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Recommended Citation

A. Doi and D. E. Day, "Conduction Polarization in Sodium Germanate Glasses," *Journal of Applied Physics*, vol. 52, no. 5, pp. 3433-3438, American Institute of Physics (AIP), May 1981.

The definitive version is available at <https://doi.org/10.1063/1.329117>

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Conduction polarization in sodium germanate glasses

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(Received 15 April 1980; accepted for publication 5 January 1981)

Only one thermally stimulated depolarization current (TSDC) peak was found in germanate glasses containing from 0.19 to 32.5 mol% Na₂O, whereas comparable silicate glasses exhibit two such peaks. Equations are developed showing that the distortion of the equilibrium Na⁺-ion distribution by an applied electrical field produces a polarization in general agreement with the observed TSDC peak. It is proposed that the TSDC peak is due to dc conduction.

PACS numbers: 72.20.Pa

I. INTRODUCTION

The thermally stimulated depolarization current (TSDC) method has recently been used to investigate^{1,2} alkali motion in simple glasses. In this technique, a sample is polarized by an applied field E_p for a time t_p at a given polarization temperature T_p and quenched to a lower temperature T_0 . Then, with the field removed, the sample is heated at a constant rate β ($= dT/dt$) and the relaxation of any polarization is detected as a current induced in the outer circuit. As a complement to TSDC, the thermally stimulated polarization current (TSPC)³ method consists of quenching a sample in thermal equilibrium to T_0 , followed by heating at a constant rate β with the field E_p applied and measuring the current induced by the buildup of polarization. Both techniques are said⁴ to give an identical peak temperature for an identical process such as dipole orientation. One of the TSDC peaks usually observed in alkali-containing glasses has been ascribed^{1,2} to the orientation of alkali-nonbridging oxygen dipoles. In the present work, the TSDC/TSPC techniques were used to investigate charge-storage mechanisms in X Na₂O·(100- X)GeO₂ glasses ($X = 0.19$ -32.5 mol).

II. EXPERIMENTAL PROCEDURES

The detailed procedures for TSDC/TSPC measurements are described elsewhere,¹ so only a brief review is given here. A glass sample ~10 by 10 by 1 mm with evaporated gold electrodes on the large surfaces was placed in a cryostat and depolarized (short-circuited) overnight before each measurement by heating to ~400 K in a vacuum of 7×10^{-3} Torr. During a measurement, the thermal gradient in the sample was minimized by flowing helium through the cryostat. The TSDC was measured with a Keithly 610B electrometer. The sample was heated from ~100 to ~475 K at a rate of 0.08 K/sec.

III. RESULTS AND DISCUSSION

Figure 1 shows typical TSDC/TSPC curves for the $X = 10$ glass. All the glasses investigated exhibited one dominant TSDC peak, which moved to lower temperatures with increasing Na₂O content, and an increasing current at higher temperatures which obeyed $i(T) = i_0 \exp - (H_c/kT)$. The temperature and activation

energy, as determined by partial discharge,^{2,4} of the TSDC peak along with the activation energy for dc conduction, H_c , as determined from the high-temperature TSPC are given in Table I.

Raman⁵ and radial distribution function⁶ studies suggest that, for $X < 18$, all the Na⁺ ions are used to charge compensate the GeO₆ octahedra, while for $X > 18$ some Na⁺ are associated with nonbridging oxygens (NBO). It might be speculated, therefore, that the TSDC peak is due to orientational polarization of sodium-GeO₆ or sodium-NBO dipoles. For such a dipolar system, the magnitude of the polarization can be expressed as⁷

$$\frac{Q}{AE_p} = \epsilon_0 \Delta \epsilon = \frac{n\mu^2}{3kT_p} \left[1 - \left(\coth \frac{H}{2kT_p} - \frac{2kT_p}{H} \right)^2 \right] \approx \frac{4n\mu^2}{3H} \quad (\text{when } H > 2kT_p), \quad (1)$$

