NaPO₃ phase are seen to be disappeared and new peaks of NaCaPO₄, CaP₂O₆, CaAl₂Si₂O₈ and NaAlSiO₄ phases are distinguished, this effect may be controlled with assumption of the depolymerization effect on the metaphosphate network. The XRD analysis of G3 sintered at 900°C showed that, Wollastonite CaSiO₃, Sodium Calcium Phosphate Ca₁₀Na(PO₄)₇ and Sodium Calcium Silicate Na₄CaSi₃O₉, CaAl₂Si₂O₈ and NaAlSi₃O₈ Phases are formed. Sodium Calcium Phosphate NaCaPO₄ crystal is analyzed as primary crystal after sintering at 850°C for 3 h. XRD investigations showed the precipitation of an additional crystalline

**Figure 3. XRD patterns of glass-ceramics G3, after sintering at 800°C, 850°C and 900°C for 3 h.****Table 3. Crystalline phases in various sample G3.**

Phases (Sintering Temperature)	Crystalline Phase
800°C	Wollastonite CaSiO ₃ -Sodium Phosphate NaPO ₃ -Amorphous Phase
850°C	Calcium Silicate Ca ₃ SiO ₅ -beta Rhenanite β-NaCaPO ₄ -Wollastonite CaSiO ₃ -Calcium Phosphate CaP ₂ O ₆ , CaAl ₂ Si ₂ O ₈ , NaAlSiO ₄ , Amorphous Phase
900°C	Wollastonite CaSiO ₃ -Sodium Calcium Phosphate Ca ₁₀ Na(PO ₄) ₇ -Sodium Calcium Silicate Na ₄ CaSi ₃ O ₉ , CaAl ₂ Si ₂ O ₈ , NaAlSi ₃ O ₈ -Amorphous Phase

phase at 900°C. Furthermore, NaCaPO₄ crystals were no longer detected. NaCaPO₄ crystals dissolved and new crystal phases (Sodium Calcium Phosphate Ca₁₀Na(PO₄)₇ and Sodium Calcium Silicate Na₄CaSi₃O₉) formed.

3.4. Microscopic Examinations

Figure 4 shows the micrographs of specimen G3 after crystallization at 800°C, 810°C (crystallization temperature), 850°C and 900°C temperatures, taken by SEM. As

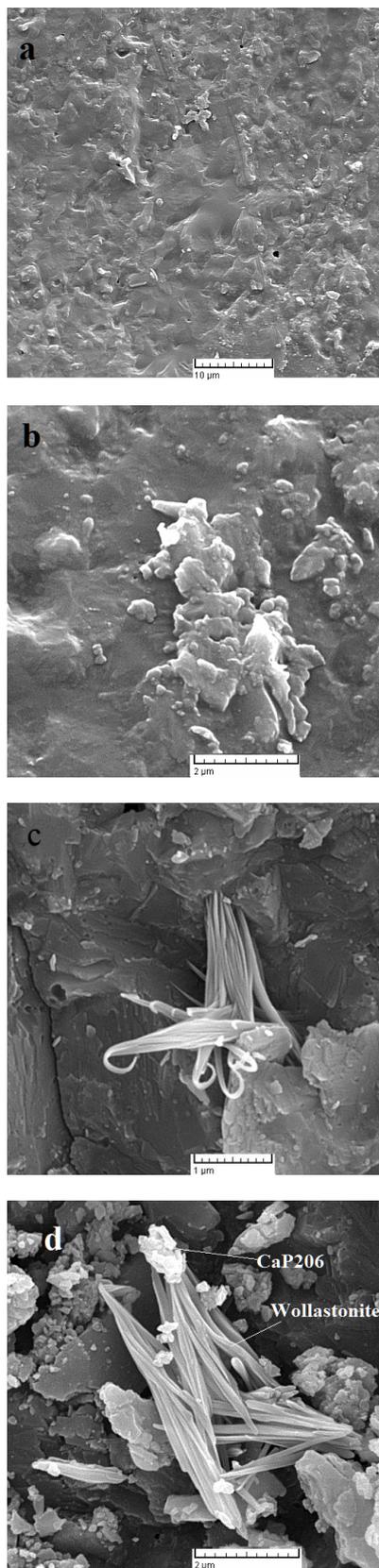


Figure 4. SEM micrographs of crystallized sample G3, sintered at: (a) 800°C; (b) 810°C; (c) 850°C and (d) 900°C.

sample (b) was sintered at crystallization temperature, it crystallized more than sample (a) as expected and bigger crystallites are formed.

At the higher temperatures at which glasses (c) and (d) were sintered, the conditions for nucleation and growth of a new crystalline phase, *i.e.* wollastonite, and CaP_2O_6 , are favorable and microstructures with good crystallinity appear. **Figure 4(d)** shows wollastonite and $\text{Na}_4\text{CaSi}_3\text{O}_9$ crystals. The EDAX analysis of G3 sintered at 850°C is shown in **Figures 5(a), (b)**. wollastonite, CaP_2O_6 are formed in samples G3 at mentioned sintering temperature. The variations of hardness versus sintering temperature for specimen G3 are shown in **Figure 6**. It is observed that increasing the temperature of sintering up to 850°C results in increasing the hardness and decreasing thereafter with increasing temperature up to 900°C.

