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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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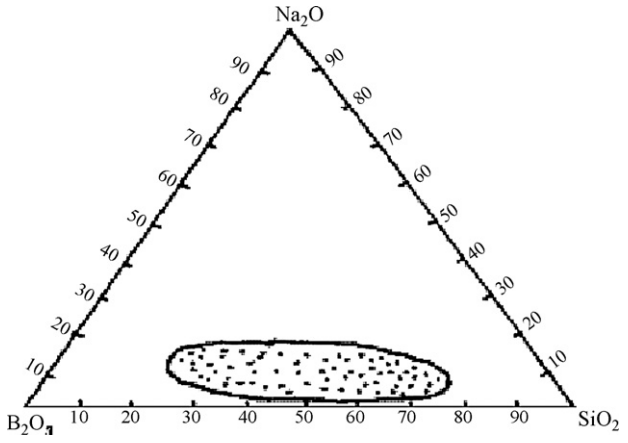

Fig. 1. Phase-separated image of the Na_2O–B_2O_3–SiO_2 system.

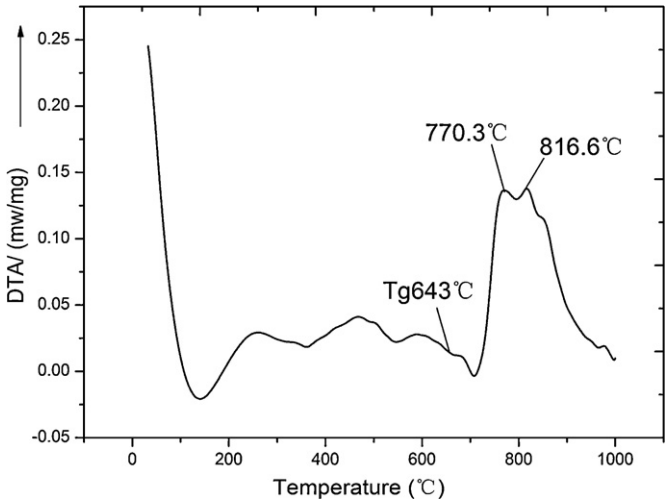

Fig. 2. The DTA curve of $7Na_2O$–$23B_2O_3$–$70SiO_2$ glass at a heating rate of 10°C min^{-1}.

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].

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.	1	2	3	4	5
Time (h)					
Temp. (°C)					
640	6	12	24		
660				6	
680					6