

Sol Gel Synthesis and Preparation of Macroporous Glass: Effect of Sodium Nitrate Addition

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Abstract: The aim of this study is to prepare gel glasses derived via acid catalyst sol-gel method based on $\text{SiO}_2\text{-CaO-P}_2\text{O}_5$ and $\text{SiO}_2\text{-CaO-Na}_2\text{O-P}_2\text{O}_5$. The synthesized gel glass powder was compacted into pellets and sintered at 1000 °C for 3 hours. The initial characteristics and sintered properties for both glasses then were analyzed. It was found that, the addition of sodium nitrate in the glass leads to foaming effect which occurred during sintering process. Thus, enables the formation of macroporous structure and expansion in thickness experienced by the glass. The pore size was approximately 300 μm by varying the sodium to calcium composition, whereas glass without sodium content only contained nanopores. The fluxing effect that occurred during sintering also caused vitrified bodies which reduced the glass porosity percentage. Glass with sodium content formed sodium related phases such as $\text{Na}_{5.27}\text{Ca}_3(\text{Si}_6\text{O}_{18})$ which increased the glass crystallinity. From this study, it shows by addition of sodium nitrate into the glass composition, macroporous glasses can be produced which potentially being used as a scaffold material.

Keywords: Bioglass, Sol-gel, Macropores, Synthesis;

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1. INTRODUCTION

Bioglass with macroporous structure is highly needed when being used as a scaffold. Minimum size required for interconnected macroporous structure to promote tissue in growth is at 100 μm while larger pore size at 300 μm enable bone in growth as well as the formation of capillary to occur [1,2]. Bioglass with macroporous structure within this range of pore size is required to fulfill the requirement as an implant scaffold. This can be achieved by preparing porous bioglass by using various methods [3-7]. Thermal treatment has the ability to influence the structural transformation and the final phase of a glass which is also important in order to improve the mechanical properties of a glass scaffold. Nevertheless, the ideal sintering temperature is much closer to the glass crystallization temperature [8]. Crystallization is said to decline the bioactivity of glass due to lower ionic dissolution *in vitro*. Besides, the highly porous nature of sol-gel glass may decline their sinter ability [9]. By the way, bioglass powder has to be sintered for production of high porous scaffolds or as coatings of implant materials. However, only few papers addressed this issue due to limitations as stated above. Melt derived bioglass, commonly used Na_2O to reduce the melting temperature [10,11].

However, low processing temperature of sol-gel method eliminates the needs of Na₂O. Because of that, simple composition of bioglass such as in binary system of SiO₂-CaO can be prepared by sol-gel technique. By the addition of network modifier cations such as sodium (Na⁺) and calcium (Ca²⁺), non-bridging oxygen (NBO) bonds can be introduced through the disruption of structure. This NBO bonds may improve the dissolution and bioactivity of bioglass [3,4]. Thus, the component of Na₂O in the sol-gel glass is still considered to be relevant. Apart from that, our observation has found that glasses with macroporous structure together with good mechanical properties can be prepared by synthesis ternary glass with the presence of specific Na₂O content prepared by sol-gel method. As it potentially used as scaffold material, further investigation needs to be carried. Thus, the aim of this study is to investigate the effect of sodium nitrate addition on the initial characteristic and sintered properties of ternary glass composition made by sol-gel method. In this study, the comparison between without sodium oxide containing glass and sodium oxide containing glass will be discussed.

2. MATERIALS AND METHODS

Bioglass in the ternary system of SiO₂-CaO-P₂O₅ and quaternary system of SiO₂-CaO-Na₂O-P₂O₅ were prepared for comparison. Bioglass without sodium nitrate content in ternary system was labeled as SiCa₄P and bioglass with the addition of sodium nitrate content in quaternary system was labeled as SiCaPN₃.

