Molecular dynamics simulation of high frequency (10^{10} to 10^{12} Hz) dielectric absorption in the Hollandite $Na_x(Ti_{8-x}Cr_x)O_{16}$

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Abstract: The charge-compensating sodium ions that reside interstitially in the one-dimensional tunnels of the hollandite $Na_x(Ti_{8-x}Cr_x)O_{16}$ are used as a simple model for a fluid. Molecular dynamics are used to calculate the motions of the ions at a range of temperatures between 200 K and 373 K. The polarization response of the system to a step-up electric field is calculated for field strengths between 7.43 MV/m and 74.3 GV/m, and converted to an ac susceptibility. A resonance absorption is found, peaking at frequencies between$4.5x10^{10}$ and $8.8x10^{10}$ Hz at 297K. The origin of the response is shown to be the anharmonically coupled ion vibrations damped by ion hopping to neighbouring sites. The relationship of the result to the experimentally observed Poley absorption is explored, and a brief comparison of the calculated dynamics to previous theoretical models is made.

INTRODUCTION

Hollandite is a non-stoichiometric material that is based on a family of compounds of general formula $A_xM_{4-x}N_yO_8$. In these materials a fraction of the cations M are replaced by a cation in a different oxidation state N, with charge neutrality maintained by the presence of interstitial monovalent cations A. A special feature of their structure is the existence of one-dimensional (1-D) tunnels within which the interstitial ions are located at specific binding sites [1,2]. The material investigated here is a sodium priderite (titania-based hollandite, $Na_x(Ti_{8-x}Cr_x)O_{16}$, (x = 1.7) [2] in which Na^+ is the tunnel ion, see Fig. 1. The ions in the lattice cage produce a potential surface with minima at the binding sites about which the sodium ions vibrate. However because of the non-stoichiometric nature not all of the possible binding sites are occupied [2,3], and the sodium ions have some freedom to move from site to site. The sodium ions therefore behave rather like a "simple fluid" with each ion moving in a potential that fluctuates because of the changing interactions with the other sodium ions.

Each Na^+ ion forms a dipole with the counter ion in the lattice cage. Na^+ ion vibrations under the action of the co-operative forces of the cage and the other Na^+ ions correspond to dipole librations if restricted to the same binding site, while displacement of the ion from site to site corresponds to rotational hopping. Dissado and Hill [4] have presented a theory for dielectric relaxation that takes into account such cooperative many-body motions and it has been shown [5] that the theory predicts an additional absorption peak at frequencies of 10^{10} to 10^{12} Hz. Peaks such as this have been observed by Poley [6], Davies [7] and others [8,9] in both liquids and solids and have been named after Poley. The theories [5,6] suggest that this peak is caused by the cooperative librations of the dipoles. Here we use Molecular Dynamic (MD) simulations to see if such motions do indeed produce the predicted Poley absorption.

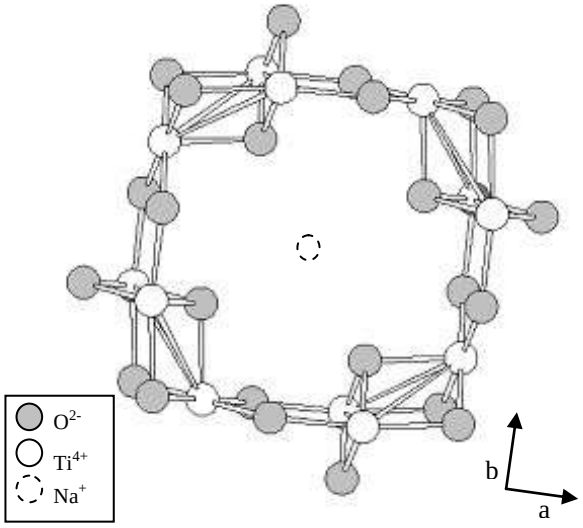


Fig. 1: Hollandite model projected slightly off the c-axis to give a clearer view of the 3-dimensional structure.

METHOD

The MD simulation has been carried out using programs that we have written specifically for the purpose. The potential between two ions is taken to have the form:

$$V_{ij}(r_{ij}) = \frac{\lambda}{r_{ij}{}^{p}} + \frac{z_i z_j e^2}{4\pi\varepsilon_0 r_{ij}} \qquad (1)$$

where z_i and z_j are the formal charge of *i*th and *j*th ions respectively, e is the unit charge, r_{ij} is the distance between the *i*th and *j*th ions. We have neglected the Van der Waals' contribution as negligible compared to the

coulombic potential. The parameters λ of the repulsive term for each ion-pair have been chosen to give as good an agreement as possible with the published 6-exponential potentials [2]. We have used a rigid-lattice approximation in which only the sodium ions are free to move. These ions are not restricted to the unit cell in which Cr^{3+} ion replaces a Ti^{4+} ion, they may also move to neighbouring cells if the site is unoccupied. Electrostatic interactions between the sodium ions along the tunnel lead to a fluctuating potential environment for the motion of the sodium ions.

