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Thermal Evolution of Na_2O-K_2O-CaO-SiO_2-P_2O_5-Al_2O_3 Glass System, and Possible Applications as Biomedical Devices

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Abstract

Bioceramics are widely used materials as filling bone and implants, which can be classified into three groups according to their reactivity with the body fluid and its interaction with the bone tissue: bioinert, resorbable or bioactive. Within the last class mentioned are bioactive glasses and glass-ceramics.

One of the most researched topics in this area is based on ensuring the ability of the implant to long term survival, as well as improves its mechanical properties. Hence, glass-ceramics are produced by a controlled crystallization of a glass, which enables to obtain very small crystallite sizes, that increases considerably the mechanical resistance and durability of the material. The SiO_2-CaO-P_2O_5-Na_2O system is the most widely used for the production of bioactive glasses, which can be added to other compounds such as Al_2O_3 that, forming part of some crystal phase in the glass- ceramic, that can provide improved mechanical properties.

In this work, two glasses were prepared starting from commercial Bioglass composition, adding potassium and aluminum. Both were included in the formulation by means of purified feldspar. Performed tests were differential thermal analysis and X-ray diffraction in order to follow up thermal transformation and to reveal the developed phases after such treatments.

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Keywords: Bioceramics, feldspar, crystallization, X ray diffraction, differential thermal analisys.

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1. Introduction

In the 70s, Hench et. al. (1973) who were studying properties of glasses formed in the Na_2O-CaO-P_2O_5-SiO_2 system, found that specific composition of these materials were able to chemically bond to bone tissue by hydroxyapatite formation in their surfaces, phase which is present in that tissue. Since that time, many studies have been done to obtain these types of materials. In turn, it has been sought to improve their mechanical properties for stronger materials, and trying to reach properties similar to bone. Interestingly also, to find a balance in the hardness / machinability ratio and thus obtain matrices that can work with traditional mechanical forming, in order to give way to a simpler way to implant, even at the time of surgery .Within this objective, bioactive glasses have been heat treated in order to crystallize phases in the glass matrix, obtaining materials, commonly called glass-ceramics, which have marked differences in mechanical properties with their predecessors. These types of material are generally produced by means of high purity raw materials. A major challenge would be to include natural raw materials in the formulation, such as quartz and feldspar. The latter, in addition to silicon, provide aluminum which can favor the formation of certain crystalline phases for obtaining biomaterials.

While it has been shown that small amounts of free aluminium as Al_2O_3 in the glass phase inhibit bone bonding (Hench et. al (1991)), this does not happen if the element is part of a crystalline phase such as an aluminosilicate (Liu et. al. (2006)). Moreover, the inclusion of the major elements of the feldspar may contribute to the formation of crystalline phases like mica, which give high machinability, and together with others crystals phases, mechanical properties would improve with respect to glass (Barrios de Arenas et. al. (2006)). In this work, silicon and aluminium were incorporated through natural quartz and feldspar, in addition other minor elements such as sodium and calcium, needed in the mixture. The objective was to evaluate the crystalline phases obtained after applying various heat treatments to glasses in P_2O_5-Na_2O-CaO-SiO_2-Al_2O_3 system.

2. Experimental

Raw materials used were sodium carbonate PA, calcium carbonate PA; monobasic ammonium phosphate PA, and natural quartz and feldspar. The amount of incorporated feldspar was set according to the amount of aluminum to be incorporated. The values were 2.5 and 5.0% by weight expressed as Al_2O_3. Samples were identified as VAl25 and VAl50, respectively. Amorphous solids were prepared starting from the basis of the bioactive glass composition (Table 1), replacing SiO_2, Al_2O_3 and K_2O from feldspar, and keeping weight percents of CaO and P_2O_5 constant in the values for Bioglass, adjusting the amounts of Na_2O. Percentages of the elements expressed as oxides are shown in Table 1. It also includes the composition of commercial Bioglass to show the composition that is split to make the previously explained changes.

Table 1. Samples compositions (w/w %)

Samples	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	P_2O_5
Bioglass®	45.0	0.0	24.5	24.5	0.0	6.0
VAl25	41.5	2.5	24.5	24.0	1.5	6.0
VAl50	38.0	5.0	24.5	23.5	3.0	6.0

The mixture was molten at 1300 °C for 2 hours in a Platinum Crucible and then cooled rapidly in distilled water to obtain glass. Mixes were previously treated at 900 °C to remove the CO_2 generated by carbonates decomposition. Glasses were ground and sieved through mesh 100. Differential thermal analysis was performed for each solid in Netzsch STA 409 equipment, at a heating rate of 10 °C/min up to 1300 °C with subsequent cooling to 10 ° C/min down to 800 °C. The assay was carried out in air atmosphere with 50 cm^3/min flow, using α-Al2O3 as reference substance. Different portions were thermally treated to 700, 800, 900, 1000 and 1100 °C for 4 hours to assess crystalline phases formed. Treated samples were identified as: VAl25-X and VAl50-X, where X is the heat treatment temperature. Glasses and glass-ceramics were characterized by X-ray diffraction (XRD) on a Philips 3010 equipment using Cu Kα radiation (λ = 1.5405 Å) at 40 kV and 35 mA and Ni filter.

