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Dielectric relaxation and ionic conductivity studies of $[N(CH_3)_4]_2Cu_{0.5}Zn_{0.5}Cl_4$

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Abstract

The complex impedance of the compound $[N(CH_3)_4]_2Cu_{0.5}Zn_{0.5}Cl_4$ have been investigated in the temperature range 443–532K and in the frequency range 200Hz–5MHz. Dielectric data were analyzed using complex permittivity ε^* and complex electrical modulus M^* for the sample at various temperatures. The modulus plot can be characterized by full width at half height or in terms of a non-experiential decay function $\phi(t) = \exp(-t/\tau)^{\beta}$. The frequency dependence of the conductivity is interpreted in term of Jonschers law: $\sigma(\omega) = \sigma_{DC} + A\omega^n$. The conductivity follows the Arrhenius relation. Hopping frequency was determined and activation energy of hopping is almost equal to the activation energy of conduction. The Z' and Z'' versus frequency plots are well fitted to an equivalent circuit model. The circuits consist of the parallel combination of bulk resistance R_p and constant phase elements CPE.

Keywords: Dielectric measurements; AC conductivity; Hopping frequency; Equivalent circuit

1. Introduction

Considerable interest has been devoted to compounds of the general formula A_2MX_4 where A is an organic cation, M a divalent metal and X a halogen. Many of these compounds exhibit successive structural phase transitions, which are associated with the reorientational dynamics of the substituted ammonium group. Interest in these compounds is rapidly increasing, as some of them exhibit interesting structural and physical properties like ferro-electricity, ferro-elasticity and low dimensional magnetism [1–8].

Preparation, infrared and Raman spectra were reported at room temperature for $[N(CH_3)_4]_2Cu_{0.5}Zn_{0.5}Cl_4$ salt. The compound crystallizes in the orthorhombic system, space group $P2_12_12$, with $Z = 4$ and $a = 13.099(3)$, $b = 13.119(2)$ and $c = 11.812(3)$ Å [9]. The crystal structure consists of alternate organic–inorganic $[(TMA)^+/(Cu)ZnCl_4{}^{2-}]$ layers and organic sheets $(TMA)^{2+}$. All Organic groups and $(Cu)ZnCl_4{}^{2-}$ are not disordered. Its main geometrical features are those commonly observed in the atomic arrangements of $(TMA)_2ZnCl_4$ and $(TMA)_2CuCl_4$. The organic–inorganic layers are centred at $y \approx 1/4$ but the organic one are observed at $y = 0$ and $y = 1/2$ (Fig. 1).

In the present work, we report the results of the electrical impedance measurements. The temperature and frequency dependence of the dielectric proprieties of the compound is studied.

2. Experimental procedure

The title compound $[N(CH_3)_4]_2Cu_{0.5}Zn_{0.5}Cl_4$ was synthesized starting from precursor $N(CH_3)_4Cl$, $CuCl_2$ and $ZnCl_2$ of high purity (more than 99.9%). The precursors were weighted in the stoichiometric proportion conforming to the following equation then dissolved in the minimum quantity of water and finally mixed.

$$2(CH_3)_4NCl + 0.5CuCl_2 + 0.5ZnCl_2 \xrightarrow{H_2O} [(CH_3)_4N]_2Zn_{0.5}Cu_{0.5}Cl_4$$

The mixture was slowly evaporated at constant temperature 300 K. After one weak, crystalline samples were obtained.

The impedance spectroscopy was performed on pellet discs of about 8 mm diameter and about 1.6 mm in thickness. Electrical impedances were measured in the frequency range from 200 Hz to 5 MHz with the TEGAM 3550 ALF automatic bridge monitored by a micro-computer between 443 and 532 K.

Complex impedance data, Z can be represented by its real, Z' and imaginary, Z'' parts by the relation $Z^* = Z' - iZ''$.

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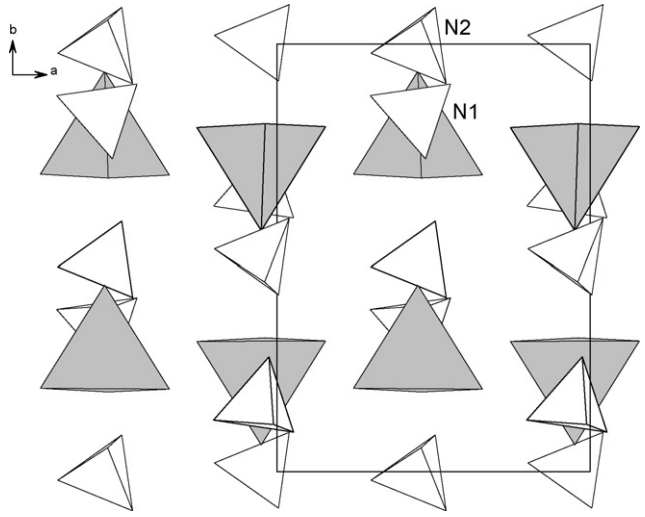

Fig. 1. [0 0 1] view of the structure of $[(CH_3)_4N]_2Zn_{0.5}Cu_{0.5}Cl_4$.