Our hollandite model consists of 30 unit cells extended along the c-axis to form a single tunnel. Twenty four titanium ions are selected at random and replaced by chromium ions. Charge neutrality is maintained by an equal number of sodium ions. These preferentially reside at interstitial sites within the same unit cell that contains a chromium ion, whose location depends upon that of the Cr^{3+} ion within the cell [2,3]. Initial positions for the ions were taken from the results of the x-ray analysis structure refinement [3]. In our MD simulations the ion dynamics were calculated using a time step of 10^{-15}s, and reflective boundaries at the ends of the tunnel. The temperature of the system is defined via the kinetic energy of the sodium ions.

The system was found to equilibrate in 5000 time steps. Ten simulations were carried out initiating with different sets of Na^+ velocities, but with the same average kinetic energy, i.e. temperature. Mean locations for the Na^+ locations were obtained by averaging over the simulations. The time development of a polarization response was obtained by performing a simulation in which a step dc electric field along the c-axis was switched on at the 5001th time step. The resulting c-axis displacement of the Na^+ from their mean locations gives the polarization of the system, whose time development was followed for 95000 time steps (= 9.5 10^{-11}s). The starting conditions here were a mean of those in the ten simulations used to obtain the Na^+ locations. The polarization current dP/dt divided by the field strength gives the dielectric response function whose one-sided Fourier transform yields the linearized frequency dependent susceptibility $\chi = \chi' - i\chi''$ [10]. Simulations were performed for temperatures in the range 200 K to 373 K, and step fields of 7.43MV/m to 74.3 GV/m.

RESULTS

During the simulation the Na^+ ions may hop back and forth between neighbouring binding sites when they are unoccupied and vibrate in the binding site in which they reside, as shown in Fig. 2. The frequency dependence of χ', see Figs 3(a) and 3(b), show clearly that the response has the form of a broadened resonance in the frequency region around 5x10^{10} Hz. An absorption peak in χ'' is associated with this feature. This is the case for all temperatures and fields investigated.

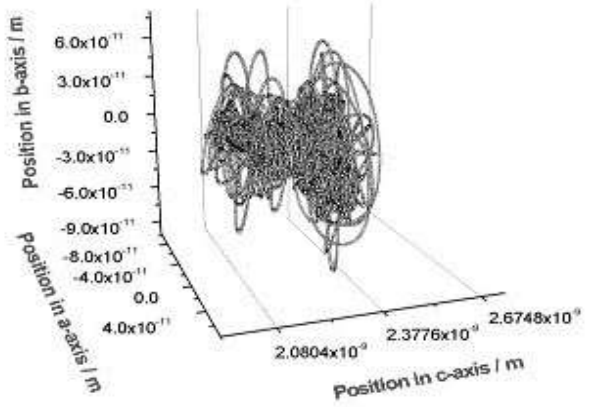


Fig 2: Trajectories of movement in three-dimensions of the 6th sodium ion in the hollandite model with a field of 743MV/m at 273K.

Resonance absorption in vibrating systems can be broadly classified as Gaussian, where there is a distribution of independent vibrations, and Lorentzian where a single fast vibration mode is damped by coupling to a range of slower vibrations. The many body nature of the forces in the Na^+ system imply that the Lorenztian should be the better description. Figures 3(b) and 3(c) show the best fits for χ' and χ'' respectively to the Lorentzian function, given in equations (2) and (3).

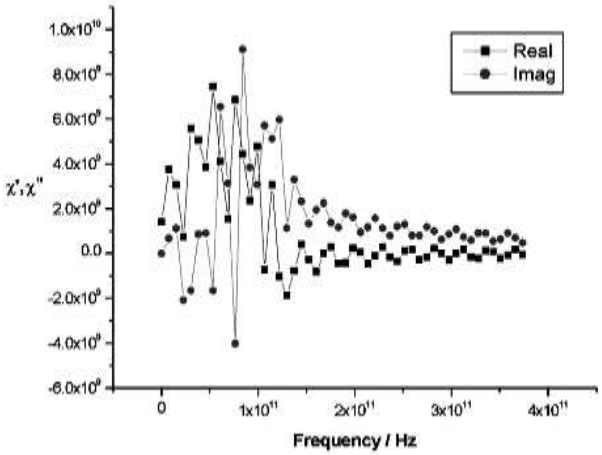
$$\chi''(x) = \frac{2A}{\pi}\frac{w}{4(x_c - x)^2 + w^2} \tag{2}$$

