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# Duality dc and frequency-dependent conductivity in ionic glasses: A possible experimental approach

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Contrary to the usual interpretations, we experimentally show that the frequency-independent (dc conductivity) and frequency-dependent (polarization conductivity) conductivities of ionic glassy conductors can be considered to be independent of each other. Indeed, after having inserted two ionic glasses ($Na_2O{\cdot}3SiO2$,$Ag_2S{\cdot}GeS_2$) between inert dielectrics, we observe that though the dc conductivity disappears, the polarization-conductivity behavior, i.e., the frequency power law, remains unchanged.

## I. INTRODUCTION

Complex-impedance spectrometry is a powerful experimental method to determine the frequency-independent conductivity of ionic solid conductors. This conductivity is known as the dc conductivity ($\sigma_{\rm dc}$) even though it is measured under an ac electric field (generally from 10 to $10^7$ Hz), which is used to prevent polarization arising from blocking electrodes. This ac measurement is also effective for investigating the frequency-dependent conductivity which is also known as the polarization conductivity [$\sigma'(\omega)$], and which is related to the dielectric losses $\varepsilon''(\omega)$ through the simple relation $\sigma'[\omega]=\varepsilon''(\omega)\omega$, where $\omega$ is the circular frequency of the applied electric field. The latter is fundamentally different from the dc conductivity since it may arise from dipole relaxations of locally trapped ions which do not participate in long-range diffusive charge transfer. The polarization conductivity is then an additional tool for understanding the microscopic hopping process and therefore, the ordering or disordering of the local structure that accompanies the oscillation of a relevant ion.[1,2] This may be an important step before understanding the more complex long-range or noncooperative hopping process, i.e., the dc conductivity process, which is likely to be more influenced by the charge-carrier coupling interaction.

To accomplish this task, it is more effective to represent the complex-impedance data in ac conductivity ($\sigma_{\rm ac}$) and permittivity ($\varepsilon'$) versus frequency plots rather than in complex-impedance planes.[3,4]

There are a number of proposed models to account for the ac conductivity in ionically conducting materials,[2,5–10] based on either series or parallel mechanisms, however, no single model correctly predicts both $\sigma_{\rm dc}$ and $\sigma'(\omega)$ behavior. The reason may be that the inherent difference between the two conductive mechanisms may preclude a possible "unified" model. Likewise, models based on the empirical Kohlraush-Williams-Watts function $\phi(t)=\exp(t/\tau)^{\beta}$ do not separate these two distinct processes, though this skewed exponential decay function can be empirically fitted by a superposition of independent simple exponential functions.[11,12] In short, most of the investigation on ac conductivity in ionic conductivity materials are based on the assumption that $\sigma_{\rm dc}$ and $\sigma'(\omega)$ conductivity mechanisms are dependent on each other. In contrast, one should consider at least a two-stage model to account for the ac conductivity, i.e., localized and nonlocalized hopping. This approach has recently been described by A. Hunt,[13] where $\sigma'(\omega)$ and $\sigma_{\rm dc}$ are explained using the "pair approximation" and percolation theories, respectively.

Our aim is to reveal the difficulties in obtaining the pure polarization conductivity because of the presence of the dc conductivity and/or the blocking electrode effect when one measures the ac conductivity. We then propose an experimental method for separating the frequency-dependent conductivity from the dc conductivity perturbation. This is desirable since it is important for understanding the ionic conductivity mechanisms.[12,14]

When one applies an ac electric field to an ionic conductor, one observes both frequency-independent and frequency-dependent behavior,[1,15,16] since ionic materials exhibit both dc conductive and dielectric properties in the same frequency range. Most ionic conductor materials are neither conductors as metals nor perfect insulators. This can be simply explained by assuming that there are two types of change carriers and all the ions do not participate in dc conductivity as predicted by the weak electrolyte model.[17] "Free" charge carriers produce frequency-independent dc conductivity within the usual frequency range, whereas "quasifree"[6] charges give rise to frequency-dependent polarization conduction. Although there are microscopic descriptions and fundamental considerations of this dual polarization-diffusion process in ionic conductive glasses[18] and crystals,[19] it is never clearly taken into account for explaining both frequency-independent and frequency-dependent behavior. The ac conductivity, i.e., the total conductivity measured from an impedance bridge, is therefore the sum of two conductivities,[4]

$$\sigma_{\rm ac}=\sigma_{\rm dc}+\sigma'(\omega)\ . \qquad (1)$$

This is a simple function accounting for two independent and different natural processes. A similar assumption

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was introduced by Johari and Pathmanathan[20] who obtained good fit to the frequency behavior of the imaginary part of the electric modulus by combining exponential conductivity relaxation ($\sigma_{dc}$) and ion-ion pair dipole relaxation [$\sigma'(\omega)$].

