

Scaling of the Conductivity Spectra in Ionic Glasses: Dependence on the Structure

A. Ghosh* and A. Pan

Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700032 India
(Received 4 August 1999)

A scaling approach in the conductivity formalism is applied to lithium tellurite glasses of different compositions. We observe that the hopping frequency can be used as the scaling frequency in the absence of well-defined dielectric loss peaks, and a universality of the scaling of the conductivity can be obtained for compositions with a similar structure. Further, the reasons behind the inapplicability of the scaling approach reported recently are elucidated in terms of structure of the glasses.

PACS numbers: 66.30.Hs

Understanding of the ionic conduction and relaxation mechanisms in ionically conducting glasses is a challenging problem [1–4]. Some authors [5] prefer to explore the relaxation dynamics in terms of conductivity spectra at different temperatures, while others contend that the modulus formalism is the best option [6]. The study of the conductivity spectra of several glasses at different temperatures leads to a scaling law which results in a time-temperature superposition [1,2]. In this regard the following expression has been used to describe the real part of the ac conductivity in glasses [7]:

$$\sigma'(\omega) = \sigma_{dc}[1 + (\omega/\omega_H)^n], \quad 0 < n \leq 1, \quad (1)$$

where σ_{dc} is the dc conductivity, ω_H is the hopping frequency of the charge carriers, and n is the dimensionless frequency exponent. Equation (1) can be obtained from the imaginary part of the complex dielectric susceptibility [8]. Recently, there have been several attempts to scale the conductivity spectra not only in terms of temperature but also in terms of composition for several glasses such as $(\text{Na}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ [1], $(\text{Na}_2\text{O})_x(\text{GeO}_2)_{1-x}$ [2], and $(\text{K}_2\text{S})_x(\text{B}_2\text{S}_3)_{1-x}$ [2].

Different workers [1,2] have considered the scaling frequency in different forms. Roling *et al.* [1] have taken $\sigma_{dc}T$ as the scaling frequency for different temperatures and $\sigma_{dc}T/x$ for different compositions, where x is the mole fraction of alkali ions for $(\text{Na}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ glasses in the composition range $0.1 \leq x \leq 0.3$ and T is the absolute temperature. They have also made use of the Barton-Nakajima-Namikawa (BNN) relation [9] while defining the crossover frequency from dc behavior to the dispersive conductivity. Sidebottom [2] has extended the above scaling approach to the case where the alkali content is very low by making use of the fact that the ion hopping length changes with the alkali content. This author has used $(\sigma_{dc}/\epsilon_0\Delta\epsilon)$ as the scaling frequency, where ϵ_0 is the free space permittivity and $\Delta\epsilon [= \epsilon(0) - \epsilon(\infty)]$ is the permittivity change from the unrelaxed baseline $[\epsilon(\infty)]$ to the fully relaxed level $[\epsilon(0)]$. This scaling frequency is again equivalent to some numerical factor times the crossover or hopping frequency according to the BNN relation [9] [see Eq. (4) below].

In this paper, we have applied a scaling approach for ionic lithium tellurite glasses using the hopping frequency as a scaling frequency. The reason behind this is twofold. First, the permittivity change under suitable approximation is given by [8]

$$\Delta\epsilon = \gamma N(qd)^2/3\epsilon_0kT, \quad (2)$$

where N is the cation density, γ is the fraction of the mobile cations, and d is the distance traversed in a single hop. Again the modified form [6] of the Nernst-Einstein equation gives the dc conductivity as

$$\sigma_{dc} = [\gamma N(qd)^2\omega_H/12\pi kTH_R], \quad (3)$$

where H_R is the Haven ratio which indicates the degree of correlation between the successive hops. Thus Eq. (2), along with Eq. (3), gives the BNN relation [9] as

$$\sigma_{dc} = (1/4\pi H_R)\epsilon_0\Delta\epsilon\omega_H. \quad (4)$$

Equation (4) can help to understand all of the changes of the conductivity spectra so far proposed [1,2], and we think for a general scaling that changes in the Haven ratio must also be taken into account. In the case of $(\text{Na}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ glasses [1] in the composition range $0.10 \leq x \leq 0.30$, the Haven ratio was more or less constant (~ 0.4 to 0.5) (Ref. [10]), whereas for $(\text{Na}_2\text{O})_x(\text{GeO}_2)_{1-x}$ glasses [2] the Haven ratio was unity as the alkali content was low enough. So in both the cases mentioned above, the Haven ratio has no role to play in the scaling of the conductivity spectra for different compositions.