$$\chi'(x) = y_0 + \frac{4A}{\pi}\frac{x_c - x}{4(x_c - x)^2 + w^2} \tag{3}$$

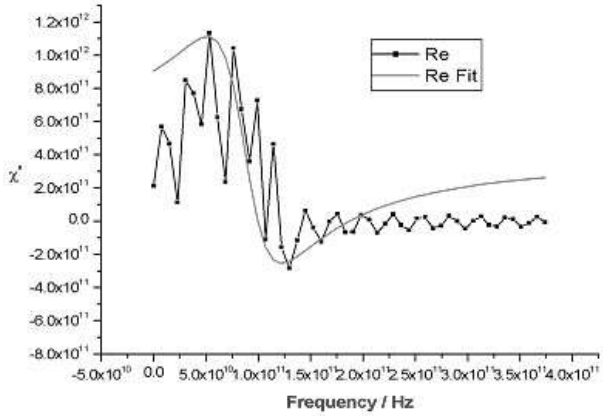
where x_c, w, A and y_0 are the parameters used for the resonant frequency, full width at ½ maximum, amplitude factor and constant respectively.

DISCUSSION

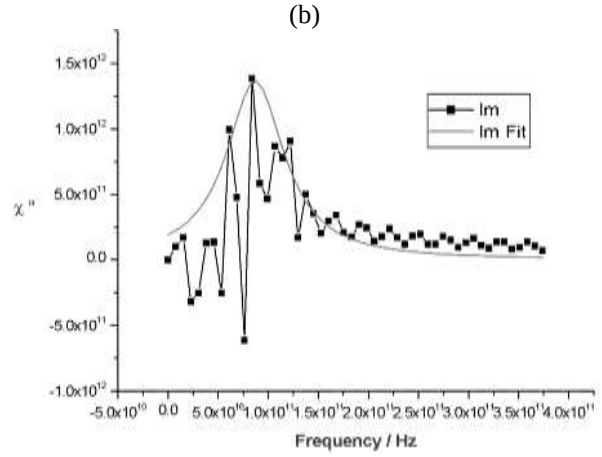
The hopping of charges between alternative sites is usually assumed to yield a relaxation peak at the hopping frequency [10]. Ionic vibrations are expected to take place at a much higher frequency and give a resonance behaviour [11]. Their influence on the hopping charges is regarded as an average series of impulses corresponding to thermal noise, giving a Debye peak. In contrast the theory of Dissado and Hill [4] envisages the hopping dipoles as coupled to displacements in the centres of motion of the vibrating system so that there is no separation between the hopping and vibration timescales. The hopping motion will then damp the extended vibrations giving a 10^{10} to 10^{12} Hz absorption peak in addition to a broadening of the relaxation peak.



(a)



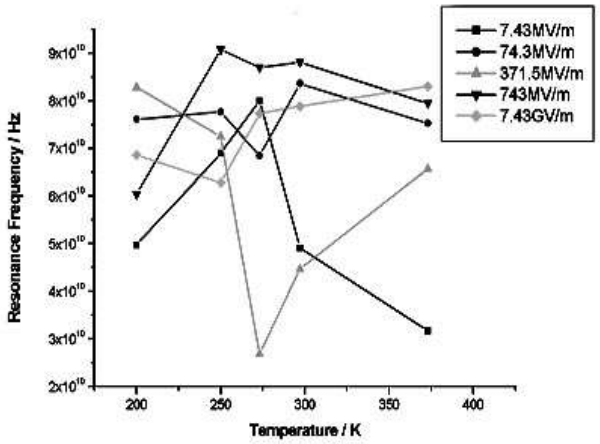
(b)



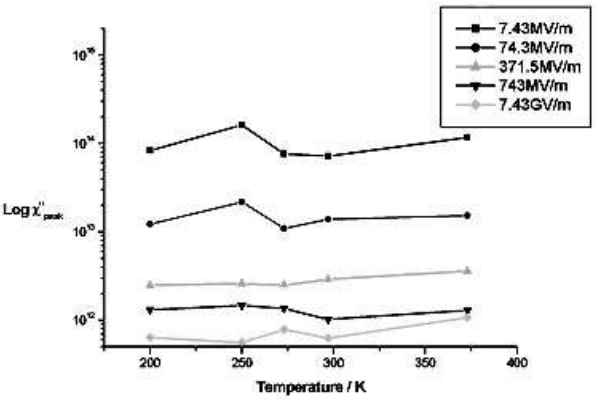
(c)

Fig. 3: (a) The real and imaginary parts of the susceptibility as a function of frequency with an electric field of 743MV/m at 273K. (b) The real part of the susceptibility with the best curve fitting to equation (3). (c) The imaginary part of the susceptibility with the best curve fitting to equation (2).

