THERMAL AND MECHANICAL PROPERTIES OF LITHIUM BORATE GLASSES IN RELATION TO THE GLASS STRUCTURE

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Abstract

In lithium borate glasses $R\text{Li}_2\text{O}\cdot\text{B}_2\text{O}_3$ ($0 \leq R < 0.4$), the following experimental results were obtained: **1**. The density increases monotonically with increasing R. **2**. Both velocities of longitudinal and transverse ultrasonic waves increase monotonically with increasing R. **3**. The elastic constants such as bulk modulus and Young's modulus increase monotonically with increasing R. **4**. The linear expansion coefficient shows a broad minimum at around $R=0.25$. **5**. The Poisson ratio shows a minimum at around $R=0.10$ and a maximum at around $R=0.20$. **6**. Each of the temperature coefficients of velocities for longitudinal and transverse ultrasonic waves shows a sharp minimum at $R=0.10$ and a sharp change in slope at $R=0.20$. The experimental results **1**, **2** and **3** can be ascribed to a change in short-range order groups. The experimental result **4** is ascribable to the most compact configuration at around $R=0.25$. The experimental results **5** and **6** are ascribable to a change in crosslink between six-membered borate rings.

Keywords: alkali metal borate glasses, borate anomaly, density, ultrasonic velocity

Introduction

Compositions of alkali metal borate glasses are usually denoted by the binary-system notation $x\text{M}_2\text{O}\cdot(1-x)\text{B}_2\text{O}_3$, where M stands for any one of alkali metals and x is the mole fraction of M_2O. Since the purpose of the present paper is to discuss the structure and physical properties with respect to unit amount of the glass former B_2O_3, the composition formula $R\text{M}_2\text{O}\cdot\text{B}_2\text{O}_3$ is used in this paper, where $R=x/(1-x)$ is the mole fraction ratio of M_2O to B_2O_3. The thermal expansivities of alkali metal borate glasses plotted against their respective compositions exhibit a minimum at around $R=0.25$ and this phenomenon is termed the 'borate anomaly' [1]. Among alkali metal borate glasses, the minimum in thermal expansivity is most prominent in lithium borate glasses. Although the structure and properties of alkali metal borate glasses have been studied extensively, the cause of the borate anomaly has not been elucidated. In order to characterize the borate anomaly, it may be necessary to examine temperature coefficients of other physical quantities having close relation to

thermal expansivity. If the density and the ultrasonic velocity of a glass are known, we can obtain many different kinds of elastic constants for the glass. Thus, the following physical quantities have been measured for lithium borate glasses $R\mathrm{Li_2O \cdot B_2O_3}$ as a function of R: **1** density and linear expansion coefficient, the latter being equivalent to the temperature coefficient of density, and **2** ultrasonic velocity and its temperature coefficient. As a result, a few different types of borate anomalies have been found.

Theoretical

By measurement of the travel times, τ_1 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_1 and c_t, of longitudinal and transverse ultrasonic waves by $c_1 = 2l/\tau_1$ and $c_t = 2l/\tau_t$, respectively. With the mass density ρ and c_1 and c_t, we can calculate elastic constants such as longitudinal modulus L, shear modulus G, bulk modulus K, Young's modulus Y, and Poisson's ratio σ by the equations [2]

$$L = \rho c_1^2, \tag{1}$$

$$G = \rho c_t^2, \tag{2}$$

$$K = L - (4/3)G, \tag{3}$$

$$Y = G(3L - 4G)/(L - G), \tag{4}$$

$$\sigma = (L - 2G)/2(L - G). \tag{5}$$

The linear expansion coefficient α is defined as $\alpha = (1/l)(\mathrm{d}l/\mathrm{d}T)$, where T is temperature. If τ_1 and τ_t are measured as a function of temperature, we can evaluate at a given temperature the temperature coefficients of travel times, $(1/\tau_1)(\mathrm{d}\tau_1/\mathrm{d}T)$ and $(1/\tau_t)(\mathrm{d}\tau_t/\mathrm{d}T)$, for longitudinal and transverse ultrasonic waves, respectively. Differentiating $c_1 = 2l/\tau_1$ and $c_t = 2l/\tau_t$ with respect to temperature, we obtain the temperature coefficients of velocities,

