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Ultrasonic velocity in sodium borate glasses

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Ultrasonic velocities in sodium borate glasses are measured as a function of composition at a frequency of 10 MHz and at a temperature of 298 K by making use of the ultrasonic pulse echo overlap method. Elastic properties of these glasses are analysed in terms of the elastic internal energy due to deformation; elastic resistances of the network-former, B_2O_3, and the modifier, Na_2O, are obtained as a function of composition from the plot of MV^2 against x_2, where M is the molar mass of sodium borate glasses, V the velocity of sound and x_2 the mole fraction of Na_2O. The elastic resistances of B_2O_3 and Na_2O are as follows: (i) for $x_2 < 0.33$, the elastic resistance of B_2O_3 is smaller than that of Na_2O; (ii) at $x_2 = 0.33$, the elastic resistances of B_2O_3 and Na_2O are equal; (iii) for $x_2 > 0.33$, the elastic resistance of B_2O_3 is greater than that of Na_2O; (iv) at $x_2 \approx 0.15$, the elastic resistances of B_2O_3 and Na_2O become respectively maximal and minimal; (v) at $x_2 \approx 0.23$, the elastic resistances of B_2O_3 and Na_2O become respectively minimal and maximal; (vi) above $x_2 = 0.36$, the elastic resistance of Na_2O becomes negative.

1. Introduction

Properties of alkali borate glasses plotted against their compositions often exhibit maxima, minima or points of inflection. This has attracted the attention of numerous investigators and various studies on the structure of these glasses have been made [1]. This paper reports on the relationship between the elasticity and the structure of sodium borate glasses.

We shall notice that sodium borate glasses are composed of the network-former, B_2O_3, and the modifier, Na_2O. The purpose of the present paper is to elucidate the way in which the network-former and the modifier contribute to the elasticity of these glasses. For this purpose, ultrasonic velocities in sodium borate glasses are measured as a function of composition, from which elastic resistances of the network-former and the modifier are obtained on the basis of a theory of elastic internal energy described in a previous paper [2]. In this theory, the elastic resistance of a component is defined as the second-order derivative of the partial molar internal energy with respect to the Lagrangean strain. This elastic resistance is useful in order to have an insight into the relationship between the elasticity and the structure of glasses. The elastic resistances of B_2O_3 and Na_2O are discussed on the basis of the Krogh-Moe structure model [3] of alkali borate glasses.

The velocity of sound in sodium borate glasses has been studied by Krause and Kurkjian [4] with the ultrasonic pulse superposition method and by Lorösch *et al.* [5] with the Brillouin scattering technique. To accomplish the above analysis, however, it is necessary to know velocities of sound concerning numerous compositions. This paper reports the velocity of sound in a series of sodium borate glasses measured with the ultrasonic pulse echo overlap method.

2. Theoretical background

We shall regard sodium borate glasses as two-component mixtures of B_2O_3 and Na_2O and denote the compositions of these glasses by the formula $x_2Na_2O \cdot x_1B_2O_3$, where x_1 and x_2 are the mole fractions of B_2O_3 and Na_2O, respectively, and $x_1 + x_2 = 1$.

First we shall summarize the theory of elastic internal energy [2] and give the formulae for expressing the elastic resistances of B_2O_3 and Na_2O. Since the ultrasonic wave propagates under adiabatic conditions, the internal energy can be chosen as the most convenient thermodynamic potential. Denoting the mean molar internal energy, the partial molar internal energy of component 1 (here B_2O_3), and the partial molar internal energy of component 2 (here Na_2O) by U_m, U_1 and U_2, respectively, we have the relation

$$U_m = U_1x_1 + U_2x_2 = (U_2 - U_1)x_2 + U_1 \quad (1)$$

Let M, V, η_α and S_m be the molar mass of the formula $x_2Na_2O \cdot x_1B_2O_3$, the velocity of sound, the Lagrangean strain of the sound wave ($\alpha = 1, 2, 3$ refers to normal strains for the longitudinal wave and $\alpha = 4, 5, 6$ refers to shear strains for the transverse wave), and the mean molar entropy, respectively. Differentiating Equation 1 twice with respect to η_α at constant S_m and using the relation

