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Temperature dependence of the near constant loss in ionic conductors: a coupling model approach

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Abstract

We analyse experimental ac conductivity data of various glassy ($61\text{SiO}_2 \cdot 35\text{Li}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ and alkali triborates of formulae $\text{M}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ with $\text{M} = \text{Li}, \text{Na}, \text{K}$ or Rb) and crystalline ionic conductors ($\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$ and yttria stabilized zirconia with a 16% molar yttria content, $(\text{Y}_2\text{O}_3)_{0.16}(\text{ZrO}_2)_{0.84}$) at temperatures ranging from 400 down to 8 K. At sufficiently low temperatures the dielectric loss is found to be almost independent of frequency, and this near constant loss (NCL) shows a weak temperature dependence in all cases. We find good agreement between the experimental data and the theoretical predictions of a new scheme for NCL based on the coupling model.

1. Introduction

At sufficiently high frequencies, ω , and/or low temperatures the ac conductivity of ionically conducting materials shows a linear frequency dependent term,

$$\sigma'(\omega) \approx A\varepsilon_0\omega, \quad (1)$$

as the dominant contribution [1, 2] where A is a magnitude. Since this term results in a dielectric loss nearly independent of frequency,

$$\varepsilon''(\omega) = \sigma'(\omega)/\varepsilon_0\omega \approx A\omega^{-\alpha}, \quad (2)$$

with α almost zero, such behaviour is usually known as near constant loss (NCL) [3–5]. In equations (1) and (2) ε_0 is the permittivity of a vacuum. Although there are other materials showing NCL behaviour at low temperatures [6, 7], it seems to be a universal feature in the case of ionic conductors [1, 4]. Evidence for its existence has been repeatedly reported over the span of several decades [8–17], although until now there have only been a few investigations of its properties [4, 18–23]. This NCL contribution appears at higher frequency than the ion

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hopping ac conductivity, $\sigma_{hop}^*(\omega)$. The latter is assumed by some workers to be represented by the Jonscher expression [6]

$$\sigma_{hop}^*(\omega) = \sigma_0[(1 + (j\omega/\omega_p)^{n_J})], \quad (3)$$

where n_J is a fractional exponent, σ_0 is the dc conductivity and ω_p is a characteristic relaxation frequency. Alternatively [24], the ion hopping ac conductivity can also be well described by the one-sided Fourier transform,

$$M^*(\omega) = \frac{j\omega\varepsilon_0}{\sigma_{hop}^*(\omega)} = M' + jM'' = M_\infty \left[1 - \int_0^\infty dt \exp(-j\omega t)(-d\Phi/dt) \right], \quad (4)$$

of the time derivative of the Kohlrausch stretched exponential function,

$$\Phi(t) = \exp[-(t/\tau)^{1-n}]. \quad (5)$$

The ion hopping contribution $\sigma_{hop}^*(\omega)$ obtained from equations (4) and (5) is similar to the Jonscher expression, equation (3), in having the dc conductivity σ_0 at low frequencies, and it increases as a power law $(\omega\tau)^n$ at high frequencies instead of as $(\omega/\omega_p)^{n_J}$ in the Jonscher expression. Both σ_0 and τ in equation (5) are found to be thermally activated with about the same activation energy E_σ . Experimental evidence indicates that the stretched exponential time dependence of electrical relaxation is caused by ion–ion correlations, and therefore $\sigma_{hop}^*(\omega)$ is a cooperative ion hopping contribution. We want to emphasize at this point that, although it is usually assumed in the literature [1–3, 14–16] that the ion hopping ac conductivity and the linear frequency term (or NCL) are additive contributions over a common frequency domain, it has recently been shown that the *total* ac conductivity in ionic conductors is not a sum of these two contributions in the frequency domain [22, 25]. Moreover, although mobile ions also seem to be responsible for the NCL the experimental facts, including its dependence on temperature and the effect of mixed alkalis, point to a different origin than the ionic hopping conductivity given by equations (3)–(5) [4]. It has been shown experimentally that the temperature dependence of the NCL is much milder than that of σ_0 or τ . The magnitude of the NCL, A , is not thermally activated and has a temperature dependence that is well described by $\exp(bT)$, with bT usually smaller than unity, or by a power law T^γ , with an exponent γ not much larger than unity [4]. On the other hand, partial replacement of alkali ions by alkali ions of a different kind has the effect of reducing the NCL [4, 15, 16] although the reduction in A is much smaller than the decrease in σ_0 due to the well known mixed alkali effect [26].

