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Elastic moduli of $XAlSiO_4$ aluminosilicate glasses: effects of charge-balancing cations

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ABSTRACT

Brillouin spectroscopy is used to investigate the elastic properties of $XAlSiO_4$ aluminosilicate glasses where X = Li, Na, K, $Mg_{0.5}$, $Ca_{0.5}$, $Sr_{0.5}$, $Ba_{0.5}$, and $Zn_{0.5}$. The Brillouin frequency shifts obtained in two different scattering geometries allow the calculation of the refractive index, the two sound velocities and Poisson's ratio. Measurements of the mass density give in turn the elastic moduli and the Debye temperature. We find that the elastic properties scale with the atomic density of the glassy network or the charge-balancing cation field strength while they negatively correlate with the glass transition temperature. Further, Poisson's ratio depends on the nature of the non-framework cations in this glass series.

1. Introduction

About 85% of the atoms in the Earth's crust are oxygen and silicon atoms forming a myriad of silicate compounds when combined with alkali, alkaline earth or other metals. Aluminum being the most abundant metal in the crust, the crucial role of aluminosilicates in earth sciences is manifest. High-value aluminosilicate glasses and glass-ceramics are widely used in currently emerging technologies due to their attractive mechanical, optical or refractory properties [1,2].

Elasticity is a fundamental property of materials and as such is used in the determination of various physical properties in glass science, such as thermal shock resistance, thermal optical coefficients or fracture toughness. Indeed, the elastic modulus gives a global view of a material stiffness and reflects both the network connectivity and the inter-atomic potentials. It is then quite surprising to observe that the elastic properties of some simple glass compositions, *e.g.* ternary aluminosilicate glasses, are not known yet. It probably relies on the difficulty of bypassing the crystallization for some compositions, and further, on obtaining sufficiently large bubble-free samples to carry on ultrasonic experiments.

In the present paper, we investigate physical properties of a series of charge-compensated aluminosilicate glasses comprising 50% mol SiO_2. The total concentration of charge compensator oxides being equal to that of alumina, the glass structure is expected to be an almost fully connected, three-dimensional, random aluminosilicate network of tetrahedral units in which the charge compensation for the negatively charged $(AlO_4)^-$ tetrahedra would be provided by the $X^{n+}_{2/n}$ cations [3–5]. Actually, these simple stoichiometric considerations must be revised since five-fold coordinated aluminum species have been shown to exist in such tectosilicate glasses [6–13], their content being related to the X cation field strength [11,13] as well as to the SiO_2 content [10,11]. High temperature data also suggest that five-fold Al concentration increases with increasing temperature in tectosilicate melts [14]. We measured density, glass transition temperature, refractive index and sound velocities from which we calculated molar volume, elastic moduli and Debye temperature. The variation of the measured physical properties in these glasses, which should reflect the influence of the charge compensator cations only, is discussed.

2. Experimental methods

2.1. Glass synthesis

The eight charge-balanced $(X^{n+}_{2/n}O^{2-}/Al_2O_3 = 1)$ aluminosilicate glasses were prepared by melting the appropriate quantities of high-purity oxide and carbonate powders according to the following protocol [15]. About 100 g of batch materials (Rectapur, Merck) was mixed and

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brunched for 60 min in alcohol using an agate mortar. The mixture was slowly heated for 24 and 72 h for alkaline earth- and alkali-bearing compositions, respectively, to decompose the carbonate, and then, heated up to 1900 K in a covered platinum crucible for a few hours in equilibrium with air. The melt was quenched in few seconds by dipping the bottom of the platinum crucible into distilled water, leading to an estimated quenching rate of ≃15 K/mn [11] across the glass transition region. This process was repeated four times to warrant the best glass homogeneity.

Glasses containing SrO and BaO oxides are hardly obtained by the above standard quenching technique due to the high liquidus temperature. Ceramic materials were then first synthesized using five melting and crunching steps [16,10]. Small amounts of materials were finally melted using an aerodynamic levitation device in air located at the CEMHTI-CNRS, Orléans, France and a CO_2 laser as the heating source [17]. The melting time was about 1 min. A high quenching rate of ≃300 K/mn [11] was obtained by simply switching off the power source. Clear glass beads with 1–5 mm in diameter were obtained.

All the glasses investigated here were annealed for at least 12 h at about 50–100 K below the estimated T_g. Chemical homogeneity was checked by microprobe analysis and Raman spectroscopy. The samples are labeled XA50.25 according to the charge balancing oxide $X^{\eta+}_{2/n}O^{2-}$ and to the composition comprising 50% mol SiO_2 and 25% mol Al_2O_3. Mass densities ρ were measured with the Archimedes' method in toluene from which we deduced molar volumes V_m. Glass transition temperatures T_g were determined from viscosity measurements. By definition, T_g corresponds to the temperature at which the viscosity is equal to 10^{12} Pa.s. Viscosity measurements were performed using a creep apparatus as detailed in [15,18,19].

