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Determination of complex-specific heat and fragility of sodium borate glasses by temperature-modulated DSC

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Abstract The frequency dependences of the complex-specific heat of the sodium borate glasses, $x\mathrm{Na_2O}\cdot(100-x)\mathrm{B_2O_3}$, where x denotes molar concentration of Na_2O, have been investigated by temperature-modulated DSC. The temperature dependences of α-relaxation time have been analyzed in Angell plot, and the fragility index has been determined. The composition dependence of the fragility index has been discussed on the basis of the variations of the structural units of the borate network. The origin of the fragility of the borate system relates to the distribution of the coordination number of boron atom.

Keywords Complex-specific heat · Fragility · Dynamic glass transition · Sodium borate glasses · Temperature-modulated DSC (TMDSC) · Structural relaxation

Introduction

The so-called Angell plot was introduced by Laughlin and Uhlmann in 1972 [1], and Angell categorized glass-forming liquids by using a concept of "fragility" as one of the most successful classifications of various glass-formers [2] on the basis of a temperature dependence of viscosity η. In the Angell plot where logarithm of η or α-relaxation time versus T_g/T, the liquids exhibiting an Arrhenius behavior are categorized into "strong" glass-forming materials and exhibiting a Vogel-Fulcher behavior are called "fragile." The deviation from an Arrhenius law is quantitatively characterized by a fragility index m defined by the following equation:

$$m = \lim_{T \to T_g} \left| \frac{\mathrm{d}\log\tau}{\mathrm{d}(T_g/T)} \right| \tag{1}$$

Although a variation of a fragility index m has been extensively discussed, an origin of the fragility is not still understood.

For alkali borate glasses, it is known that the additions of alkali metal oxide to pure B_2O_3 glass cause a marked change of the fragility from "strong" to "fragile." Since it is also known that physical properties vary remarkably over a wide composition range, there are various studies for alkali borate glasses. For instance, the intermediate structures in the borate networks were discussed by NMR and Raman spectroscopy [3–7]. The elastic properties of alkali borate glasses were investigated by ultrasonic pulse-echo overlap method and Brillouin scattering [8–11]. Recently, the non-Debye nature of thermal relaxation in lithium borate glasses was investigated by temperature-modulated DSC (TMDSC) [12] in relation with the intermediate structural units. In this context, the alkali borate glasses play an important role in glass sciences as a typical network oxide glass-forming material to understand a relationship between fundamental physical properties and glass network structures.

A viscosity or dielectric measurements are frequently used to investigate the fragility as a property of superliquid state; however, it is sometimes difficult to apply these experiments. When a material has poor glass-forming ability, the only thin and small glass samples are obtained. In this case, it is difficult to perform the viscosity measurement. In the case a material has high ionic conductivity, it is also difficult to perform the dielectric spectroscopy. In this article

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to solve these problems, the TMDSC has been employed, and the temperature evolutions of the α-relaxation time $\tau(T)$ in the vicinity of glass transition temperature T_g for the sodium borate binary glasses have been investigated by TMDSC and then determined the fragility index with Angell plot.

Experimental

Sample preparation

The composition formula of sodium borate glasses is denoted by $x\mathrm{Na_2O}\cdot(100-x)\mathrm{B_2O_3}$, where x is a molar concentration of Na_2O. All glass samples were prepared by "solution method" [10, 11] with high homogeneity in order to investigate the inherent nature of the binary system. The starting materials were analytical-reagent grade $\mathrm{NaOH \cdot H_2O}$ ($\geq$99.99% purity) and H_3BO_3 ($\geq$99.99% purity). To achieve the high homogeneity of the glass-forming materials, they were first made to react in an aqueous solution in a Teflon beaker. After complete evaporation of water of the solution in a drying oven kept at 130 °C for 1–3 days, the obtained powder was melt in the Pt crucible at 900–1100 °C depending on the composition for 1.5 h. The glass samples were obtained by quenching the melt by aluminum plates. The samples were prepared in the composition range $3 \leq x \leq 43$ mol%. We attempted to prepare the glasses with $x > 43$, but all of the melts crystallized quickly.

