

Thermally stimulated currents in lithium-sodium disilicate glasses

AKIRA DOI

Department of Inorganic Materials, Nagoya Institute of Technology, Nagoya 466, Japan

Thermally stimulated polarization and depolarization currents were measured for thin films of lithium-sodium disilicate glasses. As reported previously two thermally stimulated depolarization current peaks were found. The low-temperature peak was attributed to conduction polarization of alkali ions, while the high-temperature was attributed to localized motion of non-bridging oxygens in the alkali-depleted region near the anode rather than to space charge or interfacial polarization, as proposed earlier. Although the high-temperature peak was dominant under medium polarizing conditions, it was swept away irreversibly by biasing at extremely high electric field.

1. Introduction

The motion of alkali ions in alkali-containing oxide glasses has been studied for many years using electrical (e.g., d.c./a.c. conduction, dielectric loss), optical (far-infra-red absorption), magnetic (nuclear magnetic resonance) or mechanical (internal friction) techniques. Recent works [1-8] by thermally stimulated polarization and depolarization current (TSPC and TSDC) techniques have been directed towards correct assignment of the observed peaks in terms of an atomistic motion of alkali ions. Two TSDC peaks were found for alkali silicate glasses in the temperature range of 100 to 400 K [1, 2, 6]. Doi [1] attributed the low-temperature peak to orientational motion of alkali non-bridging oxygen dipoles and attributed the high-temperature peak to space-charge relaxation of alkali ions accumulated near the cathode during polarization. On the other hand, Hong and Day [2, 6] attributed the low-temperature peak to orientational motion of alkali non-bridging oxygen dipoles and attributed the high-temperature peak to interfacial polarization of alkali ions at the immiscible phase boundaries which they considered to be inherent in the glass structure.

However, the TSDC studies of sodium germanate glasses [7] revealed that the single peak observed cannot be attributed to the motion of sodium-anion dipoles but could possibly be attributed to the conduction polarization caused by an

elementary process of d.c. conduction itself. It was further reported [4, 8] that, when the conduction polarization model was applied to several alkali-containing oxides, at least one of the TSDC peaks for each oxide arose from conduction polarization of constituent alkalis. The purpose of the present work was to present additional data clarifying the origin of two TSDC peaks in lithium-sodium disilicate glasses, with an emphasis on the comparison of the TSPC and TSDC between thin (several micrometers thickness) and thick (about 1 mm thickness) samples.

2. Experimental procedures

A precise description of the procedures has been given elsewhere [1]. Glasses of the composition $\text{Li}_2\text{O}-2\text{SiO}_2$, $\text{Na}_2\text{O}-2\text{SiO}_2$, and $(\text{Li}_2\text{O}-\text{Na}_2\text{O})_{1/2}-2\text{SiO}_2$, abbreviated as L2S, N2S, and LN2S, were investigated. Sample numbers were labelled as L2S(1), L2S(2), etc. Circular gold electrodes were evaporated onto both sides of the samples which were of thickness about 3 to 9 μm . The only difference between the present and previous [1, 4] procedures was that the samples were deposited with gold immediately after the preparation of thin films and stored in an evacuated desiccator rather than in the usual ones with silica gel. Prior to the measurements, each sample was heated at 450 K for several hours to remove moisture and the remaining polarizations.

In our TSDC technique, the sample was biased

by an applied field, E_p , for a time, t_p , ($t_p = 15$ min) at an appropriately chosen temperature, T_p , quenched to liquid nitrogen temperature, T_0 , and with the field removed, heated to 450 K at a constant rate of 0.11 K sec^{-1} , unless otherwise specified. When a previously unpolarized sample was quenched to T_0 and heated with an applied voltage, TSPC was observed. The TSPC measurements were always made as parts of an experimental TSPC-1–TSPC-2–TSDC (T – T – T) cycle which consisted of measuring TSPC-1 up to some chosen temperature, quenching the sample to T_0 with the field still applied, and reheating a second time (TSPC-2). After cooling the samples to T_0 a third time and removing the field, E_p , TSDC was measured.

For the purpose of quantitative evaluation of the biasing effect, an unpolarized sample was heated without the field and current recorded. This background current was not reproducible and reflected the remaining polarizations; it was therefore subtracted from the currents of nearby TSPC/TSDC runs when it was not negligible. Sample thicknesses were measured with an optical microscope at a magnification of 10^3 times. The necessary information for characterizing the TSDC peaks could not be obtained from one single sample for each composition both because of the fragility of the glass films and because of an irreversible effect of biasing which we shall treat below.

