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# Thermally stimulated polarization current in sodium germanate glass

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The electrical conductivity of $X\mathrm{Na_2O} \cdot (100-X)\mathrm{GeO_2}$ glasses where $X$ is 0.19 and 27.5 mol %, was studied by means of the technique of thermally stimulated polarization current. The compositional dependence of the parameter $\sigma_0 T/n^{1/3}$, where $\sigma_0$ is the pre-exponential facor for conductivity and $n$ is the nominal concentration of sodium ions, suggests that these glasses contain some sort of inhomogeneities. This suggestion is supported by the phase diagram.

## 1. Introduction

Alkali germanate glasses are known to show a so-called "germanate anomaly", where many physical properties go through a maximum or minimum at 10 to 20 mol% alkali oxide. Evstropiev and Ivanov [1] ascribe this anomaly to a change in the coordination number of some of the Ge atoms from four to six on adding alkali, and propose that $\mathrm{GeO_6}$ octahedra share their six apices with neighbouring $\mathrm{GeO_4}$ tetrahedra to build up a network such that the octahedra increase in number up to a limiting alkali content. At alkali concentrations greater than this limiting value, there is a possibility that non-bridging oxygen atoms are generated with or without a further increase in the number of $\mathrm{GeO_6}$ octahedra. Measurements of density [2, 3], refractive index [2, 3], acoustic velocity [4], infra-red absorption [5], viscosity [6], and thermal expansion [7] support this hypothesis, although there are also properties such as permeability and diffusivity of He [8] which are related to the anomaly only indirectly, if at all.

The initial purpose of the present work was to determine whether such an anomaly is present in the electrical properties of $X\mathrm{Na_2O} \cdot (100-X)\mathrm{GeO_2}$ glasses where $X$ is 0.19 to 27.5 mol%. The thermally stimulated polarization current (TSPC) technique [9], which is said to be an easier and more reliable procedure compared with a d.c. or a.c. bridge method, was used and is composed of two sequential measurements: Firstly (TSPC-1), the sample is short-circuited and cooled to a low enough temperature, $T_0 \simeq 100\,\mathrm{K}$ to freeze-in the equilibrium configuration of constituent ions. A bias voltage is then applied across the sample, and the temperature is raised at a linear rate with respect to time up to a temperature where space charge polarization is still negligible. During heating, the sample is gradually polarized by for example a preferred orientation of alkali-nonbridging oxygen dipoles is along an applied field [10, 11]. The long-range motion of alkali which is responsible for bulk conduction, thereby producing a current in the outer circuit is recorded as a function of temperature. With a field still applied, the sample is again cooled to $T_0$ and heated a second time (TSPC-2). In this way, the conduction process can be isolated from contributions of internal polarizations which are essentially negligible during TSPC-2 [9]. The thermally stimulated depolarization current (TSDC) was also measured as necessary. This technique is a counterpart of TSPC and requires polarizing a sample at a temperature, $T_\mathrm{p}$, where internal polarization can occur easily, cooling to $T_0$ with a field applied, removing the field at $T_0$ and heating at a linear rate. The temperature of TSDC peaks thus obtained from relaxation of internal polarizations are said [12] to be identical with those of TSPC peaks.

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## 2. Experimental procedure

A description of the apparatus used is given elsewhere [9]. Gold electrodes, 0.635 cm in diameter, were deposited on both sides of samples 1 cm x 1 cm x 0.1 cm. The sample was heated from liquid nitrogen temperature, $T_0$, to 200° C at a rate of about 0.08 K $\sec^{-1}$, and the induced current in the outer circuit was measured by a Keithley 610B electrometer. In order to reduce temperature gradients within the sample during heating, helium gas flowed through the cryostat. Before entering the cryostat, the helium was dried by passing through a liquid nitrogen trap. It is important that the cryostat be free of water vapour during TSC measurements [11].

## 3. Results and discussions

Fig. 1 shows typical TSPC-1 and TSPC-2 curves for a 27.5 mol% $Na_2O$ glass, as well as a TSDC curve obtained by polarizing the sample at room temperature. The difference between TSPC-1 and TSPC-2 is believed to be due to internal polarizations. In the sodium germanate glasses investigated, only one TSDC peak was detected. The difference curve coincided almost exactly with the TSDC curve, as was expected.