To check for water contamination, the mass loss measurement was previously performed for the lithium borate glass containing 64 mol% Li_2O (64LiBO) [13], indicating that the water was driven out in the drying oven and in the first 5–10 min for melting process. In the case of the lithium borate glasses, it was concluded that the water contamination was negligible. Moreover, the actual composition of the 64LiBO was exactly analyzed by the potentiometric titration, and compared to the expected composition. It was also found that the loss of the alkali oxide during melting was negligible. Therefore, in this study for the sodium borate glasses, the actual compositions of the samples have been assumed to be identical with the expected composition.

Temperature-modulated DSC

The detail descriptions for TMDSC measurements were given in [12–14]. A modulated heating rate used in TMDSC is composed by a liner and sinusoidal heating rate, and thus a resultant heat flow also contains the linear and modulation components. From the latter, one can obtain an absolute value of a complex-specific heat $\left|C_p^*(\omega)\right|$ and a phase angle φ. Complex-specific heat $C_p^*(\omega)$ is then calculated by the following equations and separated into a real part C_p' and an imaginary part C_p'' by using a phase angle φ,

$$\begin{aligned} C_p^*(\omega) &= \left|C_p^*(\omega)\right| \cdot e^{-i\varphi} = C_p' - iC_p'', \\ C_p' &= \left|C_p^*(\omega)\right| \cos\varphi, \\ C_p'' &= \left|C_p^*(\omega)\right| \sin\varphi, \end{aligned} \tag{2}$$

In order to calculate C_P' and C_P'' correctly, the determination of a raw phase angle related to the change of thermal conductivity is necessary. Therefore, in this study, the raw phase angles were corrected as suggested by Weyer et al. [15]. The powerfulness of the phase angle correction has been shown in [16] in the case of the measurement of the complex-specific heat for the borate system.

DSC 2920 and DSC T-zero Q200 (TA Instruments, Tokyo, Japan) equipped with Liquid Nitrogen Cooling System were used to measure a complex-specific heat of the sodium borate glasses. A glass sample was put into an aluminum pan, and the mass of each sample was about 10.0 mg. Then, the sample pan was heated over T_g with the temperature control procedure; linear heating rate was 0.5 or 1.0 °C/min, temperature modulation amplitude was ±1 °C, and temperature modulation period was from 200 to 20 s. Dry nitrogen was flowed in the sample chamber as a purge gas with the flow rate of 20 mL/min during the experiments.

Results and discussion

Figure 1 shows the real and imaginary parts of the complex-specific heat with 100 s of the temperature modulation period ($x = 15$ mol%). T_g^ω is defined as a peak temperature in an imaginary part, roughly corresponding to the dynamic glass transition temperature, where ω is an angular frequency. The composition dependence of T_g^ω ($\omega = 2\pi/100$ rad/s) is shown in Fig. 2. The values of T_g^ω gradually increase with the increase in Na_2O in the composition range $0 < x \leq 19$, and shows the broad maximum between $x = 21$ and 33 mol%. In the alkali borate glass system, the random network of pure B_2O_3 glass is constructed by BO_3 triangular planar units with bridging oxygen atoms. The addition of alkali metal oxide to B_2O_3 causes a change of coordination number of boron atom from 3 to 4, resulting the formation of BO_4 tetrahedral units. Further addition of alkali oxide to B_2O_3 causes the re-change of coordination number of a boron atom from 4 to 3 with non-bridging oxygen atoms [3]. The composition dependence of T_g^ω can be explained by the change of the coordination number and the creation of non-bridging oxygen atoms.

