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Low temperature ac conductivity in the fast ionic conductor $Li_{0.18}La_{0.61}TiO_3$

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Abstract

We have performed ac conductivity measurements of the ionically conducting $Li_{0.18}La_{0.61}TiO_3$ in the frequency range 100 Hz–30 MHz and at temperatures ranging from 8 to 300 K. The power law frequency dependence, usually ascribed to ionic hopping, crosses over to a linear frequency dependence as temperature is decreased, due to a near constant loss contribution to the ac conductivity. This crossover is thermally activated, and the activation energy is related to the energy barrier that ions must overcome to jump outside their wells. This fact is discussed in terms of the vibrational mean-square displacement of ions inside their wells, at times shorter than the onset of the intersite hopping process. This points to the vibrational origin of the near constant loss term.

Keywords: Ionic conduction; Dielectric response

1. Introduction

Impedance spectroscopy is the most commonly used experimental technique to study ion dynamics in ionically conducting materials [1–8]. It supplies the complex permittivity $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, or the complex conductivity $\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega) = i\omega\epsilon^*(\omega)$, characterizing ionic motion. Ionic conductivity in the frequency domain can be usually well described by Jonscher's expression [9]:

$$\sigma^*(\omega) = \sigma_0[1 + (1\omega/\omega_p)^n] \tag{1}$$

with σ_0 the dc conductivity, ω_p a characteristic relaxation frequency, and n a fractional exponent, being σ_0 and ω_p thermally activated with nearly the same activation energy.

Much of the research activity in the field has focused on examining the long-range ion motion to find out the mechanism that limits the mobility of the ions [1–3,6]. But there is a ubiquitous contribution to that dispersive conductivity that has received little attention so far because it becomes dominant outside the commonly used experimental temperature and frequency window. This contribution consists of a nearly flat dielectric loss, $\epsilon'(\omega) \approx A$, independent of frequency in a wide frequency range, which produces an almost linear frequency dependent term of the form $\sigma'(\omega) = \omega\epsilon'(\omega) \approx A\omega$ in the complex conductivity representation. This constant loss, or nearly constant loss (NCL) term, dominates over the power law dependence of exponent n at enough low temperature or high frequencies, usually outside the commonly used experimental temperature and frequency windows.

Despite the existence of this near constant loss term was suggested more than 20 years ago [10,11], few workers have paid attention to it [12,13]. The properties investigated so far suggest that although mobile ions seem to be the ultimate cause of NCL, its origin could be different than merely ionic hopping [14]. It has been observed [14,15] that, at a fixed temperature, the change in A with ion concentration is much weaker than that of the dc conductivity. There is also a weak temperature dependence in A, almost linear, instead of the thermally activated behavior observed for the dc conductivity [14,16,17]. The effect of partially replacing one alkali ion by another alkali ion on the near constant loss is [3,14,18,19] a reduction in the value of A, but much smaller than the decrease observed in the dc conductivity due to the well-known mixed alkali effect [3]. Based on these various properties, it has been recently proposed [14] that local vibrational mean-square displacement of ions could be related to the origin of the constant loss in ionic conductors.

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Ionic transport in ionic conductors is governed by two different time scales. At the shortest times ions are vibrating in their potential wells of height E_m with a frequency ν_0 usually termed attempt frequency. The microscopic residence time is defined as $\tau_m = \nu_0^{-1} \exp(E_m/k_B T)$, such that, statistically, for times $t < \tau_m$ ions are vibrating within their sites, and for $t > \tau_m$ they leave the well. The activation energy E_m can be obtained from the low temperature side of the maximum in $1/T_1$ NMR measurements or from the temperature dependence of the dispersive ac conductivity [20]. A longer time τ_σ is defined such that for times $t < \tau_\sigma$, ions jump between sites but a stationary regime has not been achieved yet (short range ion motion), whilst for times $t > \tau_\sigma$ the dc conductivity regime or correlation limited long range motion has been reached. This characteristic electrical relaxation time τ_σ is found to be equal to $1/\omega_p$. Since both times τ_m and τ_σ are thermally activated, temperature and frequency can be adjusted to look at the various time regimes. In particular, an experiment looking for ions to be in the vibrational state should have temperature and frequency (ω) chosen such that $\omega^{-1} < \tau_m$. Since conventional ac bridges have the upper limit of the frequency in the megahertz range, low temperature measurements are necessary to look at this short time scale.

