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Ultrasonic investigation and infrared absorption of some sodium borate glasses

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Ultrasonic velocities and absorption measurements in sodium borate glasses containing Na_2O have been made using the pulse echo technique at 4, 5 and 6 MHz. Results showed an increase in velocity as the sodium oxide content (mol%) increased. The ultrasonic absorption results showed the presence of very high and well-defined peak which shifts its position to lower temperatures with increasing frequency. This suggests some sort of relaxation process and the activation energy of this process increased with increasing Na_2O concentration (mol%). The infrared absorption spectra of sodium borate glasses confirmed the results obtained by ultrasonic investigations.

1. Introduction

Glasses containing two or more different glass formers have attracted the attention of several workers [1–5] in recent years. The structure of boric oxide bears little resemblance to that of vitreous silica. Brage [6] was able to study the ultrasonic properties of glass at low temperatures and reported that ultrasonic methods had proved to be the most powerful means for understanding the unusual properties of amorphous solids at low temperatures. In pure B_2O_3, boron is triangularly coordinated with oxygen atoms. X-ray diffraction studies indicate the change of coordination from 3 to 4 as alkali oxide is added to boron oxide. Carini *et al.* [7] measured the attenuation of longitudinal sound waves in $(Ag\ I)_x(Ag_2O–B_2O_3)_{1-x}$ glasses and found a very large and high peak, whose height and temperature location change with x. They also observed a very large and high peak at higher frequencies and decreasing temperature, and suggested that the mobile ionic species strongly diffuse the ultrasonic waves; this unusually high peak could indicate the presence of anelastic effects due to mobile particles subjected to a thermally activated relaxation process. Lin and Thomas [8] investigated some borate and aluminosilicate glasses and reported the ultrasonic attenuation of longitudinal sound waves at low temperatures. Infrared absorption spectra of vanadate barium borate glasses have been obtained by Singh *et al.* [9]. They also measured the ultrasonic velocities and attenuation in these glasses. The elastic properties of these glasses as a function of composition and dissociation energy are therefore discussed in terms of a model proposed by Makishima and Mackenzie [10].

2. Experimental procedure

A conventional pulse-echo technique was used in these measurements using a Flaw Detector USM 2 and double-beam oscilloscope. Longitudinal and shear ultrasonic velocities were measured at 6 MHz and at room temperature (25 °C). Absorption measurements were carried out at three frequencies, 4, 5 and 6 MHz in the temperature range + 100 to − 160 °C. Because the ultrasonic attenuation, α, in glasses is much higher than that in metals, usually one or two echoes are observed on the oscilloscope. Accordingly, measurements were taken on a comparative basis where the variation of l^{-1} (where l is the height of the first echo on the oscilloscope) with temperature was considered because they are related to each other by

$$l = l_0 e^{-\alpha d} \quad (1)$$

where d is the distance traversed and l_0 is the amplitude of the pulse at $d = 0$.

A special sample holder for mounting the transducer and the sample was designed and constructed at the National Institute for Standards workshop and proved to be suitable for the purpose. The transducer was bonded to the specimen with an ultrasonic couplant of medium viscosity (dehydrated silicon fluid) which proved to be satisfactory over the entire range of temperatures throughout this investigation. The glass samples, provided by the Glass Laboratory of the National Research Centre, Egypt, were 2.0 cm long, ground and polished to within 2 μm.

Infrared measurements were made using Perkin–Elmer 1430 spectrophotometer. Glass powder was sieved and the fraction of particles in the size range 0.075–0.063 mm diameter was taken. The samples were prepared for spectral scanning as KBr discs.

3. Results and discussion

The composition and densities of the glasses studied and the corresponding ultrasonic propagation velocities in them are given in Table I. The densities of these

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TABLE I

Glass composition	Density (g cm^{-3})	Longitudinal velocity (m s^{-1})	Shear velocity (m s^{-1})
5.6 Na_2O–94.4 B_2O_3	1.8778	4142.0	2621.27
11.1 Na_2O–88.9 B_2O_3	1.9202	4615.9	2919.82
21.9 Na_2O–78.1 B_2O_3	2.0436	5321.5	3356.76
27.2 Na_2O–72.8 B_2O_3	2.2285	5661.5	3549.43

samples gradually rise as the mole percentage of Na_2O is increased from 5.6 to 27.2.

