

# Thermally stimulated currents in pyrex and soda-lime glasses

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Thermally stimulated current studies of commercially available soda-lime and pyrex glasses were made within the temperature range 170–700 K. Three different polarization peaks were found and compared with the peaks for alkali-rich glasses. The data were interpreted in terms of the heterogeneous distribution of alkali ions and structural rearrangement of the silicon network near the electrodes.

## 1. Introduction

The method of thermally stimulated polarization/depolarization current (TSPC/TSDC) is a novel technique for studying the motion of charge carriers in glass under the influence of an electric field. Recently, one of the authors reported from the TSPC/TSDC studies on alkali silicate glass that three different polarization peaks named P1, P2, and P3 exist in order of increasing peak temperatures within the temperature range 80–700 K [1, 2]. These three peaks were assigned as follows [1–4]: The P1-peak was due to conduction polarization of alkali ions, the P2-peak to conduction polarization of the non-bridging oxygen ions within the alkali-depleted region (ADR) near the anode, and the P3-peak to the voltage drop at ADR.

For the conduction polarization process, the TSPC/TSDC peak temperature,  $T_m$ , is related with the activation energy for conduction of the relevant charge carriers,  $H_c$ , as [3]

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

where  $k$  is Boltzmann's constant,  $\beta$  the heating rate, and  $v$  the vibrational frequency of the charge carriers. For alkali silicate [1], germanate [3], and phosphate [4] glasses the  $H_c$  values calculated from Equation 1 using the observed P1-peak temperatures agreed well with those obtained from conventional d.c./a.c. conductivity, dielectric loss or NMR measurements.

The samples studied so far were alkali-rich glasses, containing several tens of mol % of alkali oxide [1–4]. The purpose of the present work was to determine the charge carrier motion for two lower alkali-contents, commercially available glasses by the TSPC/TSDC technique.

## 2. Experimental procedures

The nominal compositions of the soda-lime and pyrex glasses used in this investigation are listed in Table I. The glasses of 0.97 to 1.30 mm in thickness were rinsed out supersonically in ethanol and deposited with gold electrodes on them. The samples were then set in a cryostat which afforded heat-cool cycles *in vacuo* in the temperature range 80 to 700 K. The applied field

was 200 V cm<sup>-1</sup>. The induced current during a TSPC/TSDC run was detected with a Takeda-Riken Model TR 8651 electrometer. The heating rate was not ideally linear, but on average was 0.16 deg sec<sup>-1</sup>.

The measurements of TSPC/TSDC were made as follows. First, the sample was heated up to 700 K with a field (TSPC), quenched to 170 K with a field still applied, and reheated a second time without field (TSDC). Although this procedure allowed us to determine the P2- and P3-peaks, the P1-peak was found only in the TSDC curve where the maximum temperature reached in the previous TSPC run was well below the P2-peak maximum.

## 3. Results and discussion

The overall data shown in the following figures were taken from the samples with gold electrodes. It was reconfirmed in the present experiment that, when evaporated silver instead of gold was used as the anode, the P3-peak was shifted to higher temperatures and the magnitude of the P2-peak was reduced drastically, in agreement with the previous finding [2, 5].

Figs. 1 and 2 show typical TSPC/TSDC curves for soda-lime and pyrex glasses. The data are summarized in Table II, which includes the peak temperatures for P1 and P2, the temperature difference between the two, the TSPC slope of the straight-line segment, and the activation energy for conduction reported in the literature [6–9]. The data on alkali silicate glasses [1, 2, 5] are also shown for comparison. The column on the far right will be discussed later.

For alkali-rich glasses the space-charge effect gives nuisance to the usual d.c. conductivity measurements, even when the applied field is not so high. Nonetheless, it can be seen from Table II that the activation energy values from the TSPC slopes were close to those for d.c. conduction [2, 5, 10], implying that the space-charge effect can be overcome by the conduction current which grows exponentially with temperature.

