

Cation Mass Dependence of the Nearly Constant Dielectric Loss in Alkali Triborate Glasses

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(Received 8 June 2001; published 11 March 2002)

Electrical ac conductivity measurements on alkali triborate glasses ($M_2O \cdot 3B_2O_3$, $M = \text{Li, Na, K, and Rb}$) were performed at temperatures down to 8 K and frequencies up to 1 GHz. All samples show a nearly constant dielectric loss (NCL), at the limit of high frequencies and/or low temperatures. The magnitude of the NCL is found to decrease as $m^{-1/3}$ with increasing alkali ion mass m . This quantitative result for the NCL, closely related to the mean-square displacement of ions, indicates that the origin of the NCL might be related to vibrational relaxation of the ions in the anharmonic potentials that cage them, and the cage is decaying very slowly with time.

DOI: 10.1103/PhysRevLett.88.125902

PACS numbers: 66.30.Hs

There has been a concerted research effort by many workers to understand the dynamics of ions in ionically conducting materials [1–15]. Experimentally, admittance spectroscopy is the most commonly used tool to probe the ion dynamics. The method allows one to obtain directly the complex conductivity of the material in the frequency domain, $\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega)$, which is related to the time dependence of the mean-square displacement for the ions, $\langle r^2(t) \rangle$, through the Laplace transform,

$$\begin{aligned} \sigma^*(\omega) &= \frac{Nq^2}{H_R kT} D(\omega) \\ &= -\omega^2 \frac{Nq^2}{6H_R kT} \int_0^\infty \langle r^2(t) \rangle e^{-i\omega t} dt, \quad (1) \end{aligned}$$

where N is the density of mobile ions, q the ion charge, k the Boltzmann constant, and T the temperature. The Haven ratio H_R has been taken to be approximately independent of frequency, since it usually varies by no more than a factor of 2 over several decades of frequency [3], and, in fact, having a value of unity at high frequencies.

In the usual experimental frequency window and temperature range, it is found that the frequency dependence of the real part of the conductivity in ionic conductors can be approximately described by the empirical expression of Jonscher [16],

$$\sigma'(\omega) = \sigma_0 [1 + (\omega/\omega_0)^n], \quad 0 \leq n < 1, \quad (2)$$

which is the sum of a constant dc conductivity $\sigma'(\omega) \approx \sigma_0$ and a fractional power-law dependence with exponent n . Both the dc conductivity and the characteristic frequency ω_0 , above which $\sigma'(\omega) \propto \omega^n$, are thermally activated, and it is well established that this frequency dependent ac conductivity originates from migration of hopping

ions. A different method to represent the experimental data based on the electric modulus [17,18] is often used. Several models have been proposed [19–22] to analyze electrical relaxation data of ionic conductors.

However, there is another contribution to the dispersion of the ac conductivity that has received less attention so far. This contribution consists of a nearly frequency independent dielectric loss, $\epsilon''(\omega) \approx A$, which corresponds to an almost linear frequency dependent term of the form $\sigma'(\omega) = \omega \epsilon_0 \epsilon''(\omega) \approx A \epsilon_0 \omega$ for the real part of the complex conductivity. At sufficiently low temperature or high frequencies, the linear term $A \epsilon_0 \omega$ dominates over the thermally activated ion hopping contribution to conductivity given by Eq. (2). The existence of a nearly constant loss (NCL) was suggested repeatedly over the span of several decades [23], and it is now considered to be a universal characteristic of ionic conductors [24], although till now there have been only a few investigations of its properties [24–27]. Measurements at low temperatures and high frequencies where the ac conductivity data are dominated by the NCL contribution are scarce.