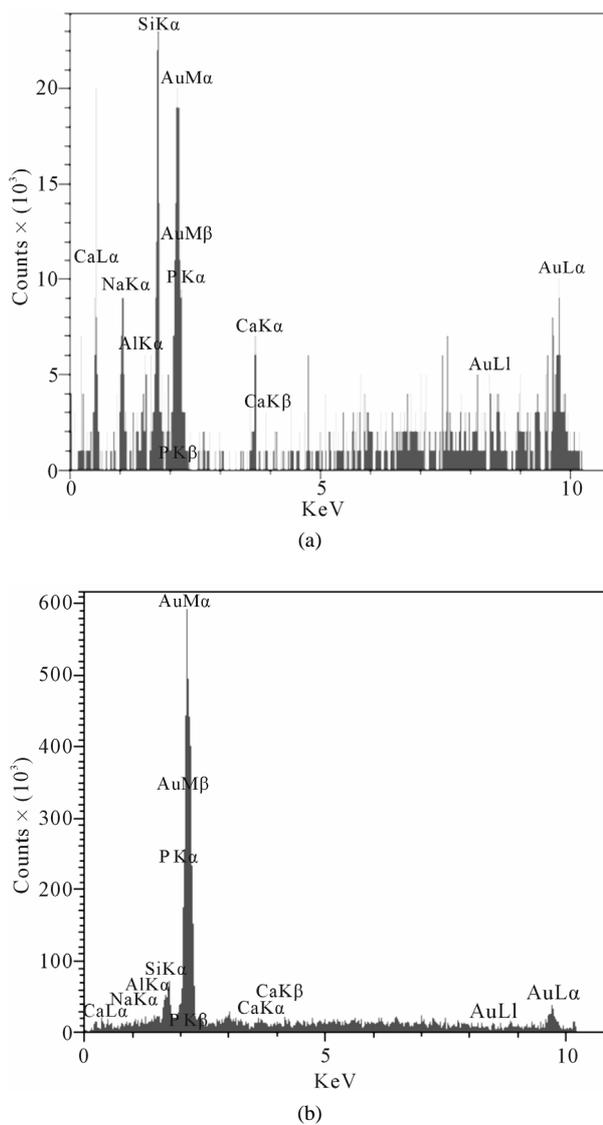


Figure 5. The EDAX analysis of sample G3: (a) Wollastonite; (b) CaP_2O_6 .

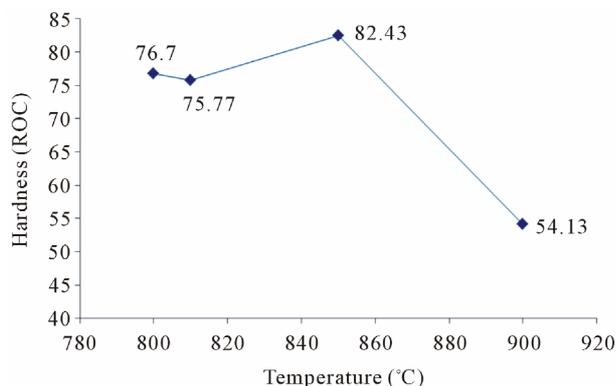


Figure 6. Variations of hardness versus temperature of sintering.

4. Discussion

The qualities of a glass-ceramic, however, depend on the kind and quantity of the crystal phase formed, as well as on the residual glass composition. In principle, the kind of crystal phase is related to the parent glass composition, but its quantity depends on the temperature the heat treatment. Therefore, the presence of an efficient nucleating agent in the correct concentration and the determination of the temperature and time of the crystallization and acquire particular importance in the formation of a glass-ceramic. Replacement of Al₂O₃ instead Na₂O cause increase crystallization temperature. Sodium oxide is a network modifier and small changes in its percentage affect significantly the melting temperature of the glass [16]. With the increase of the Al₂O₃ content in the Na₂O-CaO-P₂O₅-SiO₂ glasses, crystallization temperature gradually increases (Table 3). The crystal structure of β-Rhenanite was investigated by Jalota *et al.* [17]. This crystal phase has a polymorphic transformation from low to high form at approximately 850°C. Glass ceramics which contained NaCaPO₄ as the crystalline phase were also reported to be bioactive [18-20]. Sample G3 sintered at 850°C has maximum bending strength because Ca₃SiO₅ phase has formed at 850°C. This phase improves mechanical behavior and has potential biomaterial. With increasing sintering temperature up to 900°C, Ca₃SiO₅ phase disappeared and reduced bending strength.

5. Conclusions

Sintering behavior of Na₂O-CaO-P₂O₅-SiO₂-Al₂O₃ biological glasses containing different amounts Al₂O₃ has been investigated. The results in this study are summarized as follows:

- 1) Addition of Al₂O₃ to glass shifts the crystallisation peak to higher temperature.
- 2) Addition of alumina to glasses up to 2% mol, increases density and hardness of samples.
- 3) Sample G3 sintered at 850°C has maximum bending

strength because Ca₃SiO₅ phase has formed at 850°C.

4) The amount of Al₂O₃ in the glass ceramics and sintering temperature play an important role in controlling both phase formation and microstructures.

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