

The Effect of Microstructure on the Transport Properties of Glasses in the Sodium Silicate System

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The internal friction and DC electrical resistivity of amorphously decomposed binary sodium silicate glasses containing from 4.0 to 18.4 mole % Na_2O have been measured. The observed phase separation has little effect upon the internal friction of these glasses. The magnitude and temperature behaviour of the DC electrical resistivity is affected by the degree and type of amorphous decomposition.

1. Introduction

This report presents the data obtained from the study of acoustic absorption (internal friction) and DC electrical conductivity in amorphously decomposed sodium silicate glasses. The phase separated sodium silicate glasses have been studied in detail using a variety of methods [1]; in particular, three previous investigations of the internal friction of these glasses have been published [2-4].

The aim of the work reported here was to study the effects of a two-phase microstructure upon the transport properties. Transport is used here in the general sense of motion of ions. The DC electrical conductivity and internal friction represent two limiting cases: the electrical conductivity involves the transport of charge, in this instance Na^+ ions, over gross distances from one electrode to the other; the internal friction may involve only transfers of ions between nearest neighbours. It was our aim to determine the effects, if any, that the presence and arrangement of two dissimilar phases would have upon these transport mechanisms.

An earlier report [1] presents the background and information about microstructure germane to this system. To summarise, binary sodium silicate glasses in the composition range ~ 20 to 4 mole % Na_2O may spontaneously decompose upon cooling from a melt. The miscibility dome of this system is characterised by two regions: thermodynamically metastable and thermo-

dynamically unstable. The glasses in either of these regions have characteristic microstructures as determined by electron microscopy. Metastable glasses contain one continuous phase with more or less spherical inclusions of another phase randomly arranged throughout. For example, in the 12.6 mole % Na_2O composition, the spheroids are $\sim 0.3 \mu\text{m}$ in diameter, as seen on an electron micrograph, and have a size distribution of $\sim 0.1 \mu\text{m}$ to $0.5 \mu\text{m}$. The unstable morphology is that of two three-dimensionally interconnected phases. The unstable samples of the 12.6 mole % Na_2O composition exhibit elongated channels $\sim 0.1 \mu\text{m}$ to $\sim 0.3 \mu\text{m}$ wide distributed throughout the volume. Certain compositions can be produced by quenching and subsequent heat-treatment and have any of the three morphologies: homogeneous, metastable, or unstable.

Internal friction and DC electrical conductivity data for seven glass compositions in the immiscible region of the sodium silicate system are presented here. The data are examined to determine the effect of microstructural features on these transport properties.

2. Experimental Procedure

Melting and preparation techniques have been reported [1]. Table I lists the analysed compositions and annealing histories of the experimental glasses reported here. These glasses have a tendency to decompose upon annealing. It was

TABLE I Analysed compositions (mole %) and annealing histories of sodium silicate glasses

Composition number	Na ₂ O	SiO ₂	Annealing history
1	18.4	81.6	525° C for 15 min
2	17.6	82.4	525° C for 15 min
3	14.8	85.2	480° C for 15 min
4	12.6	87.3	500° C for 15 min
5	10.3	89.7	505° C for 45 min
6	7.2	92.8	515° C for 15 min
7	4.0	96.0	649° C for 60 min

not possible to obtain homogeneous glasses in all cases (by homogeneous is meant the absence of any noticeable structure in electron micrographs).

Internal friction measurements were performed on rough-sawn bars in the kHz frequency region. The technique entails measuring the free decay of vibrations at the natural resonant frequency of a bar [5]. Data will be presented as plots of δ , the logarithmic decrement, versus temperature. All measurements were taken with the bar hanging in the centre of a split tube furnace. The heating rate was controlled at 3° C/min and the furnace had a uniform temperature zone of $\pm 0.5^\circ$ C over the length of the bar.

Direct current electrical conductivity measurements were performed on polished squares cut from the internal friction samples. Evaporated gold electrodes were vacuum-deposited onto the squares in a three-terminal configuration. A constant voltage method was used in which 1 to 400 V were applied across the sample and the current recorded with a Keithley pico ammeter. These glasses have a propensity for absorbing water on their surfaces. To obtain representative data, both heating and cooling curves were analysed in some instances.