$$TCc_1 \equiv -(1/c_1)(\mathrm{d}c_1/\mathrm{d}T) = (1/\tau_1)(\mathrm{d}\tau_1/\mathrm{d}T) - \alpha \tag{6}$$

and

$$TCc_t \equiv -(1/c_t)(\mathrm{d}c_t/\mathrm{d}T) = (1/\tau_t)(\mathrm{d}\tau_t/\mathrm{d}T) - \alpha \tag{7}$$

for longitudinal and transverse ultrasonic waves, respectively.

The density and hence the volume of lithium borate glasses have a relationship with short-range order groups which are termed structural units [3]. Nuclear magnetic resonance (NMR) studies on lithium borate glasses have shown that the glasses in the bulk-glass formation range ($R < 0.4$) are formed by two structural units, $\mathrm{B\varnothing_3}$

and $Li^+B\varnothing_4^-$, where $\varnothing$ represents a bridging oxygen [4, 5]. Then, the glass composition can be expressed as a mixture of two structural units:

$$RLi_2O \cdot B_2O_3 = 2(1 - R)B\varnothing_3 + 2RLi^+B\varnothing_4^- \tag{8}$$

Let $M(RLi_2O \cdot B_2O_3)$ and $V_m(RLi_2O \cdot B_2O_3)$ be the molar mass and the molar volume of lithium borate glasses relative to unit amount (1 mol) of $RLi_2O \cdot B_2O_3$ respectively, and let $\rho(RLi_2O \cdot B_2O_3)$ be the density at the composition of $RLi_2O \cdot B_2O_3$. These three quantities are related by

$$V_m(RLi_2O \cdot B_2O_3) = M(RLi_2O \cdot B_2O_3)/\rho(RLi_2O \cdot B_2O_3) \tag{9}$$

Putting $R=0$ in Eq. (9), we have the relation for boron oxide glass:

$$V_m(B_2O_3) = M(B_2O_3)/\rho(B_2O_3) \tag{10}$$

Taking the ratio of Eq. (9) to Eq. (10), we have

$$V_m(RLi_2O \cdot B_2O_3)/V_m(B_2O_3) =$$

$$[M(RLi_2O \cdot B_2O_3)/M(B_2O_3)][\rho(B_2O_3)/\rho(RLi_2O \cdot B_2O_3)] \tag{11}$$

Since Eq. (8) holds, the molar volumes $V_m(RLi_2O \cdot B_2O_3)$ and $V_m(B_2O_3)$ can be expressed further in terms of the structural units:

$$V_m(RLi_2O \cdot B_2O_3) = 2(1 - R)V_m(B\varnothing_3) + 2RV_m(Li^+B\varnothing_4^-) \tag{12}$$

where $V_m(B\varnothing_3)$ and $V_m(Li^+B\varnothing_4^-)$ are the molar volumes relative to unit amount (1 mol) of the structural units $B\varnothing_3$ and $Li+B\varnothing_4^-$, respectively. Putting $R=0$ in Eq. (12), we have the relation for boron oxide glass:

$$V_m(B_2O_3) = 2V_m(B\varnothing_3) \tag{13}$$

Substituting Eqs (12) and (13) in the left-hand side of Eq. (11) and rearranging, we have finally the molar volume ratio of $Li^+B\varnothing_4^-$ to $B\varnothing_3$:

$$V_m(Li^+B\varnothing_4^-)/V_m(B\varnothing_3) =$$

$$1 - (1/R) + (1/R)[M(RLi_2O \cdot B_2O_3)/M(B_2O_3)][\rho(B_2O_3)/\rho(RLi_2O \cdot B_2O_3)] \tag{14}$$

Equation (14) gives the relationship between the density and the molar volumes of the structural units.

