Activation energy and conductivity relaxation of sodium tellurite glasses

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The electrical conductivity and conductivity relaxation of $xNa_2O-(100-x)TeO_2$ glasses have been investigated in the frequency range of 10 Hz–2 MHz and in the temperature range of 373–533 K and compared with the results of silicate and borate glasses. The Anderson-Stuart model was employed to explain the dc activation energy. The relaxation behavior of these glasses was analyzed in the light of the modulus formalism. The variation of the stretched exponential parameter with composition was explained in terms of cation-cation distance correlation. Furthermore, the structural model of tellurite glasses was employed to explain the composition dependence of the conductivity relaxation time.

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I. INTRODUCTION

TeO₂-based glasses possess many interesting physical properties such as low melting point, high dielectric constant, high refractive index, good IR transmittivity, and relatively high chemical durability which make them attractive not only from the fundamental point of view but also in terms of practical applications.¹⁻⁴ Under normal conditions, TeO₂ does not have the ability to go into the glassy state easily, yet in the presence of a modifier it does form glass easily.⁵ Neov *et al.*⁵ have shown that the role of the modifier is extremely important in the vitreous transition of tellurite melts. In this respect the tellurite glasses differ from the conventional glasses formed with glass formers such as SiO₂, GeO₂, B₂O₃, and P₂O₅. Recent studies of alkali tellurite glasses⁶ reveal the presence of different structural units for different alkali oxide contents. The glasses with low alkali content consist of a continuous random network constructed by sharing corners of TeO_4 trigonal bipyramids and TeO_{3+1} polyhedra having one nonbridging oxygen. It is worth mentioning that the notation TeO_{3+1} means that there are three short Te-O bonds and a comparatively longer Te-O bond in the TeO_{3+1} polyhedra. For the glasses with alkali content in the range 20-30 mol %, TeO₃ trigonal pyramids having nonbridging oxygen permeate the whole network. Further increase of alkali content results in isolated structural units such as $Te_2O_5^{2-}$ which coexists in the continuous network. Above 30 mol % of alkali oxide, the glass network consists of TeO₃₊₁ polyhedra and TeO₃ trigonal pyramids along with isolated structural units such as $Te_2O_5^{2-}$ and TeO_3^{2-} ions. The electrical properties of alkali tellurite glasses have been also studied.⁷⁻¹¹ These glasses have shown high ionic conductivity. It has been observed that the TeO2-based glasses containing transition metal ions have higher electronic conductivity than that of the glasses based on other conventional network formers such as P₂O₅, B₂O₃, etc.¹²⁻¹⁴ However, a few reports exist on electrical properties of the sodium tellurite glasses.¹¹ Although an interstitial mechanism for ion transport in these glasses has been proposed, there has been no attempt to our knowledge to investigate the relaxation mechanism in ionic tellurite glasses.

Our present study explores the conductivity and relaxation mechanism in sodium tellurite glasses. We have applied the Anderson-Stuart model¹⁵ to study the activation energy for different compositions and found that contribution of the strain energy to the activation energy is larger than that of the binding energy for this glass system.

II. EXPERIMENT

Glasses of compositions $xNa_2O-(100-x)TeO_2$, where x =10, 15, 20, 25, and 30 mol %, were prepared from Na₂CO₃ (Fluka, 99.5%) and TeO₂ (BDH, 98%). The mixtures of these chemicals in appropriate proportions were first heated at 450 °C for two hours for decarbonization and then melted at 750 °C for 15 min in a platinum crucible in an electric furnace. The melts were quenched by pouring them on a preheated aluminum mold. The quenched samples were immediately transferred to another furnace and were annealed for two hours at 150 °C to remove residual stresses. All the glasses were found to be yellowish in color and transparent. X-ray diffraction studies were carried out to verify the amorphous nature of the preheated samples. The differential thermal analysis was carried out to determine the glass transition temperature. The density at room temperature (298 K) was measured by Archimedes' principle using acetone as an immersion liquid. The average cation-cation distance λ_R was determined from the chemical composition and density.

