이온 전송 및 고주파 유전 흡수

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Ion Transport and High Frequency Dielectric Absorption

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Abstract : Molecular Dynamics (MD) simulations have been used to model the dynamics of the charge-compensating sodium ions in the non-stoichiometric hollandite $Nax(Ti_{8-x}Cr_x)O_{16}$. These interstitial ions reside in 'tunnels' in the crystal structure and move under the forces of both the ions making up the cage structure and the many body interactions of the other sodium ions in the tunnel. The Velocity Autocorrelation Function (VAF) of the sodium ions is calculated for a range of temperature from 250K to 1000K and converted into the linear ac-conductivity and ac-susceptibility response via Fourier transformation. A peak is found in the conductivity around $6x10^{12}$ Hz that has some of the character of a Poley absorption. Here it is shown to be due to an harmonically coupled site vibrations of the sodium atoms, which extend only over a limited range. At frequencies below the peak the conductivity tends towards a constant i.e. dc value corresponding to a constant flow of ions through the simulation cell. At high temperatures the conductivity due to this ion transport process behaves like a metal with an insulator to metal transition occurring around a specific temperature.

Key Words : Molecular dynamics, Charge-compensating sodium ions, Non-stoichiometric hollandite

1. Introduction

The fast ion conductor $Na_x(Ti_{8-x}Cr_x)O_{16}$ [1,2] is a non-stoichiometric material in which a fraction of the 4-valent titanium ions in a TiO_2 crystal are replaced by 3-valent chromium ions with the charge balance maintained by the presence of interstitial sodium ions that reside in 1-dimensional tunnels. In the present work the value of x is 1.7. Since only a fraction of the titanium ions are replaced not all of the possible sodium binding-sites along the tunnel are occupied by the sodium ions, i.e. there are empty sites between regions of occupied sites. This is rather like the situation in an ionic liquid with the difference that there are specific potential wells for the sodium (Na+) ions imposed by the structure of the crystal cage. The system therefore represents a simplified model for an ionic liquid confined to a very narrow pore. Our previous work [3] has shown that in the high-field response of this kind of system Na+ ion site-vibrations couple together in groups. The empty sites however allow some ions to detach themselves from one group and attach themselves to another

This process causes any particular vibration group to have a finite lifetime, i.e. to be damped. The oscillation frequency of the group mode is dependent upon the number of ions taking part and lies below that of an isolated individual Na+ ion. This form of behaviour occurs at short times and gives rise to an overlapping set of damped resonances at frequencies in the $3x10^{10}$ Hz to $5x10^{12}$ Hz range. This behaviour dominates at low temperatures where the Na+ ions are confined to their binding sites for a long time. At longer times or higher temperatures the ability of the Na+ to transfer along the tunnel between vibration groups should yield a net charge displacement along the tunnel, i.e. a dc-conduction.

Here we use a molecular dynamics simulation to determine the *linear* response of the Na+ ion system from its natural fluctuations defined via the velocity auto-correlation function [4], rather than the driven effects under high field. The aim is to evaluate the extent to which the natural motions of the Na+ ions are restricted to local vibrations as compared to their contribution to a conductive flow along the tunnel.

2. Simulation Method

The simulation has been carried out using programs that we have written specifically for the purpose. The contribution of the crystal lattice to the potential surface of the sodium ions is that of a series of potential wells along the tunnel with primary binding sites next to the chromium ion and secondary sites nearby. A rigid-lattice approximation is used for the ions in the crystal lattice forming the tunnel so only the sodium ions are free to move. These ions therefore move on a potential surface that has a fixed

contribution from the surrounding cage and a contribution from the coulombic interactions with the other mobile sodium ions that varies in time as their separations change. The temperature of the sodium ion system is determined in the usual way by fixing the average kinetic energy of the sodium ions in each of their three degrees of freedom to be kT. Other than that no constraints are placed on the motions of the sodium ions, which take place under the influence of the net force acting on them.

3. Results and Discussion

Simulations were performed in the temperature range from 250K to 1000K. A discrete Fourier transformation of the resulting VAF's for the c-axis velocity component yielded the c-axis component of the linear ac-conductivity [4]. An example of the frequency dependence of the real conductivity component s'(w) is shown in Fig. 1, where a peak can be seen at w ~ 3 10^{13}rad/s. This is in the frequency region below the calculated vibration frequency of a single Na+ ion, and is where localised translation-vibration modes would be expected. As in our previous work at high fields [3] this response is treated as that of a damped oscillator, for which the frequency dependent susceptibility can be described by a Lorentzian function. At frequencies below the peak the conductivity shows a trend towards a constant value related to the ability of the Na+ ion system to sustain a net flow of charge displacement along the tunnel.

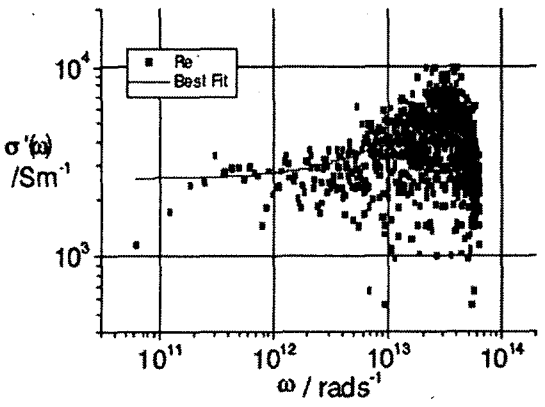

Fig. 1. Log-log plot of the c-axis component of s'(w) as a function of w, for T = 297K. The best fit to the Lorentzian function is shown by the continuous line.

The imaginary part of the susceptibility, χ"(ω) is related to the real ac-conductivity. Because of the scatter in data points following the discrete Fourier transform we determine its value from the fitted conductivity function, and an example is shown in Fig. 2.

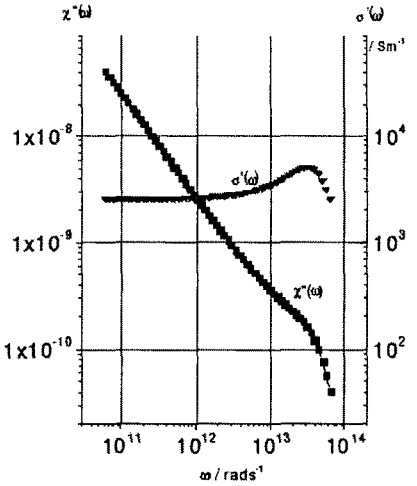

Fig. 2. The real part of the conductivity, σ'(ω) = ωχ" (ω) and the imaginary part of the susceptibility for T = 297K, plotted against frequency.

4. Conclusions

The Na+ ions oscillate in groups at low temperatures and short times with an oscillator lifetime determined by ion hopping between groups. At longer times and higher temperatures the ion hopping gives a metallic dc-conductivity and the Na+ system behaves as an ionic fluid.

Acknowledgement

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