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Effect of heat treatment on $7Na_2O–23B_2O_3–70SiO_2$ glass

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Abstract

Porous $7Na_2O–23B_2O_3–70SiO_2$ glass was successfully fabricated by acid leaching treatment and phase-separation. The 2 mol/l hydrochloric acid (HCl) solution treatment was used for 24 h. Thermal analysis and X-ray diffraction were used to identify the temperature range of heat-treatment. The average pore size and the pore volume were investigated by a nitrogen adsorption instrument, and SEM was used to characterize the appearance of the porous glass. The results show that the average size of pores changed from 3.75 nm to 3.03 nm when heat treated at 640–680 °C for 6 h. In addition, when heat treated at 640 °C for 6–24 h, the pore size fell from 3.75 nm to 3.66 nm. The surface area and pore volume become larger with the increase in both temperature and heat treatment time.

Keywords: Porous glass; Phase-separation; $7Na_2O–23B_2O_3–70SiO_2$ glass; Acid leaching thermal treatment

1. Introduction

Since 1934, the porous glasses were first fabricated by Hood and Nordberg [1], they have attracted much attention due to their flexible geometric form and porous structure, chemical inertness, optical transparency and high mechanical and thermal stability [2,3]. These special properties make porous glass a candidate for various scientific and industrial processes, such as biochemical sensors [3], optical chemosensors [4], membrane technology [5], catalysis [6] and immobilization of radioactive waste.

A porous glass could be obtained by many methods, such as sol–gel, filling, and powder sintering processes. The sol–gel method obtains porous glass through colloids and polymer gel. Tetraethyl orthosilicate and boric acid are commonly used as the precursors. It is a complex and time-consuming process besides the sample obtained through this method is small. The filling method is a good way to make the porous glass with an average diameter between 10 μm and 1 mm. The pore size of the powder after sintering process can achieve a size of 100 μm to 5 mm, but the shape of the product is limited. In the present study, porous glasses were prepared by leaching previously phase separated $7Na_2O–23B_2O_3–70SiO_2$ glass in a 2 mol/l hydrochloric acid solution for 24 h. When the initial glass was decomposed into two separated but interconnected silica-rich and sodium-rich borate phases, and then leached by acid, the borate-rich phase was washed out, and only the silica-rich phase was left as the network of the porous glass. Using the leaching method, the porous glass with bigger block, shorter time and lower cost could be obtained. The aim of this paper was to investigate the effect of the heat treatment on the $7Na_2O–23B_2O_3–70SiO_2$ glass.

2. Experimental procedure

2.1. Sample preparation

The ternary system $Na_2O–B_2O_3–SiO_2$ is a good choice for the making of porous glass [7]. Fig. 1 shows the phase-separated image of the $Na_2O–B_2O_3–SiO_2$ system. The composition for preparation of the porous glass should be in the region of the boric acid anomaly, and in this area the property of the glass is based on the ratio of V SiO_2/V B_2O_3. Considering the higher ration of SiO_2 to B_2O_3 is more suitable for the manufacturing of porous glass [8] and the melting temperature cannot be too high, so the composition used in this study is $7\%Na_2O–23\%B_2O_3–70\%SiO_2$.

The components were introduced by sodium carbonate, boric acid and quartz sand. The initial glass was melted at

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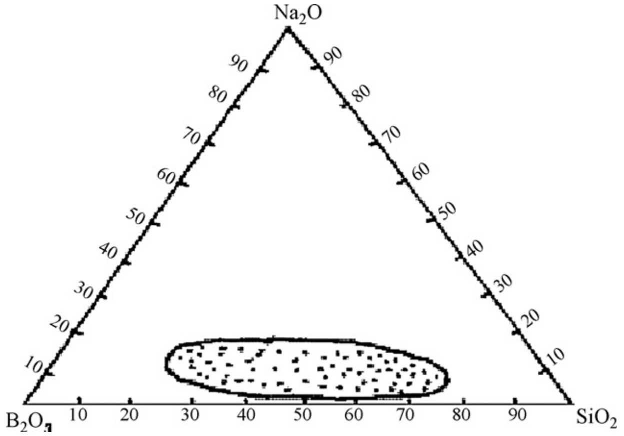

Fig. 1. Phase-separated image of the Na_2O–B_2O_3–SiO_2 system.

