JOURNAL OF MATERIALS SCIENCE **24** (1989) 1539–1542

Elastic moduli of some mixed alkali borate glasses

SANTOKH SINGH, ANAND PAL SINGH, S. S. BHATTI
Department of Physics, Guru Nanak Dev University, Amritsar-143005 (Punjab), India

Elastic moduli of mixed alkali borate glasses based on lithium and sodium oxides are calculated by measuring ultrasonic velocities and densities. For the purpose of measuring the velocity with high accuracy, the McSkimin criterion for determining the correct cyclic overlap between echoes is used. The structure of the system is discussed as a function of composition by considering the behaviour of elastic properties. Infrared studies have also been done which confirm the conclusions reached by the ultrasonic studies of the given system.

1. Introduction

The non-linear dependence of most properties of mixed alkali glasses, when one alkali is replaced by another, called the mixed alkali effect, has attracted considerable attention in glass science and technology. Much experimental evidence and theoretical explanations have been presented [1–6]. The nature of ionic diffusion, electrical conduction, internal friction, dielectric losses and mechanical properties of mixed alkali silicate glasses have been extensively investigated. However in the case of the mixed alkali borate glasses and for the Na_2O–BaO–B_2O_3 system some data have been reported [4, 7]. The elastic moduli data are limited. We present in this paper some mechanical properties of a series of Li_2O–Na_2O–B_2O_3 glasses.

2. Experimental procedure

The raw materials used were of AR-Grade. The batches were melted at a temperature above 1050° C in an electric furnace. The melt was kept for about 2 h in air at atmospheric pressure, whilst dry oxygen was bubbled through to obtain homogeneity. The glass samples were obtained by casting the melt into pre-heated cylindrical graphite moulds. The cast glass in the mould was placed in another furnace pre-heated at 550° C. Then the furnace was switched off to cool the whole assembly gradually to room temperature.

In order to measure the ultrasonic velocities, each glass sample was lapped for parallel surfaces and polished using successively finer SiC emery powders and polishing powders on a flat platform by fixing the sample in a specially designed holder. The sample length was measured with the help of a micrometer which can measure down to $1\,\mu m$. The polishing process was continued until the length of the specimen measured at the centre and four corners coincided to within $5\,\mu m$. The final length at the centre is taken to be the length of the specimen. The density of each annealed glass sample was measured by the Archimedes' principle using benzene (AR-Grade) as the immersion liquid. Infrared measurements were made using a PYE/UNICAM (SP3-300) spectrometer, with thin discs prepared by pressing the mixture of fine powdered glasses and powdered KBr under a high pressure of the order of $100\,kPa\,cm^{-2}$.

3. Results and discussion

Tables I and II show a compilation of basic data obtained with the present series of experiments.

The density, d, and the mean atomic volume (V is the mean atomic weight divided by density) of $x Li_2O \cdot (30 - x)Na_2O \cdot 70B_2O_3$ ($x = 0, 5, 10, 15, 20, 25, 30$ mol %) are shown in Figs 1 and 2, respectively, as functions of x. The variations of longitudinal (U_l) and shear (U_t) velocities with composition are shown in Fig. 3.

For $0 < x < 30$ the density and the mean atomic volume, as shown in Figs 1 and 2 decrease monotonically as the Li_2O content increases. The relationship between the atomic volume and x is almost linear where

TABLE I Composition (mol %), density (d), formula weight (M) and velocities in lithium–sodium–borate glasses

Glass sample	Li_2O (mol %)	d ($g\,cm^{-3}$)	M ($g\,mol^{-1}$)	U_l ($m\,sec^{-1}$)	U_t ($m\,sec^{-1}$)	U_m ($m\,sec^{-1}$)
LiNaBG-1	5	2.360	65.72	5952.0	3362.1	3738.8
LiNaBG-2	10	2.350	64.12	6122.1	3483.0	3872.2
LiNaBG-3	15	2.340	62.51	6265.1	3555.3	3953.0
LiNaBG-4	20	2.330	60.91	6370.2	3595.9	4000.0
LiNaBG-5	25	2.320	59.30	6527.0	3709.0	4123.0
LiBG	30	2.340	57.70	6765.5	3923.1	4353.7
NaBG	0	2.344	67.33	5710.0	3199.0	3560.5

