

ANHARMONICITY AND FRAGILITY IN LITHIUM BORATE GLASSES

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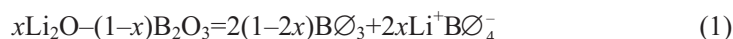
Abstract

Since the physical properties of lithium borate glasses $x\text{Li}_2\text{O}-(1-x)\text{B}_2\text{O}_3$ ($0 \leq x \leq 0.28$) vary over a wide range with the composition, this binary system is particularly suitable for studying the relationship between vibrational anharmonicity and fragility. The density, the linear expansion coefficient, the longitudinal and transverse ultrasonic velocities and their respective temperature coefficients of the velocities are measured, from which the vibrational anharmonicity in lithium borate glasses is evaluated with the help of the Grüneisen parameter at the Debye cut-off frequency and the Anderson–Grüneisen parameter: these two parameters plotted vs. composition have the same characteristics with minima at $x \approx 0.08$. The fragility is evaluated from the temperature width of the glass transition; the fragility also shows a minimum at $x \approx 0.08$. The presence of minima at $x \approx 0.08$ is ascribable to the fact that the crosslinking density between six-membered rings in the glass reaches a maximum at this composition. We show that the anharmonic parameters strongly correlate with the fragility metrics.

Keywords: anharmonicity, fragility, lithium borate glasses

Introduction

In lithium borate glasses, the physical properties such as density and velocity of sound vary over a wide range with the composition [1]. It may then be interesting to study the change in vibrational anharmonicity or in fragility in this binary system as a function of the glass composition. The compositions of lithium borate glasses are denoted by $x\text{Li}_2\text{O}-(1-x)\text{B}_2\text{O}_3$, where x is the mole fraction of Li_2O . Lithium borate glasses have been prepared in the bulk-glass formation range $0 \leq x \leq 0.28$. The short-range structure of lithium borate glasses is briefly summarized in the following on the basis of nuclear magnetic resonance (NMR) studies of boron [2–4]. Lithium borate glasses in the bulk-glass formation range are formed by two structural units, $\text{B}\emptyset_3$ and $\text{Li}^+\text{B}\emptyset_4^-$, where \emptyset represents a bridging oxygen. Then, the glass composition can be expressed in terms of the two structural units:



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The structural units combine to form different kinds of six-membered borate rings. Pure boron oxide (B_2O_3) glass consists both of six-membered boroxol rings constructed from three $B\text{O}_3$ units and of non-ring $B\text{O}_3$ units located outside boroxol rings; the mole fraction of boron atoms in boroxol rings is about 0.65 so that the mole fraction of boron atoms outside boroxol rings is about 0.35. With the initial addition of Li_2O to B_2O_3 , non-ring $B\text{O}_3$ units are preferentially converted into $B\text{O}_4^-$ units; with the further addition, boroxol rings are converted into six-membered rings with one $B\text{O}_4^-$ tetrahedron (i.e., triborate, tetraborate, or pentaborate) and into six-membered rings with two $B\text{O}_4^-$ tetrahedra (i.e., diborate).

It has been pointed out that the concept of fragility characterizing a glass-forming liquid is closely related to the anharmonicity of the resulting glassy state [5]. The present authors have measured the density and the velocity of sound in lithium borate glass as a function of composition [1] and also studied the microstructure of this glass by means of Raman spectroscopy [6, 7]. In this paper, the linear expansion coefficient and the temperature coefficients of travel times for longitudinal and transverse ultrasonic waves are measured, from which two different parameters representing anharmonicity are determined. The temperature width of glass transition is also measured and has been used to evaluate the fragility of this glass-forming liquid. We show that fragility strongly correlates with anharmonicity.

