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Thermally stimulated polarization and depolarization current (TSPC / TSDC) techniques for studying ion motion in glass

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The feasibility of studying ionic motion in glass using thermally stimulated polarization (TSPC)/depolarization current (TSDC) techniques was investigated with $4Na_2O{-}96SiO_2$ and $30PbO{-}70SiO_2$ (mol %) glasses. The TSPC peaks in these glasses were dependent on glass composition and attributed to bulk polarization. The high temperature background TSPC is shown to be due to the d.c. conductivity, whereas the TSPC/TSDC peaks in the $4Na_2O$ glass are attributed to shorter range Na^+ motion.

1. Introduction

The thermally stimulated polarization current (TSPC) and thermally stimulated depolarization current (TSDC) techniques for studying charge motion in solid dielectrics are based on the thermally activated release of trapped charge or polarization [1–5] from localized energy levels. During heating, the release of trapped charge or polarization from a dielectric produces an electrical glow curve (current peak) analogous to the more widely known glow curve observed when a thermoluminescent material is heated. The source of the thermally stimulated current may be (a) the thermal release of trapped electrons, holes or ions, (b) some type of orientational (dipole) polarization, or (c) space charge polarization. If a material contains several traps of different energy, then a corresponding number of current peaks should be observed during heating.

The TSPC technique [1, 2] involves measuring the current from a solid dielectric subjected to a steady-state (d.c.) electric field as the dielectric is heated (commonly at constant rate) from some low temperature T_0. When the solid contains a non-equilibrium concentration of trapped charge, as produced by irradiating the solid with γ-rays, X-rays, ultra-violet, etc., this charge is released thermally during heating and a current peak is produced [6–11]. Similarly, if the material contains some type of dipole, such as the impurity–vacancy complexes in alkali halides, [5, 12–14], dipole orientation commences with increasing temperature (under the applied field) and this orientational polarization produces a current peak. In either case, the temperature dependent current, $I(T)$, for a first order process is given by [1]

$$I(T) = A\exp(-E_a/kT) \times \exp\left[-B\int_{T_0}^{T}\exp(-E_a/kT')\,dT'\right] \qquad (1)$$

where E_a is an activation energy or trap depth, k is the Boltzmann constant, and A and B are constants depending upon the current source (trapped charge, dipole polarization or other) and measurement conditions (electrode area, heating rate, etc.).

The procedures for the TSDC technique, [4, 5], used primarily to study dipole polarization, differ slightly from the TSPC technique. A material containing an electrical dipole is first polarized with a d.c. field, ϵ_p, for a time, t_p, at a temperature, T_p, where dipole orientation can occur (dipole relaxation time $\tau(T_p) \ll t_p$), but space charge polarization can be avoided. The specimen is then quenched to a suitably low temperature, T_0, (e.g. 100 K) generally with the field applied, where dipole motion essentially ceases, $\tau(T_0) \gg \tau(T_p)$.

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The field is then removed and the specimen temporarily short circuited. During heating (constant or hyperbolic rates have been used), the discharge (depolarization) current is measured as a function temperature. When the dipole relaxation time, τ, varies as

$$\tau = \tau_0 \exp(E_a/kT) \tag{2}$$

the reorientation of the dipoles to their random configuration during heating produces a current, $I(T)$, given by [2, 5]

$$I(T) = (N_d \mu^2 \alpha \epsilon_p / kT_p \tau_0) \exp(-E_a/kT) \times \exp\left[(-1/b\tau_0)\cdot\int_{T_0}^{T} \exp(-E_a/kT')\,\mathrm{d}T'\right] \tag{3}$$

where N_d is the dipole concentration, μ is the dipole moment, α is a factor for the freedom of dipole orientation, b is the heating rate and the other terms have been defined.

The TSDC technique has been used to study charge trapping in chalcogenide (As_2Se_3) glasses [15–17], migration polarization in aluminophosphate glasses [18, 19], and Na^+ motion in thermally grown vitreous silica films on silicon [20–22]. In this latter study [20–22], the thermal detrapping (release) of Na^+ ions from either the Si–SiO_2 or SiO_2–Al electrode interface produced TSIC (thermally stimulated ionic current) peaks from which the trap depths and Na^+ mobility were determined.

To date, the TSPC/TSDC techniques have not been applied to alkali-containing oxide glasses. This paper describes measurements undertaken to establish the feasibility of using these techniques for studying ionic motion in glass. The effect of polarization field, type of elctrodes and measuring atmosphere are illustrated with results for $4Na_2O$–$96SiO_2$, $25Na_2O$–$75SiO_2$ and $30PbO$–$70SiO_2$ (mol %) glasses.