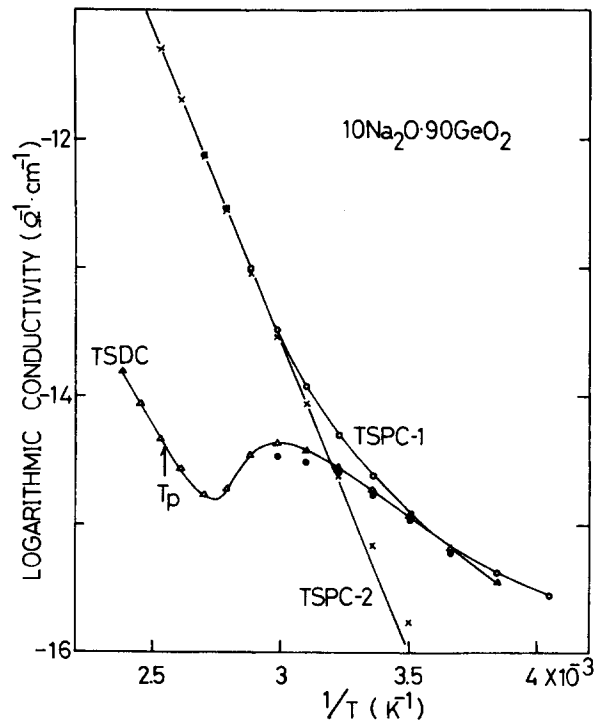


FIG. 1. TSPC-1 (first heating with applied field) and TSPC-2 (second heating with applied field) curves for $X = 10$ glass and the corresponding TSDC, where the polarizing condition is $T_p = 393$ K, $t_p = 5$ min, and $E_p = 2.44 \times 10^3$ V/cm. Closed circles correspond to the difference between TSPC-1 and TSPC-2.

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TABLE I. Data for the TSDC peak in sodium germanate glasses.

Mol% Na ₂ O	0.19	2	5	10	17.5	20	22.5	27.5	32.5
TSDC peak									
a. Temperature, T_m ($\pm 2K$)	367	349	347	336	302	264	261	230	210
b. Activation energy, H (± 1 kcal/mol)	21.7	19.0	18.4	...	15.0	13.0	14.1	12.0	...
c. Q/AE_p (10^{-12} C/V cm)	2.49	2.86	3.59	3.77	5.40	4.03	4.54	2.58	4.26
dc conduction, activation energy, H_c									
a. TSPC (Ref.8)	22.6	21.4	21.4	21.3	19.1	17.8	17.4	16.0	15.1
b. Ref. 12	...	23.5(3) ^a	23.6(5.5)	23.4	20.7(17)	20.5
Calculated values from Eq. (13)									
a. τ_0 (10^{-5} sec)	15	23-31	16	5.6-7.6	4.5-7.6	0.59-0.72	0.92	0.26	...
b. H_c (kcal/mol)	23.5	21.8-22.0	22.1	21.9-22.1	19.6-19.9	18.4	17.9	16.3	...

^aNumbers in parentheses are mol% Na₂O when composition differs from that at top of each column.

where ϵ_0 is the permittivity of free space, $\Delta\epsilon$ is the difference in the dielectric constant below and above the frequency range where relevant polarization would take place ($\epsilon_v - \epsilon_\infty$), Q is the area (charge) of the peak, A is the electrode area, H is the activation energy for the relevant polarization, n is the concentration of dipoles, and μ is the dipole moment.

The dipole distance δ_n shown in Fig. 2 was calculated from Eq. (1) using the experimentally measured TSDC peak area (charge) and activation energy H (determined by partial discharge) and assuming n was the overall Na⁺ concentration and one unit of elementary charge as the effective dipole charge. An implicit assumption is that the Na⁺ ions are homogeneously distributed and contribute equally to the TSDC peak. Analyses of the TSPC in these glasses⁸ and other data^{9,10} suggest, however, the existence of compositional microheterogeneities, at least on both sides of the $X = 18$ composition. If n in Eq. (1) is smaller than the nominal sodium content, the calculated dipolar distance is even larger than δ_n . In either case, the calculated δ is too large for any type of realistic dipole, at least for the glasses containing < 10 mol% Na₂O.

Figure 3 shows the compositional dependence of the

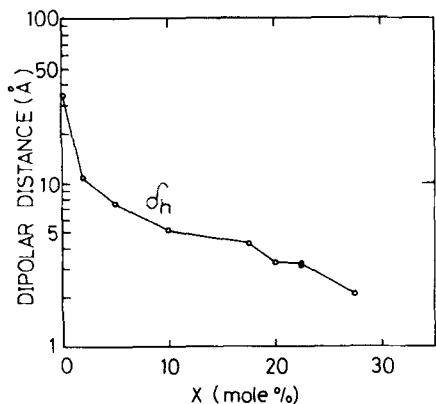


FIG. 2. Dipolar distance δ_n calculated assuming homogeneous sodium distribution and equal contribution of sodium ions to the TSDC peak. $X =$ mol% Na₂O.

activation energy for dc conduction, H_c , determined from TSPC and the temperature T_m and activation energy H of the TSDC peak. The activation energy H was determined from three partial discharges of the TSDC peak, the slope of the log current vs $-1/T$ plot of the second discharge being taken as the typical value for H . The second and third discharges typically gave about the same value for H , but the value from the first discharge was always somewhat smaller.