3. Results

3.1. Internal Friction – Low Temperature (Sodium) Peak

Internal friction data were obtained, usually, for at least three heat-treatments and two morphologies in each composition. Only selected portions of the data will be discussed in this report.

Fig. 1 is the (reduced) internal friction versus temperature data for a typical, amorphously decomposed sodium silicate glass. Graphs such as this are generated by subtracting a computer-calculated "background" loss from the raw

data [6]. As shown in fig. 1, the result is usually a pair of symmetrical maxima at $\sim 360^\circ$ K and 620° K, respectively. The question of background and peak symmetry will be discussed in a later section of this paper.

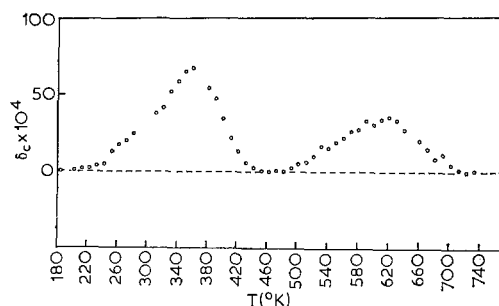


Figure 1 Reduced internal friction data of a 12.6 Na₂O glass heated 8 h at 600° C.

Considerable indirect evidence has led to the identification of the lowest temperature peak as being caused by the stress-induced diffusion of mobile sodium ions [2–4, 7, 9, 10]. In a similar manner the high temperature internal friction peak is ascribed to the motion of "non-bridging" singly ionised oxygen atoms [4, 8, 9, 10], though this conclusion is still being debated.

The reduced data of fig. 1 can be further analysed by obtaining peak heights, peak frequencies, and temperatures, and the widths of the peaks at half-maximum. Table II lists such data for all compositions heat-treated 8 h at 600° C. Two general types of microstructures were observed throughout the region of immiscibility. Within the metastable region the microstructure was characterised by discrete particles of a second phase dispersed in a continuous matrix case. Microstructures characteristic of the unstable region consisted of two independently connected phases. The morphology, unstable U, or metastable M, is indicated. Data for only one frequency are given, although many of the samples were measured at several frequencies. The main features of these data are:

- (i) Δ , which is twice the peak height at maximum, increases as the amount of soda increases;
- (ii) there is no discernible pattern or trend apparent in the width at half-maximum.

Table III lists the same data for those compositions in which more than one morphology could be developed. In the case of the 14.8 Na₂O composition, three morphologies could be

TABLE II Selected internal friction data – sodium peak

Glass	Heat-treatment	$\Delta \times 10^4$	Peak temp. ° K	Peak frequency Hz	Half width ° K	Morphology*
4.0 Na ₂ O	600° C, 8 h	26	363	5118	88	M†
7.2 Na ₂ O	600° C, 8 h	46	372	2463	84	U‡
10.3 Na ₂ O	600° C, 8 h	95	373	2109	98	U
12.6 Na ₂ O	600° C, 8 h	123	358	2125	101	U
14.8 Na ₂ O	600° C, 8 h	152	363.5	2249	113	U
17.6 Na ₂ O	600° C, 8 h	207	363	1822	117	M
18.4 Na ₂ O	600° C, 8 h	226	353	1779	96	M

*Morphologies in the unstable and metastable regions of the miscibility gap have characteristic features.

†M, metastable features.

‡U, unstable features.

TABLE III Selected internal friction data – sodium peak as a function of morphology

Glass	Heat-treatment	$\Delta \times 10^4$	Peak temp. ° K	Peak frequency Hz	Half width ° K	Morphology
12.6 Na ₂ O	600° C, 8 h	123	358	2125	101	U
	770° C, 2½ h	136	359	2968	99	M
14.8 Na ₂ O	quenched	174	368	3308	107	Homogeneous
	annealed	208	363	2780	101	U
	600° C, 8 h	170	374	3166	113	U
	600° C, 8 h	152	363.5	2249	113	U
	600° C, 8 h	186	381	3320	100	M
	600° C, 8 h	162	367.5	2795	107	M