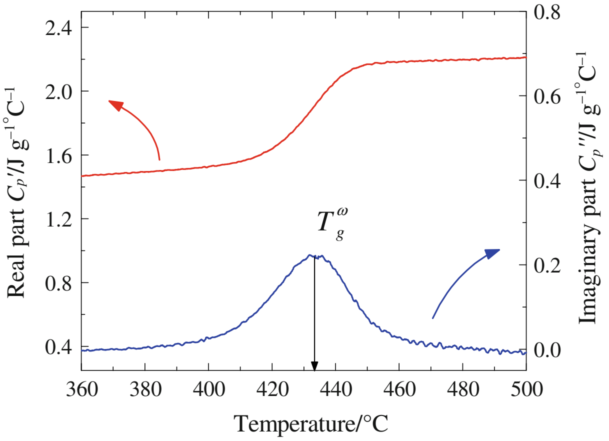

Fig. 1 Real and imaginary parts of the complex specific heat ($x = 15$ mol%). The period of the temperature modulation is 100 s

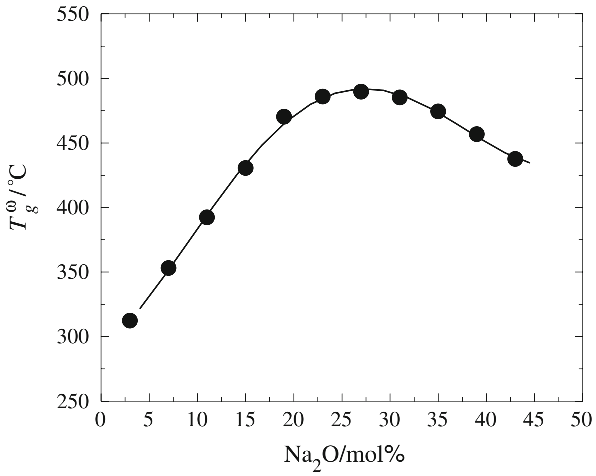

Fig. 2 Composition dependence of T_g^ω ($\omega = 2\pi/100$ rad/s), defined as a peak temperature in a imaginary part. The *solid line* is a guide for eyes

The compositional variation of the fragility with Na$_2$O has been discussed below. Firstly, the fragility index *m* should be determined quantitatively. Figure 3 shows the frequency dependences of the real and imaginary parts of the complex-specific heat ($x = 41$ mol%) by measuring with the different temperature modulation periods. A glass transition is a typical relaxation phenomenon, and thus a specific heat can be extended to a frequency-dependent physical quantity [12] in the vicinity of a glass transition temperature. In Fig. 3, the peak temperatures of the imaginary parts shift to the higher as the temperature modulation period becomes shorter. The α-relaxation time τ is most probable with the modulation period applied to the system, and can be obtained by

$$\tau = \frac{1}{\omega} = \frac{P}{2\pi}, \qquad (3)$$

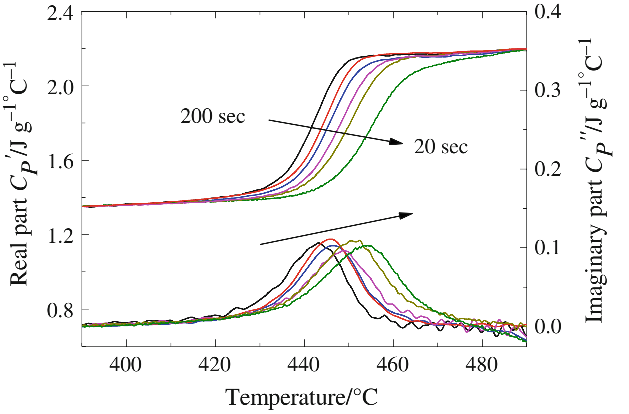

Fig. 3 Frequency dependences of the real and imaginary parts of the complex-specific heat ($x = 41$ mol%) observed by T-zero DSC Q200. The modulation period varies from 200 to 20 s

