Phase separation of borosilicate glass containing phosphorus

2011 IOP Conf. Ser.: Mater. Sci. Eng. 18 112022

(http://iopscience.iop.org/1757-899X/18/11/112022)

Phase separation of borosilicate glass containing phosphorus

Y. Ohtsuki[1], S. Sakida[2], Y. Benino[1] and T. Nanba[1]

[1]Graduate School of Environmental Science, Okayama University, Japan

[2]Environmental Management Center, Okayama University, Japan

benino@cc.okayama-u.ac.jp

Abstract Sodium borosilicate glasses containing P_2O_5 and Al_2O_3 were prepared, and the behavior of phosphorus associated with the phase separation and the effect of Al_2O_3 addition have been investigated. After the heat treatment, phase separation by spinodal decomposition was observed in the all samples. In the Al_2O_3-free glasses, phosphorus was preferentially distributed into B_2O_3-rich glass phase after the phase separation. With increasing Al_2O_3 content, the amount of phosphorus distributed into SiO_2-rich glass phase increased. According to ^{31}P MAS NMR measurements, in the Al_2O_3-containing glasses, Q^4 units free from terminal oxygen atoms were formed. It was suggested that the distribution of phosphorus depend on the PO_4 units.

1. Introduction

Phosphorus is a vital nutrient for all living organisms, and it is therefore indispensable particularly in the fertilizer manufacturing. Recently producing countries of phosphate resource such as China and USA tend to limit their exports, and hence phosphorus resources must be secured also in Japan.

Iron- and steel-making slags consist of chemical components, such as SiO_2, CaO and Al_2O_3, which are also included in widely-used commercial glasses. We focused on these components and came up with the idea that phase separation of glass, which has been used for the production of porous glasses in glass industry, could be applied to the recovery of phosphorus from iron- and steel-making slags. However, little is known concerning the distribution of phosphorus after phase separation. Then, in this study, behavior of phosphorus associated with phase separation and the effect of Al_2O_3 addition have been investigated in the ternary Na_2O-B_2O_3-SiO_2 system.

The composition of base glass, $10Na_2O \cdot 40B_2O_3 \cdot 50SiO_2$ (mol%), was chosen because the glass was soluble in hot water [1]. Chemical composition was determined with inductively-coupled plasma (ICP) emission spectroscopy. Glass structure was examined with using ^{11}B, ^{27}Al, ^{29}Si and ^{31}P MAS-NMR spectroscopies. Microstructure after phase separation was observed with scanning electron microscope (SEM). From these analyses, changes in glass structure caused by phase separation were studied, from which the distribution of phosphorus was discussed.

2. Experimental

The glasses with compositions given in Table 1 were prepared by a conventional melt-quenching method. The raw materials of reagent grade $Na_3PO_4 \cdot 12H_2O$, $NH_4H_2PO_4$, Na_2CO_3, B_2O_3, SiO_2 and Al_2O_3 were mixed thoroughly and heated at 600 °C for 30 min to remove H_2O, CO_2 and NH_3. Then, the mixture was melted in a Pt crucible at 1400 °C for 1 h. The melts were poured onto an iron plate and quenched by being pressed with another iron plate to form glass plates. Differential thermal analyses (DTA) were carried out with a heating rate of 10 K/min in order to determine glass transition and crystallization temperatures, T_g and T_x.

Heat treatments for phase separation were performed at 600 °C, which was the immiscible temperature of the corresponding glasses. After the heat treatment, the glasses were immersed in hot water or nitric acid of 1.0 N for 24 h at 90 °C, and the insoluble residues were recovered with vacuum filtration. After being rinsed in water and dried in an oven, silica-rich glasses were obtained.