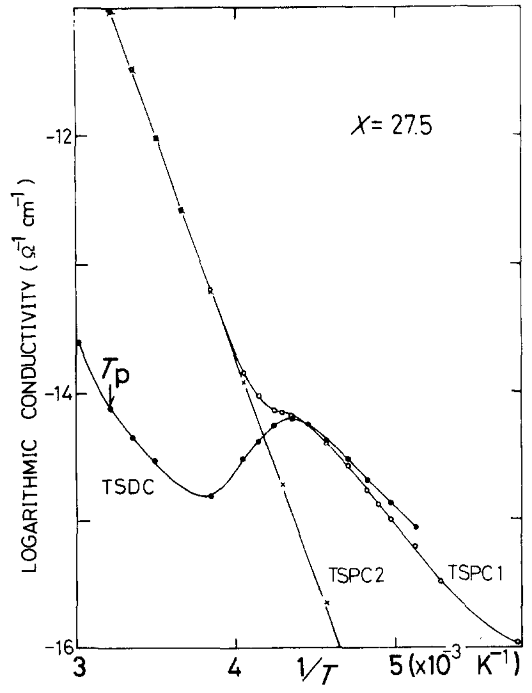

*Figure 1* Typical TSPC-1 and TSPC-2 curves for a 27.5 mol% $Na_2O$ glass, as well as a TSDC curve obtained by polarizing the sample at 312 K for 5 min, where the applied field was $2.81 \times 10^3$ V $cm^{-1}$.

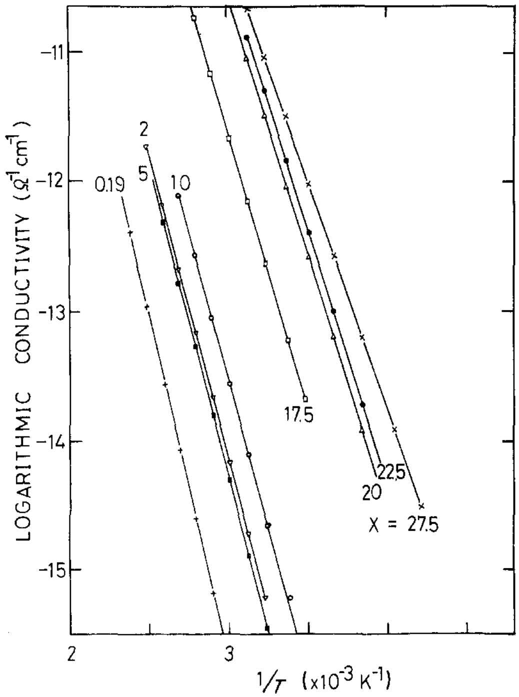

*Figure 2* Logarithmic plots of conductivity as derived from TSPC-2 against reciprocal temperature.

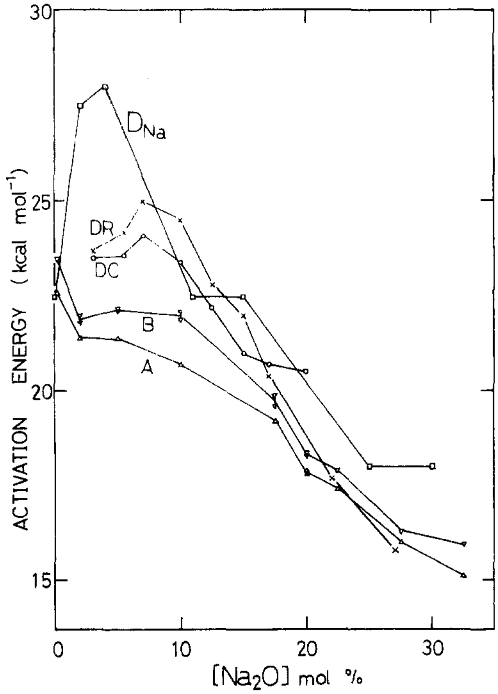

*Figure 3* Activation energies for conduction as calculated from ln σ against 1/T (labelled A) and ln (σT) against 1/T (B) plots of TSPC-2, as well as values reported for d.c. conductivity (DC) [13], dielectric relaxation (DR) [13], and sodium diffusion ($D_{Na}$) [14].

The conductivity, $\sigma$, calculated from TSPC-2 for each glass showed Arrhenius behaviour over more than four orders of magnitude of conductivity (Fig. 2). The activation energy, $H$, for conduction was calculated from

$$\sigma = \sigma_0 \exp(-H/kT), \tag{1}$$

where $\sigma_0$ is a pre-exponential factor. Fig. 3 illustrates a comparison of the activation energies calculated in this way with those reported for d.c. conductivity [13], dielectric relaxation [13] and sodium diffusion [14]. Since $\sigma_0$ is expressed theoretically as [15]

$$\sigma_0 = \frac{ne^2\lambda^2\nu}{6kT}, \tag{2}$$

where $n$ is the carrier density, $\lambda$ is the average jump distance, and $\nu$ is the oscillation frequency of charge carriers within an equilibrium position. ln $(\sigma T)$ was also plotted against $1/T$ and the activation energy recalculated. Although the values of $H$ in Fig. 3 are different from each other, the trend is the same, i.e. $H$ passes a peak or plateau at about 5 mol% $Na_2O$ and then decreases rapidly with increasing sodium content.