In this paper we investigate on the vibrational origin of the nearly constant loss term by examining electrical conductivity in the frequency range 100 Hz–100 kHz at low temperatures. We have performed complex admittance measurements of the fast ionic conductor $Li_{3x}La_{2/3-x}TiO_3$ partly because its high ionic conductivity [21–24], and partly because it has the highest value ever determined of the constant loss term [14]. We have found that, at a given frequency ω, the linear frequency term dominates the ac conductivity at the lowest temperatures, where $\omega^{-1} < \tau_m$, and a crossover to a sublinear frequency dependence occurs for $\omega^{-1} > \tau_m$ as the temperature is increased, when there is enough thermal energy for the ions to start jumping between wells. This finding provides strong evidence for a vibrational origin of NCL.

2. Experimental

Samples were prepared by heating a stoichiometric mixture of high purity $LiCO_3$, La_2O_3 and TiO_2 reagents at 1350°C in air for several hours (5–11 h) and then quenched to room temperature. Sinterized cylindrical pellets 5 mm in diameter and 1 mm thick (relative density of 0.92), with evaporated silver electrodes, were used for electrical measurements. Li content was checked by ICP analysis. Impedance spectroscopy measurements were conducted in the frequency range 20 Hz–30 MHz and for temperature range between 125 and 300 K, using precision LCR meters, HP4284A and HP4285A. Measurements were carried out under a N_2 flow to ensure an inert atmosphere. Temperature range was extended down to 8 K for frequencies in the range 100 Hz–100 kHz, mounting the sample inside a closed cycle helium cryostat. Temperature sweep rate was 1 K min^{-1}.

^{7}Li NMR spectra were obtained between 200 and 350 K in a MSL-400 Bruker spectrometer working at 155.45 MHz. Spectra were taken after irradiation of the sample with a $\pi/2$ pulse (3 μs). Determination of T_1 values was done between 170 and 500 K by using the classical (π–τ–$\pi/2$) sequence in a SXP 4/100 Bruker spectrometer, working at 10.6 MHz.

3. Results and discussion

The frequency dependence of the real part of the conductivity $\sigma'(\omega)$ of $Li_{0.18}La_{0.61}TiO_3$ for temperatures in the range 125–300 K is plotted in Fig. 1. The dc conductivity regime and the onset of the power law dependence according to Eq. (1) are observed at room temperature, and high frequencies. For the lower frequencies, conductivity decreases due to the blocking effects at grain boundaries. As temperature is reduced there is a decrease of both σ_0 and ω_p, and the power law dependence is observed for a larger frequency range, while the dc regime is shifted to lower frequencies. If temperature is further reduced an additional contribution to ac conductivity appears at high frequencies, characterized by a linear frequency dependence (NCL term). This is the dominant contribution to the dispersive ac conductivity at the lowest temperatures.

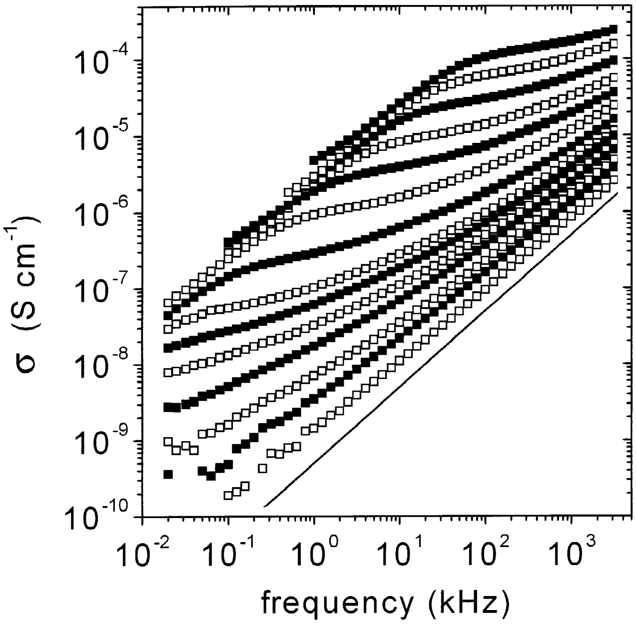

Fig. 1. Conductivity vs. frequency plots for $Li_{0.18}La_{0.61}TiO_3$ at temperatures (from top to bottom) 300, 284, 269, 252, 237, 221, 207, 194, 183, 175, 166, 153, 143, and 128 K. Solid line represents a linear frequency conductivity dependence for comparison.