U_m is the mean ultrasonic velocity

0022-2461/89 $03.00 + .12

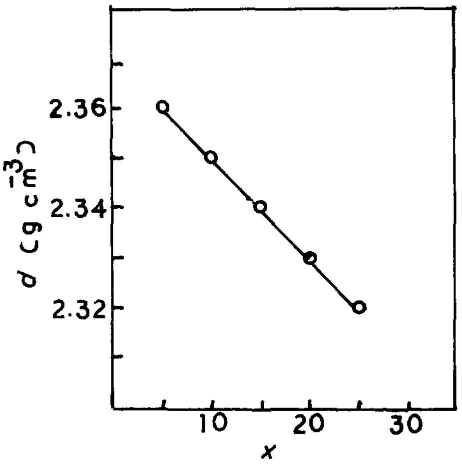

Figure 1 Density of $x\mathrm{Li_2O} \cdot (30 - x)\mathrm{Na_2O} \cdot 70\mathrm{B_2O_3}$ glasses as a function of x.

$0 < x < 30$. The increase of the longitudinal and shear velocities is shown in Fig. 3. Figs 4 and 5 show the variation of the measured bulk modulus (K_m) and the measured shear modulus (G_m). It should be noted that for K_m all the values are higher than those predicted by combining the values for end members. In Fig. 6, a plot of K_m against V on logarithmic scales is shown. Curves A and B correspond to Li_2O–Na_2O–B_2O_3 and single alkali glasses, respectively. Curve A slightly deviates from linearity, while B is represented very approximately by a straight line with a slope of -1.

For crystals having similar structures such as BeO, MgO, ZnO, CaO and SrO [8–10], it is found that K_m is proportional to V^{-1}. Also in the case of mixed alkaline earth silicate glasses Soga *et al.* [11] found that K_m is proportional to V^{-1} hence indicating that there is no essential change in network structure. It is, therefore, considered in Fig. 6 that for single alkali glasses of the same composition, there is no essential structural difference. However, as curve A slightly deviated from linearity, so the mixed alkali glasses may have a slightly abnormal behaviour and this indicates the presence of a slight mixed alkali effect. As such, no major change in structure is caused by the mixing of two types of alkali ions, in agreement with the prediction of Dietzel [5] on the basis of the difference between the field strengths of the cations.

Table III gives the main IR absorption bands of the

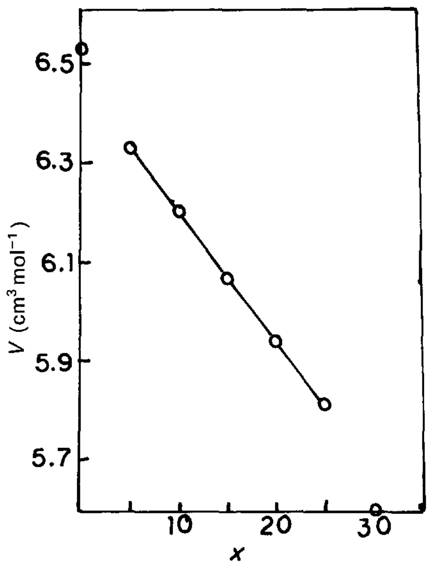

Figure 2 Mean atomic volume of $x\mathrm{Li_2O} \cdot (30 - x)\mathrm{Na_2O} \cdot 70\mathrm{B_2O_3}$ glasses as a function of x.