1480 °C for 6 h in a crucible for homogeneous mixing with these materials and then annealed at 450 °C for 4 h. And then these samples were treated in a 2 mol/l HCl solution for 24 h for acid leaching. Thence, these samples were heat treated at temperatures from 640 °C to 680 °C for various durations of 6–24 h. The heat treatment conditions are listed in Table 1. The $7Na_2O$–$23B_2O_3$–$70SiO_2$ melting tended towards phase separation into a continuously silica-rich phase and a borate-rich phase under the heat treatment stage. Subsequently, the $7Na_2O$–$23B_2O_3$–$70SiO_2$ glass containing a silica skeleton with boron oxides and highly dispersed colloidal silica particles was obtained. After the acid leaching, the removal of the borate leads to an increase in the size and volume of the pores.

Finally, the samples were washed in 5 vol% HF to eliminate the colloidal silica in the structure thence rinsed in distilled water until neutrality.

2.2. Characterization

The heat treatment temperature was examined by differential thermal analysis (DTA, NETZSCH STA 449C, RIGAKU, Japan) and X-ray diffraction (XRD, D/max-RB RIGAKU Japan). Scanning electron microscopy (SEM, JSM-5610LV RIGAKU, Japan) was used to observe the fracture surfaces morphology of the porous glass samples. The porosities of the samples were measured with a nitrogen adsorption and desorption instrument (AUTOSORB-1, Quantachrome, USA). The surface area was determined from the linear part of the Brunauer–Emmett–Teller (BET) equation in a relative pressure range (P/P_0) of the adsorption isotherms between 0.05 and 0.25 [9,10]. The total pore volume V_P was estimated from the amount of gas adsorbed at the relative pressure $P/P_0 = 0.99$, assuming that the pores were subsequently filled with condensed adsorptive in the normal liquid state. The pore size distributions of the mesoporous glasses were determined from the desorption branch of the nitrogen sorption isotherm according to the BJH (Barrett, Joyner, Halenda) method, based on the Kelvin equation, which relates the pore size with critical condensation pressure, and by assuming a straight cylindrical pore model [11].

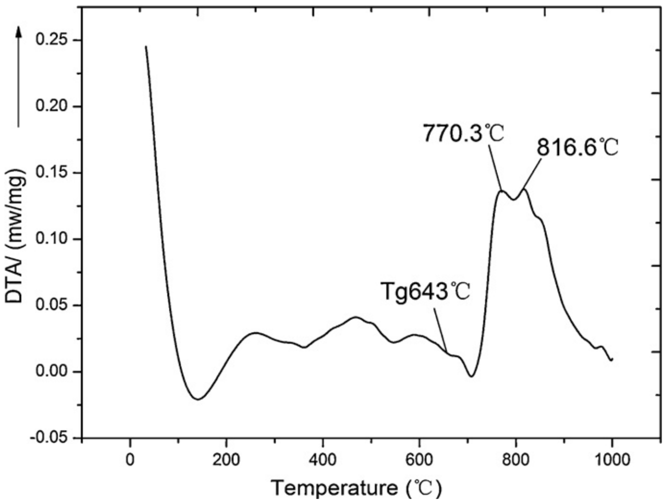

Fig. 2. The DTA curve of $7Na_2O$–$23B_2O_3$–$70SiO_2$ glass at a heating rate of 10°C min^{-1}.

3. Results and discussion

3.1. Effect of the heat treatment temperature on the $7Na_2O$–$23B_2O_3$–$70SiO_2$ porous glass

The DTA curve of $7Na_2O$–$23B_2O_3$–$70SiO_2$ glass before heat treatment at a heating rate of 10 °C min^{-1} is shown in Fig. 2. The first exothermic peak at temperature of 770.3 °C can be attributed to the crystallization of glass. The heat treatment temperature decision was referred to the DTA result and it should be lower than crystallization temperature, namely 770.3 °C.