$$(\partial^2 U_m/\partial \eta_\alpha^2)_{S_m} = MV^2 \quad (2)$$

we have

$$MV^2 = \left(\frac{\partial^2(U_2 - U_1)}{\partial \eta_\alpha^2}\right)_{S_m} x_2 + \left(\frac{\partial^2 U_1}{\partial \eta_\alpha^2}\right)_{S_m} \quad (3)$$

In what follows we shall omit the subscript S_m for brevity.

If the strain occurs under adiabatic conditions, then the elastic internal energy, namely the internal energy of the body due to the elastic deformation, increases. Suppose that a given strain, η_α, causes an increment of the elastic internal energy such that

$$\Delta U_m = \Delta U_1 x_1 + \Delta U_2 x_2 \quad (4)$$

ΔU_m, ΔU_1 and ΔU_2 being the increments of U_m, U_1 and U_2, respectively. These increments can be expressed in the forms

$$\Delta U_m = \frac{1}{2} MV^2 \eta_\alpha^2 \quad (5)$$

$$\Delta U_1 = \frac{1}{2}\left(\frac{\partial^2 U_1}{\partial \eta_\alpha^2}\right)\eta_\alpha^2 \quad (6)$$

$$\Delta U_2 = \frac{1}{2}\left(\frac{\partial^2 U_2}{\partial \eta_\alpha^2}\right)\eta_\alpha^2 \quad (7)$$

We can interpret MV^2, $\partial^2 U_1/\partial \eta_\alpha^2$ and $\partial^2 U_2/\partial \eta_\alpha^2$ as follows. The material constant MV^2 determines the elastic internal energy per unit amount of the mixture (here sodium borate glasses) generated for a given strain, and hence expresses the elastic resistance of the mixture to the deformation; likewise, $\partial^2 U_1/\partial \eta_\alpha^2$ and $\partial^2 U_2/\partial \eta_\alpha^2$ determine respectively the elastic internal energies per unit amount of component 1 and per unit amount of component 2 generated for a given strain, and hence they express the elastic resistances of the respective components to the deformation. In the above analysis, the velocity of sound is taken separately with respect to both the longitudinal velocity, V_l, and the transverse velocity, V_t.

Equation 3 gives us a method for obtaining $\partial^2 U_1/\partial \eta_\alpha^2$ and $\partial^2 U_2/\partial \eta_\alpha^2$ graphically from the curve of MV^2 against x_2. This method is illustrated in Fig. 1.

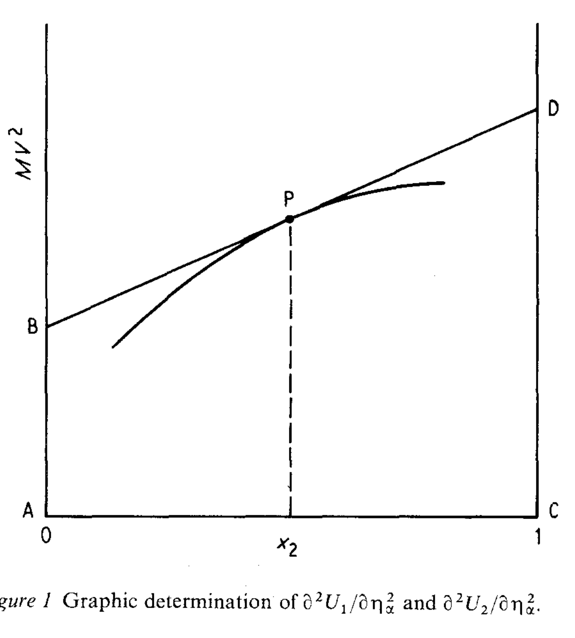

Figure 1 Graphic determination of $\partial^2 U_1/\partial \eta_\alpha^2$ and $\partial^2 U_2/\partial \eta_\alpha^2$.

