

## Hollandite $\text{Na}_x(\text{Ti}_{8-x}\text{Cr}_x)\text{O}_{16}$ 의 이온 전송과 고유전율 특성

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### Ion Transport and High Frequency Dielectric of the Hollandite $\text{Na}_x(\text{Ti}_{8-x}\text{Cr}_x)\text{O}_{16}$

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**Abstract :** 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  $6 \times 10^{12}$  Hz that has some of the character of a Coley 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 (MD) simulations, charge-compensating sodium ion, non-stoichiometric hollandite, Velocity Autocorrelation Function

#### 1. Introduction

The fast ion conductor  $\text{Na}_x(\text{Ti}_{8-x}\text{Cr}_x)\text{O}_{16}$  [1, 2] is a non-stoichiometric material in which a fraction of the 4-valent titanium ions in a  $\text{TiO}_2$  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. This is rather like the situation in an ionic liquid with the difference that there are specific potential wells for the sodium ( $\text{Na}^+$ ) 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  $\text{Na}^+$  ion site-vibrations couple together in groups.

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  $\text{Na}^+$  ion. This form of behaviour occurs at short times and gives rise to an overlapping set of damped resonances at frequencies in the  $3 \times 10^{10}$  Hz to  $5 \times 10^{12}$  Hz range. This behaviour dominates at low temperatures where the  $\text{Na}^+$  ions are confined to their binding sites for a long time. At longer times or higher temperatures the ability of the  $\text{Na}^+$  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  $\text{Na}^+$  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  $\text{Na}^+$  ions are restricted to local vibrations as compared to their contribution to a conductive flow along the tunnel.

#### 2. Experiment

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.

The sites for these replacements are chosen at random. The charge-compensating sodium ions reside on average at interstitial sites within the same unit cell that contains a chromium ion. The location of these primary binding-sites depends upon that of the chromium ion within the cell [1,2]. Initial locations for the ions in the cage structure were obtained from x-ray analysis [2]. The size of the simulation cell is small compared to a macroscopic system and we would expect in reality the motions of ions near the ends of the simulation cell to be affected by those of neighbouring ions outside of the cell.

### 3. Result 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  $w \sim 3 \cdot 10^{13}$  rad/s. This is in the frequency region below the calculated vibration frequency of a single  $\text{Na}^+$  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.

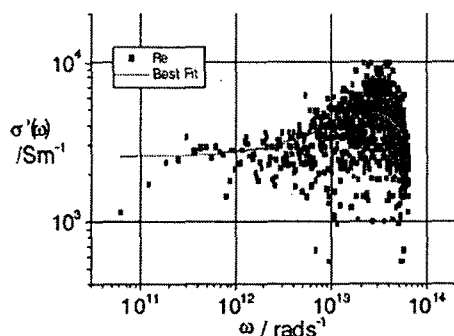


Fig. 1. Log-log plot of the c-axis component of  $s'(w)$  as a function of  $w$ , for  $T = 297\text{K}$ . The best fit to the Lorentzian function is shown by the continuous line.

In the present calculation the hopping is ionic and some energy is transferred from the vibrations to the dc-transport

process. For a Poley absorption due to polar molecules in suspension we would expect the hopping to lead to a relaxation response at lower frequencies since the mass transport of a neutral dipole does not lead to an electric current. It is suggested that the conductivity at frequencies below the resonance absorption peak, does not become constant but instead exhibits one or more fractional power law dependencies upon frequency.

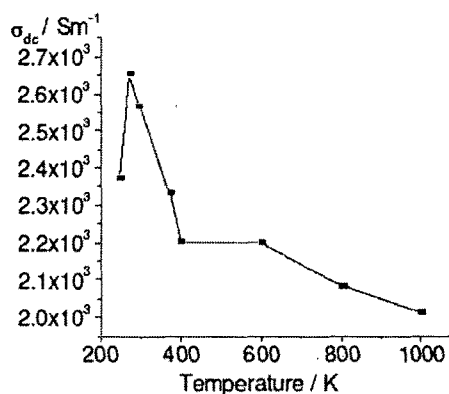


Fig. 2. Temperature dependence of  $s_{dc}$ .

### 4. Conclusion

The  $\text{Na}^+$  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  $\text{Na}^+$  system behaves as an ionic fluid.

### Acknowledgement

This work was finally supported by MOCIE program (R-2007-2-234-01).

### References

- [1] Y. Michiue and M. Watanabe, *Journal Physics Chemistry Solids*, vol. 57, pp. 547-551, 1996.
- [2] Y. Michiue and M. Watanabe, *Solid State Ionics*, vol. 79, pp. 116-119, 1995.
- [3] K. L. Khoo, L. A. Dissado, J. C. Fothergill and I. J. Youngs, Conf. Record of the 8th IEEE International Conference on Solid Dielectrics, (France), vol. 2, pp. 550-553, 2004.
- [4] R. Kubo, *J.Phys.Soc.Japan*, vol. 12, pp.570-586.