For electrical measurements, gold electrodes were deposited on both the surfaces of the disc-shaped samples of diameter $\sim 1.0-1.5$ cm and thickness $\sim 0.08-0.1$ cm by vacuum evaporation. Electrical measurements were carried out in a precision RLC meter (model 7600 Quad Tech) in the temperature range 373–533 K and in the frequency range of 10 Hz–2 MHz.

III. RESULTS AND DISCUSSION

The x-ray diffraction patterns for all glass compositions listed in Table I showed no trace of crystallinity. The molar volume V_m calculated from the density and composition and the glass transition temperature T_g determined from the differential thermal analysis curves are given in Table I. It may be noticed that with increasing Na₂O content the molar volume increases while the glass transition temperature T_g de-

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TABLE I. Molar volume, glass transition temperature, dc conductivity at 200 °C, dc activation energy, conductivity relaxation time at 200 °C, relaxation activation energy, and high frequency dielectric constant (ϵ_{∞}) for Na₂O-TeO₂ glasses.

Composition (mol %) Na ₂ O	TeO ₂	V_m (cm ³ /mol)	<i>T_g</i> (°C) ±5	$\log_{10}\sigma_{200C} \ (\Omega^{-1}\mathrm{cm}^{-1}) \ \pm 0.01$	$\begin{array}{c} \Delta E_{\sigma} \\ (\text{eV}) \\ \pm 0.02 \end{array}$	$\log_{10} \tau_{m200C}$ (sec) ± 0.01	$\begin{array}{c} \Delta E_{\tau} \\ (\text{eV}) \\ \pm 0.02 \end{array}$	$\epsilon_{\infty} (\omega = 10^7 \text{sec}^{-1}$ and $T = 472 \text{ K})$
10	90	22.3	280	-8.74	1.06	-2.76	1.06	68.6
15	85	23.0	260	-8.55	1.00	-3.26	1.02	32.7
20	80	27.4	250	-8.38	0.96	-3.20	0.94	28.3
25	75	29.2	220	-7.52	0.89	-4.10	0.87	26.4
30	70	29.0	210	-6.80	0.93	-5.04	0.96	19.2

creases highlighting the fact that more and more nonbridging oxygens are formed in the network as the concentration of alkali oxide is increased. These results are consistent with the structural studies reported earlier.⁶

The dc electrical conductivity (σ_{dc}) was computed both from the ac impedance plots as well as from the low frequency part of the conductivity isotherms. The plots of $\log_{10}\sigma_{dc}$ versus 1000 T for some compositions of sodium tellurite glasses are shown in Fig. 1. The straight lines through the data indicate the thermally activated conduction mechanism or so-called Arrhenius behavior. The corresponding activation energy ΔE_{σ} calculated from the slopes of the Arrhenius plots are given in Table I.

We have compared in Figs. 2(a) and 2(b), the dc conductivity at 200 °C and ΔE_{σ} , respectively, of sodium tellurite glasses with those of sodium ion containing glasses formed with other network formers such as SiO₂, ^{16,17} P₂O₅, ¹⁸ and B₂O₃ (Refs. 19 and 20) in a wide composition range. It can be seen from Fig. 2(a) that tellurite glasses exhibit intermediate conductivity nearly equal to that of borate glasses but less than the silicate and phosphate glasses at a particular temperature. The activation energy ΔE_{σ} for conduction also



FIG. 1. Temperature dependence of the dc conductivity of the different compositions of Na_2O -TeO₂ glasses shown.



FIG. 2. (a) Composition dependence of the dc conductivity at 200 °C for the tellurite, silicate, phosphate, and borate glasses. (b) Composition dependence of the dc activation energy for the tellurite, silicate, phosphate, and borate glasses.

TABLE II. Average cation-cation distance, relaxation parameter β , strain energy, binding energy, calculated dc activation energy, and experimental dc activation energy for Na₂O-TeO₂ glasses.