Simulation of the dynamics of a single Na^+ ion with the other ions held rigid as well as the lattice cage gives a harmonic vibration frequency of $4x10^{12}$ Hz. The simulated absorption peaks in χ" (resonance frequency) obtained for the complete ionic system lie between $4.5x10^{10}$ and $8.8x10^{10}$ Hz at 297K. Therefore the anharmonic coupling of the Na^+ motions has progressively connected larger groups of ions and extended the vibrations to lower frequencies as suggested by Dissado and Hill [4]. Ion hopping will break the connection of an ion with one cluster of coupled vibrations and link it to another, thereby providing the damped resonance-like behaviour observed in Fig. 3. The ion hopping can be taken to be equivalent to the friction between annulus and disc in the Itinerant Oscillator model [12], however this model treats the coupling between the oscillator and the vibrations as random impulses and does not include the anharmonic coupling we have shown to be important, as implied in [8].



(a)



(b)

Fig. 4: (a) The resonance frequency as a function of temperature (b) The peak of χ" as a function of temperature for a range of electric field (7.43MV/m – 7.43GV/m).

The absorption peaks obtained lie at the lower end of Poley's predicted range, which is typically observed in polar liquids in the 1.2 - 70 cm^{-1} ($3.6x10^{10}$ – $2.1x10^{12}$ Hz) region at room temperature [6]. It would therefore be reasonable to assume that our calculated absorption corresponds to what would be the Poley absorption for this material. However our calculated resonance frequency and resonance peak height are essentially independent of temperature, see Fig. 4 (a) & (b). In contrast Johari [8] deduced that the Poley absorption frequency in ice clathrate crystals decreased with an

increase in temperature and Noskova at al [13] obtained the same result from a restricted rotator model. Furthermore Johari [8] found that the resonance peak height increased with temperature whereas Noskova et al [13] found and absorption peak that decreased with the increase in temperature. Although the changes are small and possibly not detectable in our calculation it is therefore not certain that we can equate our calculated behaviour with the Poley absorption in liquids. It is possible that the high field required by our simulations has created a Poley-type behaviour, however the absorption decreased with an increase in field, Fig. 5, which suggests that it was not a consequence of the field strength. Also the correlation function approach used in the MD simulation of a similar material [14], gave a linear response peak around the same frequency.

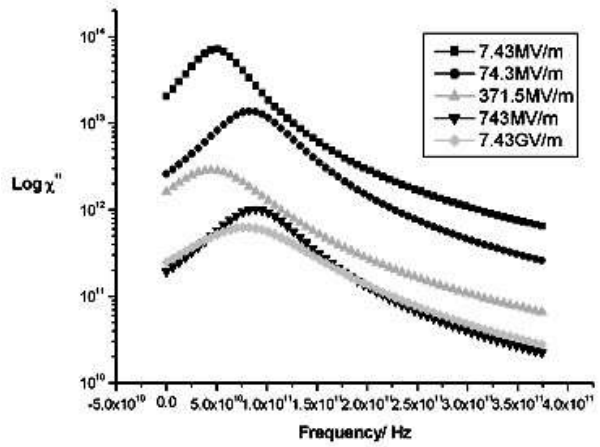


Fig. 5: Imaginary part of the susceptibility at 297K fitted to equation (2) has been plotted for a range of electric field (7.43MV/m – 7.43GV/m).

CONCLUSIONS

Anharmonic coupling between vibrating ions extends the vibration modes to lower frequencies and gives rise to a broad resonance in the frequency region between 4.5×10^{10} and 8.8×10^{10} Hz at 297K. The 'damping' associated with the resonance absorption was the result of ion hopping to unoccupied neighbouring sites, causing the ion to be disconnected from its original group vibration and connected to another. The calculated absorption frequency agreed well with Poley's prediction of an absorption typically observed in polar liquids in the 1.2 - 70 cm^{-1} (3.6×10^{10} – 2.1×10^{12} Hz) region at room temperature, but it could not be definitively assigned to this process because the predicted temperature dependence seems to be different from that found in experiment.

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