Effects of CaO on Properties of $\text{P}_2\text{O}_5$-CaO-Na$_2$O Glasses and Glass Ceramics

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Abstract

This project is aimed at producing calcium phosphate glass ceramic for bone substituting applications. Effects of calcium content on the thermal parameters, physical properties, phase formation and microstructures of $\text{P}_2\text{O}_5$-CaO-Na$_2$O glass ceramics were studied. Three glass compositions of fixed $\text{P}_2\text{O}_5$ content were prepared by conventional melt quenching method at 1200°C. Thermal parameters of each glass were studied by differential thermal analysis (DTA). The glass powder was pressed into pellets and subsequently sintered at 550, 600 and 650°C. Afterward, the density of the glass ceramic samples was measured by Archimedes’ method. Phase investigation and micro structural study were performed by XRD and SEM, respectively. The DTA traces provided heat treatment temperatures in a range of 550-650°C. XRD results revealed that calcium phosphate and sodium phosphate were formed in the glass ceramics.

Key words: Calcium phosphate, Glass ceramic, Bone substituting

Introduction

Calcium phosphate glasses have a potential use as bone substituting applications, because of their chemical composition is closely similar to that of natural bone. They have bioresorbable property enable this glass to be dissolved in physical fluids. The implant glass can be slowly replaced by regenerate tissue and has good biocompatibility and non toxicity.$^{(1-2)}$

Calcium phosphate glasses from a ternary $\text{P}_2\text{O}_5$-CaO-Na$_2$O system have been studied in terms of thermal property, dissolution property and cytotoxicity. These glasses were found to exhibit low melting point, low glass transition temperature and low crystallization temperature, depending on the amount of $\text{P}_2\text{O}_5$ and CaO contents in the glass compositions.$^{(3-6)}$ It was also reported that CaO has a strong effect on reduction of the CaO dissolution rate in distilled water because this oxide improves the phosphate network strength when cross-link formation between the non-bridging oxygen of two different chains by Ca$^{2+}$ ion. As well as in simulated body fluid (SBF), the dissolution rate showed the same tendency as in distilled water. The cytotoxicity of this glass decreased with increasing CaO and decreasing $\text{P}_2\text{O}_5$ content.$^{(3)}$ In conclusion, the suitable composition from this glass system was found in the samples where $\text{P}_2\text{O}_5$ more than 40 mol% especially at 45 mol% of $\text{P}_2\text{O}_5$, which was easily melted and had good biocompatibility. It also possessed low melting point, low glass transition, low softening point, low crystallization temperature and consequently low processing temperature.$^{(4-6)}$

In this project, effects of calcium oxide (CaO) content on the thermal parameters, physical properties, phase formation and microstructures of the $\text{P}_2\text{O}_5$-CaO-Na$_2$O glasses and glass ceramics, with fixed amount of 45 mol% $\text{P}_2\text{O}_5$ and various ratios of CaO:Na$_2$O, were investigated.

Materials and Experimental Procedures

Glass Melting

Three glass compositions from the $\text{P}_2\text{O}_5$-CaO-Na$_2$O were prepared using (NH$_4$)$_2$HPO$_4$, CaCO$_3$ and Na$_2$CO$_3$ as starting materials. Ternary

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diagram as shown in Figure 1, illustrates the three compositions of 45P_2O_5-32CaO-23Na_2O, 45P_2O_5-36CaO-19Na_2O and 45P_2O_5-40CaO-15Na_2O. The starting powders were weighed following the desired glass compositions. The batch of each composition was melted in an alumina crucible using an electric furnace at 1200°C with 1 hour dwell time. The melts were quenched by pouring them onto a stainless steel mould in air and pressing another stainless steel plate onto the melt for avoiding crystallization. The automatic milling machine was employed for grinding the prepared phosphate glasses into fine powder. The powder of each glass composition was subsequently examined by differential thermal analysis (DTA: Stanton redcroft DTA model 673-4) using Al_2O_3 as reference.

**Glass Ceramic Preparation**

The prepared glass powders from 2.1 were pressed into pellets of 15 mm in diameter and 1 gram in weight and were subsequently sintered at 500-650°C for 2 hours. The densities of the resulting glass ceramics were measured via Archimedes’s method using ethyl-alcohol as a medium because this phosphate glass can be easily dissolved in water. Phase formation and microstructures of the resulting glass ceramics were investigated by X-ray diffraction (XRD: Siemen D-500) and scanning electron microscopy (JSM-6335F), respectively.

**Results and Discussion**

**Thermal Parameters of P_2O_5-CaO-Na_2O Glasses**

DTA traces of the quenched samples of 45P_2O_5-32CaO-23Na_2O, 45P_2O_5-36CaO-19Na_2O and 45P_2O_5-40CaO-15Na_2O are shown in Figure 2. The glass transition temperatures: T_g(s) of these glasses are in the range of 440-455°C. It is also noticed that this T_g slightly increases with increasing CaO content. This tendency has a good agreement with their density data where the density of the quenched glass increases with increasing CaO concentrations as can be clearly illustrated in Figure 3.