Fig. 3 shows the XRD patterns of the $7Na_2O$–$23B_2O_3$–$70SiO_2$ glass heat treatment at various temperatures for 6 h. The crystals were formed when the glass sample was treated at 750 °C. The result indicates that the glass still maintained the amorphous state when the heat treatment at temperature below 710 °C. Therefore, for maintaining the amorphous state the heat treatment temperature must be set at temperature lower than 710 °C.

Table 1
Heat treatment condition s for 6 h.

No. Time (h) Temp. (°C)	1	2	3	4	5
640	6	12	24		
660				6	
680					6

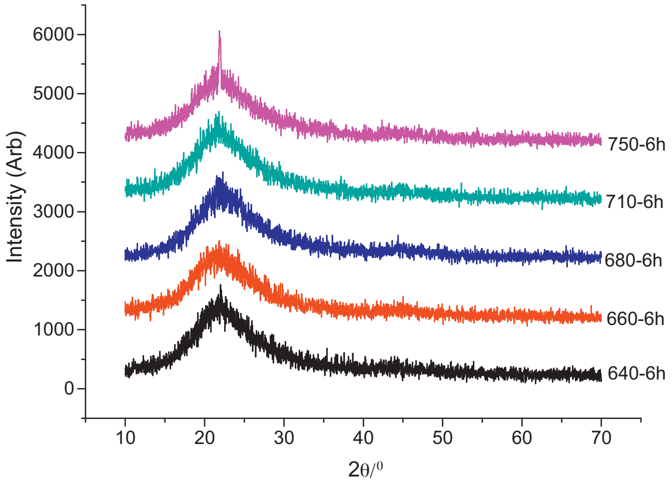

Fig. 3. XRD patterns of $7Na_2O–23B_2O_3–70SiO_2$ glass heating treatment at various temperatures for 6 h.

The SEM micrographs of the samples treated at various temperatures for 6 h are shown in Fig. 4 which indicates that the pore size increases with the heat treatment temperature increasing. From Fig. 4, result is that the heat treatment temperature is a very important factor for the fabrication of porous glass. If the temperature is too low, the appropriate phase structure cannot be obtained. Furthermore, with the result of XRD, the crystallization occurs when treated at 750 °C for 6 h. Therefore, for maintained the amorphous state and appropriate phase structure, the heat treatment temperature was thus set at 640–680 °C.

The BET surface area, pore volume and average pore size were calculated from nitrogen adsorption and listed in Table 2. The BET surface areas and pore volumes increased with the temperature as listed in Table 2. In addition, the pore size first increased and then decreased. This result is due to the viscosity decreases of the glass owing to temperature increase, which leads to the silica-rich and sodium-rich borate phases separate completely, more borate moves into the spaces of the silica, and created the aperture becomes larger. Moreover, when the temperature increases significantly, the content of the silica-rich phase in the glass is higher after phase separation and then the borate phase is hard to be completely washed out after the acid leaching and the silica particles are engendered more easily. This also causes the increase in surface area and the decrease in pore size.

Fig. 5(a) illustrates the pore size distribution curve of $7Na_2O–23B_2O_3–70SiO_2$ glass heat treatment at various temperatures for 6 h. It can be found that a concentrated distribution between 2.5 and 5 nm and the pore size is in mesoporous range. In addition, the result of Fig. 5(a) also shows that the peak of the diameter is nearly 5 nm for sample treated at 680 °C, which is smaller than at 660 °C. This result is due to the high treatment temperature causing a mixing between the two separate phases and creating the small pores.

