Intermediate-range structure in ion-conducting tellurite glasses

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Abstract — 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.

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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 obtaining a 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
\[
\frac{\sigma(\nu)}{\sigma_{dc}} = F(\nu/\nu_0),
\]
for the conductivity spectra \( \sigma(\nu) \), expresses the TTSP in frequency space, with \( \sigma_{dc} \) the dc conductivity, \( \nu_0 \) 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 \( \alpha \). More recently, this kind of universality has been demonstrated for the conductivity spectra of poly-electrolyte 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 alkali 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 scales 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): \(\text{TeO}_2\), \(V_2\text{O}_5\), \(\text{MoO}_3\), and \(\text{Na}_2\text{CO}_3\) or \(\text{Li}_2\text{CO}_3\). The amorphous character of each resulting solid, \(0.8\text{Na}_2\text{O}-0.2[0.5\text{V}_2\text{O}_5\cdot0.5\text{MoO}_3]^{-2}\text{TeO}_2\), with \(T_g = 518\text{K}, \) and \(0.8\text{Li}_2\text{O}-0.2[0.5\text{V}_2\text{O}_5\cdot0.5\text{MoO}_3]^{-2}\text{TeO}_2\) with \(T_g = 525\text{K}, \) was tested by X-ray diffraction analysis and confirmed by the differential scanning calorimetry (DSC). Glass disks of thickness ranging between 0.5 and 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. For the systems under study these contacts give a blocking interface with respect to the ions species in the electrolyte, they cannot cross the interface or exchange charge with the electrode. There is accumulation or depletion of ions near the electrodes, leading to the formation of space-charge layers where the voltage drops [11]. The conductivity of each sample \(\sigma\) was determined, as a function of the frequency \(\nu\), by standard ac impedance methods using a Novocontrol BDS-80 system. We have explored the electrical response at five distinct values of the temperature \(T\): 313 K, 373 K, 413 K, 453 K, and 493 K. For every \(\nu\), we applied a voltage \(V(t) = V_0 \cos(2\pi \nu t)\) with an amplitude \(V_0 = 100\text{ mV}\), small enough to ensure that the results do not depend on this perturbation throughout the frequency range.

The experimental conductivity spectra of the obtained compounds are plotted in fig. 1. A simple inspection of this figure shows that, as the frequency increases, \(\sigma(\nu)\) undergoes the usually expected crossover from a nearly constant conductivity (out of the plot scale for the lower temperatures), to a power-law behavior. However, a closer look (insets) reveals that an oscillatory modulation appears at larger frequencies (\(\nu \sim 1\text{ MHz}\)). The amplitude of these oscillations decreases with the increase of temperature, and becomes negligible for high enough \(T\) (see footnote 1).

**Interpretation.** – Ion conducting glasses can be considered as weak electrolytes where a density \(\rho\) of ions, which depends on temperature, becomes mobile and explore the sample in a random walk (RW) [12]. Two basic hopping mechanisms have been proposed [13]. In the first, the so-called network hopping, the diffusing ion moves by jumps in a random network consisting only of bridging oxygens (BOs). These hoppings involve little conformational change in the network, and have a relatively small activation energy \(\Delta E_{\text{network}} \approx 0\). In the second mechanism, referred to as intrachannel hopping, the alkalis are mainly coordinated with non-bridging oxygens (NBOs), and mobile ions diffuse in a network of conducting channels, which results in connecting NBOs together. These jumps do entail important modifications in the local NBO and BO configurations, and a comparatively high activation energy \(\Delta E_{\text{ion}} \gg \Delta E_{\text{network}}\) 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 BOs does not percolate the sample but consists in 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 it were trapped in a cage and

\footnote{These modulations were also obtained for tellurite glasses with other ion carriers (Ag, Cu, Mg) at different concentrations, as well as, for silicates modified with Na or Li.}

Fig. 1: (Color online) Experimental ac electrical conductivities as a function of the frequency at five different temperatures: 493 K (red squares), 453 K (green up-triangles), 413 K (blue circles) 373 K (black stars), and 313 K (cyan down-triangles). The experimental conductivity spectra of the obtained compound. Lower panel: 0.8Li\(_2\)O...
with an escape time \( \tau \). In addition, if the typical linear size of a cage is not so large, \( \tau \sim \exp(E_{ic}/k_B T) \) \((k_B \text{ is the Boltzmann constant})\), 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 \( \tau \), 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

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

where \( \beta = 1/k_B T \), \( d \) is the substrate dimension, \( \epsilon \) is the ion charge, and \( H_R \) is the Haven ratio, which expresses the multi-particle correlations \([14]\). A simple dimensional analysis of eq. (2) leads to

\[
\Delta^2 r(t) \sim t^\eta \Leftrightarrow \sigma(\nu) \sim \nu^{1-\eta},
\]

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

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 \( \Delta E_{ic} \). 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 the cell typical size. In what follows, we will 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 \([15]\).

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 decrease of the diffusion coefficient with the increase of the length scale produces an oscillating modulation in \( \Delta^2 r(t) \) \([16]\), 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 \( \lambda \) are introduced as parameters \([17]\). 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. \([17]\). For concreteness, we have chosen \( L = 2 \) and \( 1 + \lambda = 20 \), 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) (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, 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 $T \lesssim T_g$. 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.

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 $T \lesssim T_g$. 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.

Note that the use of other estimates will modify only the separation between the sets of data points in the vertical direction.

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 $T_2 = 2T_1$ (blue upper symbols). A dash-dotted line with slope of 1 was drawn to guide the eye.

(b) Conductivity spectra calculated with the data in (a). A dash-dotted line with slope of 1 was drawn to guide the eye.
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