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Temperature dependence of the ionic conductivity in $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$: Arrhenius versus non-Arrhenius

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We report on the temperature dependence of the ionic conductivity at low temperatures in the crystalline lithium ionic conductor $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$. Time domain measurements of the electric modulus have been performed to investigate ion dynamics in the frequency range 10^{-5} – 10^2 Hz and for conductivity values in the range 10^{-14} – 10^{-8} S/cm. Ionic conductivity shows an Arrhenius temperature dependence below 300 K and down to 120 K, in contrast to the non-Arrhenius behavior found at higher temperatures, demonstrating that the temperature dependence of ionic conductivity in $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$ cannot be described by a Vogel–Fulcher–Tammann law. © 2003 American Institute of Physics. [DOI: 10.1063/1.1568169]

The practical applications of ionic conductors in batteries, sensors, and other devices have motivated the increasing research efforts in this field in the last two decades.^{1–10} Although substantial work has been directed to experimental and theoretical aspects of the dynamics of ions in ionically conducting materials, there remain important open questions.¹¹ One of the important subjects that is still unsolved concerns the temperature dependence of the ionic conductivity. Although it is well known that the dc conductivity of many ionic conductors displays an Arrhenius temperature dependence, $\sigma_{\text{dc}} = \sigma_{\infty} \exp(-E_{\sigma}/k_B T)$, over large temperature ranges, recently, departures from this behavior have been observed in some ionic conductors, consisting of a decrease of the apparent activation energy, E_{σ} , as the temperature is increased.^{12–17} The nature and details of this temperature dependence are of fundamental interest and deserve attention.

$\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO) is a crystalline lithium ionic conductor with an outstanding dc conductivity at room temperature of 10^{-3} S/cm,^{18–20} showing a non-Arrhenius temperature dependence of the dc conductivity. Previous work has shown a non-Arrhenius behavior in the temperature range 200–500 K,^{18–23} and the temperature dependence of the dc conductivity was empirically described by a Vogel–Fulcher–Tammann (VFT) law, $\sigma_{\text{dc}} = \sigma_{\infty} \exp(-E_{\sigma}/k_B(T-T_0))$. The same expression has been also used to fit experimental data of other ionic conductors, but its physical significance is not clear.^{15–17} The VFT law is often used to describe the temperature dependence of the relaxation times of the primary relaxation process in supercooled liquid undergoing the glass transition.^{24,25} The parameter T_0 , which describes the non-Arrhenius behavior, is usually between 50 and 60 K lower than the glass transition temperature T_g .²⁶ But no theoretical explanation exists for a VFT law for the dc conductivity in ionic conductors. Moreover, the validity of the VFT expression to describe experimental data in a broader tem-

perature range remains an open question, especially at low temperatures, where the dc conductivity values are very low and difficult to accurately determine even with high precision impedance bridges.

dc conductivity values of ionic conductors cannot be measured directly due to the onset of blocking effects at the electrodes. Instead, the dc conductivity is determined from the analysis of ac conductivity data measured by impedance bridges. The frequency dependence of ac conductivity spectra of ionic conductors is usually described by the so-called Jonscher expression,²⁷

$$\sigma^*(\omega) = \sigma_{\text{dc}}(1 + (j\omega/\omega_p)^n). \quad (1)$$

At any temperature, the real part of the conductivity shows a power-law frequency dependence at high frequencies, characterized by a fractional exponent n which is usually in the range 0.6–0.8. Lowering the frequency, below a characteristic frequency ω_p , this power-law dependence ceases and eventually turns into a constant value for the real part of the conductivity, which is the dc conductivity, σ_{dc} . Both σ_{dc} and ω_p show a similar temperature dependence, pointing to a common origin in ion hopping, and the ratio $\sigma_{\text{dc}}/\omega_p$ is usually on the order of the absolute permittivity at high frequencies, $\epsilon_0\epsilon_{\infty}$, (10^{-11} – 10^{-10} F/cm). Therefore, in order to accurately determine the low dc conductivity values in the range 10^{-14} – 10^{-10} S/cm, we would need high precision impedance bridges able to operate at very low frequencies, typically within the mHz and μ Hz ranges. This is why dc conductivity values in the range 10^{-14} – 10^{-10} S/cm are scarce in literature. Recently, another possibility has been proposed based on performing electric modulus measurements in the time domain, since the region of small frequencies or long times is naturally well suited for this technique.^{28–31} The electric modulus, $M^*(\omega)$, is related to the conductivity by the simple relation

$$M^*(\omega) = i\omega\epsilon_0/\sigma^*(\omega), \quad (2)$$

with ϵ_0 the permittivity of a vacuum, and given by the expression

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$$M^*(\omega) = M_\infty \left(1 - \int_0^\infty (-d\Phi/dt) e^{-j\omega t} dt \right). \quad (3)$$

M_∞ is the inverse of the high-frequency dielectric permittivity ϵ_∞ , and the relaxation function $\Phi(t)$ is the decay of the electric field \mathbf{E} at a constant displacement vector \mathbf{D} .³² The electric modulus is measured in the time domain by probing $\Phi(t)$. This can be achieved by creating a step function in $\mathbf{D}(t)$ [$\mathbf{D}(t) = \mathbf{0}$ for $t < 0$ and $\mathbf{D}(t) = \mathbf{D}_0$ for $t \geq 0$] and measuring the electric field inside the sample as a function of time, $\mathbf{E}(t)$.^{28–31} The frequency dependence of the conductivity and the value of the dc conductivity can be obtained by using Eqs. (1)–(3).