It is apparent from Equation 1 that, once the temperature of the P1-peak maximum is determined experimentally,  $H_c$  can be calculated with good accuracy even when  $v$  is not so accurate. The vibrational

TABLE I Glass samples and their nominal compositions

Glass	Manufacturer	Nominal compositions
Soda-lime	Japan Sheet Glass	73 SiO <sub>2</sub> , 1.7 Al <sub>2</sub> O <sub>3</sub> , 0.09 Fe <sub>2</sub> O <sub>3</sub> , 7 CaO, 4 MgO, 14 Na <sub>2</sub> O (wt %)
Pyrex	Schott (West Germany)	80.6 SiO <sub>2</sub> , 12.6 B <sub>2</sub> O <sub>3</sub> , 4.15 Na <sub>2</sub> O, 2.2 Al <sub>2</sub> O <sub>3</sub> , 0.1 CaO, 0.1 Cl, 0.05 MgO, 0.04 Fe <sub>2</sub> O <sub>3</sub> (wt %)

TABLE II Summary of TSPC/TSDC data for soda-lime and pyrex glasses, as well as reported data for alkali disilicate glasses [1, 2, 5]

Glass	$T_m$ (Peak temperature) (K)		Peak temperature difference (K)	TSPC slope (kcal mol <sup>-1</sup> )	Reported activation energy for conduction (kcal mol <sup>-1</sup> )	Calculated activation energy for conduction from Equation 1 using $T_m$ for P1 (kcal mol <sup>-1</sup> )
	P1	P2				
Soda-lime	274	336 ± 6	62 ± 6	18.4 ± 0.8	20.6 [6], 23.5 [7], 19.1 [9]	18.2
Pyrex	302	372 ± 3	70 ± 3	21.1 ± 0.9	22.2 [6], 18.4 ± 0.6 [8], 22.4 [9]	20.2
Li <sub>2</sub> O · 2SiO <sub>2</sub>	218 ± 6	263	45 ± 6	15.6 ± 0.8	14.6–14.9	14.8 ± 0.4
Na <sub>2</sub> O · 2SiO <sub>2</sub>	237 ± 6	287	50 ± 6	15.7 ± 1.1	14.0–15.0	15.6 ± 0.4
(NaLiO) · 2SiO <sub>2</sub>	325 ± 6	383	58 ± 6	—	20.0–22.0	22.3 ± 0.7

frequencies of alkali ions in alkali-poor glasses are not known, but will be not so much different from the values for alkali-rich glasses since the cation motion band for the (Na<sub>2</sub>O)<sub>x</sub> · P<sub>2</sub>O<sub>5</sub> glass merely shifted from  $6.78 \times 10^{12}$  to  $5.70 \times 10^{12}$  Hz when  $x$  changed from 1.26 to 0.46 [11]. When the value of  $\nu$ ,  $6.90 \times 10^{12}$  Hz, for sodium vibration in Na<sub>2</sub>O · SiO<sub>2</sub> glass [12] was adopted to our glasses, the calculated  $H_c$  values are in good agreement with the reported ones (Table II).

For the pyrex glass the P3-peak was not found in the first TSPC curve of the previously unpolarized sample, but was found in the subsequent runs made with the same polarity (Fig. 3). In the figure the corresponding TSDC curves are not shown for clarity.

Considering the faint but definite appearance in soda-lime glass (Figs. 1 and 4) and sharp appearance in alkali-rich glasses as Na<sub>2</sub>O · 2SiO<sub>2</sub> [2] and Li<sub>2</sub>O · 2SiO<sub>2</sub> [5] of the P3-peaks even in the first TSPC curves, the absence of the P3-peak for the pyrex glass may presumably be due to its low alkali content. As stated above, the P3-peak was assigned as being due to the formation of ADR near the anode as alkali conduction proceeds. It was already demonstrated that the density of alkali ions in ADR was very low, some  $10^{-4}$  or less than that in the bulk [5, 13]. The lower the alkali content of the glass, the wider will be the distribution of the jump distance of alkali ions for conduction. More energy will be required for depleting alkali ions with larger jump distance from ADR. In the