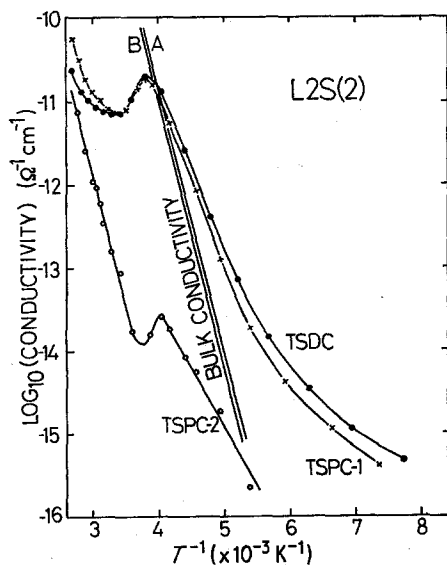


Figure 1 T – T – T cycle for Sample L2S(2), where E_p is 1.2 kV cm^{-1} . Curves A [9] and B [10] are d.c. conductivities for thick 30 mol% Li_2O –70 mol% SiO_2 glass samples.

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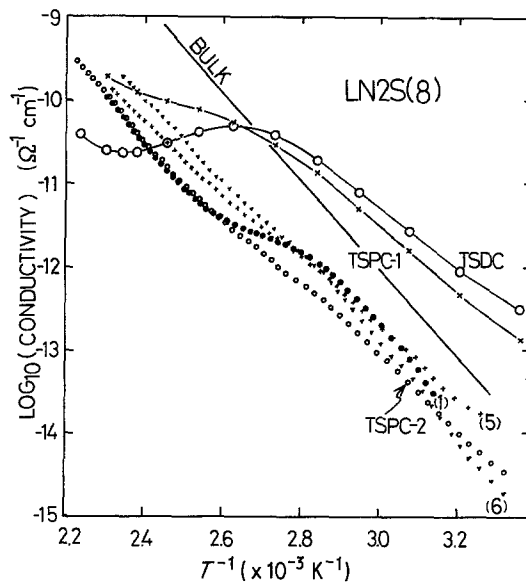


Figure 2 T – T – T cycle for Sample LN2S(8), where E_p is 2.0 kV cm^{-1} . TSPC-2 curves for Samples LN2S(1), LN2S(5) and LN2S(6) are also shown, where E_p is $2.0 \pm 0.1 \text{ kV cm}^{-1}$. The curve marked "BULK" corresponds to TSPC-2 of thick $(\text{Li}_2\text{O}-\text{Na}_2\text{O})_{1/2}-3\text{SiO}_2$ glass [11].

3. Results and discussion

Typical T – T – T cycles for L2S, LN2S, and N2S are shown in Figs 1 to 3. Curves representing d.c. conductivities for thick ($\sim 1 \text{ mm}$) glass samples [6, 9–11] are also shown for comparison. The general results obtained for the three glasses are as follows. First, the single peaks in TSPC-1 and

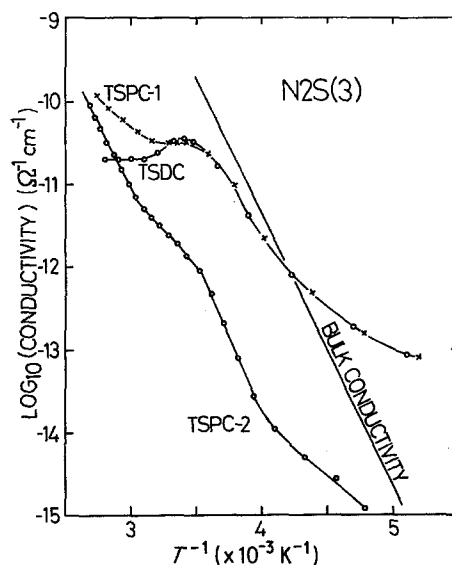


Figure 3 T – T – T cycle for N2S(3), where E_p is 1.2 kV cm^{-1} . Bulk conductivities, as measured from d.c. conduction and TSPC for thick Na_2O – 3SiO_2 glass samples [6, 12], are also shown.

TSDC, hereafter called the P2-peak, have almost the same peak temperatures and magnitudes. Second, a weak but definite peak appears in TSPC-2 at or slightly below the peak temperature of the P2-peak. This is in sharp contrast with corresponding curves for thick glasses [2, 3, 5-7] where these curves are fairly linear up to some $10^{-9} \Omega^{-1} \text{cm}^{-1}$, from the slopes of which the activation energies for conduction are determined. Fig. 4 shows how the $T-T-T$ cycle for L2S varies with applied voltage. The TSDC curves are omitted for clarity, but have maxima at identical temperatures as in the corresponding TSPC-1 curves. The shift of the P2-peak to higher temperatures with increasing E_p is also shown in Fig. 5. Similar results are observed for both N2S and LN2S (see Figs 6 and 7).

