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Impedance Analysis of a.c. Conductivity of $Rb_4Cu_{16}I_{7+x}Cl_{13-x}$ Superionic Conductor

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Abstract

The Determination of Hopping Rates and Carrier Concentrations in $Rb_4Cu_{16}I_{7+x}Cl_{13-x}$ Superionic Conductor *Non-stoichiometric superionic conductor $Rb_4Cu_{16}I_{7+x}Cl_{13-x}$ has been synthesized by solid state reaction. The frequency response of frequency dependent conductivity have been measured by a.c. complex impedance bridge methods in the temperature range 200-460K K. The a.c. conductivity of superionic materials takes the form, $\sigma=\sigma(0) + A\omega^n$. The carrier hopping rate ω_p is obtained from the new expression $\sigma(0)= A\omega_p^n$, and the carrier concentration is estimated from $\sigma(0)$. The contribution of creation and migration terms to the activation energy from conduction may be determined from the thermal activation of $\sigma(0)$ and ω_p and the corresponding entropy terms quantified. In this paper , conductivity data is analyzed, to obtain the carrier concentration and hopping rates of $Rb_4Cu_{16}I_{7+x}Cl_{13-x}$*

Abstrak

Penentuan Waktu Loncatan *Hopping* dan Konsentrasi Pembawa Muatan Listrik pada Konduktor Superionik $Rb_4Cu_{16}I_{7-x}Cl_{13-x}$ *Konduktor superionik tidak-stoikiometrik $Rb_4Cu_{16}I_{7-x}Cl_{13-x}$ telah berhasil disintesa melalui reaksi padatan. Respon frekuensi konduktivitas arus bolak-balik telah diukur menggunakan metode jembatan impedansi kompleks pada daerah temperatur 200-460 K. Konduktivitas arus bolak-balik suatu konduktor superionik memiliki bentuk fungsional $\sigma=\sigma(0) + A\omega^n$. Waktu loncatan 'hopping' ω_p diperoleh dari ekspresi baru $\sigma(0)= A\omega_p^n$, sedangkan konsentrasi pembawa muatan listrik dapat diestimasi dari konduktivitas arus searah $\sigma(0)$. Kontribusi yang diakibatkan oleh pengaruh efek migrasi dan pembentukan pembawa muatan listrik terhadap enersi aktivasi konduksi ion bahan dapat ditentukan dari aktivasi termal $\sigma(0)$ and ω_p dan pengkuantifikasian suku-suku entropi. Pada tulisan ini disajikan analisis data konduktivitas untuk memperoleh konsentrasi pembawa muatan listrik dan waktu loncatan hopping ion pada $Rb_4Cu_{16}I_{7+x}Cl_{13-x}$.*

Introduction

Ionic solids have been a subject of study of physics for a long past. The transport in such materials is partly or wholly governed by ions. Such materials having high ionic conductivity are called fast ionic conductors and have found wide application in solid state devices such as batteries, capacitors, timers, pacemakers, etc. Recently, one of the technologically very important electrolyte material for all solid state batteries is the Cu-based battery. This battery utilizes the

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$Rb_4Cu_{16}I_{7-x}Cl_{13-x}$ compound as solid electrolyte. The non - stoichiometric superionic conductor of $Rb_4Cu_{16}I_{7-x}Cl_{13-x}$, first synthesized by Takahashi *et al* [1] has a room-temperature conductivity of 0.34 $\Omega^{-1}cm^{-1}$. So far this is the highest known room-temperature ionic conductivity of any superionic conductors. The conductivity of an ionic conductor is determined by both the concentration of the mobile ions and the rate at which they are able to hop from site to site in the material. The a.c. conductivity $\sigma(\omega)$ is found to vary with angular frequency ω as:

$$\sigma(\omega) = \sigma(0) + A\omega^n \qquad (1)$$

where $\sigma(0)$ is the d.c. conductivity, A is a temperature dependent parameter and n is found to take values 0 and 1. Jonscher [2] has suggested that this power law is a 'universal' property of materials that is related to the dynamics of hopping conduction. Almond *et al* have shown [3], that there is a simple relationship between $\sigma(0)$ and A. The conductivity $\sigma(\omega)$ can then be expressed as

$$\sigma(\omega) = K\omega_P + K\omega_p^{1-n}\omega^n \qquad (2)$$

Here K is a temperature dependent prefactor which relates $\sigma(0)$ and ω_P. From the theory of random walk, one obtains:

$$\sigma(0) = K\omega_P = (Ne^2a^2/kT)\gamma c(1-c)\omega_p \qquad (3)$$

where γ is geometrical factor, c is the concentration of mobile ions on N equivalent lattice sites per unit volume, a is the hopping distance, e is the electronic charge, k is the Boltzmann constant, T is the absolute temperature and ω_p is the hopping rate of ions. The above relationships have been used to analyze a.c. conductivity data from $Rb_4Cu_{16}I_{7-x}Cl_{13-x}$ superionic conductor.