A clear rise in velocity is seen (Fig. 1) with the rise in Na_2O content (mol %). This trend fits well with the earlier observations at 10 MHz for binary barium borate glass [1]. The increase in velocity is mainly caused by the increase in the backing density due to a decrease in B_2O_3 content (mol %). In the lower region, the boron atoms with a co-ordination number of 3 predominate and makes B_2O_3 soft and easily deformed by stress. Near the maxima, boron atoms change from three-fold CN (B^{3+}) to four-fold CN (B^{4+}). A similar explanation has been reported by Yun and Bary [2, 3] for sodium boro-silicate glasses.

Figs 2–5 show the relation between ultrasonic absorption and temperature at the three ultrasonic frequencies. Over the whole temperature range, there is only one sharp and well-defined peak which appeared, always in the low-temperature region between − 45 and − 73 °C. The position of the peak shifts to lower temperatures with increasing frequency. The presence of this peak reveals the presence of some sort of relaxation process. From the shift of the position of the peak with increasing frequency, the activation energy associated with this relaxation process, as well as the relaxation frequency, were calculated according

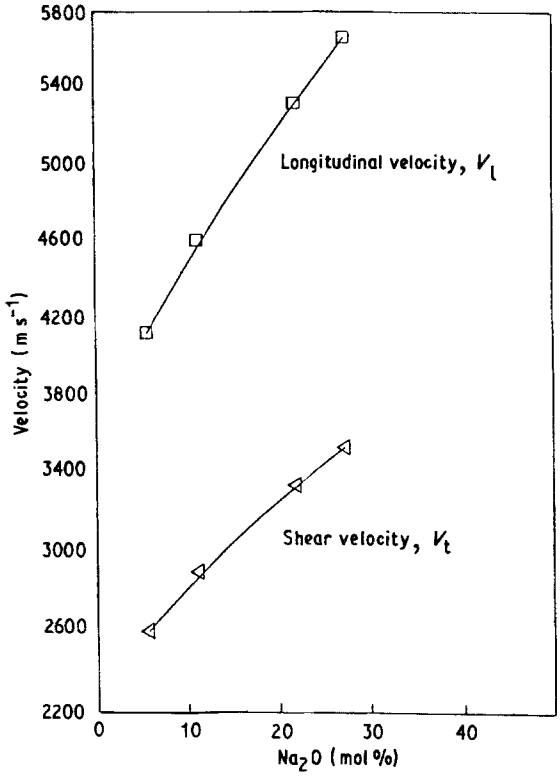

Figure 1 Variation of longitudinal and shear ultrasonic velocities with Na_2O content.