When the polarizing temperature is lowered, the low-temperature P1-peak emerges out of the overlapping P2-peak (see Figs 5, 6 and 8). For the conduction polarization model [7], the peak temperature, T_m , and the activation energy for conduction, H_c , have been related by

$$\frac{H_c}{kT_m^2} = \frac{\nu}{\beta} \exp(-H_c/kT_m), \quad (1)$$

where k is Boltzmann's constant, β is the heating rate and ν (Hz) is the hopping frequency of charge carriers in their potential wells. For example,

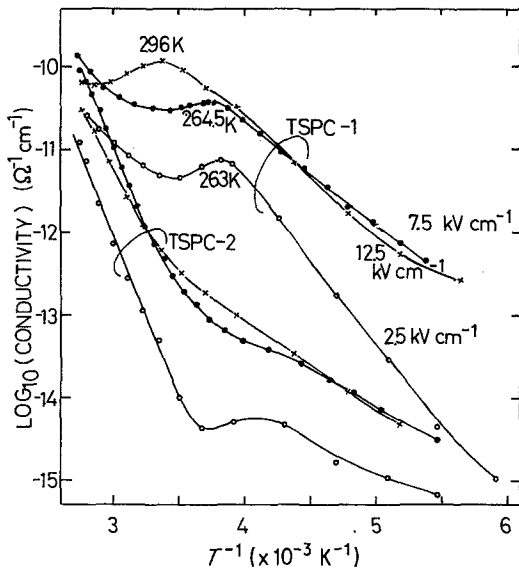


Figure 4 $T-T-T$ cycles for Sample L2S(3) for three different E_p values: open circles correspond to $E_p = 2.5 \text{ kV cm}^{-1}$, closed circles correspond to $E_p = 7.5 \text{ kV cm}^{-1}$, and crosses correspond to $E_p = 12.5 \text{ kV cm}^{-1}$. Although TSDC curves are omitted for clarity, they have maxima at temperatures identical to those of TSPC-1.

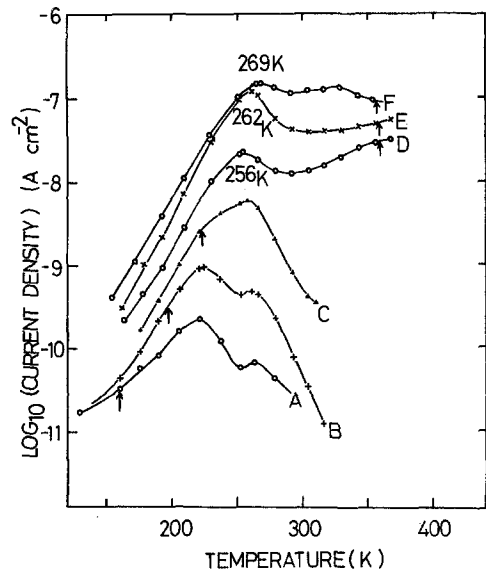


Figure 5 TSDC curves for Sample L2S(3). Curves A to D illustrate the appearance of the low-temperature peak as T_p decreases, where E_p is 2.5 kV cm^{-1} . The arrows indicate T_p . Curves D, E, and F show the shift of the peak temperature with increase in E_p : (D) 2.5 kV cm^{-1} , (E) 5.0 kV cm^{-1} , and (F) 10 kV cm^{-1} .

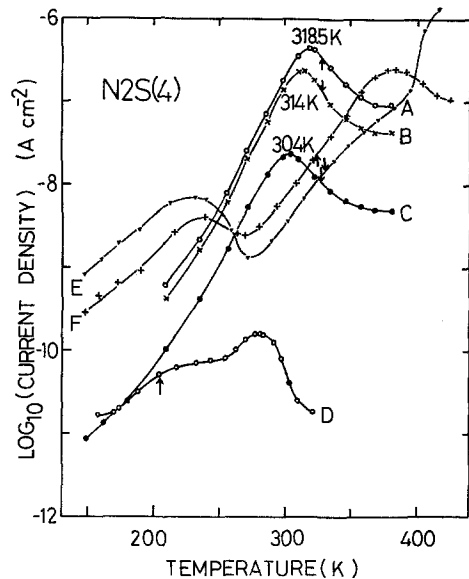


Figure 6 TSDC curves for Sample N2S(4). Curves A to C show the shift of the peak temperature with increase in E_p : (A) 6.7 kV cm^{-1} , (B) 4.0 kV cm^{-1} , (C) 1.3 kV cm^{-1} . When T_p is lowered, the low-temperature peak appears (Curve D, where E_p is 1.3 kV cm^{-1}). When the sample is biased by 67 kV cm^{-1} (Curve E), the P2-peak is drastically swept away and the P1-peak reappears (Curves E and F where, in the latter, E_p is 13 kV cm^{-1}). The arrows indicate T_p .