TABLE IV Selected internal friction data – oxygen peak

Glass	Heat-treatment	$\Delta \times 10^4$	Peak temp. ° K	Peak frequency Hz	Half width ° K	Morphology
4.0 Na ₂ O	600° C, 8 h	22	623	5215	132	M
7.2 Na ₂ O	600° C, 8 h	36	596.5	2489	137	U
10.3 Na ₂ O	600° C, 8 h	54	613	2126	120	U
12.6 Na ₂ O	600° C, 8 h	60	618	2859	114	U
14.8 Na ₂ O	600° C, 8 h	68	613.5	2822	113	U
17.6 Na ₂ O	600° C, 8 h	88	617	1810	117	M
18.4 Na ₂ O	600° C, 8 h	110	647	3647	101	M

studied and data for two frequencies are listed. There is little doubt that the morphology, in this composition at least, influences the height, position, and shape of the absorption maxima. The sensitivity of peak maxima to measuring frequency will be discussed later.

3.2. Internal Friction – High Temperature (Oxygen) Peak

The behaviour of the high temperature peak is

essentially the same as that noted above for the low temperature peak. Minor differences in behaviour with composition and morphology might be attributable to difficulties in fitting the background. Tables IV and V are analogues of tables II and III, respectively.

3.3. Internal Friction – Activation Energies

It is generally assumed that the internal friction of alkali ion-containing glasses can be described

TABLE V Selected internal friction data – oxygen peak as a function of morphology

Glass	Heat-treatment	$\Delta \times 10^4$	Peak temp. ° K	Peak frequency Hz	Half width ° K	Morphology
12.6 Na ₂ O	600° C, 8 h	60	618	2859	114	U
		68	625.5	5760	109	U
14.8 Na ₂ O	770° C, 2½ h	74	609	2964	103	M
	quenched	118	623	3308	132	Homogeneous
	annealed	86	628	2761	87	U
	600° C, 8 h	68	613.5	2822	113	U
		96	620	3148	104	U
710° C, 4 h	54	617	2232	142	U	

by a Debye curve or a sum of Debye-type curves. This implies that, for a single relaxation process,

$$\delta = \frac{\Delta \omega \tau}{1 + (\omega \tau)^2} \quad (1)$$

where δ is the observed internal friction, Δ is a constant, known as the relaxation strength, ω is the angular frequency, and τ is a characteristic relaxation time. The quantity τ is further assumed to be thermally activated, viz:

$$\tau = \tau_0 \exp\left(\frac{q}{RT}\right), \quad (2)$$

where τ_0 is considered constant, R is the universal gas constant, T is the absolute temperature, and q is an activation energy. These equations are for the case of a single relaxation time or mechanism. If measurements are made at several frequencies, the quantities τ_0 and q can be calculated. The precision of determining the magnitudes of these parameters depends critically upon:

- (i) the number of frequencies scanned;
- (ii) the accuracy of the temperature measurements;
- (iii) the method and reliability of subtracting background curves.

The error caused by the first two points can be readily estimated. The last point is less easily dealt with. The method described by Field and Redwine [6] yields reproducible results. Statistical analysis of the computer curve fit accounts for 98% of the points used. Only 2% of the variation cannot be accounted for by the curve. Assuming the background curves are correct and valid, the activation energies quoted in table VI are estimated to be accurate within $\pm 5\%$.

3.4. DC Electrical Measurements

Table VII is a compilation of resistivities at $T = 100^\circ \text{C}$ for the compositions and heat-

TABLE VI Activation energy, q , determined from internal friction measurements on selected samples

Glass	Heat-treatment	Sodium peak q (kcal/mole)	Oxygen peak q (kcal/mole)	Morphology
7.2 Na ₂ O	600° C, 1 h	22.6	46.5	U
12.6 Na ₂ O	600° C, 1 h	16.9	38.9	U
	600° C, 8 h	16.1	32.2	U
14.8 Na ₂ O	600° C, 8 h	11.3	22.5	U
	710° C, 4 h	14.3	21.6	M