Recently, various correlations were found between parameters that characterize the ion hopping conductivity contribution and the magnitude of the NCL [28]. Although the ions themselves seem to be responsible for the NCL contribution to the real part of the conductivity, the experimental facts point to a different origin than ionic hopping as a contribution given by Eq. (2) [28]. For example, it has been found that the magnitude of A has temperature dependence much milder than the dc conductivity σ_0 [28–30]. Partial replacement by alkali ions of a different kind has the effect of reducing the NCL [3,28,31,32], but the reduction in A is much smaller than the corresponding decrease in σ_0 from the commonly called mixed alkali effect [3].

Moreover, the crossover from a linear to a fractional power-law frequency dependence of ac conductivity has recently been shown [33] to be thermally activated, with activation energy identifiable with the microscopic potential barrier at the sites where ions reside, considerably smaller than the dc conductivity activation energy. It was found that for a given temperature, the NCL is the dominant contribution at frequencies greater than the characteristic single ion independent jump frequency, i.e., at short times when an ion is still localized and vibrating within the potential well or the cage. From these facts, it has been proposed that vibrational relaxation within the cage reflected by the mean-square displacement of ions is somehow related to the origin of the constant loss in ionic conductors [28,33].

In the context of this interpretation of the NCL [28,33], it is of interest to measure the dependence of the NCL on the mass of the mobile ions in otherwise identical glasses. From previously reported [34] conductivity data of the ionically conducting glasses $0.25\text{Li}_2\text{O} \cdot 0.75\text{GeO}_2$ and $0.2\text{K}_2\text{O} \cdot 0.8\text{GeO}_2$, it can be inferred that the NCL is larger for lighter ions, at least for the family of germanate glasses. However, this result cannot be used for any quantitative test because the purpose of that work was not directed towards the study of the alkali mass dependence of the NCL, and the concentration of the alkali ions is not the same in the two germanate glasses. In this paper we report an experimental study on a family of ionic glasses that enables a determination of the dependence of the NCL on the mobile ion mass. Such information is heretofore lacking in the literature.

Recently, mid- and far-infrared absorption spectra of the family of alkali borate glasses with the chemical formula $M_2\text{O} \cdot 3\text{B}_2\text{O}_3$ (where M stands for Li, Na, K, and Rb) have shown that the cages for the different alkali ions are quite similar [35]. In fact, from the analysis of far-infrared absorption peaks due to localized vibrations of alkali ions, the very same value is obtained for the spring constant k defining the potential of the cages [35]. This result makes the family of the ionically conducting alkali triborate glasses an ideal system to investigate the dependence of the NCL on the alkali mass. We report here on the results of such an investigation. We find, for the first time, that the NCL in ionic conductors decreases systematically with increasing mass of the mobile ions. This experimental finding suggests the NCL originates from loss during the time regime while the ion is still confined in the cage and the cage is decaying very slowly (vibrational relaxation). It supports the vibrational relaxation interpretation of the NCL because the mean-square displacement of the ion, which is proportional to the magnitude of the vibrational relaxation loss, decreases with increasing ion mass. The results could be instrumental for others to build a rigorous theoretical explanation of the NCL in ionic conductors.

Glasses have been prepared from stoichiometric ground mixtures of B_2O_3 and alkali carbonates by melting in platinum crucibles in an electric furnace at 1100°C for

ca. 20 min. The liquids were quenched by pouring into 10 mm diameter, cylindrical brass molds, followed by annealing at ca. 10°C below T_g . The resulting glass cylinders were cut with a low speed diamond saw (Isomet by Buehler) into 1 mm thick disks. Individual sample dimensions have been measured with an accuracy of $\pm 10 \mu\text{m}$. Midinfrared reflectance and Raman spectra (not shown) of these specimens confirmed the glass stoichiometry and an absence of crystallites. Immediately after preparation, the samples were coated with mineral oil (which had been stored over metallic sodium) to exclude surface hydrolysis and were stored in a desiccator. Prior to electrode evaporation, the oil coating was removed by rinsing with trichloroethane. Silver electrodes, 7 mm in diameter, were evaporated on the flat surfaces of the samples. We have performed complex admittance measurements in the audio frequency range (100 Hz–100 kHz) at low temperatures (8–300 K) by using a closed cycle helium cryostat and precision LCR meter HP4284. High frequency complex admittance measurements from 1 MHz to 1 GHz were obtained at room temperature with an HP4291A impedance analyzer.