2. Experimental procedures and apparatus

2.1. TSDC measurements

A typical measurement sequence is shown in Fig. 1a where a dipole orientation process has been assumed for purposes of illustration. The specimen is first polarized with a d.c. field, ϵ_p, at temperature, T_p, for a time t_p. T_p should be high enough for dipole alignment, but low enough to avoid significant space charge polarization. The specimen, with ϵ_p still applied, is quenched to a low temperature $T_0 \ll T_p$ ($T_0 \sim 100$ K), where dipole motion is essentially negligible. At T_0, ϵ_p is removed, the two electrodes are temporarily short circuited (~ 1 min), and the specimen is connected to an electrometer. As the specimen is heated at a constant rate (0.05 to 0.1 K sec^{-1} is generally suitable), the discharge current is recorded as a function of temperature. As shown in Fig. 1a, one, or more, current peaks are observed as the dipoles assume their random orientation.

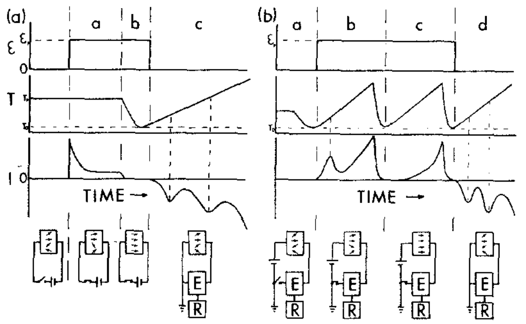

Figure 1 Schematic representation of TSDC and TSPC measurements. (a) TSDC measrement: (i) polarization, (ii) quenching, (iii) TSDC measurement and (b) measurement: (i) quenching, (ii) TSPC-1, (iii) TSPC-2, (iv) TSDC-3. E: electrometer and R: recorder.

2.2. TSPC measurements

The sequence for this measurement is shown in Fig. 1b and the procedure described below again assumes a dipole orientation process. The specimen is first quenched to a low temperature T_0 (~ 100 K) where a battery, the specimen, and an electrometer are connected in series. The specimen is then heated at a constant rate, b, and as the dipoles become oriented the current increases and reaches a maximum. This current is denoted as TSPC-1, where 1 designates the first heating. The specimen is then requenched to T_0, with the ϵ_p still applied, and reheated a second time at a constant rate, this current being denoted as TSPC-2. No current peak due to dipole orientation is observed, since the dipoles became oriented during the first heating. TSPC-2 can be used for calculating the d.c. conductivity of the specimen [23].

The specimen is again quenched to T_0 with the ϵ_p still applied. The ϵ_p is then removed and the electrodes temporarily short-circuited for ~ 1 min. after which the specimen is connected to an electrometer in the manner for measuring TSDC. While heating the specimen at a constant rate, the TSDC curve is recorded as a function of temperature. At T_m, a peak identical to that in TSPC-1 should be observed as the dipoles become randomly oriented.

2.3. Apparatus

The apparatus for measuring the thermal current included an electrometer*, an X–Y recorder, and a cell (Fig. 2) which could be evacuated to ~ 15 μm Hg and heated from 78 to 600 K. Glass discs 1.2 to 2.5 cm in diameter and 0.05 to 0.2 cm thick were cut and ground from larger annealed rods. Gold electrodes, 0.635 cm in diameter, were evaporated onto both sides of the disc. The disc was held between two brass electrodes and two alumina plates. This assembly was held together by a metal frame which was attached to an inner copper tube (for supporting the electrode assembly). The entire assembly was placed in an outer copper container that provided added electrical shielding and which could be evacuated or filled with dry helium (during heating).