If at some point $P(x_2, MV^2)$ on the curve a tangent is drawn, it cuts the ordinate at $x_2 = 0$ at the point B and the ordinate at $x_2 = 1$ at the point D such that $AB = \partial^2 U_1/\partial \eta_\alpha^2$ and $CD = \partial^2 U_2/\partial \eta_\alpha^2$.

3. Experimental procedure

3.1. Glass preparation

A series of sodium borate glasses denoted by the formula $x_2Na_2O \cdot x_1B_2O_3$ was prepared in the glass formation range such that $0 \leq x_2 \leq 0.38$ [6] and at such intervals that the increment of x_2 equals 0.02. In order to obtain good transmission of ultrasonic waves, it is necessary to prepare glasses with high homogeneity and without strains or bubbles.

Electronic-grade sodium hydroxide (more than 97.0% purity, the main residual being sodium carbonate) and boric acid (more than 99.7% purity) were used as the starting materials. The sodium hydroxide was used in the form of an aqueous solution whose concentration had been determined with a potentiometric titration method. With the aim of preparing glasses with high homogeneity, amounts of the sodium hydroxide solution and the boric acid calculated to give 30 g in the melts were perfectly dissolved into water in a beaker made of polytetrafluoroethylene. The solution was transferred to a dry box and after the complete evaporation of the water a chemically reacted powder was obtained.

By making use of an SiC resistance electric furnace, the powder was fused in a 20 cm^3 platinum crucible which was placed in an alumina crucible. The fusion was carried out at temperatures from 900 to 1300 °C for about 4 h with occasional stirring using a platinum wire; these temperatures were lowered as x_2 increased. The melt was then poured into a cylindrical graphite mould 15 mm in diameter and 23 mm in depth which had been preheated at the glass transition temperature in an electric muffle furnace. This glass transition temperature was determined from Shelby's experimental points [7] through which a smooth curve was drawn. Subsequently, the cast glass in the mould was held at the glass transition temperature for 2 h, then cooled at a rate of 1 K min^{-1} to room temperature while passing dry nitrogen through the muffle furnace; a programmable temperature regulator was used for this temperature–time schedule. The residual melt was poured on to an aluminium plate and later used for chemical analysis. Sometimes small bubbles were observed in the cast glasses, but these were not used in the present experiments. The glass of each composition was stored in a hermetic vial.

The compositions of all the glasses were analysed with respect to both x_1 and x_2 with a neutralization titration described in the previous paper [2]. Each composition was determined by five analyses; the probable error was less than 1.3×10^{-4} mole fraction for all the compositions studied.

Although the density, ρ, of each glass is not the requisite quantity for the present theory, it is necessary in order to calculate the elastic constant. For this reason, the density of the cast glass was also measured at 298 K by a hydrostatic weighing method described in the previous paper [2]. The error in the measurements of density was within $8 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$.

3.2. Ultrasonic velocity

In order to measure the ultrasonic velocity, each glass specimen must have a pair of end faces that are flat and mutually parallel. Each glass was first ground on a glass plate using SiC abrasives by setting it in a holder to maintain the two faces parallel, and subsequently polished by hand with fine alumina abrasive and machine oil on a flat glass plate. During polishing, the length of the specimen was occasionally measured at the centre and the four corners with a micrometer reading to 1 μm. The polishing was continued until the lengths of five portions coincided to within 2 μm; the final length at the centre was taken as the length of the specimen. Dimensions of polished glasses were 15 mm in diameter and normally 12 mm long. Inspection with a strain viewer showed that all the specimens were transparent and almost free from stress.