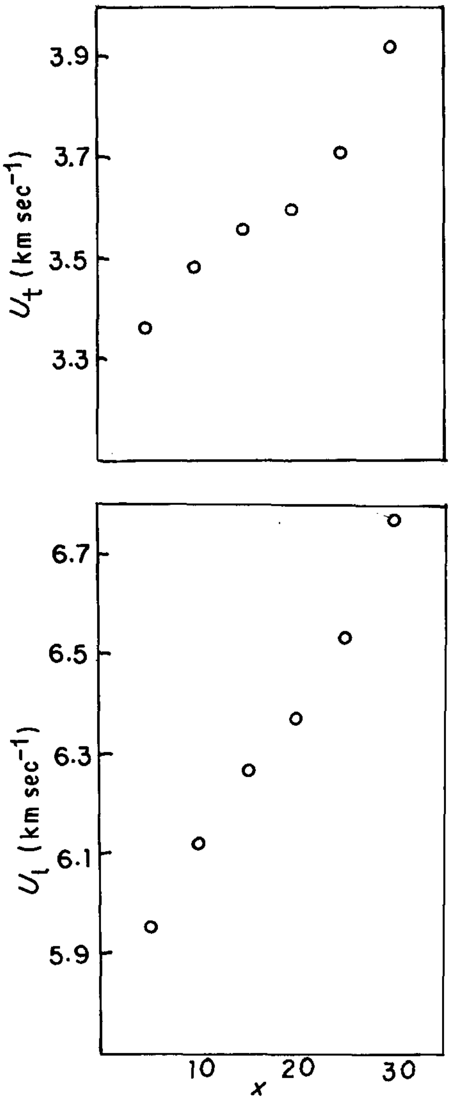

Figure 3 Wave velocities in $x\mathrm{Li_2O} \cdot (30 - x)\mathrm{Na_2O} \cdot 70\mathrm{B_2O_3}$ glasses as a function of x.

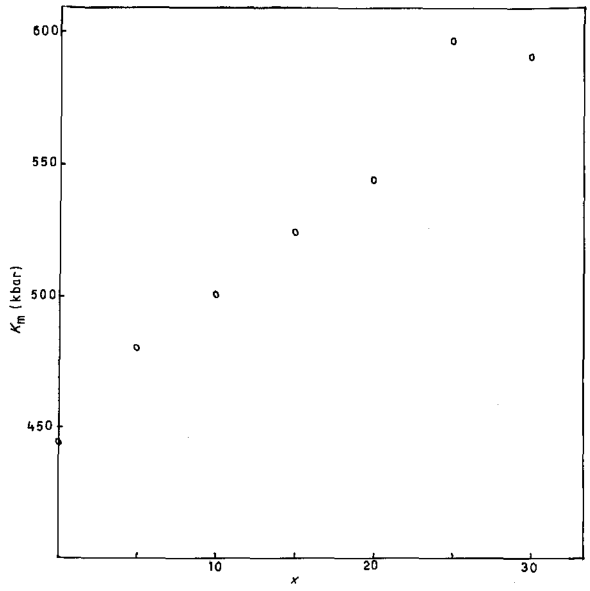

Figure 4 Bulk modulus of $x\mathrm{Li_2O} \cdot (30 - x)\mathrm{Na_2O} \cdot 70\mathrm{B_2O_3}$ glasses as a function of x.