Experimental

A series of lithium borate glasses was prepared in the bulk-glass formation range $0 \leq R < 0.4$ without strains or bubbles in order that they might transmit ultrasound sat-

isfactorily. A powder synthesized chemically from $LiOH \cdot H_2O$ and H_3BO_3 was fused in a 20 cm^3 platinum crucible at temperatures from 1050 to 1300°C for about 4 h by heating in an 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 strain 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 [6]. 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 [7] 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 of 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 which had been calibrated against the thermal expansivity of a platinum rod.

Results and discussion

The experimental results can be summarized as follows:

Figure 1 shows the density as a function of R. The density increases monotonically with increasing R. The density of lithium borate glasses has been studied extensively in the literature [3], six independent data on the density of lithium borate glasses are summarized over a wide composition range $0 \le R \le 2.75$. Although the composition range of the present study is restricted to the bulk-glass formation range $0 \le R < 0.4$, this composition range is studied in detail by preparing fifteen different compositions of glasses. The density values of the present study are in close agreement with those reported in the literature [3].

Figure 2 shows the longitudinal velocity and the transverse velocity as a function of R. Both velocities increase monotonically with increasing R.
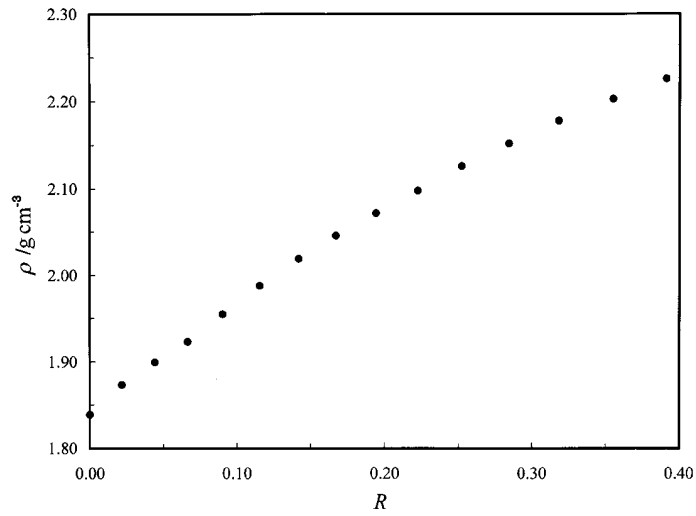
Fig. 1 Density ρ of lithium borate glasses as a function of R
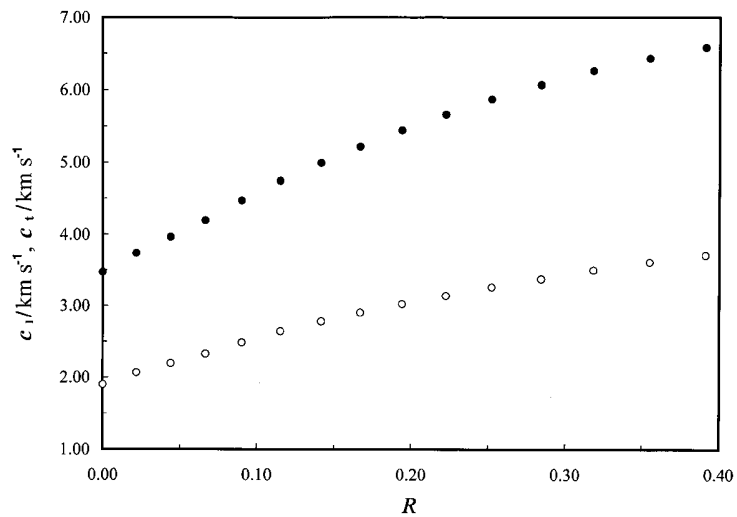

Fig. 2 Longitudinal velocity c_l (●) and transverse velocity c_t (○) of ultrasound in lithium borate glasses as a function of R

Figure 3 shows the longitudinal modulus, the shear modulus, the bulk modulus, and the Young modulus as a function of R. These elastic constants increase monotonically with increasing R.