X-ray diffraction (XRD) measurement was carried out to confirm the crystallization. Chemical compositions of the specimens, such as the glasses before phase separation, the solutions and insoluble residues after immersed in hot water or nitric acid were determined by ICP emission spectroscopy. Transmittance change was evaluated at a wavelength range of 250 - 750 nm. Phase separation was confirmed by SEM observation, where the specimens were etched in 5% HF solution for 30 s. Local structures around Si, B, P and Al atoms were investigated with ^{29}Si, ^{11}B, ^{31}P and ^{27}Al MAS-NMR measurements, respectively. For the ^{29}Si and ^{31}P MAS-NMR measurements, 0.1 mol% of Fe_2O_3 was added to the glass batches in order to shorten the relaxation time. NMR measurements were carried out at 7.05 T on a Varian Unity Inova 300 spectrometer, and the respective conditions of ^{29}Si, ^{11}B, ^{31}P and ^{27}Al NMR measurements were as follows: frequency = 59.6 MHz, 96.2 MHz, 121.4 MHz and 78.2 MHz, sample spinning speed = 5.0 kHz (all), pulse duration = 4.0 μs, 0.6 μs, 4.0 μs and 0.6 μs, repetition time = 1.0 s (all), chemical shift standard = poly dimethyl siloxane (PDMS), BPO_4, $NH_4H_2PO_4$ and aq.$AlCl_3$.

3. Results

3.1 Changes due to heat-treatment

Figure 1 shows the SEM photographs of the surfaces of the heat-treated samples. Regardless of P_2O_5 or Al_2O_3, typical morphologies due to spinodal decomposition are commonly confirmed. In the DTA curves of the glasses No. 4 and 5, an exothermic peak due to crystallization was commonly observed below 600 °C (See T_x in Table 1). As shown in Figure 2, $AlPO_4$ crystal is precipitated in these glasses after heat treatment.

Table 1. Nominal and analytical compositions (mol%), T_g and T_x (°C) of the samples.

No.	**Na_2O**	**B_2O_3**	**SiO_2**	**P_2O_5**	**Al_2O_3**	**T_g**	**T_x**
1	10 (8.2)	40 (36.9)	50 (54.9)	-	-	469	-
2	10 (8.8)	40 (37.8)	47 (50.6)	3 (2.8)	-	450	-
3	8 (7.1)	40 (36.9)	47 (50.9)	3 (2.9)	2 (2.3)	444	-
4	7 (5.9)	40 (36.7)	47 (51.0)	3 (3.0)	3 (3.4)	433	533
5	6 (4.8)	40 (36.0)	47 (51.7)	3 (3.0)	4 (4.5)	423	535

( ): analytical composition

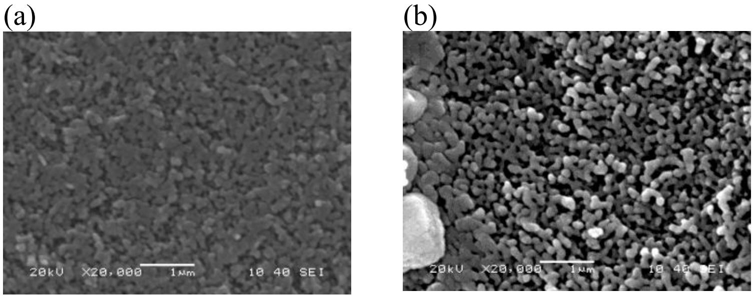

Figure 1. SEM photographs of the surfaces of the glasses heated at 600 °C for 16 h. (a) glass No. 1 (b) glass No. 3

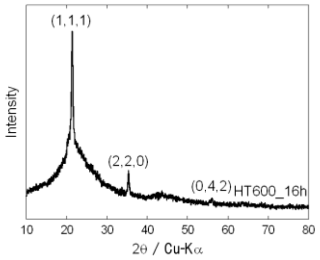

Figure 2. XRD pattern of glass No. 5 heated at 600°C for 16 h.

