Effect of alkaline and alkaline-earth cations on the compressibility of aluminosilicate glasses

R. G. Kuryaeva
V. S. Sobolev Institute of Geology and Mineralogy of the Siberian Branch of the RAS, Novosibirsk

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Introduction. Glasses are models of deep-seated melts. Of special interest are glasses that along with other oxides contain Al₂O₃. The traditional model for the structure of alkali (alkaline-earth) aluminosilicate glasses holds that aluminum goes into tetrahedral coordination as a network former when the molar ratio Al₂O₃/M(M₂)O=1. The cations of alkaline and alkaline-earth elements in such glass compensate charge in the alumo-oxygen tetrahedrons AlO₄⁻¹, and is not formed connection with the non-bridge atoms of oxygen. In other words, the structure of such glass must be completely polymerized. However, there is a number of the experimental works, which testify about the presence in such glass of the non-bridge atoms of oxygen [Riebling, 1966; Stebbins, Xu, 1997].

In a number of works it was also shown that the properties of aluminosilicate glasses and melts depend on what cations, one- or double-charged, enter into their structure. Works [Webb, Courtial, 1996; Kress, et al., 1988] show that the bulk moduli of melts in the CaO–Al₂O₃–SiO₂ system are, in general, higher than those in the Na₂O–Al₂O₃–SiO₂ system. Kuryaeva [Kuryaeva, 2004] reported that the compressibility of tholeiite basalt glass is lower than that of the glass with alkaline basalt composition. The former, in addition to net formers, contains mainly cations of alkaline-earth elements. The composition of the latter is similar to that of tholeiite basalt glass but contains mainly cations of alkaline metals. However, natural glass of alkaline and tholeitic basalt, besides the oxides of silicon, aluminum and alkaline (alkaline-earth) cations, contain other components, which also could influence the compressibility of glasses.

In this work, for the purpose of the confirmation of the assumption about different compressibility of aluminosilicate glass and melts, which contain the cations of alkaline or alkaline-earth elements expressed previously, the compressibilities of two identical aluminosilicate glasses Na₂O•Al₂O₃•6SiO₂ and CaO•Al₂O₃•6SiO₂ are compared. The obtained results are discussed from the point of view of the different degree of polymerization of their structural network.

Experimental technique and results. Glasses of Na₂O•Al₂O₃•6SiO₂ and CaO•Al₂O₃•6SiO₂ compositions were synthesized and studied in the works [Kuryaeva, 2009; Kuryaeva, Surkov, 2010].

The refractive index at high hydrostatic pressures was measured by the technique described in detail in our previous works [Kuryaeva, Kirinskii, 1997; 1998], with the use of the polarizing interference microscope MPI-5 and the apparatus with the diamond anvils. The measuring method of the refractive indices of sample n, under pressure is based on the pressure-induced change in the optical path difference \( \Phi \) caused by the sample under study. The optical path difference \( \Phi \) and the refractive indices of sample n, and the medium n, in our case a methanol-ethanol 4:1 alcohol mixture, are related by the expression \( \Phi = (n_x - n) t \) (1). Expression (1) shows that a decrease in \( \Phi \) results from the change in the ratio between the refractive indices of sample \( n_x \) and the medium \( n \) (under pressure, the refractive index of the liquid increases much more rapidly than the refractive index of the glass).

Changes in the relative densities of glass has been calculated from the experimental values of the refractive indices with the use of Mueller photoelasticity theory [10] according to the following equation:

\[ \Delta d/d = 6n_0 \Delta n/(n^2 - 1)(n^2 + 2)(1 - A) \]

where \( A = -(\Delta R/R_0)/\Delta d/d \) is Mueller strain–polarizability constant. The value of the strain–polarizability constant for aluminosilicate glasses is obtained to be \( A = 0.24 \) [Kuryaeva, 2004]. The fig.1 demonstrates the values of relative density of the studied glasses within the pressure range up to 6.0 GPa.

Discussion. Fig. 1 shows the pressure-induced changes in the relative density of NaAlSi₃O₈ glass [Kuryaeva, Surkov, 2010] together with the data for CaAl₂Si₆O₁₆ glass [Kuryaeva, 2009].
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It is seen from fig. 1 that the compressibility of glass containing Na is higher than the compressibility of glass containing Ca. One of the critical variables that control the properties of silicate glasses and melts, such as a viscosity and compressibility, is the degree of polymerization. The difference in the compressibility of glasses under high pressure suggests different degrees of polymerization.