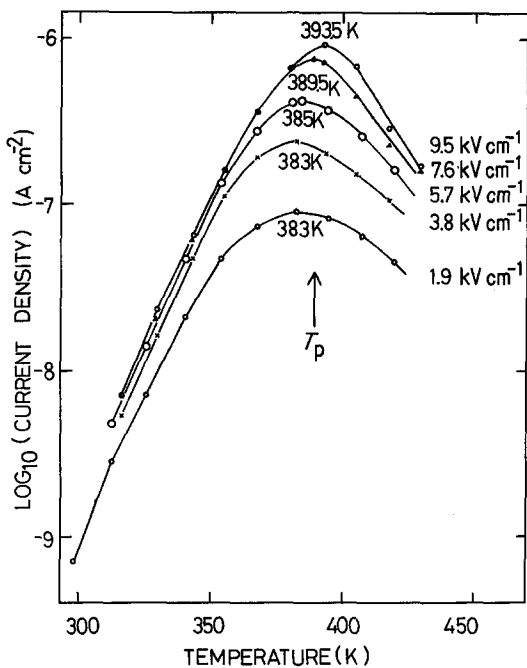


Figure 7 TSDC curves for Sample LN2S(6), illustrating shift of the peak temperature with E_p , where T_p is 389 K.

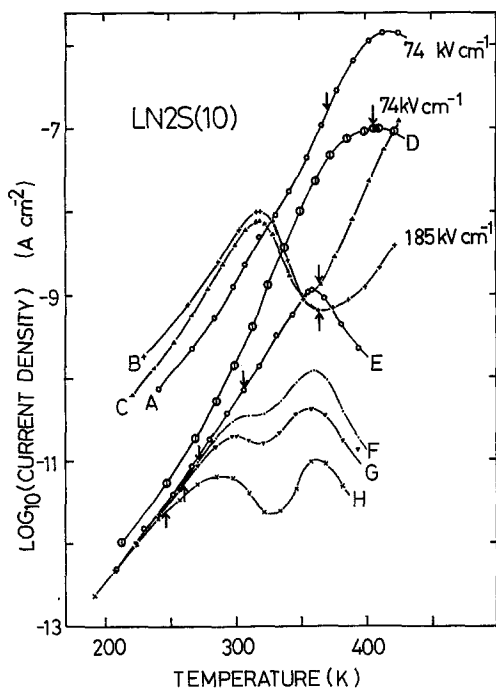


Figure 8 TSDC for Sample LN2S(10). Curves D to H show the appearance of the P1-peak by lowering T_p , where E_p is 3.7 kV cm^{-1} . Curves A to C illustrate how the application of a high electric field (185 kV cm^{-1} , Curve B) erases the overlapping P2-peak, where Curves A and D to H are before biasing at 185 kV cm^{-1} . Arrows indicate T_p .

substitution of 62.4 kJ mol^{-1} for H_c of L2S [13], $1.46 \times 10^{13} \text{ Hz}$ for ν of lithium ions [14], and 0.13 K sec^{-1} for β gives a calculated peak temperature of 219 K, in fair agreement with the P1-peak (Fig. 5). For every glass investigated the P1-peak is almost hidden behind the dominant P2-peak at moderate polarizing conditions of E_p and T_p . However, when the sample is biased by an extremely high electric field, the P2-peak is reduced irreversibly and the P1-peak emerges (see Figs 6, 8 and 9). In other words, the P1-peak is cleaned. The only noticeable difference of the mixed alkali glass LN2S, from L2S and N2S is that in the former a rather higher electric field is necessary for cleaning the P1-peak. Figs 10 to 12 show variations of the peak temperature and magnitude of polarization (the area under the peak) for the cleaned P1-peak as a function of E_p . Initially, the magnitude of polarization rises almost linearly with an applied field up to 20 kV cm^{-1} or more, but levels off afterwards. The activation energies for conduction, as determined from Equation 1 using the peak temperatures of the cleaned P1-peak are given in Table I. There is no report on the compositional dependence of ν in alkali silicate glasses, but it is assumed that ν changes only slightly, as in sodium phosphate glasses [17] and the values of ν for lithium and sodium metasilicate

