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Thermodynamic Prediction of Spinodal Decomposition in Multi-component Silicate Glass for Design of Functional Porous Glass Materials

Abstract: The authors have investigated metastable phase separation in multi-component silicate glass for the fabrication of porous glass from multi-component slag. Spinodal decomposition forms an interconnected microstructure in glass spontaneously, and porous glass is obtained by leaching one of the decomposed phases with an acid solution. This porous glass can be used for a filter to remove impurities in polluted water or air. In this study, the metastable miscibility gap was predicted in multi-component silicate glass using thermodynamic analyses where glass was regarded as a super-cooled liquid phase. Occurrence of spinodal decomposition was observed in annealed glass, and it corresponded to the predicted miscibility gap. Then, we fabricated porous glass using spinodal decomposition in multi-component borosilicate glass and by removing one of the decomposed phases. Furthermore, for the creation of functional porous glass applicable for environmental purification, the spinodal decomposition was prepared in multi-component borosilicate glass containing titanium oxide based on the predicted metastable miscibility gap in multi-component silicate glass.

Keywords: spinodal decomposition, porous glass, slag, multi-component silicate systems, Gibbs energy

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1 Introduction

To fabricate functional glass materials using slag as by-products of metallurgical processes or ash melting processes, the authors have investigated the phase separation in multi-component oxide glass which contains fundamental components in slag [1–6].

Figure 1 shows a schematic diagram for the production of porous glass using phase separation in glass from a single glass phase obtained from slag. Phase separation in glass represents a phenomenon in which a single glass phase spontaneously decomposes into two or more glass phases with different compositions under heat-treating process. Especially, spinodal decomposition forms three-dimensional interconnected microstructure by different glass phases. Then, the porous glass can be obtained by leaching one of those phases with an acid solution. Since its pore size can be controlled at a nano-scale level, the porous glass can be expected for widespread applications, such as a filter to remove impurities from polluted water or air. Thus, slag can be transformed into value-added functional glass materials using phase separation in oxide glass.

To generate phase separation in glass obtained from slag, the composition ranges for spinodal decomposition must be evaluated for multi-component slag systems. Previous experimental and predicting studies had revealed the occurrence of phase separation in various binary and ternary silicate glasses [7–13]. Additionally, the fabrication of porous glass had been attempted using spinodal decomposition in several oxide glass including multi-

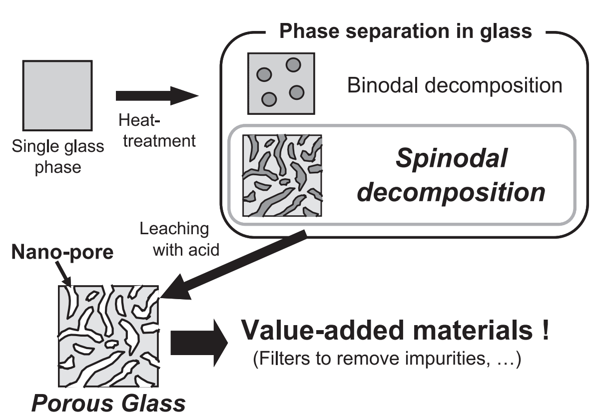

Fig. 1: Schematic diagram to create porous glass using phase separation in glass obtained from slag.

component system [14–16]. However, it is difficult to empirically predict the metastable phase separation in multi-component oxide systems such as slag. Therefore, it is necessary to perform a thermodynamic evaluation to determine the metastable phase separation in multi-component oxide systems.

For evaluating phase equilibria in various oxide systems, thermodynamic analyses have been carried out using Gibbs energy as a function of composition and temperature. In recent years, thermodynamic databases have been developed to calculate the temperature and composition dependences of Gibbs energies in different phases in oxide systems, so that multi-phase equilibria including liquid phase can be successfully predicted in multi-component oxide systems [17–20]. However, no attempts have been made to predict metastable phase separation in multi-component oxide systems on the basis of thermodynamic analyses.