Dielectric relaxation studies¹¹ show only one peak for many glasses, and there are few which reveal two dielectric loss peaks. If H is truly smaller than H_c , then the relevant polarization should produce an additional peak at higher frequencies than the usual one whose activation energy is

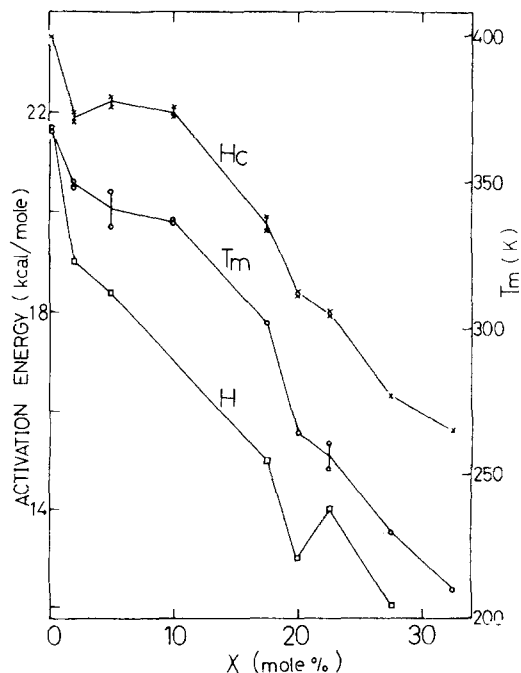


FIG. 3. Compositional dependence of the activation energy for dc conduction H_c from TSPC and the temperature T_m and activation energy H for the TSDC peak. $X =$ mol% Na₂O.

TABLE II. Magnitude of polarization $\Delta\epsilon$ for glasses of similar composition as calculated from dielectric relaxation (Ref.11) and from TSDC (Ref. 14).

Composition (mol%)	$\Delta\epsilon$ (dielectric loss)	Composition (mol%)	$\Delta\epsilon$ (TSDC)
15Na ₂ O-85SiO ₂	16.0	14.6Na ₂ O-85.4SiO ₂	14.1
30Na ₂ O-70SiO ₂	27.0	25Na ₂ O-75SiO ₂	25.5
15Na ₂ O-85B ₂ O ₃	9.2	16Na ₂ O-84B ₂ O ₃	14.9
16Na ₂ O-74B ₂ O ₃ -10SiO ₂	7.5	14.7Na ₂ O-68.9B ₂ O ₃ -16.4SiO ₂	16.6
10Na ₂ O-25B ₂ O ₃ -65SiO ₂	17.0	11.7Na ₂ O-15.1B ₂ O ₃ -73.2SiO ₂	21.2
16Na ₂ O-10CaO-74SiO ₂	27.0	15Na ₂ O-10CaO-75SiO ₂	26.0
3Na ₂ O-97GeO ₂ (Ref. 12)	17.5	2Na ₂ O-98GeO ₂ (This work)	28.1

almost identical with H_c . Furthermore, the measured $\Delta\epsilon$ of the dielectric loss peak^{11,12} and that calculated from the TSDC peak are of comparable magnitude as shown for some glasses in Table II. The partial discharge or the initial rise method¹³ gives an activation energy for the low-temperature portion of a partially discharged TSDC peak, and, in some glasses,¹⁴ the results indicate a distribution in the activation energy. Thus, it is difficult to state the typical value of H . It is a plausible hypothesis that conduction itself gives rise to both the TSDC and dielectric loss peaks; they have the same origin and the same activation energy H_c . The following is the tentative description of how conduction can produce a TSDC peak.