Mixing of reagents was involved during synthesis of bioglass powder for both systems via sol-gel method. This sol-gel method involved series addition of reagents where 40 ml of deionized water was mixed with 1 ml of nitric acid (HNO₃, 1M, Sigma Aldrich) and a precursor contained 10 ml of tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄, Sigma Aldrich). This mixture was stirred using magnetic stirrer and it was allowed to react for 40 min before added with 2 ml of tetraethyl phosphate (TEP, OP(OC₂H₅)₄, Merck). After 30 min stirring, 8 g of calcium nitrate tetrahydrate (Ca(NO₃)₂, 4H₂O, Merck) then added into the solution mixture and it was allowed to react for another 40 min. For the preparation of bioglass in quaternary system, it was differentiated by adding 5 g of calcium nitrate tetrahydrate (Ca(NO₃)₂, 4H₂O, Merck) and the solution mixture was allowed to react for 20 min before added with 3 g of sodium nitrate (NaNO₃, Merck) and it was allowed to react for another 20 min. The final solution that obtained then casted into plastic container and gel formation was observed after solution was left at ambient temperature for three days. Aging process then took place for 24 hours at 60 °C before proceed to drying process for another 2 days at 120 °C. The dried powder obtained was directed to the thermal stabilization process in muffle furnace for 3 hours at 600 °C with heating rate of 5 °C/min in order to remove any residues that contained in the powder. A fine gel glass powder was obtained by grinding using agate and mortar and preliminary analysis of the powder which involved Thermal Gravimetric Analysis (TGA, Rigaku Thermo plus Evo) and Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer) were carried out.

The powder was then compacted into cylindrical pellet with diameter and thickness of about 12.00 mm and 3.00 mm respectively. The compacted pellets were sintered at 1000 °C with soaking time and heating rate of 3 hours and 5 °C/min respectively. Further analyses such as Scanning Electron Microscopy (SEM, JOEL Model JSM-6460LA), X-ray Diffraction (XRD, BRUKER D2 PHASER), FTIR and Archimedes test (HR-250AZ) were carried out.

3. RESULTS AND DISCUSSION

3.1 Initial characterizations.

Fig. 1 (a) and (b) show the TGA and FTIR analysis for gel glass powder thermal stabilized at 600 °C respectively. The increment of sodium nitrate content resulted increased in nitrate residual within the glass matrix as indicated by infrared spectrum. This lead to the highest decomposition to occur at temperature range between 600 °C to 900 °C for the sample with presence of sodium nitrate in their glass matrix as shown

on TGA graph. Samples contained sodium nitrate was observed to be effectively stable above 900 °C due to the decomposition of by product occurred. This was approved by Arcos et al. which showed nitrates decomposed approximately at 680 °C [12]. Increase in the sodium nitrate content lead to the increment of Si-O-Ca non-bridging oxygen (NBO) bond which indicated by FTIR [12-14]. This NBO bond should be advantages for bioactivity property of a scaffold.

