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Electrical conductivity relaxation in lithium doped silver iodide

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Abstract

We report on electrical conductivity relaxation measurements of single crystal lithium doped silver iodide ($Li_xAg_{1-x}I$, $0 \le x \le 0.2$) by Admittance Spectroscopy, in the frequency range 20 Hz to 1 MHz and at temperatures between 270 and 330 K. A power-law frequency dependence of the ac conductivity is observed at low temperatures and/or high frequencies, which is characteristic of the effects of ion–ion correlation in ion hopping. An analysis of the frequency dependence of the electric modulus shows that the time decay functions for the electric field relaxation are well described by stretched exponential functions of the form $\exp[-(t/\tau)^{1-n}]$. By increasing lithium content, ionic conductivity values do not change significantly, but the exponent n is found to decrease from $n = 0.54$ (for $x = 0$) to $n = 0.23$ (for $x = 0.2$). This result points to weaker correlation effects among silver ions when the lithium content is increased.

Keyword: Ionic conductivity

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1. Introduction

Among ionic compounds, silver iodide is a typical example of a superionic conductor.[1] This material undergoes a first-order superionic transition at 420 K from the low-temperature β-AgI phase (thermodynamically stable below 420 K) to the α-AgI phase at higher temperature, while the ionic conductivity increases by more than three orders of magnitude at the phase transition. The α phase exhibits a highly disordered cation distribution, and an essentially rigid crystal framework provided by the anion sublattice.[2] Silver ions move easily through this structure with a low activation energy giving rise to high ionic conductivity values. A phenomenological theory was proposed by Huberman[3] which accounts for the temperature dependence of the conductivity. It is based on randomly distributed Frenkel pairs which are generated by Ag-ions leaving their normal sites and going to available interstitial sites when increasing temperature. However, the ionic conductivity in the low-temperature phase (the β-AgI phase) is not so well understood: Arrhenius plots of the dc conductivity of β-AgI by Cava and Rietman[4] show a curvature near the β-to-α phase transition which defies interpretations in terms of simple activated behavior, and no evidence has been found of a pretransition silver sublattice melting in the vicinity of the β-to-α phase transition. In other words, it is not known yet how the disorder in the Ag^+-sublattice may drive the transition to the fast-ion conducting phase with increasing temperature,[5] and open questions still remain regarding the silver ion dynamics, in particular concerning the existence and importance of ion–ion correlation effects in the ionic conduction process. Although ion–ion correlation effects on ionic conductivity have been extensively investigated in ionic glasses, where disorder is an intrinsic feature, and are known to be responsible for the non-Debye behavior of conductivity relaxation, not much attention has been paid to the study of the electrical conductivity relaxation at low temperatures in crystalline ionic conductors characterized by a positional disorder in the sublattice of mobile ions.[6]

On the other hand, doping AgI with other alkali salts has been a subject of research for decades looking for higher ionic conductivity values. It is well-known that alkali salts react with AgI to form other AgI-type solid electrolyte compounds, such us MAg_4I_5 ($M = K$, NH_4, Rb, $K_{1-x}Cs_x$) rather than form solid solutions.[7,8] Other salts, such as NaI, do not dissolve in AgI, although doping with NaI was found to stabilize the β-to-α phase boundary of AgI at 420 K.[9] Doping with alkali sites is expected also to modify the degree of positional disorder in the silver

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ion sublattice, and thus, these materials may also be helpful in providing information on silver ion dynamics and in determining the importance of ion–ion correlations in the ion hopping process.

We present here a study of the electrical conductivity relaxation in lithium doped single crystal silver iodide ($Li_xAg_{1-x}I$, $0 \le x \le 0.2$) by Admittance Spectroscopy measurements at temperatures below the solid electrolyte transition temperature in order to investigate the importance of ion–ion correlations. Admittance Spectroscopy measurements provide a direct way to investigate electrical conductivity relaxation in ionic conductors. At a given temperature, these measurements provide both conductivity and permittivity data as a function of frequency, and are widely used to obtain the response function for the electric field relaxation in the time domain.[10,11] It is well known that the asymptotic behavior of the response function at short times follows power laws of the form t^{-n} and then results in a dispersive conductivity depending on frequency as ω^n. Such a dispersive behavior of the conductivity has been interpreted as a consequence of ion-ion correlations in the ion conduction process, and the value of the exponent n has been proposed to be a measure of the degree of ion–ion correlations.[12] Within this framework the exponent n would be 0 for a totally uncorrelated ion hopping process, in which ions hop randomly and independently one from each other, and n would take larger values with the increasing importance of ion–ion correlations in ion dynamics. As stated above, doping silver iodide with alkali salts is expected to modify the degree of correlations among silver ions in the ion hopping process, and in fact we observe a significant increase in the value of the exponent n when the lithium content is decreased. This finding suggests that, when lithium content decreases, the positional disorder in the silver ion sublattice is favored, which might explain the enhanced correlations in silver ion motion.