Parameters representing anharmonicity

The anharmonic vibration of atoms in a solid material has often been evaluated in terms of Grüneisen parameter [8]. Let T , p , and V be thermodynamic temperature, pressure, and volume, respectively. If anharmonic terms of atomic vibration are not present, the cubic expansion coefficient defined as $\alpha_v = (1/V)(\partial V/\partial T)_p$ vanishes and the compressibility defined as $\kappa = -(1/V)(\partial V/\partial p)_T$ is independent of temperature and pressure [9]. Let ν be the frequency of atomic vibration. Grüneisen [10] defined the so-called Grüneisen parameter, γ , in two different ways (Eq. 10 of Grüneisen's original paper [10]):

$$\gamma = -\frac{1}{\alpha_v} \frac{\partial \ln \nu}{\partial T} \quad (2)$$

and

$$\gamma = \frac{1}{\kappa} \frac{\partial \ln \nu}{\partial p} \quad (3)$$

Equation (2) represents the change in vibrational frequency with temperature, while Eq. (3) represents the change in vibrational frequency with pressure.

Grüneisen [10] also defined another set of parameters representing anharmonicity (Eqs (29) and (36a) of Grüneisen's original paper [10]) by

$$\delta_s = -\frac{1}{\alpha_v} \left(\frac{\partial \ln K_s}{\partial T} \right)_p \quad (4)$$

and

$$\delta_T = -\frac{1}{\alpha_v} \left(\frac{\partial \ln K_T}{\partial T} \right)_p \quad (5)$$

where K_s and K_T are adiabatic bulk modulus and isothermal bulk modulus, respectively. The parameters δ_s and δ_T are often called Anderson–Grüneisen (A–G) parameters [11, 12]. If anharmonic terms are not present, the elastic constants such as bulk modulus are independent of temperature and pressure [9]. It may thus be understood that Eqs (4) and (5) represent anharmonic properties.

In this paper, we evaluate the anharmonicity of lithium borate glasses on the basis of Eqs (2) and (4). By measuring the travel times, τ_l and τ_t , for one round trip of longitudinal and transverse ultrasonic waves in a specimen whose length is denoted by l , we obtain the velocities, c_l and c_t , of longitudinal and transverse ultrasonic waves from $c_l=2l/\tau_l$ and $c_t=2l/\tau_t$, respectively. In order to determine the parameters given by Eqs (2) and (4), we measured the linear expansion coefficient $\alpha_l=(1/l)(dl/dT)$ and the temperature coefficients of travel times, $(1/\tau_l)(d\tau_l/dT)$ and $(1/\tau_t)(d\tau_t/dT)$, for longitudinal and transverse ultrasonic waves, respectively. Differentiating $c_l=2l/\tau_l$ and $c_t=2l/\tau_t$ with respect to temperature, we obtained the temperature coefficients of the velocities for longitudinal and transverse ultrasonic waves:

$$k_l \equiv (1/c_l)(dc_l/dT) = -(1/\tau_l)(d\tau_l/dT) + \alpha_l \quad (6)$$

and

$$k_t \equiv (1/c_t)(dc_t/dT) = -(1/\tau_t)(d\tau_t/dT) + \alpha_l \quad (7)$$

It is possible to define the Debye cut-off frequency ν_D even in the case of glasses [13] so that we can evaluate Eq. (2) at ν_D :

$$\gamma_D = -\frac{1}{\alpha_v} \frac{\partial \ln \nu_D}{\partial T} \quad (8)$$

The Debye cut-off frequency can be expressed as

$$\nu_D = \left(\frac{6\pi^2 N}{V} \right)^{1/3} c_D \quad (9)$$

where N is the number of atoms in the volume V and c_D is the Debye mean velocity given by

$$c_D = \left\{ \frac{1}{3} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \right\}^{-1/3} \quad (10)$$

Differentiating Eq. (10) with respect to temperature, we have the expression for the temperature coefficient of the Debye mean velocity:

$$k_D \equiv \frac{\partial \ln c_D}{\partial T} = \frac{c_D^3}{3} \left(\frac{k_1}{c_1^3} + \frac{2k_t}{c_t^3} \right) \quad (11)$$