Since the magnitude of the dc conductivity, as well as the characteristic relaxation frequency of ionic hopping contribution to complex conductivity, is thermally activated, the NCL will become the dominant contribution to $\sigma'(\omega)$ at sufficiently high frequencies or low temperatures. For the usual measurement range (frequencies up to a few megahertz), it is necessary to perform complex admittance measurements well below room temperature to obtain a dominant contribution from the NCL in typical ionic conductors. At room temperatures, the NCL contribution can be seen only if the measurement frequency is extended up to the gigahertz range. Figure 1 shows conductivity versus frequency plots at 300 K, from 1 MHz up to 1 GHz, for the four alkali triborate glasses studied in this work. Note that the experimental conductivity data have been shifted vertically to separate from each other for clarity. It can be readily observed that a linear frequency dependence of the ac conductivity is found for all samples over this frequency range. Best fits are obtained for a frequency dependence of the form $\sigma'(\omega) = A\varepsilon_o\omega^p$, with an exponent $p = 0.99 \pm 0.03$ for all samples. The magnitude A of the NCL at 300 K is thus obtained for each alkali borate from these fits.

Figure 2 shows conductivity versus temperature plots, at five different fixed frequencies between 1 and 100 kHz, for the lithium triborate glass. It can be observed that the data sets at low temperature are spaced according to a linear frequency dependence, $\sigma'(\omega) = \omega\varepsilon_o\varepsilon''(\omega) \approx A\varepsilon_o\omega$, with the magnitude A of the NCL only weakly dependent on temperature. In fact, over a wide temperature range, it increases very slowly. The NCL is found to be the dominant contribution to the conductivity in the frequency range from 1 kHz to 1 GHz at temperatures from 8 K to about 250 K. This can be seen in the inset where $\varepsilon''(\omega)$ is

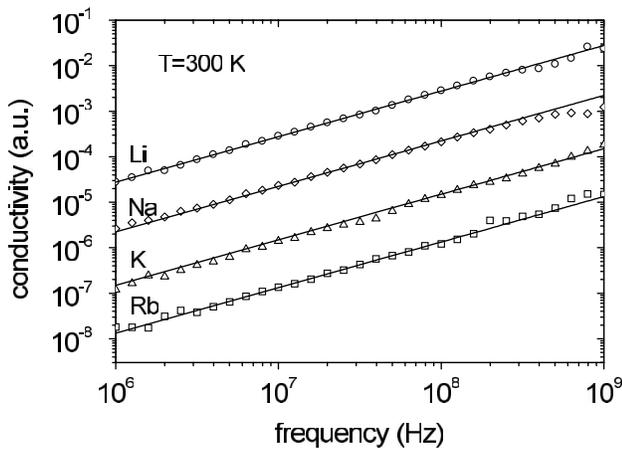


FIG. 1. Frequency dependence of the real part of the conductivity, $\sigma'(\omega)$, at room temperature and frequencies in the range 1 MHz–1 GHz, for the alkali triborate glasses $M_2O \cdot 3B_2O_3$, with $M = \text{Li, Na, K, and Rb}$. Data sets corresponding to $M = \text{Li, Na, and K}$ have been multiplied by 1000, 100, and 10, respectively, for clarity. Solid lines represent best fits to a linear frequency dependence, i.e., a constant loss contribution to the conductivity.

plotted against T . The data from the five different frequencies collapse onto a single curve at low temperature, indicating that $\varepsilon''(\omega)$ is truly independent of frequency and is a genuine NCL. Nevertheless, the experimental $\varepsilon''(\omega)$ data for the different frequencies in the inset can be seen to diverge at higher temperatures. Equivalently, $\sigma'(\omega)$ in the main figure starts to deviate from a linear frequency dependence at the higher temperatures, due to the crossover