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 [8]. The apparatus used was constructed in the present author's laboratory and the circuitry has been described in a previous paper [9]. X-cut and Y-cut quartz transducers were used for the generation and detection of the longitudinal and transverse waves, respectively; the fundamental frequency of the transducers was 10 MHz, the electrode being in the form of a single-ended connection with a diameter of 10 mm. The transducer was bonded to the specimen on one of the two parallel faces with phenyl benzoate [10]. The specimen with the transducer attached was set in a hermetic specimen holder and controlled at 25 °C by placing the holder on a water bath.

McSkimin [11] proposed a criterion for determining the correct cyclic overlap between echoes with the purpose of measuring the ultrasonic travel time with high accuracy. The McSkimin criterion was extended in the previous paper [2] to become applicable to ordinary glass specimens, and this was used in the present measurements. Once a pair of echoes are properly overlapped according to the McSkimin criterion, it is possible to measure the ultrasonic travel time within an error of 0.02% for round trips greater than 5 μs [11]. Since the velocity of sound is equal to the propagation distance divided by the travel time and the error in the measurements of sample length is within 0.02%, the error in the present measurements of ultrasonic velocity is within 0.04%.

4. Results

Table I compiles the basic data obtained with the present series of experiments. The velocities of sound measured by Krause and Kurkjian [4], by Lorösch *et al.* [5], and by the present author are shown in Fig. 2, from which we see that these three sets of experimental data are in close agreement.

With the theory of elastic internal energy, we can now obtain $\partial^2 U_1/\partial\eta_\alpha^2$ and $\partial^2 U_2/\partial\eta_\alpha^2$ which represent respectively the elastic resistances of B_2O_3 and Na_2O. Fig. 3 shows the plots of MV_l^2 and MV_t^2 against x_2. We see that both plots change in a similar manner with an increase in x_2. Applying the method shown in Fig. 1 to the curve of MV_l^2 plotted against x_2, we obtain $\partial^2 U_1/\partial\eta_\alpha^2$ and $\partial^2 U_2/\partial\eta_\alpha^2$ concerning the longitudinal wave ($\alpha = 1, 2,$ or 3) and these are shown as

TABLE I Analysed composition, molar mass, density and ultrasonic velocities of longitudinal and transverse waves of sodium borate glasses at 298 K

x_2	M ($\mathrm{g\,mol^{-1}}$)	ρ ($\mathrm{g\,cm^{-3}}$)	V_l ($\mathrm{km\,s^{-1}}$)	V_t ($\mathrm{km\,s^{-1}}$)
0	69.62	1.838	3.469	1.901
0.0197	69.47	1.888	3.748	2.063
0.0411	69.31	1.933	3.988	2.199
0.0619	69.15	1.972	4.207	2.322
0.0818	68.99	2.014	4.410	2.439
0.1021	68.84	2.047	4.564	2.520
0.1222	68.69	2.077	4.705	2.595
0.1428	68.53	2.106	4.842	2.663
0.1622	68.38	2.131	4.957	2.721
0.1818	68.23	2.159	5.078	2.785
0.2016	68.08	2.186	5.197	2.857
0.2207	67.93	2.218	5.318	2.936
0.2396	67.79	2.251	5.438	3.017
0.2599	67.63	2.285	5.554	3.096
0.2795	67.48	2.316	5.655	3.162
0.2991	67.33	2.340	5.721	3.204
0.3196	67.18	2.364	5.765	3.228
0.3399	67.02	2.380	5.779	3.229
0.3594	66.87	2.386	5.744	3.196