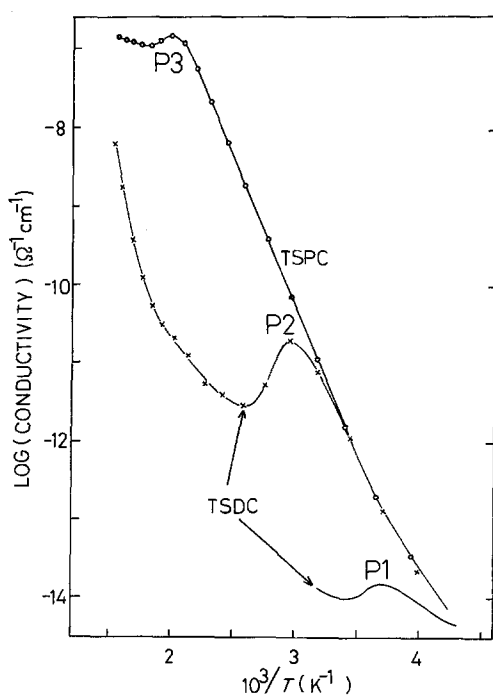


Figure 1 First TSPC/TSDC curves for soda-lime glass. Three peaks labelled P1, P2, and P3 were found.

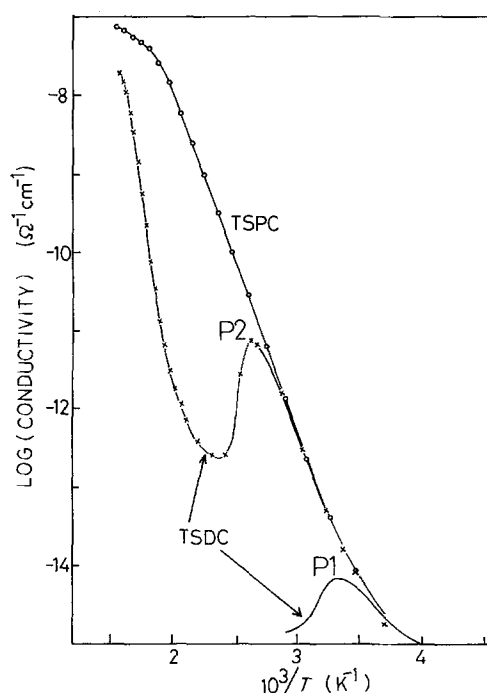


Figure 2 First TSPC/TSDC curves for pyrex glass. The P3-peak was not detected.

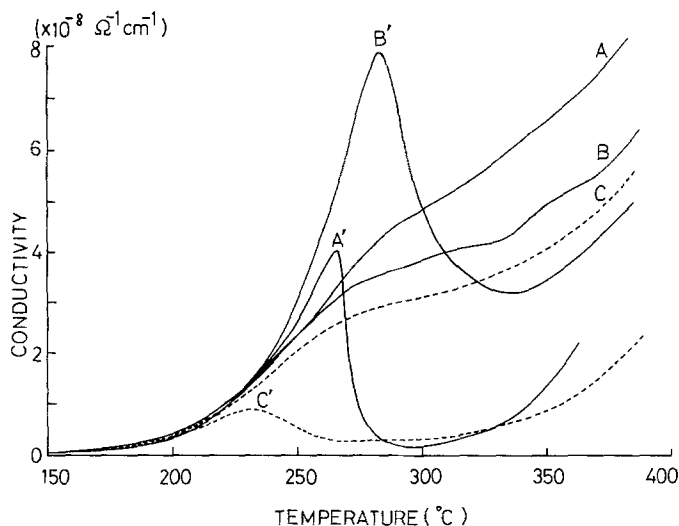


Figure 3 TSPC curves for three previously unpolarized samples of pyrex glass. The second TSPC runs (A', B', C') were made the next day after the first runs (A, B, C) were done, with the same electrode polarity. Corresponding TSDC curves are not shown for clarity.

pyrex glass, therefore, a wide temperature range must be spanned for evacuating overall sodium ions from ADR. In other words, the necessary condition for observing the P3-peak would be to generate ADR within a temperature range as narrow as possible. The IR measurement [13] suggests that the formation of ADR accompanies rearrangement of the silicon network near the anode. This structural change would afford easier movement of the sodium ions in ADR, leading to the observation of the P3-peak in the subsequent TSPC runs.

