Intermediate Range Structure in Ion-Conducting Tellurite Glasses

M. A. Frechero

Sección Fisicoquímica, INQUISUR-UNS-CONICET and Departamento de Química, Universidad Nacional del Sur, Avenida Alem 1253, 8000 Bahía Blanca, Argentina

L. Padilla, H. O. Mártin, and J. L. Iguain*

Instituto de Investigaciones Físicas de Mar del Plata (IFIMAR) and Departamento de Física FCEyN,

Universidad Nacional de Mar del Plata, Deán Funes 3350, 7600 Mar del Plata, Argentina

We present ac conductivity spectra of tellurite glasses at several temperatures. For the first time, we report oscillatory modulations at frequencies around MHz. This effect is more pronounced the lower the temperature, and washes out when approaching the glass transition temperature T_g . We show, by using a minimal model, how this modulation may be attributed to the fractal structure of the glass at intermediate mesoscopic length scales.

PACS numbers: 66.30.H-, 61.43.Hv

Over the last 30 years, the study of the atomic structure of inorganic glasses has revealed a very rich order both from a local point of view (individual polyhedron coordination), as at intermediate range (the way polyhedra are connected among them). Of course, it keeps long range disorder, as all of us interpret glassy materials. Many experiments have exposed a quasi-periodicity in the network, including a kind of channels of network modifiers, in a direct relationship with ionic transport mechanisms. However, the comprehension of the relaxation laws in these materials is still incomplete, and many questions remain unanswered [1].

Conductivity spectroscopy is a widely employed technique to investigate ion dynamics at different time and length scales [2], and considerable effort has been dedicated to obtain an universal behavior bringing the spectra to collapse on a single curve. A scaling law without arbitrary parameters was first proposed in Ref. [3] for single ion conducting glasses, and then slightly modified to account for glasses with a wide variation of alkali content [4]. However, that the shape of the spectra is not universal but depends on glass composition was later shown in Ref. [5].

For one given compound, a simple scaling law can be obtained on the basis of the time-temperature superposition principle (TTSP), stating that, at a temperature T, only one characteristic time scale exists: the crossover time between sub-diffusive and normal diffusive ion behavior. The form

$$\sigma(\nu)/\sigma_{dc} = F\left(\nu/\nu_0\right),\tag{1}$$

for the conductivity spectra $\sigma(\nu)$, expresses the TTSP in frequency space, with σ_{dc} the dc conductivity, ν_0 the crossover frequency (both temperature dependent), and F the scaling function (which depends on the compound).

In 1985, Summerfield proposed that $\nu_0 = \sigma_{dc}T$ for amorphous semiconductors [6]. This assumption has also been shown to be valid on some single ion conducting glasses [3–5, 7], but cannot be applied generally. The conductivity spectra fail to collapse as suggested by Summerfield not only for various mixed alkali glasses [8] but also for single ion tellurite glasses [9]. In the latter case the universal form of the spectra is obtained by adopting $\nu_0 = \sigma_{dc} T/T^{\alpha}$, at the cost of introducing a new parameter α . More recently, this kind of universality has been demonstrated for the conductivity spectra of polyelectrolyte complexes [10].

In this Letter, we report an oscillatory behavior observed in electrical conductivity measurements on tellurite glasses at frequencies around 1 MHz. These glasses have a mainly ionic conductivity behavior, with the alkaline cations as charge carriers. Generally, at frequencies above 100 Hz and temperatures below the glass transition temperature T_g , there is little dispersion in the electrical conductivity and the response of the system is related to the immediate vicinity of the alkali cation. The presence of an oscillating modulation is a clear indication of the existence of several relevant length scale in the ion diffusion problem, and that simple scaling forms as Eq. (1) cannot be applied. We propose an interpretation of this phenomenon based on the structure of the glass at intermediate mesoscopic length scales.

