Compressibility of the $CsAlSi_3O_8$ glass in the comparison with those for the glasses of albite and orthoclase compositions

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The refractive index for $CsAlSi_3O_8$ glass in the pressure range up to 6.0 GPa using a polarization-interference microscope and an apparatus with diamond anvils was measured and the values of compressibility $(d-d_0)/d$ were estimated. The results were compared with the previous data for the albite $(NaAlSi_3O_8)$ and orthoclase $(KAlSi_3O_8)$ glasses. Isothermal initial bulk modulus $(K_{t,\ 0})$ of glasses decreases in a series of Na^+, K^+, Cs^+ alkali metal cations. This change in $K_{t,\ 0}$ indicates an increase in the degree of polymerization of the structural network of glasses in the order Na^+, K^+, Cs^+. The increase in $K'_t = \partial K_t/\partial P$ for glasses in the same series can be explained by the fact that the voids are occupied by K^+, Cs^+ cations, which have a larger orbital radius than Na^+, and more strongly inhibit compression. For glass containing Cs^+ a denser packing structure containing three-membered rings of tetrahedra exhibits additional resistance to compression.

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

Introduction. Silicate and aluminosilicate melts are the dominant phases in the Earth's crust and mantle. Glasses are models of magmatic liquids. Investigation of the properties of various compositions of glasses at high pressures is important for understanding the role of deep melts in magmatic and volcanic processes [*Mysen, 1990; Agee and Walker, 1988*]. A change in the composition of silicate glasses and melts affects the properties that depend on the degree of polymerization, such as viscosity [*Hochella and Brown, 1984; Toplis et al., 1997*] and compressibility [*Webb and Courtial, 1996; Kress, 1988; Kuryaeva and Kirkinskii, 2001*].

For $Al_2O_3 \bullet M(M_2)O \bullet xSiO_2$ glasses with the ratio of $Al_2O_3/M(M_2)O = 1$ the increase in silica content results in an increase in viscosity [*Hochella and Brown, 1984; Toplis et al., 1997*] and compressibility [*Webb and Courtial, 1996; Kress, 1988; Kuryaeva and Kirkinskii, 2001*]. The glasses in which the ratio of $Al_2O_3/M(M_2)O \neq 1$ have a lower compressibility than the glasses with the ratio of $Al_2O_3 /M(M_2)O = 1$, all other things being equal [*Kress, 1988; Kuryaeva 2008*]. Aluminosilicate glasses of the $Al_2O_3 \bullet M(M_2)O \bullet xSiO_2$ composition containing the cations of alkaline earth elements have a lower compressibility compared to those containing cations of alkali metals [Kuryaeva, 2004; Kuryaeva and Surkov, 2010]. And finally, the replacement of the cations Na^+ by K^+ in the $MAlSi_3O_8$ glass was accompanied by an increase in compressibility [*Kuryaeva, 2011*].

In this work we report new results concerning the pressure-dependent behavior of the refractive index and the compressibility for $CsAlSi_3O_8$ glass in the pressure range 0–6.0 GPa . To determine the effect of replacing alkali metal cations in series M = Na, K, Cs on the properties of the $M_2O \bullet Al_2O_3 \bullet 6SiO_2$ glasses, the obtained data were compared with the data for the previously studied $NaAlSi_3O_8$ [*Kuryaeva and Surkov, 2010*] and $KAlSi_3O_8$ [*Kuryaeva, 2011*] glasses.

Experimental technique and results. $CsAlSi_3O_8$ glass was synthesized by melting the corresponding oxides and carbonates of special-purity grade at a temperature of 1600–1650 °C for 1 hour in a platinum crucible. Then, the glass was ground in a mortar made from a hard alloy, melted once more, and quenched in water. No annealing of the glass was carried out.

In the experiments polished glass plates 40–50 μm in length and width and 15–20 μm in thickness were used. The samples were polished with diamond pastes on a cardboard.

