Analysis of ion conduction and relaxation in Na$_2$NbCdP$_3$O$_{12}$ glass

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Abstract. The ac conductivity of ionic conducting Na$_2$NbCdP$_3$O$_{12}$ is studied over the frequency range of 100Hz to 1MHz at different temperatures. The conduction mechanism of the material is studied using the concept of mismatch and relaxation (CMR) model and the length scale of the ion transport process is studied from the many particle displacement function <$R(t)^2$> for various temperature. The non-Debye relaxation mechanism and ionic conduction is analysed through the anomalous relaxation function and it is compared with CMR.

1. Introduction
The dynamics of mobile ion in ionic conducting disordered materials is one of the prime interests of physics and material research. AC impedance spectroscopy is one of the common experimental techniques used to study the dynamics of mobile ion in the applied electric field. It is quite complex to extract the clear picture of dynamics and relaxation of mobile ions. There are several empirical formulas and relaxation models are available to study the conduction mechanism and non-Debye electrical relaxation process [1]. Among them concept of mismatch and relaxation (CMR) [2] and anomalous relaxation function [3, 4] are relatively new models.

Na$^+$ superionic conductors (NASICON) have a major role in electrochemical research due to their wide applications such as batteries, gas sensors, fuel cells etc [5]. Niobium based phosphate (Na$_4$NbP$_3$O$_{12}$) glass have an appreciable ionic conductivity even at room temperature. In the present study the ac electrical data of NASICON type Na$_2$NbCdP$_3$O$_{12}$ glass is investigated for ion conduction mechanism using the CMR and anomalous relaxation models, then the physical picture and limitations of these models are studied and compared.

2. Experiment
The ion conducting NASICON type glass Na$_2$NbCdP$_3$O$_{12}$ were synthesized by melt quenching method from the analytical grade of Na$_2$CO$_3$, Nb$_2$O$_5$, CdO and NH$_4$H$_2$PO$_4$. The sample was characterized with XRD, FT-IR and DSC and it was reported earlier [6]. The ac impedance measurements were carried out in the frequency range of 100Hz to 1MHz using HIOKI-3532 LCR Hi-TESTER over the temperature range 393K to 513K. The real part of complex conductivity can be obtained from the impedance data using $\sigma'(\omega)=G(\omega)\times d/S$, where d is the thickness and S is the area of cross section of the sample. G(\omega) is the conductance of the sample obtained by using LCR meter.

3. Electrical relaxation and ion transport
Several representations of impedance spectroscopic data are used to study the electric relaxation mechanism worldwide. Many models are formulated based on the ac conductivity behavior, and it is the most used representation for ionic conducting materials. The ac conductivity data of most of the materials shows the similar feature that the real part of conductivity shows a frequency independent character for low frequencies and above certain characteristic frequency the conductivity shows frequency dependence and the characteristic frequency increases with increase of temperature. Correspondingly complex impedance shows a depressed semicircle which is the signature of the non-Debye relaxation [5]. The Na$_2$NbCdP$_3$O$_{12}$ glass sample also shows the similar feature.

3.1. Concept of mismatch and relaxation

The CMR model explains the ac conductivity dispersive regime as a consequence of correlated forward backward jumps of mobile ions. Due to the mutual repulsive interaction, the mobile ions will retain some distance each other. A mismatch of arrangement of ions will occur due to the jumping of ion to its neighboring site. This mismatch is reduced either by the rearrangement of neighboring mobile ions or by the backward jump of the ion to its original position. This leads to the correlated forward-backward jumps and consequently the dispersive regime in ac conductivity spectra. The CMR describes the ion dynamics mathematically by two coupled rate equations

$$\begin{align*}
-\frac{dg(t)}{dt} &= A_g^4(t)W(t) \\
-\frac{dW(t)}{dt} &= -BW(t)\frac{dg(t)}{dt}
\end{align*}$$

(1)

where $W(t)$ is time dependent correlation factor which represent the probability of an ion to be still in the new position occupied directly after the jump and $g(t)$ normalized mismatch function which describes a normalized distance between the actual position of an ion and the position where its neighbors expect it to be. The function $g(t)$ varies with time as $g(0)=1$ to $g(\infty)=0$. CMR is a model which incorporates the high frequency plateau in the ac conductivity $\sigma(\omega)$. The parameter $A$ is an internal frequency proportional to high frequency limit of the conductivity $\sigma(\omega)$, and $B$ determines the ratio $\sigma(0)/\sigma(\infty)=\exp(-B)$ and $K$ is the shape parameter which is mostly close to 2. The ac conductivity is related with the correlation factor by linear response theory as

$$\sigma(\omega) = \sigma(\infty) \left(1 + \int_{0}^{\infty} \frac{dW(t)}{dt} \cos(\omega t) dt \right)$$

(2)

The model shows a good microscopic picture of ion dynamics through “single particle route” and “many particle route” [2].