In the case of $(\text{Li}_2\text{O})_x(\text{TeO}_2)_{1-x}$ glasses we cannot neglect the change in the Haven ratio even in the composition range $0.10 \leq x \leq 0.30$ from the structural point of view. The coordination of boron in borate glasses changes from 3 to 4, increasing the network linkages with increasing alkali content [11], whereas in the case of the tellurite glasses the Te coordination changes from 4 to 3 by the cleavage of network [12]. As a consequence of increasing network linkages an interstitialcy mechanism will be expected for hopping of alkali ions for borate glasses, making the Haven ratio almost constant in the composition region mentioned

above. However, for tellurite glasses, the cleavage of the network linkage will result in the presence of vacant sites and this vacancy mechanism will introduce the change in the Haven ratio. This is why the scaling formalism of Roling *et al.* [1] was unable to merge all of the conductivity isotherms into a single master curve for lithium tellurite glasses even in the higher composition range.

Second, it is not possible to correlate the scaling frequency with the permittivity change for heavy metal oxide glasses as they do not possess well-defined dielectric loss peaks, and as a consequence the values of the static dielectric constant could not be obtained from the frequency dependence of dielectric data. Thus we propose to scale the frequency axis with respect to the hopping frequency (ω_H) which, through the usage of Eq. [4], automatically takes into account the Haven ratio change and the permittivity change implicitly. The advantage of using hopping frequency as the scaling frequency is that it is not specifically delimited by the composition range or the type of glass.

Lithium tellurite glasses of compositions $(\text{Li}_2\text{O})_x(\text{TeO}_2)_{1-x}$, where $x = 0.10, 0.15, 0.20, 0.25,$ and 0.30 , were prepared from Li_2CO_3 and TeO_2 . The appropriate mixtures of these chemicals were taken in a platinum crucible, heated at 450°C for 2 h for decarbonization and then melted at a temperature in the range of $680\text{--}760^\circ\text{C}$, depending on the composition in air, for about 15 min (chosen for minimum evaporation loss). Determination of the final composition by the atomic absorption showed that the changes in the TeO_2 content due to evaporation loss were within 1–3%. The amorphous nature of the samples were confirmed from x -ray diffraction. Conductivity measurements were carried out on the gold-coated samples of thickness $\sim 0.3\text{--}1.0$ mm and diameter $\sim 10\text{--}15$ mm using a precision RLC meter (model 7600, QuadTech) in a wide frequency range of 10 Hz–2 MHz and in the temperature range of 373 K to just below glass transition temperature.

The first point of interest is to note whether the conductivity spectra merge into a single master curve when the conductivity axis is scaled with respect to σ_{dc} and the frequency axis with respect to ω_H . To verify this, the hopping frequency was computed by fitting Eq. (1) to the experimental data, and then each conductivity isotherm for the glass series $(\text{Li}_2\text{O})_x(\text{TeO}_2)_{1-x}$ with $0.10 \leq x \leq 0.30$ is scaled. In the fitting procedure σ_{dc} , ω_H , and n were varied simultaneously to get the best fits. The values of n obtained from the best fits are in the range 0.60–0.65, increasing with an increase in Li_2O content. The values of σ_{dc} agreed well with those determined from the complex impedance plots [13]. A perfectly superposed master curve for the conductivity spectra is obtained for each composition and a plot is shown in Fig. 1 for $x = 0.30$. Thus the relaxation mechanism is found to be temperature independent under conductivity formalism.