2. Experimental

Single crystals of chemical composition $Li_xAg_{1-x}I$, $0 \le x \le 0.2$ were prepared by solvent casting technique. No further thermal treatments were made to the samples before measurements. Silver electrodes were painted in the samples for electrical measurements. Admittance Spectroscopy measurements were performed in the frequency range 20 Hz to 3 MHz using precision LCR meter HP4284A, and at different fixed temperatures between 270 and 330 K. Measurements were carried out under a N_2 gas flow to ensure an inert atmosphere.

3. Results and discussion

The frequency dependence of the electrical conductivity $\sigma^*(\omega)$ in ionically conducting materials can be usually well described by using the Jonscher expression[13]:

$$\sigma^*(\omega) = \sigma_0 \left[1 + \left(\frac{j\omega}{\omega_p}\right)^{n_J}\right] \qquad (1)$$

where σ_0 is the dc conductivity, ω_p is a characteristic relaxation or crossover frequency, and n_J is a fractional exponent between 0 and 1. Thus, a non-dispersive dc conductivity σ_0 is expected for $\omega \ll \omega_p$ and a crossover to a power-law dependent ac conductivity of the form ω^{n_J} when the frequency is increased. Fig. 1 shows the frequency dependence of the real part of the ac conductivity $\sigma'(\omega)$ at several fixed temperatures for the sample of composition $Li_{0.2}Ag_{0.8}I$. As expected, a power-law dependence is observed at the highest frequencies and a crossover to a non-dispersive *dc* regime occurs at lower frequencies, with the crossover frequency ω_p increasing with temperature. The values of the dc conductivity can be readily obtained from the frequency independent plateaus showed by these isothermal data sets at the lowest frequencies. An Arrhenius plot of the dc conductivity is shown in the inset of Fig. 1, where it can be observed that dc conductivity is thermally activated. A linear fit to these experimental data gives an activation energy $E_\sigma = 0.50 \pm 0.02$ eV for the ionic conductivity. The inset also shows for comparison the dc conductivity values of an additional sample with a lower lithium content ($x = 0.0025$) and those of undoped silver iodide (AgI). It can be observed from the figure that ionic conductivity does not change significantly when doping silver iodide with lithium up to $x = 0.2$. This result discards a mixed alkali effect[6] in the ionic conductivity and points to silver ions as the effective charge carriers. Moreover, this result points to the number or fraction of silver ions that contribute to the dc ionic conductivity at these temperatures below the superionic transition is small, and remains essentially constant when increasing lithium content up to $x = 0.2$.

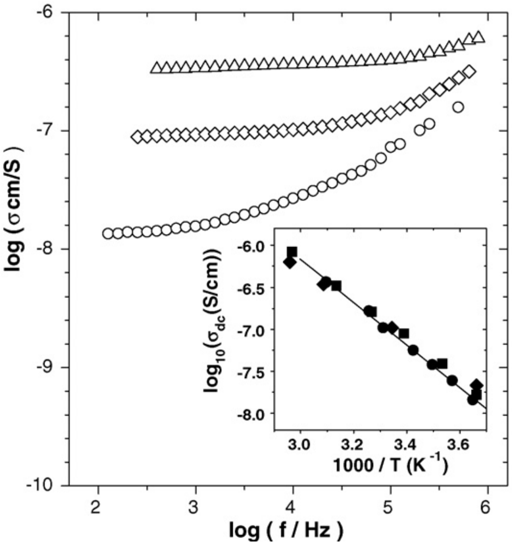

Fig. 1. Main panel shows the frequency dependence of the real part of the conductivity at several temperatures (323 K (△), 302 K (◇) and 274 K (○)) for a lithium doped silver iodide single crystal of composition $Li_xAg_{1-x}I$ with $x = 0.2$. An Arrhenius plot of the dc conductivity is shown in the inset for the same sample (●), for a lower lithium content, $x = 0.0025$, (▲) and for undoped silver iodide, AgI (■).