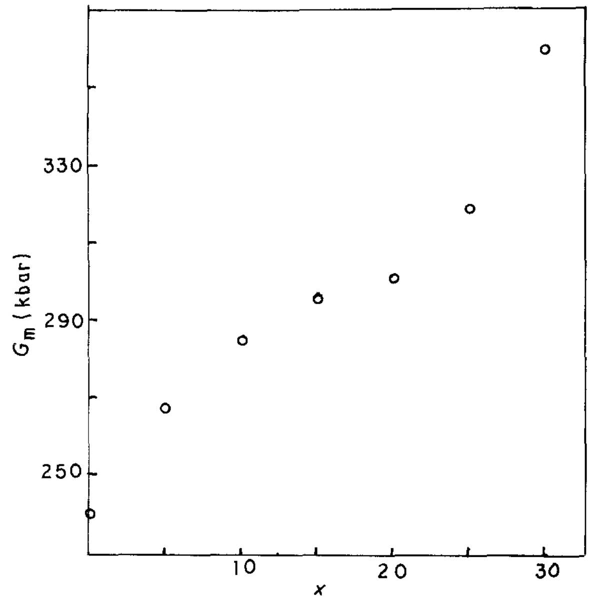

Figure 5 Shear modulus of $x\text{Li}_2\text{O} \cdot (30 - x)\text{Na}_2\text{O} \cdot 70\text{B}_2\text{O}_3$ glasses as a function of x.

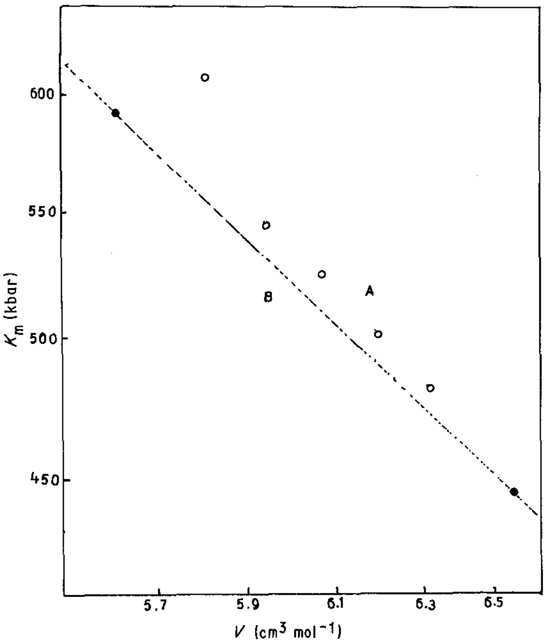

Figure 6 Relation between bulk modulus and mean atomic volume: (○) $x\text{Li}_2\text{O} \cdot (30 - x)\text{Na}_2\text{O} \cdot 70\text{B}_2\text{O}_3$, (●) single alkali glass.

series of lithium sodium borate glasses along with that of B_2O_3 reported by Hogarth *et al.* [12].

According to Anderson *et al.* [13] the peaks at 1460, 1200 and 780 cm^{-1} are related to BO_3 triangles. The weaker peaks at 1115, 1030, 930 and 740 cm^{-1} for B_2O_3 reported by Anderson *et al.* correspond closely with four peaks in danburite and pentaborate, which are assigned to BO_4 tetrahedra. The peak at 1250 cm^{-1} [13, 14] is characteristic of the B–O–B linkage in which both borons are triangularly coordinated and broad peak at 1333 to 1428 cm^{-1} shows the presence of tetrahedrally coordinated boron in the structure.

Many peaks of B_2O_3 have disappeared in the formation of the glass. However the following bands are found (a) a fairly broad strong band from 1230 to 1415 cm^{-1}, (b) a broad weaker band from 800 to 1000 cm^{-1} and (c) a strong band at 690 cm^{-1}. Hogarth *et al.* suggest that the bands at 1220 to 1440 cm^{-1} and 950 to 1100 cm^{-1} for $ZnO–B_2O_3$ system belong to tetrahedrally coordinate borons. As such the bands observed here from 1230 to 1415 cm^{-1} and at 800 to 1000 cm^{-1} seem to belong to [=B–O–B=] group in which one of the boron atoms is tetrahedrally coordinated.