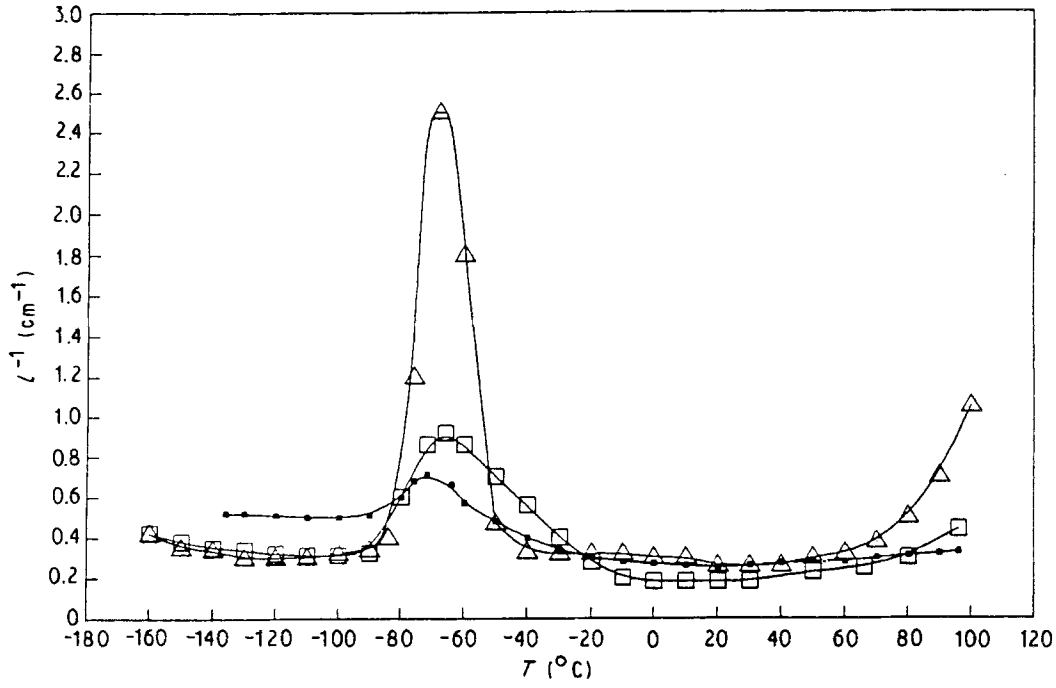

Figure 2 Relation between l^{-1} and T for a glass sample with the composition containing 5.6 mol % Na_2O, at (□) 4 MHz, (△) 5 MHz, (●) 6 MHz.

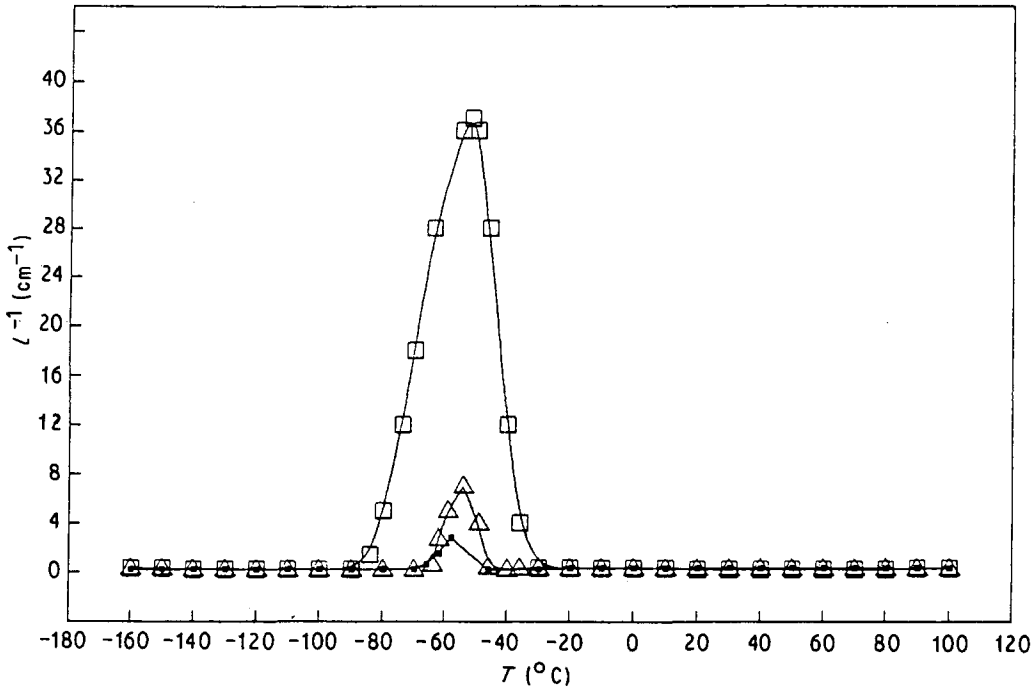

Figure 3 Relation between l^{-1} and T for a glass sample with the composition containing 11.1 mol % Na_2O, at (□) 4 MHz, (△) 5 MHz, (●) 6 MHz.