Materials and Methods

The samples of $Rb_4Cu_{16}I_{7-x}Cl_{13-x}$ were prepared by solid state reaction. The appropriate quantities of CuCl, CuI and RbCl were mixed together, ground and pressed into pellets, and heated for 24 hours in - pyrex tubes and then quenched.Rietveld refinements of the x-ray diffraction intensities show x to be in the range between 0.1-0.2. Details of sample preparation and structural characterization have been presented elsewhere[4]. A.C. impedance measurements were performed using a high-precission LCZ meter (Hioki 3531Z-Japan) in the frequency range of 45 Hz - 1.0 MHz, in the temperature range 200 K - 460 K. Conductive silver paint is painted on the surfaces of the pellet samples to make good Ohmic contacts.

The powder samples for electrical conductivity were pressed at 700 $kgcm^{-2}$ into cylindrical pellets; the geometrical data is as follow, length is equal to 1.70 mm and the diameter is around 13.0 mm.

Results and Discussion

The conductivity data pattern at several temperatures for $Rb_4Cu_{16}I_{7+x}Cl_{13-x}$ is shown in Fig. 1. The experimental data at the higher temperatures and higher frequencies show a conductivity dispersion associated with electrode polarisation effects.

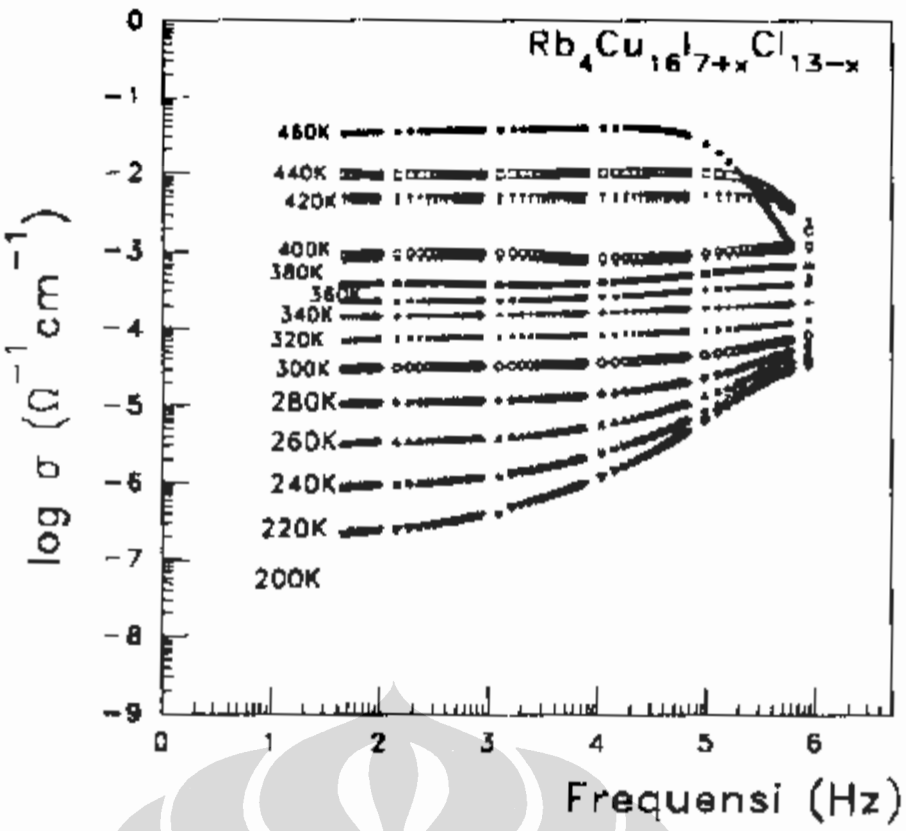

Fig. 1 Conductivity data for $Rb_4Cu_{16}I_{7-x}Cl_{13-x}$ at various temperatures.

From the graph in Fig.1, the values of d.c. conductivity, $\sigma(0)$, are estimated, and plotted in conventional Arrhenius format as $\sigma(0)$ vs. $1000/T$ in Fig.2., where T is the absolute temperature. a.c. conductivity data at 11 temperatures between 200 and 400 K were found to fit equation (1),using the values of $\sigma(0)$, A and n shown in table 1.