The strong band at 960 cm^{-1} belongs to the B–O–B linkage in which both boron atoms are triangularly coordinated. As the glasses are hygroscopic so the

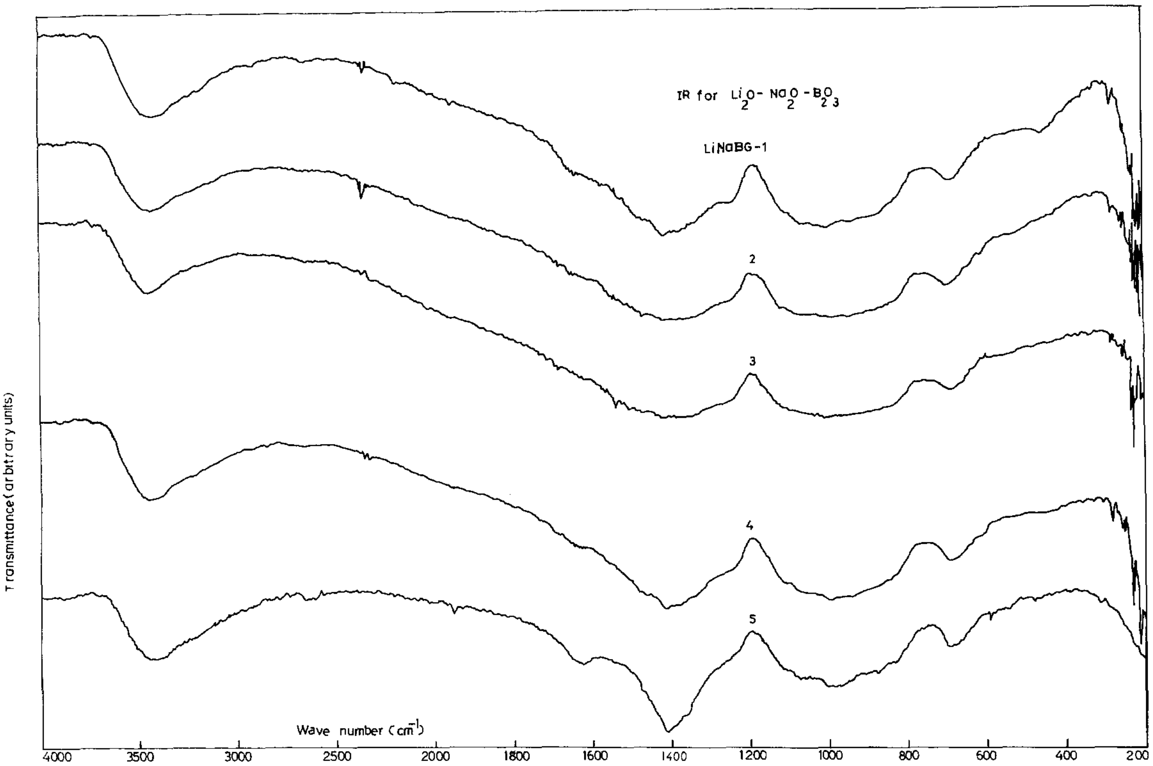

Figure 7 Room temperature infrared absorption spectra of $x\text{Li}_2\text{O} \cdot (30 - x)\text{Na}_2\text{O} \cdot 70\text{B}_2\text{O}_3$ glasses.

TABLE II Mean atomic volume (V), measure elastic moduli for lithium–sodium–borate glasses

Glass sample	V (cm^3 mol^{-1})	L_m (kbar)	E_m (kbar)	G_m (kbar)	K_m (kbar)	σ_m
LiNaBG-1	6.329	836.1	675.4	266.8	480.4	0.226
LiNaBG-2	6.201	860.8	718.9	285.1	500.6	0.261
LiNaBG-3	6.071	918.5	746.7	295.7	524.2	0.263
LiNaBG-4	5.941	945.4	763.0	301.3	543.7	0.266
LiNaBG-5	5.809	988.4	805.4	319.2	607.5	0.262
LiBG	5.604	1071.1	897.9	360.1	591.0	0.247
NaBG	6.528	764.2	610.0	239.9	444.3	0.271

L_m is the measured dynamic longitudinal modulus of elasticity.
E_m is the measured Young's modulus.

