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Microwave-assisted phase separation of alkali-borosilicates in the production of nanoporous glasses

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The influence of a hybrid thermal processing on the spinodal decomposition of sodium borosilicate glasses was investigated. The pore diameter of the resulting porous glasses is a function of the parameters of the thermal treatment. One result of this study was the inversion of the phase separation under preservation of the external shape of glass monoliths. Furthermore by using microwaves in addition to thermal radiation it was possible to generate temperature gradients in the samples and so gradients in pore size too. The glass templates were heated with microwaves in a tube furnace consisting of a resonant rectangular waveguide (TE103). Additionally the tube wall was heated by thermal radiation. The heating control was realized by steering the input power and the frequency of a 200 W semiconductor source. The regulation was performed with a HOMER 3-stub tuner, which simultaneously measured the impedance by reflected wave analysis and the actual template temperature with an IR-sensor. Various temperature-time courses of the hybrid furnace led to different pore size gradients. This was discussed by analyzing specific properties like mean pore diameter, surface area and pore volume. Further effects like the pore orientation and properties of the pore walls were determined by scanning electron microscopy and focused ion beam (FIB).

Keywords: porous glasses, microwave heating.

1. Introduction

Porous glasses based on phase-separated alkali-borosilicates have a variety of advantageous properties. They have high chemical, thermal and mechanical stability.

Porous glasses are also characterized by narrow pore size distribution. The pore sizes can be adjusted in the range between 1 and 1000 nm selectively. In addition, due to their surface consisting of silanol groups, porous glasses offer the possibility for various surface modifications. This opens up a wide range of applications for these materials, for example in sensor technology, chromatography and membrane technology [1, 2].

In this study, the influence of microwave heating on the phase separation and the pore structures of these alkali-borosilicate glasses were examined. The effect of microwaves on the spinodal decomposition of other systems could be already shown [3].

2. Experiment

2.1. Porous glass

A sodium borosilicate glass with the composition 70 wt% SiO_2, 23 wt% B_2O_3 and 7 wt% Na_2O was used for the experiments. Due to the manufacturing process of this glass (slow cooling from the melt) it has some interesting features. These include the absence of mechanical stresses in the glass and the optical opalescence due to the uncontrolled phase separation during the cooling of the melt. Without further temperature treatments this initial glass results in a nanoporous glass with a pore size of about 40 nm. This pre-separated glass was used deliberately for these experiments because the influences of the temperature treatment could be estimated relatively easily by changes in the optical opalescence.

The annealing experiments with conventional heating (by radiation) were performed in a furnace (N11/H/P300, Nabertherm). After thermal treatment, the glass blocks were cut into ultra thin plates with a thickness of 0.2 mm using an annular precision (Annular 55, Logitech) and a diamond band saw (SAW 15, Logitech). Finally, the glass plates were leached with hydrochloric acid (1 N or 3 N) at 90 °C and, if necessary with sodium hydroxide (0.1 N) at room temperature in special Teflon baskets. The general preparation procedure of nanoporous glass monoliths was described in previous articles [1, 4].

The characterization of the prepared porous glass plates was performed using nitrogen sorption (Quantachrome Autosorb iQ) and mercury intrusion (Quantachrome Poremaster).

2.2. Hybrid heating system

The aim of the hybrid oven concept was the investigation of the influence of electromagnetic waves on the phase separation of sodium borosilicate glasses. Therefore, a conventional oven and a microwave oven were combined. This was necessary because borosilicates couple only weakly with the electromagnetic field at low temperatures.

The hybrid furnace developed in this study consists of a tube furnace (Gero) and a microwave applicator. The core of the microwave oven is a special waveguide to

Fig. 1. Hybrid furnace.