Consider first that conduction proceeds by an interstitialcy mechanism, as has been proposed from isotope effect measurements.¹⁵ The concentration of available "lattice" sites is assumed equal to the concentration of mobile Na⁺ ions. When a lattice site is vacant, the Na⁺ ion previously occupying this site is somewhere on a nearby interstitial site. Under thermal equilibrium, a Na⁺ ion should have an equal probability of occupying any of the nearest-neighbor interstitial sites, so the probability distribution may be spherical around the lattice site. The number of Na⁺ ions jumping out of any given site surrounded by an energy barrier H_c is usually expressed as¹⁶

$$K = \nu \exp(-H_c/kT), \tag{2}$$

where ν is the vibrational frequency and any distribution in H_c is ignored for simplification. The number of Na⁺ ions

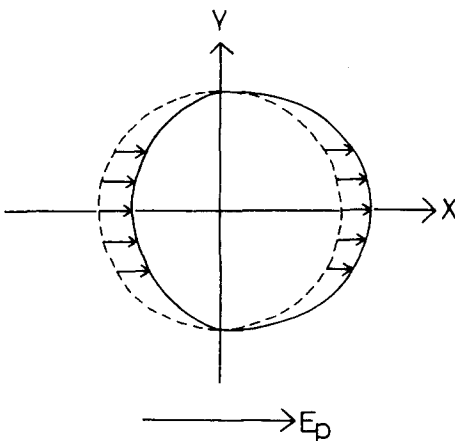


FIG. 4. Two-dimensional representation of the probability distribution of Na⁺-ion jump directions around a lattice site to nearest-neighbor interstitial sites before (dotted line) and after (solid line) applying bias field E_p .

jumping from a given lattice site to a nearest-neighbor interstitial site in the direction of the applied field is the following:

$$K_+ = \frac{1}{6}\nu \exp[-(H_c - eE_p\lambda/2)/kT], \tag{3}$$

while the number of Na⁺ ions jumping from a lattice site to a nearest-neighbor interstitial site in the direction opposite to the applied field is as follows:

$$K_- = \frac{1}{6}\nu \exp[-(H_c + eE_p\lambda/2)/kT], \tag{4}$$

where 6 results from the number of possible jump directions and λ is the jump distance.

When the system is biased by an applied field E_p , the probability distribution of jump directions from a given lattice site to nearest-neighbor interstitial sites is distorted from a spherical distribution, as shown in Fig. 4. Here we assume that any available site for conduction can accommodate one or more Na⁺ ions, so the effect of adjacent occupied sites on the probability distribution is neglected. The distortion can be expressed, therefore, as

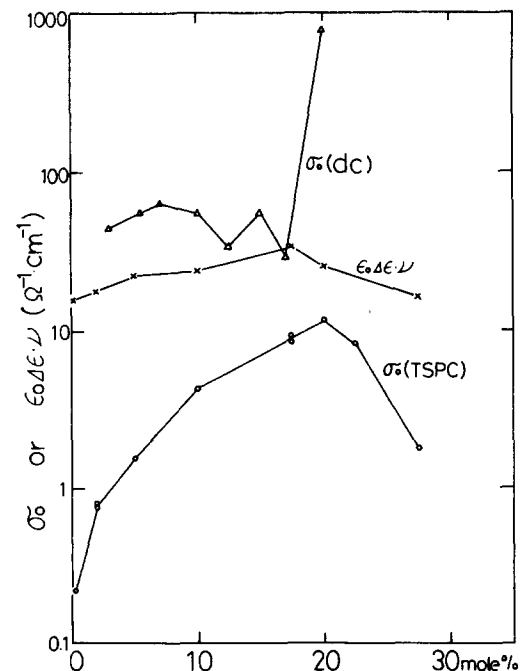


FIG. 5. Compositional dependence of $\epsilon_0\Delta\epsilon\nu$ and the preexponential factor for conductivity σ_0 as derived from TSDC (Ref. 8) and from dc conduction (Ref. 12), where $\epsilon_0\Delta\epsilon$ is the magnitude of polarization determined from the TSDC peak and ν is the Na⁺-ion jumping frequency chosen as $\nu = 6.3 \times 10^{12}$ Hz (Ref. 20).

$$\frac{K_+ - K_-}{K} = \frac{1}{3} \sinh\left(\frac{eE_p\lambda}{2kT}\right) \approx \frac{eE_p\lambda}{6kT}, \quad (5)$$

when $eE_p\lambda \ll 2kT$. An identical situation holds for the probability distribution of jump directions of a Na^+ ion from a given interstitial site to nearest-neighbor lattice sites. A distortion like this produces a dipole moment $e\lambda(K_+ - K_-)/K$, so the saturated polarization P is as follows:

$$P = ne\lambda \left(\frac{K_+ - K_-}{K}\right) = \frac{ne^2\lambda^2}{6kT} E_p, \quad (6)$$

where n is the concentration of mobile Na^+ ions. Equation (6) holds for other dc conduction mechanisms as well, if each jump of a conductive Na^+ ion can be treated as independent of the jumps of nearby ions.