The present paper reviews our trials on predicting phase separation in multi-component silicate glass and fabricating porous glass using spinodal decomposition in oxide glass [1–6]. The SiO_2-CaO-MgO-Na_2O and SiO_2-CaO-Al_2O_3-Na_2O systems have been first selected, because SiO_2, CaO, MgO and Al_2O_3 are fundamental components of most industrial slags, and Na_2O enables these slags to be molten at a low temperature. To predict the metastable miscibility gap including spinodal decomposition for these multi-component silicate systems, thermodynamic analyses have been performed where glass is regarded as a super-cooled liquid phase. To verify the occurrence of the metastable phase separation in those systems, experimental studies have been carried out by annealing the glasses of which compositions are included in the predicted miscibility gap and by observing microstructure in annealed glass with the transmission electron microscopy. Then, we have prepared porous glass using spinodal decomposition in multi-component borosilicate glass, and by removing one of the decomposed phases with acid leaching.

2 Trial 1 – prediction of metastable phase separation in multi-component silicate systems [1–3]

In general, liquid-liquid immiscibility is evaluated from the Gibbs energy curve of the liquid phase. Therefore, it is expected that composition ranges for phase separation and spinodal decomposition in glass can be estimated from Gibbs energy of the super-cooled liquid phase.

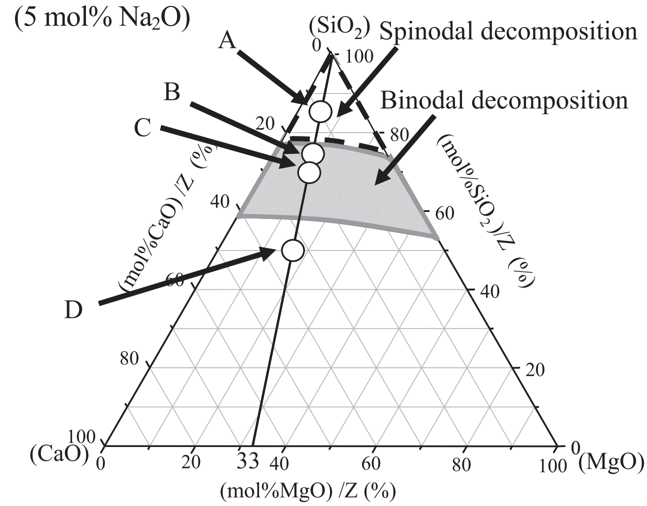

Fig. 2: Calculated composition ranges of spinodal and binodal decomposition in the SiO_2-CaO-MgO-5 mol% Na_2O system at 948 K. (Z = mol% (SiO_2 + CaO + MgO), A-D: glass compositions used in experimental studies)

Figure 2 shows the calculated results of the metastable miscibility gap including spinodal decomposition in the SiO_2-CaO-MgO-5 mol% Na_2O system, where the sum of the molar concentrations of all components except Na_2O is converted to unity. The detail calculating procedure of the miscibility gap is described in our previous papers [1–2]. Gibbs energy of the super-cooled liquid phase in this system was obtained using thermodynamic databases for molten oxide systems developed by Pelton *et al.* [18–20] Figure 2 indicates that spinodal decomposition occurs in the composition range surrounded by the dotted line, which is located at the high SiO_2 concentration area.