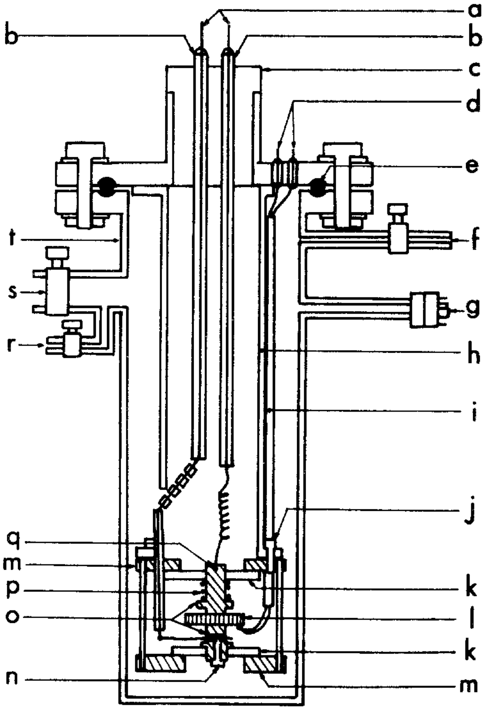

Figure 2 TSDC/TSPC measuring apparatus. a: copper wire to electrodes. b: alumina tube. c: Teflon insulation. d: thermocouple. e: O-ring. f: helium inlet. g: pressure guage. h: inner copper tube. i: thermocouple spaghetti. j: screw. k: insulating alumina plate. 1: glass specimen. m: metal frame. n: set screw. o: electrode. p: spring. q: set screw. r: helium outlet. s: to vacuum pump, and t: copper container.

The temperature was measured with a chromel–alumel thermocouple in contact with a portion of the uncoated surface of the glass disc. During a measurement, the cell contained dry helium (~ 1 atm.) to improve heat transfer and minimize temperature gradients. The temperature was ±1K for a heating rate of 0.05 to 0.1 K sec^{-1}. The reproducibility of the current maximum temperature, T_m, was ±3 K for the same heating rate.

The accuracy to which the current could be measured by the electrometer was ±2% of full scale for 1×10^{-11} to 0.3 A and ±4% of full scale for 1×10^{-14} to 3×10^{-12} A. Currents $< 5 \times 10^{-14}$ A could not be measured accurately and currents $< 1 \times 10^{-13}$ A could not be accounted for quantitatively. The reproducibility of the peak current (height) was within ± 10%.

During a TSDC measurement, the resistance of the shunt resistor in the electrometer was kept at least two orders of magnitude less than the specimen resistance, so that the charge in the specimen was freely discharged.

3. Results and discussion

3.1. Bulk versus surface polarization

To establish that the currents measured were due to bulk polarization of the glass and not simply electrode effects, three different experiments were performed. In the first experiment, an alumina disc (99.9% Al_2O_3) of the same material used to insulate the two electrodes was placed between the electrodes, polarized at 420 K and the TSDC measured. An essentially constant background current $< 5 \times 10^{-14}$ A was measured between 100 K and 550 K. This was taken to be the background of the system.

In the second experiment, the TSDC from an unpolarized 30PbO glass disc was measured, Curve A in Fig. 3. This specimen was then polarized at 420 K, quenched to 100 K and the TSDC measured on heating to 463 K, during which a peak at 416 K was observed, Curve B in Fig. 3. The specimen was then repolarized, but with the field reversed. As expected, the TSDC measured on heating, Curve C in Fig. 3, was the reverse of Curve B with the same peak temperature and magnitude. After several polarization and discharge cycles, the TSDC was measured without polarization and was essentially the same as Curve A, Fig. 3. These

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*Keithley Instruments, Model 610B Electrometer, Cleveland, Ohio, USA.

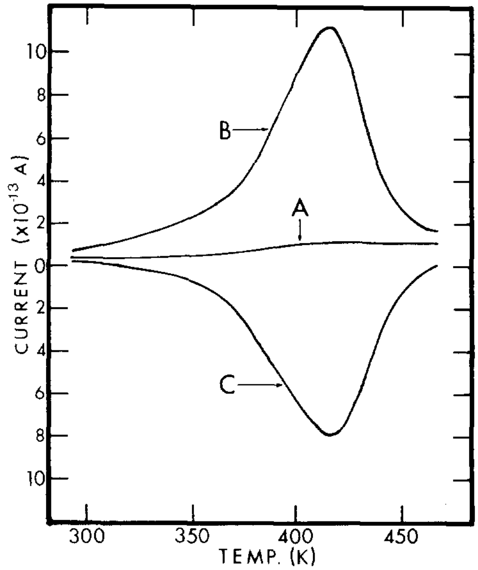

Figure 3 The effect of polarization field polarity, 30PbO–70SiO$_2$ (mol%) glass. Curve A: background, no polarization. Curve B: $T_p = 418 \pm 2$ K and $\epsilon_p = +3813$ V cm^{-1}. Curve C: $T_p = 418 \pm 2$ K and $\epsilon_p = -3813$ V cm^{-1}. For all measurements $b = 0.07$ K sec^{-1} and $t_p = 1200$ sec.

results demonstrate the reversibility of the TSDC peak, its dependence upon the polarity of the applied d.c. field, and show that repeated polarization produced no detectable permanent changes in the glass.