An alternative way to analyze ion dynamics in ionic conductors from Admittance Spectroscopy measurements is to use the so-called electric modulus formalism, which provides a time domain image of the effects of ion–ion correlations on the conductivity relaxation.[14–17] The electric modulus $M^*(\omega)$ is related to the conductivity $\sigma^*(\omega)$ and permittivity $\varepsilon^*(\omega)$ through $M^*(\omega) = 1/\varepsilon^*(\omega) = j\omega\varepsilon_0/\sigma^*(\omega)$, with ε_0 the permittivity of vacuum. It is straightforward to obtain the time decay function $\Phi(t)$ of the electric field inside the material at a constant displacement vector from the experimental admittance data in the frequency domain. The electric field decay function $\Phi(t)$ is related to the frequency dependence of the electric modulus by the following expression:

$$M^*(\omega)=\frac{1}{\varepsilon^*(\omega)}=\frac{1}{\varepsilon_\infty}\left[1-\int_0^\infty\left(-\frac{\mathrm{d}\Phi}{\mathrm{d}t}\right)\exp^{-\mathrm{j}\omega t}\,\mathrm{d}t\right], \qquad (2)$$

where ε_∞ is the high-frequency dielectric permittivity.[12–14] Kohlrausch–Williams–Watts (KWW),[11] "stretched" exponential decay functions of the form:

$$\Phi(t)=\exp\left(-\left(\frac{t}{\tau}\right)^{1-n}\right) \qquad (3)$$

are observed in ionically conducting materials, where τ is a thermally activated characteristic relaxation time for the hopping ion dynamics, and $0 \le n < 1$. Disordered materials like ionically conducting glasses and polymers show this "stretched" exponential behavior in the electrical conductivity relaxation, showing the importance of ion–ion correlations in the ion hopping process.[18,19] The parameter n has been proposed to be close to 1 for strongly correlated ion motion and equals to 0 for completely random and independent Debye-like ion hops.[20]

Fig. 2 shows electric modulus plots, as a function of frequency and at several temperatures, for the sample of composition $\mathrm{Li_{0.2}Ag_{0.8}I}$. It can be observed that the imaginary part of the electric modulus, $M''(\omega)$, shows an asymmetric peak which can be fitted to expressions (2) and (3). It is interesting to note the nearly absent "constant loss" contribution in experimental data,[21,22] which is ubiquitous in ionic conductors and thus always results in a departure of experimental data from KWW fits at enough high frequencies and low temperatures. Solid lines in the figure are best fits to a KWW relaxation function, and the parameter n can be obtained from these fits. Note that n values are obtained from these KWW fits over the whole frequency range (about four orders of magnitude) and not only from the high frequency branches of electric modulus peaks. We want to emphasize that it is the value of the exponent n which accounts for the width of the peaks in the imaginary part of the electric modulus, and this width is fairly well resolved from the experimental data. Interestingly, the value of n is found to decrease when increasing the lithium content in the sample. Fig. 3 shows the electric modulus spectra at room temperature for three samples with different lithium content. By simple inspection of the peaks in the log–log plots of Fig. 3 one can see that, while the slope of the low frequency side of the peaks is about 1 for the different samples, the negative slope at the high frequency sides increases with lithium content, and the peak becomes narrower. We would like to emphasize that the value of the high frequency permittivity, ε_∞, has no influence on the change of the shape of the modulus peaks, since it remains almost constant $\varepsilon_\infty = 7 \pm 1$ independent of temperature or lithium content. As a consequence, the stretched exponential parameter n, obtained from the fits to Eqs. (2) and (3), decreases strongly when increasing the lithium content x in $\mathrm{Li}_x\mathrm{Ag}_{1-x}\mathrm{I}$, taking values $n = 0.54 \pm 0.01$ for $x = 0$, $n = 0.41$ for $x = 0.0025$, and $n = 0.23 \pm 0.01$ for $x = 0.2$. As afore mentioned, there are different models [8–10,12] that have proposed that the exponent n describes the non-Debye or "stretched" exponential relaxation, and it is determined by the slowing down of the electrical conductivity relaxation process as a result of correlated ion hopping. Thus, the observed decrease of n when doping silver iodide with lithium ions points to a smaller degree of ion–ion correlations in silver ion motion. Since ion–ion correlations are expected to be enhanced for a higher degree of disorder in the mobile ion sublattice, we speculate on the