The occurrence of phase separation was experimentally investigated for the glasses A-D, of which compositions are indicated by circle marks in Figure 2, by preparing phase-separated glasses and by observing microstructures in those glasses. Figure 3 shows electron micrographs of the glasses A-D annealed for 192 h at 948 K, and it depicts the microstructure formed by phase separation. In glass A, interconnected microstructure corresponding to spinodal decomposition was observed. The cross-section of the interconnected structure is estimated to be 80 to 100 nm in diameter. In glasses B and C, particle structures corresponding to binodal decomposition were observed. As the composition of glass D was out of the predicted miscibility gap, no specific microstructure was observed after heat-treating. Since the electron diffraction patterns for each specimen in Figure 3 indicate no evidence for the presence of crystalline phases, and it follows that these specimens were glassy in the observed microscopic area. Above experimental results indicate that the

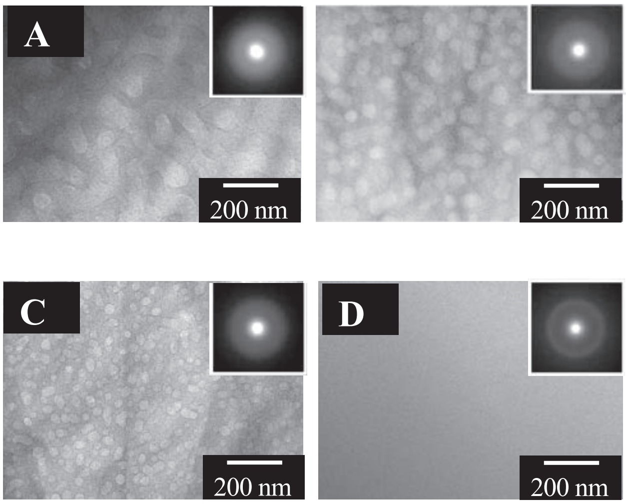

Fig. 3: Transmission electron micrographs of glasses after heat-treating at 948 K for 192 h [2].

microstructures detected in the annealed glasses can be attributed to the phase separation in glass, and that phase separation including spinodal decomposition occurs in the SiO_2-CaO-MgO-Na_2O glasses in accordance with the predicted metastable miscibility gap shown in Figure 2.

Furthermore, the composition dependence of the size of the decomposed microstructure was investigated in the phase separation of SiO_2-CaO-MgO-Na_2O glass [2]. Table 1 summarizes the experimental results, where the solid circles denote the glass compositions in which spinodal decomposition was detected, the double circles denote the binodal decomposition, and the open circles show where the phase separation was not observed in the annealed glasses with the relevant composition. The cross-section or size of these microstructures in the glass samples are also given in this table. Table 1 indicates that the size of the microstructures in the glasses decreases as the composition ratio of CaO/MgO decreases under a given heat-treatment conditions (948 K, 192 h). Consequently, it has been found that the size of microstructures formed by phase separation can be controlled by manipulating the initial glass composition, as well as thermal conditions of heat-treating process.

CaO / MgO molar composition ratio	Mole fraction of SiO_2: 1.0 ← Spinodal decomposition → 0.8 ← Binodal decomposition → 0.6 … 0.4
90 /10	● (100 nm) — ◎ (50 nm) — ○
67 /33	● (80 nm) — ◎ (50 nm) — ◎ (30 nm) — ○
25 /75	● (40 nm) — ○ — ○

●: Spinodal decomposition, ◎: Binodal decomposition,, ○: No phase separation

Table 1: Composition dependence of microstructures formed by phase separation in SiO_2-CaO-MgO-Na_2O glass. (Annealing condition: 948 K, 192 h) [2]

We also predicted spinodal decomposition in the SiO_2-CaO-Al_2O_3-5 mol% Na_2O glass [3]. Figure 4 shows the calculated metastable miscibility gap in this system, where the sum of the molar concentrations of all components except Na_2O is converted to unity. Similar to the result in the SiO_2-CaO-MgO-Na_2O system, the occurrence of the spinodal decomposition was predicted at a high SiO_2 composition. Figure 5 shows the electron micrograph of heat-

