

RELATIONSHIP BETWEEN THE COMPRESSIBILITY OF GLASSES OF THE $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$ SYSTEM AND THE DEGREE OF POLYMERIZATION OF SILICON - ALUMINUM – OXYGEN NETWORK

Kuryaeva R.G. (IGM SB RAS)

rufina@uiggm.msc.ru; phone: (383) 333-08-99

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

Introduction. Glasses are models of deep-seated melts. Of special interest are glasses that along with other oxides contain Al_2O_3 . It is generally accepted that Al^{3+} ions, like Si^{4+} ions, are network formers. In glasses containing sufficiently large amount of alkali (M^+) and alkaline-earth (M^{2+}) cations, Al^{3+} have a tetrahedral coordination. Within this approach, aluminosilicate glasses containing identical mole fractions of Al_2O_3 and $\text{M}(\text{M}_2)\text{O}$ should have a totally polymerized structure, that is maximal degree of polymerization.

The degree of polymerization is among the most critical variables that control the properties of silicate glasses and melts, such as a viscosity and compressibility. In several works [1, 2] it was shown that the viscosity of the $\text{M}(\text{M}_2)\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$ melts decreases considerably with a decrease in the content of SiO_2 , suggesting different degrees of polymerization of this system melts [3]. The compressibility of $\text{M}(\text{M}_2)\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$ glasses should be changeable with a decrease in x . The goal of this work is to study the effect of silica content on the compressibility glasses with ratio $\text{CaO}/\text{Al}_2\text{O}_3=1$. In this work a comparison between the data concerning to the pressure-dependent behavior of relative densities for (a) $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ [4], (b) $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ [5] and (c) $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ [6] glasses are reported.

Experimental technique and results. The glasses of (a), (b) and (c) compositions ($d=2.69 \pm 0.02$ g/cm³, $d=2.60 \pm 0.02$ g/cm³ and $d=2.45 \pm 0.02$ g/cm³, correspondingly) have been obtained by melting of high pure oxides in a platinum crucible during 1 hour at 1550 °C. Then the glass was rubbed in a hardalloy mortar and remelted with further quench in water. No annealing of the glass was performed.

The refractive index was measured at atmospheric and high hydrostatic pressures by the procedure described in detail in [7, 8] with the use of polarization – interference microscope and apparatus with diamond anvils ($n_o(a)=1.575 \pm 0.003$, $n_o(b)=1.529 \pm 0.003$ and $n_o(c)=1.504$). Thin (15-30 mkm) flat-parallel plates were used for measurements. Optical path difference Φ and the refractive indices of the object n_x and the surrounding medium (methanol-ethanol mixture 4:1, in our case) are related by the expression $\Phi=(n_x-n)t$. The method is based on the change of optical path difference Φ under pressure, caused by the sample. It can be seen from the expression that a decrease in the Φ results from the change in the ratio between n_x and n (the refractive index of the liquid increases significantly faster under pressure than the glass refractive index). Determinations of pressure and refractive index are in error by $\sigma P = \pm 0.05$ GPa and $\sigma n_x = \pm 0.003$, correspondingly. Relative densities of glasses have been calculated from the experimental values of the refractive indices with the use of Mueller photoelasticity theory [9] according to the following equation: $\Delta d/d = 6n\Delta n/(n^2-1)(n^2+2)(1-A)$, 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 $A=0.24$ [10]. 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 change in the relative density of (a) $\text{CaAl}_2\text{Si}_2\text{O}_8$ [4], (b) $\text{CaAl}_2\text{Si}_4\text{O}_{12}$ [5] and (c) $\text{CaAl}_2\text{Si}_6\text{O}_{16}$ [6] glasses. The pressure - induced behavior of the properties of the (b) and (c) glasses somewhat differs from the behavior of the glass (a). Unlike (b) and (c) glasses, (a) $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass has a crystal analog - anorthite. Experiment shows that the refractive index of glass (a) at initial increase in pressure to 0.1 GPa drastically increases to $n=1.596$, which is close to crystal anorthite. The value of relative change density increases dramatically to $(d-d_0)/d=0.0376$ (fig. 1). This phenomenon was not observed for other glasses.

The structure of the $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass was studied by various methods. The experimental RDF's (radial distribution functions) [11] showed that the structure of the $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass is similar to that of the crystalline analog and is built up of four-member rings of SiO_4 and AlO_4 tetrahedra that are joined together in a more or less ordered manner. The similarity of the glass and crystal structures and the tendency toward the attainment of an equilibrium state by the system, most likely, explain the initial increase in the refractive index to the value close to the refractive index of the crystalline anorthite.