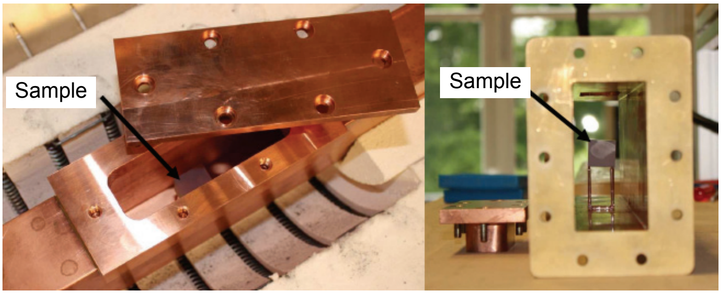

Fig. 2. Position of the glass sample inside the copper waveguide.

achieve a linearly polarized microwave field. A waveguide made of aluminum could not be used because of the low melting point. Therefore, a waveguide of oxygen-free copper has been designed. Through its good heat radiation adsorption in the whole infrared range and high thermal conductivity, it was perfectly suited to guarantee nearly homogeneous temperature distribution. The microwave field was generated by a semiconductor source with 200 W and a frequency of 2.45 GHz. Since borosilicates couple only weakly with the electromagnetic field at low temperatures, a resonance cavity (TE103) has to be used. The control was performed with a HOMER 3-stub tuner, which simultaneously analyzed the impedance of the reflected wave and the actual sample temperature (with IR sensor). Thus, the power and frequency of the semiconductor source were controlled. A picture of the hybrid furnace is shown in Fig. 1. The glass samples with a cube geometry (edge length 20 mm) were placed at the maximum of the electric field (position in the waveguide, see Fig. 2).

3. Results

3.1. Conventional heating

Prior to the experiments with microwave heating, the temperature and time constants of the inversion of phase separation were determined. For that purpose, the glass blocks with the same geometry (10 mm × 10 mm × 20 mm) were heated to a target temperature with a heating rate of 10 $K min^{-1}$ and annealed for a certain holding time. After this

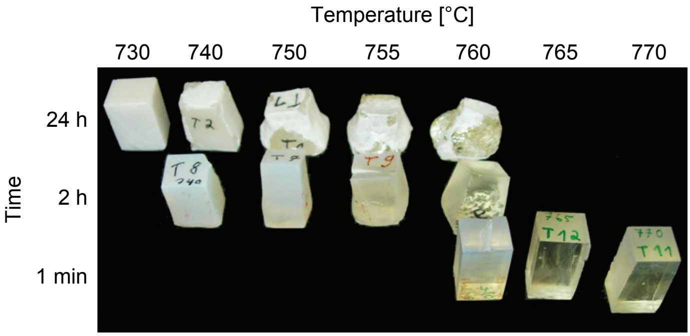

Fig. 3. Overview of the experiments to determine the temperature and time constants of the reverse phase separation.

holding period, the furnace was opened and the glass blocks were removed to cool down to room temperature. An overview of this series of experiments provides Fig. 3.

The external shape of the glass blocks was ensured for a holding time of 24 hours up to a temperature of 730 °C. An inversion of the phase separation of the glasses could be found only above a temperature of about 755 °C. Therefore, the holding time was shortened to 2 hours. So, the geometrical shape remained up to a temperature of 740 °C and the inversion of phase separation required temperatures above 755 °C. In the test series with a holding time of one minute the external shape of the glass could be realized up to a temperature of 770 °C. The glass block with a target temperature of 760 °C shows already the onset of the inversion of phase separation, but only the glass block with a target temperature of 770 °C appears completely transparent without opalescence. Thus it can be concluded that, for a glass with composition 70 wt% SiO_2, 23 wt% B_2O_3 and 7 wt% Na_2O, an inversion of the phase separation is possible while preserving the external shape of the glass. It can be concluded that the temperature is the dominant parameter and so just short periods of time are sufficient to obtain an initial glass with a reduced degree of phase separation.

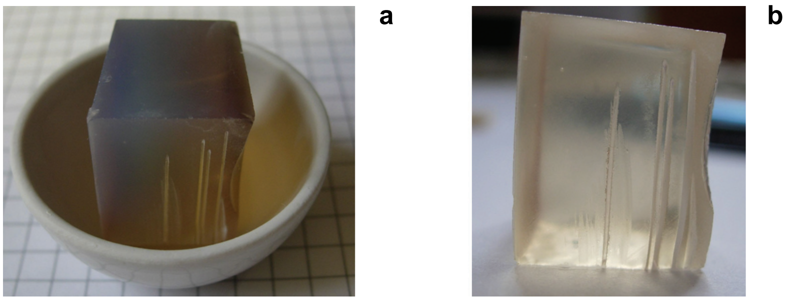

Fig. 4. Glass block before (**a**) and after thermal treatment at 770 °C (**b**) with different degree of opalescence.