Composition (mol %)		λ_R (Å)	β	ΔE_S (eV)	ΔE_B (eV)	ΔE_{σ} (eV)	ΔE_{σ} (eV)±0.02
Na ₂ O	TeO ₂	±0.03	± 0.01			calculated	experimental
10	90	5.70	0.77	1.00	0.06	1.06	1.06
15	85	5.02	0.75	0.88	0.12	1.00	1.00
20	80	4.84	0.72	0.85	0.14	0.99	0.96
25	75	4.60	0.63	0.81	0.15	0.96	0.89
30	70	4.31	0.63	0.76	0.21	0.97	0.93

obeys similar trends i.e., the tellurite glasses possess intermediate activation energy ΔE_{σ} nearly equal to that of borate glasses but greater than that of silicate glasses. For example, for glasses with 25 mol % Na₂O the conductivities at 200 °C for silicate, ^{16,17} phosphate, ¹⁸ borate, ¹⁹ and tellurite glasses, respectively, are $3.8 \times 10^{-6} \ \Omega^{-1} \ cm^{-1}$, $2.3 \times 10^{-6} \ \Omega^{-1} \ cm^{-1}$, $6.02 \times 10^{-8} \ \Omega^{-1} \ cm^{-1}$, and $3.03 \times 10^{-8} \ \Omega^{-1} \ cm^{-1}$. The activation energies for conduction for the corresponding systems are 0.68, 1.16, 0.85, and 0.90 eV, respectively.

The activation energy for different compositions of the present tellurite glasses was calculated in the framework of the Anderson-Stuart model¹⁵ and compared with the experimentally observed values. According to the Anderson-Stuart model and the total activation energy, ΔE_{σ} is the sum of two parts:

$$\Delta E_{\sigma} = \Delta E_B + \Delta E_S, \qquad (1)$$

where ΔE_B is the electrostatic binding energy and ΔE_S the strain energy which are given by

$$\Delta E_B = \beta' Z Z_0 e^2 / \gamma(r+r_0), \quad \beta' = (2.1-r)/3.5, \quad (2a)$$

$$\Delta E_S = 4 \pi G_D (r - r_D)^2 \lambda, \qquad (2b)$$

where β' and γ are parameters, with the latter being set equal to the relative dielectric constant ϵ_{∞} ; Z,r and Z₀,r₀ are the charges and radii, respectively, of the cation and oxygen anion, r_D is the "doorway" radius, G_D the shear modulus of the glass, and λ represents the average jump distance between the cation sites. The shear modulus for tellurite glasses were calculated form the Young's modulus and Poisson's ratio reported by Lambson et al.²¹ and was approximately equal to 2.06×10^{11} dyn/cm² and the corresponding doorway radius was assumed to be more or less equal to that of silicate glasses that is $r_D = 0.62$ Å. λ was assumed to be given by the average cation-cation distance λ_R (Table II) calculated from the composition and density. The assumption is justified because in the Anderson-Stuart model an ion would be recaptured in an interstice adjacent to one in which it has been freed. The calculated values of ΔE_B , ΔE_S , and ΔE_{σ} are given in Table II. The results in Table II show that ΔE_S is higher than ΔE_B for all compositions of the present sodium tellurite glasses indicating that these glasses behave as strong electrolytes.²² These results were found to be strikingly different when compared with ΔE_B and ΔE_S of sodium silicate¹⁵ and sodium borate²³ glasses where ΔE_B was found to be higher than the ΔE_s contribution.