treatment studied. Included for comparison are relaxation strengths, temperatures of peak maxima, and measuring frequencies from the internal friction experiments. In sharp contrast to the steady increase in relaxation strength with increasing sodium content, the DC electrical resistivity decreases rapidly between the 4 Na₂O and the 7.2 Na₂O compositions, and then the magnitude falls off slowly. The 4 Na₂O sample consists of small, roughly spherical droplets about 400 Å in diameter dispersed in a continuous matrix. From the phase diagram the continuous phase must be silica-rich. The resistivity of $\sim 10^{13} \Omega \text{cm}$ is reasonable for a composition so low in sodium [11]. The 18.4 Na₂O sample exhibits the inverse microstructure: silica-rich droplets dispersed in a continuous soda-rich phase. The spheroids of the 600° C 8 h sample are roughly 600 Å in diameter, but there seem to be fewer of them than in the corresponding 4 Na₂O sample. A resistivity of $\sim 10^8 \Omega \text{cm}$ at $T = 100^\circ \text{C}$ seems quite reasonable for this sample [7, 11].

The behaviour of the resistivity for compositions lying between these two end points can be explained on the basis of the amount and distribution of two phases present with electrical

TABLE VII Sodium silicate system DC electrical resistivity and internal friction maxima

Glass	Heat-treatment	ρ (373° K) Ω cm	Δ	T_p ° K	F_p Hz
4.0 Na ₂ O	600° C, 8 h	2.44×10^{13}	26×10^{-4}	363	5118
7.2 Na ₂ O	600° C, 8 h	5.33×10^9	46×10^{-4}	372	2463
			32×10^{-4}	398	3498
10.3 Na ₂ O	600° C, 8 h	4.43×10^9	95×10^{-4}	373	2109
12.6 Na ₂ O	annealed	1.78×10^9	92×10^{-4}	373	2716
	600° C, 8 h	6.9×10^{10}	108×10^{-4}	368	2862
			123×10^{-4}	358	2125
	770° C, 2½ h	8.98×10^8	136×10^{-4}	359	2968
14.8 Na ₂ O	annealed	3.88×10^7			
	600° C, 8 h	1.78×10^8	152×10^{-4}	363.5	2249
			130×10^{-4}	357	2855
	710° C, 4 h	1.74×10^8	188×10^{-4}	374	2247
17.6 Na ₂ O	600° C, 8 h	9.51×10^7	207×10^{-4}	363	1822
18.4 Na ₂ O	600° C, 8 h	1.77×10^8	220×10^{-4}	353	1779
			306×10^{-4}	363	3711

properties similar to 4 Na₂O and 18.4 Na₂O. The various heat-treated samples of 12.6 Na₂O are good examples of the effect of microstructure on the electrical properties. The sample treated for 8 h at 600° C contains, from the phase diagram and the application of the lever rule, about 40% by volume of a phase rich in soda. It has been shown previously that both phases in these glasses are three-dimensionally interconnected and continuous [1]. If this soda-rich phase is actually the same soda-rich phase as is present in 18.4 Na₂O, we would expect that most of the current would be transported by carriers in this phase and that the magnitude of the resistivity should be higher than the 18.4 Na₂O sample. This is indeed the case as the data in table VII indicate. A 12.6 Na₂O sample, heated at 770° C for 2½ h exhibits a metastable phase morphology. Due to the fact that the miscibility line is curved, the "end-point" composition" for this temperature, contains less than 18.4 moles Na₂O. We would estimate, then, that the resistivity should be similar in magnitude to that of 18.4 Na₂O, but slightly higher. The data confirm this assumption.

Fig. 2 is a plot of the natural logarithm of the resistivity versus the reciprocal of the absolute temperature for 14.8 Na₂O. Note the marked deviations from a single straight line. The regions of different slope have been interpreted as reflecting changes in the activation energy and concentration of carriers [8].

Table VIII exhibits the activation energies derived from a least-squares fit to a straight line of $\ln \rho$ versus $1/T$ over various temperature intervals. The general feature observed in these

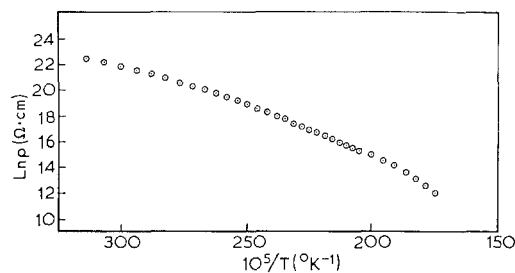


Figure 2 DC electrical resistivity versus temperature for a 14.8Na₂O glass heated 4 h at 710° C.

data is two regions, each characterised by a different magnitude of the activation energy. At low temperatures the activation energy is typical of ionic transport; i.e. ~ 16 kcal/mole. At high temperatures (typically, 150 to 250° C) the energies range from 25 to 44 kcal/mole. Activation energies and DC electrical resistivities are accurate to within $\pm 5\%$. The pre-exponential terms are much less accurate due to their extreme sensitivity to the curve-fitting.