Experimental result of the ac conductivity of the sample is best fitted for the equation (1) and (2) of CMR model for various temperatures and it is shown in figure 1. The parameter $K$ shows temperature independence with a value $K=2.1$. $\sigma(\omega)$ and hence parameter $A$ increases with increase of temperature. The high frequency plateau is not observed in glass, since the vibrational contribution dominates to the hopping motion of ions at high frequency. The $W(t)$ and $g(t)$ response with time for the sample at 423K is shown in figure 2. Information on the length scales of ion transport process can be obtained from mean-square displacement. Many particle displacement function $<R^2(t)>$ is proportional to the mean-square displacement of the center of charge of the mobile ions by definition. Through linear response
theory, the microscopic property of the material \(<R^2(t)\rangle\) can be obtained from real part of conductivity as [7]

\[
\langle R^2(t) \rangle = \frac{12k_B T}{Nq^2} \int_0^t \frac{d\tau \sigma'(\tau)}{\tau} \sin(2\pi \omega \tau) d\tau \tag{3}
\]

Where \(k_B\) is the Boltzmann constant, \(N\) is the carrier density, \(q\) is the charge of the carrier and \(T\) is absolute temperature. \(<R^2(t)\rangle\) for the sample Na\(_2\)NbCdP\(_3\)O\(_{12}\) at different temperature is obtained from \(\sigma'(\omega)\) using equation (3) and it is shown in figure 3. At longer time scale \(<R^2(t)\rangle\) is linearly dependent on time, this is the characteristics of random walk motion of mobile ions and it corresponds to a frequency independent conductivity. In short time scale \(<R^2(t)\rangle\) shows sublinear dependency on time which reflects the forward-backward correlations in ion dynamics and it corresponds to the dispersive region of ac conductivity. Crossover length \(\xi\) is defined as the average distance that the ions have to cover in order to overcome the forces causing backward correlation. \(\xi\) increases with the increase of temperature and its order is a few Angstrom for the sample and it is shown in inset of figure 3.

3.2. Anomalous relaxation function

Anomalous relaxation model has the relaxation function \(\phi^*(t) = \exp(-t/\tau^*)\) with \(\tau^* = \tau_D/(i\tau_D)^{1-g}\), \(i = \sqrt{-1}\) and \(0 < g \leq 1\), where \(\tau_D\) is the Debye relaxation time. The non-Debye response is the consequence of the parameter \(g\). In the impedance representation the model has the simple functional form

\[
Z^* = R/(1 + i\omega \tau_D)^g \tag{4}
\]

where \(R\) is the bulk resistance. When \(g = 1\) the relaxation mechanism will be Debye type and the imaginary part of the relaxation time vanishes. The model has the functional form \(\sigma^*(\omega) = \sigma_0 (1 + i\omega \tau^*)\) in conductivity representation. According to the model collective motions of hopping ions due to ion-ion interaction are non-random process and it is attributed trapping of charge carriers in disordered host lattice and it is accounted in terms of exponent \(g\). During conduction the ion have to go through several reiterated forward backward ion hopping. The phase factor \(i^{(1-g)}\) slows down the \(\tau_D\) by the factor of \((1/\tau_D)^{1-g}\) which incorporate the non-Debye response [3, 4]. The parameters of the model is extracted by fitting complex impedance data with equation (4) and it is shown in figure 4(a)&(b).
conductivity and hopping are thermally activated process which shows Arrhenius behavior is shown in figure 5 and figure 6. The activation energy for conduction is $0.92 \pm 0.05\text{ eV}$ and for hopping $1.05 \pm 0.05\text{ eV}$. The exponent $g=1$ corresponds to the fast relaxation process of mobile charge carriers $n_c q$ and the exponent $0<g<1$ corresponds to slow relaxation process with $g n_c q$ hopping charges and $(1-g)n_c q$ trapped charge carriers. With increase of temperature the number of hopping charge is expected to increase. The sample has $g$ values which are independent of temperature, even though hopping charge may be increasing due to increase of free charge carrier $n_c$ with temperature. For hopping ion have to overcome a barrier energy of $E_h$, due to the interaction among the charges $g n_c q$ and $(1-g)n_c q$ it alters to $E_h-(gq)bE/2$ and $E_h+(gq)bE/2$, where $E$ is the applied field and $b$ is the hopping distance. The hopping rate of the charge carrier in fast process is given by $1/\tau^f=1/\tau_0 \exp(-E_h/k_BT)$ and for slow process $1/\tau^s=1/\tau_0 \exp(-gE_b/k_BT)$ where $E_b$ is the activation energy for fast hopping process.

4. Conclusion
The dynamics of Na$^+$ ion in the Na$_2$NbCdP$_7$O$_{12}$ is studied with the CMR and anomalous relaxation function. $<R^2(t)>$ and crossover length strengthen the concept of ion dynamics. Both the models are commensurate with the linear response theory and dynamics contains similar features like forward-backward correlated hopping. The microscopic ion transport is mathematically formulated in CMR and shows a good physical picture, but it lacks physical interpretation of some parameter $K$ and it is relatively harder to handle for the experimental data due to mathematical complexities. Anomalous relaxation function gives simple functional form in all representations of complex impedance and it gives better physical picture in terms of hopping and trapped charges. Anomalous relaxation function quantitatively describes non-Debye relaxation and site energy variation through a single exponent $g$.

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