The relation between the volume and relative pressure of the samples treated at various temperatures for 6 h are shown in Fig. 5(b). A hysteresis between the adsorption and desorption

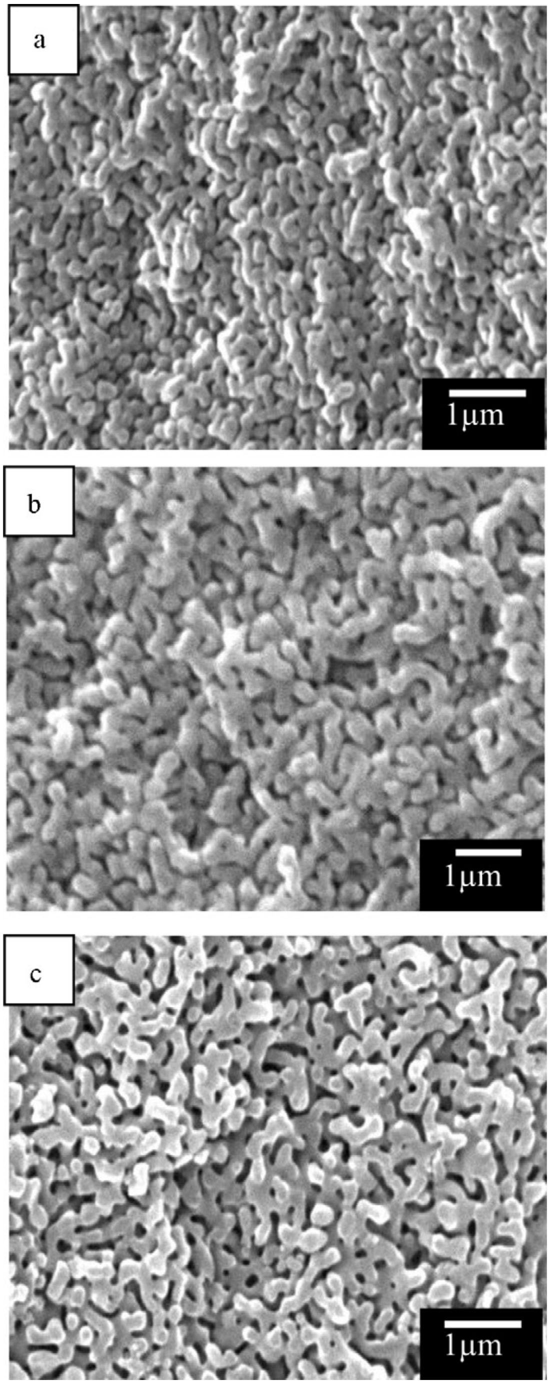

Fig. 4. SEM micrographs of the porous $7Na_2O–23B_2O_3–70SiO_2$ glass leaching in 2 mol/l HCl solution for 24 h and heat treatment at various temperatures for 6 h: (a) 640, (b) 660, and (c) 680 °C.

Table 2
Pore structure of samples treatment at various temperatures for 6 h.

Temperature (°C)	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cc\ g^{-1}$)	Average pore diameter (nm)
640	121.1	0.114	3.75
660	131.5	0.125	3.79
680	164.6	0.125	3.03