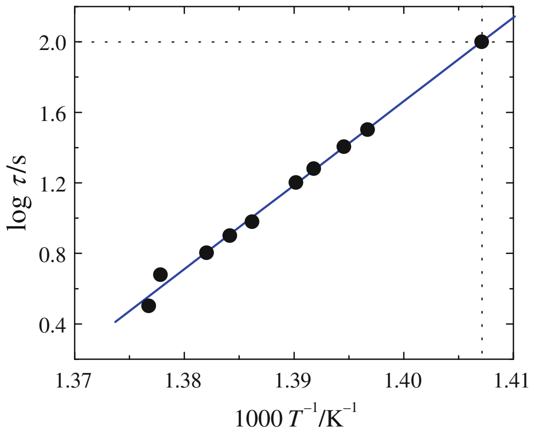

Fig. 4 Arrhenius plot of the α-relaxation times τ and peak temperatures of the imaginary parts ($x = 41$ mol%). The *straight line* is the fit by a least square method

where *P* is the temperature modulation period. From the values obtained for τ and peak temperatures of the imaginary part, the Arrhenius plot has been performed as shown in Fig. 4. The values of T_g have been determined by the extrapolation from the present experimental data, where T_g is defined as the temperature when τ becomes 100 s. Then, the horizontal axis in Fig. 4 is normalized by the value of T_g determined; such normalized Arrhenius plot is called Angell plot. The Angell plots of $x = 11$ and 41 mol% are shown in Fig. 5, from which the fragility index *m* can be calculated by Eq. 1 corresponding to the steepness of the linear curve. As seen in Fig. 5, the steepness increases with the increase in Na$_2$O, namely the change of the fragility from "strong" to "fragile" with the increase in Na$_2$O content has been clearly observed.

The composition dependence of *m* is shown in Fig. 6, where the solid circles denote the results by the TMDSC

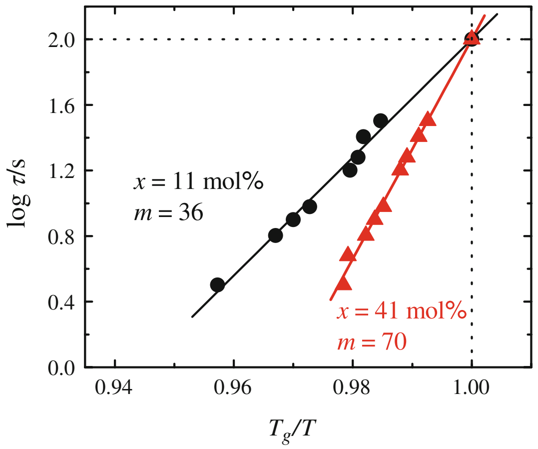

Fig. 5 Angell plot of the glasses with $x = 11$ and 41 mol%. The *horizontal axis* is normalized by T_g determined by the Arrhenius plot. The *straight lines* are the fits by a least square method

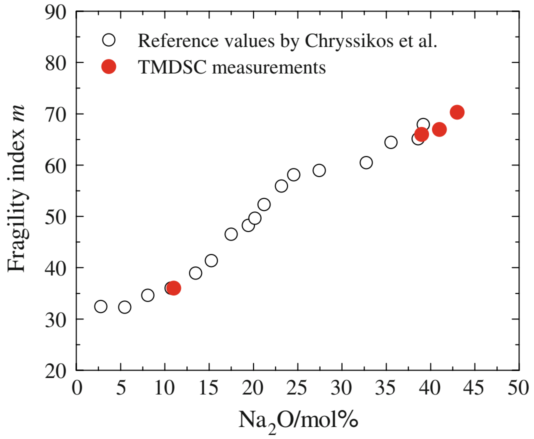

Fig. 6 Composition dependence of the fragility index *m*. *Solid circles* denote the results of the TMDSC measurements. *Open circles* denote the reference values summarized by Chryssikos et al. [17]

measurements and the open circles denote those of the viscosity measurements summarized by Chryssikos et al. [17] as the reference values. The results by the TMDSC measurements are in good agreement with those of the viscosity measurement, and this fact shows the reliability and powerfulness of the TMDSC to investigate the fragility in the vicinity of T_g.