Figure 4 shows the linear expansion coefficient together with the molar volume $V_m(R\text{Li}_2\text{O}\cdot\text{B}_2\text{O}_3)$ given by Eq. (9). These two sets of quantities resemble each other closely in shape with broad minima at around $R=0.25$. The linear expansion coefficient of the present study is in close agreement with that reported by Shelby [1].
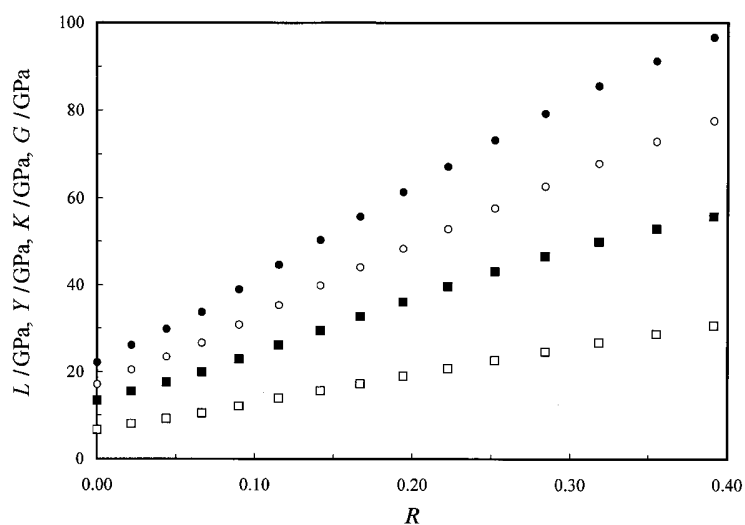
Fig. 3 Longitudinal modulus L (●), shear modulus G (□), bulk modulus K (■), and Young's modulus Y (○) of lithium borate glasses as a function of R
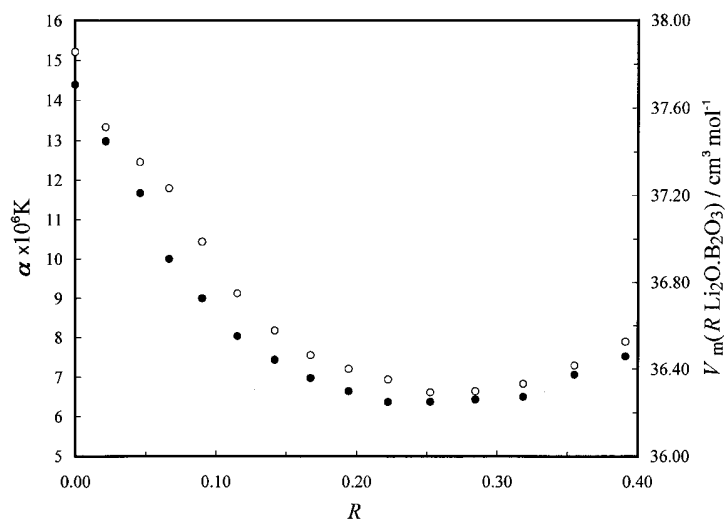

Fig. 4 Linear expansion coefficient α (●) and molar volume $V_m(R\mathrm{Li_2O \cdot B_2O_3})$ (○) of lithium borate glasses as a function of R

Figure 5 shows the Poisson ratio as a function of R. The Poisson ratio shows a minimum at around $R=0.10$ and a maximum at around $R=0.20$.