The NCL behaviour has often been explained in the past in terms of asymmetric double-well potential (ADWP) configurations and attributed to the motion of groups of ions [16, 18, 20]. Recently, it has been proposed that the origin of the NCL stems from the vibrational relaxation of ions within their cages, before they start hopping and contributing to the long-range ion transport [4, 22]. Most recently, NCL was identified with the very slow decay of the cage in the short time regime, when the probability for successful independent hopping of the ions out of their potential wells is small [27, 28]. There are also different theoretical models [29, 30] that propose no formal separation between the Jonscher term and the NCL such that the latter is just the consequence of ionic hopping but on a very short timescale [31, 32].

In order to further understand the NCL behaviour it is necessary to perform new and systematic studies of the ac conductivity of different ionic conductors at low temperatures and/or high frequencies. By investigating the properties of the NCL we shall obtain new insight regarding its nature and origin. Since ion hopping is a thermally activated process, while the NCL has a much weaker temperature dependence, the contribution given by equations (3)–(5) becomes negligible at sufficiently low temperatures. Then the NCL becomes the dominant contribution to the ac conductivity in the experimental frequency window. For the usual measurement range of frequencies up to a few megahertz, and in typical ionic conductors, it

is then necessary to perform complex admittance measurements well below room temperature to obtain a dominant contribution from the NCL.

In this paper we report on the temperature dependence of the NCL in various glassy ($61\text{SiO}_2\cdot 35\text{Li}_2\text{O}\cdot 3\text{Al}_2\text{O}_3\cdot \text{P}_2\text{O}_5$ and alkali triborates of formulae $\text{M}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ with $\text{M} = \text{Li}, \text{Na}, \text{K}$ or Rb) and crystalline ionic conductors ($\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$ and yttria stabilized zirconia (YSZ) with a 16% molar yttria content, $(\text{Y}_2\text{O}_3)_{0.16}(\text{ZrO}_2)_{0.84}$). In the new model for NCL [27, 28] based on the coupling model (CM), its weak temperature dependence has been explained [28], and an approximate but explicit expression for it has been given. We compare the theoretical temperature dependence with experimental measurements and find good agreement. A corollary of the theoretical temperature dependence is the prediction that there is an approximate anticorrelation between A and the activation energy for independent hops, $E_a \equiv (1 - n)E_\sigma$, when considering different ionic conductors of the same class. Experimental data from the family of alkali borate glasses are used to verify this approximate anticorrelation. All these findings support the idea that the NCL originates from a very slow decay of the cages due to few and infrequent independent ion hops in the short time regime.

2. Experimental details

Samples of YSZ were oriented (100) single crystals supplied by ESCETE with composition $\text{ZrO}_2 - 16 \text{ mol}\% \text{Y}_2\text{O}_3$ and $10 \text{ mm} \times 5 \text{ mm} \times 1 \text{ mm}$ in size. Ceramic samples of composition $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$ 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) before quenching to room temperature. Sintered cylindrical pellets 5 mm in diameter and 1 mm thick, with evaporated silver electrodes, were used for the electrical measurements. The Li content was checked by ICP analysis. Silver electrodes were evaporated on the flat surfaces of the samples prior to electrical measurements. Complex admittance was measured in the audio frequency range (100 Hz–100 kHz) by using an HP4284 precision *LCR* meter. Sample preparation and experimental details for the electrical conductivity measurements of $61\text{SiO}_2\cdot 35\text{Li}_2\text{O}\cdot 3\text{Al}_2\text{O}_3\cdot \text{P}_2\text{O}_5$ and alkali triborate glasses with chemical formula $\text{M}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ (where M stands for $\text{Li}, \text{Na}, \text{K}$ or Rb) are given elsewhere [23, 33].