Fig. 2(a) shows conductivity vs. temperature plots at different fixed frequencies. For clarity, we have removed conductivity data affected by blocking effects at high temperatures and low frequencies. At the highest temperatures the dc ionic conductivity regime is observed in this representation by data at different frequencies collapsing in a single curve. As temperature is lowered, the power law dependent term of the ionic ac conductivity (see Eq. (1)) becomes dominant. This takes place at lower temperatures the higher the frequency, and data sets separate from each other. At this stage ions are hopping outside their wells, but a stationary regime has not been achieved yet, since $\omega^{-1} < \tau_{\sigma}$. When decreasing temperature towards 100–125 K and down to the lowest temperatures examined, the NCL term becomes the dominant contribution to the ac conductivity. This NCL term manifests in Fig. 2(a) as a linear dependence of ac conductivity, which is found to be proportional to the frequency of measurement. The NCL regime is characterized by a weak temperature dependence of the ac conductivity. The best fits of experimental data over a wide temperature range are obtained by using an exponential temperature dependence ($\sigma = \sigma_A \exp(aT)$). Such fits are represented as solid lines in Fig. 2(a) for the different frequencies.

The linear frequency dependence can be chosen as a criterion to determine, at each frequency, a crossover temperature where the NCL term becomes the dominant contribution to the ac conductivity. The crossover points were obtained as the highest temperature where a linear frequency dependence was observed within a 10% accuracy. These crossover points are represented in Fig. 2 as open squares. In order to analyze the temperature dependence of the so defined crossover points, the same conductivity data of Fig. 2(a) have been plotted in Fig. 2(b) in an Arrhenius fashion. An activation energy $E = 0.17 \pm 0.01$ eV is obtained from this representation. Fig. 3 shows the temperature dependence of the NMR spin-lattice relaxation rate T_1^{-1}, measured at 10 MHz, and the line-width of the central transition T_2^{-1}. A cancellation of dipole Li–Li interactions happens when the correlation time of Li motion is smaller than $\langle \Delta\omega^2 \rangle^{-1/2}$ (motional narrowing effect), producing the decrease observed between 180 and 220 K in the T_2^{-1} curve. T_1^{-1} vs. $1000/T$ displays a maximum at about 270 K with different slopes at both sides of the maximum, 0.25 and 0.16 eV, for the high and

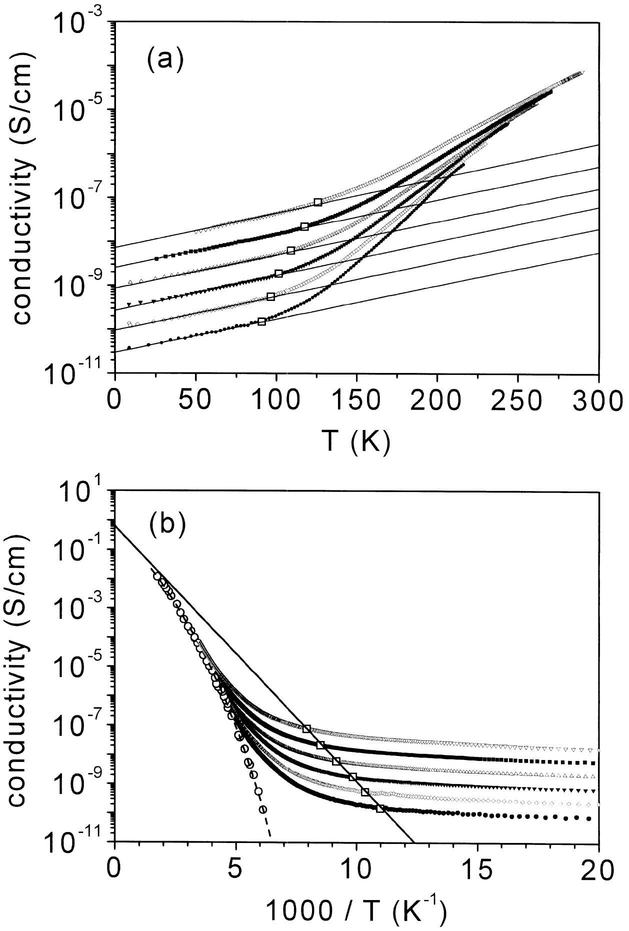

Fig. 2. Conductivity vs. temperature plots for $Li_{0.18}La_{0.61}TiO_3$. Conductivity data are shown for different frequencies (300 Hz, 1, 3, 10, 30 and 100 kHz, from bottom to top) in a linear temperature scale (a) and in an Arrhenius plot (b). Open squares in both plots represent the crossover between the linear frequency dependent conductivity (constant loss regime), and the power law regime of Eq. (1) which is due to ionic hopping. Solid lines in (a) are fits to an exponential temperature dependence of ac conductivity data in the constant loss regime. Open circles in (b) are dc conductivity data, and the solid line is a fit to an Arrhenius law for the temperature dependence of crossover points.