Differentiating the natural logarithm of Eq. (9) with respect to temperature, we have

$$\frac{\partial \ln v_D}{\partial T} = k_D - \frac{\alpha_v}{3} \quad (12)$$

so that γ_D can now be calculated from

$$\gamma_D = \frac{1}{3} - \frac{k_D}{\alpha_v} \quad (13)$$

We shall consider the A-G parameter defined by Eq. (4). With the mass density ρ , c_1 and c_t , the adiabatic bulk modulus K_s can be expressed as

$$K_s = \rho [c_1^2 - (4/3)c_t^2] \quad (14)$$

Differentiating Eq. (14) with respect to temperature, we have

$$(\partial K_s / \partial T)_p = 2\rho [c_1^2 k_1 - (4/3)c_t^2 k_t] - \alpha_v K_s \quad (15)$$

so that the A-G parameter δ_s can be calculated from

$$\delta_s = 1 - \frac{2\rho}{\alpha_v K_s} [c_1^2 k_1 - (4/3)c_t^2 k_t] \quad (16)$$

Experimental

A series of lithium borate glasses was prepared in the bulk-glass formation range $0 \leq x \leq 0.28$ without strains or bubbles in order that they might transmit ultrasound satisfactorily. A powder synthesized chemically from LiOH·H₂O and H₃BO₃ was fused in a 20 cm³ platinum crucible at temperatures from 1050 to 1300°C for about 4 h by heating in a SiC resistance electric furnace. The melt was then poured into a cylindrical graphite mold, 15 mm in diameter and 30 mm deep, which had been preheated at 300°C in an electric muffle furnace. Subsequently, the cast glass in the mold was cooled at a rate of 1 K min⁻¹ to room temperature. The residual melt was poured onto an aluminum plate and later used for chemical analysis and for differential thermal analysis (DTA). Each cast glass was annealed at the glass transition temperature determined by DTA.

The density of each annealed glass was measured at 298 K by a hydrostatic weighing method using a silicon single crystal as the density standard. Each annealed glass was ground and polished to give a pair of end faces that were flat and parallel. Inspection with a strain viewer showed that all specimens were transparent and free

from strains or bubbles. The ultrasonic travel time was measured at a frequency of 10 MHz and at a temperature of 298 K by means of the pulse-echo overlap method [14]. X-cut and Y-cut quartz transducers resonating at a fundamental frequency of 10 MHz were used for the longitudinal wave and for the transverse wave, respectively. The transducer was bonded to the specimen on one of the two parallel faces with phenyl benzoate and used for both generation and detection of ultrasound. Adjacent two echoes were overlapped according to the McSkimin criterion [15] in order that the ultrasonic travel time could be measured within an error of 0.02%. The velocities, c_l and c_t , of longitudinal and transverse ultrasonic waves were determined at 298 K from τ_l and τ_t measured in this way and the specimen length measured with a micrometer reading to 1 μm . Subsequently, τ_l and τ_t were measured as a function of temperature in the temperature range 0 to 60°C. Both τ_l and τ_t changed linearly with temperature so that $(1/\tau_l)(d\tau_l/dT)$ and $(1/\tau_t)(d\tau_t/dT)$ were evaluated from their respective slopes at 298 K. After the ultrasonic properties had been measured for each glass, the linear expansion coefficient was determined in the temperature range 50 to 150°C by a standard horizontal vitreous silica dilatometer; the change in specimen length with temperature was measured by a differential transformer. The dilatometer was calibrated beforehand vs. the thermal expansivity of platinum [16] by making use of a platinum rod.