To quantify the degree of the inversion of phase separation more glass blocks were thermal treated at 770 °C with a holding time of a minute. One of those glass blocks is exemplary shown in Fig. 4.

The best result was achieved with the glass block *A*, which was extracted with 3 N hydrochloric acid for 2 hours at 90 °C, after sawing it into 0.2 mm thick plates. The characterization by nitrogen sorption (see Fig. 5 for pore size distribution by density functional theory (DFT) method) provides the following structure data. The sample was characterized by a specific surface area of 253 $m^2 g^{-1}$, a pore volume of 0.13 $m^3 g^{-1}$ and pores with a diameter smaller than 5 nm. In addition, a second sample (*B*) was prepared, which differs by a slower cooling after thermal treatment and an additional treatment with sodium hydroxide solution from sample *A*. This glass has pores with a diameter smaller than 15 nm.

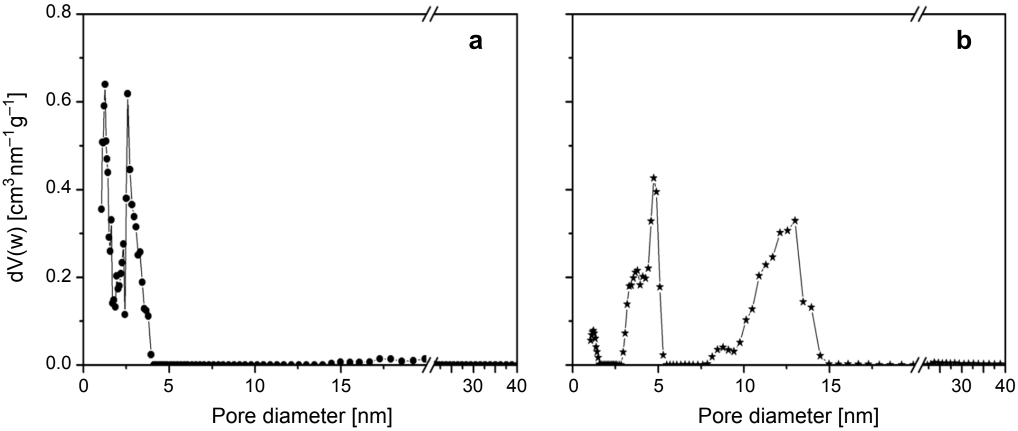

Fig. 5. Pore size distributions by DFT-method of glass block *A* (**a**) and glass block *B* (**b**).

Thus, it is possible to produce a glass with a lower pre-separation from a glass with an advanced phase separation (d_P approximately 40 nm), by a controlled thermal treatment. These systematic pre-investigations were absolutely necessary for the later studies using the hybrid heating concept.

3.2. Hybrid heating

For the microwave heating experiments with the hybrid furnace, the following parameters were varied: the temperature of the tube furnace, the intensity of the electromagnetic field and the duration of the microwave treatment. Thereby the power of the microwave was regulated as a function of the measured sample surface temperature (IR-sensor). The first test series were run with a duration time of 45 minutes, the second with 5 minutes. Additionally the temperature of the tube furnace and the sample

T a b l e 1. Parameters for the hybrid heating experiments.

Sample	Temperature tube furnace [°C]	Temperature IR-sensor [°C]	Duration time [min]
PG 01	600	600	45
PG 02	630	650	45
PG 04	630	675	45
PG 10	630	650	5
PG 11	630	675	5
PG 12	630	700	5
PG 13	630	700	5

surface temperature (associated to that the strength of the electromagnetic field) were varied. An overview of these test series provides Tab. 1.

The resulting sample blocks were cut into 0.2 mm thick membranes, and then extracted with 1 N HCl at 90 °C for 3 h and with 0.1 N NaOH at room temperature for 2 hours. In Figure 6, two extracted membranes are shown.