It is interesting to note that ΔE_B for tellurite glasses increases with the increase of the Na₂O content in the compositions in sharp contrast to silicate¹⁵ and borate²³ glasses, while ΔE_s decreases with the increase of the Na₂O content similar to silicate glasses¹⁵ but opposite to borate glasses.²³ The reason for such behavior is that the dielectric constant for tellurite glasses (Table II) is much higher than that of silicate¹⁵ and borate²³ glasses and decreases with the increase of the Na₂O content and thus the contribution of ΔE_B [Eq. (2a)] to the total activation energy for tellurite glasses is smaller and increases slightly with the increase of the Na₂O content and most of the contribution to the total activation energy comes from ΔE_s in contrast to silicate and borate glasses. The striking difference between the variation of ΔE_B with composition for tellurite glasses and that of the borate and silicate glasses rises principally from the variation of the dielectric constant with composition. In tellurite glasses the high dielectric constant arises from the highly polarizable Te⁴⁺ ions and hence decreases with the increase of the Na₂O content in the network, while in silicate and borate glasses the dielectric constant contains the contribution from the partially ionic and partially covalent nonbridging oxygen-sodium bonds and increases slowly with the increase of the Na₂O content in the compositions. As pointed out in Sec. I, the network structures for tellurite glasses loosen with the increase of the Na₂O content in the compositions and hence the energy required to dilate elastically the structure decreases with the increase of the Na₂O content, resulting in a decrease of ΔE_s with the increase of the Na₂O content in the compositions.

Typical conductivity isotherms of the $25Na_2O-75TeO_2$ glass composition are shown in Fig. 3, which exhibits a frequency-independent conductivity (i.e., dc conductivity) at lower frequencies and a dispersive conductivity at higher frequencies. Other glass compositions also showed a similar behavior. The transition from the frequency-independent to frequency-dependent conductivity indicates the onset of a relaxation phenomenon which is here analyzed in the framework of the modulus formalism.²⁴

According to Macedo *et al.*²⁴ the electric modulus was defined as the electric analog of the dynamical mechanical modulus and was related to the complex permittivity $\epsilon^*(\omega)$ by

$$M^{*}(\omega) = 1/\epsilon^{*}(\omega) = \{\epsilon'(\omega) - i\epsilon''(\omega)\} |\epsilon^{*}(\omega)|^{2}$$
$$= M'(\omega) + iM''(\omega)$$
$$= M_{\infty} \left[1 - \int_{0}^{\infty} e^{-i\omega t} \{d\phi(t)/dt\} dt \right], \qquad (3)$$

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FIG. 3. Isothermal frequency spectra of the conductivity for 25Na₂O-75TeO₂ glass at several temperatures.

where $M'(\omega)$ and $M''(\omega)$ are the real and imaginary parts of the electric modulus, $M_{\infty} = 1/\epsilon_{\infty}$ is the inverse of the highfrequency dielectric permittivity and the function $\phi(t)$ gives the time evolution of the electric field within the dielectrics and was related to time by the decay function proposed by Kohlrausch, Williams, and Watts²⁵ and is given by

$$\phi(t) = \exp[-(t/\tau_m)^\beta], \quad 0 < \beta < 1 \tag{4}$$

where τ_m was defined as the most probable relaxation time and β is the stretched exponential parameter.

Isothermal frequency spectra of the modulus for the 25Na₂O-75TeO₂ glass are displayed in Fig. 4. Other glass compositions also showed a similar behavior. It is noticed that at high frequencies the real modulus M' tends to a frequency-independent constant value M_{∞} which decreases



FIG. 4. Isothermal frequency spectra of the modulus for $25Na_2O$ -75TeO₂ glass at several temperatures. The solid curves are best fits to Eq. (3).



FIG. 5. Temperature dependence of the conductivity relaxation time of all compositions of Na₂O-TeO₂ glasses shown.

slightly with the increase of temperature. The value of ϵ_{∞} $= 1/M_{\infty}$ estimated at a frequency of 10⁷ sec⁻¹ and at a temperature of 472 K is shown in Table I. The transition from long-range to short-range mobility of ions is manifested by a peak in $M''(\omega)$ spectra²⁶ and the peak frequency ω_m is given by $\omega_m \tau_m \approx 1$, where τ_m is the most probable conductivity relaxation time. The values of τ_m were obtained from the peak of $M''(\omega)$ spectra. It can be seen in Table I that the values of τ_m at 200 °C show a decreasing trend with the increasing alkali content which can be explained on the basis of the structural model⁶ mentioned in Sec. I according to which at lower compositions a continuous network of TeO_4 trigonal bipyramids with a very few TeO_{3+1} polyhedra are present. Consequently, the Te-O⁻ sites (which are the preferential sties for conducting sodium ion) associated with TeO₃₊₁ polyhedra are also less in number. This makes the