Experimental- The samples were prepared by a standard melt quenching technique from initial mixtures of proper quantities of components (99.99%) pure): TeO_2 , V_2O_5 , MoO_3 , and Na_2CO_3 or The amorphous character of each result- Li_2CO_3 . ing solid, $0.6Na_2O-0.4[0.5V_2O_50.5MoO_3]-2TeO_2$, with $T_g = 535.7K$, and $0.6Li_2O-0.4[0.5V_2O_50.5MoO_3]-2TeO_2$ with $T_a = 539.5K$, was tested by X-ray diffraction analysis and confirmed by the Differential Scanning Calorimetry (DSC). Glass disks of thickness ranging between 0.5 - 1.0 mm, were cut from the obtained cylinder and polished with very fine quality lapping papers. The electrodes for electrical measurements were made using silver conducting paint to which metallic leads were attached. The conductivity of each sample σ was determined, as a function of the frequency ν , by standard a. c. impedance

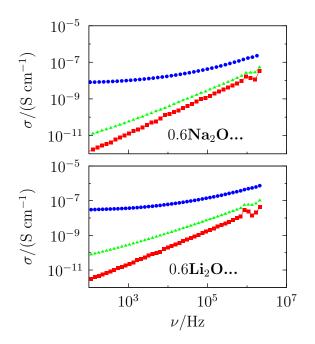


FIG. 1. (Color online) Experimental a. c. electrical conductivities as a function of the frequency at three different temperatures: 223K (red squares), 353K (green triangles), 473K (blue circles). Top panel: $0.6Na_2O-0.4[0.5V_2O_50.5MoO_3]-2TeO_2$ compound. Lower panel: $0.6Li_2O-0.4[0.5V_2O_50.5MoO_3]-2TeO_2$ compound. Errors are smaller than symbol sizes

methods using a Novocontrol BDS-80 system. We have explored the electrical response at three distinct values of the temperature T: 223K, 353K and 473K. The applied voltages $V(t) = V_a \cos(2\pi\nu t)$ with a small amplitude $V_a = 100$ mV ensured a linear response throughout the frequency range.

The experimental conductivity spectra of the obtained compounds are plotted in Fig. 1. A simple inspection of this figure reveals that, as the frequency increases, $\sigma(\nu)$ shows not only the usually expected crossover from a nearly constant conductivity (out of the plot scale for the lower temperatures), to a power-law behavior, but also that an oscillatory modulation appears at larger frequencies ($\nu \sim 1$ MHz). Note also that the amplitude of the oscillations decreases with the increasing of temperature, and becomes negligible for high enough T.

Interpretation- Ion conducting glasses can be considered as weak electrolytes where a density ρ of ions, which depends on temperature, becomes mobile and explore the sample in a random walk (RW) [11]. Two basic hopping mechanisms have been proposed [12]. In the first, the so called *network hopping*, the diffusing ion moves by jumps in a random network consisting only on bridging oxygens (BO). These hoppings involve little conformational change in the network, and have a relatively small activation energy $\Delta E_{net} (\approx 0)$. In the second mechanism, referred to as *intrachannel hopping*, the al-

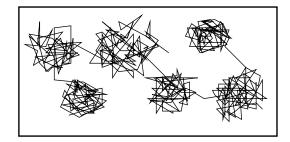


FIG. 2. Sketch of single ion diffusion in an oxide glass. At short distances, the behavior is dominated by hoppings in a network of BO's only; with a very small activation energy ΔE_{net} . When this network does not percolate the sample, jumps among NBO's, with a high activation energy $\Delta E_{\text{ic}} (\gg \Delta E_{\text{net}})$, play a role.

kalies are mainly coordinated to non-bridging oxygens (NBO), and mobile ions diffuse in a network of conducting channels, which results of connecting NBO's together. These jumps do entail important modifications in the local NBO and BO configurations, and a comparatively high activation energy ΔE_{ic} ($\gg \Delta E_{net}$) results. Though there exist materials where the ionic transport can be represented with one of these two ideal networks (compensated aluminosilicates, the first; silicates, the second), in general, both mechanisms are present.