4. Discussion

4.1. The Effect of Amorphous Phase Decomposition

If one plots Δ , twice the sodium peak maximum, versus hours of heat-treatment at 600° C, the curve initially decreases and then increases to a more or less constant value after 16 h at 600° C. This behaviour was noted for most of the compositions. The minimum in the peak height moves to longer times as the sodium content

TABLE VIII Activation energies from DC electrical resistivity measurements

Glass	Heat treatment	Temperature interval ° C	E_A kcal/mole	$\ln \rho_0$
18.4 Na ₂ O	600° C, 8 h	65–147	16.12	– 2.8
		188–276	44.20	– 34.6
12.6 Na ₂ O	annealed 600° C, 8 h 770° C, 1½ h	184–280	30.84	– 16.59
		158–200	32.50	– 17.5
		135–205	31.03	– 22.6
14.8 Na ₂ O	annealed 607° C, 8 h 710° C, 4 h	40–172	15.96	– 4.1
		209–269	32.50	– 21.88
		85–294	28.20	– 17.2
		107–236	15.65	– 0.91
		248–296	25.49	– 10.47
7.2 Na ₂ O	600° C, 8 h	188–246	26.04	– 9.1
4.0 Na ₂ O	600° C, 8 h	129–212	24.80	– 1.7

increases. The minima occur at 2, 4, 8, and 16 h for 7.2 Na₂O, 12.6 Na₂O, 14.8 Na₂O, and 17.6 Na₂O, respectively. This behaviour could be caused by:

- (i) changes in the volume fractions of the two phases;
- (ii) changes in the composition of the phases;
- (iii) a varying rate of decomposition:

The explanation for this behaviour is not forthcoming from these data. Only one piece of evidence applies directly to this question, and it points to a changing volume fraction in unstable morphologies. In fact, the behaviour of the volume fraction of the soda-rich phase with time, for 7.2 Na₂O and 12.6 Na₂O compositions, is identical to the change in Δ with time.

Aside from this change in the peak height with time of heat-treatment, which is undoubtedly due in some way to the developing microstructure, amorphous decomposition seems to have little or no effect upon the internal friction spectra of these glasses. Tables III and V indicate small changes in the height, position, and shape of the maxima as the morphology is manipulated, but some or all of these differences might be due to compositional variations or the effect of fictive temperature. This negative result demonstrates again that the internal friction is sensitive only to short range forces upon mobile ions. The gross differences observed in the structure with electron microscopy are variations of groupings thousands of angstrom units long. Internal friction measurements are sensitive to changes of atomic ordering near tens of angstroms. Averages of long wavelength dependent properties, i.e. elastic moduli and softening points, are quite sensitive to the degree and type of amorph-

ous phase decomposition, as has been shown earlier [1].

It is reassuring to note that the electrical properties are sensitive to the phase separation. DC electrical measurements are the type of long range averages of many ion "jumps" that should show the effect of phase separation. The reason that the magnitude of the electrical resistivity and activation energy does not change much from the 7.2 Na₂O to the 17.6 Na₂O compositions is probably due to the continued presence of one continuous soda-rich phase in all of those compositions. Most of the current will be carried by that phase whenever it is present.

The rather obvious curvature of the resistivity with temperature and the occurrence of two activation energies in different temperature regions have been ascribed to changes in the concentration of carriers and activation energies. At high temperatures this may include contributions from sodium ions in the silica-rich regions of the lattice. It should be mentioned here that only one region of dielectric constant dispersion was noted for compositions containing 12.6 Na₂O and 7.2 Na₂O.* This is in contrast with Charles's findings in some lithium silicate glasses [7, 12]. We specifically looked for two regions of dispersion similar to those Charles noted in his lithium silicate specimen No. 1 (6.7 mole % lithia, remainder silica [12]) but were unable to find any.