## II. EXPERIMENTAL APPROACH FOR SEPARATING THE DC CONDUCTIVITY FROM THE POLARIZATION CONDUCTIVITY

According to the previous remarks, we believe that new methods are needed to determine $\sigma'(\omega)$ independently from the dc conductivity. Then we are able to conclude whether or not the polarization conductivity and the dc conductivity are different in nature.

There are several possible experimental methods for observing the "true" dielectric relaxation, i.e., a non-$\sigma_{dc}$-influenced frequency-dependent conductivity. For this purpose, we undertook a "new" method of conductivity measurements by placing the ionic material between two insulators, i.e., thin films of Mylar, stuck to the sample with a commerical epoxy glue (Fig. 1). Silver paste is painted on the outside surface of the Mylar and then the sample is wired to an impedance meter (Hewlett-Packard 4192A). Before taking data on such a sample, we verified that the system silver-Mylar-glue behaved as a true capacitor and did not exhibit a dielectric loss peak in the measuring frequency range (100 Hz–13 MHz). Such an inert dielectric insert is commonly used in thermally stimulated depolarization current techniques (TDSC).[21–23]

The ac conductivity of our samples, $Na_2O{\cdot}3SiO_2$ and $Ag_2S{\cdot}GeS_2$ glasses, in their new configuration is measured and compared with the data obtained from the usual ac conductivity measurements (Figs. 2 and 3), i.e., the ionic material between two gold deposited electrodes. We see from this plot that the new configuration lowers the absolute value of $\sigma'(\omega)$ (about one order of magnitude) without affecting the frequency power law, $s=0.67-0.70$, in either case. The magnitude change of $\sigma'(\omega)$ can be explained if one considers that the dielectric insert is equivalent to a resistance much higher than the ionic conductor and does not modify its geometric factors. Therefore, resulting from a "voltage loss" at each side of the ionic conductor and from a decrease of the apparent dielectric constant of the studied system, the polarization conductivity is lowered. However, the dc conductivity is lowered so much more that it disappears. We show in Fig. 4 that the temperature variation of the parameter $s$ using both sample configurations is equivalent, within the studied temperature range.

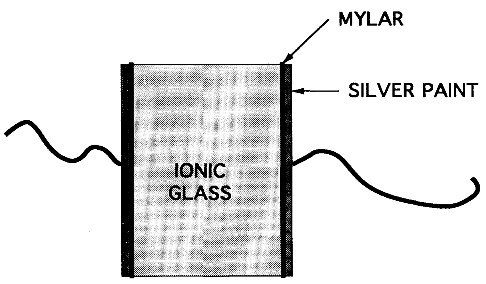

FIG. 1. Sample between inert dielectric insert.

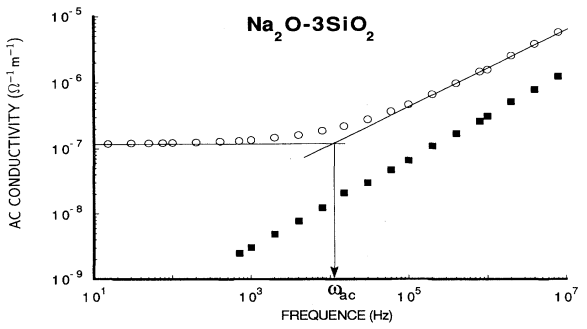

FIG. 2. Comparison of conductivities of $Na_2O{\cdot}3SiO_2$; in a usual configuration (empty circles) and in the configuration shown in Fig. 1 (filled squares) at room temperature.

These results confirm two facts. On the one hand, Eq. (1) is verified on a real system as a proof that the polarization conductivity $\sigma'(\omega)$ may not be strongly dependent on the dc conductivity. This is consistent with our earlier assumption and should be considered in future dielectric relaxation investigations, particularly for ionic glasses. On the other hand, the so-called relaxation peak $\tau_{ac}$ or hopping rate $\omega_{ac}$ (Ref. 24), which is defined as the frequency where the value of $\sigma_{dc}$ is equal to $\sigma'(\omega)$ (see Figs. 2 and 3), is mainly related to the dc conductivity and not to any kind of dipole relaxation time or local hopping rate; under its new configuration the sample does not exhibit any relaxation peak. Experiments are currently in progress to establish the reproducibility of our data and to see if any kind of relaxation peak appears within the studied frequency range with increasing or decreasing temperature.