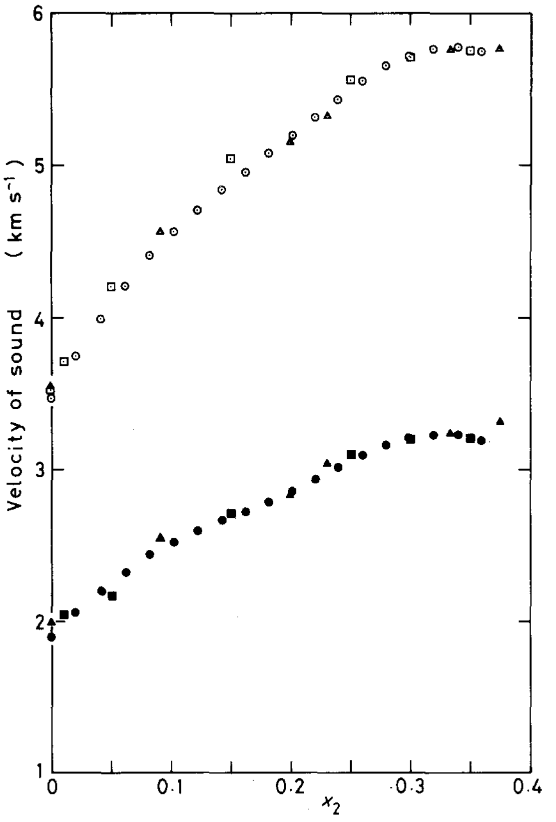

Figure 2 Velocities of sound in sodium borate glasses as a function of x_2: (○) V_l and (●) V_t measured by the present author; (□) V_l and (■) V_t measured by Krause and Kurkjian [4]; (△) V_l and (▲) V_t measured by Lorösch *et al.* [5].

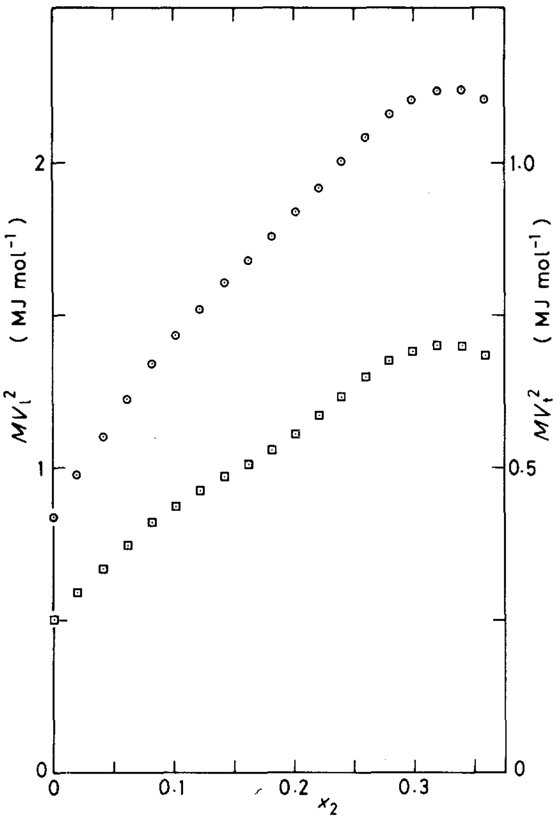

Figure 3 (⊙) MV_l^2 and (□) MV_t^2 as a function of x_2.

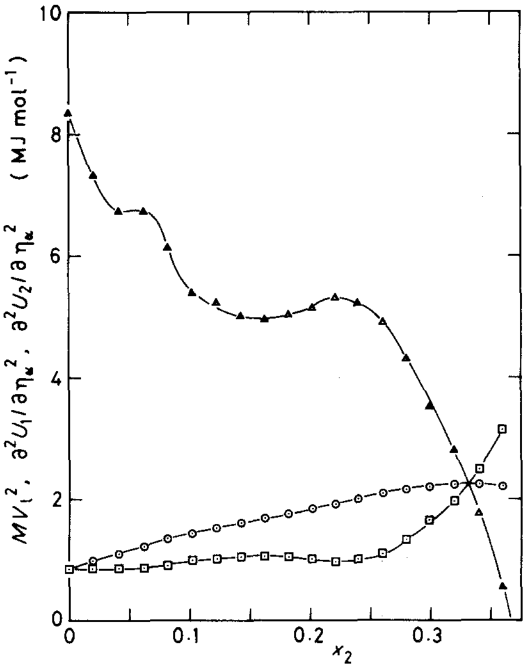

Figure 4 (□) $\partial^2 U_1/\partial\eta_\alpha^2$ and (△) $\partial^2 U_2/\partial\eta_\alpha^2$ concerning the longitudinal wave as a function of x_2. For the sake of comparison, the plot of (⊙) MV_l^2 against x_2 is also included in this figure.

