



Compressibility of magnesium silicate glasses in comparison with those of aluminosilicate glasses



R.G. Kuryaeva*

Sobolev Institute of Geology and Mineralogy, SB of the RAS, 3 Prosp. Akad. Koptyuga, 630090 Novosibirsk, Russian Federation

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ABSTRACT

The refractive index of the $\text{Na}_2\text{MgSi}_6\text{O}_{14}$ glass in the pressure range up to 6.0 GPa has been measured using a polarization-interference microscope and an apparatus with diamond anvils. The changes in relative density which characterize the compressibility of the glass have been estimated in the pressure range under investigation from the measured refractive indices within the framework of the theory of photoelasticity. The results have been compared with the data previously obtained for the $\text{NaAlSi}_3\text{O}_8$ and $\text{CaAl}_2\text{Si}_6\text{O}_{16}$ glasses. A comparison of the changes in relative density of the aluminosilicate and magnesium silicate glasses has been demonstrated that the difference in the compressibility is not so much significant as should be expected from the replacement of network-forming ions by modifiers ions. Estimated by different methods the degree of depolymerization of the $\text{Na}_2\text{MgSi}_6\text{O}_{14}$ glass ($\text{NBO}/T \cong 0.2$) is compared to those for the aluminosilicate glasses. The decrease in the compressibility in the series $\text{NaAlSi}_3\text{O}_8$, $\text{CaAl}_2\text{Si}_6\text{O}_{16}$, $\text{Na}_2\text{MgSi}_6\text{O}_{14}$ glasses is in agreement with an increase of the degree of depolymerization in the same series.

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1. Introduction

Silicate glasses are widely applied in science, technology, and household owing to their cheapness, availability, relatively easy industrial production and great diversity of properties. To achieve various properties of glasses, oxides of such elements as Al, B, Mg, Ca, Na, and K are added to the main component (SiO_2). Each oxide component imparts certain properties to the glasses. For example, it is known that introduction of CaO and ZnO increases the chemical stability and mechanical strength of glass. However, the purposeful synthesis of noncrystalline silicate materials with a wide set of predetermined features can be realized only on the basis of deep insight into the structure of silicate melts and glasses.

The random network model [1,2] is assumed as the basis for understanding of the structure and properties of silicate glasses and melts. According to this model, all positively charged ions are divided into network formers (mainly tetrahedrally coordinated to oxygen) and modifiers which are coordinated to more than four oxygen atoms. The modern model suggests that in aluminosilicate glasses Al^{3+} ions along with Si^{4+} play the part of network formers [3]. The presence of “compensating charge” alkali and alkaline-

earth cations allows stabilization of aluminum in tetrahedral coordination. At $M^{n+}/n\text{Al} = 1$, glasses or melts must have a completely polymerized structure. At $M^{n+}/n\text{Al} < 1$, excess of aluminum ions can remain tetrahedrally coordinated with formation of tricluster oxygen [4,5] (tricluster is tri-coordinated oxygen linked with three $[\text{Si,Al}]\text{O}_4$ tetrahedra [e.g. 6]), or play the part of modifiers, with fivefold or sixfold coordination to oxygen [6,7]. It is proposed in Refs. [5,8] that some of triclusters can be present in the compositions with $M^{n+}/n\text{Al} = 1$. At $M^{n+}/n\text{Al} > 1$, the excess amount (with respect to aluminum) of alkali and alkaline-earth cations will play the part of modifiers that destroy the network and decrease its degree of polymerization. The presence of modifiers has a significant influence on glass properties. A decrease in the degree of polymerization of glass network leads to a drop in glass vitrification temperature, while the coefficient of thermal expansion increases. Owing to the appearance of less directed bonds in glass structure, the framework becomes weaker and one can observe a tendency to form a denser packing, which influences on glass compressibility under pressure. Within the framework of the standard model, Mg^{2+} , similar to Ca^{2+} , is considered to be a modifier. As for the role of Mg^{2+} in silicate glasses, it is not clear so far.

In Ref. [9] the survey of the data concerning to the properties of magnesium silicate glasses is made, from which one can suggest that Mg^{2+} ions play a particular part in the structure of silicate glasses and melts. For example, it is reported in Refs. [10–13] that in

* Tel.: +7 89139229323.

E-mail address: rufina@igm.nsc.ru.

magnesium-aluminosilicate systems at least not all Mg^{2+} ions compensate the charge in aluminum–oxygen tetrahedra, due to which these glasses and melts were found to have a rather high content of $^{\text{V}}\text{Al}$ and $^{\text{VI}}\text{Al}$ compared to those in which Mg^{2+} ions are replaced by Ca^{2+} or alkali cations. Moreover, in Refs. [13,14] the authors show that Mg^{2+} ions can compete with Al^{3+} ions for the part of network formers.

Viscosity and compressibility are the properties, which reflect the degree of polymerization of glasses and melts. Comparison of the elastic properties of silicate glasses containing aluminum and the glasses in which Al is replaced by Mg [15–17] showed that the difference in the properties of Al- and Mg-bearing glasses is not so much significant as should be expected from the replacement of network-forming ions by modifier ions. This fact suggests a sufficiently high degree of polymerization of magnesium silicate glasses and the role of Mg^{2+} ions in the structure as network formers. Earlier [17] the dependence of the compressibility on the degree of depolymerization for aluminosilicate glasses was found. The comparison of the compressibility of magnesium silicate glasses with those of the aluminosilicate glasses makes it possible to estimate their degree of depolymerization and to understand the role of magnesium in the silicate systems (what part of the Mg^{2+} ions are network formers and what part are modifiers, which determine the degree of depolymerization). For this purpose it is necessary to accumulate more experimental data on the compressibility of magnesium silicate and aluminosilicate glasses of various composition (for example, with the different content of SiO_2).