We do think that a local dipole relaxation, arising from short-range hopping of quasifree charge carriers, must exist in all the ionic solids if it is not overlapped by some kind of nonlocal diffusion process. Indeed, a localized hopping process is likely to take place in all ionic solids

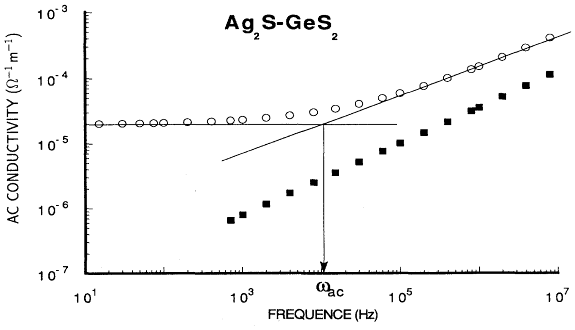

FIG. 3. Comparison of conductivities of $Ag_2S{\cdot}GeS_2$; in a usual configuration (empty circles) and in the configuration shown in Fig. 1 (filled squares) at room temperature.

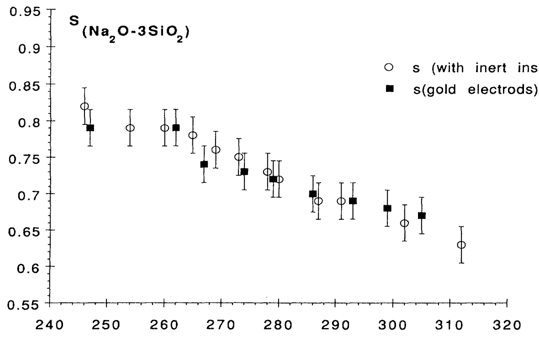

FIG. 4. Temperature variation of $s$ for $Na_2O\cdot 3SiO_2$ in both sample configurations.

since there are not only free charge carriers. From the data of Herous[25] and Namikawa,[26] we believe that this local mechanism exists in all cases even though it is only observed in cases of low ionic concentration glasses having very poor conductivity.

Although Lee *et al.*[27] did not mention any relaxation peak at all in both bi- and tri-lithium borate glasses, Wang and Nowick[22] reported two relaxation peaks in low concentrations in an yttria-doped ceria solid solution. The first one was ascribed to a local dipole polarization while the second, with the same activation energy as $E_{\sigma_{dc}}$, was obviously due to the dc conductivity. Likewise, Hong and Day[28] showed that, by TDSC experiment, sodium silicate glasses exhibit two peaks, assigned to local motions, for which the activation energies are lower than $E_{\sigma_{dc}}$. However, they also reported that these peaks could be strongly disturbed by high-temperature background due, once again, to $\sigma_{dc}$.

## III. DISCUSSION AND CONCLUSION

Although more experimental results are desirable, it appears, as far as we know, that neglecting the influence of the local dipole relaxation[29] led many authors to overlook the possibility that the frequency-dependent conductivity mechanisms could be basically different from $\sigma_{dc}$. It seems more and more reasonable to account for the ac conductivity by considering two kinds of ionic populations, hence two different frequency behaviors. The relation between both populations is not straightforward. However, neglecting, initially, the possible interdependence does allow proper treatment of the experimental data. Even if both conductivities are based on hopping processes, the scales remain different. In fact, as indicated by the Ngai relation,[30] both mechanisms lead to two distinct activation energies, one for a microscopic or local noncoupling hopping process and a second for a long-range hopping and diffusion mechanism, which take into account correlations and couplings between charge carriers. Likewise, two activation energies can be observed from the temperature dependence of the NMR $T_1$ spin-lattice relaxation time.[14] Meanwhile, we do not think these two activation energies are closely related via the parameters, which only depends on the dielectric properties of the material. It would be more prudent to simply write, as it has been often done, that $E_{\sigma_{dc}}$ is the sum of an activation energy $E_m$ of mobility and of an energy $E_c$ required to create free charge carriers from quasifree or bound ions. As we showed from the recent paper,[2,31] accounting for the polarization conductivity behavior in ionically conducting materials, $E_c$ may be determined by studying $\sigma'(\omega)$ itself and by using a "pair approximation" model. The $E_c$ activation energy may be then assimilated to the binding energy of the quasifree ion in its double potential well, that is, the energy required to extract the charge carrier from its site.