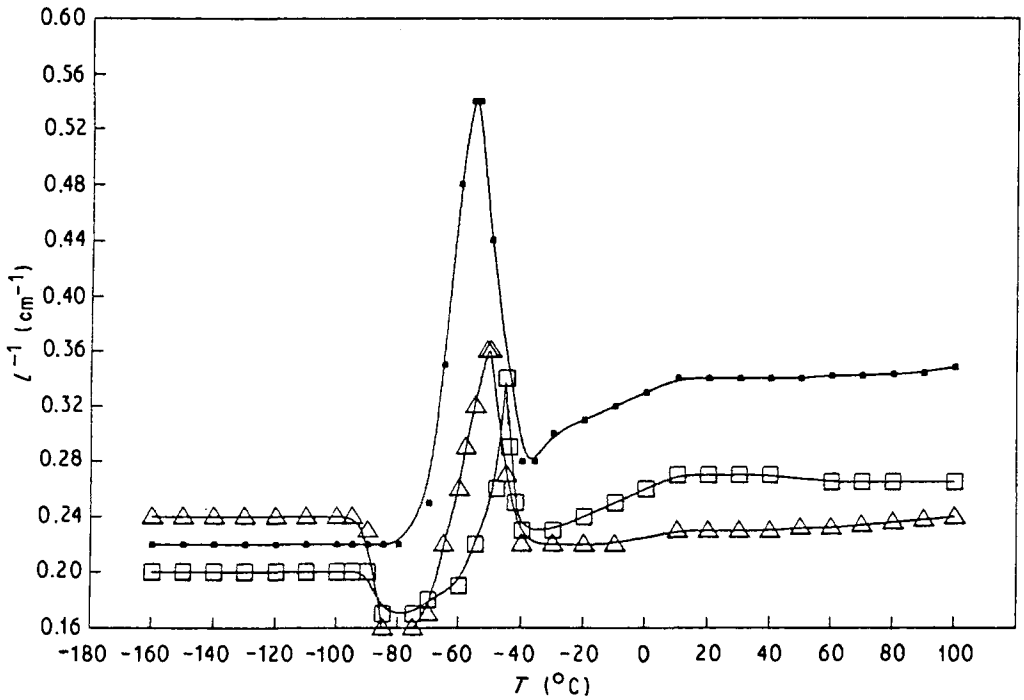

Figure 4 Relation between l^{-1} and T for a glass sample with the composition containing 21.9 mol % Na_2O, with (□) 4 MHz, (△) 5 MHz, (●) 6 MHz.

to the Arrehenius equation

$$f = f_0 e^{-W/KT_m} \quad (2)$$

where f is the applied frequency, f_0 is the relaxation frequency, W is the activation energy associated with the process, K is the Boltzmann constant, and T_m is the maximum temperature (peak temperature at which the maximum absorption occurs).

Figs 6–9 give the relation between $\ln f$ and the reciprocal of temperature, T_m^{-1}. All curves show a linear relation, given as straight lines and which satisfies the Arrehenius equation. Table II gives the maximum temperature, T_m, the activation energy, and the relaxation frequency, f_0, for the four glass samples. From these results, it appeared that there is an increase in activation energy with increasing Na_2O concentration. This suggests a structural relaxation involving a major topological structural reconstruction and this suggestion agrees well with the conclusion arrived at by Chen [11].

The infrared spectra of these Na_2O–B_2O_3 glasses show bands in the range 300–2000 cm^{-1}, as shown in