Results and discussion

Figure 1 shows the density and the linear expansion coefficient as a function of composition. The density increases monotonically with composition, while the linear expansion coefficient shows a broad minimum at around $x=0.20$. Figure 2 shows the longitudinal and transverse velocities and their respective temperature coefficients. Each of the velocities increases monotonically with composition while each of the temperature coefficients shows a sharp minimum at $x=0.08$. Figure 3 shows the anharmonic parameters, γ_D

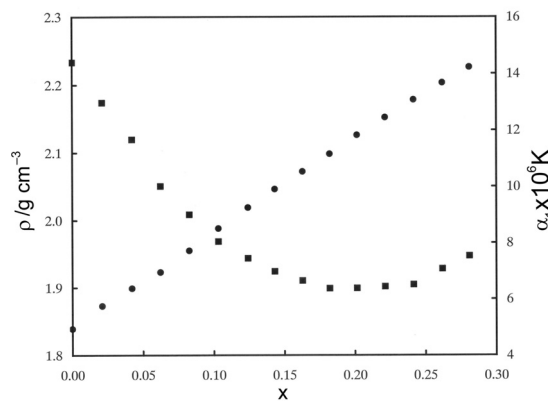


Fig. 1 Density ρ ● – and linear expansion coefficient α_1 ■ – of lithium borate glasses vs. x

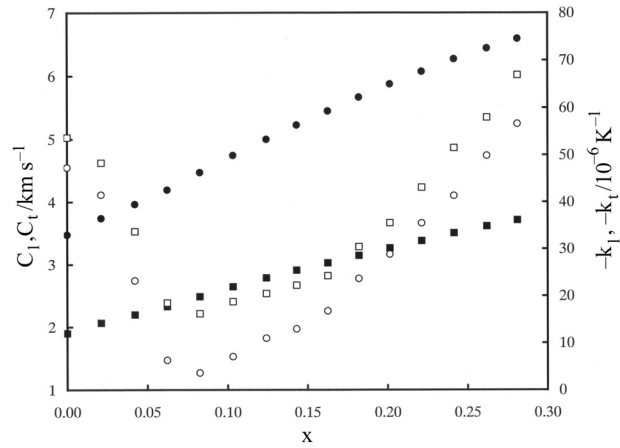


Fig. 2 Longitudinal velocity c_l ● – transverse velocity c_t ■ – temperature coefficient of longitudinal velocity k_l ○ – and temperature coefficient of transverse velocity k_t □ – in lithium borate glasses vs. x

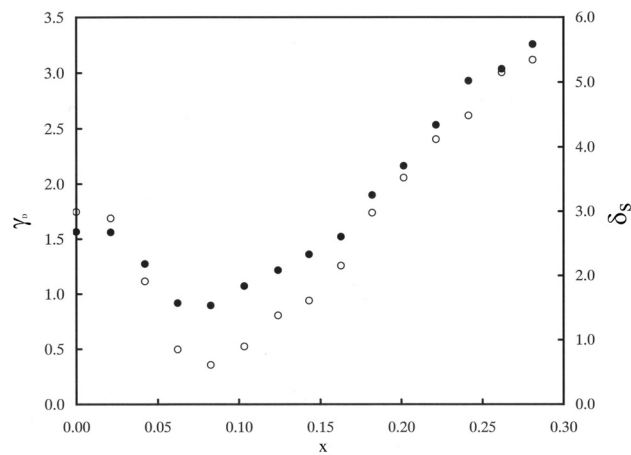


Fig. 3 Grüneisen parameter γ_D ● and A-G parameter δ_S ○ – of lithium borate glasses vs. x

and δ_S , as a function of composition. These two sets of parameters plotted vs. composition have the same characteristics with minima at around $x = 0.08$.