Assuming the charge carriers (sodium ions) are homogeneously distributed and contribute equally to $\sigma$, and that the jump distance equals the separation between the carriers, then, approximately, $(4/3)\pi(\lambda/2)^3 n \approx 1$, such that

$$n\lambda^2 \approx (6/\pi)^{2/3} n^{1/3}. \tag{3}$$

In Equation 2, the temperature factor can be eliminated by plotting ln $(\sigma T)$ against $1/T$ rather than the ln $\sigma$ against $1/T$ plot, to obtain a temperature independent term $\sigma_0 T$. If the assumption of a homogeneous distribution of charge carriers is correct, the parameter

$$R = \frac{\sigma_0 T}{n^{1/3}} = \frac{e^2 \nu}{6k}\left(\frac{6}{\pi}\right)^{2/3} \tag{4}$$

should be dependent on $\nu$ only. The measurement by far-infra-red spectroscopy [16] revealed, however, that $\nu$ changes little for the various glasses; $\nu = 195\,\text{cm}^{-1}$ for $Na_2O \cdot V_2O_5$, $212\,\text{cm}^{-1}$ for $Na_2O \cdot P_2O_5$, $220\,\text{cm}^{-1}$ for $Na_2O \cdot B_2O_3$ and $Na_2O \cdot 2B_2O_3$, and $230\,\text{cm}^{-1}$ for $Na_2O \cdot SiO_2$. Therefore, the parameter $R$ can be used roughly as a measure of homogeneity of the glass structure, since $R$ must be smaller than an ideal value (Equation 4) whenever some charge carriers are localized and cannot contribute to conduction.

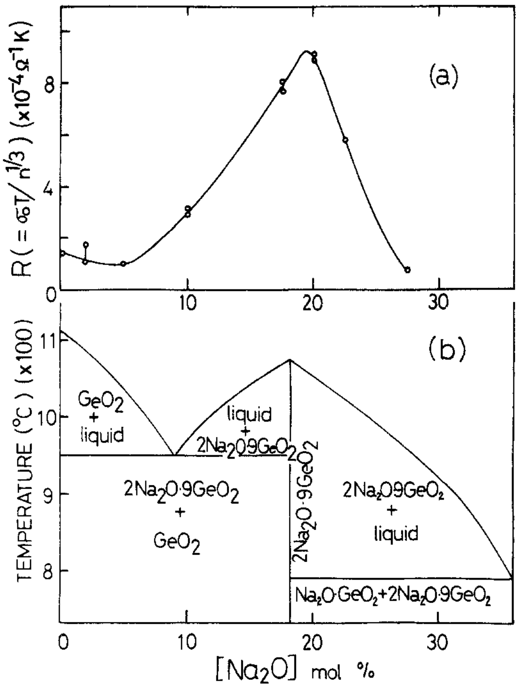

*Figure 4* Compositional dependence of the ratio $R$ ($= \sigma_0 T/n^{1/3}$) and the corresponding phase diagram [2].

Fig. 4 shows the compositional dependence of $R$ in the sodium germanate glasses as calculated from the electrical conductivity and composition, as well as the $Na_2O$–$GeO_2$ phase diagram [2]. Ideally, $R$ is $3.1 \times 10^{-3}\,\Omega^{-1} \cdot \text{K}$ for the sodium germanate glasses when $\nu$ is taken to be $220\,\text{cm}^{-1}$. Based on the difference between the calculated and experimental values for $R$, Fig. 4 indicates that the highest degree of sodium inhomogeneity would occur on both sides of the composition $2Na_2O \cdot 9GeO_2$ ($X = 18$). Even at $X = 18$, $R$ is only about 1/3 that calculated for a homogeneous sodium distribution.

There are conflicting opinions regarding phase separation in these glasses. Studies of density [17] and electric moduli [18] have been interpreted as indicating an absence of phase separation. However, Shelby [19] interpreted the compositional dependence of the viscosity of these glasses in terms of a clustering of the sodium ions at low sodium content. Also, Reishakhrit and Tolstoi [20] suggested the existence of a sodium-rich microphase from the fluorescence of Nd doped sodium germanate glasses.

Most of the glasses in this study were examined by TEM, especially $X = 5$, after etching in several etchants and at magnifications up to $\times 10^5$. However, no discernable phase separation or microheterogeneity was observed under the wide variety of conditions employed. Although the values of $R$ are suggestive of alkali inhomogeneities and the compositional dependence of $R$ correlates reasonably well with the $Na_2O$–$GeO_2$ phase diagram, these inhomogeneities are apparently not readily detected by normal electron microscopy.

## 4. Conclusion

Analyses of the TSPC curves of $X\text{Na}_2\text{O} \cdot (100-X)$ $\text{GeO}_2$ glasses in terms of the parameter $R$ $(= \sigma_0 T/n^{1/3})$, where $\sigma_0 T$ is the temperature independent term as evaluated from the Arrhenius' plots of TSPC-2, suggest an inhomogeneous distribution of sodium ions in these glasses. Supporting evidence is provided by the phase diagram.

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