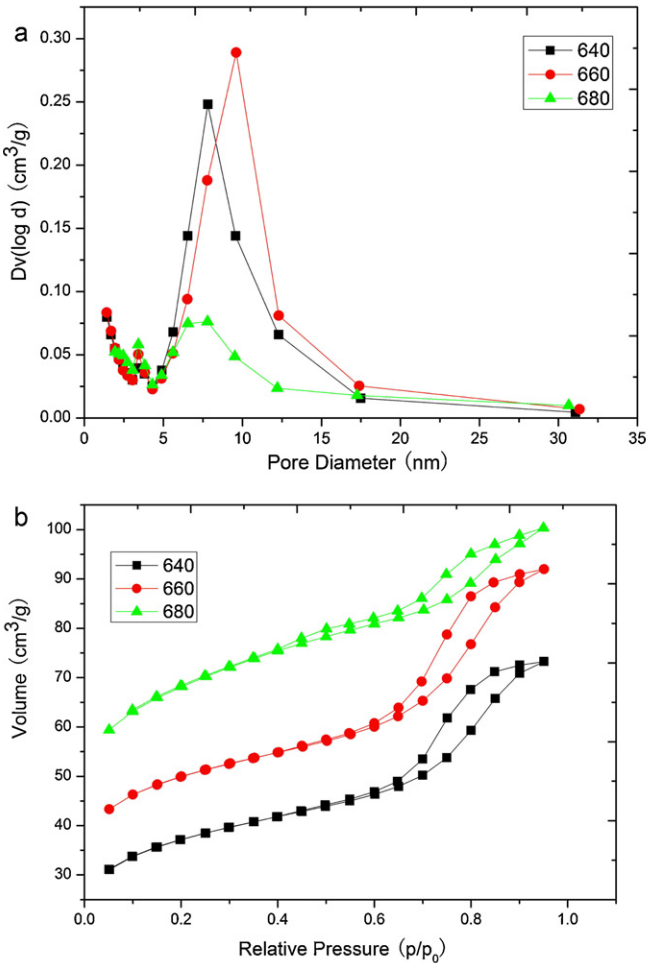

Fig. 5. (a) Pore size distribution curve and (b) N_2 adsorption isothermal curve of the porous $7Na_2O$–$23B_2O_3$–$70SiO_2$ glass leaching heat treatment at various temperatures.

was found in all curves. The form and characteristics of the hysteresis loops are type IV, due to the capillary condensation taking place in the mesopores. Moreover, the initial part of these isothermal curves occur because of monolayer–multilayer adsorption through the pore structure [12].

3.2. *Effect of time on the $7Na_2O$–$23B_2O_3$–$70SiO_2$ porous glass*

Fig. 6 shows the SEM micrographs of the $7Na_2O$–$23B_2O_3$–$70SiO_2$ glass samples leaching in 2 mol/l HCl at 640 °C for various durations. It can be found that the surfaces of the samples have a connective pore structure, and the pore size increases with the duration time increasing from 6 to 12 h. On the other hand, when the duration time increases from 12 to 24 h, the pore size seems slightly decreased and there are some larger partials agglomerated on the surface, which resulted in the surface was not uniformly flat. This result is due to the partial dissolution of $7Na_2O$–$23B_2O_3$–$70SiO_2$ glass leaching in 2 mol/l HCl when the duration time increase from 12 to 24 h. The BET surface area, pore size and pore volume fraction for $7Na_2O$–$23B_2O_3$–$70SiO_2$ glass leaching in 2 mol/l HCl solution for various times are listed in Table 3.