In short, the internal friction spectra are affected most by the total amount of sodium present in the glass and only slightly by the separation into two phases of varying composition and arrangement. The DC electrical resistivities reflect both the composition and the

* Data not included in tables.

arrangement of the two phases.

Fig. 3 is a plot of Δ , twice the peak height, versus soda content for samples of sodium silicate glass heated for 8 and 16 h at 600° C. Dotted lines are drawn at the approximate compositions separating metastable and unstable morphologies. Notice that these lines nearly correspond to the transitions between straight line portions of the graph for the 8 h samples. It may be that the effects of morphology upon the internal friction are stronger, but more subtle than we thought. It should be pointed out, however, that in no other heat-treatment sequence did the data appear this regular. For example, data for 16 h treatments at 600° C are represented on fig. 3 as a straight line. Indeed, the acute sensitivity of these peak maxima to measuring frequency makes the task of comparing data from composition to composition very difficult.

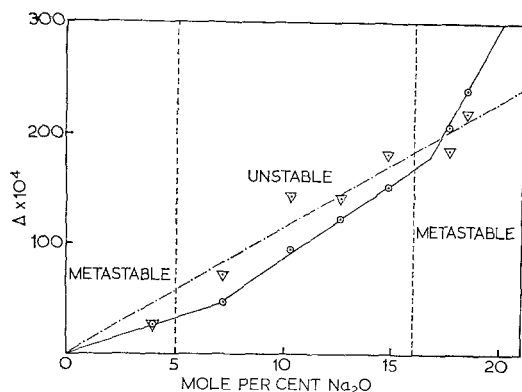


Figure 3 Relaxation strength (twice peak maximum) of sodium silicate glasses heated 8 h (circles) and 16 h (triangles) at 600° C versus % Na₂O.

4.2. Peak Shape and Background

Fig. 1, which illustrates the internal friction data for one composition of 12.6 Na₂O, exhibits two quite symmetrical peaks. Generating a background curve for such a spectrum is quite easy and straightforward. Fig. 4 shows similar data for a 14.8 Na₂O composition. It is easy to see here that the sodium peak at least, is *not* symmetrical; it has a tail which extends to low temperatures.

The question to be answered is whether or not this tail is real, and if it is, what is the cause of this asymmetry. The reality of this asymmetry in a peak ascribed to alkali ion motion can be

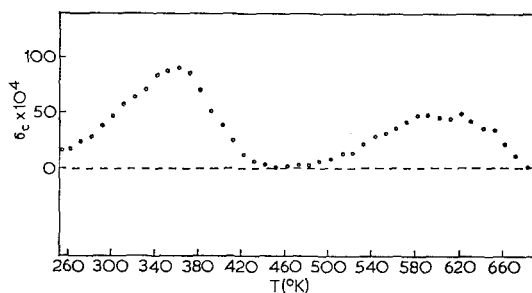


Figure 4 Reduced internal friction data of a 14.8Na₂O glass versus temperature.

corroborated by its appearance in all our data on compositions containing 14.8 mole % Na₂O or more and, in torsional pendulum experiments conducted by other authors [9]. Its cause can only be speculated upon. One mechanism comes to mind immediately; a contribution from mobile sodium ions in the silica-rich phase. Two peaks in these glasses attributable to sodium were never resolved, but a calculation based on an activation energy appropriate to a silica-rich composition has suggested that it is possible for the two maxima to overlap in temperature. It might be possible to resolve separate peaks with torsional pendulum data if they exist.

In addition to having a "tail" which extends to low temperatures, this system is extraordinarily sensitive to measuring frequency. The height of the sodium peak in a 12.6 or 14.8 Na₂O composition will nearly double as the measuring frequency is doubled. This *might* be taken as evidence that the distribution of relaxing centres is not symmetrical. Another possibility is the superposition of a second peak on the major relaxation. This second peak would presumably be due to the relaxation of sodium ions from the minor phase. Such relaxations would have different activation energies and thus a different temperature and frequency behaviour from the principal relaxation. This explanation is attractive because it requires no modification or asymmetry of the actual distribution of energy sites.

