Vestnik Otdelenia nauk o Zemle RAN, VOL. 3, NZ6061, doi:10.2205/2011NZ000191, 2011

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
rufina@igm.msc.ru, tel.: 8 (383) 333 0899

Key words: aluminosilicate glasses, high pressures, compressibility of glasses and melts, structure of glasses and melts.

Citation: Kuryaeva R.G. (2011), Effect of alkaline and alkaline-earth cations on the compressibility of aluminosilicate glasses, *Vestn. Otd. nauk Zemle, 3*, NZ6061, doi:10.2205/2011NZ000191.

Introduction. Glasses are models of deep-seated melts. Of special interest are glasses that along with other oxides contain Al_2O_3.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 $Al_2O_3/M(M_2)O=1$. The cations of alkaline and alkali-earth elements in such glass compensate charge in the alumo-oxygen tetrahedrons AlO_4^{-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 $CaO–Al_2O_3–SiO_2$ system are, in general, higher than those in the $Na_2O–Al_2O_3–SiO_2$ system. Kuryaeva [5 *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 tholeiitic 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 alkali-earth elements expressed previously, the compressibilities of two identical aluminosilicate glasses $Na_2O•Al_2O_3•6SiO_2$ and $CaO•Al_2O_3•6SiO_2$ 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 $Na_2O•Al_2O_3•6SiO_2$ and $CaO•Al_2O_3•6SiO_2$ 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, Kirkinskii,* 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_x under pressure is based on the pressure-induced change in the optical path difference Φ caused by the sample under study. The optical path difference Φ and the refractive indices of sample n_x 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 Φ 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: $\Delta d/d = 6n\Delta n/(n^2-1)(n^2+2)(1-\Lambda)$, where $\Lambda = -(\Delta R/R_0)/(\Delta d/d)$ is Mueller strain –polarizability constant. The value of the strain–polarizability constant for aluminosilicate glasses is obtained to be Λ=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 $NaAlSi_3O_8$ glass [*Kuryaeva, Surkov,* 2010] together with the data for $CaAl_2Si_6O_{16}$ glass [*Kuryaeva,* 2009].

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 $Na_2O–Al_2O_3–SiO_2$ from $Al_2O_3/Na_2O=1$ to the excess of Al_2O_3 , studied by Riebling [*Riebling,* 1966] and Toplis et al. [*Toplis, et al.,* 1997] evidences that $NaAlSi_3O_8$ 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 $(Si,Al)O_4$ 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 $Na_2O–Al_2O_3–SiO_2$, 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 Al_2O_3 relative to Na_2O.

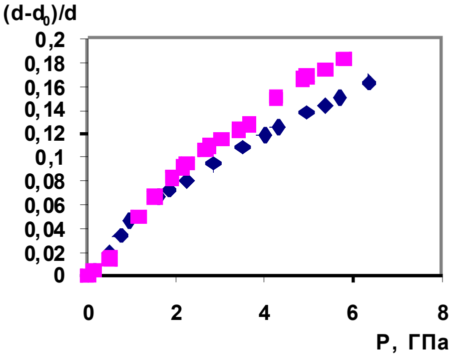

Fig.1. Dependence of the relative change in the density *(d-d₀)/d* on the pressure *P* for the glasses: diamonds are $CaO•Al_2O_3•6SiO_2$ [*Kuryaeva,* 2009], open squares are $Na_2O•Al_2O_3•6SiO_2$ [*Kuryaeva, Surkov,* 2010]

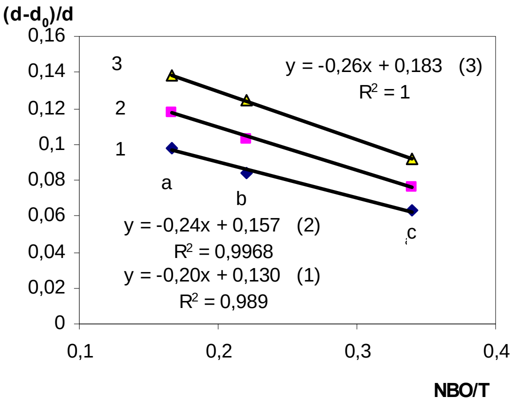

Fig. 2. Relationship between the change in relative density *(d-d0)/d* and degree of depolymerization *NBO/T* for: *a* – $CaAl_2Si_6O_{16}$ glass [*Kuryaeva,* 2009], *b* – $CaAl_2Si_4O_{12}$ glass [19 *Kuryaeva,* 2008], *c* – $CaAl_2Si_2O_8$ glass [20 *Kuryaeva, et al.,* 2007]. Data obtained at pressures: 1 – *P* = 3.0 GPa, 2 – *P* = 4.0 GPa, 3 – *P* = 5.0 GPa

Glasses of the system $CaO–Al_2O_3–SiO_2$ 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.

$$2CaAl_2Si_2O_8 \rightarrow \underset{\text{tricluster}}{Ca_{0.5}Al_2SiO_{5.5}} + 1.6Ca_{0.5}AlO_2 + \underset{\text{modifier}}{0.4AlO_{1.5}} + \underset{\text{nonbridging oxygen}}{0.7CaO} + 3SiO_2 \qquad (3)$$

According to equation (3), $CaO•Al_2O_3•2SiO_2$ 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 $CaO•Al_2O_3•xSiO_2$. Glass of $CaO•Al_2O_3•6SiO_2$ composition contains ~2.20 % *NBO*, 1.55 % of which result from the formation of triclusters. On the assumption that in the system $M(M_2)O•Al_2O_3•xSiO_2$ the percentage of triclusters depends only on the content of SiO_2 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 $CaO•Al_2O_3•6SiO_2$ and $Na_2O•Al_2O_3•6SiO_2$. 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

$$3NaAlSi_3O_8 \rightarrow \underset{\text{tricluster}}{0.75Si_2AlO_{5.5}} + 7.5SiO_2 + 2.25NaAlO_2 + \underset{\substack{\text{nonbridging}\\ \text{oxygen}}}{0.75NaO_{0.5}} \qquad (4)$$

The degree of depolymerization of $NaAlSi_3O_8$ glass calculated from equation (4) yields *NBO/T*=0.063.

Fig. 2 shows the linear approximation of dependencies of relative changes in density $(d\text{-}d_0)/d$ on the degree of depolymerization *NBO/T* for glasses of the system $CaO{\bullet}Al_2O_3{\bullet}xSiO_2$ (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 $Na_2O{\bullet}Al_2O_3{\bullet}xSiO_2$. Table presents $(d\text{-}d_0)/d$ 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. The changes in the relative density $(d\text{-}d_0)/d$ in albite glass (experimental and calculated using linear equations given in Fig. 3) at pressures P =3, 4, 5 GPa

P (GPa)	$(d\text{-}d_0)/d$ ± 0,0035 (experimental)	$(d\text{-}d_0)/d$ (calculated)	Deviation of calculated values from experimental values (rel.%)
3.0	0.1155	0.1175	1.7
4.0	0.1410	0.1420	0.7
5.0	0.1690	0.1665	1.5

Conclusions. The obtained results show that glasses as well as melts with the ratio $Al_2O_3/M(M_2)O=1$ containing Na^+ cations have higher compressibility compared to that of similar glasses containing Ca^{2+} cations. The compressibilities of glasses agree with the values of the degree of depolymerization *NBO/T* calculated considering the triclusters for glasses containingo Na^+ and calculated considering the triclusters and highly coordinated aluminum for glasses containing Ca^{2+}.

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