3. Results and discussion

The temperature dependence of the dielectric loss of $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$ is shown in figure 1 for several fixed frequencies from 300 Hz to 30 kHz and in the temperature range from 150 down to 8 K. It can be observed that, at low temperatures, the experimental data sets are almost frequency independent according to a genuine NCL behaviour, $\varepsilon''(\omega) \approx A$. At the highest temperatures, the conductivity data change to assume a sublinear frequency dependence (see equation (3)) and $\varepsilon''(\omega)$ becomes strongly frequency dependent. In a similar fashion, figure 2 shows the temperature dependence of the dielectric loss of YSZ with a 16% molar yttria content. Each data set was obtained by varying the temperature from 150 to 400 K at constant frequency ranging from 1 to 100 kHz. It can be observed that $\varepsilon''(\omega)$ is clearly an NCL up to almost room temperature in this frequency range. Figure 3 shows plots of the imaginary part of the dielectric permittivity versus temperature, at eight different fixed frequencies between 50 Hz and 10 kHz, and in the temperature range from 8 to 210 K, for the lithium silicate glass $61\text{SiO}_2\cdot 35\text{Li}_2\text{O}\cdot 3\text{Al}_2\text{O}_3\cdot \text{P}_2\text{O}_5$ (data after [33]). An NCL behaviour is also evident from the figure. In all of the samples analysed, the magnitude $\varepsilon''(\omega) \approx A$ of the NCL was found to be only weakly dependent on temperature. It can be observed from figures 1–3 that the

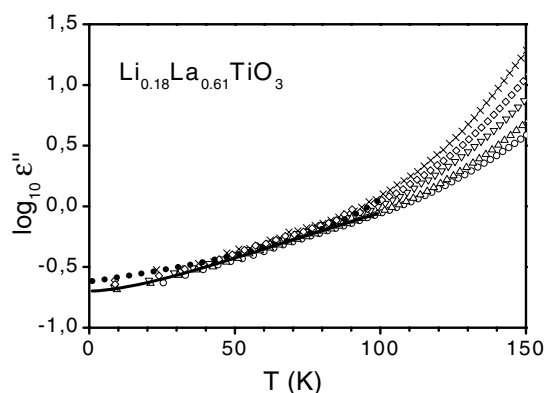


Figure 1. Temperature dependence of the dielectric loss, $\varepsilon''(\omega)$, at fixed frequencies for $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$. The experimental data are shown for different frequencies (300 Hz (\times), 1 kHz (\diamond), 3 kHz (∇), 10 kHz (Δ) and 30 kHz (\circ)) on a linear temperature scale. At low temperatures, data at the different frequencies are almost frequency independent, $\varepsilon''(\omega) \approx A$. Only at the highest temperatures, when ionic hopping contributes to the diffusion, does any frequency dependence become noticeable. Solid circles and the solid line represent fits to equations (10) and (12) respectively (see the text).

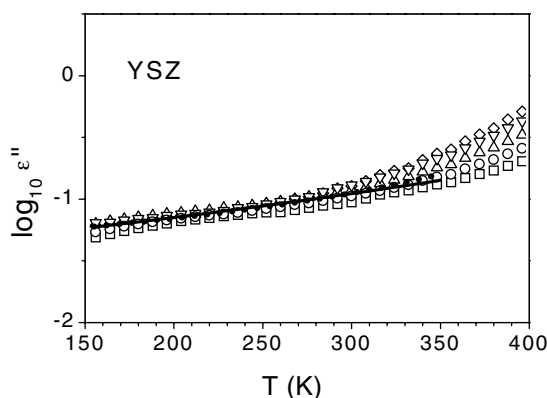


Figure 2. Temperature dependence of the imaginary part of the permittivity, $\varepsilon''(\omega)$, at fixed frequencies for $(\text{Y}_2\text{O}_3)_{0.16}(\text{ZrO}_2)_{0.84}$. The experimental data are shown for different frequencies (1 kHz (\diamond), 3 kHz (∇), 10 kHz (Δ), 30 kHz (\circ) and 100 kHz (\square)) on a linear temperature scale. The data are almost independent of frequency indicating the NCL behaviour, $\varepsilon''(\omega) \approx A$, in this temperature range. Solid circles and the solid line represent fits to equations (10) and (12) respectively (see the text).

weak temperature dependence of the NCL can be approximately described by an exponential function of temperature of the form $A \propto \exp(bT)$, although reasonable fits were also obtained to a power law temperature dependence $A \propto T^\gamma$. It is always found that the NCL shows a weak temperature dependence, yet stronger than linear [4], and no theoretical explanation for such behaviour has been given so far. We present in the following a qualitative theory for the NCL, based on the CM [34–36], that predicts [27, 28] its temperature dependence.