2.2. Brillouin scattering

Brillouin scattering experiments were performed using a standard triple-pass tandem interferometer of the Vernier type designed by JRS Scientific Instruments [20]. A single line diode-pumped solid-state laser operating at $\lambda_0 = 532.03$ nm was used to excite the samples with a power of 150 mW at the sample surface. A single photon counting avalanche photo-diode was used to record the Brillouin spectra which were taken at room temperature in both backscattering and symmetric platelet scattering geometry [21] without any polarization analysis. The backscattered light was collected by a high numerical aperture aspheric lens (NA = 0.38). In the platelet geometry, the scattered light was collected at $\theta = 50^{\circ}$ to the incident laser beam by the same aspheric lens. However, the aperture was limited to a curved slit according the spurious geometrical broadening of the Brillouin lines to the resolution of the spectrometer [22]. All the measurements were performed on samples that were optically polished on two opposite parallel faces.

For isotropic materials in backscattering geometry, sound velocities v are related to the measured Brillouin frequency shifts ν_B by the following equation:

$$v = \frac{\nu_B \lambda_0}{2n}, \tag{1}$$

where λ_0 is the incident laser wavelength in air and n is the refractive index of the sample at λ_0. The measured Brillouin lineshapes were analyzed taking into account the slight downshift of the frequency line arising from the finite aperture [23]. In the symmetric platelet geometry, the Brillouin equation reads:

$$v = \frac{\nu_B \lambda_0}{2\sin(\theta/2)}. \tag{2}$$

Selection rules governing Brillouin scattering in isotropic materials show that longitudinal modes only are visible in perfect backscattering geometry whereas both transverse and longitudinal modes can be measured in the symmetric platelet configuration. With combining measurements in both geometries, it is possible to obtain the two sound velocities v_L, v_T and the refractive index of the sample at λ_0. The value of θ was obtained using the Brillouin scattering from the longitudinal mode of a high purity silica glass sample (Suprasil F300, <1 ppm OH) in both geometries (Eq. (1) and (2)) and its known refractive index $n = 1.4607$ at 532 nm. We found $\theta = 49.80^{\circ} \pm 0.16^{\circ}$.

3. Results

3.1. Thermo-physical properties

Table 1 summarizes the measured values of the glass transition temperature T_g and the mass density ρ, as well as the calculated molar volume V_m of the eight tectosilicate glasses. Alkali containing glasses share an almost constant ρ value with a variation of about 1% around 2.46 g.cm^{-3} whereas the mass density of the alkaline earth glasses increases significantly with the increasing molar weight of the charge compensator oxide, from about 2.68 to 3.30 g.cm^{-3}. Conversely, the atomic density which is inversely proportional to V_m decreases with increasing charge compensator cation size for both the alkali and the alkaline earth glasses. As shown in Fig. 1, V_m decreases non-linearly for increasing cation field strength. The latter is here defined as the ratio of the formal charge z divided by the square of the effective cation radius r [32]. Coordination numbers C.N. and corresponding effective radii r [24] used to calculate the cations field strengths z/r^2 are reported in Table 1 for the eight charge-balancing cations. z/r^2 increases along the series $K^+ < Na^+ < Li^+$ and Ba^{2+} $Sr^{2+} < Ca^{2+} < Mg^{2+}$. Accordingly, the cation field strength of the small transition metal cation Zn^{2+} is close to the one of Mg^{2+}. This trend in V_m probably reflects a tighter binding of oxygens to the lighter charge compensator cations, as expected from their larger field strength.

Fig. 2 displays the glass transition temperature as a function of the cation field strength. T_g decreases with z/r^2, both for alkali and alkaline earth glasses, but with very different slopes. For alkali-bearing or alkaline earth-bearing glasses, T_g is thus strongly influenced by the radius of the charge compensator cation. These trends are mostly in line with the viscosity of silica-richer $XAlSi_3O_8$ melts close to T_g which increases in the order Li < Na < Ca < Mg < K [33]. We note however that for the $XAlSiO_4$ glasses here investigated, the T_g of the Ca-bearing glass is higher than the T_g of the Mg compound, in agreement with the smaller radius of the later cation. Such remarkable variations of T_g reveal a strong coupling between the aluminosilicate backbone and the non-framework cation introduced to charge-balance Al in tetrahedral coordination. It has indeed been shown that increasing the field strength of charge compensator cations leads to increasing perturbations and weakening of the aluminosilicate framework [34]. While the trends observed independently for the alkali- or alkaline earth-bearing glasses follow this simple scenario, the substitution of alkaline earth for alkali cations cannot be reconciled with it. The T_g variations could also result from modifications of the aluminosilicate network topology and/or differences in (Si, Al) distributions between alkali- and alkaline earth-bearing glasses [33,35].

3.2. Elastic properties

Fig. 3 shows the Brillouin scattering spectrum from the calcium-bearing aluminosilicate glass obtained in the platelet scattering geometry. For all glasses, both transverse acoustic (TA) and longitudinal acoustic (LA) Brillouin doublets were clearly observed with significant variations of their relative scattered intensities. The intense central unshifted peak is the Rayleigh line, whereas the outer pair of peaks arises from the Rayleigh ghosts of the first order transmitted by the tandem interferometer.

Poisson's ratio v can be readily obtained from the measured Brillouin frequency shifts of the longitudinal ν_{B_L} and the transverse ν_{B_T} modes in