a function of x_2 in Fig. 4. These values of $\partial^2 U_1/\partial\eta_\alpha^2$ and $\partial^2 U_2/\partial\eta_\alpha^2$ are obtained by fitting a quadratic function to three adjacent points of the (x_2, MV_l^2) data and by calculating the tangential line to the quadratic curve. For the sake of comparison, the plot of MV_l^2 against x_2 is also included in Fig. 4. Similarly, from the curve of MV_t^2 plotted against x_2 we obtain

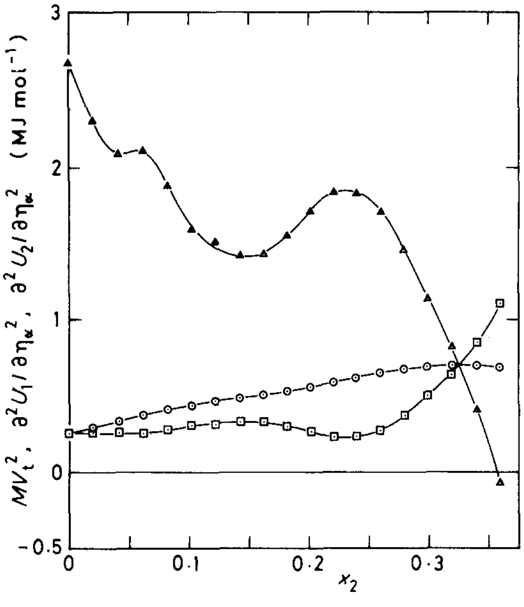

Figure 5 (□) $\partial^2 U_1/\partial\eta_\alpha^2$ and (△) $\partial^2 U_2/\partial\eta_\alpha^2$ concerning the transverse wave as a function of x_2. For the sake of comparison, the plot of (⊙) MV_t^2 against x_2 is also included in this figure.

$\partial^2 U_1/\partial\eta_\alpha^2$ and $\partial^2 U_2/\partial\eta_\alpha^2$ concerning the transverse wave ($\alpha = 4$, 5, or 6) as shown in Fig. 5.

We see from Figs 4 and 5 that the change in $\partial^2 U_1/\partial\eta_\alpha^2$ against x_2 depends hardly appreciably on the difference between the longitudinal and the transverse waves, and so does the change in $\partial^2 U_2/\partial\eta_\alpha^2$ against x_2. We can summarize, with respect to both the longitudinal and the transverse strains, the elastic resistances of B_2O_3 and Na_2O in sodium borate glasses as follows.

1. When $x_2 < 0.33$, we see that $\partial^2 U_1/\partial\eta_\alpha^2 < \partial^2 U_2/\partial\eta_\alpha^2$, indicating that the elastic resistance of B_2O_3 is always smaller than that of Na_2O in this composition range.
2. At $x_2 = 0.33$, we see that $\partial^2 U_1/\partial\eta_\alpha^2 = \partial^2 U_2/\partial\eta_\alpha^2$, indicating that the elastic resistances of B_2O_3 and Na_2O are equal at this composition.
3. When $x_2 > 0.33$, we see that $\partial^2 U_1/\partial\eta_\alpha^2 > \partial^2 U_2/\partial\eta_\alpha^2$, indicating that the elastic resistance of B_2O_3 now becomes greater than that of Na_2O in this composition range.
4. At $x_2 \approx 0.15$, $\partial^2 U_1/\partial\eta_\alpha^2$ and $\partial^2 U_2/\partial\eta_\alpha^2$ show respectively a maximum and a minimum, indicating that the elastic resistances of B_2O_3 and Na_2O become respectively maximal and minimal at this composition.
5. At $x_2 \approx 0.23$, $\partial^2 U_1/\partial\eta_\alpha^2$ and $\partial^2 U_2/\partial\eta_\alpha^2$ show respectively a minimum and a maximum, indicating that the elastic resistances of B_2O_3 and Na_2O become respectively minimal and maximal at this composition.
6. Above $x_2 = 0.36$, $\partial^2 U_2/\partial\eta_\alpha^2$ takes negative values. This indicates that the component Na_2O becomes unstable to elastic deformation.

