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Super-protonic phase transition and fast ionic conductivity of Li^+ in $[Li_{0.2}(NH_4)_{0.8}]_2TeCl_6$

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Abstract

The differential scanning calorimetry diagram of $[Li_{0.2}(NH_4)_{0.8}]_2TeCl_6$ showed one anomaly at 526 K accompanied with a shoulder at 505 K. The conductivity plot exhibits two anomalies at 496 and 526 K, which characterize the beginning and the end of the crossing to superionic conductor state. The low temperature conduction is ensured essentially by Li^+. A sudden jump confirms the presence of a superionic protonic transition related to the fast motion of Li^+ and H^+ ions. Above 526 K, the high temperature phase is characterized by high electrical conductivity ($10^{-3}\ \Omega^{-1}\ m^{-1}$) and low activation energy ($E_a < 0.3$ eV).

The dielectric constant evolution as a function of frequency and temperature revealed the same anomaly.

Transport properties in this material appear to be due to Li^+ and H^+ ions' hopping mechanism.

Keywords: Phase transition; Permittivity; Modulus spectroscopy; DSC

1. Introduction

Numerous hexahalometallates of formula A_2MX_6, where A is an alkali, B a tetravalent metal, and X a halogen, crystallize in the cubic K_2PtCl_6 (antifluorite) structure with space group $Fm\bar{3}m$. Many undergo one or more phase transitions [1]. Most investigations have been taken by spectroscopic or calorimetric methods [2], relatively few by diffraction while electrical conductivity studies have never been undertaken on these salts.

The low equivalent weight and the high electropositive nature of Li gives high cell voltage and energy density of advanced electrochemical devices, pave the way for an intense search of a good Li^+ ion conductor by a crystal chemical substitution retaining the basic antifluorite structure. Substitutional studies in the $[Li_x(NH_4)_{1-x}]_2TeCl_6$ system have indicated that the cubic crystal exists up to $x = 0.2$. The last was characterized by X-ray diffraction and examined by IR and Raman vibrational spectroscopy and DSC thermal technique [3].

In the present paper we report electric behaviour and phase transition nature of the $[Li_{0.2}\ (NH_4)_{0.8}]_2TeCl_6$ mixed compound. The partial substitution of Li^+, despite the low ratio, renders possible the superionic conduction in this material at high temperature.

2. Experimental

From the mixed solutions of LiCl, NH_4Cl and TeO_2 in conc. HCl with the molar ratio 1 : 1 : 1, bright yellow crystals grew within several days using a desiccator filled with conc. H_2SO_4 as water absorber. As the crystals of the hexachlorotellurate (IV) are very sensitive to moisture, they were protected by paraffin-oil.

The differential scanning calorimetry measurements were performed between 300 to 530 K with a DCS METTLER TA4000 at a heating speed of 10 K min^{-1}. Electrical impedances measurements were realized in the range 5 KHz–13 MHz using a Hewlett-Packard 4192 ALF automatic bridge monitored by a HP vectra microcomputer. Dense translucent pellets (8 mm in diameter, 1–1.2 mm in thickness) were used for measurements. The pellet was covered with graphite electrodes.

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3. Structural proprieties

The structure of this family of salts was first deduced by Wyckoff and Posnjak [4]. The Te atoms lie on the 4(a) sites of the $Fm\bar{3}m$ (O_h^5) space group with $a = 10.3572(16)$ Å, surrounded by an octahedron of chlorine atoms in the 24(e) positions with coordinates $(x,0,0)$ and $x \approx 0.2504$. The Li or N atoms occupy the 8(c) (1/4, 1/4, 1/4) sites, as shown in Fig. 1. The H atoms belonging to the ammonium group exhibit a three-fold disorder about [1 1 1]. The cohesion of the atomic arrangement is ensured by hydrogen and ionic bonding (N–H…Cl and Li^+–Cl^-).

Comparison with $(NH_4)_2TeCl_6$ compound lets us assume that the structure is amenable to extensive crystal chemical substitutions retaining the basic structure, by suitable modification of the framework cations: the larger unit cell volume and the extension of the cavity around Li/N atoms pave the way for a good Li^+ ion conduction.