In these samples, the influence of the microwave field is clearly recognizable by different degrees of opalescence within the respective membranes (circular areas). Therefore, for characterization the membranes were broken just in the way that

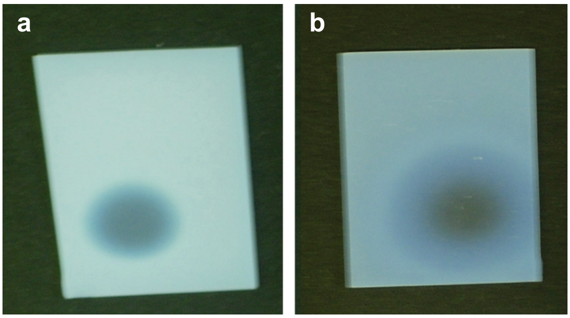

Fig. 6. PG 12 (**a**) and PG 13 (**b**) membrane.

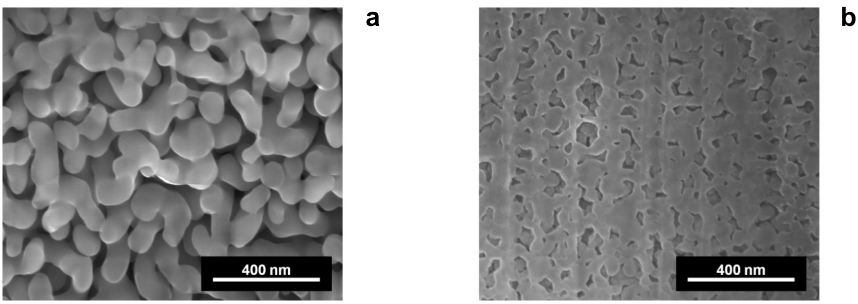

Fig. 7. SEM pictures of sample PG 12, outer region – no microwave influence (**a**), circular area – microwave influence (**b**).

Table 2. Results of the hybrid heating experiments.

Sample	BET-surface area[a] $[m^2 g^{-1}]$	Pore volume[a] $[cm^3 g^{-1}]$	Mean pore diameter[b] [nm]	Mean pore diameter[a] [nm]
PG 01	35	0.36	45.0	47.5
PG 02	70	0.14	58.2	4.9
PG 04	102	0.16	58.6	3.1
PG 10	103	0.11	46.9	5.3
PG 11	140	0.13	48.1 (8.4)	4.9
PG 12	143	0.10	43.8	4.7
PG 13	177	0.15	47.9	4.7

[a] From nitrogen sorption;
[b] From mercury intrusion.

the circular area was separated from the rest of the membrane. The circular area was characterized with nitrogen adsorption and the rest was used for mercury intrusion. For sample PG 12, SEM-pictures were shown in Fig. 7.

The results of nitrogen low-temperature adsorption and mercury-intrusion are summarized in Tab. 2. The samples PG 01, PG 02 and PG 04 show the influence of a higher temperature under a constant holding time. Thus the average pore diameter is shifted to higher values with increasing temperature. Another observation was that the temperature of the sample PG 01 was still too low to initiate a reverse phase separation. In contrast, the samples PG 02 and PG 04 show already pores smaller than 10 nm in the nitrogen sorption pore size distribution, which are caused by the inversion of the phase separation in the glass under influence of the microwaves (see Fig. 8). The temperature which is required for this inversion was determined to a value higher than 750 °C. So it can be concluded that in these glass blocks this temperature was reached or exceeded during the microwave treatment. But the surface temperature of

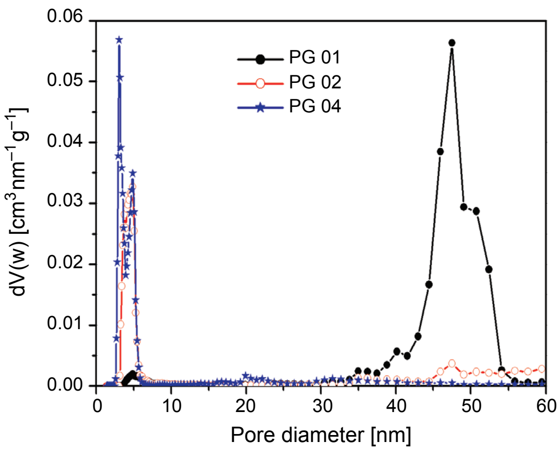

Fig. 8. DFT pore size distribution for samples PG 01, PG 02 and PG 04.