FIG. 6. Plots of M'/M_{∞} and M''/M''_{max} for 25Na₂O-75TeO₂ glass for the same temperatures as shown in Fig. 5.



FIG. 7. Composition dependence of the cation-cation distance for borate, silicate, and tellurite glasses.

ions mobile over long distances at lower frequencies only. A further increase in frequency results in a spatial confinement of the ions in their potential wells. So the frequency of the transition being lower increases the relaxation time by the relation $\omega_m \tau_m \approx 1$. As the alkali content increases more and more TeO₃ trigonal pyramids with nonbridging oxygen are formed in the network which obviously increases the number of sites for the mobile ion. Thus the ions remain mobile over long distances even at higher frequencies, thereby resulting in a decrease in the relaxation time. Figure 5 shows that the conductivity relaxation time also obeys the Arrhenius behavior and the corresponding activation energy ΔE_{τ} is shown in Table I. It can be noticed that the activation energy for conduction is more or less equal to the activation energy for the relaxation time which may be due to the fact that an ion has to overcome the same barrier while conducting as well as while relaxing consistent with the fluctuation-dissipation theory. A master plot for the 25Na₂O-75TeO₂ glass is shown in Fig. 6 by scaling each frequency by ω_m and the corresponding $M'(\omega)[M''(\omega)]$ by $M_{\infty}[M''max]$. The near perfect overlap of the data at different temperatures on a single master curve indicates that all the dynamic processes occurring at different frequencies exhibit the same thermal activation energy or in the other way the relaxation mechanism involved is temperature independent. Other glass compositions also showed a similar behavior.

The stretched exponential parameter β of the relaxation function shown in Table II was determined by fitting Eq. (3) to the modulus data following Moynihan *et al.*²⁷ The solid curves in Fig. 4 are the best fits to the modulus spectra. The variation of β from 0.75 for x = 10 mol % to 0.63 for x= 30 mol % is in conformity with Martin's results²⁶ according to which as the cation-cation distance decreases with increasing sodium oxide content (Fig. 7), the cation-cation interaction increases, resulting in the lowering of β with in-



FIG. 8. Composition dependence of the stretched exponential parameter β for borate, silicate, and tellurite glasses.

creasing content of Na₂O in these compositions. The values of β for tellurite glasses were compared in Fig. 8 with those for the sodium borate and sodium silicate glasses. The values of β for 25 mol % of Na₂O for silicate,²⁸ borate,²⁹ and tellurite glasses are 0.50, 0.53, and 0.63, respectively. This can be explained with reference to Fig. 7, which shows that cationcation distance is larger for sodium tellurite glasses than that for silicate and borate glasses. Thus the interaction between cations for tellurite glasses is lower than that for borate or silicate glasses and hence a higher value of β for tellurite glasses is observed compared to its value for borate or silicate glasses.

IV. CONCLUSIONS

We reported a thorough study of the electrical conductivity and the conductivity relaxation of sodium tellurite glasses along with a comparison with those of other glasses having the same modifier Na₂O. The Anderson-Stuart model was employed for the calculation of the activation energy. We observed that the strain energy contribution to the activation energy for tellurite glasses is much higher than the binding energy part unlike silicate or borate glasses. The decrease of the conductivity relaxation time with increasing content of Na₂O was explained in the framework of the structural model⁶ of tellurite glasses. The variation of the relaxation parameter β with composition was compared with those of borate and silicate glasses and was explained in terms of correlation between cation-cation distance.

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