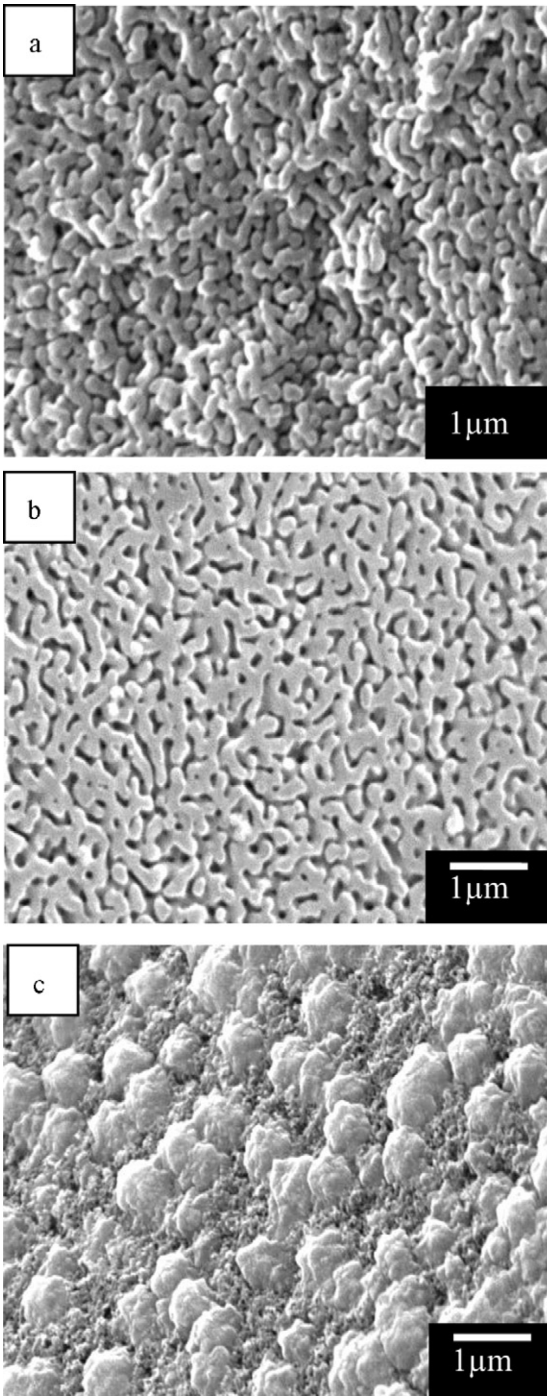

Fig. 6. SEM microstructures of the porous sodium-borosilicate glasses treated with 2 mol/l HCl for 24 h and at 640 °C for various times: (a) 6 h, (b) 12 h, and(c) 24 h.

Table 3
Pore structure of samples heat treatment at 640 °C for various times.

Time (h)	BET surface area ($m^2 g^{-1}$)	Pore volume ($cc g^{-1}$)	Average pore diameter (nm)
6	121.1	0.114	3.75
12	135.0	0.127	3.77
24	132.3	0.121	3.66

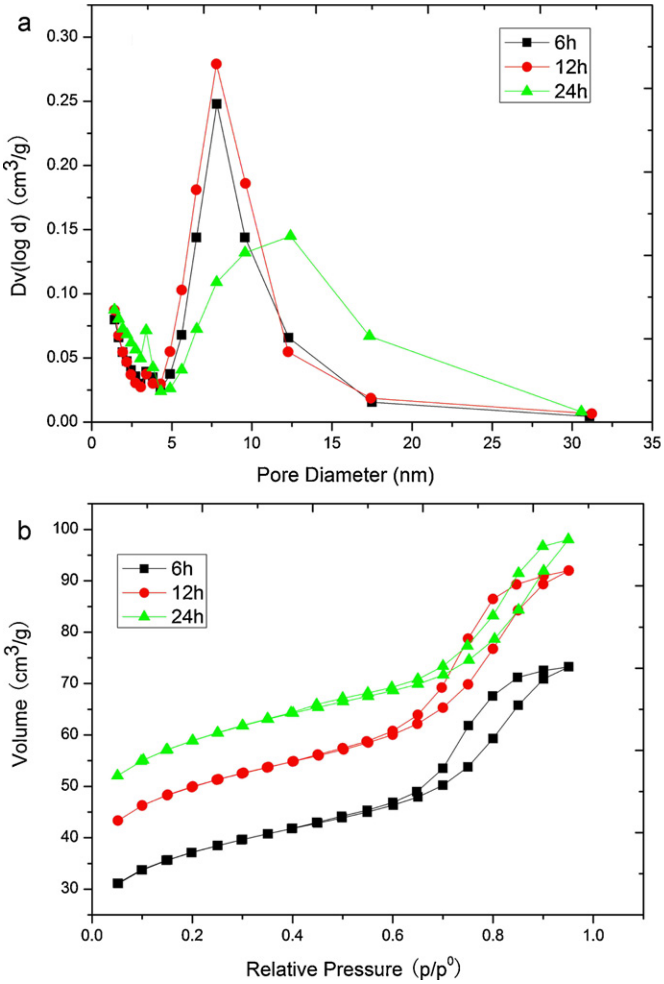

Fig. 7. (a) Pore size distribution curve and (b) N_2 adsorption isothermal curve of the porous $7Na_2O–23B_2O_3–70SiO_2$ glass at 640 °C for various heat treatment times.