3. Results and discussion

3.1. Differential Thermal Analysis

Differential thermal analyses of VAl25 and VAl50 are shown in Figures 1 and 2, respectively. Table 2 contains data of characteristics temperatures obtained in this test.

Table 2. Characteristic temperatures of VAl25 and VAl50 obtained by differential thermal analysis.

Muestras	Tg_1	Tp	Tg_2	Tl_1	Tl_2
VAl25	512	708	962	1172	1189
VAl50	508	642	967	1092	1184

Where Tg: glass transition temperature, Tp: crystallization peak temperature and Tl: liquidus temperature.

Using extracted data, we can see that glass transition temperatures are close in both samples. After the characteristic temperature mentioned, an exothermic peak is observed, corresponding to glass crystallization. VAl50 sample begins to crystallize at a lower temperature that VAl25 (Table 2). Crystallization peaks in both glasses, when temperature was uprising, are in a fairly narrow range. This would indicate that the crystallization quickly occurs in both glasses, so that a priori would indicate that crystallization occurs in the entire volume of glass (Hölland et. al. 2002).

Following the observed peak, a second glass transition temperature is recorded, corresponding to second amorphous phase because of a glass-in-glass phase separation.

The crystallization peak of the second phase is not observed because the solid begins to melt a few degrees above. Then, two endothermic peaks become visible corresponding to complete melting of two phases developed during the test. When the melts cool down, two exothermic peaks appeared in both samples, corresponding to separated glass phases crystallization. With naked eye it is seen that the peak at upper temperature is bigger than the one at lower temperature, and gives us an idea of the relative amounts of each amorphous phase.

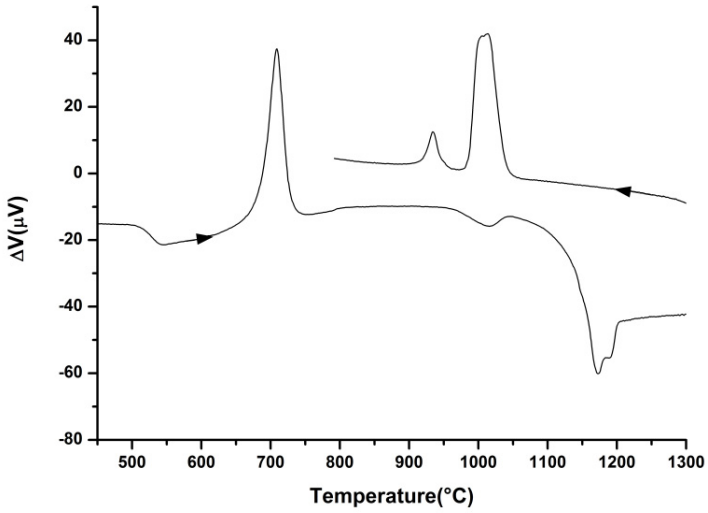

Figure. 1. Differential thermal analysis of VAl25 glass

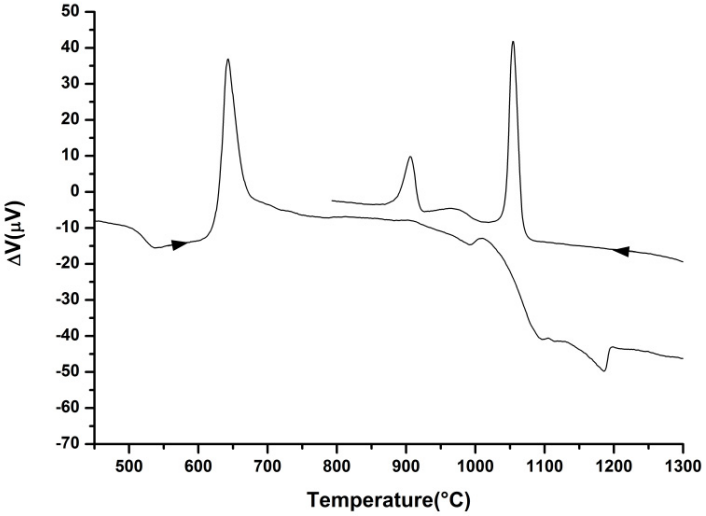

Figure. 2. Differential thermal analysis of VAl50 glass

3.2. X-ray diffraction

Diffractograms of VAl25 and VAl50 glasses and glass-ceramics obtained with rising temperatures are shown in figures 3 and 4, respectively.