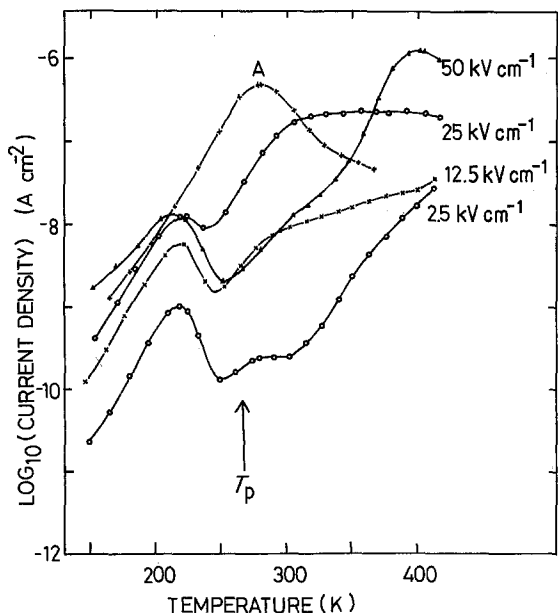


Figure 9 TSDC curves for Sample L2S(3), showing how the dominant P2-peak (Curve A, where E_p is 15 kV cm^{-1}) is swept away and the P1-peak emerges after applying an electric field of 50 kV cm^{-1} .

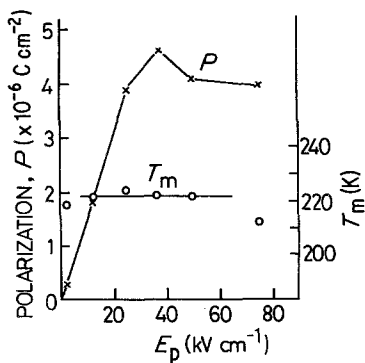


Figure 10 Variations of the peak temperature and magnitude of polarization for the P1-peak of Sample L2S(3) as a function of E_p after the sample was biased at 50 kV cm^{-1} .

glasses [14] are adopted. In mixed alkali glasses, the hopping frequencies of alkali ions are said [18] to be unaffected by the introduction of the second alkali into the glass structure. As seen in Table I, the activation energies calculated from Equation 1 are in good agreement with the reported values [9–13]. It is thus concluded that the P1-peak arises by conduction polarization of mobile alkali ions, as has been proposed before [4].

If an ohmic condition of $eE_p\lambda \ll 2kT_p$, where e is the electronic charge and λ is the hopping distance, is fulfilled, the magnitude of conduction polarization, P , after its saturation is of the form [7]

$$P = \frac{ne^2\lambda^2 E_p}{6kT_p}, \quad (2)$$

where n is the density of conductive alkali ions.

Assuming that all the alkali ions in each glass contribute to the P1-peak after it is cleaned and that the hopping distance equals the separation

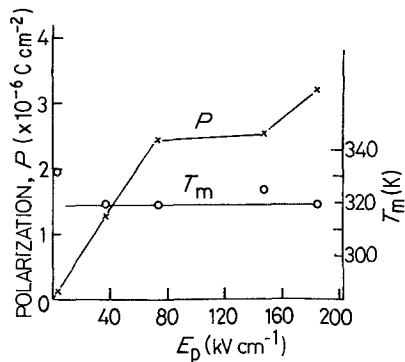


Figure 11 Variations of the peak temperature and magnitude of polarization for the P1-peak of Sample LN2S(10), as a function of E_p , after the sample was biased at 185 kV cm^{-1} .

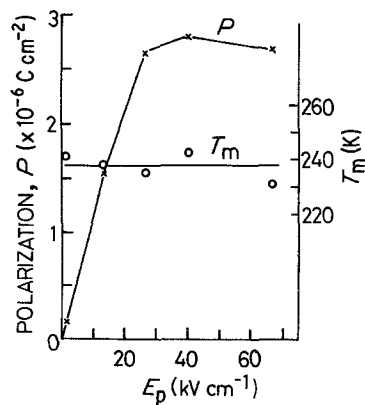


Figure 12 Variations of the peak temperature and magnitude of polarization for the P1-peak of Sample LN2S(10), as a function of E_p after the sample was biased at 67 kV cm^{-1} .