In this article, using this time domain technique in a crystalline ionic conductor, we report results of electrical relaxation in LLTO. This allows us to extend the frequency range down to 10^{-5} Hz and measure conductivity values down to the range of 10^{-14} S/cm. The temperature range where the dc conductivity can be obtained is now extended at low temperatures down to 120 K. We find an Arrhenius behavior down to the lowest temperature with an activation energy $E_\sigma = 0.36 \pm 0.02$ eV (34.7 kJ/mol), which unambiguously shows that the non-Arrhenius behavior reported earlier is a saturation effect at high temperatures, and there is not a physical basis to describe the non-Arrhenius behavior in terms of a VFT at low temperatures.

Ceramic LLTO samples were prepared by solid-state reaction at 1350 °C and then quenched to room temperature. Sinterized cylindrical pellets 12 mm in diameter and 1 mm thick, with evaporated silver electrodes, were used for electrical measurements. Further experimental details on sample preparation have been published elsewhere.^{20,22} The experimental setup to measure the electric modulus in the time domain has been described in detail by Richert *et al.*^{28–31} The step in \mathbf{D} can be achieved experimentally with a step in charge in the electrodes of the capacitor (formed by the solid sample and contacts), implemented connecting a voltage supply U_0 for a short time (20 μ s) and then isolating the circuit for $t > 0$. A value of 4 V has been used here as the initial voltage (U_0) to set the charge. The sample was placed in a static Cryo Vac cryostat, and a Teflon coaxial line and a low noise triaxial cable connect the sample and the Keithley 6517 electrometer. All measurements were conducted under a helium gas atmosphere.

Figure 1 shows the decay of the voltage across the sample due to the relaxation of the electric field inside the crystalline ionic conductor LLTO. The main relaxation observed in Fig. 1 is caused by lithium ions developing a long-range motion by hopping and compensating the field created by the external charge. This dc conductivity or long-range ionic transport process completely cancels the external charge in glasses,²⁹ but the blocking of charge carriers in the grain boundaries of the ceramic LLTO prevents the electric field from going to zero (Fig. 1). The frequency dependence of the electric modulus is obtained by using Eq. (3) and it involves a Fourier transform of the data measured in the time domain for the electric-field decay. In Fig. 2, electric modulus spectra at several temperatures are plotted in a log–log scale (open symbols). We have included for comparison previous measurements of the electric modulus spectra at higher

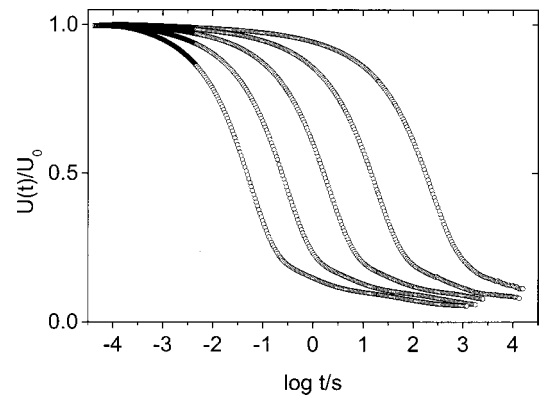


FIG. 1. Normalized time decay of the voltage $U(t)/U_0$ across the sample due to the relaxation of the electric field \mathbf{E} at constant displacement vector \mathbf{D} in $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$. Different data sets correspond to different temperatures (160 K, 150 K, 141 K, 131 K, and 121 K from the left- to the right-hand side).

temperatures (solid symbols in Fig. 2) as obtained in the frequency domain by using a conventional impedance bridge.^{20,22} The relaxation or time decay function of the electric field is reflected in the shape of the electric modulus spectra. The imaginary part $M''(\omega)$ shows a peak with a maximum at a characteristic frequency which is inversely proportional to the temperature dependent relaxation time of the electric-field decay function. By using Eq. (2), conductivity spectra are readily obtained from electric modulus data. Since many readers are more familiar with the conductivity representation, we have plotted, in Fig. 3, the real part of the conductivity as a function of frequency for the same temperatures presented in Fig. 2. It can be observed that the experimental data are well described by fits to the Jonscher expression [Eq. (1)], represented by solid lines in Fig. 3. There is a power-law dependence of the conductivity at high frequencies, characterized by an exponent n close to 0.6, and a crossover to a conductivity plateau when the frequency is lowered. Only at the lowest frequencies experimental data depart from the fits due to the onset of charge blocking effects. Fits of conductivity data to the Jonscher expression allow obtaining the value of the dc conductivity at each temperature. The power of time domain measurements to experi-

