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Thermally stimulated current studies of conduction polarization in several alkali-containing oxides

There have been several recent investigations [1–3] of alkali motion in simple glasses using the method of thermally stimulated depolarization current (TSDC). In this technique, a sample is polarized by an applied field at an appropriately chosen temperature, and quenched to a lower temperature where the polarization can be frozen-in. Then, with the field removed, the sample is heated at a linear rate as the induced current in the outer circuit is detected by depolarization. As a complement to TSDC, the method of thermally stimulated polarization current (TSPC, [4]) consists of quenching a sample, followed by heating with the field applied and measuring the current induced by the buildup of polarization. These techniques have been developed for studying orientational motion of impurity-vacancy dipoles in ionic crystals [4, 5]. Hence the TSDC peaks of alkali-containing oxide glasses were liable to be interpreted in terms of orientational depolarization of alkali-nonbridging oxygen dipoles [1, 2]. Recent work [6] on the single TSDC peak in sodium germanate glass suggests, however, that the peak is due to polarization caused by conduction itself (conduction polarization) and not to orientational motion of sodium–GeO_6^- or sodium–nonbridging oxygen dipoles.

The conduction polarization model [6] is explained shortly as follows. A conductive ion jumps by thermal activation from any given site to nearest-neighbour sites with a probability

$$\eta = \nu \exp(-H_c/kT), \qquad (1)$$

where ν is an oscillation frequency of the ion within a potential well surrounded by an energy barrier H_c. When a sample is biased by an applied field, the probability distribution for a conductive ion to occupy any of the nearest-neighbour sites must be different from a distribution without a field. Such a move from a normal to a distorted distribution of conductive ions is responsible for a TSPC peak, while the reverse move produces a TSDC peak. Both techniques are said [4, 6] to give an almost identical peak temperature, T_m, for which the relationship

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

holds, where β is the heating rate. The purpose of the present work was to re-interpret published TSDC/TSPC data of several alkali-containing oxides in terms of the conduction polarization model.

Fig. 1 shows a TSDC curve of $4Na_2O{\cdot}96SiO_2$ glass polarized at around 403 K [2]. Hong and Day

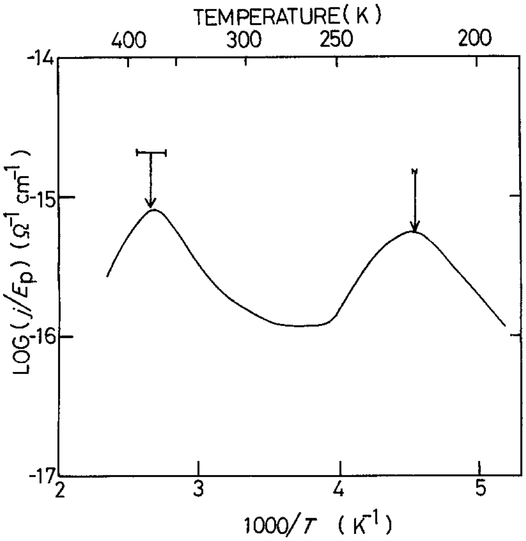

Figure 1 TSDC of $4Na_2O{\cdot}96SiO_2$ glass polarized at around 403 K (Hong and Day [2]). The arrows indicate calculated peak temperatures.

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[2] attributed the 220 K peak to orientational motion of sodium-nonbridging oxygen dipoles and the 373 K peak to sodium motion within alkali-rich droplets which produces interfacial polarization at the immiscible phase boundaries.

The peak temperature for the conduction polarization process was estimated from Equation 2. The heating rate, β, is 0.07 degree sec^{-1} and the activation energy for conduction is 24.8 kcal mol^{-1} (d.c. conduction [7]) or 26.5 to 27.0 kcal mol^{-1} (TSPC [8]). Concerning ν of this glass, a value of 230 cm^{-1} for $Na_2O{\cdot}SiO_2$ glass [9] was selected for convenience because it was assumed that ν changes only slightly for the change in composition as in sodium phosphate glasses [10]. T_m was calculated to be 376 ± 15 K, which is very close to the 373 K peak.

$4Na_2O{\cdot}96SiO_2$ glass is phase-separated [7], containing isolated sodium-rich droplets embedded in a sodium-poor matrix. If the 373 K peak is due to conduction polarization of sodium ions in the sodium-poor matrix, there should be another conduction polarization peak by sodium motion within sodium-rich droplets. Since the chemical composition of sodium-rich droplets resembles that of $Na_2O{\cdot}3SiO_2$ glass [7, 11], H_c of 14.9 kcal mol^{-1} (TSCP [8]) or 15.0 kcal mol^{-1} (d.c. conduction [12]) was used to estimate T_m from Equation 2. T_m thus calculated, 220 to 221 K, is almost identical to the 220 K peak. Although the reported activation energy for this peak, 7 to 10 kcal mol^{-1} [2], as determined from partial discharge, is far below H_c of $Na_2O{\cdot}3SiO_2$ glass, it is noted that partial discharging gives a distribution in activation energies while d.c./a.c. conduction, dielectric relaxation or TSPC gives a single activation energy which is located higher than the most probable value of the distribution [13].