**Phase Formation of P_2O_5-CaO-Na_2O Glass Ceramics**

Phase formation study of P_2O_5-CaO-Na_2O glass ceramics sintered at 550-650°C were carried out by XRD. The XRD patterns of each composition
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with various sintering temperature are shown in Figure 4 (a-b). It can be seen that all glass ceramics have amorphous phase coexist with some crystal phases, which are two calcium phosphate phase of Ca3P2O7 (JCPDS file No. 73-0440) and \( \beta \)-Ca3P2O7 (JCPDS file No. 03-0604) and two sodium phosphate phases of NaPO3 (JCPDS file No. 11-0650), NaPO3 (JCPDS file No. 76-0788). The two NaPO3 phases are monoclinic with difference in their unit cell parameters. The one with JCPDS file No. 11-0650 has \( a = 15.38 \), \( b = 3.504 \), \( c = 7.078 \) Å and \( \beta = 93.870^\circ \), while the latter has \( a = 12.120 \), \( b = 6.200 \), \( c = 7.078 \) Å and \( \beta = 92.000^\circ \).

The two NaPO3 are major phases in the glass ceramics, containing CaO content of 32 (Figure 4(a)) and 36 mol\% (Figure 4(b)) of all sintering conditions. The amount of coexisting phases of Ca3P2O7 and \( \beta \)-Ca3P2O7 was found to increase with increasing sintering temperature. The XRD patterns of the sintered glass ceramics with CaO content of 40 mol\% (Figure 4(c)) show different result comparing to that of the lower CaO content samples as described above. The samples sintered at higher temperature of 600 and 650°C contain \( \beta \)-Ca3P2O7 as a major phase, which may be attributed to the exothermic peaks at high temperature of more than 600°C (Figure 2). The \( \beta \)-Ca3P2O7 enables these glass ceramics to be suitable in biorealorbed applications.

Density and Microstructure of P2O5-CaO-Na2O Glass Ceramics

The relationships between density and sintering temperature of the glass ceramics with different compositions are graphically illustrated in Figure 5. It can be seen that the trends of the glass ceramics with 32 and 36 mol\%CaO are similar while that of the glass ceramics with 40 mol\%CaO exhibits differently. For the glass ceramics with lower CaO content (32 and 36 mol\%), the density decreases with increasing sintering temperature. This implies that the crystallization processes of these glasses at the temperature between 550-600°C, involves the mass transport of many atoms for formation of crystal phase, leaving many free volumes and pores in the glass matrix, thus caused the reduction in bulk density of the sintered pieces. While the glass ceramics with 40 mol\%CaO content, has a higher range of crystallization temperatures between 606-630°C, therefore at 600°C the sintering process had no effect from crystallization, giving rise to the proper mechanism in densification of the sintered piece with the highest value of density. Further increase of sintering temperature to 650°C then minimized the density value of the glass ceramics as a result of crystallization.

Figure 6 shows the microstructures of the glass ceramics sintered at 650°C for all compositions. It can be seen that, at low density sample (low CaO content) has the highest porosity and the average
pore size of about 20 μm, while the higher CaO content sample exhibits dense microstructure. This result has a good consistency with their density data. Even though the glass ceramic with 40 mol%CaO sintered at 650°C has the highest density value, the glass ceramic with 32 mol%CaO, having interconnected pores of micron in size, is of interest as porosity is important properties for bone tissues regenerate, cell increase and drug delivery in artificial bone.\textsuperscript{(7-8)}

![Figure 5](image)

**Figure 5.** Density of P\textsubscript{2}O\textsubscript{5}-CaO-Na\textsubscript{2}O glass ceramics at different sintering temperatures.

**Conclusions**

Glasses and glass ceramics from P\textsubscript{2}O\textsubscript{5}-CaO-Na\textsubscript{2}O system were successfully produced. DTA result suggested the suitable range of sintering temperatures which were between 550-650°C. Phase identification study revealed the formation of Ca\textsubscript{2}P\textsubscript{2}O\textsubscript{7}, β-Ca\textsubscript{2}P\textsubscript{2}O\textsubscript{7} and two phase of NaPO\textsubscript{3}. The amount of CaO in the glass ceramics and sintering temperature play an important role in controlling both phase formation and microstructures. Two interesting glass ceramics were achieved from this research. The first one is from the 45P\textsubscript{2}O\textsubscript{5}-32CaO-23Na\textsubscript{2}O composition and sintered at 650°C as it has good interconnected pores of ~20 μm in size, which is useful for bone tissue regeneration. The second one is from the 45P\textsubscript{2}O\textsubscript{5}-40CaO-15Na\textsubscript{2}O composition and sintered at the same temperature. This sample offers the highest density value with β-Ca\textsubscript{2}P\textsubscript{2}O\textsubscript{7} as a major phase which plays an important part in controlling bioresorbable properties.

![Figure 6](image)

**Figure 6.** Microstructures the glass ceramics sintered at 650°C: (a) 45P\textsubscript{2}O\textsubscript{5}-32CaO-23Na\textsubscript{2}O, (b) P45\textsubscript{2}O\textsubscript{5}-36CaO-19Na\textsubscript{2}O and (c) 45P\textsubscript{2}O\textsubscript{5}-40CaO-15Na\textsubscript{2}O.

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