To understand the composition dependence of m, the theoretical model for the fragility proposed by Vilgis [18, 19] is useful. In the model, Vilgis suggested that the degree of the fragility relates to the distribution of the coordination number of a key element. For instance, a silica glass SiO_2 belongs to the "strong" since it has a fixed covalent bonding of Si atom, which is 4-coordinated with oxygen atoms. On the other hand, *o*-terphenyl, one of the well-known molecular glass-formers, belongs to the typical "fragile" since its coordination number fluctuates from 11 to 16. In the case of the alkali borate system, the coordination number of boron atom fluctuates from 3 to 4 with the compositions. In our previous studies for lithium borate glasses, the fragility index m has been investigated by TMDSC over a wide composition range up to $x = 64$ mol%, and its composition dependence has been discussed by the Vilgis model [16, 20].

The distribution $F(x)$, or variance in this study, of the coordination number of boron atom as a function of x can be calculated using Eq. 4 on the basis of the discrete probability theory,

$$\begin{aligned} &F(x) = \left(3 - \overline{Z}(x)\right)^2 \cdot N_3(x) + \left(4 - \overline{Z}(x)\right)^2 \cdot N_4(x), \\ &\overline{Z}(x) = 3 \cdot N_3(x) + 4 \cdot N_4(x), \\ &N_3(x) + N_4(x) = 1, \end{aligned} \tag{4}$$

where $\overline{Z}(x)$ is a mean coordination number of boron atom and $N_3(x)$ or $N_4(x)$ is a fraction of 3- or 4-coordinated boron atom, respectively. In the lithium borate system, the trend of the composition dependence of m and distribution of coordination number of boron atom have been similar, and thus this result indicated that the origin of the fragility relates to the degree of the variation of the coordination number of a system. Namely, a distribution of a coordination number of a glass forming materials controls a degree of a temperature evolution of α-relaxation time, or fragility.

In this article, the distribution of coordination number of boron atom of sodium borate glasses has been calculated by Eq. 4. The values of $N_4(x)$ are taken from the results of the NMR study by Bray and O'Keefe [3]. The composition dependence of the distribution is shown in Fig. 7. The behavior in Fig. 7 is roughly similar to that of Fig. 6 in the composition range studied, in the way that the shapes of both curves increase with the increase in Na_2O. Considering the shapes in more detail, the former $m(x)$ increases continuously and shows the bump between $x = 20$ and 35 mol%, whereas the latter $F(x)$ increases rather monotonous way. To make clear the correlation, the fragility $m(F)$ is plotted as a function of the distribution of the coordination number $F(x)$ in Fig. 8. The plots in Fig. 8 were attempted to be fitted by a quadratic function by Eq. 5 for simplicity,

$$m(F) = m_0 + cF^2, \tag{5}$$

where m_0 and c are constant as the fitting parameters. The solid line in Fig. 8 shows the fitted curve by Eq. 5. The fitting result suggests that there is a simple positive correlation between the fragility and the coordination number. The cases in sodium borate glass system also have provided the experimental evidence to support the prediction by Vilgis as in the case of the result of lithium borate glasses.

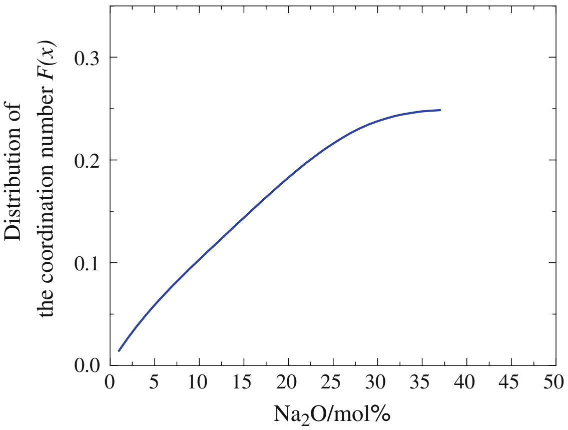

Fig. 7 Composition dependence of the distribution of the coordination number of boron atom calculated by the NMR results by Bray and O'Keefe [3]