Once the pyrex glass sample was polarized to the temperatures above the P3-peak maximum, the P3-peak appeared definitely afterwards even when the polarity was reversed. Some structural rearrangement would occur also in the region near the cathode during the first TSPC run by, possibly, the alkali accumulation. If the silicon network near the original cathode were to be free from the structural change, it would have been difficult to generate ADR near the original cathode within a narrow temperature range where the polarity is reversed in the subsequent runs. Our hypothesis is partially substantiated by the potential probe

experiment [14] in which the development of the potential drop was shown near the cathode as alkali conduction proceeded.

Table III shows data for four repetitive TSPC/TSDC runs of the pyrex glass sample C. The closeness of the areas covered by the P3-peak and by the TSDC curves supports the previous explanation [2] that the TSDC current, other than the P1- and P2-peaks, would arise from back-diffusion of alkali ions into ADR.

For both soda-lime and pyrex glasses, a scatter of the initial TSPC curves from sample to sample was small at low temperatures but became larger at temperatures higher than the P3-peak maximum (Figs. 3 and 4). This, as well as a scatter of the location and the magnitude of the P3-peak, would reflect a microheterogeneous distribution of sodium ions in ADR which because of the very restricted volume of ADR cannot be averaged over as in the bulk.

From previous papers [3, 15] it is shown that the ratio of the pre-exponential factor of the frequency at dielectric loss maximum ( $f_{mo}$ ) to that of d.c. conductivity ( $\sigma_0$ ) is

$$\frac{f_{mo}}{\sigma_0} = \frac{6kT}{2\pi e^2 \lambda^2 n} \quad (2)$$

where  $n$  is the density of mobile alkali ions and  $\lambda$  the jump distance. Since the magnitude of conduction polarization for the P1-peak is [3]

$$P = \frac{ne^2 \lambda^2}{6kT_p} E_p \quad (3)$$

the ratio  $f_{mo}/\sigma_0$  can be rewritten as

$$\frac{f_{mo}}{\sigma_0} = \frac{E_p}{2\pi P} \quad (4)$$

when the ratio is determined at the polarization temperature,  $T_p$ , at which the system is polarized by the applied field,  $E_p$ . The calculated values of the ratio, using the areas covered by the P1-peaks, are listed in Table IV for both glasses as well as for alkali trisilicate glasses [16, 17]. Fig. 5 shows the observed ratio of  $f_{mo}/\sigma_0$  as a function of alkali content for many alkali-containing oxide glass systems [18]. In view of the scatter of the  $f_{mo}/\sigma_0$  values the agreement between

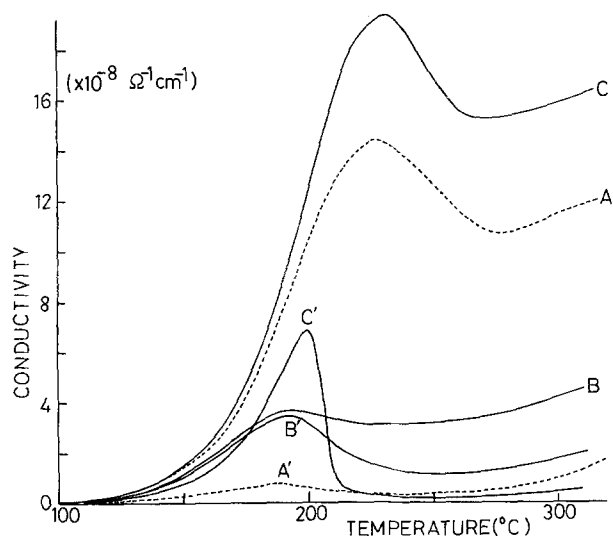


Figure 4 TSPC curves for three previously unpolarized samples of soda-lime glass. The second TSPC runs (A', B', C') were made the next day after the first runs (A, B, C) were done, with the same electrode polarity. Corresponding TSDC curves are not shown for clarity.