As further verification that bulk polarization was being observed, the third experiment was performed on two different glasses. After an initial TSDC measurement, a 30PbO glass was repolarized at 420 K and quenched to ~295 K (with the d.c. field applied). The field was then removed, the specimen removed from the apparatus, and the gold electrodes and ~10 μm of each surface ground off. After evaporating new electrodes onto the previously polarized specimen (specimen was heated slightly during electrode evaporation), it was replaced in the apparatus and the TSDC measured a second time without any additional polarization. As expected for bulk polarization, the second curve, TSDC-2 in Fig. 4, was essentially identical to the first, TSDC-1, since the glass removed was small compared to the total thickness (750 μm). If polarization had been confined to a thin surface layer only, then the peak for TSDC-2 would have been smaller or absent.

The results for a similar experiment using a 4Na$_2$O glass are given in Table I. In this case a significant portion of each surface was removed after polarization, but the charge remaining (79%) for the TSDC peak at 370 K was essentially proportional to the remaining sample volume (86.4%) and there was no change in peak temperature. These results clearly establish that polarization had occurred in the bulk and was not confined to just a thin surface layer.

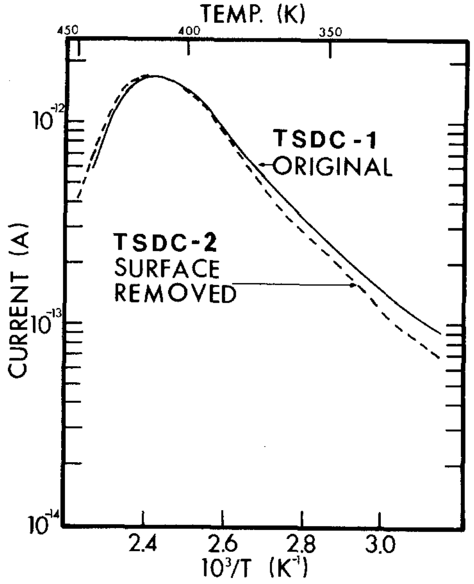

Figure 4 Comparison of TSDC peak in a 30PbO–70SiO$_2$ (mol%) glass before and after surface removal. ———: original, without surface removal after polarization. – – – –: with surface removal (10 μm each side) after polarization. $T_p = 419 \pm 1$ K, $t_p = 1200$ sec, $\epsilon_p = 7000$ V cm^{-1} and $b = 0.07$ K sec^{-1}.

TABLE I Comparison of charge (polarization) and specimen volume of a TSDC peak in a 4Na$_2$O–96SiO$_2$ glass (mol%)

Parameter	TSDC-1*	TSDC-2†	Ratio (TSDC-2/TSDC-1) (%)
Specimen thickness (cm)	0.180	0.156	86.4
Specimen volume (cm^3)	0.0572	0.0494	86.4
Total charge (C)	5.02×10^{-10}	3.97×10^{-10}	79.0
Maximum current I_{max} (A)	9.1×10^{-10}	6.4×10^{-13}	70.3
Temperature at I_{max} (K)	369	370	

*Initial measurement, no surface removed.

†Specimen repolarized using same conditions as TSDC-1, and then electrodes and surface removed.

3.2. Effect of water vapour

Water vapour reduces the electrical resistance of a glass surface and could, therefore, affect the current measured. A $25Na_2O$ glass was used to determine the effect of surface moisture, since this glass has a relatively low chemical durability. TSPC/TSDC measurements were performed both with and without preheating the cell and specimen under vacuum (~ 373 K overnight) or passing the helium through a cold trap prior to its introduction into the cell. Measurements performed without preheating or the cold trap, showed a current peak at 250 K (dotted curve in Fig. 5). When the cell was evacuated and held at 373 K overnight and the helium passed through a liquid nitrogen cold trap, the TSPC/TSDC curves in Fig. 5 were reproducible and the peak at 250 K was absent.

For the purpose of eliminating the peak at 250 K, which is attributed to water vapour, and obtaining reproducible data, the cell is kept moisture-free by heating the specimen and cell under vacuum above 373 K overnight and passing the helium through a liquid nitrogen cold trap to remove residual water vapour.