Nevertheless, investigations on $\sigma'(\omega)$ strongly rely on the thermal dependence of the parameter $s$ (Refs. 9, 32, and 33) which turns out to be the key issue of this study. However, up to now, discrepancies reported on the temperature dependence of $s$ does not lead to an obvious choice between various interpretations. Such an effort should be made and we think the simple experimental method presented here will allow a better determination of the value of $s$ and thereby will provide new insights to understanding the field of ac conductivity. Other experimental methods, such as TDSC and short transient current, should be used to complement our approach.

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[1] J. C. Guintini, J. V. Zanchetta, and F. E. G. Henn, Solid State Ionics **28-30**, 142 (1988).

[2] F. Buet, J. C. Giuntini, F. E. G. Henn, and J. V. Zanchetta, Philos. Mag. B **66**, 77 (1992).

[3] A. K. Jonscher, J. Mater. Sci. **13**, 553 (1978).

[4] S. R. Elliott, Solid State Ionics **27**, 131 (1988).

[5] R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **53**, 958 (1984).

[6] L. A. Dissado and R. M. Hill, Solid State Ionics **22**, 331 (1987).

[7] S. R. Elliott and A. P. Owens, Philos. Mag. B **30**, 777 (1989).

[8] K. Funke and R. Hoppe, Solid State Ionics **40-41**, 200 (1990).

[9] S. R. Elliott and F. E. G. Henn, J. Non-Cryst. Solids **116**, 1036 (1990).

[10] P. Mass, J. Petersen, A. Bunde, W. Dietrich, and H. E. Roman, Phys. Rev. Lett. **66**, 52 (1991).

[11] J. R. MacDonald, J. Appl. Phys. **61**, 700 (1987).

[12] See discussion session on glassy ionics, J. Non-Cryst. Solids **131-133**, 1113 (1991).

[13] A. Hunt, J. Phys. Condens. Matter **3**, 7831 (1991).

[14] C. A. Angell, Chem. Rev. **90**, 523 (1990).

[15] A. K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea

Dielectrics, London, 1983).

[16] D. P. Almond and A. R. West, Solid State Ionics **23**, 27 (1987).

[17] D. Ravaine and J. L. Souquet, Phys. Chem. Glasses **18**, 27 (1977).

[18] R. J. Charles, J. Appl. Phys. **32**, 1115 (1961).

[19] P. Abelard and J. F. Baumard, Phys. Rev. B **26**, 1005 (1982).

[20] G. P. Johari and K. Pathmanathan, Phys. Chem. Glasses **29**, 219 (1988).

[21] J. Vanderschueren and J. Gasio, *Thermally Stimulated Relaxation in Solids* (Springer-Verlag, Berlin, 1979).

[22] D. Y. Wang and A. S. Nowick, Phys. Chem. Solids **44**, 639 (1983).

[23] F. E. G. Henn, J. C. Guintini, F. Buet, J. V. Zanchetta, and J. Vanderschueren, J. Phys. (Paris) **2** (Suppl. 10), 145 (1992).

[24] D. P. Almond, Mater. Chem. Phys. **23**, 211 (1989).

[25] L. Herous, J. Appl. Phys. **29**, 1639 (1958).

[26] H. Mamikawa, J. Non-Cryst. Solids **18**, 173 (1975).

[27] W. K. Lee, S. Arason-Unger, A. S. Nowick, and H. J. Jain, J. Non-Cryst. Solids **44**, 197 (1990).

[28] C. M. Hong and D. E. Day, J. Am. Ceram. Soc. **64**, 61 (1981).

[29] B. Bates and J. C. Wang, Solid State Ionics **28-30**, 115 (1988).

[30] K. I. Ngai and S. W. Martin, Phys. Rev. B **40**, 10 550 (1990).

[31] F. E. G. Henn, D. A. Stevenson, N. Jiang, R. Buchanan, and W. Waschman (unpublished).

[32] A. Pradel and M. Ribes, J. Solid State Chem. **96**, 247 (1992).

[33] W. K. Lee, J. F. Liu, and A. S. Nowick, Phys. Rev. Lett. **67**, 1159 (1991).