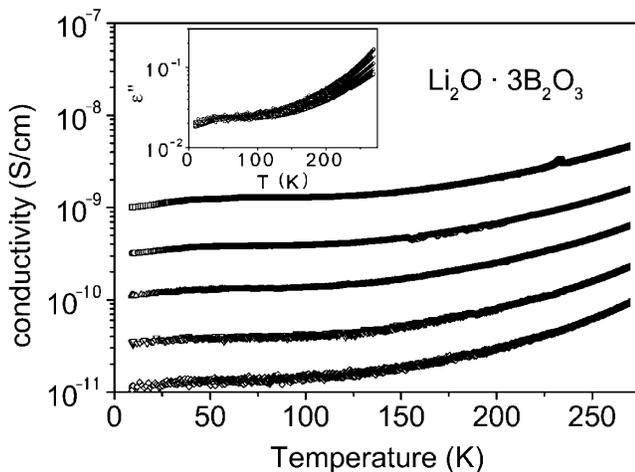


FIG. 2. Temperature dependence of the real part of the conductivity, $\sigma'(\omega)$, at fixed frequencies for $\text{Li}_2\text{O} \cdot 3\text{B}_2\text{O}_3$. Conductivity data are shown for different frequencies (1, 3, 10, 30, and 100 kHz, from bottom to top) in a linear temperature scale. At low temperatures, data at the different frequencies are spaced according to a linear frequency dependence. This is emphasized in the inset, where we have plotted the imaginary part of the permittivity, or dielectric loss, $\varepsilon''(\omega) = \sigma'(\omega)/\varepsilon_0\omega$, for the same frequencies, showing that these losses are nearly frequency independent, $\varepsilon''(\omega) \approx A$. Only at the highest temperatures, for which ionic hopping contributes to the diffusion, does any frequency dependence [see Eq. (2)] become noticeable.

to a fractional power-law dependence, Eq. (2), reflecting ions have already hopped out of their cages [33].

The dependence of the nearly constant loss on the mass of alkali ions is presented in Fig. 3. We have plotted data at two different temperatures, 300 and 60 K, and both data sets show a similar trend: the magnitude of the NCL decreases slightly but systematically as the alkali mass increases. The observed change in A is much smaller than that found for the dc conductivity. At 300 K, while A varies by about a factor of 2, the dc conductivity decreases by more than 3 orders of magnitude, in changing the alkali ion mass from lithium to rubidium. This fact, together with the contrast between the weak temperature dependence of the NCL and the thermally activated behavior of the dc conductivity, suggests that the NCL is related to the ions, but has a different origin than the dc conductivity. However, changes in both quantities are not unrelated, since samples with a higher dc conductivity show also a higher value of A . This correlation between the magnitude of A and the dc conductivity value found for the family of alkali triborates is consistent with the previously published observation [28] that ionic conductors showing high values of the NCL are all superionic conductors, having very high dc conductivities even at room temperature.

Previous experimental results [33] suggested that the NCL arises from ions vibrating within their anharmonic cages, before any significant number of them has hopped to adjacent vacant sites at low temperature or short times (high frequencies). Accordingly, the still localized ions give rise to the NCL from their vibrational displacements in very slowly decaying cages. Other experimental facts