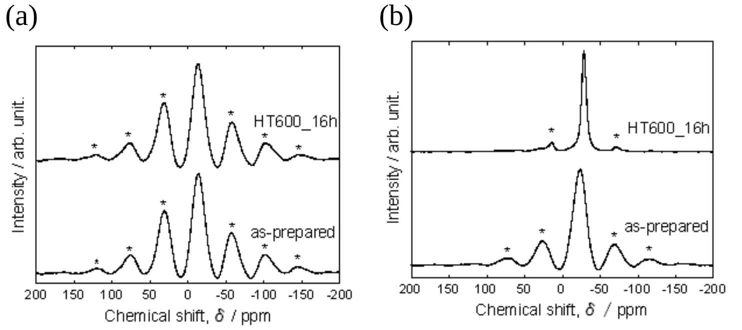

Figure 3. ^{31}P MAS NMR spectra of glasses before and after the heat-treatment. (a) glass No. 2 (b) glass No. 5
* : spinning side band

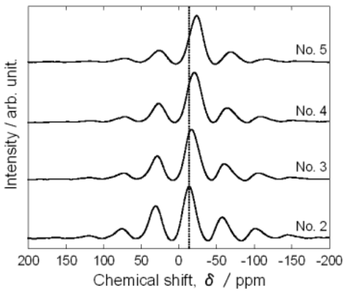

Figure 4. ^{31}P MAS NMR spectra of as-prepared glasses

3.2 MAS NMR analysis

Figure 3 shows ^{31}P MAS NMR spectra before and after the heat-treatment. For the glass No.2, a peak at $\delta \approx -14$ ppm is observed, which is assigned to pure Q^2_P unit, Q^2_P unit connected to one four-coordinated boron or Q^3_P unit connected to four-coordinated boron [2, 3], where *n* in Q^n_X means the number bridging oxygen (BO) connected to the X atoms. Comparing the spectra for before and after the heat-treatment in Figure 3 (a), no change is observed on the environment of PO_4 network. However, in the glass No. 5, a significant change is observed, that is, a peak at $\delta \approx -24$ ppm in the as-prepared glass shifts to $\delta \approx -29$ ppm after the heat-treatment. The sharp peak at −29 ppm is assigned to Q^4_P in $AlPO_4$ crystal [4]. The relative fractions of P in $AlPO_4$ crystal to total phosphorus were not determined. Comparing as-prepared glasses (Figure 4), the peak shifts to a higher magnetic field side with increasing Al/Na ratio.

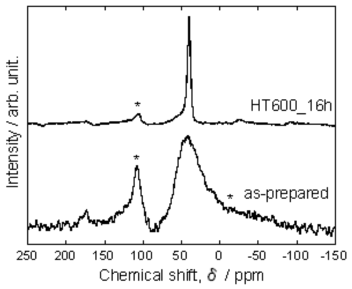

Figure 5. ^{27}Al MAS NMR spectra of glasses before and after the heat-treatment.
* : signals from rotor

Figure 5 shows ^{27}Al MAS NMR spectra of the glass No. 5 before and after the heat-treatment, which shows that Al atoms are mainly present as AlO_4 unit in glasses. The peak at −39 ppm after the heat-treatment is also assigned to Q^4_{Al} in $AlPO_4$ crystal [4], indicating the precipitation of $AlPO_4$ crystal. According to a rough estimation by the peak area, the relative fractions of the glassy and crystalline Al species are 0.34 and 0.66, respectively.

3.3 ICP analysis

Table 2 shows the chemical compositions of the glass phases after phase separation obtained from ICP analysis. These compositions were estimated as follows; B_2O_3-rich phase is soluble in hot water, and hence the composition of B_2O_3-rich phase is determined from the concentration of the elements in the solution after hot-water treatment. SiO_2-rich phase is insoluble in hot water but soluble in HF solution, and hence the insoluble solids after hot-water treatment were dissolved by HF solution, from which the composition of SiO_2-rich phase was determined.