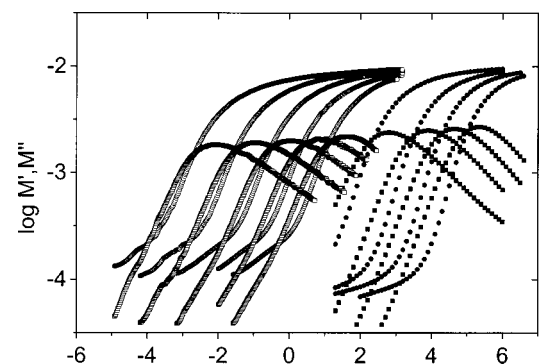


FIG. 2. Spectra of the real (open circles) and imaginary part (open squares) of the electric modulus of $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$ obtained from time domain data of Fig. 1 (121 K, 131 K, 141 K, 150 K, and 160 K from the left- to the right-hand side). Solid symbols represent spectra of real and imaginary parts of the electric modulus at higher temperatures (191 K, 212 K, 232 K, and 256 K from the left- to the right-hand side) obtained from frequency domain measurements using a conventional impedance bridge.

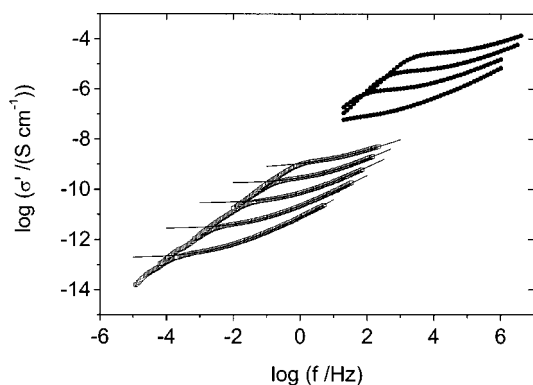


FIG. 3. Real part of the conductivity of $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$, at the same temperatures of Fig. 2, from time domain (open squares) and frequency domain (solid circles) measurements. Lines are fits to the Jonscher behavior [Eq. (1)] for data not affected by blocking effects.

mentally access low conductivity and low-frequency data is evident in Fig. 2. Experimental data are obtained in a low-frequency range 10^{-5} – 10^2 Hz, which is completely covered by using this time domain technique, and conductivity values down to 10^{-14} S/cm are probed.

The temperature dependence of the dc conductivity in LLTO is shown in an Arrhenius plot in Fig. 4. Open squares in Fig. 4 correspond to experimental data obtained by using time domain measurements, and open circles are data obtained from measurements in the frequency domain by using a conventional impedance bridge in the frequency range 20 Hz–5 MHz. Previous analysis of these data at temperatures above 180 K show a non-Arrhenius behavior of the conductivity, and a VFT law was proposed to describe the temperature dependence.^{20,22} However, our measurements in the time domain allow us to extend the temperature range down to 120 K and the dc conductivity clearly shows an Arrhenius behavior below room temperature down to the lowest temperature, with an activation energy $E_\sigma = 0.36 \pm 0.02$ eV. The

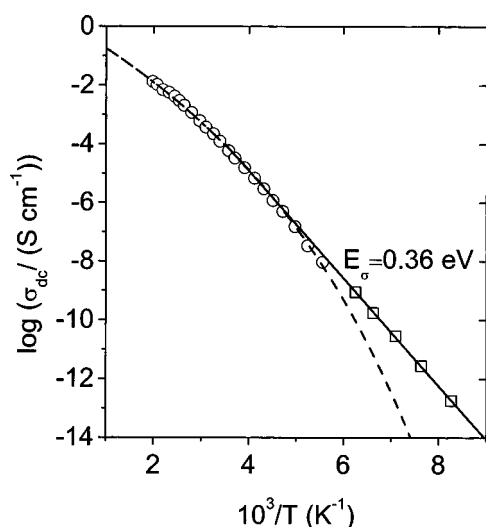


FIG. 4. Arrhenius plot of the dc conductivity of $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$ showing data obtained from frequency domain measurements with a conventional impedance bridge (open circles) and from time domain measurements of the electric modulus (open squares). An activation energy $E_\sigma = 0.36 \pm 0.02$ eV is obtained in the temperature range 120–300 K while a non-Arrhenius temperature dependence is observed above room temperature.

non-Arrhenius temperature dependence of the dc conductivity is then restricted to temperatures approximately above 300 K.^{18–23} This behavior is consistent with the observed saturation of dc conductivity values at high temperatures in fast ionic conductors.^{33,34} The activation energy starts to decrease when a dc conductivity value of about 10^{-3} S/cm is reached. However, at low temperatures, over a large temperature range (120 K–300 K), the dc conductivity shows an Arrhenius behavior while varying 10 orders of magnitude. This result definitely excludes the possibility of using a VFT law to describe the temperature dependence of the dc conductivity in LLTO, and suggests that the previous fits to VFT expressions of dc conductivity data in ionic conductors might be just due to the limited temperature and conductivity ranges available from conventional measurements in the frequency domain.

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