In the first stages of the diffusive motion, ion migration occurs mainly by network hopping due to energetic reasons. However, if the random network of BO's does not percolate the sample but consists on disconnected regions, after a typical time t_1 , the ion will reach the border of one of these regions, the diffusion will slow down, and the particle will behave as if trapped in a cage and with an escape time τ . In addition, if the typical linear size of a cage is not so large, $\tau \sim \exp(E_{ic}/k_BT)$ (k_B is the Boltzmann constant), and we expect the behavior of mobile ions sketched in Fig. 2. Thus, at intermediate times t ($t_1 < t < \tau$), the ion mean-square displacement behaves as $\Delta^2 r(t) \sim t^{\eta}$, with a very small RW exponent $(\eta \simeq 0)$, because of the effect of the cages. For times longer than τ , the ions become able to explore the whole sample, and normal diffusion results $(\eta \simeq 1)$ if large-scale homogeneity is assumed.

According to the linear response theory, the conductivity spectrum is related to the ion mean-square displacement by

$$\sigma(\nu) = -2\pi^2 \nu^2 \frac{\beta \rho e^2}{dH_R} \lim_{\epsilon \to 0^+} \int_0^\infty dt \, \Delta^2 r(t) \cos(2\pi\nu t) e^{-\epsilon t},\tag{2}$$

where $\beta = 1/k_BT$, *d* is the substrate dimension, *e* is the ion charge, and H_R is the Haven ratio, which expresses the multi-particle correlations [13]. A simple dimensional analysis of Eq. (2) leads to

$$\Delta^2 r(t) \sim t^\eta \Leftrightarrow \sigma(\nu) \sim \nu^{1-\eta}, \tag{3}$$

and then, the above mentioned change in the kinetics of diffusion is reflected in the behavior of the function $\sigma(\nu) \sim \nu^{\zeta}$, which, as the frequency increases, undergoes the crossover $\zeta \simeq 0 \longrightarrow \zeta \simeq 1$.

Long-time or short-frequency ion behavior can be captured by modeling the substrate as a set of cells of convenient size, separated by energetic barriers of height ΔE_{ic} . However, to understand the mechanisms responsible for the oscillations appearing at higher frequencies, we have to watch inside these cells, at distances larger than atomic radius but smaller than cell typical size. In what follows, we show that the experimental results in Fig. 1 can be qualitatively reproduced if we assume that the BO network has a fractal structure, similar to the well-known Vicsek model [14].

For a single particle diffusing on a self-similar substrate, a hierarchical set of length-dependent diffusion coefficients $\{D^{(n)}, n \in \mathbb{N}\}$ exists, with $\{D^{(n)}/D^{(n+1)} =$ $1 + \lambda, n \in \mathbb{N}\}$, and where $\lambda > 0$ is a constant; meaning that the RW mean-square displacement behaves as $\Delta^2 r(t) \sim D^{(n)}t$, for $\sqrt{\Delta^2 r}$ in the range (L^n, L^{n+1}) , where L is the basic length of the fractal. The decreasing of the diffusion coefficient with the increasing of the length scale produces an oscillating modulation in $\Delta^2 r(t)$ [15], and, according to Eq. (2), also in $\sigma(\nu)$. Note that oscillations in the mean-square displacement at short times imply oscillations in the conductivity at high frequencies.

The most relevant aspects of RW in a self-similar structure can be effectively captured by a one-dimensional model, in which L and λ are introduced as parameters [16]. Thus, to keep our approach simple we consider a particle moving on a periodic lattice in one dimension, with the unit cell as sketched in Fig. 3. At every time step the particle can hop to a nearest neighbor lattice site. The hopping rates depend on the initial and final sites only and are represented in the drawing by vertical segments or barriers. Two kinds of barriers exist. The topological barriers (dashed segments) correspond to the network hopping processes. Their rates, which do not depend on temperature and decrease with the length scale, were obtained from the minimal self-similar model in Ref. [16]. For concreteness, we have chosen L = 2and $1 + \lambda = 20$, leading to $k_1/k_0 = 2.56 \times 10^{-2}$ and $k_2/k_0 = 6.41 \times 10^{-4}$. The energetic barriers (full segments) correspond to the intrachannel hopping processes occurring at a rate $q = k_0 \exp(-E_{ic}/k_B T)$.