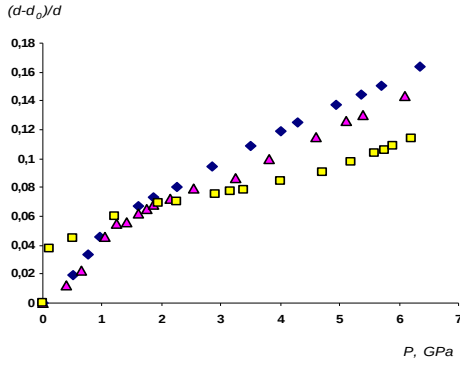


Fig.1. Dependence of the relative change in the density $(d-d_0)/d$ on the pressure P for the $\text{CaO Al}_2\text{O}_3 x\text{SiO}_2$ glasses: diamonds are $\text{CaO Al}_2\text{O}_3 6\text{SiO}_2$ [6], triangles are $\text{CaO Al}_2\text{O}_3 4\text{SiO}_2$ [5], open squares are $\text{CaO Al}_2\text{O}_3 2\text{SiO}_2$ [4]

Fig.1 shows that ruling out the initial abrupt jump of relative density for anorthite glass, pressure has a greater influence on the density of the $\text{CaAl}_2\text{Si}_6\text{O}_{16}$ glass. In other words, in the pressure range 2.0-6.0 GPa the compressibility of the $\text{CaO Al}_2\text{O}_3 6\text{SiO}_2$ glass is higher than that of $\text{CaO Al}_2\text{O}_3 4\text{SiO}_2$ and $\text{CaO Al}_2\text{O}_3 2\text{SiO}_2$ glasses. Webb S. and Courtiel P. [12] used ultrasonic interferometric method to study the influence of composition on the compressibility of melts in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ with varying contents of SiO_2 and varying $\text{Al}_2\text{O}_3/\text{CaO}$ ratios at normal pressure. It was shown that compressibility of melts decreases on addition of modifier ions and increases on addition of net-forming ions. These data suggest that in our case higher compressibility is evidence of a lesser number of non-bridging oxygen atoms, hence, of a greater degree of polymerization of $\text{CaO Al}_2\text{O}_3 6\text{SiO}_2$ glass.

The degree of polymerization can be calculated from a formula (1) with regard to the formation of triclusters [13] and highly coordinated aluminum [14]. The formula (1) was proposed in [15, 16].

$$NBO/T = [2(O + 0.833 \cdot O_{t2}) + 3(0.167 \cdot O_{t2}) - 4(T - 0.1 \cdot T_2)] / (T - 0.1 \cdot T_2) \quad (1),$$

where O is the total number of gram-ions of oxygen in the composition of modifier oxides and network forming oxides that do not form triclusters (all oxides except for Al_2O_3); O_{t2} is the number of gram-ions of oxygen in the composition of oxides that form triclusters in whose oxygen tetrahedra the charge is compensated by doubly charged cations, T is the total number of gram-ions of all network formers in the oxides that form or do not form triclusters, T_2 is the number of gram-ions of network formers in the composition of oxides forming triclusters.

Results of calculations NBO/T are given in tab. 1 together with the values $(d-d_0)/d$, which characterize compressibility of glasses at pressures $P=4.0, 5.0$ and 6.0 GPa. Tab.1 shows that compressibility of glasses under pressure is consistent with the degree of polymerization calculated at normal pressure. With increasing relative number of nonbridging oxygen atoms, the rigidity of framework decreases. Distortion of the framework, in turn, results in a more compact packing and, hence, in a lower compressibility of glass under pressure.