The distortion as described by Eq. (5) leads to a microscopic distribution of Na^+ ions within the glass which is different from their distribution without field. That is, the elementary process of dc conduction motivates a move from a normal to a distorted distribution of Na^+ ions which is responsible for a TSPC peak, while the reverse move produces a TSDC peak. The relevant polarization is dynamic in the sense that each mobile Na^+ ion moves perpetually, but the overall polarization remains constant. This type of distortion or polarization is established when mobile Na^+ ions jump from their respective equilibrium sites at least once during the time the glass is biased by E_p and then remains unchanged for a given temperature and E_p . For example, the state of the system at $T = T_m$ during a TSPC measurement is that some fraction of Na^+ ions jump from their original sites and contribute to dc conduction, while some are still frozen in, the classification being of statistical origin.

Therefore, for any conduction mechanism, the buildup of polarization at a given temperature T follows the equation

$$\frac{dP(t)}{dt} = -\frac{1}{\tau} \left(P(t) - \frac{ne^2\lambda^2}{6kT} E_p \right), \quad (7)$$

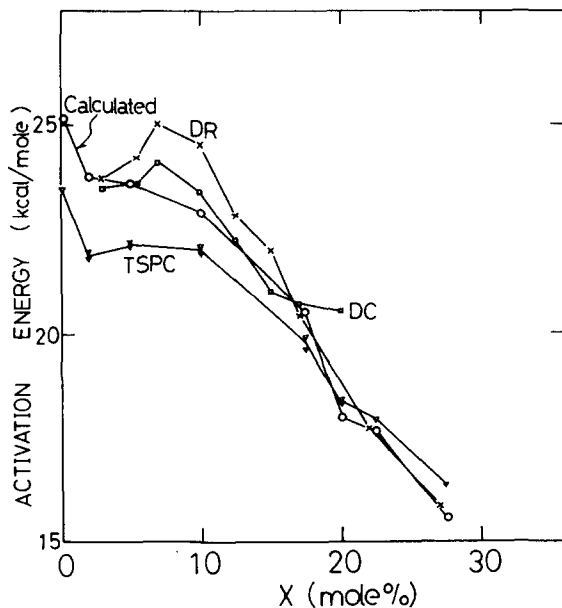


FIG. 6. Compositional dependence of the activation energy for the TSDC peak as calculated from Eq. (13) and labeled "Calculated," and the activation energy for dc conduction from TSPC (Ref. 8); from dc conduction, DC (Ref. 12); and from dielectric relaxation, DR (Ref. 12). $X = \text{mol\% Na}_2\text{O}$.

TABLE III. Comparison of jumping frequency ν from far infrared (Ref. 20) and the frequency $2\pi f_{m_0}$ at the dielectric loss maximum (Ref. 11).

Composition	ν (Hz) (Ref. 20)	Composition	$2\pi f_{m_0}$ (Hz) (Ref. 11)
$\text{Li}_2\text{O}\cdot\text{SiO}_2$	1.46×10^{13}	$30\text{Li}_2\text{O}\cdot 70\text{SiO}_2$	6.28×10^{13}
$\text{Na}_2\text{O}\cdot\text{SiO}_2$	6.90×10^{12}	$30\text{Na}_2\text{O}\cdot 70\text{SiO}_2$	7.91×10^{12}
$\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$	6.60×10^{12}	$\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$	4.96×10^{14}

where

$$\tau = 1/K = \tau_0 \exp(H_c/kT) \quad (8)$$

is a relaxation time for Na^+ -ion jumps. Assuming $P(t) = 0$,

at $t = 0$, then

$$P(t) = \frac{ne^2\lambda^2 E_p}{6kT} \left[1 - \exp\left(-\int_0^t \frac{dt}{\tau}\right) \right]. \quad (9)$$