From the result of Table 3, it can be found that the surface area, pore volume and pore size are all decreased when the duration time attained to 24 h. This is because when the temperature was fixed at 640 °C, the phase separation in the $7Na_2O–23B_2O_3–70SiO_2$ glass was treated complete when duration for 6–12 h, and this phenomenon leads the particles of sodium-rich borate phase to become larger, and all of these particles become concentrating in the skeleton, which causes the acid leaching improvement and the growing of the pore size. In addition, when the leaching time further increase to 24 h, the mixing and partial dissolution occurs with the silica-rich and the sodium-rich borate phases. Therefore, the smaller particles were found, and the pore size decreases.

Fig. 7 shows the results of the BET analysis of the $7Na_2O–23B_2O_3–70SiO_2$ glass heat treated at 640 °C for various durations. It can be found that the hysteresis loops are also type IV, which similar to that in Fig. 5. In addition, the desorption curves indicates that the distribution of pore size is concentrated at sizes between 2.5 and 5 nm. Moreover, in the pore size distribution curve of Fig. 7(a), the pore sizes are more nearly 2.4 nm and a higher peak between 5 and 15 nm is found when heat treated for 6 and 12 h. Moreover when treated at 640 °C for 24 h, the peak between 5 and 15 nm is lower than treated at 640 °C for 12 h. This phenomenon is due to the treated time is too long to prevent from the phase separation, created leaching harder and thus the pore size decreases and the distribution of the pore size is not as concentrated as in the samples obtained in a shorter treatment time.

4. Conclusions

The porous glasses were obtained by acid leaching and heat treatment based on the $7Na_2O–23B_2O_3–70SiO_2$ glass. When the heat treatment temperature increasing, the porous skeleton was enhanced and the pore size becomes larger. The same phenomena were found when the processing time was prolonged under the same heat treatment temperature. The pore volume increased with the heat treatment temperature increasing, however, a suitable duration time is needed to obtain a maximum value when heat treated at a fixed temperature.

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References

[1] W. Qian, S. Hang, C. Haifeng, Preparation of a macro-pore porous glass bead carrier, J. Sichuan Univ. 30 (2002) 99–102.

[2] D. Enke, F. Janowski, W. Schwieger, Porous glasses in the 21st century—a short review, Microporous Mesoporous Mater. 60 (2003) 19–30.

[3] M. Hermann, U. Gottschalk, Large-scale immobilization of antibodies on porous glass carriers, Bioforum 3 (2000) 172.

[4] W.J. Haller, Study on the production of porous glass, Nature 206 (1965) 693.

[5] I. Altug, M.L. Hair, Porous glass as an ionic membrane, J. Phys. Chem. 72 (1968) 599–603.

[6] X. Li, X.P. Wu, H.R. Chen, Hierarchically porous bioactive glass scaffolds synthesized with a PUF and P123 cotemplated approach, Chem. Mater. 19 (2007) 4322–4326.

[7] W. Haller, D.H. Blackburn, Metastable immiscilility surface in the system $Na_2O–B_2O_3–SiO_2$, J. Am. Ceram. Soc. 53 (1970) 34–39.

[8] W. Haller, D.H. Blackburn, J.H. Simmons, J. Am. Ceram. Soc. 57 (1972) 120.

[9] J.J. Han, J. Ruan, J.D. Liu, X.J. Zhao, Preparation and performance analysis of controllable aperture glasses, Mater. Sci. Eng. A 102 (2006) 24.

[10] J.L. Hedrick, R.D. Miller, C.J. Hawker, K.R. Carter, W. Volksen, D.Y. Yoon, M. Trollsas, Templating nanoporosity in thin-film dieletric insulators, Adv. Mater. 10 (1998) 1049.

[11] E.P. Barrett, L.G. Joyner, P.H. Halenda, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, J. Am. Chem. Soc. 73 (1951) 373.

[12] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R. Pierotti, J. Rouquerol, T.A. Siemieniewska, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, Pure Appl. Chem. 57 (1985) 603.