Thermodynamic properties of K₂Si₄O₉ and Na₂Si₄O₉ glasses quenched from melts at high pressures and high temperatures

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Abstract

Calorimetric study was performed to measure relative enthalpies of alkali tetrasilicate glasses quenched from melts at various pressures. The high-pressure K₂Si₄O₉ and Na₂Si₄O₉ glasses were obtained by quenching the melts at about 2273-2473 K in the pressure range from 3 to 12 GPa. The enthalpies of the glasses were measured by a differential drop-solution calorimetry method in 2PbO·B₂O₃ solvent, using a Calvet-type microcalorimeter. Densities of the glasses were also measured by the Archimedes method. Relative enthalpies and densities in the K₂Si₄O₉ and Na₂Si₄O₉ glasses increase with increasing the synthesis pressure. Compared with those of the 1 atm-glass, relative enthalpy and density of the K₂Si₄O₉ glass synthesized at 8 GPa are higher by 28.1 kJ/mol and 11.0 %, respectively, and those of Na₂Si₄O₉ glass higher by 33.1 kJ/mol and 25.1 %, respectively. These large enthalpy increases are consistent with pressure-induced structural changes in K₂Si₄O₉ and Na₂Si₄O₉ glasses in which the proportion of five- and six-coordinated Si increases with pressure: total abundance of the high-coordinated Si increases up to about 12 % in all of Si in the Na₂Si₄O₉ glass synthesized at 12 GPa and about 5 % in the K₂Si₄O₉ glass at 5.5 GPa. In contrast to these large enthalpy changes in the alkali tetrasilicates, enthalpy increase in NaAlSi₃O₈ glasses quenched from melt at 1.5-2.5 GPa was only 2-3 kJ/mol, because only a small structural change in the medium range (decrease of mean T-O-T angles) occurred in this pressure range.

Introduction

Structures and physical properties of silicate melts at high pressures and high temperatures are of great importance for fundamental understanding of magmatic processes in the earth’s crust and mantle. Like crystalline silicates, it has been confirmed that structures of silicate melts and glasses change with pressure. At relatively low pressures, medium-range structures in silicate melts change: Si-O-Si angles decrease and thus sizes of (SiO₄)₄ rings decrease in silicate melts with fully polymerized networks (e.g., Hemley et al., 1994). In partially depolymerized silicate melts such as alkali silicates, change in connectivity of SiO₄ tetrahedra occurs at the low pressures (Xue et al., 1991). At higher pressures, however, short-range structures change drastically: coordination of cations increases in both of the fully and partially polymerized silicate melts. For example, Si coordination changes with increasing pressure from four-fold to five- and six-fold in alkali silicate glasses quenched from the melts.
at high pressures and high temperatures (Stebbins and McMillan, 1989; Xue et al., 1991). Studies on structures of silicate melts and glasses at high pressures have been recently reviewed by Wolf and McMillan (1995). In contrast to the structural studies, physical properties of these high-pressure melts and glasses have not yet been fully investigated.

Thermodynamic properties (enthalpy, heat capacity, entropy, volume, etc.) of silicate glasses and melts have been studied extensively in recent two decades (e.g., Richet and Bottinca, 1986; Navrotsky, 1995, as reviews). However, the thermodynamic properties of silicate melts stable at high pressures and of glasses quenched from the high-pressure melts have not yet been measured, except for those of NaAlSi$_3$O$_8$ glasses quenched from the melt at pressures below 3 GPa (Navrotsky et al., 1982).

In this study, we have measured enthalpies and densities of two kinds of alkali tetrasilicate glasses, K$_2$Si$_4$O$_9$ and Na$_2$Si$_4$O$_9$, quenched from the liquids at high pressures and high temperatures, using high-temperature calorimetry for enthalpy and the Archimedes method for density. These alkali silicates were chosen, because the glasses having five- and six-coordinated Si can be quenched to ambient conditions, as described above. The obtained experimental results on enthalpy and density are discussed in relation to the structural features of the high-pressure glasses.