Let us assume that at a low enough temperature T_1 the structure where mobile ions diffuse can be modeled by a periodic array of the unit cells in Fig. 3. We fix T_1 by asking that the corresponding intrachannel transition rate is $q(T_1) = 10^{-12}k_0$. For this substrate, the RW mean-square displacement as a function of time, obtained by Monte Carlo simulations, is shown in Fig. 4-a

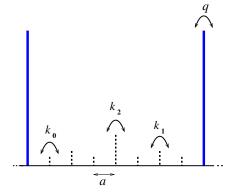


FIG. 3. A one-dimensional unit cell. The topological hopping rates k_i (i = 0, 1, 2) represent network hoppings. They are built in a self-similar manner and do not depend on temperature. The energetic hopping rate $q = k_0 \exp(-E_{ic}/k_BT)$ accounts for intrachannel jumps.

(lower data points). The results were averaged over 10^4 independent runs with random initial positions. Three different regimes can be clearly observed. At short times, $\Delta^2 r(t)$ exhibits a sub-diffusive power-law behavior modulated by log-periodic oscillations due to the self-similar structure of the unit cell. At intermediate times, it shows a plateau, caused by the constraint in diffusion imposed by the energetic barriers. Finally, at long enough times $(\gg 10^{12}/k_0), \Delta^2 r(t) \sim t$. As explained in Ref. [16], the crossovers among the length scales $\ell_n = a2^n$, for n = 0, 1, and 2, cause a sub-diffusive behavior modulated by oscillations. At distances larger than 8a, the substrate can be considered as periodic, and the diffusion becomes normal.

At a higher temperature, we consider the possibility of some level of randomness in the BO network, which we introduce in the model by shuffling the locations of the topological barriers. Although the so-obtained substrate will depend on the probability distribution function involved in the shuffle procedure, it has been shown that, in the limit of full randomization, the oscillating modulation is washed out but the RW exponent remains as in the self-similar substrate [17]. By using the MC protocol described above, we have studied the RW of a single particle at a temperature $T_2 = 2T_1$, giving an intranetwork hopping rate $(k_0 \text{ units}) q(T_2)/k_0 = (q(T_1)/k_0)^{1/2} = 10^{-6}$. We have used a substrate in which the topological barriers are randomized in the 30% of the cells (the other 70%remain ordered as in Fig. 3). These values are arbitrary but useful to appreciate the trend of the effects of randomness. The corresponding numerical RW mean-square displacement is plotted as a function of time in Fig. 4-a (upper data points). As compared with the behavior at T_1 , the amplitude of the oscillations decreases because of randomness, and the normal diffusion regime is reached at a shorter time due to the increasing of the rate q.

Using the data in Fig. 4-a, we have calculated the corresponding electrical conductivities, by numerical inte-

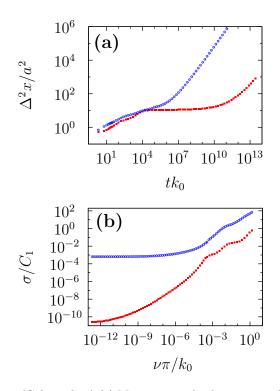


FIG. 4. (Color online) (a) Mean-square displacement as function of time for the one-dimensional minimal model at two temperatures T_1 (red-lower symbols) and $T_2 = 2T_1$ (blueupper symbols). (b) Conductivity spectra calculated with the data in (a).

gration of Eq. (2), which can be rewritten as

$$\sigma(\nu;\beta) = -C_1 \left(\beta \rho / \beta_1 \rho_1\right) I(\nu;\beta) . \tag{4}$$

Here ρ_1 is the carrier density at the inverse temperature $\beta_1 = 1/k_B T_1$, C_1 is a reference conductivity $C_1 = 2e^2k_0a^2\beta_1\rho_1/H_R$, and $I(\nu;\beta)$ is the non-dimensional function

$$I(\nu;\beta) = \lim_{\epsilon \to 0^+} \int_0^\infty dt \, k_0 \, \left(\frac{\nu\pi}{k_0}\right)^2 \frac{\Delta^2 r(t;\beta)}{a^2} \cos(2\pi\nu t) e^{-\epsilon t}.$$
(5)