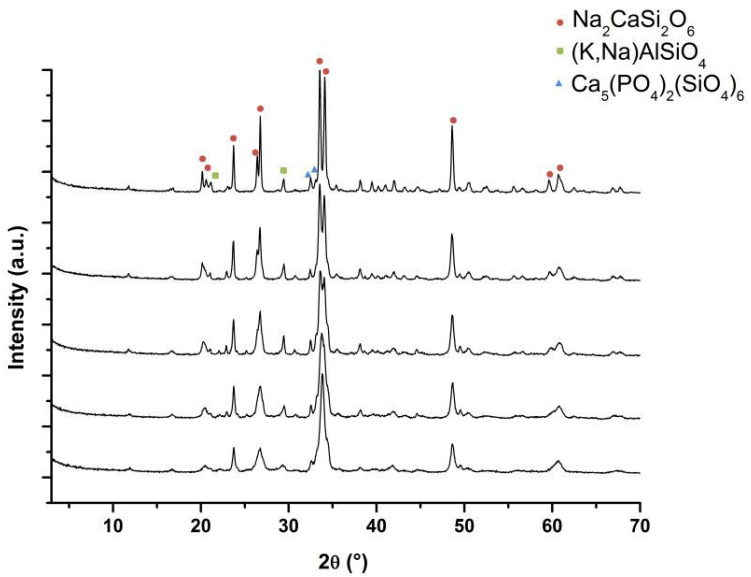

Figure 3. VAl25 glass and glass-ceramics diffractograms

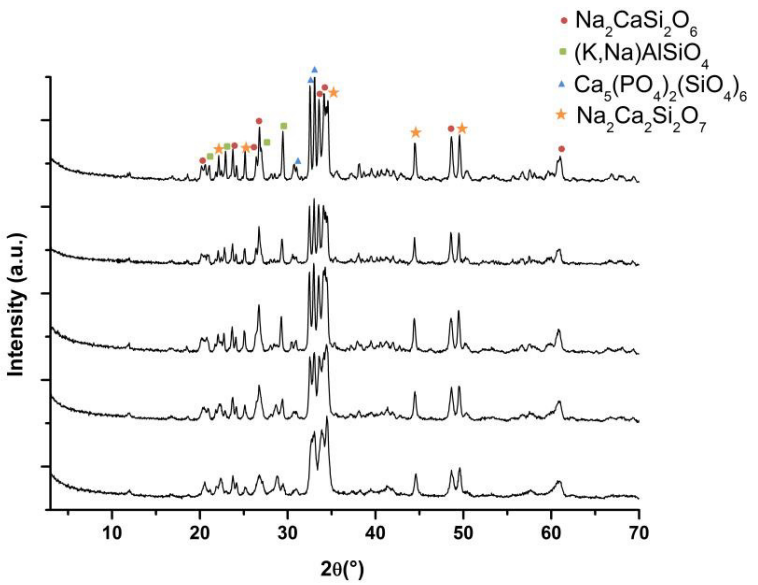

Figure 4. VAl50 glass and glass-ceramics diffractograms

X-ray diffraction was performed to both glass powders, in order to ensure lack of crystalline structure, which is verified by the appearance of typical halo in X-ray patterns of amorphous solids (Figures 3 and 4). It can be seen that heat treatment up to 700 °C caused VAl25 complete crystallization, in agreement with differential thermal analysis result.

With increasing thermal treatments temperatures, the formed phases are the same. The observable difference is referred to the microstructure, where the peaks become narrower with temperature, which indicates crystal growth of the developed phases.

Phases formed were sodium calcium silicate ($Na_2CaSi_2O_6$), nepheline ($(Na,K)AlSiO_4$) and calcium silicophosphate ($Ca_5(PO_4)_2(SiO_4)_6$ (Figure 3). Sodium calcium silicate has also been found by Lefebvre et. al. (2007) after Bioglass heat treatment and is a phase that has bioactive behavior (Pleit et. al. (1991)). A calcium silicophosphate of similar stoichometry was found to be bioactive, due to the formation of a hydroxyapatite layer when it is in contact with Simulated Body Fluid (Lu et. al. (2010)).

With respect to VAl50 heat treatments, the same behavior as VAl25 was observed with increasing heat treatment temperature. Developed phases were the same as VAl25 with an additional silicate phase, $Na_2Ca_2Si_2O_7$ (Figure 4). Comparing the heights of the peaks of both thermally treated glasses up to 1100 °C, we could conclude that there is a higher quantity of calcium and silicophosphate and nepheline a lower amount of $Na_2CaSi_2O_6$ in VAl50 regarding VAl25. The second amorphous phase did not crystallize and there were no new phases developed with increasing temperature.

4. Conclusions

Both compositions showed glass-in-glass phase separation. The three developed phases by heat treatments in both glasses were the same, except an additional crystalline phase, $Na_2Ca_2Si_2O_7$, obtained in 1100 °C thermal treatment of VAl50. The relative amounts of each crystalline phase formed in the two samples were different.

The addition of aluminum by feldspar became part of a crystalline phase developed in the two compositions, and this could positively influence the bioactivity. The presence of $Na_2CaSi_2O_6$ and Ca_5 $(PO_4)_2(SiO_4)_6$ phases could

promote bioactivity on both glass ceramics. Still remains a more detailed study of the transformations undergone by both bioactive glasses and their bioactive properties.

Acknowledgements

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