4. Calorimetric study

A typical result of calorimetric study is presented in Fig. 2 which shows the diagram obtained while heating and cooling recently prepared crystals. The heating curve shows one endothermal and intense peak at 526 K accompanied by a shoulder at 505 K . The enthalpy of the sum is $\Delta H = 4.53$ J mol^{-1}. The cooling curve shows one transition at 514 K with an enthalpy equal to -2.6 J mol^{-1}.

5. Electrical proprieties

Dense translucent pellets (8 mm in diameter, 1–1.2 mm in thickness) were used for measurements. Graphite electrodes were deposited.

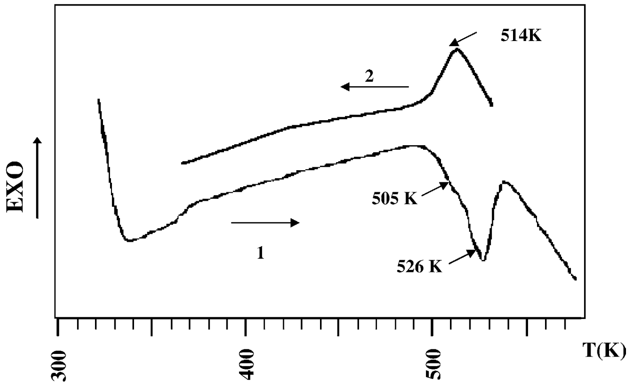

Fig. 2. Differential scanning calorimetry of $[Li_{0.2}(NH_4)_{0.8}]_2TeCl_6$. (1) Sample heating; (2) Sample cooling.

A combined analysis using both the complex impedance and the complex modulus formalisms present advantages over the earlier methods. This theme has been further developed in the present paper on the $[Li_{0.2}(NH_4)_{0.8}]_2TeCl_6$ material. Our measurements were realized in the temperature range 300 to 550K.

Some complex impedance spectra Z'' vs. Z' recorded at various temperatures are presented in Fig. 3. The complex impedance plane data show a non-depressed semi-circle for all frequency and temperature variations. This behaviour confirms that no electrode phenomenon is present. The resistance is determined by extrapolation at frequency equal to zero from the Z'' vs. Z' circle arc centred under the Z' axis because at this frequency the equivalent circuit of our material presents only a resistant behaviour. The coefficient $\alpha(0,33$ rad) which characterizes the deviation of the cole–cole from the Deby law is determined from the complex impedance spectrum.

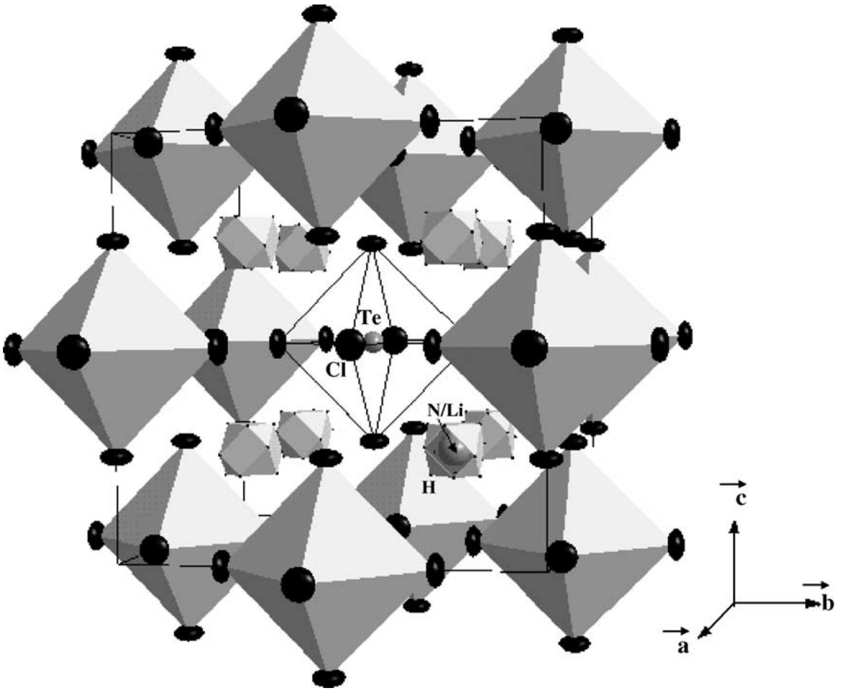

Fig. 1. Room temperature cubic unit cell of $[Li_{0.2}(NH_4)_{0.8}]_2TeCl_6$.