The density of mobile ions depends strongly on temperature. It has been reported that ρ increases in a factor of around 10² when T is doubled from 200K to 400K [11]. As we want to relate T_1 with the lowest temperature of our measurements (see Fig. 1), we use a value of 50 as a good estimate of the factor in parentheses in Eq. (4), when $T_1 \simeq 200K$, and $\beta = \beta_2 = \beta_1/2$. We neglect the possible variation of H_R with the temperature. The numerical conductivity spectra are plotted in Fig. 4-b. Let us remark the good qualitative agreement between model and experiment.

In summary, we report for the first time the experimental ac conductivity spectra of tellurite glasses showing oscillatory modulations at frequencies around MHz, which reflect a non-trivial structure of the glass at mesoscopic distances. In order to account for these oscillations, we introduce a minimal model describing ion diffusion in a one-dimensional substrate with a short-length fractal structure; self-similar at low enough T, and fully disordered for $T \leq T_g$. We find a very good qualitative agreement between theoretical and experimental results, which supports our hypothesis that a fractal structure exists in oxide glasses at intermediate length scales.

Acknowledgments- We are grateful to the Grupo de Física de Materiales Complejos - UCM for kindly sharing their Novocontrol BDS-80 system. This work was supported by UNMdP and CONICET (PIPs 041 and 431).

* iguain@mdp.edu.ar

- P. S. Salmon, Nat. Mater. 1, 87 (2002). G. N. Greaves and S. Sen, Adv. Phys. 56, 1 (2007). F. Sanda and S. Mukamel, J. Chem. Phys. 127, 154107 (2007).
- [2] K. Funke and C. Cramer, Current Opinion in Solid State and Materials Science 2, 483 (1997).
- [3] B. Roling, A. Happe, K. Funke, and M. D. Ingram, Phys. Rev. Lett. 78, 2160 (1997).
- [4] D. L. Sidebottom, Phys. Rev. Lett. 82, 3653 (1999).
- [5] B. Roling, C. Martiny, Phys. Rev. Lett. 85, 1274 (2000).
- [6] S. Summerfield, Philos. Mag. B 52, 9 (1985). N. Balkan,
 P. N. Butcher, W. R. Hogg, A. R. Long, and S. Summerfield, *ibid.* 51, L7 (1985).
- [7] D. Zielniok, H. Eckert, and C. Cramer, Phys. Rev. Lett. 100, 035901 (2008).
- [8] C. Cramer, S. Brückner, Y. Gao, and K. Funke, Phys. Chem. Chem. Phys. 4, 3214 (2002). A. W. Imre, S. Voss, and H. Mehrer, *ibid.* 4, 3219 (2002).
- [9] S. Murugavel, B. Roling, Phys. Rev. Lett. 89, 195902 (2002).
- [10] A. W. Imre, M. Schönhoff, and C. Cramer, Phys. Rev. Lett. **102**, 255901 (2009).
- [11] J.-L. Souquet, M. L. F. Nascimento, and A. C. M. Rodrigues, J. Chem. Phys. **132**, 034704 (2010).
- [12] G. N. Greaves, K. L. Ngai, Phys. Rev. B 52, 6358 (1995).
- [13] S. Havlin and A. Bunde, in *Fractals and Disordered Systems* (Springer, 1996). A. Heuer, M. Kunow, M. Vogel, and R. D. Banhatti, Phys. Chem. Chem. Phys. 4, 3185 (2002).
- [14] T. Vicsek, Fractal Growth Phenomena (2nd Edition), World Scientific, Singapore (1992).
- [15] L. Padilla, H. O. Mártin, and J. L. Iguain, Phys. Rev. E 82, 011124 (2010).
- [16] L. Padilla, H. O. Mártin, and J. L. Iguain, EPL 85, 20008 (2009).
- [17] L. Padilla, H. O. Mártin, and J. L. Iguain, Phys. Rev. E 83, 020105(R) (2011).