It is evident from the foregone discussion that, in $4Na_2O{\cdot}96SiO_2$ glass, at least two peaks must be observed in the dielectric loss spectrum, one of ~ 15 kcal mol^{-1} and an other of ~ 25 kcal mol^{-1} activation energies. To date, no dielectric measurements have been reported for this glass. However, supporting evidence is provided by $7.5Li_2O{\cdot}92.5SiO_2$ glass where two dielectric loss peaks are observed [14]. The low-frequency peak has an activation energy of 29.6 kcal mol^{-1} which equals H_c of $7.5Li_2O{\cdot}92.5SiO_2$ glass, while the high-frequency peak has an activation energy of 15.6 kcal mol^{-1} which resembles H_c of $30Li_2O{\cdot}70SiO_2$ glass, 14.6 to 15.5 kcal mol^{-1} [12] to which the composition of lithium-rich droplets approximates. Accordingly, Charles [14] associated the low-frequency peak with the lithium-poor matrix and the high-frequency peak with isolated, lithium-rich phases.

In summary, it is concluded that the 220 K peak is due to conduction polarization of sodium ions in sodium-rich droplets while the 373 K peak is due to conduction polarization of sodium ions in the sodium-poor matrix.

The TSPC peaks of lithium–sodium borosilicate glasses were analysed [15] in terms of thermal release of the carriers (electrons and/or holes) from trapping centres. These trapping centres were specified only as some unknown gap states from structural defects or band tail states [15]. All the samples except 914, whose composition is $24Na_2O{\cdot}30B_2O_3{\cdot}47SiO_2$, have batch compositions of 15 to $20Na_2O{\cdot}14$ to $19Li_2O{\cdot}18$ to $24B_2O_3{\cdot}30$ to $38SiO_2$. To samples 906 and 907 Fe_2O_3 was added. To samples 910 and 911, NiO was added. To samples 902 and 905 Fe_2O_3 + NiO was added and nothing was added to sample 913. For those glasses of high alkali content, however, it may be natural to assume an ionic rather than electronic conduction. Accordingly, the TSPC peaks were re-examined on an ionic basis. The activation energies for ionic conduction, determined from the high-temperature part of the TSPC [15], are listed in Table I. All the samples except 914 contained both lithium and sodium ions as charge carriers. Due to the difference in ionic radii between them, it was assumed that the motion of sodium ions was the rate-determining step for conduction, and an oscillation frequency of 225 cm^{-1} was selected as an average between 220 cm^{-1} for sodium meta- and di-borate glasses and 230 cm^{-1} for sodium metasilicate glass [9]. Thus, using $\beta = 0.16$ degree sec^{-1}, the peak temperature for conduction polarization was calculated (Table I). Smooth TSPC curves were obtained only for samples 911 and 913, but two overlapping peaks can be identified for almost every sample. The dominant peak temperature of overlapping peaks, which was close to the calculated one [15], is also listed in Table I. The agreement is rather good, except for samples 906

TABLE I Calculated peak temperatures for conduction polarization in lithium–sodium borosilicate glasses using the reported activation energies for conduction, H_c [15]. The dominant peak temperatures [15], which are close to the calculated ones, are also included

Parameter	Sample							
	902	905	906	907	910	911	913	914
H_c (ev) [15]	0.74	0.66	0.79	0.73	0.86	0.86	0.84	0.44
Dominant peak temperature (K) [15]	266.6	229.8	298.5	263.1	292.4	296.3	285.7	—
Calculated peak temperature (K)	258	230	274	253	297	297	291	154

and 907 where the reproducibility of the position and shape of the curves was said [15] to be poor. Fig. 2 shows, as an example, the TSPC curve and the calculated peak temperature for sample 911. Published data are almost indifferent as to whether the samples contain a transition metal or not. It is concluded, therefore, that at least one of the TSPC peaks is due to ionic rather than electronic conduction.

When Li^+-doped MgO crystals [16] were annealed at high temperature and then cooled slowly. Lithium ions were distributed randomly and the charge neutrality was provided by impurities of some sort [17]. But, when the crystals were quenched from above 1400 K, there existed microgalaxies [17] composed of Li_2O precipitates surrounded by dense, substitutional Li^+ compensated by holes to form $[Li]^0$ centres. Isolated $[Li]^0$ centres, as generated by X- or γ- irradiation on slowly cooled crystals, were unstable above 220 K. On the other hand, $[Li]^0$ centres within the microgalaxy, produced without recourse to X- or γ-irradiation, were stable up to 900 K because of the potential barrier against the escape of the holes from the microgalaxy [16]. Eisenberg *et al.* [16] tried to explain the TSDC peak in terms of a Maxwell–Wagner type of polarization, in which the carriers of electric conductivity, σ, within the microgalaxy were emitted holes from $[Li]^0$ centres, and the relaxation time, τ, for polarization is pro-