Figure 6 shows the temperature coefficients of longitudinal and transverse velocities. Each of these temperature coefficients shows a sharp minimum at $R=0.10$ and a sharp change in slope at $R=0.20$.
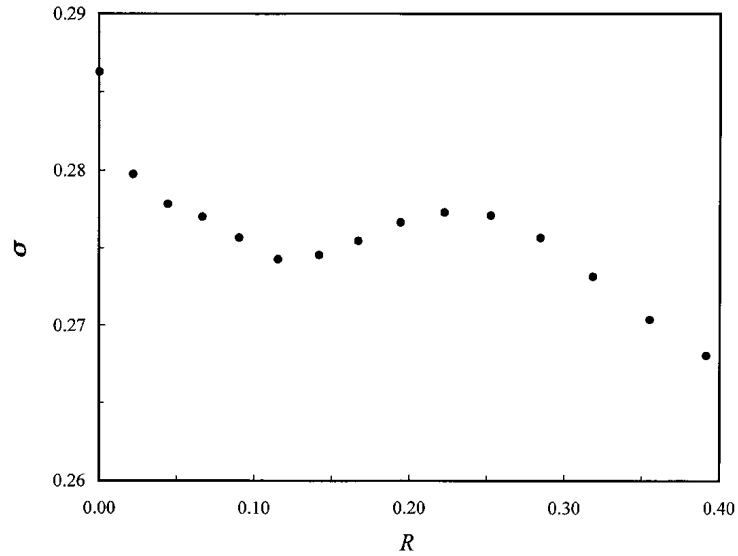
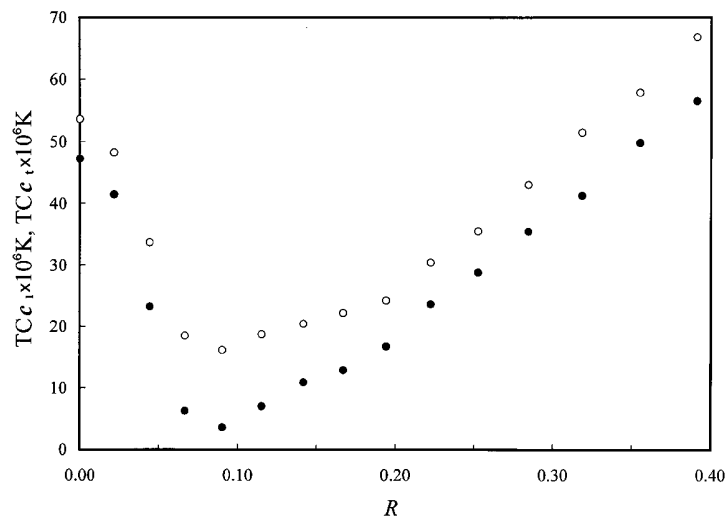**Fig. 5** Poisson's ratio σ of lithium borate glasses as a function of R

Fig. 6 Temperature coefficients of velocities, TCc_l (●) and TCc_t (○), for longitudinal and transverse ultrasonic waves in lithium borate glasses as a function of R

The structure of alkali metal borate glasses elucidated by a high-resolution NMR spectroscopy [8] may be summarized as follows:

1 – It is possible to resolve simultaneously three different boron sites: ring $B\varnothing_3$ units located inside six-membered boroxol or borate rings, non-ring $B\varnothing_3$ units located outside the rings, and $B\varnothing_4^-$ units.

2 – Pure boron oxide glass consists both of six-membered boroxol rings constructed from three $B\varnothing_3$ units and of non-ring $B\varnothing_3$ 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.

3 – With the initial addition of alkali metal oxide to boron oxide, non-ring $B\varnothing_3$ units are preferentially converted into $B\varnothing_4^-$ units; with the further addition, boroxol rings are converted into six-membered rings with one $B\varnothing_4^-$ tetrahedron (i.e., triborate, tetraborate, or pentaborate) and into six-membered rings with two $B\varnothing_4^-$ tetrahedra (i.e., diborate).