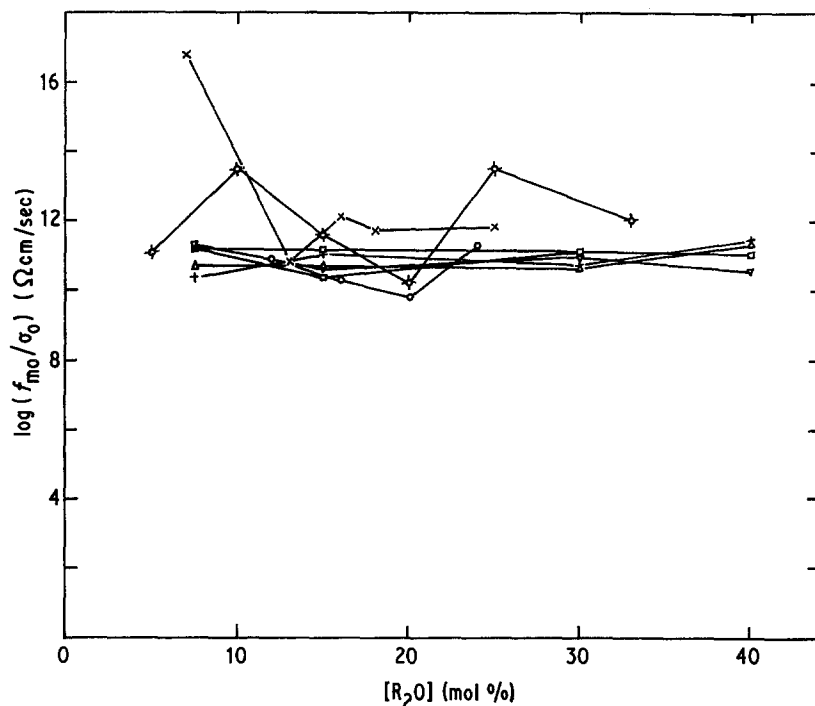


Figure 5 The ratio of the pre-exponential factors of the frequency at dielectric loss maximum and of d.c. conductivity for various alkali-containing oxide glass systems [18]. ( $\square$ )  $x\text{Li}_2\text{O} \cdot (100-x)\text{SiO}_2$ , ( $\Delta$ )  $x\text{Na}_2\text{O} \cdot (100-x)\text{SiO}_2$ , ( $\nabla$ )  $x\text{K}_2\text{O} \cdot (100-x)\text{SiO}_2$ , ( $+$ )  $x\text{Rb}_2\text{O} \cdot (100-x)\text{SiO}_2$ , ( $\circ$ )  $x\text{Na}_2\text{O} \cdot 10\text{CaO} \cdot (90-x)\text{SiO}_2$ , ( $\ominus$ )  $x\text{Na}_2\text{O} \cdot (100-x)\text{B}_2\text{O}_3$ , ( $\times$ )  $x\text{Na}_2\text{O} \cdot 10\text{SiO}_2 \cdot (90-x)\text{B}_2\text{O}_3$ .

calculation (Table IV) and observation (Fig. 5) is rather good.

If alkali ions are homogeneously distributed and  $\lambda$  is equal to the separation between two nearest-neighbour alkali ions, the average jump distance is

$$\lambda_{\text{av}} = \left( \frac{6}{\pi N} \right)^{1/3} \quad (5)$$

where  $N$  is the density of overall alkali ions. The unknown factor in Equation 3,  $n\lambda^2$ , is estimated from the magnitude of the P1-peak and listed in Table IV in the reduced form  $n\lambda^2/N\lambda_{\text{av}}^2$ . The data for thin films of alkali disilicate glasses of several  $\mu\text{m}$  in thickness after biasing with more than several tens of  $\text{kV cm}^{-1}$  at high temperatures [1] are also shown for comparison. It is apparent from Table IV that some of alkali ions cannot contribute equally to the electrical conduction for thick glass samples, but (possibly) can do so for thin films. It implies that, in thin films, similar structural change as discussed above would take place by biasing with extremely high field, thus permitting participation of the overall alkali ions to the P1-peak.

From the magnitude,  $P$ , of the P2-peak we can estimate the corresponding dielectric constant  $\epsilon$  as

$$\epsilon = \frac{P}{\epsilon_0 E_p} \quad (6)$$

where  $\epsilon_0$  is the permittivity of free space. The calculated values for  $\epsilon$  were  $\sim 4 \times 10^4$  for soda-lime and  $\sim 1 \times 10^4$  for pyrex glasses. The dielectric measurements of alkali-containing oxide glasses revealed the existence of two types of dispersions. The large dielectric constant at lower frequencies is called electrode polarization [19] while the small dielectric constant at higher frequencies is ascribed to conduction polarization of alkali ions, i.e. to the P1-peak [3, 4]. Since the dielectric constant for the soda-lime glass comes close to  $10^4$  and possibly levels off with decreasing frequencies [19], the lower-frequency dispersion may be due to conduction polarization of the non-bridging oxygen ions in ADR, i.e. to the P2-peak. It is noted that the "genuine" dielectric constant for the relevant dispersion must be evaluated from Equation 6 using the effective electric field at ADR, rather than the applied field.