The second point of interest is whether the BNN relation given by Eq. (4) is obeyed in the case of $(\text{Li}_2\text{O})_x(\text{TeO}_2)_{1-x}$ glasses. To this end we have plotted $\log_{10}\sigma_{\text{dc}}$ versus

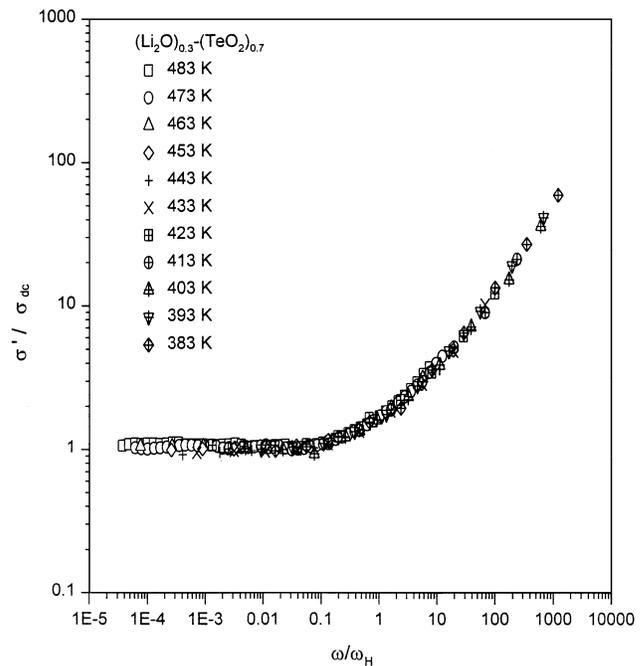


FIG. 1. The frequency spectra of the real part of conductivity $\sigma'(\omega)$ for different temperatures (shown) for a typical $(\text{Li}_2\text{O})_{0.30}(\text{TeO}_2)_{0.70}$ glass composition. The conductivity and frequency axes are scaled by dc conductivity and hopping frequency, respectively, obtained from the best fits of Eq. (1) to the conductivity spectra.

$\log_{10}\omega_H$ (where the values of σ_{dc} and ω_H were obtained from the best fits as mentioned above) in Fig. 2 for different glass compositions. The solid lines are the least squares straight line fits, all of which give a slope equal to unity, implying that the dc and ac conductions are correlated for lithium tellurite glasses. An irregular variation of the data points for $x = 0.15$ and a different value of the constant in Eq. (4) for $x = 0.10$ arise from their different structural behaviors which will be pointed out later.

Finally, the conductivity spectra are selected for each of the compositions at an arbitrary temperature and are exhibited in Fig. 3. It can be observed that, except for $x = 0.10$ and 0.15 , the spectra for all other compositions superpose on a single master curve. This result is quite surprising with regard to the universality of the scaling of the conductivity spectra [1,2]. The superposition of all of the conductivity spectra for different compositions on a single master curve reported by Roling *et al.* [1] and Sidebottom [2] simply means the compositional independence of the electrical relaxation mechanism, which is in sharp contrast with the correlation of the stretched exponential parameter β (which measures the deviation of relaxation from the ideal Debye type) with composition [14]. The values of β reported for the lithium tellurite glass [13] are found to vary sharply for $x = 0.10$ and 0.15 and level off to a constant value for $x \geq 0.20$. Thus the superposition of the conductivity spectra for different compositions