Table 1. Parameters obtained in fitting a.c. conductivity measurements of $Rb_4Cu_{16}I_{7-x}Cl_{13-x}$ to $\sigma(\omega) = \sigma(0) + A\omega^n$.

Temperature (K)	$\sigma(0)(\Omega^{-1}cm^{-1})$	$A(\Omega^{-1}cm^{-1}rad^{-1/n})$	n
200	5.15×10^{-8}	2.84×10^{-9}	0.65
220	1.95×10^{-7}	2.02×10^{-8}	0.51
240	7.95×10^{-7}	1.41×10^{-7}	0.37
260	2.91×10^{-6}	7.38×10^{-7}	0.25
280	1.00×10^{-5}	2.37×10^{-6}	0.15
300	3.00×10^{-5}	4.17×10^{-6}	0.08
320	6.00×10^{-5}	1.15×10^{-6}	0.05
340	1.2×10^{-3}		0.04
360	1.9×10^{-3}		0.06
380	3.3×10^{-3}		0.06
400	6.8×10^{-3}		0.02

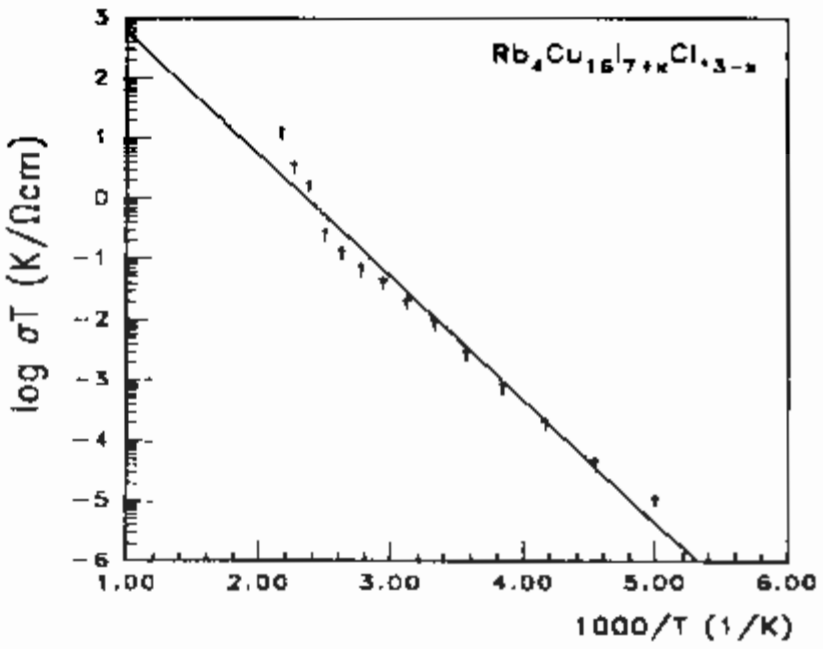

Fig.2. Arrhenius plot of the d.c. conductivity. The solid line is a least-squares fit to the data

The values of the parameter A are also shown plotted as AT vs. $1000/T$ in fig. 3. It was observed from table 1, that the values of $\sigma(0)$. A and n are strongly dependent upon temperature, albeit for n significant change is true only for temperatures below 300 K. similar to the situation in Na β-Alumina[5]. Both $\sigma(0)$ and A are therefore thermally activated, the calculated thermal activation energy E_a, are 17.0 kJ/mol (0.18 eV) and 17.2 kJ/mol respectively. These values are close to each other. The ion hopping rates ω_p are plotted in fig. 4 as function of temperatures. A considerable smooth slope change is observed for temperatures above 280 K. Kanno *et al*[6] reported smooth slope changes in the conductivity curves of $Rb_4Cu_{16}I_{7-x}Cl_{13-x}$ over a wide range of temperatures (110K-300K), due to structural changes in the sample. Detailed structural study using neutron diffraction techniques by the same author showed that the movement of a copper ion from a Cu(1) site through faces shared by tetrahedra to four neigbouring sites namely , the Cu(3) site, another Cu(1) site or one of two Cu(2) site constitutes the most likely ion conduction mechanism in the samples.