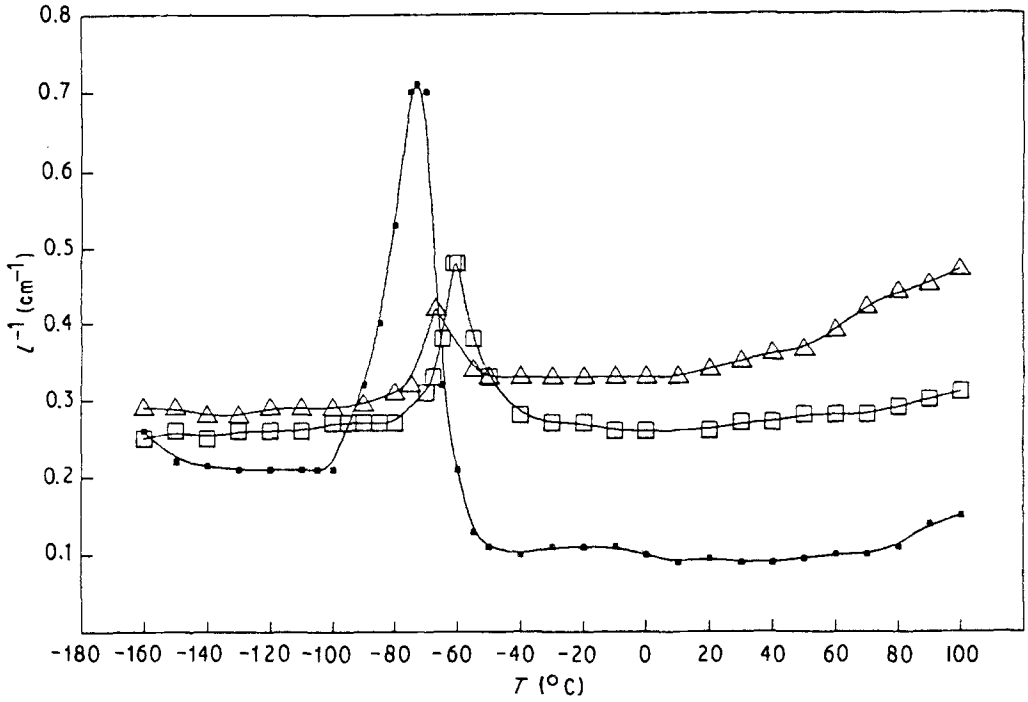

Figure 5 Relation between l^{-1} and T for a glass sample with the composition containing 27.2 mol % Na_2O, at (□) 4 MHz, (△) 5 MHz, (●) 6 MHz.

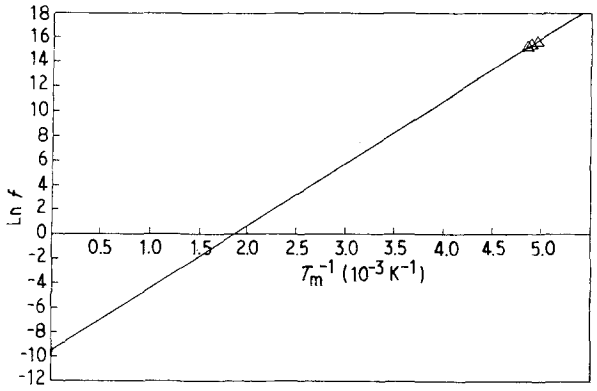

Figure 6 Plot of ln$f$ against T_m^{-1} for a glass sample with the composition containing 5.6 mol % Na_2O.

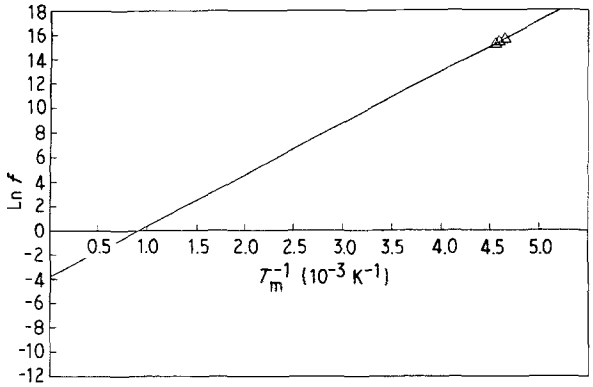

Figure 8 Plot of ln$f$ against T_m^{-1} for a glass sample with the composition containing 11.1 mol % Na_2O.