#### 4. Conclusion

In the TSPC/TSDC curves of the soda-lime and pyrex glasses, we found three peaks named P1, P2, and P3

TABLE III Data of four repetitive TSPC/TSDC runs made with an identical polarity at one-day intervals for pyrex glass sample C

	1		2		3		4	
	TSPC	TSDC	TSPC	TSDC	TSPC	TSDC	TSPC	TSDC
Overall area of the curve ( $\text{C cm}^{-2}$ )	$9.34 \times 10^{-3}$	$1.2 \times 10^{-3}$	$3.22 \times 10^{-3}$	$1.3 \times 10^{-3}$	$2.64 \times 10^{-3}$	$1.32 \times 10^{-3}$	$2.21 \times 10^{-3}$	$1.0 \times 10^{-3}$
P2 Peak temperature (K)		376		374		369		373
Area ( $\text{C cm}^{-2}$ )		$2.29 \times 10^{-7}$		$1.98 \times 10^{-7}$		$1.73 \times 10^{-7}$		$1.59 \times 10^{-7}$
P3 Peak temperature (K)			527		528		531	
Area ( $\text{C cm}^{-2}$ )			$1.30 \times 10^{-3}$		$1.30 \times 10^{-3}$		$1.28 \times 10^{-3}$	

TABLE IV The values of the ratios  $f_{mo}/\sigma_0$  and  $n\lambda^2/N\lambda_{av}^2$ , as calculated using the areas covered by the P1 peaks and  $N$ , the density of overall alkali ions

Glass	$N$ (cm <sup>-3</sup> )	$\frac{f_{mo}}{\sigma_0}$ ( $\Omega$ cm sec <sup>-1</sup> )	$n\lambda^2/N\lambda_{av}^2$
Pyrex	$8.9 \times 10^{20}$	$7.5 \times 10^{10}$	0.14
Soda-lime	$3.1 \times 10^{21}$	$3.0 \times 10^{10}$	0.22
R <sub>2</sub> O · 3SiO <sub>2</sub> [16, 17]	$(0.99-1.33) \times 10^{22}$	$(7.0-13.2) \times 10^{10}$	0.043-0.048
Thin films of R <sub>2</sub> O · 2SiO <sub>2</sub> [1]	$(1.73-1.87) \times 10^{22}$	$(0.14-0.45) \times 10^{10}$	1.1-2.6

within the temperature range from 170 to 700 K. Based on the previous assignment for these peaks [1-5], the following conclusions were made.

1. As the nominal alkali content is decreased, the distribution of the jump distance of alkali ions for conduction becomes wider, so wider temperature range must be spanned for evacuating overall alkali ions from ADR. This can be the reason for the absence of the P3-peak in the first TSPC curve of the previously unpolarized sample of the pyrex glass.

2. In ADR the scatter of the distribution of alkali ions from sample to sample cannot be averaged over as in the bulk, hence a scatter of the peak position and the magnitude of the P3-peak from sample to sample would occur.

3. Structural rearrangement of the silicon network would take place at both regions near the electrodes during the first TSPC run, by which easier movement of alkali ions would be afforded in the subsequent runs within ADR.

4. From the discussion of the ratio  $n\lambda^2/N\lambda_{av}^2$ , it is suggested that no overall alkali ions contribute equally to the P1-peak for thick glass samples, but possibly do so for thin films after biasing with extremely high electric field. This high-field effect can be explained in terms of the same structural change as stated in point 3 above.

5. The large dielectric constant at low frequency, as large as  $\sim 10^4$ , for alkali-containing oxide glasses may be due to conduction polarization of the non-bridging oxygen ions in ADR, i.e. to the P2-peak.

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