For the lack of more evidence to the contrary, the peaks were obtained using a self-consistent method of generating a background curve, and all further analysis assumed the internal friction maxima to be symmetrical. As will be discussed below, a method does exist for deriving quantitative comparisons between the sodium and the oxygen peak assuming them to be symmetrical.

4.3. Quantitative Comparison of Internal Friction Peaks

A convenient visualisation of internal friction is to imagine a loosely bound ion, such as sodium in sodium silicate glasses, absorbing energy from an elastic wave and jumping or hopping to a higher energy site within the material. After a characteristic time, τ , the ion may "relax" back into its original configuration. In glasses one can postulate a range of energies available to any given ion. For lack of data to the contrary, it can be assumed that the distribution function describing the range of energies is bell-shaped, a Gaussian curve. Such a distribution function is called a "log normal" distribution.

Nowick and Berry [13], in an excellent paper, have analysed the effect such a distribution would have upon internal friction measurements such as are presented here. They describe explicitly the mechanism by which one can extract three quantities, β , Δ_j , and τ_m , from a knowledge of mean activation energy, peak position, and magnitude. The quantity β is the width of the curve in decades of the logarithm of τ ; if β equals zero the process causing the relaxation is single-valued. The larger β the more relaxation times or energy sites – or processes – required to explain the experimental curves. The factor Δ_j is the relaxation strength, a measure of the magnitude of the relaxation. Finally, τ_m is the mean relaxation time; the relaxation time in seconds characteristic of the majority of the relaxing centres. It should be reiterated that such an analysis *assumes* a symmetrical peak for the experimental data. As we have seen for all sodium silicate glasses containing greater than 14.8 mole % of soda, this is *not* true. Nevertheless, Nowick and Berry's techniques and methods have been used to analyse three

compositions as a first approximation. The results for β and Δ_j are tabulated in table IX. The most striking feature of these data is the decrease in β from ~ 4 in the 7.2 Na₂O glass to ~ 2.4 in the 14.8 Na₂O composition. This indicates that the distribution of sites in the 14.8 Na₂O glass is sharper than that of the 7.2 Na₂O composition. The distribution of energy sites (or energies) narrows even more markedly in the high temperature peak attributed to O⁻ ion migration.

Forry, using a similar analysis on data from glasses containing 17 to 34% Na₂O, reported an opposite trend of β with composition [2]. The reason for this anomaly is not known. Both β and Δ_j are quite sensitive to the values of mean activation energy and peak width used in the calculation. In any event, the curves for the composition greater than 14.8 Na₂O are *not* symmetrical. No great confidence can be placed on calculations based on symmetrical peaks in this portion of the sodium silicate system.

5. Conclusions

- (i) Amorphous phase decomposition affects those transport properties which depend on long-range order or averages over the sample volume.
- (ii) The electrical conductivity involves the transport of charged (Na⁺) ions over large distances. The microstructural features produced by amorphous phase decomposition (the amounts, distributions and compositions of phases present) determine the magnitudes of the electrical conductivity and the activation energies for conduction.
- (iii) The initial friction involves, primarily, transport of ions (Na⁺) between nearest neighbours. The total amount of sodium present determines the magnitude and appearance of

TABLE IX Relaxation parameters

Glass	Heat-treatment	Morphology	Peak*	β	$\Delta_j \times 10^3$
7.2 Na ₂ O	600° C, 1 h	U	Low	4.1	9.7
			High	4.0	6.7
12.6 Na ₂ O	600° C, 1 h	U	Low	4.4	28.9
			High	3.4	15.9
			Low	3.4	24.9
			High	2.3	10.5
14.8 Na ₂ O	600° C, 8 h	U	Low	2.4	25.5
			High	1.0	9.5
	710° C, 4 h	M	Low	2.5	32.0
			High	1.3	10.0

*"Low" refers to the low temperature or sodium peak. "High" refers to the high temperature O⁻ relaxation.

internal friction spectra for these glasses.

The presence of a second phase may exert a minor influence upon the shape of the spectrum i.e. (a) an asymmetrical peak, and (b) changes in peak height with time of heat treatment.

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