The CM for ionic conductors in most previous applications [34–36] considers only the case when all of the mobile ions have a high probability of hopping out of their cages. All of them are ready to hop with a relaxation rate τ_0^{-1} to neighbouring sites but their interactions

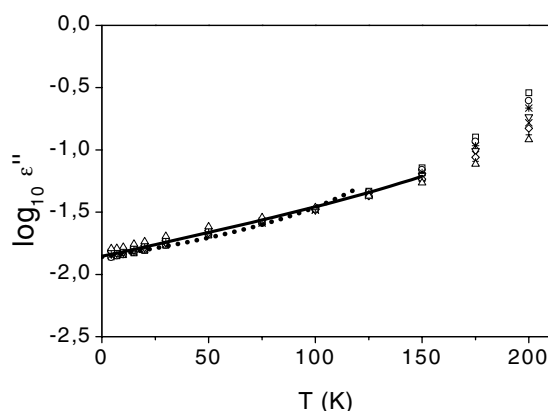


Figure 3. Temperature dependence of the dielectric loss, $\varepsilon''(\omega)$, at fixed frequencies for $61\text{SiO}_2\cdot 35\text{Li}_2\text{O}\cdot 3\text{Al}_2\text{O}_3\cdot \text{P}_2\text{O}_5$. The experimental data are shown for different frequencies (50 Hz (\square), 100 Hz (\circ), 200 Hz ($*$), 500 Hz (∇), 1 kHz (\times), 2 kHz (\diamond), 5 kHz ($+$) and 10 kHz (\triangle)) on a linear temperature scale. The losses are nearly frequency independent, $\varepsilon''(\omega) \approx A$. Only at the highest temperatures, when ionic hopping contributes to the diffusion, does any frequency dependence become noticeable. Solid circles and the solid line represent fits to equations (10) and (12) respectively (see the text).

and correlations make the simultaneous independent hopping of each ion impossible. The result is a slowed-down cooperative motion of all the ions with heterogeneous dynamics. The correlation function is changed at some time t_c from the linear exponential,

$$\Phi(t) = \exp(-t/\tau_0), \quad (6)$$

for independent hops to the stretched exponential function, $\exp[-(t/\tau)^{1-n}]$ (equation (5)). The relation between τ and τ_0 is given by

$$\tau = [t_c^{-n} \tau_0]^{1/(1-n)} \quad (7)$$

with $t_c \approx 2$ ps determined previously from high frequency measurements for ionic conductors [37–40]. Experimental evidence for the existence of such a change of dynamics in the neighbourhood of t_c is found from the high frequency and high temperature electrical conductivity measurements of Cramer *et al* [37–39] on molten CKN, glassy $0.44\text{LiBr}\text{--}0.56\text{Li}_2\text{O}\text{--}\text{B}_2\text{O}_3$ and other glasses, after the ω^2 -dependent vibrational absorption contribution is removed from the data. The temperature must be high enough that there is no intervening NCL, and the cooperative ion hopping term (having at high frequencies a ν^n -dependence for the ac conductivity) crosses over directly to the independent ion hopping term (having a frequency independent conductivity). Other evidence for a change of dynamics near $t_c \approx 2$ ps is found from the change of the temperature dependence of the dc conductivity of many ionic conductors when it exceeds about 1 S cm^{-1} [41, 42]. Other support comes from quasielastic neutron scattering (time of flight) measurements which give information on the short time behaviour (in the picosecond and sub-picosecond range) of the ionic diffusion coefficient as a function of temperature in superionic glasses [43–45].