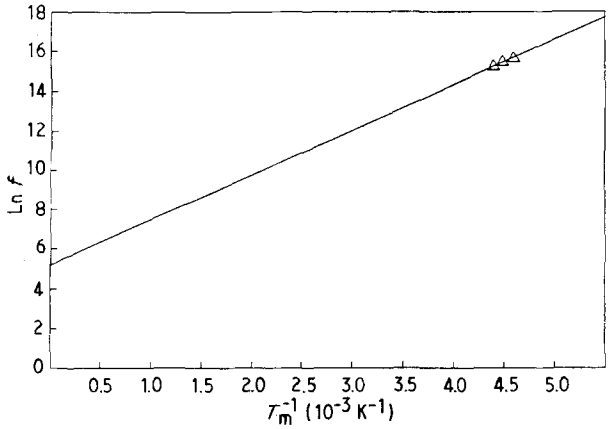

Figure 7 Plot of ln$f$ against T_m^{-1} for a glass sample with the composition containing 21.9 mol % Na_2O.

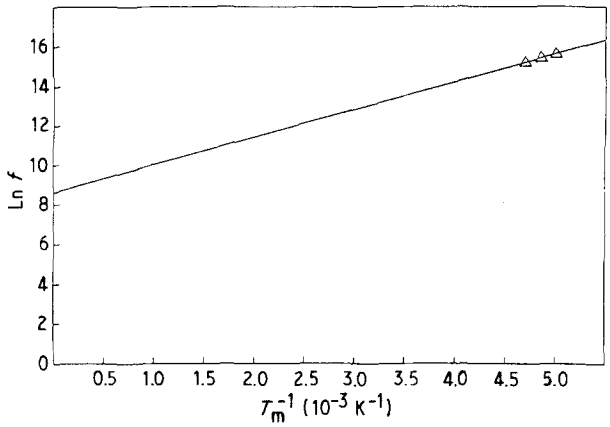

Figure 9 Plot of ln$f$ against T_m^{-1} for a glass sample with the composition containing 27.2 mol % Na_2O.

Fig. 10. Strong and medium absorption bands appeared due to a number of causes, such as bridging and non-bridging oxygen vibration to sodium and to boron ions. Fig. 10 shows that by increasing the Na_2O concentration from 5.6 mol % to 27.2 mol %, the strong absorption bands at 645, 551, 461 and 369 cm^{-1}, disappeared at high concentrations. This may be due to the change in the symmetry of boron atoms, and the vibrations characteristic of these bands become infrared inactive vibrations. In order to confirm this, the change in the intensity of the infrared bands with changing boron concentration was plotted and is

TABLE II

Glass composition (mol %)	Applied frequency (10^6 Hz)	Maximum temperature, T_m (°C)	Activation energy (10^{-2} J)	Relation frequency, f_0 (Hz)
5.6 Na_2O–94.4 B_2O_3	4	− 67	66.27	7.485×10^{-5}
	5	− 68		
	6	− 71		
11.1 Na_2O–88.9 B_2O_3	4	− 53	57.99	2.24×10^{-2}
	5	− 55		
	6	− 58		
21.9 Na_2O–78.1 B_2O_3	4	− 45	33.125	1.64×10^{3}
	5	− 50		
	6	− 55		
27.2 Na_2O–72.8 B_2O_3	4	− 60	19.329	57.10×10^{2}
	5	− 67		
	6	− 73		