**Experimental Methods**

*Sample synthesis*

Glasses with K$_2$Si$_4$O$_9$ and Na$_2$Si$_4$O$_9$ compositions were synthesized at 1 atm and high temperatures using reagent grade chemicals as follows, and were used as starting materials for high pressure synthesis of the dense glasses. K$_2$CO$_3$ and silicic acid (SiO$_2$•11wt%H$_2$O) were mixed in molar ratio of 1:4, heated at 973 K for 3 days and subsequently at 1373 K for 2 hours, and then quenched in liquid nitrogen. Similarly, Na$_2$CO$_3$ and silicic acid were mixed in molar ratio of 1:4, heated up to 1473K and held at the temperature for 2 hours, and quenched in liquid nitrogen. Both of the glasses were confirmed to be free from quench crystals by microscopic observation and powder x-ray diffraction. EPMA analyses were made for the sintered crystalline samples (K$_2$Si$_4$O$_9$ wadeite and a high-pressure phase of Na$_2$Si$_4$O$_8$) synthesized at high pressures and high temperatures using the K$_2$Si$_4$O$_9$ and Na$_2$Si$_4$O$_9$ glasses, confirming K/Si and Na/Si atomic ratios of 0.50 within the analytical errors.

The dense high-pressure glasses were synthesized from the glasses prepared at 1 atm, by means of a multi-anvil apparatus at Gakushuin University. Tungsten carbide anvils of truncated edge length of 8 mm were used together with a MgO octahedron of 14 mm in edge. The starting materials were put into a cylindrical Re furnace/capsule, which was placed in a central part of the octahedron and surrounded with a LaCrO$_3$ sleeve for thermal insulation. Two LaCrO$_3$ endplugs were placed at both ends of the furnace, with two Pt discs between the sample and endplugs. Pressure calibration was made by the method described by Suzuki and Akaogi (1995). Moreover, pressure was calibrated at 2273 K, using the coesite-stishovite
transition boundary by Zhang et al. (1993). Presicion of pressure was about ±0.2 GPa. In some representative runs, temperature was measured by a Pt/Pt-13%Rh thermocouple up to about 1973 K, and extrapolated at higher temperature with the obtained electric power - temperature relationship. In most of the synthesis runs, temperature was estimated with this relationship without direct measurement by the thermocouple.

The sample assembly of the octahedron was heated at 973 K for 2 hours in Ar gas just before each high-pressure synthesis run to remove absorbed water in the sample. Then the sample was compressed to desired pressure of 3.0-12.0 GPa, heated at about 2273-2473 K for about 10 min, and quenched isobarically within 1 sec down to temperature below 373 K. Pressure was released slowly to 1 atm for several hours to recover the sample. The synthesized glass in the central part of the furnace was easily separated from quench crystals which occurred in both ends and/or outer part of the sample. In all of the Na₂Si₄O₉ runs, the amount of quench crystals, which were not well characterized, was very small. In the K₂Si₄O₉ runs, the amount of quench crystals (wadeite) was increased with pressure. Weights of the synthesized K₂Si₄O₉ glasses were about 70-80 mg at 3.0 and 5.5 GPa, and 11 mg at 8.0 GPa. The Na₂Si₄O₉ glasses of about 90-115 mg were synthesized at 5.5, 9.0, and 12.0 GPa. The high-pressure glass samples thus obtained were examined by microscopic observation and powder x-ray diffraction, confirming no crystals in the samples. EPMA analysis of the quenched glasses confirmed that the compositions were K₂Si₄O₉ and Na₂Si₄O₉, though the analysis was a little less accurate than for the crystalline samples due to alkali volatilization associated with electron beam damage of the glasses.