The independent relaxation time $\tau_0(T)$ of the CM can be calculated using equation (7) from the experimental values of τ and $(1-n)$, obtained from fitting $M^*(\omega)$ data by equations (4) and (5), and using $t_c = 2$ ps. The interpretation of $\tau_0(T)$ given by the CM is the relaxation time for an ion, vibrating in its potential well, to exit by overcoming the energy barrier E_a through thermal activation. If τ has an Arrhenius temperature dependence and n is constant over a temperature region, then it follows from equation (7) that $\tau_0(T)$ should also have an Arrhenius

temperature dependence, $\tau_0(T) = [t_c^n \tau^{1-n}] = \tau_\infty \exp(E_a/kT)$ over the same temperature range. It is easy to verify from equation (7) that the product, $(1 - n)E_\sigma$, is the activation enthalpy E_a for the independent hop relaxation time τ_0 . From the simple nature of τ_0 , the reciprocal of its prefactor τ_∞ must be identifiable with the angular frequency of vibration for the ion inside the well. An example indicating that τ_0 is indeed the thermally activated relaxation time for an ion to hop out of its potential well is provided by a CM analysis of conductivity relaxation and hyper-Raman scattering data for yttria stabilized zirconia [42].

On the other hand, it has been recently suggested [27, 28] that the NCL originates from a slow decay of the cages during a time regime when most ions remain caged and successful independent hops are rare events. Molecular dynamics simulations of this time regime show that the mean square displacement of ions increases slowly with time in response to the decay of the cage [28]. Therefore, an NCL behaviour is expected from the following approximate (neglecting cross-correlations and assuming that the Haven ratio is not unity) relation between mean square displacement and complex conductivity:

$$\sigma^*(\omega) = -\omega^2 \frac{Nq^2}{6kT} \int_0^\infty \langle r^2(t) \rangle e^{-j\omega t} dt, \quad (8)$$

where N is the density of mobile ions, q the ion charge, k the Boltzmann constant and T the temperature. For a slowly varying mean square displacement of the form $\langle r^2 \rangle \propto ct^\alpha$ with α small, equation (8) gives $\sigma^*(\omega) \propto \omega^{1-\alpha}$ and $\varepsilon''(\omega) \propto \omega^{-\alpha}$, an NCL behaviour. In the limiting case of a mean square displacement that would increase logarithmically with time as $\langle r^2 \rangle \propto \log t$, the dielectric loss $\varepsilon''(\omega)$ would be practically flat and $\sigma^*(\omega) \propto \omega^{1.0}$.

At sufficiently short times, when most of the ions are still caged, the successful jumps out of cages are *independent* of each other in the framework of the CM. This is because there are very few ion jumps and therefore no cooperative dynamics are involved. The independent ion jumps have a rate $1/\tau_0$. It is then expected that, at times much shorter than τ_0 when ion jumps are rare events, the decay of the cages or the increase of $\langle r^2 \rangle$ with time has to be very slow, resulting in the NCL [28]. The NCL terminates at some time t_{x1} , when the successful independent ion hops become significant and there is a more rapid increase of $\langle r^2 \rangle$ with time. Still t_{x1} has to be much smaller than τ_0 because the latter is the characteristic time for the ions to leave their cages. In fact, this has recently been shown to be the case in several ionic conductors [46] for which the availability of extensive broad frequency range experimental data for the electrical conductivity makes possible a comparison of t_{x1} and τ_0 . The NCL exists in the short time (high frequency) regime, $t_{on} < t < t_{x1}$. From experimental data showing the NCL extending to very high frequencies, the onset time of the NCL, t_{on} , is found to be of the order of 10^{-11} – 10^{-12} s. The value of t_{x1} is the time beyond which the experimental data, $\sigma'(\omega)$, departs from its approximate linear dependence. Since t_{x1} is found to be much less than τ_0 , there are few successful independent ion jumps out of their cages throughout the period $t_{on} < t < t_{x1}$. Therefore the probability that an ion has jumped out of its cage at time t_{x1} , determined by $1 - \exp(-t_{x1}/\tau_0)$, is still close to zero, and it has the same value for all temperatures by the convention used to define the NCL termination at t_{x1} . Hence t_{x1} has the same thermally activated temperature dependence as τ_0 , in agreement with previous experimental results [22], and it is written out explicitly here as $t_{x1}(T) = \tau_\infty \exp(E_a/kT)$.