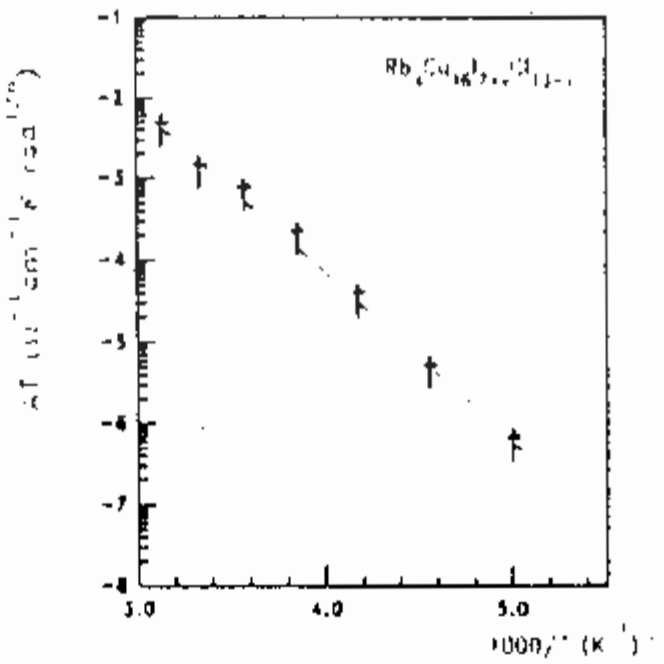

Fig. 3. Arrhenius plot of AT vs. $1000/T$ from the data given in Table 1.

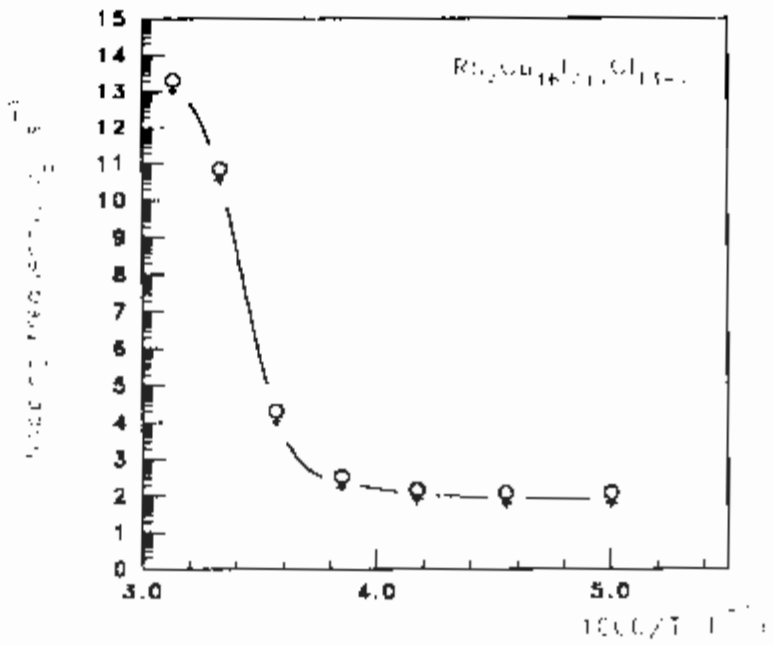

Fig. 4. Arrhenius plot of ion hopping rates ω_p.

Assuming temperature indepen - dence, the net carrier concentration C′=C(1-C)N could be estimated from equation [3], using the average value a = 1.611 Å and γ = 0.33,our estimate falls in the range ~ 8.5 - 16 %, roughly correspond to x values of 0.1-0.2.

In an earlier work, Almond *et al*[5] contended that dynamical properties of ionic materials like β-alumina , may be unified by the use of the "universal" dielectric response theory. In each case the response observed is attributed to the effects that many-body interaction amongst the ions have on relaxation processes. Dissado and Hill[7], have developed a microscopic theory which shows that in interactive many-body systems, dielectric perturbations decay after a short time as t^{n}, rather than exponentially with time t. This in the frequency domain, explains the ω^{n} dispersion in the conductivity, which has been suggested as a "universal" law by Jonscher. In this work it was shown that $Rb_4Cu_{16}I_{7-x}Cl_{13-x}$ appears to be an example whose response is in support of this theory. Furthermore, the strong dependence of conductivity on the frequency ω, especially at temperatures below 280 K, may be explained by the anomaly of excess heat capacity with a maximum at about 190 K, associated with noncooperative mechanism of Cu ions redistribution in the crystal lattice[6].

Conclusion

Using the analysis metods outlined above, we were able to utilize the dynamical characteristics of a.c. conduc - tivity, such as activation energies and ion hopping frequencies. D.c. contributions to the overall conductivity have been estimated, and power law relationships between conductivity and frequency have been established for $Rb_4Cu_{16}I_{7+x}Cl_{13-x}$.

Smooth slope-changes have been observed in the Arrhenius plot of ω_p vs. T. The physical origin of this behaviour may be attributed to copper ion redistribution mechanism in the crystal lattice, as well as to conduction ions interaction in the samples. The results presented in this work seem to support the "universal" law of dielectric response in superionic conductors.

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