3.3. Typical TSPC/TSDC results

Data for a $4Na_2O$ glass are shown in Fig. 6. The specimen was cooled initially to ~ 100 K, the field (2523 V^{-1} cm) applied, and the specimen heated to ~ 403 K (TSPC-1 curve), recooled to ~ 100 K with the field applied and reheated (TSPC-2 curve), and then recooled a third time to ~ 100 K where the field was removed and reheated (TSDC-3 curve). The important aspects of these results are: (a) a peak at 220 K is present for TSPC-1 but is missing in TSPC-2, (b) a large and reproducible current (TSPC-1 and 2) is observed at higher temperature whose temperature dependency is

$$i = i_0 \exp(-E_a/kT), \tag{4}$$

(c) the TSDC-3 curve contains two peaks, a peak at 220 K corresponding to that observed for TSPC-1 and a second peak at 373 K which was hidden by what is called the high temperature background (HTB) current for TSPC-1 and 2, and (d) the TSPC-2 and TSDC-3 curves when added together are essentially identical to TSPC-1. There is excellent reproducibility in the HTB for repeated TSPC measurements, as illustrated in

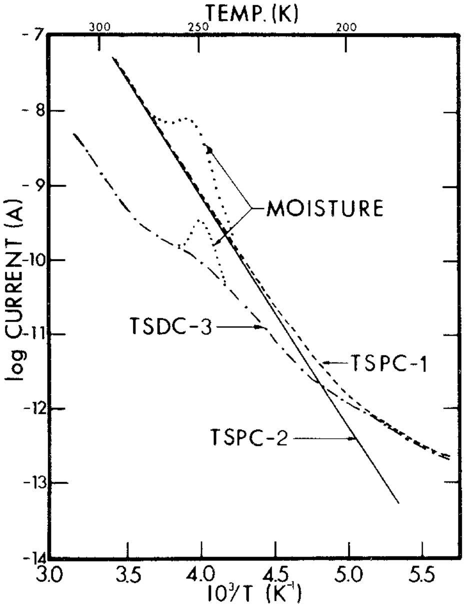

Figure 5 Effect of water vapour in the measuring system for a $25Na_2O-75SiO_2$ glass. – – – –: TSPC-1. ———: TSPC-2. —·—·—: TSDC-3, measured in dry helium with or without guard ring, $\epsilon_p = 811\ V\ cm^{-1}$. Peak shown by dotted line (· · · · ·) attributed to water vapour in measuring system.

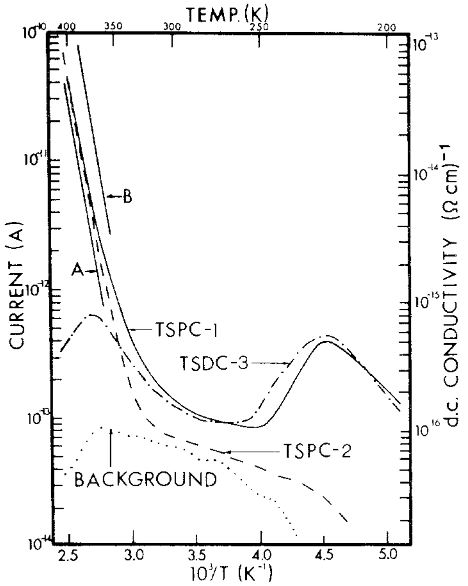

Figure 6 Typical TSPC/TSDC curves for $4Na_2O-96SiO_2$ glass. ———: TSPC-1. – – – –: TSPC-2. —·—·—: TSDC-3. $\epsilon_p = 2523\ V\ cm^{-1}$ and $b = 0.07\ K\ sec^{-1}$. Dotted (· · · · ·) line is the background, no polarization, curve. Curves A and B are the d.c. conductivity for $5Na_2O-95SiO_2$ glass [24].

Fig. 6, which would not be the case if significant space charge polarization developed during the previous heating cycles. Space charge (or electrode) polarization does not become significant until >600 K, for this glass. In glasses of higher alkali content (~ 25 mol% Na_2O), the current deviates from Equation 4 when the conductivity is $\geqslant 10^{-7}$ $(\Omega\,cm)^{-1}$ i.e., above 373 K.

The d.c. conductivity calculated from the HTB, particularly for TSPC-2, agrees well with that determined by more complicated a.c. or d.c. techniques. The right-hand scale in Fig. 6 corresponds to the d.c. conductivity calculated from the HTB of the TSPC-2 curve. Lines A and B represent the conductivity [24] for a $5Na_2O$ glass. The TSPC technique is a convenient method of measuring the d.c. conductivity between 10^{-7} and 10^{-15} $(\Omega\,cm)^{-1}$ (the upper limit being determined by space charge polarization, whereas the lower limit is determined by electrometer sensitivity and background noise).