between the alkali ions, the hopping distance is calculated from $(4/3)\pi(\lambda/2)^3 n_0 \approx 1$, where n_0 is the nominal density of alkali ions. These values for λ and those for E_p , T_p and P of the cleaned P1-peaks within linear portions of the P against E_p plots (see Figs 10 to 12) were used to calculate the densities of conductive alkalis given in Table II. The values of n calculated from Equation 2 are, however, several times larger than the nominal densities. Possible errors in the electrode area and sample thickness reduce the calculated density at best to 70 per cent. There is no experimental evidence either that the hopping distance equals the separation between the alkali ions or that alkali ions are homogeneously distributed within the glass structure. High-field conduction measurements in alkali silicate glasses [19] show hopping distances of about 2.5 to 3.0 nm. Alternatively, as one of other possible means for reducing the calculated density to a value below the nominal one, the hypothesis in deriving Equation 2 [7] that conductive ions hop in any three-dimensional direction can be modified to admit that the motion of alkali ions is restricted, at least in part, to some preferential paths along which conduction would take place. This modification reduces the denominator 6 of Equation 2 to a smaller number. However, it is evident from Table II that once the samples are biased by an extremely high electric field, almost all the alkali ions in our glasses come to take part in conduction.

Fig. 13 illustrates how the application of high electric field (66.5 kV cm^{-1}) across N2S(4) causes an irreversible change of the T - T - T cycle. Provided the effect of biasing by an extremely high

TABLE I Activation energies for conduction, as determined from Equation 1 using peak temperatures of the "cleaned" P1-peak

Sample	T_m (K)	β ($^{\circ}$ sec $^{-1}$)	ν ($\times 10^{12}$ Hz [14])	Calculated H_c (kJ mol $^{-1}$)	Reported H_c (kJ mol $^{-1}$)	Reference
L2S(3)	212–224	0.13	14.6 (Li)	60.3–63.6	61.1 62.0 62.4	[9] * [10] * [13]
LN2S(10)	319–331	0.11	14.6 (Li) 6.90 (Na)	92.1–95.9 90.4–93.8	100.9 83.7–92.1	[11] † [15]
N2S(4)	231–242.5	0.20	6.90 (Na)	63.6–67.0	58.6–60.7 62.8	[16] ‡ [12] §

*30 mol% Li₂O–70 mol% SiO₂.

†(Li₂O–Na₂O)_{0.5}–3SiO₂.

‡30 mol% Na₂O–70 mol% SiO₂.

§Na₂O–3SiO₂.

electric field across the samples were merely to sweep out the overlapping P2-peaks, each Curve B of the T – T – T cycle should not have exceeded the corresponding Curve A. Fig. 13 suggests that the P1-peak is irreversibly increased by the application of a high electric field. That means that some localized alkali ions become mobilized by the biasing effect and contribute to d.c. conduction. Such an irreversible change of the P1-peak is also demonstrated in Fig. 8, where the cleaned curve, Curve C, surmounts the corresponding curve before cleaning, Curve A, in the temperature range of the P1-peak.

Consider next the effect of different sample thicknesses on the TSPC and TSDC curves. The thicknesses of the samples in the present work are 10^{-3} times smaller than those used in the work of Day [2, 3, 5–7]. For an applied field of greater than 1 kV cm^{-1} at moderate polarizing temperatures, space charges would be built up at both electrodes. Since both the polarizing conditions derived by Day and derived in this work are comparable, the amount of space charge built up would also be comparable if the other conditions are the same. For thick glass samples the high-temperature portion of TSPC-2 is said [2, 6] to agree well with the d.c. conductivity. On the other hand, the TSPC-2 curves in the pre-

sent work are between one and three orders of magnitude smaller than the bulk conductivities (see Figs 1 to 3). It is easy to interpret this in terms of the deterioration of an effective field on charge carriers in the interior of a sample by space charges built at both electrodes during polarization. However, in view of the fact that linear portions of the polarization against E_p plots (see Figs 10 to 12) can be described well by using an apparent rather than an effective field, we may assume that space charges become influencing in deteriorating an effective field only when E_p is very large. Scattered TSPC-2 curves from sample to sample of the same composition, as in Fig. 2, would reflect the scatter in microheterogeneities of the glass structure from sample to sample which becomes more noticeable as the sample thickness decreases. It is possible then that the microheterogeneous structure is responsible, through unknown mechanisms, for the great reduction observed in our TSPC-2 currents.

Coincidences of the peak temperature and the magnitude of polarization for the P2-peak in TSPC-1 and TSDC (see Figs 1 to 4) suggest that the relevant polarization occurs by either the dipolar [1] or the conduction polarization [7] process and not by the space charge or interfacial processes, as proposed earlier [1, 6] because the relaxation

TABLE II Comparison of density of conductive alkalis as calculated from Equation 2 using magnitude of polarization for the "cleaned" P1-peak and nominal density of alkalis