The refractive index at high hydrostatic pressures was measured by the technique described in detail in our previous works [*Kuryaeva and Kirkinskii, 1994; Kuryaeva and Kirkinskii, 1997*], 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 [*Mueller, 1935*] 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 $\Lambda=0.24$ [*Kuryaeva, 2004b*]. The Fig.1 demonstrates the values of relative density of the studied glasses within the pressure range up to 6.0 GPa.
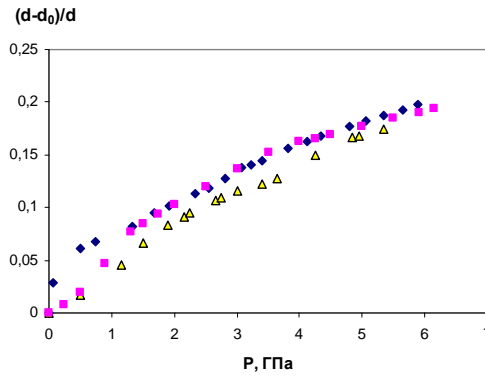
(d-d$_0$)/d

Fig. 1. Pressure dependence of the relative change in the density $(d-d_0)/d$ (compressibility) of glasses: diamonds – CsAlSi$_3$O$_8$, squares – KAlSi$_3$O$_8$, triangles – NaAlSi$_3$O$_8$.

Discussion. We analyzed the available literature data on the change in the compressibility of alkali silicate glasses and melts in the series Li, Na, K, Rb, Cs. To compare the compressibilities of various glasses and melts the values of the initial bulk modulus $K_{t(T),0}$ (at normal pressure) and the values of the derivative of the bulk modulus with respect to pressure $K_{t(T)}'= \partial K_{t(T)}/\partial P$ are often used. Using ultrasonic methods in papers [*Rivers and Carmichael, 1987; Webb and Dingwell, 1994*] the values of the initial bulk modulus for alkali silicate [*Rivers and Carmichael, 1987*] and for alkaline titanosilicate melts [*Webb and Dingwell, 1994*] were determined. Obtained in these works data attest to the fact that for melts the initial bulk modulus decreases, therefore, the initial pressure coefficient of the compressibility increases in the order Li, Na, K, Rb, Cs. The change in the bulk modulus is consistent with the decrease in the electronegativity of the cations of alkali metals in the same order. With decreasing electronegativity of alkali metal cations, bonding between Si and O increases in the fragment $\equiv$Si$-$O$^-$M$^+$, but decreases in the adjacent $\equiv$Si$-$O$-$Si$\equiv$ bonds. Hence, the Si$-$O network is in general weaker and the rotation around the Si$-$O$-$Si bonds is easier [*Revesz, 1972*]. Thus, with the decreasing electronegativity of alkali metal cations in silicate glasses, conformational changes during compression occur with increasing ease.

The same change in the compressibility in the order of Na, K, Cs, are to expected for aluminosilicate systems in which the alkali metal cations compensate the charge in aluminum-oxygen tetrahedra. Aluminosilicate glasses and melts with the ratio of $Al_2O_3/(M)M_2O=1$ contain a number of nonbridging oxygen atoms [*Stebbins and Xu, 1997*] due to the formation of triclusters [*Toplis et al., 1997*]. The smaller the electronegativity of the singly charged cation, the more stable are the aluminum complexes and the lower is the probability of the formation of triclusters and, respectively, the lower is the possibility of forming nonbridging oxygen atoms. That is, for MAlSi$_3$O$_8$ glasses, the degree of polymerization increases in the series of alkali metals Na, K, Cs, and the compressibility increases in the same order, as well.

Fig. 1 shows that the relative change in the density $(d-d_0)/d$ of the KAlSi$_3$O$_8$ glass in the pressure range of 2.0–6.0 GPa is indeed greater than that for the NaAlSi$_3$O$_8$ glass. The values $(d-d_0)/d$ for the

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$KAlSi_3O_8$ and $NaAlSi_3O_8$ glasses are consistent with the concept of change in the compressibility in a series of alkali metals according to the change in values of electronegativity. A further increase in the compressibility was expected for more polymerised glass of the $CsAlSi_3O_8$ composition. However, the compressibility of the $CsAlSi_3O_8$ glass does not significantly differs from that of the $KAlSi_3O_8$ glass in the pressure range of 2.0–6.0 GPa. This is probably due to unaccounted factors that have an opposite effect on the compressibility, as compared to the effect of the degree of polymerization. To such factors can be attributed an increase in the ionic radius of the cation of alkali metal, which earlier has already been noted in the work [*Kuryaeva, 2011*] and the structure of $CsAlSi_3O_8$ glass, which contains the small rings of the tetrahedron [*McMillan et al, 1998*].