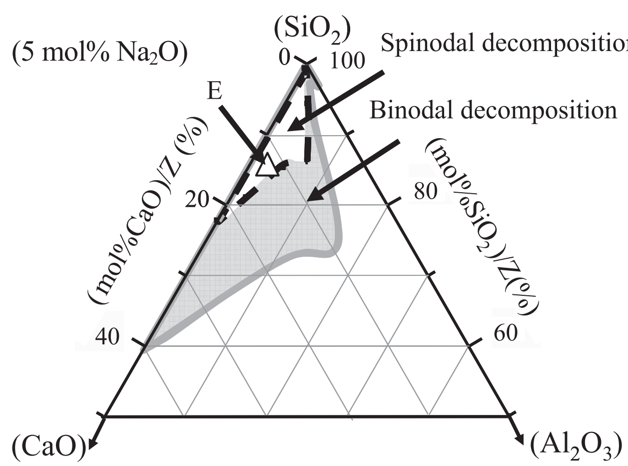

Fig. 4: Calculated composition ranges for spinodal and binodal decomposition in the SiO_2-CaO-Al_2O_3-5 mol% Na_2O system at 993 K. (Z = mol% (SiO_2 + CaO + Al_2O_3), E: glass composition used in experimental studies)

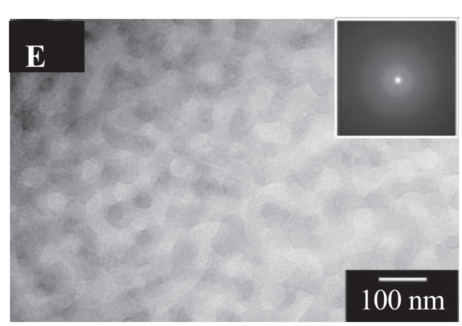

Fig. 5: Transmission electron micrograph of glass E annealed at 993 K for 96 h.

treated glass E, where the glass composition is included in the predicted miscibility gap shown in Figure 4. Development of interconnected microstructure was observed, and it indicates that the spinodal decomposition occurs in the SiO_2-CaO-Al_2O_3-Na_2O glass according to the predicted metastable immiscibility region.

3 Trial 2 – fabrication of porous glass using phase separation in multi-component glass containing B_2O_3 [3–4]

To produce porous glass using the spinodal-decomposed glass, one of the decomposed phases need to be removed. First, we conducted the leaching process for the annealed SiO_2-CaO-MgO-Na_2O glass A in which spinodal decomposition was detected, and it was found that the proportion of the glass sample dissolved into acid solution was quite low [3]. The fact that the separated phases in glass A contain high SiO_2 concentrations may make it difficult to leach one of the phases selectively with acid solutions.

It should be noted that in the spinodal decomposition in glasses containing B_2O_3, one of the separated phases contains a lot of B_2O_3 and can be leached out with acid solutions [13–16]. In our study, to selectively remove one of the decomposed phases, a multi-component borosilicate glass composition was designed by partially substituting molar concentration of SiO_2 with B_2O_3 in the silicate glass where the spinidal decomposition had been observed [3].

Table 2 shows the chemical composition of the multi-component borosilicate glass F prepared for the fabrication of porous glass using the metastable spinodal decomposition. The chemical composition of the glass F was designed by replacing 30 mol% of SiO_2 with $BO_{1.5}$ in the silicate glass composition E, which is included in the predicted metastable miscibility gap shown in Figure 4.

Figure 6 shows the microstructures of (a) two-phase glass, and (b) porous glass obtained from the SiO_2-CaO-Al_2O_3-Na_2O-B_2O_3 multi-component glass F. A microstructure with interconnectivity was observed in the two-phase glass, and it corresponds to the spinodal decomposition. Then, a three-dimensional interconnected porous structure was observed, indicating that one of the decomposed phases formed by spinodal decomposition in the borosilicate glass was selectively removed with an acid solution. The chemical composition analysis for the glass dissolved into acid solution revealed that a lot of B_2O_3 in glass F was dissolved into acid and that the remaining porous glass contains high concentration of SiO_2. Consequently, porous glass with high concentration of SiO_2 was obtained by spinodal decomposition in multi-component borosilicate glass and by leaching one of the separated phases selectively with an acid solution. Since the multi-component oxide systems investigated in this study contain fundamental components of slag, it is expected that porous glass materials can be created from slag using spinodal decomposition in glass.