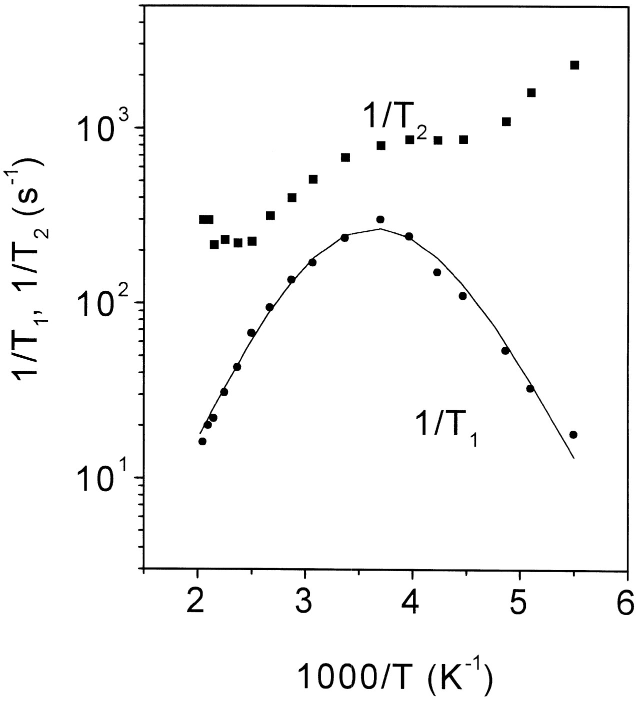

Fig. 3. NMR relaxation rates T_1^{-1} and T_2^{-2} vs. $1000/T$ for $Li_{0.18}La_{0.61}TiO_3$ measured at 10.6 MHz. The solid line was calculated from conductivity data at the same frequency (see Ref. [25]).

low temperature sides, respectively. While the high temperature side is related to long-range ion mobility, the slope of 0.16 eV at low temperatures gives the microscopic potential energy barrier, E_m, that ions must overcome to leave their wells [25].

Interestingly, the activation energy $E = 0.17 \pm 0.01$ eV obtained for the thermally activated behavior of crossover points in Fig. 2(b) is the same value obtained for the microscopic energy barrier for ionic hopping, E_m, obtained from NMR spin-lattice relaxation [25]. Moreover, the extrapolation to high temperatures of conductivity data at the crossover yields a value of about 1 S cm^{-1}, the same value obtained from the extrapolation to high temperatures of dc conductivity (see Fig. 2(b)). This extrapolation of dc conductivity data to infinite temperature is determined by the Nernst–Einstein equation, $\sigma_{0\infty} = (Nq^2 d^2 \nu_0)/(6\, k_B T)$, in terms of the attempt frequency ν_0, typically in the range 10^{12}–10^{13} s^{-1}, and for usual mobile ion concentrations $N \approx 10^{21}$–10^{22} cm^{-3} and physical ionic jump distances d of a few angstroms. It is found then that, at a fixed temperature, the NCL term is observed for frequencies $\omega > \tau_m^{-1} = \nu_0 \exp(-E_m/k_B T)$, as can be observed in Fig. 2(b). In other words, for a given frequency the NCL regime is found at temperatures low enough that ions can not jump from site to site. The near constant loss term is the dominant contribution to ac conductivity when Li ions remain vibrating in their potential wells, before ionic hopping starts. The value of the constant loss, A, would be determined by the vibrational mean-square displacement of ions inside their wells.

4. Conclusions

In summary, we have examined ac conductivity data of the fast ionic conductor $\mathrm{Li}_{0.18}\mathrm{La}_{0.61}\mathrm{TiO}_3$ at low temperatures in the audio frequency range. We have found a crossover from a power-law frequency dependence to a linear frequency dependence or near constant loss, as temperature is decreased for a given frequency. This crossover is found to be determined by the microscopic residence time τ_m that ions remain inside their wells, so that NCL dominates ac conductivity for $\omega > \tau_m^{-1}$. This finding provides strong evidence for the near constant loss to be due to the local vibrational mean-square displacement of ions inside their wells.

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