Again from the definition of t_{x1} , the mean square displacement $\langle r^2 \rangle_{NCL}$ corresponding to the NCL increases by the *same* small amount in the period $t_{on} < t < t_{x1}(T)$, at *all* temperatures. However, because t_{x1} is thermally activated, this same increase of $\langle r^2 \rangle_{NCL}$ is spread over a number of decades of time given by $[\log_e(t_{x1}) - \log_e(t_{on})]/2.303$. Therefore the mean square displacement is inversely proportional to $\log_e(t_{x1}/t_{on})$. From this and the relation between conductivity and mean square displacement (equation (8)), we deduce that the magnitude of

the NCL measured by A in equations (1) and (2) is given by the proportionality relation,

$$A \propto \frac{1}{E_a} [1 - (kT/E_a) \log_e(t_{on}/t_{\infty})]^{-1}, \quad (9)$$

or

$$A \propto \frac{1}{E_a} [1 - (T/T_0)]^{-1}, \quad (10)$$

with

$$T_0 = E_a/k \log_e(t_{on}/t_{\infty}). \quad (11)$$

Note that T_0 is a positive number because $\log_e(t_{on}/t_{\infty})$ is a positive number from the fact that $t_{x1} \ll \tau_0$, and hence t_{∞} is even shorter than the prefactor of τ_0 , τ_{∞} , which is the reciprocal of a vibrational attempt frequency. Thus the weak temperature dependence of the NCL is captured by our interpretation of the origin of the NCL within the framework of the CM.

Solid circles in figures 1–3 are fits to equation (9) (or (10)). The activation energy E_a was fixed at the value calculated by $E_a = (1 - n)E_{\sigma}$ from electrical conductivity measurements made at higher temperatures, where ionic hopping is the dominant contribution to the ac conductivity (see equation (2)). These values of E_a/k are 2000 K for $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$, 7200 K for YSZ with 16% yttria content and 3150 K for $61\text{SiO}_2 \cdot 35\text{Li}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$. We can estimate that t_{on} is of the order 10^{-11} s and that t_{∞} is in the range 10^{-14} – 10^{-16} s, much shorter than τ_{∞} . Therefore the value of $\log_e(t_{on}/t_{\infty})$ should typically be in the range 7–12. The values of $\log_e(t_{on}/t_{\infty})$ obtained from the fits are, however, a bit larger i.e. 15.82 for $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$, 15.42 for YSZ with 16% yttria content and 18.95 for $61\text{SiO}_2 \cdot 35\text{Li}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$. Therefore the T_0 values are 126.4 K for $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$, 466.9 K for YSZ and 166.2 K for $61\text{SiO}_2 \cdot 35\text{Li}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$. The fits to equation (10), deduced from the CM [27, 28], accurately describe the temperature dependence of the NCL observed in the experimental data. However it seems, from the low values obtained for T_0 in these fits, that the temperature dependence of the NCL is actually a bit stronger than predicted by independent ion hopping in the time regime $t < t_{x1} \ll \tau_0$. We can try to account for this by including an additional T^a factor and rewrite equation (10) as