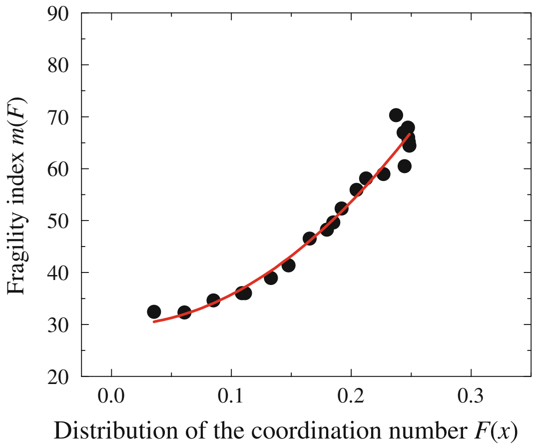

Fig. 8 Correlation between the fragility and coordination number of boron atom. The *solid curve* is the fit of an empirical quadratic function by a least square method

It should be discussed on the temperature effect on the coordination changes of boron atoms, since the experiments by TMDSC used in this article scan a temperature range over T_g, whereas the reference values of the coordination number of boron atom used for the calculation are those in the glassy state. The recent studies of the high-temperature neutron diffraction [21] and Raman spectroscopy [22] have discussed on the temperature-induced boron coordination change in a glassy state and liquid. In [21], it has been revealed that the fraction of 4-coordinated boron atom, $N_4(x)$, of 35.8 $K_2O{\cdot}64.2B_2O_3$, decreases from 0.40 in glassy state to 0.32 in melt at 1200 K. In this study, the TMDSC observed the temperature dependences of α-relaxational process in the vicinity of T_g (but, $T > T_g$) in such a region $0.95 < T_g/T < 1$ (see Fig. 5). In this narrow region, it can be assumed that the structures of the sodium borate supercooled liquids investigated by TMDSC should be identical to those of the glasses, namely the temperature effects on the coordination change of boron atom can be ignored. One of the evidence to prove the validity of such assumption is the study of the high-temperature Raman spectroscopy by Yano et al. [22], where the temperature variation of the fraction of the 4-coordinated boron, N_4, has been presented (see Fig. 4 of [22]), indicating the N_4 at the glassy state is not different from that in the vicinity of T_g. The coordination number starts to convert from 4 to 3 at higher temperature far above T_g.

Conclusions

The complex-specific heat of sodium borate glasses, $x\text{Na}_2\text{O}{\cdot}(100-x)\text{B}_2\text{O}_3$, has been investigated by TMDSC. The values of T_g^{ω} drastically vary with Na_2O composition, and the composition dependence relates to the change of the coordination number of boron atom.

The compositional variations of the fragility have been investigated by observing the frequency and temperature dependences of the complex-specific heat in the vicinity of the glass transition temperature T_g. The α-relaxation time and peak temperature of the imaginary part of the complex-specific heat have been analyzed with Angell plot, and then the degree of fragility has been characterized by fragility index m. The values of m obtained by TMDSC measurement have been in good agreement with those of viscosity measurement. The TMDSC is a powerful tool to investigate the temperature evolution of the α-relaxation time in the vicinity of T_g.

The clear correlation between the fragility *m(x)* and the distribution of the coordination number of boron atom *F(x)* has been revealed for the case of sodium borate glass system. The composition dependence *m(x)* can be explained by the distribution of the coordination number of boron atom. Namely, the distribution of the coordination number of the glass forming materials may control the degree of the temperature evolution of α-relaxation time, or fragility.

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