TABLE III The main absorption band positions of lithium–sodium–borate glasses

Glass sample	Absorption band positions (cm^{-1})					
	Strong			Weak	Strong	
LiNaBG-1	–	–	690	800 to 1000	1230 to 1415	3420
LiNaBG-2	–	–	690	800 to 1000	1230 to 1415	3420
LiNaBG-3	–	–	690	800 to 1000	1230 to 1415	3420
LiNaBG-4	–	–	690	800 to 1000	1230 to 1415	3420
LiNaBG-5	–	–	690	800 to 1000	1230 to 1415	3420
B_2O_3	550	650	700	1200	1450	3220

band at 3420 cm^{-1} are due to the -OH groups in the glass. The main observations of the infrared absorption spectra of these glasses shows that all the bands remain as such. Hence the IR spectra confirm the conclusion that there is no drastic change in structure due to the mixing of two types of alkali ions.

The expected structure of the given glassy system may involve having saturated amounts of BO_4 tetrahedra and BO_3 triangles. Their amounts are expected to remain as such as we replace one alkali ion with another. However there are some physical properties which show a systematic variation with composition that probably reflect variations in the closeness of packing. For example, large cations expand the network and form comparatively weak bonds, while small cations form strong bonds and increase the elastic constants. The ionic radius of lithium is 0.06 nm while that of sodium is 0.095 nm. Hence elastic moduli (except Poisson ratio, σ) as in Table II, show an increase as Li_2O replaces Na_2O. The Poissons ratio which is a measure of cross-link densities [9], remains almost invariant with composition, as expected, because there is no change in structure with composition.

References

1. J. R. HENDRICKSON and P. J. BRAY, *Phys. Chem. Glasses* **13** (1972) 43, 107.
2. K. MATUSITA, S. SAKKA, A. OSAKA, N. SOGA and M. KUNUGI, *J. Non-Cryst. Solids* **16** (1974) 308.
3. D. E. DAY, *ibid.* **21** (1976) 343.
4. K. MATUSITA, T. WATANAKE, K. KAMIYA and S. SAKKA, *Physics Chem. Glasses* **21** (1980) 78.
5. A. H. DIETZEL, *ibid.* **24** (1983) 172.
6. W. J. TH. VAN GEMERT, H. M. J. M. VAN ASS and J. M. STEVELS, *J. Non-Cryst. Solids* **16** (1974) 281.
7. S. S. BHATTI and SANTOKH SINGH, *Acustica* **65** (1988) 261.
8. R. OTA, N. SOGA and M. KUNUGI, *J. Ceram. Soc. Jpn* **81** (1973) 156.
9. O. L. ANDERSON, E. SCHREIBER, R. C. LIEBERMANN and N. SOGA, *Rev. Geophys.* **6** (1968) 491.
10. N. SOGA, R. OTA and M. KUNUGI, Proceedings 1971 International Conference on Mechanical Behaviour of Materials, Vol. 9, p. 366.
11. N. SOGA, C. HISAMOTO and M. KUNUGI, 14th Symposium of the Glass Division of the Ceramic Association of Japan, 6 (Nagoya-1973).
12. C. A. HOGARTH and M. M. AHMED, *J. Mater. Sci.* **2** (1983) 649.
13. S. ANDERSON, R. L. BOHON and D. D. KIMPTON, *J. Amer. Ceram. Soc.* **38** (1955) 370.
14. P. E. JELLYMAN and J. P. PROCTOR, *Trans. Soc. Glass Technol.* **39** (1955) T173.
15. B. BRIDGE, N. D. PATEL and D. N. WATERS, *Phys. Status Solidi* (*a*) **77** (1983) 655.

Received 21 January
and accepted 9 September 1988