The shift of maximum viscosity in the system Na₂O–Al₂O₃–SiO₂ from Al₂O₃/Na₂O=1 to the excess of Al₂O₃, studied by Riebling [Riebling, 1966] and Toplis et al. [Toplis, et al., 1997] evidences that NaAl₅Si₃O₁₆ glass contains a certain number of nonbridging oxygen (NBO) atoms. In the work of Stebbins J.F. and Xu Z. [Stebbins, Xu, 1997] the presence of nonbridging oxygen atoms results from the formation of a tricluster oxygen (oxygen coordinated to three (Si,Al)O₄ tetrahedra), which was reported earlier by Lacy [Lacy, 1963]. The presence of five- and six-coordinated aluminum might be also the reason for the formation of nonbridging oxygen atoms. However in glasses of the system Na₂O–Al₂O₃–SiO₂, obtained by quenching from melt at atmospheric pressure, no evidence was found for the existence of five and six-coordinated aluminum [Stebbins, Sykes, 1990; Sykes, et al., 1993; Allwardt, et al., 2005]. The lack of [⁵]Al and [⁶]Al in the ambient pressure glasses of this system may support the conclusion of Toplis et al. [Allwardt, et al., 2005], which suggests that the presence of triclusters rather than [⁵]Al and [⁶]Al is responsible for the shift of maximum viscosity of melts away from the charge balanced join toward an excess of Al₂O₃ relative to Na₂O.

Glasses of the system CaO–Al₂O₃–SiO₂ contain a highly coordinated aluminum [Neuville, et al., 2004], in contrast to glasses containing Na. Kuryaeva [Kuryaeva, 2009] proposed a schematic equation (3) that considers the formation of triclusters, nonbridging oxygen atoms (~4.5 %) and highly coordinated aluminum (~10 %) for anorthite glass.

\[
2\text{CaAl}_2\text{Si}_2\text{O}_5 \rightarrow \text{Ca}_0.5\text{Al}_2\text{Si}_5\text{O}_{16} + 0.4\text{AlO}_{1.5} + 0.7\text{CaO} + 3\text{SiO}_2 \tag{3}
\]

According to equation (3), CaO•Al₂O₃•2SiO₂ glass contains 4.4% nonbridging oxygen atoms with ~30 % of the total number of NBO resulting from the formation of highly coordinated aluminum and ~70 %, from the formation of triclusters. Using a similar equation, one can calculate the number of NBO for other glasses of the system CaO•Al₂O₃•xSiO₂. Glass of CaO•Al₂O₃•6SiO₂ composition contains ~20 % NBO, 1.55 % of which result from the formation of triclusters. On the assumption that in the system M(M₂)O•Al₂O₃•xSiO₂ the percentage of triclusters depends only on the content of SiO₂ and is independent on the charge of the network-modifying ion, the number of NBO resulting from the formation of triclusters will be the same (1.55 %) in CaO•Al₂O₃•6SiO₂ and Na₂O•Al₂O₃•6SiO₂ glasses. Unfortunately, no experimental
data were found on the exact percentage of NBO in albite glass. Calculations by the method of molecular orbitals for albite glass [Stein, Spera, 1995] yield 4–7% tricluster oxygen and 2–5% nonbridging oxygen atoms. The content of NBO determined using NMR in the work of Oestrike et al. [Oestrike, et al., 1987] is estimated as a “defective level” which seems to be ~1–2%, and does not disagree with the value of 1.55%. For albite glass, the following schematic reaction (4) for the formation of triclusters and nonbridging oxygen atoms can be written down

\[
3\text{NaAlSi}_3\text{O}_8 \rightarrow 0.75\text{Si}_2\text{AlO}_{5.5} + 7.5\text{SiO}_2 + 2.25\text{NaAlO}_2 + 0.75\text{NaO}_{0.5} \quad (4)
\]

The degree of depolymerization of NaAlSi3O8 glass calculated from equation (4) yields NBO/T = 0.063.

Fig. 2 shows the linear approximation of dependencies of relative changes in density \((d-d_0)/d\) on the degree of depolymerization NBO/T for glasses of the system CaO•Al2O3•xSiO2 (x=2, 4, 6) at \(P = 3, 4\) and 5 GPa. The values of the relative change in density and the degree of depolymerization were obtained and calculated in [Kuryaeva, 2008; 2009; Kuryaeva et al., 2007;]. If the degrees of depolymerization are estimated correctly, these dependencies must, most likely, be appropriate for glasses of the system Na2O•Al2O3•xSiO2. Table presents \((d-d_0)/d\) values for albite glasses, obtained experimentally and calculated using the equations given in fig. 2 for NBO/T = 0.063. Deviation (< 2 rel.%) of experimentally obtained data from the calculated values does not exceed the experimental error.

<table>
<thead>
<tr>
<th>(P) (GPa)</th>
<th>((d-d_0)/d \pm 0.0035) (experimental)</th>
<th>((d-d_0)/d) (calculated)</th>
<th>Deviation of calculated values from experimental values (rel.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>0.1155</td>
<td>0.1175</td>
<td>1.7</td>
</tr>
<tr>
<td>4.0</td>
<td>0.1410</td>
<td>0.1420</td>
<td>0.7</td>
</tr>
<tr>
<td>5.0</td>
<td>0.1690</td>
<td>0.1665</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Conclusions. The obtained results show that glasses as well as melts with the ratio Al2O3/M(M2)O=1 containing Na+ cations have higher compressibility compared to that of similar glasses containing Ca2+ cations. The compressibilities of glasses agree with the values of the degree of depolymerization NBO/T calculated considering the triclusters for glasses containing Na+ and calculated considering the triclusters and highly coordinated aluminum for glasses containing Ca2+.

References