When the temperature is raised at a constant rate, $T = T_0 + \beta t$, then the TSPC current j is the following:

$$j = \frac{dP(t)}{dt} = \frac{\beta ne^2\lambda^2 E_p}{6kT^2} \left\{ \left(1 + \frac{T}{\beta\tau} \right) \exp\left[-\frac{1}{\beta\tau_0} \int_{T_0}^T \exp\left(\frac{-H_c}{kT}\right) dT \right] - 1 \right\}. \quad (10)$$

At low temperatures, Eq. (10) is approximated by¹⁷

$$j \approx \frac{ne^2\lambda^2 E_p}{6kT\tau_0} \exp\left[-\frac{H_c}{kT} - \frac{1}{\beta\tau_0} \int_{T_0}^T \exp\left(\frac{-H_c}{kT}\right) dT \right]. \quad (11)$$

Similarly, the TSDC current j' is given by¹³

$$j' = \frac{ne^2\lambda^2 E_p}{6KT_p\tau_0} \exp\left[-\frac{H_c}{kT} - \frac{1}{\beta\tau_0} \int_{T_0}^T \exp\left(\frac{-H_c}{kT}\right) dT \right]. \quad (12)$$

On differentiating Eq. (11), the temperature of the maximum TSPC current, T_m , is obtained as

$$\frac{H_c}{kT_m^2} = \frac{1}{\beta\tau_0} \exp\left(\frac{-H_c}{kT_m}\right) + \frac{1}{T_m} \approx \frac{1}{\beta\tau_0} \exp\left(\frac{-H_c}{kT_m}\right) \quad (13)$$

for $H_c \gg kT_m$. Similarly, the temperature of the TSDC maximum obtained by differentiating Eq. (12) is exactly the same as Eq. (13). Equation (13) was originally derived for orienta-

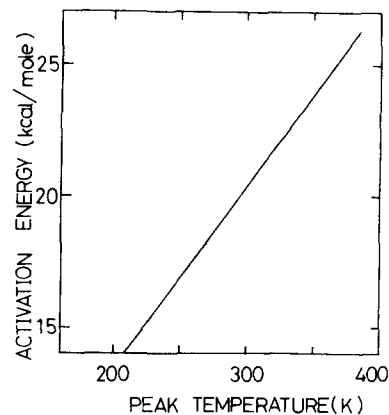


FIG. 7. Relation of the activation energy and temperature of TSDC peak calculated from Eq. (13) using $\beta = 0.08 \text{ K/sec}$ and $\tau_0 = 1.6 \times 10^{-13} \text{ /sec}$.

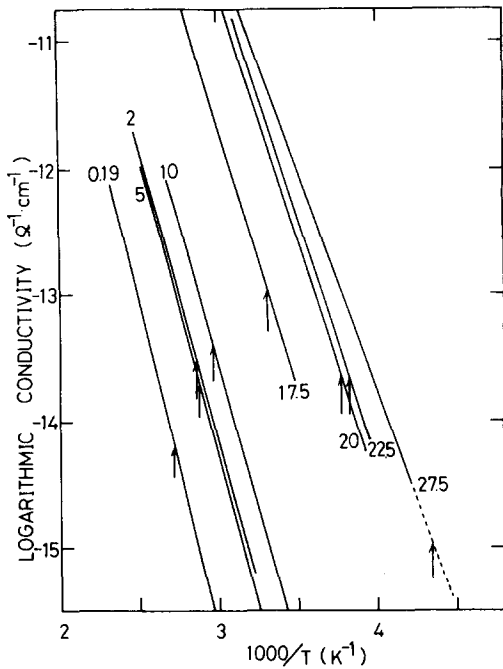


FIG. 8. dc conductivity of $X\text{Na}_2\text{O}\cdot(100-X)\text{GeO}_2$ glasses as determined from TSPC-2. Number for each line is mol% Na_2O and the arrow corresponds to temperature of the TSDC peak maximum, T_m .

tional polarization¹³ but holds for conduction polarization as well.