In order to determine the way in which the elasticity of lithium borate glasses is related to the microstructure, a microscopic theory should be constructed. In a previous paper [9], the relationship between the elasticity and the structure of lithium borate glasses has been analyzed in terms of the three structural units, $B\varnothing_3$, $Li^+B\varnothing_4^-$ and $Li^+B\varnothing_2O^-$, where O^- represents a non-bridging oxygen; on the assumption that these structural units exhibit their inherent elastic properties and hence have their respective elastic constants, the elastic constants of the structural units are defined on the basis of a thermodynamic equation of a deformed body. From this analysis, it is concluded that the structural unit $B\varnothing_3$ is converted only into the structural unit $Li^+B\varnothing_4^-$ in the composition range $0 \leq R < 0.4$ in the way expressed by Eq. (8). Thus, the present experimental results **1**, **2** and **3** represent this monotonic change in the short-range order structure.

The above experimental results **4**, **5** and **6** do not arise only from the change in the short-range order but may stem from an intermediate-range effect or from a long-range effect. The anomalous behavior of the linear expansion coefficient may be interpreted on the basis of the behavior of the molar volume $V_m(R\text{Li}_2\text{O}\cdot\text{B}_2\text{O}_3)$. Since this molar volume is taken relative to 2 mol of boron atoms, it follows that the molar volume is equal to the volume relative to 2 mol of $B\varnothing_3$ and $Li^+B\varnothing_4^-$. It seems that, at around $R=0.25$, these two structural units combine to form the most compact configuration such as pentaborate group for which $R=0.20$ or tetraborate group for which $R=0.25$. This most compact configuration causes the minimum in thermal expansivity at around $R=0.25$.

Equation (14) gives us a knowledge about the way in which the two structural units combine to form an intermediate-range structure. Figure 7 shows $V_m(Li^+B\varnothing_4^-)/V_m(B\varnothing_3)$ plotted *vs*. R; for comparison, in Fig. 7 is also shown $V_m(Na^+B\varnothing_4^-)/V_m(B\varnothing_3)$, the value of which is calculated from the density of sodium borate glasses [10]. Since $V_m(Li^+B\varnothing_4^-)$ is much smaller than $V_m(B\varnothing_3)$ in the initial composition range $0 < R < 0.10$, it follows that lithium ions are initially incorporated in holes outside the boroxol rings. The findings by the high-resolution NMR spectroscopy indicate that this incorporation converts non-ring $B\varnothing_3$ units located outside the boroxol rings into $Li^+B\varnothing_4^-$ units, which results in an increase in crosslink between boroxol rings. Above $R \approx 0.10$, $B\varnothing_4^-$ tetrahedra are included in six-membered rings by transforming boroxol rings into pentaborate, tetraborate, triborate groups, and so forth. Figure 7 also shows a slight change in the slope at around $R=0.22$, which indicates that the ring structure may change around this composition.
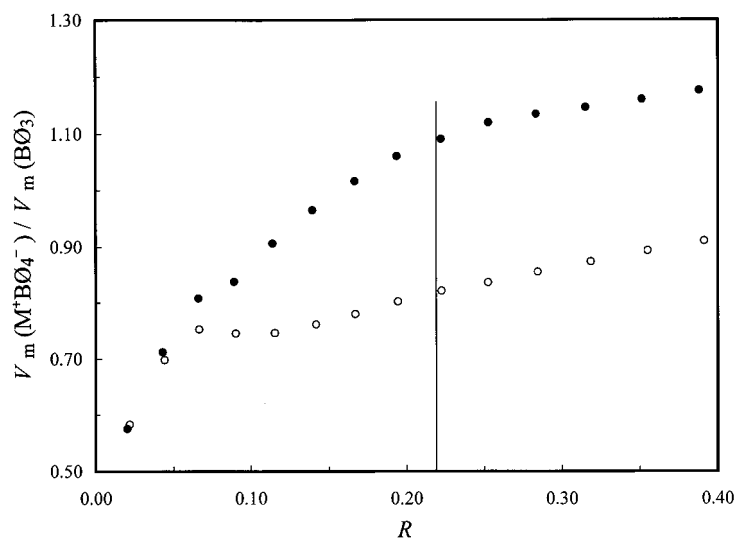
Fig. 7 $V_m(M^+B\varnothing_4^-)/V_m(B\varnothing_3)$ plotted *vs*. R, where M represents Li (○) and Na (●). The vertical line shows the composition of $R=0.22$ at around which both plots change their respective slopes