Table 1

Relative changes in the density $(d-d_0)/d$ and degrees of polymerization NBO/T for $\text{CaAl}_2\text{Si}_6\text{O}_{16}$ [6], $\text{CaAl}_2\text{Si}_4\text{O}_{12}$ [5] and $\text{CaAl}_2\text{Si}_2\text{O}_8$ [4] glasses at pressures $P= 4.0, 5.0, 6.0$ GPa

Glass composition	NBO/T	$(d-d_0)/d$	$(d-d_0)/d$	$(d-d_0)/d$
		$P=4.0$ GPa	$P=5.0$ GPa	$P=6.0$ GPa
$\text{CaAl}_2\text{Si}_6\text{O}_{16}$	0.167	0.118	0.140	0.156
$\text{CaAl}_2\text{Si}_4\text{O}_{12}$	0.222	0.103	0.124	0.142
$\text{CaAl}_2\text{Si}_2\text{O}_8$	0.342	0.084	0.094	0.112

Most likely, the degree of polymerization of glasses under pressure will differ from the values reported in Table, as the structure of glasses can change under pressure to form a more compact state, up to a change in the coordination number of ions. Considerable pressure-induced changes in the coordination number of Al^{3+} are related, mainly, to the compositions with a great excess of alkaline or alkaline-earth elements with respect to Al_2O_3 . S.K.Lee et al. [17] report that the greater degree of polymerization of structural network, the lesser the amount of pressure-induced highly coordinated aluminum. Since all studied glasses have a rather high degree of polymerization, it is unlikely to expect sharp anomalies on the curves of pressure dependencies of refractive index and change in the relative density of aluminosilicate glasses suggesting overall structural changes. The sharp anomalies on the curves were not observed really. Unfortunately, our experimental data obtained for glasses of investigated compositions do not give us a clear answer about the changes taking place in a structure and, hence, about the change in the degree of polymerization of structural net in the studied range of pressures. We can only say that, for glasses with a high degree of polymerization of structural net, the NBO/T values calculated for normal conditions reflect the ability of glasses to compress under pressure.

References

1. Hochella M.F., Brown G.E. // *Geochim. Cosmochim. Acta*. 1984. V. 48. P. 2631.
2. Kushihiro I. // *Carnegie Institution of Washington Year Book*. 1981. V. 80. P. 339.
3. Giordano D., Dingwell D.B. // *Earth and Planetary Science Letters*. 2003. V. 208. P. 337.
4. Kuryaeva R.G., Kirkinskii V.A., Surkov N.V. // *Geokhimiya*. 2007. No 3. P. 348. [*Geochim. Int.* (Engl. Transl.) 2007. V. 45. P. 308].
5. Kuryaeva R.G. // *Fiz. Khim. Stekla*. 2008. No 1. P. 48. [*Glass Phys. Chem.* 2008. V. 34. P. 37].
6. Kuryaeva R.G. // *J. Non-Cryst. Sol.* 2009. V. 355. P. 159.
7. Kuryaeva R.G., Kirkinskii V.A. // *Prib. Tekh. Eksp.* 1998. No 3. P. 145. [*Instrum. Exp. Tech.* (Engl. Transl.) 1998. V. 41. P. 430].
8. Kuryaeva R.G., Kirkinskii V.A. // *Phys. Chem. Minerals*. 1997. V. 25. P. 48.
9. Mueller H. // *Physics*. 1935. V. 6. P. 179.
10. Kuryaeva R.G. // *Fiz. Khim. Stekla*. 2004. V. 30. P. 713. [*Glass Phys. Chem.* 2004. V. 30. P. 523].
11. Taylor M., Brown G.E. // *Geochim. Cosmochim. Acta*. 1979. V. 43. P. 61.
12. Webb S., Courtial P. // *Geochim. Cosmochim. Acta*. 1996. V. 60. P. 75.
13. Lacy E.D. // *Phys. Chem. Glasses*. 1963. V. 4. P. 234.
14. Neuville D.R., Cornier L., Massiot D. // *Geochim. Cosmochim. Acta*. 2004. V. 68. P. 5071.
15. Kuryaeva R.G. // *Fiz. Khim. Stekla*. 2004. V. 30. P. 212. [*Glass Phys. Chem.* 2004. V. 30. P. 157].
16. Kuryaeva R.G. // *Fiz. Khim. Stekla*. 2006. V. 32. P. 690. [*Glass Phys. Chem.* 2006. V. 32. P. 505].
17. Lee S.K., Cody G.D., Fei Y., Mysen B.O. // *Geochim. Cosmochim. Acta*. 2004. V. 68. P. 4189.

Electronic Scientific Information Journal "Vestnik Otdelenia nauk o Zemle RAN" № 1(27) 2009

ISSN 1819 – 6586

Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2009

URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2009/informbul-1_2009/magm-21e.pdf

Published on July, 1, 2009

© *Vestnik Otdelenia nauk o Zemle RAN, 1997-2009*

All rights reserved