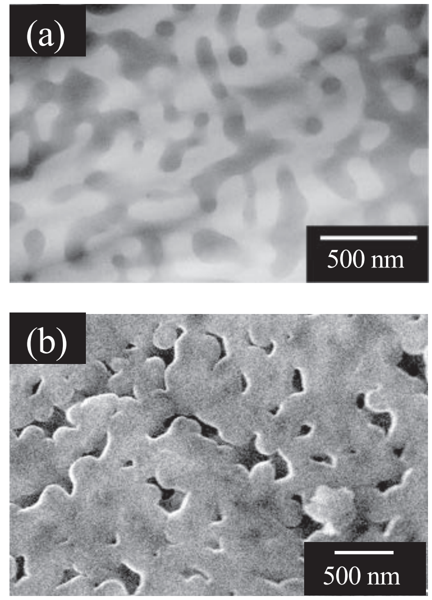

Fig. 6: Electron micrographs of glass F: (a) after heat treatment at 993 K for 96 h, (b) after leaching of two-phase glass with a 1 M HCl solution [3].

(mol%)	SiO_2	CaO	Al_2O_3	Na_2O	B_2O_3
E	80.8	11.7	2.5	5.0	–
F	59.7	13.8	2.9	5.9	17.7

Table 2: Selected glass compositions in SiO_2-CaO-Al_2O_3-Na_2O and SiO_2-CaO-Al_2O_3-Na_2O-B_2O_3 systems to produce porous glass using spinodal decomposition.

4 Trial 3 – preparation of porous glass containing titanium oxide applicable for environmental purification [5]

It has been found that tetrahedrally coordinated titanium oxides implanted into inorganic materials aid in the removal of air-based pollutants by photocatalytic reac-

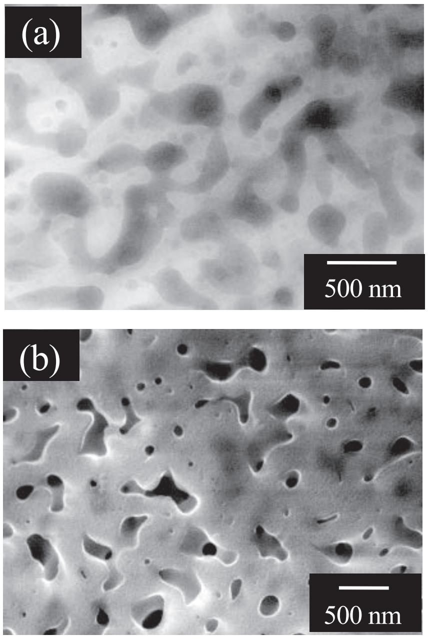

Fig. 7: Electron micrographs of glass G (65.0 SiO_2-13.0 CaO-2.8 Al_2O_3-5.6 Na_2O-11.1 B_2O_3-2.5 mol% TiO_2): (a) after heat-treatment at 993 K for 96 h (b) after acid leaching with 1 M HCl solution [5].

tions [21]. To obtain porous glass containing tetrahedrally coordinated titanium oxides, we investigated the distribution and the coordination state of titanium oxides in the glass phases formed by spnodal decomposition in multi-component glass. A multi-component borosilicate glass G, which contains titanium oxide, was prepared by partially substituting SiO_2 with $BO_{1.5}$ and small amount of TiO_2 in the SiO_2-CaO-Al_2O_3-Na_2O glass composition E where the spinodal decomposition had been observed. This borosilicate glass was heat-treated to promote spinodal decomposition, and the two-phase microstructure in the annealed glass was observed as shown in Figure 7 (a). An interconnected microstructure was detected, and it corresponds to the spinodal decomposition. The elemental analysis of this two-phase microstructure by energy dispersion spectroscopy indicated that the decomposed phase with higher concentration of SiO_2 contains smaller proportion of titanium oxides than the other phase.