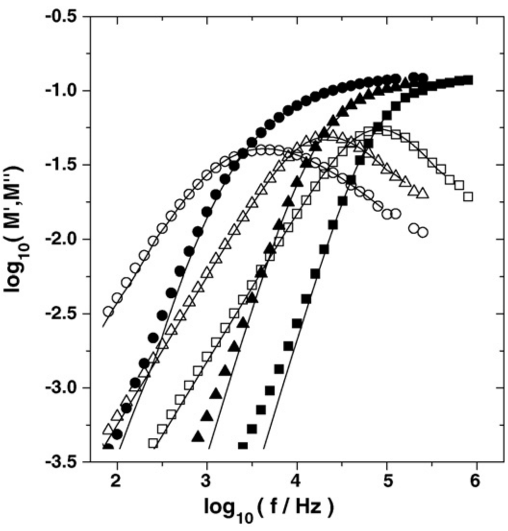

Fig. 2. Frequency dependence of the real part (solid symbols) and the imaginary part (open symbols) of the electric modulus for $\mathrm{Li_{0.2}Ag_{0.8}I}$, at several temperatures: 323 K (■, □), 302 K (▲, △) and 274 K (●, ○). Solid lines represent best KWW fits.

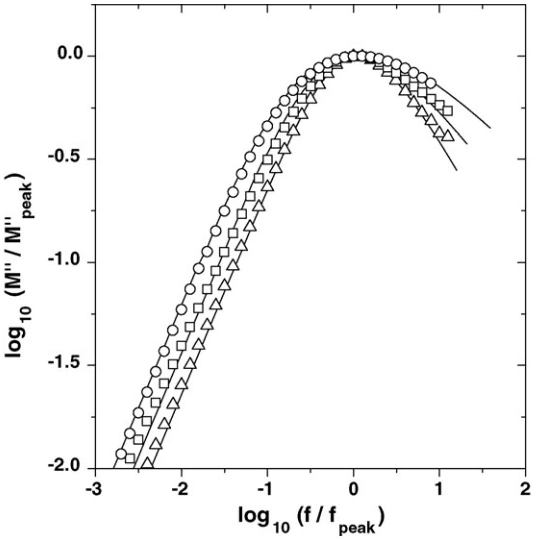

Fig. 3. Frequency dependence of the imaginary part of the electric modulus at room temperature for $\mathrm{Li}_x\mathrm{Ag}_{1-x}\mathrm{I}$ with different lithium contents: $x = 0.2$ (△), $x = 0.0025$ (□) and $x = 0$ (○). Experimental data have been normalized to peak height and peak frequency values in order to compare the different peak widths. The solid lines represent best KWW fits.

possibility of a reduction of positional disorder in the silver ion sublattice when increasing the lithium content as the reason for the observed behavior in the electrical conductivity relaxation. Raman and NMR techniques have been shown to be appropriate to study structural disorder and ion dynamics in other ionically conducting materials,[23] and such measurements are currently under way to further investigate this issue.

4. Summary

We have performed electrical conductivity relaxation measurements of lithium doped single crystal silver iodide at temperatures below the superionic transition and investigate the possible existence and importance of ion–ion correlation effects in the ion diffusion process. Conductivity and electric modulus plots were obtained as a function of frequency, at fixed temperatures, by Admittance Spectroscopy measurements. We have found that in all cases conductivity relaxation is well described by stretched exponential functions characterized by a fractional exponent n whose value decreases significantly by increasing lithium content. According to different well established models for explaining conductivity relaxation in ionic conductors, we interpret our results in terms of the decrease in the degree of ion–ion correlations among mobile silver ions when increasing the lithium content.

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