This paper reports the results of the investigation of the pressure dependence of the refractive index and the compressibility of the $\text{Na}_2\text{MgSi}_6\text{O}_{14}$ glass with the high content of SiO_2 (75 mol.%). This glass was chosen since earlier the experimental data on the density and compressibility of aluminosilicate glasses of a similar composition, which are necessary for the comparison, were obtained [18,19].

2. Materials and methods

2.1. Preparation of the glass samples

Glass of the $\text{Na}_2\text{MgSi}_6\text{O}_{14}$ composition was synthesized by melting the corresponding oxides of special-purity grade at a temperature of 1650–1700 °C for 2 h 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. The glass had density $d = 2.45 \pm 0.05 \text{ g/cm}^3$ (the glass density was measured by hydrostatic weighing).

The experiments were performed with polished glass plates 40–50 μm in length and width. The samples were polished with diamond pastes on a cardboard. The plates were treated as plane-parallel plates when interference fringes characteristic of a “wedge” were absent.

2.2. Measurement of refractive index at atmospheric and high pressures

The refractive index and the thickness of initial glass were determined with the use of a microscope polarizing interference (MPI-5, Poland optical plant) by measuring the optical path difference Φ in three different media (namely, in air with the refractive index $n_1 = 1.0002$, in toluene with the refractive index $n_2 = 1.495$ and in ethanol with the refractive index $n_3 = 1.365$) according to the method of “interference fringes with a large image splitting” [20]. The path difference Φ was measured with an error $\pm 0.02 \mu\text{m}$ at the wavelength $\lambda = 0.546 \mu\text{m}$. The refractive index n_x and the thickness m of the glass sample under investigation at

atmospheric pressure were determined to be as follows: $n_x = 1.485 \pm 0.002$, $m = 23.1 \pm 0.1 \mu\text{m}$. The errors were calculated under the assumption that the errors in the determination of n_1 , n_2 and n_3 are negligible.

The refractive index at high hydrostatic pressures was measured by the technique described in detail in our previous works [20–22] with the use of the polarizing interference microscope MPI-5 and the apparatus with the diamond anvils. A plate of the $\text{Na}_2\text{MgSi}_6\text{O}_{14}$ glass was loaded in the hole of stainless steel gasket together with ruby spheres (1 or 2) and methanol–ethanol mixture (4:1 volume ratio) as pressure transmitting medium. At the moment of the loading of liquid the disturbance of parallelism is possible between the anvils and the sample, which is easily controlled visually by using the interference-polarization microscope. This sample is not suitable for the measurement, since a dark border appears on the edge of the sample and the interference fringes are distorted. In this case the liquid is moved away from the hole, and the procedure of the arrangement of the sample between the anvils and the loading of the mixture of alcohols is repeated.

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:

$$\Phi = (n_x - n)m \quad (1)$$

The measuring method is based on the pressure-induced change in the optical path difference Φ caused by the sample under study. 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). To obtain n_x , it is necessary to know the path difference Φ , refractive index of the medium n , sample thickness m at specified pressure. The path difference Φ was measured at each pressure by the method of “interference fringes with a large image splitting” [20]. The refractive index of the methanol–ethanol (4:1) alcohol mixture n_0 was measured at atmospheric pressure and room temperature using a refractometer with the error ± 0.0002 . The change in the refractive index of the alcohol mixture at specified pressure was determined by the equation $\Delta n = AP + BP^{1/2} + CP^{1/3}$ with constants $A = -0.0222 \text{ GPa}^{-1}$, $B = 0.2134 \text{ GPa}^{-1/2}$, and $C = -0.075 \text{ GPa}^{-1/3}$. The pressure dependence of the refractive index for the alcohol mixture was reported in Refs. [20,21]. The error in the measurement of refractive index for the methanol–ethanol (4:1) alcohol mixture n in the pressures range up to 6.0 GPa was ± 0.001 . The sample thickness m obtained at atmospheric pressure was used when calculating the refractive index from Formula (1). The change in the thickness of the sample under pressure was disregarded because according to the estimates reported for silicate glasses in our previous papers [21,22] the decrease in the thickness of silicate glasses in the studied range of pressures introduces a systematic error into calculations of refractive index comparable to the error in the measurements. The pressure was determined from a shift in the R_1 luminescence line of ruby Refs. [23,24]. The pressure was measured before and after measuring the path difference. The uncertainty in the determination of pressure P was $\pm 0.05 \text{ GPa}$. In order to avoid any random errors, the measurement of the refractive index of glass was conducted, at least, in three samples. The obtained dependences of refractive index on the pressure were compared between each other. The obtained results were considered satisfactory if the curves coincided within the experimental error. The refractive index n_x for the $\text{Na}_2\text{MgSi}_6\text{O}_{14}$ glass was measured at pressures up to 6.0 GPa with the error ± 0.003 . This error involves the error in the determination of refractive index of the methanol–ethanol (4:1) alcohol mixture.

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