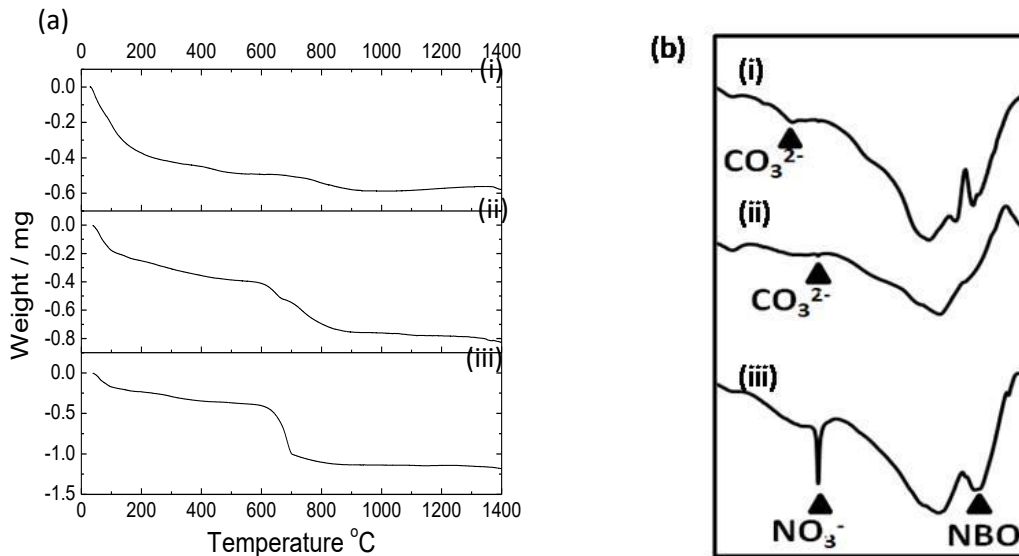


Fig. 1 (a) TGA and (b) FTIR analyses of gel glass for (i) SiCa₄P, (ii) with addition of sodium nitrate and (iii) with addition of more sodium nitrate (SiCaPNa₃) thermal stabilized at 600 °C

3.2 Physical and morphological properties.

Table 1 displays the dimensional changes in thickness and diameter as well as porosity and densification using Archimedes principle for gel glass pellets sintered at 1000 °C. The SiCa₄P shrank in both thickness (9.85 %) and diameter (9.93%) due to the densification of the particle that occurred upon sintering process. Meanwhile, SiCaPNa₃ shrank in diameter (4.35%) but expanded in thickness (60.53%). Scanning electron microscopy (SEM) reveals the SiCa₄P existed in nanoporous sized while SiCaPNa₃ was in macroporous sized with pore size approximately achieved 300 μm throughout both surface and cross section of the sintered gel glass pellet. This phenomenon of macroporous formation occurred due to the gas released and eventually created such foaming effect once the gel glass pellet undergo sintering process at this temperature. This factor also caused the expansion in thickness of sintered SiCaPNa₃.

For Archimedes test, water is used as the medium. SiCa₄P showed 41.1374% porosity which is higher compared to SiCaPNa₃ at only 6.8346%. The presence of sodium nitrate content in SiCaPNa₃ showed this sample experienced partially melted on its surface due to the fluxing effect and lead to vitrified body after sintered. This factor lead to the major reduction in porosity percent of the sintered gel glass due to the SiCaPNa₃ that was impermeable to water and it only allowed water to passes throughout the pores. These indicated that SiCa₄P was able to absorb more water than SiCaPNa₃. This suggested that, Archimedes principle using water as a medium is not very suitable in order to determine the porosity percent of these samples.

Table 1 Dimensional changes, porosity and densification analyses for sol-gel glass pellet sintered at 1000 °C

Properties	SiCa ₄ P	SiCaPNa ₃
Thickness shrinkage (%)	9.85	60.53 (Expand)
Diameter shrinkage (%)	9.93	4.35
Bulk density (g/cm ³)	1.3971	1.1383
Apparent porosity (%)	41.1374	6.8346
Densification (%)	58.8626	93.1654