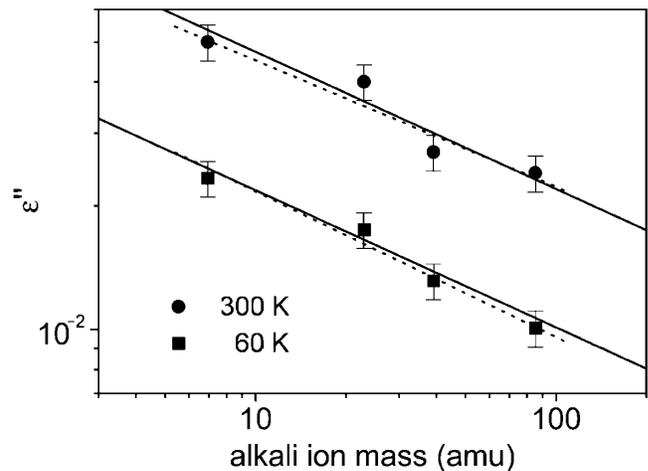


FIG. 3. Mass dependence of the dielectric loss $\varepsilon''(\omega) \approx A$ at 60 and 300 K for the alkali triborate glasses analyzed in this work. The values of A at 60 and 300 K were obtained, respectively, from conductivity data at 10 kHz and 100 MHz. The magnitude of the NCL increases by a factor of 2 in changing the alkali ion from rubidium to lithium. Dotted lines are fits to a power-law dependence of the form m^{-a} with exponents $a = 0.35 \pm 0.03$ and 0.31 ± 0.05 at 60 and 300 K, respectively. Solid lines represent a dependence of the form $m^{-1/3}$, which describes within error for the experimental data.

also point to such vibrational relaxation of ions in anharmonic potentials as the origin of the NCL [28]. Best fits to a power-law dependence on the alkali mass of the value of A obtained in this work for the alkali triborates are shown in Fig. 3 (dashed lines): exponents $a = 0.35 \pm 0.03$ and 0.31 ± 0.05 are obtained for A values at 60 and 300 K, respectively. In fact, solid lines in Fig. 3 represent a mass dependence of the form $m^{-1/3}$, which accounts within experimental error, and at both temperatures, for the observed change in the magnitude of the NCL with the mass of the alkali ion. This finding might be related to the anharmonicity of the potential that cages the ion, since it is well known that the characteristic mean-square displacement of an ion vibrating in a cage defined by a harmonic potential, according to the equipartition theorem, is independent of the mass of the ion [36]. Rigorous theoretical work is necessary for a satisfactory understanding of the origin of NCL and its properties, and our current interpretation based on anharmonicity of the cages must be considered as tentative at the present stage. Nevertheless, the mobile ion mass dependence of NCL found experimentally in this work should be an important fact to be considered in the construction of a viable theory.

In summary, we have analyzed the cation mass dependence of the nearly constant loss in a family of alkali triborate glasses having exactly the same composition. We determined the magnitude of the NCL by measuring their ac conductivity at frequencies up to 1 GHz at room temperature and also at low temperatures for frequencies in the audio frequency range. At any fixed temperature, the magnitude of the nearly constant loss systematically decreases with increasing alkali ion mass from lithium to rubidium, following a power-law dependence of the form $m^{-1/3}$. This result is consistent with the proposal that NCL in ionic conductors originates from the vibrational relaxation of the ions in very slowly decaying anharmonic cages [28,33].

C.L. thanks NRL for hospitality during his stay. A. R. and C.L. thank J. Santamaria for stimulating discussions. Financial support from CICYT Grant No. MAT98-1053-C04 is acknowledged. The work performed at NRL was supported by ONR.

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- [1] C. A. Angell, *Chem. Rev.* **90**, 523 (1990).
 - [2] See the collection of papers in *J. Non-Cryst. Solids* **131-133** (1991); **172-174** (1994); **235-238** (1998).
 - [3] P. Maass, M. Meyer, and A. Bunde, *Phys. Rev. B* **51**, 8164 (1995).
 - [4] K. L. Ngai, *J. Non-Cryst. Solids* **203**, 232 (1996).
 - [5] J. Kinsc and S. W. Martin, *Phys. Rev. Lett.* **76**, 70 (1996).
 - [6] K. L. Ngai and A. K. Rizos, *Phys. Rev. Lett.* **76**, 1296 (1996).