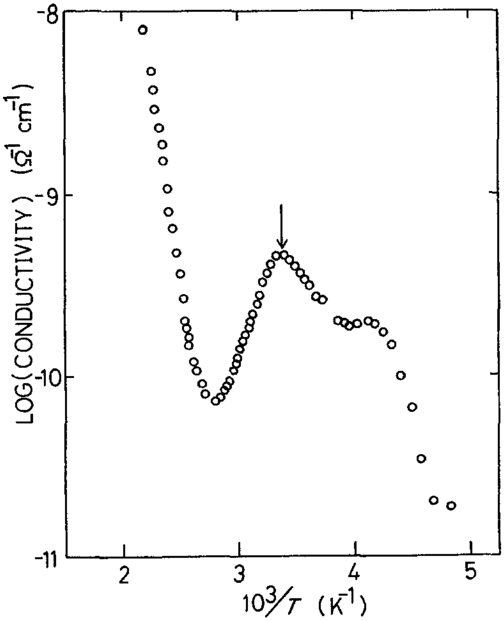

Figure 2 TSPC of sample 911 whose composition is $15.109Na_2O \cdot 14.449Li_2O \cdot 18.346B_2O_3 \cdot 29.61SiO_2 \cdot 22.48NiO$ (Catchings [15]). The arrow indicates the calculated peak temperature.

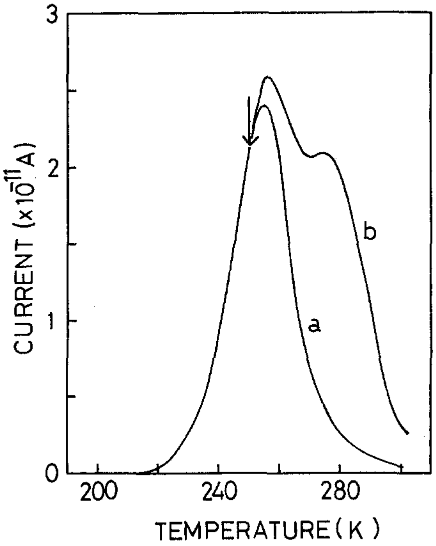

Figure 3 TSDC of MgO : Li^+ crystal quenched from 1573 K (Eisenberg *et al.* [16]). The polarization temperature is (a) 245 K or (b) 280 K. The arrow indicates the calculated peak temperature.

portional to $1/\sigma$ [14]. Therefore, from dielectric loss measurements of τ against $1/T$ or from initial-rise analyses of the TSDC, an ionization energy of $[\mathrm{Li}]^0$ centres can be evaluated.

A single peak in the dielectric loss spectrum has a relaxation energy of 0.73 eV and an oscillation frequency of 197 cm^{-1} [16], the latter being about one-half of an oscillation frequency of 385 to 485 cm^{-1} for lithium ions in various oxide glasses [9]. Equation 2 was used to calculate T_m for the polarization which is relevant to a single loss peak. T_m thus calculated, 250 K, is proximate to the 255 K peak (Fig. 3). If the polarization arises by ionic conduction within $\mathrm{Li_2O}$ precipitates rather than by ionization of $[\mathrm{Li}]^0$ centres, the activation energy for conduction in $\mathrm{Li_2O}$ crystal must be equal to or close to 0.73 eV. A.c. conductivity measurements [18] reveal H_c of 0.72 to 0.77 eV for four samples out of six of $\mathrm{Li_2O}$ polycrystals. Therefore, it seems better to ascribe the relevant polarization as arising from ionic conduction within $\mathrm{Li_2O}$ precipitates rather than ionization of $[\mathrm{Li}]^0$ centres within micro-galaxies.

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Grain-boundary deformation behaviour in a metastable beta-titanium alloy

Recent studies of tensile and bending fracture in heat-treated Ti–4.5 Al–5 Mo–1.5 Cr (CORONA 5) weld metal have shown that room-temperature sliding can occur at grain-boundary alpha/transformed-beta interfaces [1]. The mechanism of sliding differs fundamentally from that reported for grain-boundary sliding during high-temperature creep, and appears to involve highly localized, shear-induced deformation at the grain-boundary alpha/transformed-beta interface. In order to determine the universality of this phenomena for titanium alloys the present programme investigated the deformation behaviour of the metastable-beta titanium alloy Ti–15 V–3 Cr–3 Al–3 Sn.

Studies were conducted on sheet material approximately 2 mm thick which was given one of two different heat treatments:

(1) solution heat-treated at 788° C/3 h-WQ to obtain an entirely beta microstructure;

(2) solution heat-treated at 788° C/3 h-WQ + aged at 675° C/6 h-AC, which resulted in a Widmanstätten plus grain-boundary alpha microstructure in a retained beta matrix.

Following thermal treatments, blanks were machined into bend specimens, mechanically polished through 600 grit SiC paper, and electropolished at −45° C in a perchloric acid

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