For all three glasses the initial isothermal bulk modulus $(K_{t,0})$ and the derivative of the bulk modulus with respect to pressure $K_{t(T)}' = \partial K_{t(T)}/\partial P$ in the pressure range with a normal behavior of the pressure coefficient of the compressibility were calculated using experimental data and the isothermal Birch-Murnaghan equation. The isothermal Birch-Murnaghan equation of state has the form:

$$P=(3/2)K_{t,0}\{(d/d_0)^{7/3} – (d/d_0)^{5/3}\}\{1 - \tfrac{3}{4}(4 – K'_t) \,[(d/d_0)^{2/3} – 1]\},$$

where P is the pressure, d is the density of the glass at a pressure P, d_0 is the density of the glass at atmospheric pressure, $K_{t,0}$ is the initial isothermal (at normal pressure and room temperature) bulk modulus of the glass, K'_t is the derivative of the isothermal bulk modulus with respect to pressure. The results of the calculations of $K_{t,0}$ and K'_t are presented in Table 1.

Table 1. The change of $K_{t,0}$, and K'_t for $MAlSi_3O_8$ glasses in the series M = Na [*Kuryaeva and Surkov, 2010*] , K [*Kuryaeva, 2011*], Cs (data from this article.) The orbital radii of alkali metal cations $r_{op\delta}^{M+}$ are defined in [*Weber and Cromer, 1965*]. The values of the degree of depolymerization NBO / T are defined in [*Kuryaeva, 2004a; Kuryaeva, 2011*].

M	$K_{t,0}$ ГПа	K_t'	$r_{op\delta}^{M+}$ Å	NBO/T
Na	16.5	6.0	0.278	0.083
K	13.0	7.0	0.592	0.045
Cs	12.3	7.5	0.921	

The Table 1 shows that in aluminosilicate glasses ($MAlSi_3O_8$) the initial bulk modulus $K_{t,0}$ decreases in the order Na, K, Cs. This trend seems to be explained by the fact that a decrease in the depolymerization of the structural network NBO/T (the ratio between the number of nonbridging oxygen atoms and the number of network formers) in the series Na, K, Cs has a dominant influence on the compressibility of the glass at low pressures.

The positive effect of the increasing degree of polymerization in the series of Na, K, Cs on the compressibility of the glasses may be weakened by the influence of factors that contribute to a decrease in compressibility. These factors include: a significant increase in the orbital radius of cations in the series Na, K, Cs, and changes in the glass structure in favor of the formation of three-membered rings for glasses containing Cs. The greater the radius of the cation the greater is its resistance to compression with increasing pressure. A small increase in the derivative of the bulk modulus with respect to pressure (K'_t) in the series aluminosilicate glasses (Table 1) and the convergence of curves $(d-d_0) / d$–P at pressures above 4.0 GPa for the $NaAlSi_3O_8$ and $KAlSi_3O_8$ glasses (Figs. 1) can be attributed to this factor.

A structure containing three-membered rings (as in the $CsAlSi_3O_8$ glass) is less compressible than the structure containing six-membered rings of tetrahedra (as in the $MAlSi_3O_8$ glasses, M = Na, K) as the three-membered ring have smaller angles of T–O–T bonds and larger packing density compared to six-membered rings [*Revesz, 1972*]. An additional negative influence of the latter factor on the ability of $CsAlSi_3O_8$ glass to shrink under pressure can significantly reduce the increase in the compressibility due to the changes in the degree of polymerization of the structural network. The coincidence of the curves $(d-d_0)/d – P$ for the $KAlSi_3O_8$ and $CsAlSi_3O_8$ glasses in the pressure range of 2.0–6.0 GPa (Figs. 1) can be explained by the fact that for the $CsAlSi_3O_8$ glass the negative effect of factors that reduce compressibility compensates a positive effect on the compressibility of a higher degree of polymerization of its structure.

Conclusion. For $MAlSi_3O_8$ glasses (M=Na, K, Cs) isothermal initial bulk modulus $(K_{t,0})$ decreases in the series of alkali metal cations Na^+, K^+, Cs^+. This change in $K_{t,0}$ indicates that the degree of polymerization of the structural network of alkali aluminosilicate glasses increases, according to the order Na, K, Cs. The increase in the cation radius in the series of alkali metals and particularly the presence of the three-membered rings in the structure of the aluminosilicate glasses containing Cs have an adverse

effect on the increase of the compressibility of the MAlSi$_3$O$_8$ glasses which is due to the increasing degree of polymerization of the structural network, in the order Na, K, Cs.

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