Figure 4 shows schematically part of the DTA heating curve in the vicinity of glass transition, where T_g , T_p and T_e are the onset temperature, the peak temperature and the end temperature of glass transition, respectively. Let η be the viscosity of a glass-forming liquid at a temperature T above T_g . The concept of fragility is defined from the dependence of $\log \eta$ on T/T_g [17] and one of the fragility metrics is the steepness index m [18]:

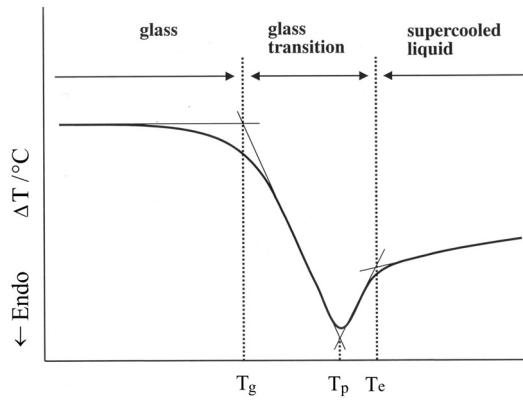


Fig. 4 Schematic DTA heating curve in the vicinity of glass transition

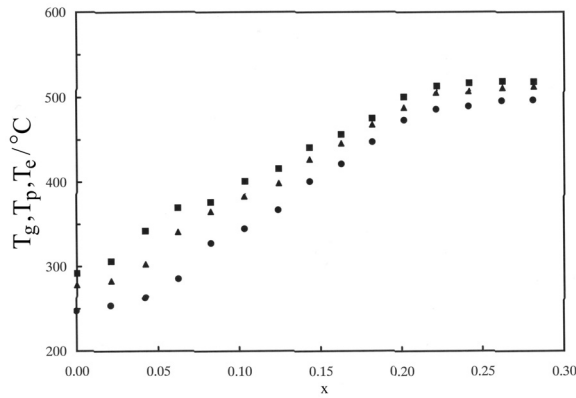


Fig. 5 T_g • - T_p ▲ and T_e ■ - of lithium borate glasses vs. x

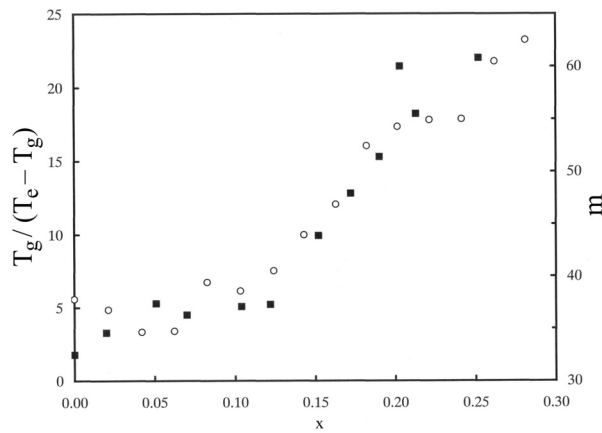


Fig. 6 Two fragility metrics, $T_g / (T_e - T_g)$ o and m ■ - of lithium borate glasses vs. x

$$m = \lim_{T \rightarrow T_g} \frac{d \log \eta}{d(T_g/T)} \quad (17)$$

Since $\log(\eta/\text{Pas}) \approx 11.3$ at T_g and $\log(\eta/\text{Pas}) \approx 9.2$ at T_c [19], the approximate relation $m \approx 2.1 T_g/(T_c - T_g)$ holds. We can then evaluate the fragility in this temperature range of glass transition approximately from $T_g/(T_c - T_g)$ [20]. Figure 5 shows T_g , T_p and T_c as a function of composition. Figure 6 shows the two fragility metrics, $T_g/(T_c - T_g)$ and m , the latter data being the literature value determined from the viscosity measurements [18]. Except for the composition region of low x , there is a close connection between these two fragility metrics. In Fig. 7, we compare the fragility metrics $T_g/(T_c - T_g)$ with the anharmonic parameter γ_D . The correlation between $T_g/(T_c - T_g)$ and γ_D is very good in the whole composition region. Since $T_g/(T_c - T_g)$ correlates closely also with the anharmonic parameter δ_s , we show here only the correlation between $T_g/(T_c - T_g)$ and γ_D . In conclusion, these results show that the fragility metrics $T_g/(T_c - T_g)$ and m strongly correlate with the anharmonic parameters γ_D and δ_s .