The TSDC curves depend greatly on glass composition and polarization conditions. For instance, lead silicate glasses (30 to 50 mol% PbO) show only one current peak (Fig. 4); however, two TSDC peaks are detectable in most sodium silicate glasses, Fig. 6, when properly polarized. For polarization temperatures where $T_p \gg T_m$, the peaks are hidden by the HTB current and are only faintly resolved bumps on the TSDC curve (Fig. 5).

Several polarization processes can be anticipated for alkali silicate glasses and associated with the TSDC/TSPC peaks observed in the $4Na_2O$ glass. The first consists of the orientation of the alkali ions around the non-bridging oxygens (NBO) as proposed by Charles [25, 26] i.e., a type of alkali$^+$–(NBO)$^-$ dipole orientation where the alkali ion jumps to other equivalent sites about the NBO to which it is bonded, but the NBO is anchored. This type of alkali ion motion is consistent with the characteristics of the TSDC peak at 220 K in Fig. 6, since this peak was observed in TSPC-1 (dipoles oriented) was absent in TSPC-2 (dipoles still oriented), but was again observed in TSDC-3 when the specimen was reheated with the ϵ_p removed (randomization of dipoles). Furthermore, the activation energy for this peak, 7 to 10 kcal mol^{-1}, is reasonably close to the strain energy for sodium ion movement [27, 28], and the compositional dependence of the peak magnitude correlates well with the Na^+–(NBO)$^-$ dipole concentration calculated [29] for glasses containing 4 to 25 mol% Na_2O.

In glasses consisting of two immiscible phases of different electrical characteristics, such as the 30PbO and $4Na_2O$ glasses which are both phase separated [30, 31], some type of polarization can be expected at the interface of the immiscible phases. In the case of the $4Na_2O$ glass, which contains isolated sodium-rich droplets (~ 400 Å in diameter) distributed in a sodium-poor matrix [31], the difference in sodium ion mobility can be envisaged to cause interfacial polarization at the phase boundaries. Tentatively, the TSDC peak at 373 K in the $4Na_2O$ glass is attributed to an interfacial polarization of this type whereby the higher mobility of the sodium ions in the droplet results in their polarization relative to the matrix.

The excellent agreement between the HTB portion of the TSPC curves and the electrical conductivity [24] shows that the alkali ion movement being measured is the long range alkali ion motion corresponding to that responsible for d.c. conductivity. In the $4Na_2O$ glass, this general drift of the sodium ions becomes appreciable at about the same temperature where the 373 K TSDC peak is located. This provides an excellent example of the usefulness of the TSDC technique since the polarization (alkali motion) associated with the 373 K peak is hidden by the start of the HTB when the glass is heated with an applied field (TSPC) and only becomes evident when the general drift motion of the alkali ions is eliminated by removal of the field (TSDC). Thus, in conventional a.c. techniques where an applied field must be used, the polarization detected by TSDC may be difficult to separate from the "conduction" motion caused by the applied field.

4. Conclusions

The thermally stimulated currents measured in this investigation are concluded to result from polarization processes occurring within the glass bulk rather than at the electrode only where the polarization would be confined to a thin surface layer. From the results obtained for the $4Na_2O$ glass, the TSDC technique appears particularly useful for investigating alkali ion motion in glass, since the absence of an applied field reveals features of alkali ion motion that may often be obscured by the general drift of alkali ions (conduction) that occurs with an applied field.

The TSDC/TSPC peaks for the $4Na_2O$ glass are interpreted on the basis of a type of alkali motion differing primarily in terms of distance, i.e., the TSDC peak at 220 K is due to the short range motion of a Na^+ ion around a given, immobile NBO; whereas, the 373 K TSDC peak is due to Na^+ ion motion within the alkali-rich droplets which produces interfacial polarization at the immiscible phase boundaries. The HTB consists of Na^+ ion motion corresponding to that for d.c. conductivity and over considerably larger distances.

Care must be taken to ensure that any moisture within the system (sample surfaces, cell, and gas atmosphere) has been removed prior to measurement. An overnight vacuum bake-out at ~373 K is adequate to eliminate the TSDC/TSPC peak at 250 K, which is a certain indication of moisture contamination, and to obtain reproducible TSDC/TSPC data.

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