- [7] P. Maass, M. Meyer, A. Bunde, and W. Dieterich, *Phys. Rev. Lett.* **77**, 1528 (1996).
- [8] B. Roling, A. Happe, K. Funke, and M. D. Ingram, *Phys. Rev. Lett.* **78**, 2160 (1997).
- [9] P. Lunkenheimer, A. Pimenov, and A. Loidl, *Phys. Rev. Lett.* **78**, 2995 (1997).
- [10] C. León *et al.*, *Phys. Rev. B* **54**, 184 (1996); C. León *et al.*, *Phys. Rev. B* **56**, 5302 (1997).
- [11] K. L. Ngai and C. T. Moynihan, *Bull. Mater. Res. Soc.* **23**, 51 (1998).
- [12] D. L. Sidebottom, *Phys. Rev. Lett.* **82**, 3653 (1999).
- [13] K. L. Ngai and C. León, *Phys. Rev. B* **60**, 9396 (1999).
- [14] T. B. Schroder and J. C. Dyre, *Phys. Rev. Lett.* **84**, 310 (2000).
- [15] A. Ghosh and A. Pan, *Phys. Rev. Lett.* **84**, 2188 (2000).
- [16] A. K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectric Press, London, 1983).
- [17] C. T. Moynihan, L. P. Boesch, and N. L. Laberge, *Phys. Chem. Glasses* **14**, 122 (1973).
- [18] F. S. Howell, R. A. Bose, P. B. Macedo, and C. T. Moynihan, *J. Phys. Chem.* **78**, 639 (1974).
- [19] K. L. Ngai, *Phys. Rev. B* **48**, 13481 (1993); K. L. Ngai, G. N. Greaves, and C. T. Moynihan, *Phys. Rev. Lett.* **80**, 1018 (1998).
- [20] J. R. Macdonald, *J. Chem. Phys.* **115**, 6192 (2001).
- [21] K. Funke, *Prog. Solid State Chem.* **22**, 111 (1993).
- [22] J. C. Dyre, *J. Appl. Phys.* **64**, 2456 (1988).
- [23] G. C. Garton, *Discuss. Faraday Soc.* **42A**, 161 (1946); A. E. Owen, *Prog. Ceram. Sci.* **3**, 77 (1963); J. M. Stevels, *Handb. Phys.* **20**, 372 (1957); J. Wong and C. A. Angell, *Glass Structure by Spectroscopy* (Dekker, New York, 1976).
- [24] W. K. Lee, J. F. Liu, and A. S. Nowick, *Phys. Rev. Lett.* **67**, 1559 (1991).
- [25] C. Cramer, K. Funke, and T. Saatkamp, *Philos. Mag. B* **71**, 701 (1995).
- [26] K. L. Ngai, H. Jain, and O. Kanert, *J. Non-Cryst. Solids* **222**, 383 (1997).
- [27] R. Casalini, K. L. Ngai, and C. M. Roland, *J. Chem. Phys.* **112**, 5181 (2000).
- [28] K. L. Ngai, *J. Chem. Phys.* **110**, 10576 (1999).
- [29] C. León, M. L. Lucía, and J. Santamaría, *Phys. Rev. B* **55**, 882 (1997).
- [30] A. S. Nowick, A. V. Vaysleb, and W. Liu, *Solid State Ion.* **105**, 121 (1998).
- [31] D. L. Sidebottom, P. F. Green, and R. K. Brow, *Phys. Rev. Lett.* **74**, 5068 (1995).
- [32] H. Jain and X. Lu, *J. Non-Cryst. Solids* **196**, 285 (1996).
- [33] C. León, A. Rivera, A. Várez, J. Sanz, J. Santamaria, and K. L. Ngai, *Phys. Rev. Lett.* **86**, 1279 (2001).
- [34] H. Jain and S. Krishnaswami, *Solid State Ion.* **105**, 129 (1998).
- [35] G. D. Chryssikos, L. Liu, C. P. Varsamis, and E. I. Kamitsos, *J. Non-Cryst. Solids* **235-237**, 761 (1998).
- [36] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, 1995), p. 387.