**Enthalpy and density measurements**

Enthalpies of drop-solution of the K₂Si₄O₉ and Na₂Si₄O₉ glasses were measured by a differential drop-solution calorimetry, using a twin Calvet-type microcalorimeter kept at 976 ±1 K. A 2PbO·B₂O₃ solvent was used for the enthalpy measurements. The method of the solvent preparation and the calorimeter are described in Akaogi et al. (1990). In the differential drop-solution calorimetry, a powder sample of about 5-16 mg was put into a silica glass capsule of about 3-6 mg with a Pt wire of about 105-135 mg, and these were dropped from room temperature into one side of calorimeter. Simultaneously, the silica glass capsule and the Pt wire without the sample were dropped into the other side of the calorimeter. Because of the similar weights, heat effects of the silica glass capsules and the Pt wires in both sides were almost cancelled. Then the heat effect for drop-solution process of the powder sample was obtained. More detailed description of the differential drop-solution calorimetry method is given by Akaogi and Ito (1993).

Densities of the K₂Si₄O₉ and Na₂Si₄O₉ glasses were measured by the Archimedes method using a Berman density torsion balance. Several small pieces (about 4-15 mg in total) of each glass sample were put on a Pt mesh and the weight was measured in air and in carbon tetrachloride (CCl₄). The glass density was calculated from the measured weights and density of CCl₄.
### Table 1. Measured densities and enthalpies of drop-solution of $K_2Si_4O_9$ glasses.

<table>
<thead>
<tr>
<th>Synthesis Pressure</th>
<th>$\Delta H^0_{\text{d-s}}$ (kJ/mol)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 atm</td>
<td>196.9±7.7[9]</td>
<td>2.37±0.01</td>
</tr>
<tr>
<td>3.0 GPa</td>
<td>181.0±8.0[8]</td>
<td>2.49±0.04</td>
</tr>
<tr>
<td>5.5 GPa</td>
<td>179.4±3.6[8]</td>
<td>2.54±0.03</td>
</tr>
<tr>
<td>8.0 GPa</td>
<td>168.8±9.2[2]</td>
<td>2.63±0.04</td>
</tr>
</tbody>
</table>

Number in brackets is the number of runs.

### Table 2. Measured densities and enthalpies of drop-solution of $Na_2Si_4O_9$ glasses.

<table>
<thead>
<tr>
<th>Synthesis Pressure</th>
<th>$\Delta H^0_{\text{d-s}}$ (kJ/mol)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 atm</td>
<td>165.7±5.2[4]</td>
<td>2.35±0.05</td>
</tr>
<tr>
<td>5.5 GPa</td>
<td>158.7±3.4[3]</td>
<td>2.65±0.01</td>
</tr>
<tr>
<td>9.0 GPa</td>
<td>144.0±6.1[8]</td>
<td>2.88±0.02</td>
</tr>
<tr>
<td>12.0 GPa</td>
<td>132.6±5.9[5]</td>
<td>2.94±0.03</td>
</tr>
</tbody>
</table>

Number in brackets is the number of runs.

### Results and Discussion

Tables 1 and 2 summarize the measured enthalpies by the differential drop-solution runs and the densities of the $K_2Si_4O_9$ and $Na_2Si_4O_9$ glasses, respectively. Figure 1 shows the relationship between the measured densities and the synthesis pressures of $K_2Si_4O_9$ glasses, and Figure 2 between the measured enthalpies and the synthesis pressures. Similarly, Figures 3 and 4 show the relationships for $Na_2Si_4O_9$ glasses. The densities of $K_2Si_4O_9$ and $Na_2Si_4O_9$ glasses increase with increasing pressure. This densification results from structural changes in $K_2Si_4O_9$ and $Na_2Si_4O_9$ melts at high pressures and high temperatures, because it is accepted that as the first approximation the quenched glass structures of these alkali silicates retain the melt structures at the glass transition temperatures at high pressure (Xue et al., 1991). Figures 2 and 4 indicate that the measured enthalpies of drop-solution decrease with increasing the synthesis pressure. Since the enthalpy of drop-solution is difference between the sample at 298 K and the dissolved sample in the solvent at 976 K, difference between the measured enthalpy of drop-solution ($\Delta H_{\text{d-s}}$) of the 1 atm-glass and that of the high-pressure glass is difference in enthalpy of formation at 298 K ($H^0_\text{298}$) between the glasses,

\[
\Delta H_{\text{d-s}}^0(\text{1 atm-glass}) - \Delta H_{\text{d-s}}^0(\text{h.p. glass}) = H^0_\text{298}(\text{h.p. glass}) - H^0_\text{298}(\text{1 atm-glass})
\]