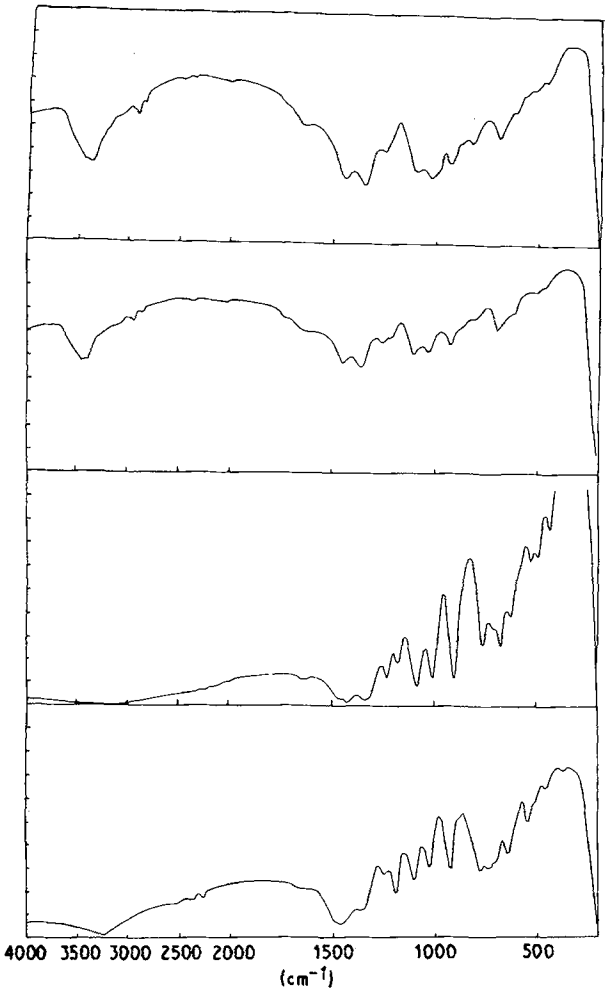

Figure 10 The infrared spectra of Na_2O–B_2O_3 glasses.

shown in Fig. 11. From this figure, it can be seen that the intensity decreased with decreasing boron content up to 88.9 mol %, then the intensity increased, and finally it decreased. This indicates that, at a concentration of 72.8 mol % B_2O_3, the symmetry of boron atoms changes, leading to different modes of symmetry vibrations (represented by dashed and solid lines). Thus the change in the intensity of the lines at 1482, 1250 and 1106 cm^{-1} confirms the presence of two types of symmetry vibration in this concentration region.

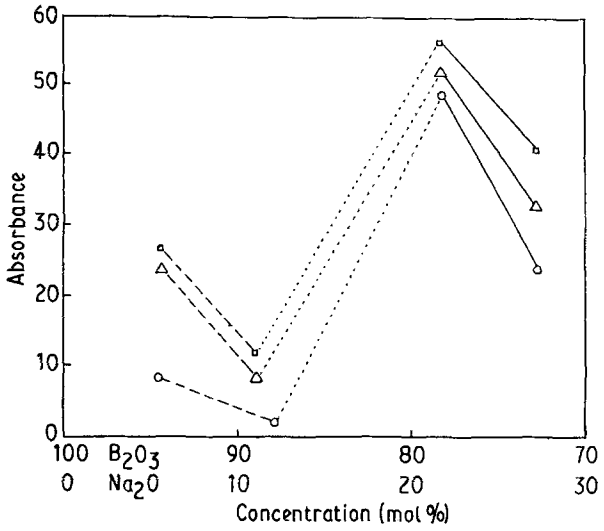

Figure 11 Effect of concentration of sodium borate glasses and the absorbance of the (○) 1482, (△) 1250 and (□) 1106 cm^{-1} bands.

This trend supports results obtained from ultrasonic measurements as far as the change in co-ordination number is concerned.

References

1. S. S. BHATTI and S. SANTOKH, *J. Pure Appl. Ultrason.* **8** (1986) 101.
2. Y. H. YUN and P. J. BARY, *J. Non-Cryst. Solids* **27** (1978) 363.
3. *Idem, ibid.* **30** (1978) 45.
4. L. D. BOGOMOLOVA, I. K. PAVLUSHINA and A. V. ROSHCHINO, *ibid.* **58** (1983) 99.
5. L. D. BOGOMOLOVA, M. P. GLASSOVA, O. E. DUBATOVKO, S. I. REIMAN and S. N. SPASIBKINA, *ibid.* **58** (1983) 71.
6. G. BRAGE, in "Ultrasonic Symposium", Annoplis, MD, USA (1976) p. 83.
7. G. CARINI, M. CUTONI, M. FEDERICO and G. GALLI, *Solid State Commun.* **44** (1982) 1427.
8. M. J. LIN and R. L. THOMAS, "Phonon Scattering in Condensed Matter" (Plenum, Providence, NY, 1980).
9. A. P. SINGH, S. GURJIT and S. S. BHATTI, *J. Pure Appl. Ultrason.* **11** (1989) 49.
10. A. MAKISHMIA and J. D. MACKENZIE, *J. Non-Cryst. Solids* **12** (1973) 35.
11. H. S. CHEN, *J. Appl. Phys.* **49** (1978) 3289.

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