$$A \propto K_0 + K \frac{T^a}{E_a} [1 - (T/T_0)]^{-1}, \quad (12)$$

where the constant K_0 accounts for a non-zero mean square displacement existing at $T = 0$ K. This additional T^a factor, if a were close to unity, could be rationalized in terms of a temperature dependence on a vibrational contribution to the mean square displacement that is similar to a Debye–Waller factor. In the case of an ion vibrating in a non-decaying cage, the vibrational contribution to the mean square displacement is found to be approximately proportional to T^a , with a close to unity in general and $a = 1$ for a harmonic well. The same is also true for the corresponding dielectric loss associated with this vibrational contribution. In the case of slowly decaying cages, we can still have this temperature factor determining the magnitude of the dielectric loss in addition to the factor $[1 - (T/T_0)]^{-1}$ contributed by the independent ion hopping in the time regime $t < t_{x1} \ll \tau_0$. Solid curves in figures 1–3 are fits to equation (12) and the fitting parameters are shown in table 1. Equation (12) fits better the experimental data and the T_0 parameters thus obtained lead, by using equation (11), to values for $\log_e(t_{on}/t_{\infty})$ of 7.65 for $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$, 10.91 for YSZ with 16% yttria content and 12.50 for $61\text{SiO}_2 \cdot 35\text{Li}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$, which are more reasonable values than those obtained by fitting to equation (10). However, it is worth emphasizing that an accurate description of the observed temperature dependence of the NCL for the three samples analysed is obtained over

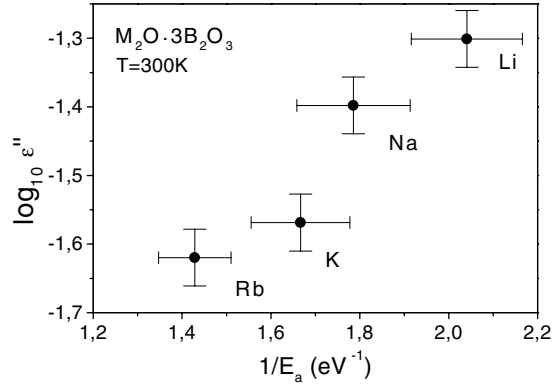


Figure 4. The magnitude of the NCL, $\epsilon''(\omega) \approx A$, at 300 K as a function of the reciprocal of the single ion independent activation energy, $1/E_a$, for the family of alkali triborate glasses $M_2O \cdot 3B_2O_3$ (where M stands for Li, Na, K or Rb).

Table 1. Parameters obtained from the fits to equation (12) of the experimental NCL data shown in figures 1–3.

	K_0	K	a	T_0 (K)
$Li_{0.18}La_{0.61}TiO_3$	0.2	2.8×10^{-4}	1.59	261.6
$(Y_2O_3)_{0.16}(ZrO_2)_{0.84}$	0.038	1.8×10^{-5}	1.35	660
$61SiO_2 \cdot 35Li_2O \cdot 3Al_2O_3 \cdot P_2O_5$	0.014	1.1×10^{-4}	1.02	252

a wide temperature range by using equation (10) which contains only two fitting parameters, T_0 and a proportionality factor.

We note also from equation (10), which is derived from the CM, that at constant temperature, A should decrease with increasing E_a provided other factors that determine the absolute value of A are the same for all ionic conductors. If this condition holds for some ionic conductors, then an approximate anticorrelation between A and E_a may exist at constant T . In order to test the validity of this anticorrelation we have analysed the magnitude of the NCL for members of the family of alkali triborate glasses $M_2O \cdot 3B_2O_3$ (where M stands for Li, Na, K or Rb). In this family of glasses, where the mobile ion M is the only variable, we should have similar values for other factors determining the value of A , except E_a . Therefore, at constant T we would expect an approximate anticorrelation to hold. Such an anticorrelation does indeed exist as can be seen from a plot of the magnitude A of the NCL versus $1/E_a$ (figure 4). We mention in passing that the systematic decrease of the NCL, observed when changing the alkali ion from lithium to rubidium, had been reported as a mass dependence of the NCL [23]. From the present perspective, such a decrease in the NCL when increasing the mass of the alkali ion arises from the observed increase of the activation energy, $E_a = (1 - n)E_\sigma$, for the relaxation time of independent ion hops in the CM.

4. Conclusions

In summary, we have analysed the temperature dependence of the NCL in several ionic conductors and found good agreement between the experimental data and the theoretical predictions from a recently proposed model for NCL based on ion coupling. An approximate anticorrelation between the magnitude of the NCL and the activation energy for independent

ion hops is also verified experimentally. Our results thus give additional support to the idea that the NCL originates from the slow decay of cages during a time regime when most of the ions remain caged and independent jumps are rare events. Nonetheless, we point out that there are also other contributions that can give rise to NCL and these may be relevant for describing data obtained under different conditions (such as at low temperatures and high frequencies) to those used in the present work.

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