As shown in Table 2, phosphorus in the Al_2O_3-free glass No. 2 is preferentially distributed into B_2O_3-rich glass phase after the phase separation. On the other hand, in the Al_2O_3-containing glasses No. 3 and No. 5, phosphorus is distributed also into SiO_2-rich glass phase. In addition, the amount of phosphorus distributed into SiO_2-rich glass phase increases with increasing Al/Na ratio. Moreover, aluminum is preferentially distributed into SiO_2-rich glass phase.

However, in the case of acid treatment, phosphorus and aluminum were completely eluted in all samples, suggesting that P and Al species both in glassy and $AlPO_4$ crystalline phases were insoluble to hot water but soluble to acid.

Table 2. Analytical composition of the glass phases after phase separation

(a) SiO_2-rich phase (mol%)

No.	Na_2O	B_2O_3	SiO_2	P_2O_5	Al_2O_3
2	0.0	4.2	95.7	0.1	-
3	2.1	0.4	93.1	1.1	3.3
5	2.6	0.6	87.9	3.5	5.5

(b) B_2O_3-rich phase (mol%)

No.	Na_2O	B_2O_3	SiO_2	P_2O_5	Al_2O_3
2	18.1	73.1	2.8	6.0	-
3	10.6	81.7	2.3	5.3	0.0
5	7.0	89.1	1.7	2.2	0.0

4. Discussion

From the results of ICP analysis, it was suggested that phosphorus was preferentially distributed to B_2O_3-rich glass phase after phase separation, and with increasing Al_2O_3 content, however, the amount of phosphorus distributed into SiO_2-rich glass phase increased. According to ^{31}P MAS NMR measurements, the peak shifted to a higher magnetic field side with increasing Al_2O_3 content, which meant that Q^4_P units free from terminal oxygen atoms increased. It was therefore suggested that the distribution of phosphorus depended on the states of PO_4 units. Furthermore, Q^4_P units increased with increasing Al/Na ratio, i.e. the amount of Q^4_P units formed related to not only Al content but also Na content [5].

As shown in Table 2, aluminum were not confirmed in B_2O_3-rich glass phase. Aluminum existed in AlO_4 unit, so it was considered that SiO_4 unit was replaced by AlO_4 unit [6], and Na^+ ion in SiO_2-rich glass phase compensate the negative charge of AlO_4 unit not-neighboring to PO_4 unit.

5. Conclusion

Sodium borosilicate glasses containing P_2O_5 and Al_2O_3 were prepared by a conventional melt-quenching method, and behavior of phosphorus associated with the phase separation and the effect of Al_2O_3 addition have been investigated. After the heat treatment, phase separation by spinodal decomposition was confirmed by SEM observation, and precipitation of $AlPO_4$ crystal was also found in Al_2O_3-containing samples. ^{31}P MAS NMR spectra suggested that P atoms were essentially present in Q^2_P or Q^3_P species, and Q^4_P species formed by addition of Al_2O_3. From ICP analysis, in Al_2O_3-free glasses, phosphorus was preferentially distributed into B_2O_3-rich glass phase after the phase separation. On the other hand, with increasing Al_2O_3 content, the amount of phosphorus distributed into SiO_2-rich glass phase increased. It was suggested that the distribution of phosphorus depended on the existing state of PO_4 units.

References

[1] Hammel J J and Allersma N L 1974 *U.S. Patents* 3 843 341
[2] Elbers S Strojek W Koudelka L and Eckert H 2005 *Solid State Nucl. Magn. Reson.* **27** 65
[3] Zeyer-Dusterer M Montagne L Palavit G and Jager C 2005 *Solid State Nucl. Magn. Reson.* **27** 50
[4] Müller D Jahn E and Ladwlg G 1984 *Chem. Phys. Lett.* **109** 332
[5] Cody G D Mysen B Saghi-Szabo G and Tossell J A 2001 *Geochim. Cosmochim. Acta* **65** 2395
[6] Du W -F Kuraoka K Akai T and Yazawa T 2000 *J. Mater. Sci.* **35** 4865