Therefore, the decrease of enthalpy of drop-solution in Figures 2 and 4 indicates that the enthalpy of formation of glass increases with the synthesis pressure. In Figure 5, the enthalpies of high-pressure glasses relative to that synthesized at 1 atm are plotted as functions of molar volumes. The molar volumes of the glasses were calculated from the measured densities. Figure 5 shows that the glasses of smaller molar volumes synthesized at higher pressures are higher in relative enthalpy, and are therefore energetically less stable at 1 atm and 298 K.

Based on the $^{29}$Si MAS-NMR studies of glasses quenched from melts at high pressures and high temperatures, Xue et al. (1991) showed that melt structures of $K_2Si_4O_9$ and $Na_2Si_4O_9$ change with pressure as follows. At low pressure below about 4 GPa, mean Si-O-Si angles for $Q^3$ and $Q^4$ species in $Na_2Si_4O_9$ melt decrease with increasing pressure, where $Q^n$ indicates a SiO$_4$ tetrahedron having n bridging oxygens shared with other tetrahedra. Above about 6 GPa, however, five- and six-coordinated silicons (denoted $^{[5]}$Si and $^{[6]}$Si, respectively) appear. The abundance of these high-coordinated Si increases with increasing pressure. The total amount of $^{[5]}$Si and $^{[6]}$Si in $Na_2Si_4O_9$ melt is below the detection limit (≤0.3 %) at 4
Thermodynamic properties of $K_2Si_4O_9$ and $Na_2Si_4O_9$ glasses quenched at high pressures

**Fig. 1.** Measured density vs. synthesis pressure for $K_2Si_4O_9$ glasses.

**Fig. 3.** Measured density vs. synthesis pressure for $Na_2Si_4O_9$ glasses.

**Fig. 2.** Relationship between measured enthalpy of drop-solution and synthesis pressure for $K_2Si_4O_9$ glasses.

**Fig. 4.** Relationship between measured enthalpy of drop-solution and synthesis pressure for $Na_2Si_4O_9$ glasses.

GPa and about 15% at 12 GPa. For the $K_2Si_4O_9$ melt, the same structural changes with pressure occur, but the $^{[5]}$Si and $^{[6]}$Si appear at lower pressure: the total abundance of $^{[5]}$Si and $^{[6]}$Si is about 2% at 4 GPa, 6% at 6 GPa, and therefore tends to increase with pressure. Xue et al. (1991) proposed that the $^{[5]}$Si and $^{[6]}$Si are synthesized by the following reactions

$$Q^3 + Q^4 \rightarrow Q^{4+} + ^{[5]}Si$$

$$2Q^3 + Q^4 \rightarrow 2Q^{4+} + ^{[6]}Si$$

where $Q^{4+}$ is a SiO$_4$ species associated with three $^{[4]}$Si and one $^{[5]}$Si (or $^{[6]}$Si) neighbors.

It is highly expected that similar structural changes occurred in the $K_2Si_4O_9$ and
Na$_2$Si$_4$O$_9$ glasses synthesized in this study to those by Xue et al. (1991), though the synthesis conditions, particularly the run temperature, quenching rate, and decompression rate, were not the same. To confirm the structural similarity, we synthesized at the same conditions as those for the enthalpy and density measurements the sufficient amounts of the K$_2$Si$_4$O$_9$ and Na$_2$Si$_4$O$_9$ glasses for the $^{29}$Si MAS-NMR measurements, which were performed by Dr. H. Maekawa, Hokkaido University. The measurements showed quite similar results to those by Xue et al. (1991). In our glasses, the total abundance of $^{29}$Si and $^{28}$Si increases with pressure up to about 12% at 12 GPa for Na$_2$Si$_4$O$_9$ and to about 5% at 5.5 GPa for K$_2$Si$_4$O$_9$ (H. Maekawa, private communication).