The equations for the dielectric constant, ε', the dielectric loss, ε'', the real electrical modulus M' and the imaginary electrical modulus M'' can be shown as

$$M' = -\omega C_0 Z'' \quad (1)$$

$$M'' = \omega C_0 Z' \quad (2)$$

$$\varepsilon' = \frac{M'}{M'^2 + M''^2} \quad (3)$$

$$\varepsilon'' = \frac{M''}{M'^2 + M''^2} \quad (4)$$

where $C_0 = \varepsilon_0 S/e$ and the ε_0 is the permittivity of the free space, S the electrolyte–electrode contact area, e the thickness of the sample ($e = 1.6$ mm) and $\omega = 2\pi f$, f being the frequency in Hz.

3. Results and discussion

3.1. Modulus studies

The variations of real M' and imaginary part of M'' of electrical modulus are depicted in Figs. 2 and 3, respectively. The value of M' reaches a constant value $M'_\infty = 1/\varepsilon'_\infty$ at high frequencies. At low frequencies, it approaches to zero. It can be seen that the interfacial effects tend to be eliminated in modulus representation [10]. M'' shows a slightly asymmetric peak at each temperature. The peak shifts toward higher frequencies with increasing temperature. The presence of such relaxation peaks in the M'' plots indicates that the samples are ionic conductors [11].

The frequency ω_c, at which the maximum of M'' occurs, defines the relaxation time τ_c by the relation $\tau_c\omega_c = 1$. The variation of the relaxation time with temperature can be described by an Arrhenius plot [12] and given as $\tau_c = \tau_0 \exp(E_c/kT)$ (Fig. 4), where E_c is the activation energy for the relaxation process ($E_c = 0.65(1)$ eV), k the Boltzmann constant and τ_0 is the pre-exponential factor ($\tau_0 = 1.28 \times 10^{-12}$ s).

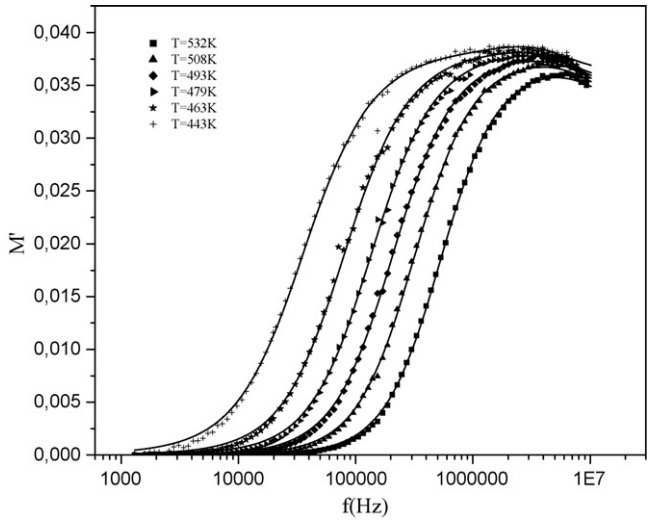

Fig. 2. Frequency dependence of the real part of electric modulus at several temperatures.

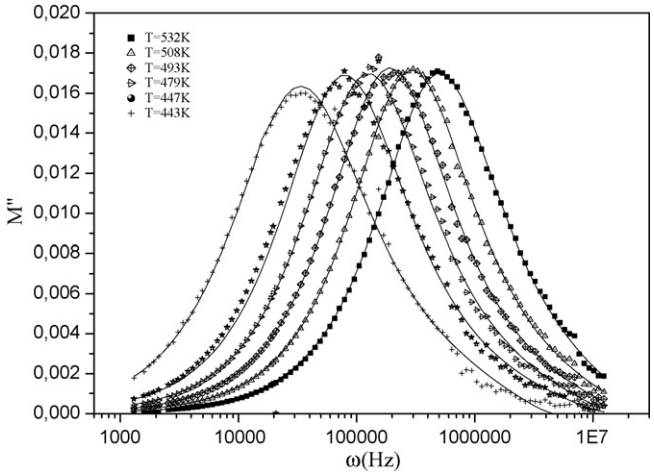

Fig. 3. Frequency dependence of the imaginary part of electric modulus at several temperatures.

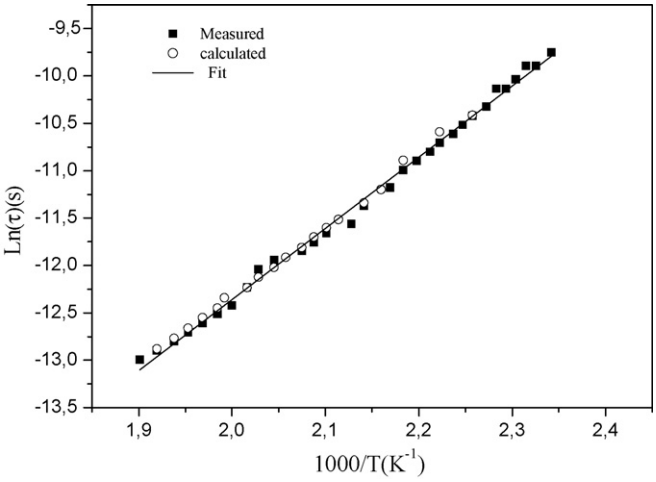

Fig. 4. Temperature dependence of relaxation time τ.