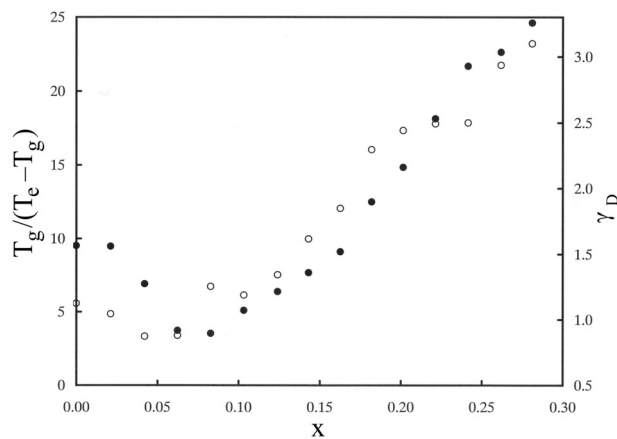


Fig. 7 Correlation between $T_g/(T_c - T_g)$ ○ and γ_D ●

An analysis [21] of the crosslinking density in lithium borate glasses gives a reason why the minima are present at $x \approx 0.08$. In the composition range $0 \leq x \leq 0.08$, lithium ions are initially incorporated in holes outside the boroxol rings. This incorporation converts non-ring BO_3 units located outside the boroxol rings into Li^+BO_4^- units, which results in an increase in crosslink between boroxol rings. Above $x \approx 0.08$, BO_4^- tetrahedra are preferentially included in six-membered rings by transforming boroxol rings into pentaborate rings, tetraborate rings and so forth, which results in a decrease in the crosslinking density between the rings. As a result, the crosslinking density of lithium borate glasses reaches a maximum at $x \approx 0.08$. If we assume that anharmonicity and fragility decrease as crosslinking density increases, the presence of minima at $x \approx 0.08$ is ascribable to the maximum crosslinking density at this composition.

Low-frequency Raman scattering spectra in glasses exhibit two characteristic features: the boson peak in the THz region and the quasi-elastic light scattering (QELS) with a characteristic width on the order of a few hundreds GHz [7]. Glass has a nanostructure formed from cohesive nanodomains (pseudophases or clusters, the size being 0.5–2 nm) and from the interfacial soft zones (connective tissues) [22, 23]. The boson peak is ascribable to an acoustic vibration localized in the cohesive nanodomain. QELS is ascribable to a fast relaxation process localized in the interfacial soft zones between cohesive domains. Since the acoustic vibration of the cohesive domains is weakly coupled to the surrounding soft zones, the energy of the boson peak oscillation is dissipated. In fact, damping of the boson peak is relatively high and also the lineshape of the observed boson peak is generally broad due to high damping [6]. This damping vibration makes the vibration of boson peak anharmonic.

The present authors have studied the low-frequency Raman scattering spectra (boson peak and QELS) of lithium borate glasses [6, 7]. Although a detailed discussion [7] of the relationship between anharmonicity and fragility is beyond the scope of the present paper, the ratio of the integral over the QELS spectrum to that over the boson peak is proportional to γ^2 , where γ is the third order anharmonic coefficient or Grüneisen parameter; furthermore, the Grüneisen parameter determined from this ratio correlates closely with the steepness index m .

Anharmonic intermolecular potential is considered to be a major cause of glass transition [5]; structural α -relaxation, fast relaxation, and boson peak are interrelated by the anharmonicity of the intermolecular potential. In fact, there is a strong correlation between the non-exponentiality parameter $n \equiv 1 - \beta_\alpha(T_g)$ where $\beta_\alpha(T_g)$ is the stretch exponent at T_g in the Kohlrausch–Williams–Watts function, the steepness index representing fragility, and the vibrational anharmonicity represented in terms of the mean square displacement of the Debye–Waller factor [5].

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