Porous glass containing titanium oxide was obtained from two-phase glass G with spinodal decomposition by leaching one of the separated phases with an acid solution. The microstructure on the surface of the porous glass is shown in Figure 7 (b). The porous structure with three-dimensional interconnectivity was obtained, and it corresponds to the microstructure in the two-phase glass G. The Ti-K edge X-ray absorption spectrum was measured to examine the coordination state of titanium oxides dispersed in the porous glass, and the result revealed the presence of tetrahedrally coordinated titanium oxide [5]. Therefore, it was indicated that titanium oxides in the porous glass may induce photocatalytic reaction to remove air pollutants.

5 Future target – prediction of metastable phase separation in oxide systems containing B_2O_3

For the creation of porous glass using spinodal decomposition in glass, we designed multi-component borosilicate glass compositions semi-empirically by partly replacing SiO_2 with B_2O_3 in the silicate glass composition where spinodal decomposition had been detected. If one could predict the glass compositions for spinodal decomposition in multi-component oxide glass containing B_2O_3 by thermodynamic analyses, it should be much effective to design the appropriate composition for fabricating porous glass materials.

We have conducted thermodynamic analyses to estimate phase separation in multi-component borosilicate glass compositions used for producing porous glass, by calculating Gibbs energy of the super-cooled liquid phase. However, the calculated result indicated that the phase separation would not occur in the SiO_2-CaO-Al_2O_3-Na_2O-B_2O_3 glass F, although the spinodal decomposition had been observed in this glass after heat treatment [4]. Thus, the calculated result of the possibility of metastable phase separation does not coincide with the experimental results in multi-component oxide glass containing B_2O_3. To precisely evaluate the metastable miscibility gap, the temperature and composition dependence of the Gibbs energy function of the liquid phase, including super-cooled liquid state, should be optimized in multi-component borosilicate systems.

6 Concluding remarks

Thermodynamic analyses were conducted to predict composition ranges for phase separation and spinodal decomposition in multi-component silicate glass, where glass was regarded as a super-cooled liquid phase. The metastable miscibility gaps in the SiO_2-CaO-MgO-Na_2O and SiO_2-CaO-Al_2O_3-Na_2O systems were obtained by calculating the Gibbs energy of the metastable liquid phase. The occurrence of spinodal decomposition in those silicate glasses was verified by observing microstructures in heat-treated glasses, and these experimental results corresponded to the predicted miscibility gaps. Furthermore, it was found that the size of the microstructures formed by the phase separation depends on the initial glass compositions. In the phase separation in SiO_2-CaO-MgO-Na_2O glass, the size of microstructure decreased as the composition ratio of CaO to MgO decreased.

To remove one of the decomposed phases and to fabricate a porous glass, the leaching process was performed for the two-phase glasses formed by spinodal decomposition. A Multi-component borosilicate glass was prepared by partially replacing SiO_2 with B_2O_3 in the silicate glass compositions where the occurrence of the spinodal decomposition had been detected. Since one of the decomposed phases by spinodal decomposition in the borosilicate glass can be leached out with an acid solution, porous glass with three-dimensional interconnected structure was successfully obtained.

Furthermore, for the fabrication of porous glass containing applicable for environmental purification, multi-component borosilicate glass was designed by partially substituting SiO_2 with B_2O_3 and small amount of TiO_2 in the silicate glass composition included in the predicted miscibility gap. Spinodal decomposition was detected in the borosilicate glass after heat-treating, and it was found that the decomposed glass phase with high concentration of SiO_2 contains low content of titanium oxide. Porous glass containing titanium oxides was successfully obtained by removing one of the decomposed phases with acid leaching. Titanium oxides in the porous glass were terahedrally-coordinated, which may induce photocatalytic reactions to remove air-based pollutants.

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