Figure 5 shows that the enthalpies of K$_2$Si$_4$O$_9$ and Na$_2$Si$_4$O$_9$ high-pressure glasses relative to those of the 1 atm-glasses increase with decreasing the molar volumes. For K$_2$Si$_4$O$_9$, the enthalpy change between the 1 atm-glass and 8 GPa-glass is 28.1 kJ/mol with the density increase of 11.0 %, and for Na$_2$Si$_4$O$_9$ 33.1kJ/mol between 1 atm-glass and 12 GPa-glass with the density increase of 25.1%. It is very likely that these enthalpy increases result from the structural changes described above.

It is interesting to compare the observed enthalpy changes in the high-pressure glasses with those in phase transitions in crystalline materials. For the coesite-stishovite transition in which all of Si change from four-fold to six-fold coordination, the enthalpy change for Si$_4$O$_9$ at 298 K is 151 kJ/mol, with the density increase of 47.0 % (Akaogi et al., 1995). The enthalpy increase of 92 kJ/mol and density increase of 9.6 % are reported for the pyroxene-garnet transition in Mg$_3$Si$_2$O$_9$ in which 75 % of Si changes from four-fold to six-fold and 75 % of Mg changes from six-fold to eight-fold (Akaogi et al., 1992; Yusa et al., 1993). The observed enthalpy changes in the K$_2$Si$_4$O$_9$ and Na$_2$Si$_4$O$_9$ glasses are in order of magnitude consistent with those of the above solid-state phase transitions, when we consider the proportions of high-coordinated Si. However, such comparison may be too simple, because other structural changes such as formation of weakly bound alkali ions occur together with the formation of high-coordinated Si. In addition, the change of Si-O-Si angle also occurs at relatively low pressures. Therefore, further investigation is required for quantitative analysis of the enthalpies of high-pressure glasses in terms of the structure.

The enthalpy changes obtained in this study can also be compared with those in NaAl-
Si$_3$O$_8$ glasses quenched from melt at high pressures and high temperatures. Navrotsky et al. (1982) reported that the glasses quenched from albite melt at 1.5 and 2.5 GPa are denser by 2.9-6.1% and higher in enthalpy by about 2.3-3.3 kJ/mol. Their results are also plotted in Figure 5. It has been confirmed that higher coordinated Al and Si than four were not observed in the NaAlSi$_3$O$_8$ glasses quenched at pressures below 4 GPa (Ohtani et al., 1985; Stebbins and Sykes, 1990). Instead, a slight decrease of the mean T-O-T angles (T=Si, Al) was observed (Mysen et al., 1980). It is interesting that increase in enthalpy with decreasing molar volume in Figure 5 is very small in NaAlSi$_3$O$_8$ glasses in the pressure range up to 2.5 GPa and in Na$_2$Si$_4$O$_9$ glasses up to 5.5 GPa. This suggests that structural changes in medium range (decrease of T-O-T angles) are associated with much smaller enthalpy change, compared with the change in Si coordination, but are accompanied with considerably large volume decrease. Compared with Na$_2$Si$_4$O$_9$ and NaAlSi$_3$O$_8$ glasses, a larger increase in enthalpy with decreasing molar volume is observed in K$_2$Si$_4$O$_9$ glasses in the pressure range up to 5.5 GPa. This may be related with higher abundance of high-coordinated Si in K$_2$Si$_4$O$_9$ glasses than in Na$_2$Si$_4$O$_9$ and NaAlSi$_3$O$_8$ glasses at the low pressure range, as described above.

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References


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