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Rheological and thermodynamic properties of alkaline earth oxide bearing silicate glasses: Implication of structural role of Mg^{2+} in peralkaline glasses

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ABSTRACT

We investigate the rheological and thermodynamic features of SiO_2– Al_2O_3– Bi_2O_3– Na_2O– MeO glasses (Me = Mg, Ca, Sr and Ba) using calorimetry and viscosity measurements. The results show a striking phenomenon: the glass containing MgO shows an obvious deviation in glass transition temperature T_g, configurational heat capacity ΔC_p and dynamic fragility m from the linear tendency of glasses containing Ca^{2+}, Sr^{2+} and Ba^{2+} ions. It is also found that the content of non-bridging oxygen decreases accompanying a increase of bridging oxygen content when CaO is substituted by MgO from the O 1s XPS data. This implies that Mg^{2+} serves as intermediate rather than network modifier like other alkaline earth cations in the studied silicate glass. Furthermore, the configurational entropy $S_c(T)$ based on the theories of Adam-Gibbs (AG) and iso-structural viscosity (η_{iso}) shows that the structural role of Mg^{2+} in the studied silicate glass does not change much with temperature. This is verified by the unique infrared absorption band (~1055 cm^{-1}) of fast-quenched glass Mg.

1. Introduction

The structure and dynamical properties of glass-forming liquids has been a long-standing subject of the condensed matter physics and material science [1]. Mg is a major constituent in most magmas and many commercial glasses, and its multiple coordination in silicate glasses is of interest and importance in both theory and practice. Mg^{2+} was found to be present in four-, five-, and six-fold coordination in silicate glasses depending on the glass composition and the experimental techniques employed [2–6]. Extensive effort have been devoted to clarifying what determine the structural role of Mg^{2+} in silicate glasses using EXAFS [7], NMR spectroscopy [8–10], high pressure x-ray diffraction [11] and MD simulation technique [12]. However, there is considerable disagreement between certain studies on structural role of Mg^{2+} due to the lack of unambiguous information on its local environment.

Most information about the structure of silicate liquids has come from the study of that of silicate glasses at the glass-transition temperature (T_g). In-situ high-temperature ^{25}Mg NMR shows that Mg^{2+} may undergo a change in coordination in silicate liquids with decreasing temperature [10]. However, it is difficult to collect the ^{25}Mg NMR spectra in the high-temperature range because of its low resonance frequency. Viscosity and heat capacity data, which are easily obtained, has been widely recognized that they are intimately related to the structure of silicate liquid, and become the most promising approaches to the prediction of structural relaxation time and the relationship between property and melt structure [13–15]. In particular, the configurational entropy (S_c) derived from Adam-Gibbs (AG) model, is sensitive to the structure change of silicate liquids. In details, the S_c can be seen as separated into two parts, i.e., chemical and topological parts. The chemical contribution originates in the mixing of different elements and it is independent of temperature. However, the contribution from the topological arrangement is related to the distribution in bond angles and length, the various coordination states, the way bridging and non-bridging oxygens bonded to Si and intermediate range order as well.

In this work, we will investigate the structural role of Mg^{2+}

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using viscosity as the fundamental tool by comparing the rheological and thermodynamic parameters of peralkaline silicate glasses containing Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions. To lower the crystallization tendency, we introduce a small amount of Al_2O_3 and Bi_2O_3 into the glass compositions to enhance their higher glass-forming ability and stability (compared to alkali and alkaline earth oxides) [16,17]. Four compositions containing MgO, CaO, SrO or BaO were studied to quantify the effect of alkaline earth cations on viscosity. These data were then combined with calorimetric data and interpreted within the framework of the Adam-Gibbs theory to shed more light on the relationship between configurational entropy and structure of Mg^{2+} bearing peralkaline silicate glass in a wide temperature range.

2. Experimental

The glasses in this work have the following composition (mol%): $64SiO_2- 1.8Al_2O_3- 2.2Bi_2O_3- 24Na_2O- 8MeO$ system (Me = Mg, Ca, Sr and Ba). The glasses containing MgO or CaO or SrO or BaO are hereafter designated as Mg, Ca, Sr and Ba, respectively. The raw materials are reagent grade chemicals (SiO_2, Al_2O_3, Bi_2O_3, Na_2CO_3, MgO, $CaCO_3$, $SrCO_3$ and $BaCO_3$). It is noted that MgO is used instead of $MgCO_3$ to avoid the reaction between $MgCO_3$ with H_2O at high temperature [18]. The mixtures of raw materials were completely melted in a lidded platinum crucible placed in an electric furnace at 1693 K for 2 h. Subsequently, the melts were cast onto a stainless steel mold and then annealed in a furnace slightly below their respective glass transition temperatures for 1 h. In addition, the fast-quenched glasses were obtained by pouring the glass melts into cold water in order to maintain the structure in liquid state.

The isobaric heat capacity (C_p) of the glasses was measured by using a differential scanning calorimeter (DSC) (Setaram STA Labsys evo) in N_2 atmosphere. All the samples underwent two runs of up- and downscans at 10 K/min. The C_p curve for each measurement was calculated relative to the C_p curve of a sapphire reference material after subtraction of a correction run with empty crucible.