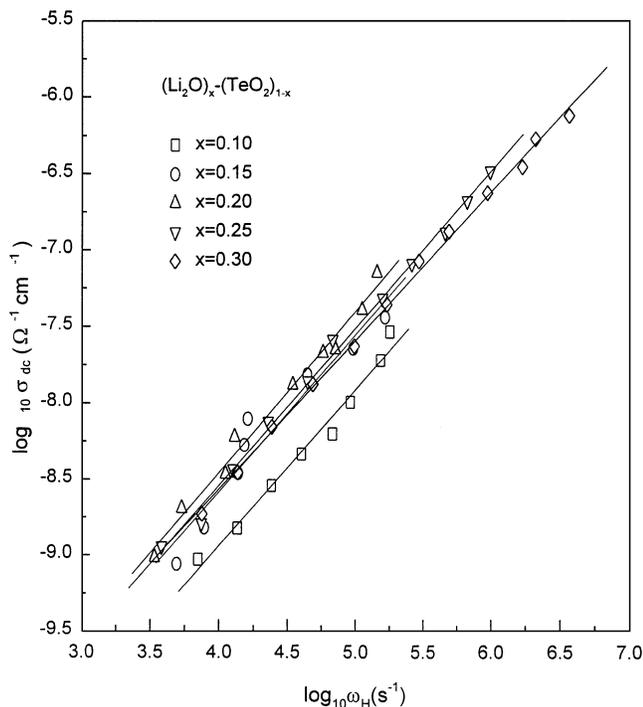


FIG. 2. The dc conductivity (σ_{dc}) versus hopping frequency ω_H for different $(\text{Li}_2\text{O})_x(\text{TeO}_2)_{1-x}$ glass compositions. The values of σ_{dc} and ω_H were obtained from the best fits of Eq. (1) to the conductivity spectra. The solid lines are the least squares straight line fits.

depends on the composition range or, strictly speaking, on the structure of the glasses.

The above results are supported by measurements [15] of the ^{125}Te Lamb-Mössbauer factor for tellurite glasses. According to these measurements the stiffness threshold

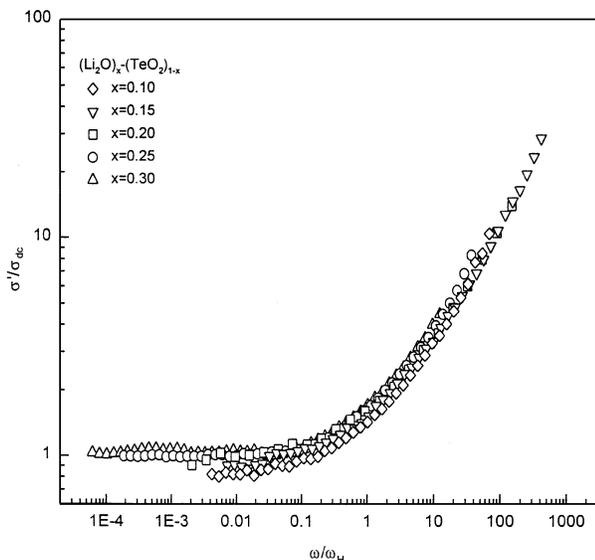


FIG. 3. The plot of $\log_{10}(\sigma'/\sigma_{dc})$ versus $\log_{10}(\omega/\omega_H)$ at a fixed temperature of 433 K for all of the glass compositions shown in the inset.

for alkali tellurite glasses occurs at a critical composition $x_c = 0.18$, above which the glass softens because the number of mechanical constraints/atoms becomes less than three, the available degrees of freedom/atoms [16]. In counting constraints [15], the alkali is taken to be onefold coordinated and the bond bending constraints of nonbridging oxygen is omitted since it is intrinsically broken. This results in the displacement of atoms from their equilibrium position without much cost in energy. This displacement is composition independent [15], making the relaxation mechanism composition independent. Below the critical composition, a composition dependent rigid network prevails and the displacement of the atoms from their equilibrium position cost strain energy, making the relaxation mechanism composition dependent.

In summary, the hopping frequency is considered as a more appropriate parameter for the scaling of the conductivity spectra for the glasses, where no dielectric loss peaks or static dielectric constant value can be obtained. This appears quite justified as the change in hopping length with composition is manifested in the change in the hopping frequency which takes into account the correlation effects between successive hops through the Haven ratio [17]. A universal scaling of the conductivity with respect to composition can be achieved only for a limited composition range, where the structure does not change drastically.

One of the authors (A. P.) acknowledges partial financial support from CSIR (India).

*Author to whom correspondence should be sent.

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