Sample	P ($\times 10^{-7}$ C cm $^{-2}$)	E_p (kV cm $^{-1}$)	T_p (K)	λ (nm)	Calculated n ($\times 10^{22}$ cm $^{-3}$)	Nominal n_0 ($\times 10^{22}$ cm $^{-3}$)
L2S(3)	2.8	2.5	267	0.468	4.4	1.87
LN2S(10)	1.3	3.7	373	0.477	1.9	1.76
N2S(4)	1.3	1.3	325	0.479	4.6	1.73

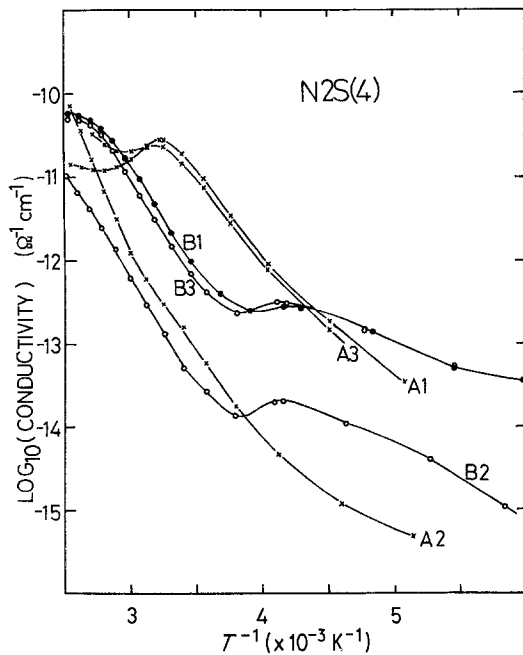


Figure 13 T - T - T cycles for Sample N2S(4), with E_p of 1.3 kV cm^{-1} . In-between cycles of A1, A2 and A3 and B1, B2 and B3, the sample was biased at 66.5 kV cm^{-1} .

times for polarizing and depolarizing the dielectric cannot be identical for both processes. Some data of the magnitude of polarization for the P2-peak before it was swept away by applying an extremely high electric field across samples are given in Table III. The large amount of polarization for the P2-peak compared with that for the P1-peak (20 to 500 times as large) denies interpretation in terms of the motion of constituent ions in the interior of a sample. The general results observed, which the hypothetical model for the P2-peak must fulfill, are as follows:

(a) the P2-peak becomes saturated for given E_p , as is verified by the coincidences of the position and height of the peak for TSPC-1 and TSDC;

(b) in spite of its saturation for given E_p , the P2-peak shifts to higher temperatures with increasing E_p ; and

(c) the P2-peak disappears irreversibly when the applied field is extremely high.

A potential drop within a very narrow region near the anode where alkali ions are depleted would develop a high electric field [20], even when the potential drop does not have so much influence on the deterioration of an effective field on the charge carriers in the interior of a sample. Evolution of the oxygen gas from the anode was detected when glasses were biased by high electric

TABLE III Magnitude of polarization for the P2-peak before it was swept away by the biasing effect of high electric field

Sample	P (C cm^{-2})	E_p (kV cm^{-1})
L2S(1)	5.4×10^{-6}	1.7
L2S(2)	5.6×10^{-6}	1.2
LN2S(6)	4.8×10^{-5}	1.9
LN2S(8)	5.5×10^{-5}	2.1
N2S(2)	1.6×10^{-5}	1.8
N2S(3)	1.7×10^{-5}	1.2

field at high temperatures [21, 22]. In the experimental conditions used, therefore, a tentative interpretation for the P2-peak is that the localized motion of non-bridging oxygens in the alkali-depleted region under high effective field is responsible for the P2-peak. This type of motion of non-bridging oxygens is different in nature from those of alkali ions in that the former anions are bound to the glass network by strong Si-O bonding, while alkali ions are relatively free to move, whence the motion of non-bridging oxygens should distort the network directly. Larger distortion of the glass network within the alkali-depleted region near the anode, by applying higher E_p , requires more energy for its relaxation and, hence, the TSPC/TSDC peak shifts to higher temperatures. Once the applied field is extremely high, there is a possibility that some of non-bridging oxygens in the alkali-depleted region move long distances to the anode and evolve as the oxygen gas. In the subsequent TSPC/TSDC runs, therefore, the P2-peak is drastically reduced and the P1-peak emerges out of the overlapping P2-peak.

If the T_p -dependence of polarization for the P2-peak is of the form or of similar form to Equation 2 the change of polarization and the consequent induced current, dP/dt , for both the P1- and P2-peaks during the TSPC-2 run should be as shown in Fig. 14 [23, 24]. That is, a peak should be observed just below the peak temperature of the relevant polarization, and current inversion [23, 24] takes place afterwards. The appearance of a faint peak at or slightly below the peak temperature of the P1- or P2-peaks during the TSPC-2 run (see Figs 1 to 4 and 13) agrees well with this expectation. The absence of this phenomenon in thick glass samples [3, 5, 6] is due probably to the overwhelming conduction currents in the TSPC-2 runs.