Equation (6) gives

$$P/E_p = \epsilon_0 \Delta \epsilon = ne^2 \lambda^2 / 6kT. \quad (14)$$

Since a theoretical expression for the conductivity σ is the following¹⁸:

$$\begin{aligned} \sigma &= \sigma_0 \exp(-H_c/kT) \\ &= (ne^2 \lambda^2 \nu / 6kT) \exp(-H_c/kT), \end{aligned} \quad (15)$$

the relation

$$\epsilon_0 \Delta \epsilon \nu = \sigma_0 \quad (16)$$

should hold. There is no reported compositional dependence of ν in sodium germanate glasses, but it is assumed ν changes only slightly as in sodium phosphate glasses.¹⁹ A value of $\nu = 6.3 \times 10^{12}$ Hz was selected²⁰ for convenience as an average ν to calculate $\epsilon_0 \Delta \epsilon \nu$. Figure 5 shows that $\epsilon_0 \Delta \epsilon \nu$ lies between the two σ_0 values as derived from TSPC⁸ and dc conduction.¹²

As is apparent from the TSPC/TSDC curves for the $X = 10$ glass in Fig. 1, the conductivity at the TSPC or TSDC peak maximum, defined by $\sigma_m(\text{TSPC}) = j(T_m)/E_p$ or $\sigma_m(\text{TSDC}) = j'(T_m)/E_p$, is always smaller than the dc conductivity at T_m , $\sigma(T_m)$. This is because, from Eqs. (11), (12), and (15),

$$\begin{aligned} \sigma_m(\text{TSDC}) &= \sigma(T_m) \frac{T_m}{T_p} \exp\left[-\frac{1}{\beta \tau_0} \int_{T_0}^{T_m} \exp\left(\frac{-H_c}{kT}\right) dT\right] \\ &\leq \sigma_m(\text{TSPC}) = \sigma(T_m) \exp\left[-\frac{1}{\beta \tau_0} \int_{T_0}^{T_m} \exp\left(\frac{-H_c}{kT}\right) dT\right] \\ &< \sigma(T_m). \end{aligned} \quad (17)$$

It is to be noted that, although dc conduction and at least one of the TSPC/TSDC peaks originate from the same elemen-

tary process, the nature of the current is different. The former measures ionic flow per unit time through the electrodes and is independent of β , while the latter is the polarization-induced current which is dependent upon β .

A simple correlation between the conductivity σ and the frequency f_m at a dielectric loss maximum is as follows²¹:

$$2\pi \epsilon_0 \Delta \epsilon f_m = \sigma, \quad (18)$$

where

$$f_m = f_{m0} \exp(-H_c/kT). \quad (19)$$

Since the polarization considered here is due to dc conduction, σ in Eq. (18) must be the dc conductivity.

Equations (16) and (18) give

$$2\pi f_{m0} = \nu. \quad (20)$$

Table III compares values of ν reported²⁰ from far-infrared measurements and those¹¹ for f_{m0} for several glasses. The agreement is rather good considering the difficulty in obtaining reliable f_m or f_{m0} values.²²

To check whether the TSDC peak was due to polarization produced by the Na^+ -ion motion described previously, τ_0 was calculated from Eq. (13) using the experimental H_c values. The calculated τ_0 values in Table I are, in some cases, in rather poor agreement with the expected values of about $(1.4 - 1.7) \times 10^{13}$ sec, as estimated from the infrared data.²⁰ Consequently, H_c was recalculated from Eq. (13) assuming $\tau_0 = 1.6 \times 10^{-13}$ sec. The recalculated H_c is very close to the reported values, as shown in Fig. 6 and Table I. The relation between H_c and T_m in Fig. 7 indicates only a small change in the ratio H_c/kT_m , from 33.9 to 34.4 as T_m increases from 230 to 370 K. Since the preexponential factor σ_0 for the conductivity lies within $1-100 \Omega^{-1} \text{ cm}$ in many glasses,¹¹ the conductivity at T_m is expected to be $\sim 2 \times 10^{-15}$ to $2 \times 10^{-13} \Omega^{-1} \text{ cm}$, in fair agreement with the data shown in Fig. 8.

IV. SUMMARY

The data and speculations presented herein are in general agreement with the hypothesis that the dominant TSDC peak in sodium germanate glasses is due to polarization caused by the dc conduction of Na^+ ions rather than to orientational polarization of Na-NBO or Na-GeO_6 dipoles. Since nothing is known at present about the heterogeneous structure of these glasses, no reliable estimate of λ and n as a function of sodium content can be made.

ACKNOWLEDGMENTS

The authors express their appreciation to M. Tomozawa, Rensselaer Polytechnic Institute, and J. E. Shelby, Jr., Sandia Laboratories, for providing some of the glasses used in this study. This work was supported by the National Science Foundation, Grants NSF DMR 77-13002 and NSF DMR 79-18425.

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