It is pointed out that Poisson's ratio decreases as the crosslinking density of the glass network increases [11]. Figure 5 means then that the crosslinking density of lithium borate glasses is maximal at $R=0.10$ and minimal at $R=0.20$. The analysis of $V_m(Li^+B\varnothing_4^-)/V_m(B\varnothing_3)$ (Fig. 7) has shown that non-ring $B\varnothing_3$ units are first converted into $B\varnothing_4^-$ tetrahedra until $R\approx0.10$, which results in a maximum crosslinking density between boroxol rings at around $R=0.10$. The minimum in the crosslinking density at the pentaborate composition of $R=0.20$ may arise from the effect that $B\varnothing_4^-$ units are preferentially included in the six-membered rings of pentaborate group, which results in a decrease in the crosslinking density between the rings.

The behavior of the temperature coefficients of ultrasonic velocities can be interpreted by the same principle as the behavior of Poisson's ratio. Figure 6 shows that both temperature coefficients of the velocities tend to decrease as R is increased in the composition range $0<R<0.10$. Krause and Kurkjian [12] point out that TCc_l and TCc_t defined by Eqs (6) and (7) are positive in B_2O_3 glass while they are negative in tetrahedrally coordinated glasses such as SiO_2 glass and GeO_2 glass. We see from the analysis of $V_m(Li^+B\varnothing_4^-)/V_m(B\varnothing_3)$ that boroxol rings are gradually linked together by tetrahedral $B\varnothing_4^-$ units with an increase in R in the first composition range $0<R<0.10$. As a result, the temperature coefficients of velocities are decreased by the crosslinkage due to the $B\varnothing_4^-$ tetrahedra located outside the boroxol rings. Above $R\approx0.10$, the temperature coefficients increase because $B\varnothing_4^-$ tetrahedra are now included in six-membered rings. The sharp change in the slope at $R=0.20$ may be ascribed to a change in the ring structure.

References

1 J. E. Shelby, J. Am. Ceram. Soc., 66 (1983) 225.
2 W. P. Mason, Physical Acoustics and the Properties of Solids, D. Van Nostrand, Princeton 1958, p. 13.
3 M. Shibata, C. Sanchez, H. Patel, S. Feller, J. Stark, G. Sumcad and J. Kasper, J. Non-Cryst. Solids, 85 (1986) 29.
4 G. E. Jellison Jr., S. A. Feller and P. J. Bray, Phys. Chem. Glasses, 19 (1978) 52.
5 S. A. Feller, W. J. Dell and P. J. Bray, J. Non-Cryst. Solids, 51 (1982) 21.
6 E. P. Papadakis, Physical Acoustics, eds. W. P. Mason and R. N. Thurston, Academic Press, New York 1976, Vol. 12, Chap. 5, p. 277.
7 H. J. McSkimin, J. Acoust. Soc. Am., 33 (1961) 12.
8 J. W. Zwanziger, R. E. Youngman and M. Braun, Borate Glasses, Crystals and Melts, eds. A. C. Wright, S. A. Feller and A. C. Hannon, Society of Glass Technology, Sheffield 1997, p. 21.
9 M. Kodama, T. Matsushita and S. Kojima, Jpn. J. Appl. Phys., 34 (1995) 2570.
10 M. Kodama, J. Mater. Sci., 26 (1991) 4048.
11 B. Bridge, N. D. Patel and D. N. Waters, Phys. Status Solidi (a), 77 (1983) 655.
12 J. T. Krause and C. R. Kurkjian, J. Am. Ceram. Soc., 51 (1968) 226.