Although the 180 K peak was dealt with in the last paper [4] for LN2S, it was missing in the pre-

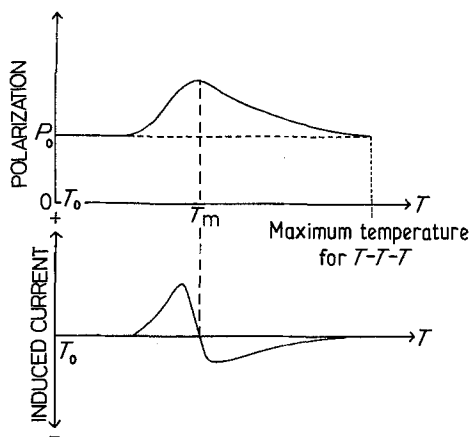


Figure 14 Schematic diagram (not shown to scale) of how the polarization, P , and the consequent induced current, dP/dt , change with temperature during the TSPC-2 run.

sent samples. Therefore the 180 K peak must be due to surface- or impurity-related polarization.

4. Conclusion

Two TSDC peaks for thin glass films of L2S, N2S, and LN2S are analysed with the help of $T-T-T$ measurements. The low-temperature peak, the P1-peak, is attributed to conduction polarization of alkali ions in the interior of a sample. The high-temperature peak, the P2-peak, is attributed to localized motion of non-bridging oxygens in the alkali-depleted region near the anode. The P2-peak shifts to higher temperatures with increase in E_p . When the applied field becomes extremely high, some of non-bridging oxygens move long distances to the anode and are neutralized there, whence the P2-peak is drastically reduced in subsequent TSPC/TSDC runs.

References

1. A. DOI, *J. Appl. Phys.* **50** (1979) 1291.
2. C. M. HONG and D. E. DAY, *J. Mater. Sci.* **14** (1979) 2493.
3. *Idem*, *J. Appl. Phys.* **50** (1979) 5352.
4. A. DOI, *Jap. J. Appl. Phys.* **19** (1980) 2085.
5. A. DOI and D. E. DAY, *J. Mater. Sci.* **15** (1980) 3047.
6. C. M. HONG and D. E. DAY, *J. Amer. Ceram. Soc.* **64** (1981) 61.
7. A. DOI and D. E. DAY, *J. Appl. Phys.* **52** (1981) 3433.
8. A. DOI, *J. Mater. Sci.* **16** (1981) 2028.
9. R. J. CHARLES, *J. Amer. Ceram. Soc.* **46** (1963) 235.
10. H. NAMIKAWA, *J. Non-cryst. Sol.* **14** (1974) 88.
11. A. AGARWAL, PhD thesis, University of Missouri-Rolla, USA (1980).
12. V. PROVENZANO, L. P. BOESCH, V. VOLTERRA, C. T. MOYNIHAN and P. B. MACEDO, *J. Amer. Ceram. Soc.* **55** (1972) 492.
13. J. R. HENDRICKSON and P. J. BRAY, *J. Chem. Phys.* **61** (1974) 2754.
14. G. J. EXARHOS and W. M. RISEN, Jr, *Sol. Stat. Commun.* **11** (1972) 755.
15. W. MÜLLER-WARMUTH, F. KRÄMER and H. DUTZ, 9th International Congress on Glass Science Technology (Institute de Verre, Paris, 1971) p. 303.
16. R. J. CHARLES, *J. Amer. Ceram. Soc.* **49** (1966) 55.
17. G. J. EXARHOS, P. J. MILLER and W. M. RISEN, Jr, *J. Chem. Phys.* **60** (1974) 4145.
18. G. B. ROUSE, Jr, P. J. MILLER and W. M. RISEN, Jr, *J. Non-cryst. Sol.* **28** (1978) 193.
19. J. P. LACHARME and J. O. ISARD, *J. Non-cryst. Sol.* **27** (1978) 381.
20. P. M. SUTTON, *J. Amer. Ceram. Soc.* **47** (1964) 219.
21. D. E. CARLSON, K. W. HANG and G. F. STOCKDALE, *ibid.* **55** (1972) 337.
22. K. TAKIZAWA, *ibid.* **61** (1978) 475.
23. T. MIZUTANI, Y. SUZUOKI and M. IEDA, *J. Appl. Phys.* **48** (1977) 2408.
24. A. LINKENS, P. PAROT, J. VANDERSCHUEREN and J. GASLOT, *Compt. Phys. Commun.* **13** (1978) 411.

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