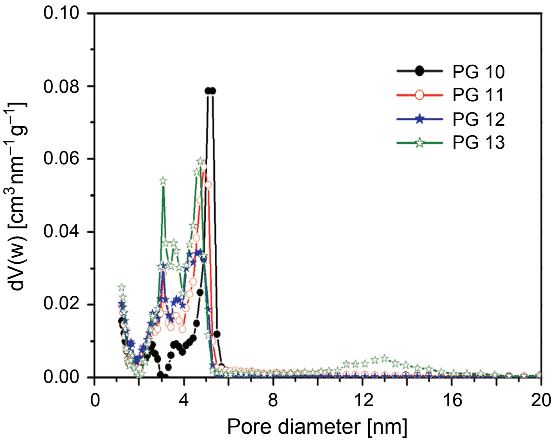

Fig. 9. DFT pore size distribution for samples PG 10, PG 11, PG 12 and PG 13.

these glass blocks, which was measured with the IR-sensor, was markedly lower. Therefore, this is the proof for the generation of a large temperature gradient within the glass block.

The second series with the samples PG 10 to PG 13 was exposed to microwave radiation for only 5 minutes. Nevertheless, in all these samples, small pores below 10 nm could be detected by means of DFT pore size distribution (see Fig. 9).

In case of sample PG 11 the resulting bimodal pore structure is clearly visible in the pore size distribution graph from mercury intrusion (Fig. 10).

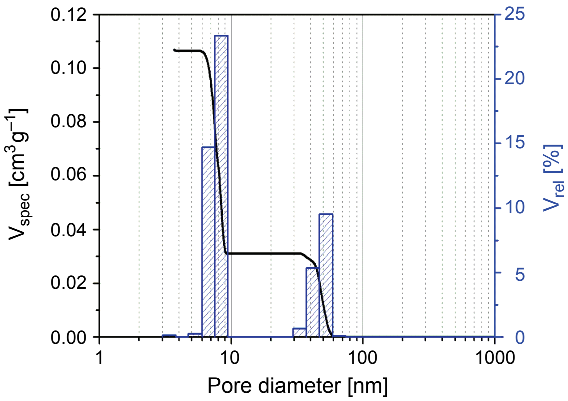

Fig. 10. Pore size distribution from mercury intrusion of sample PG 11.

To detect possible additional effects related to the high frequency electromagnetic field, like pore deformation or pore orientation, some samples were characterized by environmental scanning electron microscopy (ESEM) and focused ion beam (FIB). But such effects could not be detected yet and work is still in progress.

4. Conclusions

Sodium borosilicate glasses with the composition 70 wt% SiO_2, 23 wt% B_2O_3 and 7 wt% Na_2O are suitable for inversion of the phase separation under preservation of the external shape of the glass by a thermal treatment above 750 °C.

The use of hybrid furnace process led to the production of membranes with gradients in the pore size. This can be attributed to high temperature gradients during the thermal treatment. Fortunately, the extent and the magnitude of the gradient can be influenced by controlling the parameters of the hybrid furnace. The orientation of the pore system in a preferred direction due to the influence of microwave radiation could not yet be determined. Further systematic studies regarding the effect of microwaves on the phase separation in alkali borosilicate glasses (mechanism, other glass compositions) are still in progress.

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References

[1] JANOWSKI F., ENKE D., *Porous glasses*, [In] *Handbook of Porous Solids*, Schüth F., Sing K.S.W., Weitkamp J. [Eds.], Vol. 3, Wiley-VCH, Weinheim, 2002, pp. 1432–1542.

[2] ENKE D., JANOWSKI F., SCHWIEGER W., *Porous glasses in the 21st century – A short review*, Microporous and Mesoporous Materials **60**(1–3), 2003, pp. 19–30.

[3] WILLERT-PORADA M., *Microwave effects on spinodal decomposition*, Materials Research Society Symposium – Proceedings, Vol. 430, 1996, pp. 403–409.

[4] ENKE D., FRIEDEL F., JANOWSKI F., HAHN T., GILLE W., MÜLLER R., KADEN H., *Ultrathin porous glass membranes with controlled texture properties*, Studies in Surface Science and Catalysis **144**, 2002, pp. 347–354.

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