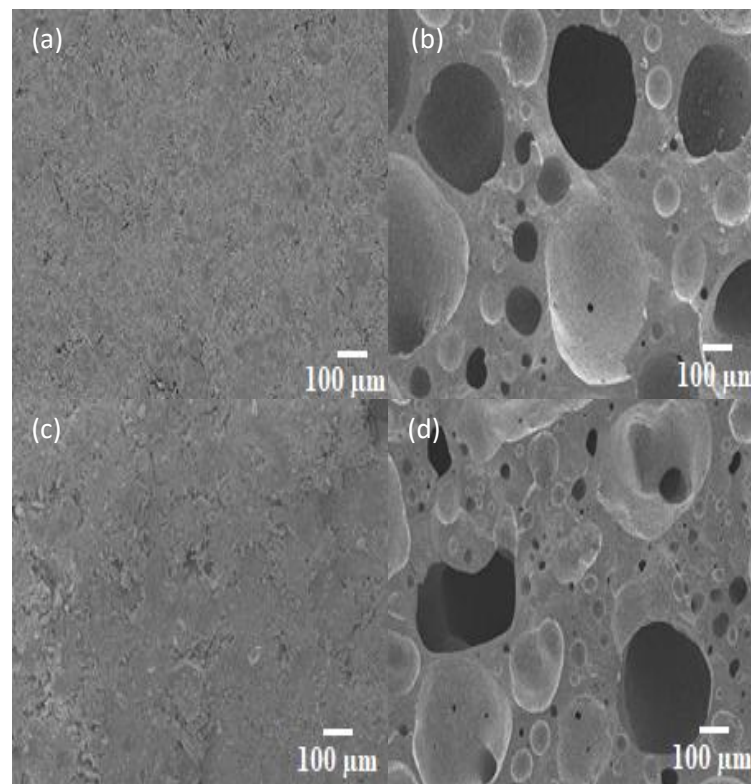


Fig. 2 Surface morphology for (a) SiCa₄P and (b) SiCaPNa₃ and cross section morphology for (c) SiCa₄P and (d) SiCaPNa₃ sintered at 1000 °C

3.3 Phases and structural properties.

Fig. 3 shows the diffractograms of gel glass powder sintered at 1000 °C. The percent of crystallinity for SiCa₄P was 66.6% while for SiCaPNa₃ was 71.5%, which indicate an increased in sample crystallization with the presence of sodium content. The SiCa₄P contained calcium silicate (CaSiO₃) as the main phase (40.7%) meanwhile for SiCaPNa₃ is tetracalcium catena-hexaphosphate(V) (Ca₄(P₆O₁₉)) phase (39.2%). For SiCa₄P, all the phases formed were related to calcium such as dicalcium silicate (Ca₂(SiO₄)), dicalcium diphosphate(V) (Ca₂(P₂O₇)), decacalcium hexakis(phosphate(V)) oxide (Ca₁₀(PO₄)₆O) and calcium silicate (CaSiO₃). However, for SiCaPNa₃ most of the phases formed were sodium-related such as sodium calcium cyclo-hexasilicate (Na_{5.27}Ca₃(Si₆O₁₈)), sodium peroxide (NaO₂) and disodium dicalcium disilicate (Na₂Ca₂(Si₂O₇)). This indicates the formation of new phases as sodium nitrate was added into the sol-gel glass matrix. This sodium related

phase proved the presence of Na₂O in SiCaPNa₃. With the presence of sodium related phases, bioactive glass monolith with enhanced mechanical strength and adequate biodegradability would be achieved [15].