Incidentally, the two curves of $\partial^2 U_2/\partial\eta_\alpha^2$ against x_2 shown in Figs 4 and 5 have points of inflection at $x_2 = 0.05$. The cause of these inflection points is unclear at present and will not be discussed in this paper.

5. Discussion

We shall discuss the above elastic properties on the basis of the Krogh-Moe structure model [3] of alkali borate glasses. This model is now supported by studies by means of such experimental techniques as nuclear magnetic resonance [12–14] and Raman scattering [15] and the change in the amount of each borate group as a function of x_2 is summarized in a simple graph by Griscom [1].

We shall first interpret elastic property No. 1 in the list given in Section 4 above. In the composition range $x_2 < 0.33$, boron atoms change from the three-fold to the four-fold coordination of oxygen atoms by addition of the modifier to form a three-dimensional connection of the network. The mechanical condition that $\partial^2 U_1/\partial \eta_\alpha^2 < MV^2 < \partial^2 U_2/\partial \eta_\alpha^2$ for $x_2 < 0.33$ means that the glasses in this composition range are composed of soft B_2O_3 and hard Na_2O. This indicates that the modifier is enclosed within the network in such a way that the modifier prevents the deformation of the surrounding soft network.

We shall next interpret elastic property 3. In the composition range $x_2 > 0.33$, the three-dimensional connection of the network has been partly broken up by the formation of non-bridging oxygen ions. The mechanical condition that $\partial^2 U_1/\partial \eta_\alpha^2 > MV^2 > \partial^2 U_2/\partial \eta_\alpha^2$ for $x_2 > 0.33$ indicates that the glasses in this composition range are now composed of hard B_2O_3 and soft Na_2O. This indicates that Na_2O is not enclosed within the network but situated outside a partly destroyed borate network, which leads to the modifier being easily deformed by the application of stress. Moreover, the fact that the elastic resistance of B_2O_3 in the range $x_2 > 0.33$ is much greater than that in the range $x_2 < 0.33$ indicates that the component B_2O_3 forms into smaller rigid borate groups in the range $x_2 > 0.33$.

Elastic property 2 indicates the intermediate state between the above two states. The glass at this composition is the most rigid throughout the composition range studied, since each of MV_l^2 and MV_t^2 shows the greatest value at $x_2 = 0.33$. The Krogh-Moe model shows that the borate network at $x_2 = 0.33$ is made up mainly of diborate group.

We shall next consider elastic property 4 at the composition of $x_2 = 0.15$. Alkali borate glasses often exhibit borate anomalies near this composition [1]. The fact that the elastic resistance of B_2O_3 is maximal at this composition indicates that the borate network becomes rigid to a high degree. The Krogh-Moe model shows that, at the composition of $x_2 = 0.15$, the three different species of boroxol ring, tetraborate group and diborate group exist in large quantities at the same time. It seems therefore that a combination of these three borate groups forms the rigid network. Consequently, the degree to which the modifier prevents the deformation of the surrounding rigid network decreases. The minimum in the thermal expansion coefficient near $x_2 = 0.15$ [7] may be attributed to the occurrence of this rigid network.