Equilibrium viscosity was measured by beam-bending (in low-temperature region) and concentric cylinder (in high-temperature region) experiments. For beam-bending experiments, bars of 60 mm length and 3 mm × 5 mm cross section were cut from the bulk glasses. The bars were bent in a symmetric three-point forced bending mode with 50 mm open span at a constant heating rate of 5 K/min (BBV-1000, Orton, America). The low viscosity data ($<10^3$ Pa s) in high temperature range are measured using the SRV-1600 cylinder concentric viscometer (Orton, America) under the atmospheric condition. During cooling of the melts at an interval of 25 K, every viscosity value was recorded until the melt was held on at the isolated temperatures for 30 min in order to insure the equilibrium state. The standard glass NIST SRM 717A was used for calibration of the viscometers [19]. Good agreement was achieved between the measured and the standard values. The error range of the viscosity measurement is $\Delta\log_{10}\eta = \pm 0.05$ (η in Pa s).

X-ray Photoelectron Spectroscopy (XPS) was performed in a VG Escalab MK spectrometer, using monochromatic Mg-K_α X-ray ($h\upsilon = 1253.6$ eV). The pressure inside the analyzer chamber was $\sim 2 \times 10^{-8}$ pa. Surface charging was minimized by flooding the surface with low energy electrons. The C1s peak at 284.8 eV was used as a charge reference to calibrate the binding energies.

The infrared absorption spectra of the fast-quenched glasses were measured at room temperature in the wavenumber range 400–1600 cm^{-1} by a Fourier Transform computerized infrared spectrometer type JASCO Corp., FT/IR-430, Japan. The samples were investigated as fine powders which were mixed with KBr in the ratio (1:100 mg glass powder to KBr respectively). The weighed mixture was then subjected to a pressure of 5 ton/cm^2 to produce clear homogenous discs. The IR spectra were measured immediately after disc preparation.

3. Results and discussion

Fig. 1(a) shows the heat capacity curves obtained from the first and second upscans, for fast-quenched glass Mg, which are denominated C_{p1} and C_{p2}, respectively. The C_{p1} curve reflects thermal history of the fast-quenched process, and the C_{p2} curve reflects the thermal history determined by the cooling rate of 10 K/min. The fictive temperature T_f of fast-quenched glass Mg is obtained using area-matching method, especially, T_g is equal to the T_f value for which the glass underwent a thermal history with cooling rate of 10 K/min [21–23]. Similarly, the T_g values of glasses containing Ca^{2+}, Sr^{2+} and Ba^{2+} ions can be obtained from C_{p2} curves as shown in the inset of Fig. 1(a). In addition, the configurational heat capacity $\Delta C_p = C_{pl} - C_{pg}$, are also determined using the C_p data [25,26], in which C_{pg} is the heat capacity value of glass at T_g, C_{pl} is the offset value of the C_p overshoot above the glass transition range. It is shown that C_p of the liquid state fluctuates in a narrow range when temperature is increased up to around 1200 K, thus C_{pl} value can approximately represent the heat capacity of the liquid state. T_g and ΔC_p are plotted as a function of ionic radius of alkaline earth cations (r) in Fig. 1(b) and listed in Table 1. They are found to increase linearly in the order of glasses Ba < Sr < Ca, this is in agreement with the previous observations that T_g and ΔC_p increase with increasing field strength of the network-modifying ca ions in the melt [27,28]. Whereas glass Mg deviates obviously from this tendency for both T_g and ΔC_p, this indicates that Mg^{2+} plays a different structural role from other three alkaline earth cations in the studied glasses. In general, Ca^{2+}, Sr^{2+} and Ba^{2+} ions have the same structural role acting as network modifier in silicate glasses, the linear increase in T_g and ΔC_p of three glasses is due to the fact that the overall network is strengthened due to the enhanced attraction of Me^{2+} ions to their surrounding structural groups of $[SiO_4]$ tetrahedra with decreasing the r value. However, partial Mg^{2+} may be 4- or 5-fold coordinated in glass Mg, this indicates that MgO, rather than depolymerizing the silicate network by acting as a network modifier, is behaving in part, as an intermediate oxide. In this case Mg^{2+} is entering the silicate network, removing network modifying ions for charge compensation and resulting in the observed polymerization of the silicate network. On the other hand, the lower bond strength of Mg–O compared to Si–O weakens the glass network. Consequently, a lower potential energy barrier needs to be overcome for the glass structure to rearrange to be in equilibrium state with temperature in the glass transition range.

Measured Viscosity (η) data for the four glass compositions are shown as a function of T_g/T in Fig. 2(a). For all the glass melts it is clear that the temperature dependence of η over the studied temperature range presents a non-arrhenius characteristic. Moreover, as shown in the inset of Fig. 2(a), glass melts containing Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions show different responses of η to the temperature change, which is dependent on the temperature ranges. In the low-temperature (LT) region, the η value increases in the order of glasses Ba < Sr < Mg < Ca. As temperature increases, the strength of the chemical bonds, including the network-forming ions and the network-modifying ions become weaker and more unstable, and hence leading to a decrease in viscosity. However, four glass melts show a different η dependence on composition in the HT region compared with that in the LT region, i.e., η increases in the order of glasses Ba < Sr < Ca < Mg in the HT region.

Furthermore, the degree of viscosity change with temperature can be expressed by dynamic fragility (m), since m is a measure of the deviation of the melt flow behavior from Arrhenian behavior. In