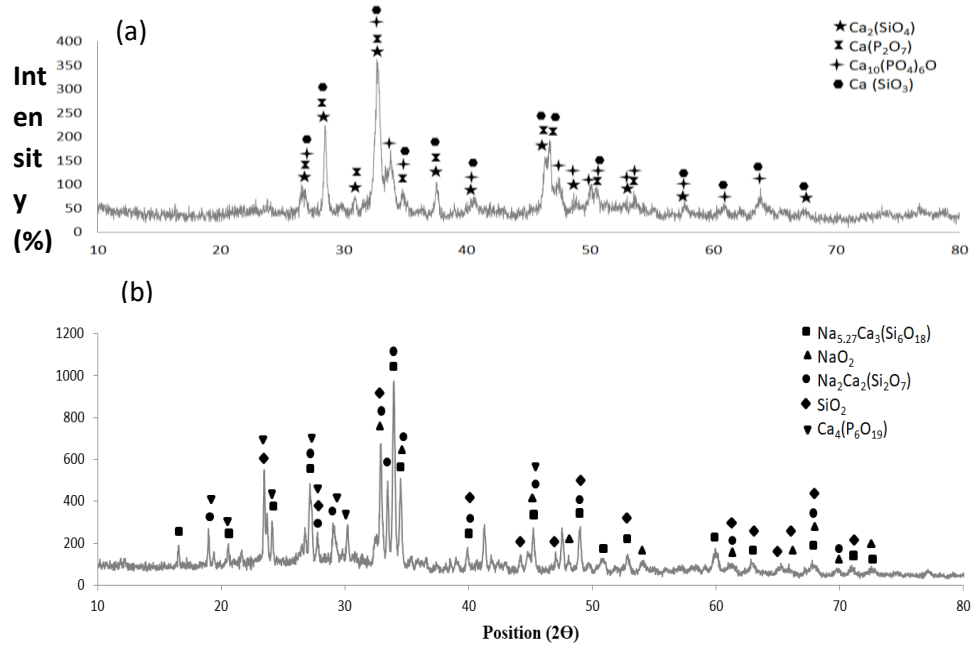


Fig. 3 XRD analysis for (a) SiCa₄P and (b) SiCaPNa₃ sintered at 1000 °C

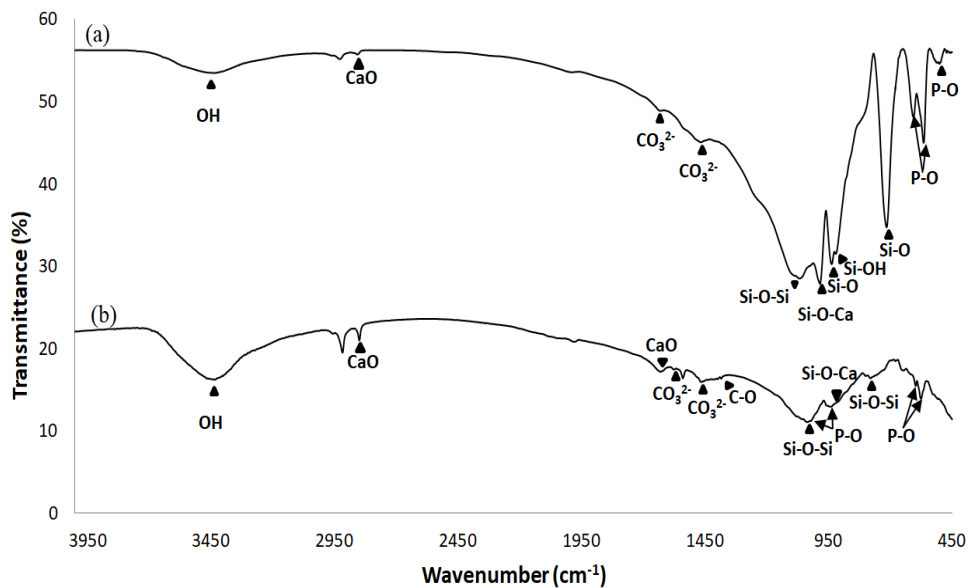


Fig. 4 FTIR spectrum for (a) SiCa₄P and (b) SiCaPNa₃ sintered at 1000 °C

4. SUMMARY

Fig. 4 shows the Fourier transform infrared (FTIR) spectrum of gel glass sintered at 1000 °C. In both samples, peak related to P-O bond were observed to correspond with XRD spectra. This proved the presence of phosphate crystalline phase in both samples. It was found that, peak that related to nitrate was fully decomposed as indicated by TGA analysis. From the graph, silicate (Si-O) and phosphate (P-O) spectral band intensity were reduced. This is caused by the addition of sodium nitrate into the glass matrix increased the non-bridging oxygen (NBO) structure thus reducing those glass networking structures. This would enhance the *in vitro* bioactivity property of this glass monolith.

5. CONCLUSION:

Macroporous monolith with the additions of sodium nitrate into ternary sol-gel derived glass composition ($\text{SiO}_2\text{-CaO-P}_2\text{O}_5$) was successfully prepared. The initial properties of sodium-contained glass were compared to the typical ternary glass composition. The macroporous structure formation can be related to foaming effect occurred during sintering. The addition of sodium nitrate in this ternary glass composition leads to the formation of macro-sized pores, formed sodium-related phases which increased glass crystallinity besides decreased the glass networking structures. Thus, it was possible to prepare macroporous glass structure by addition of sodium nitrate, which replaced calcium oxide content in the sol-gel composition with sintering at 1000 °C.

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