We shall next consider elastic property 5 at the composition of $x_2 = 0.23$. At this composition, the borate network becomes soft again and at the same time the degree to which the modifier prevents the deformation of this soft network becomes greater. The Krogh-Moe model shows that, at the composition of $x_2 = 0.23$, the boroxol ring has completely disappeared and the tetraborate and diborate groups exist almost in a one-to-one ratio. It seems therefore that this one-to-one combination of tetraborate group and diborate group forms this soft network.

Finally we shall consider elastic property 6. Strictly, $\partial^2 U_2/\partial \eta_\alpha^2$ for the transverse wave becomes negative above $x_2 = 0.36$ (Fig. 5) and $\partial^2 U_2/\partial \eta_\alpha^2$ for the longitudinal wave shows a tendency to become negative above $x_2 = 0.37$ (Fig. 4). If $\partial^2 U_2/\partial \eta_\alpha^2 < 0$, we see from Equation 7 that $\Delta U_2 < 0$ always with respect to any strain. This mechanical condition means that the component Na_2O becomes unstable to elastic deformation. Owing to this elastic instability of Na_2O, it becomes difficult for Na_2O to form glasses with B_2O_3. As a result, sodium borate melts tend to crystallize above $x_2 = 0.36$; the upper limit of the glass formation range ($0 \leq x_2 \leq 0.38$) may be attributed to this elastic instability of Na_2O.

6. Conclusions

The ultrasonic velocity in sodium borate glasses denoted by the formula $x_2Na_2O \cdot x_1B_2O_3$ was measured as a function of x_2 from which the elastic resistances of the network-former, B_2O_3, and the modifier, Na_2O, were obtained on the basis of the elastic internal energy. The elastic resistances of B_2O_3 and Na_2O were interpreted in terms of the Krogh-Moe structure model and the following conclusions were obtained.

1. In the composition range $x_2 < 0.33$, the elastic resistance of Na_2O is always greater than that of B_2O_3. This mechanical condition indicates that the modifier is enclosed within the network in such a way that the modifier prevents the deformation of the surrounding soft network.

2. At $x_2 = 0.33$, the elastic resistances of B_2O_3 and Na_2O are equal. The glass at this composition is the most rigid. The Krogh-Moe model suggests that the network of this rigid glass is composed mainly of diborate groups.

3. In the composition range $x_2 > 0.33$, the elastic resistance of B_2O_3 becomes greater than that of Na_2O. This mechanical condition indicates that Na_2O is not enclosed within the network but situated outside a partly destroyed borate network. Moreover, the elastic resistance of B_2O_3 in the range $x_2 > 0.33$ becomes much greater than that in the range $x_2 < 0.33$, indicating that B_2O_3 forms into smaller rigid borate groups in the range $x_2 > 0.33$.

4. At $x_2 \approx 0.15$, the elastic resistances of B_2O_3 and Na_2O become respectively maximal and minimal. This mechanical condition indicates that the borate network becomes rigid to a high degree and the degree to which the modifier prevents the deformation of the surrounding network decreases. The Krogh-Moe model suggests that a combination of boroxol ring, tetraborate group and diborate group forms this rigid network. Owing to this rigid network, the

thermal expansion coefficient shows a minimum near $x_2 = 0.15$.

5. At $x_2 \approx 0.23$, the elastic resistances of B_2O_3 and Na_2O become respectively minimal and maximal. This mechanical condition indicates that the borate network becomes soft to a high degree and the degree to which the modifier prevents the deformation of the surrounding network increases. The Krogh-Moe model suggests that a one-to-one combination of tetraborate group and diborate group forms this soft network.

6. Above $x_2 = 0.36$, the elastic resistance of Na_2O becomes negative. This mechanical condition means that the component Na_2O becomes unstable to elastic deformation. As a result, sodium borate melts tend to crystallize above $x_2 = 0.36$.

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