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AC conductivity and dielectric behavior in lithium and sodium diphosphate $LiNa_3P_2O_7$

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ABSTRACT

This work presents some electrical properties based on the impedance measurements as well as the dielectric constants and electric modulus. In order to through light in the electrical conductivity and dielectric properties of $LiNa_3P_2O_7$, we have carried out complex impedance spectroscopy technique in the frequency range 200 Hz–5 MHz at various temperatures (613–719 K). The complex impedance diagram at different temperatures showed a single semicircle, implying that the response originated from a single capacitive element corresponding to the grains. ac and dc conductivities were studied to explore the mechanisms of conduction. It can be seen from the experimental data that the ac conductivity of this compound is proportional to ω^s ($s < 1$), the value of s is to be temperature-dependent, which has a tendency to decrease in temperature. Activation energy values deduced from both dc conductivity and hopping frequency are in the order of $E_a = 0.95$ eV and $E_a = 0.89$ eV respectively. The near value of activation energies obtained from the hopping frequency and equivalent circuit confirms that the transport is through ion hopping mechanism dominated by the motion of the Li^+ ion in the structure of the investigated material.

1. Introduction

Organic and inorganic phosphates have several applications in different areas because of their use as, ceramic, ferroelectric, electric, solid electrolytes, catalysis and non-linear optic materials NLO [1].

Pyrophosphate constitutes the largest family of condensed phosphates and a great number of compounds of different stoichiometrie [2]. It has also a waked great interest relation to its potential technological applications [3,4] it can be used as catalysts [5], ionic conductors [6], and some of them have been proposed as cathode materials for lithium batteries [7–9]. In deed there are a large number of crystalline materials containing P_2O_7 groups in the literature for example the new non-centrosymmetric NCS diphosphate compounds with the general formula $LiM_3P_2O_7$ (Li: monovalent, M = Na, K. . .monovalent) which are potentially applicable as NLO materials. For optical applications in telecommunication, optical data storage and information processing make particularly the NCS materials of strategic importance especially when endowed with electrical conduction properties [10].

In this paper the electrical relaxation and the conduction mechanism in $LiNa_3P_2O_7$ is examined by ac and dc conductivity. The results of the dielectric properties and conductivity measured by varying the temperature and frequency are described.

2. Experimental section

2.1. Solid-state synthesis

The polycrystalline compound $LiNa_3P_2O_7$ was obtained by standard solid state reactions. Analytical grade reagent with 99% purity of Li_2CO_3, Na_2CO_3 and $NH_4H_2PO_4$ were used as raw materials. These materials were mixed in stoichiometric ratio and progressively heated from room temperature to 473 K at first step in order to expel NH_3, H_2O and CO_2. The calcined powder was then pressed into cylindrical pellets, heated once at 573 K for 8 h and finally at 813 K for 24 h.

2.2. X-ray powder diffraction

X-ray powder diffraction pattern was recorded using a Philips PW 1710 diffractometer operating with copper radiation Kα = 1.5418 Å. Units cells parameters of the synthesized compound have been refined by the least square method from the powder data.

2.3. Impedance measurements

The electrical measurements were performed using a two platinum electrode configuration. The ceramic $LiNa_3P_2O_7$ sample was pressed into pellets of 8 mm diameter and 1.2 mm thickness using 3 t/cm^2 uniaxial pressure. Electrical impedances were measured in the frequency ranging from 200 Hz to 5 MHz with the TEGAM 3550 ALF automatic bridge monitored by a microcomputer and a temperature controller. Measurements were carried out at temperatures from 613 K to 719 K.

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3. Results and discussions

3.1. Powder X-ray analysis

The structure of $LiNa_3P_2O_7$ solid was investigated by Shi et al. [11]. They found that the samples crystallize in the orthorhombic space group $C222_1$ with the unit cells: $a = 5.4966(2)$ Å, $b = 9.1365(4)$ Å, $c = 12.2764(5)$ Å.

At room temperature, the X-ray diffractogram (XRD) (Fig. 1) of powder $LiNa_3P_2O_7$ was reinvestigated. The peaks have been successfully indexed in the orthorhombic system with $C222_1$ space group. The lattice parameters were refined and the calculated values are in well agreement with the literature and found to be: $a = 5.5003(3)$ Å, $b = 9.1325(4)$ Å, $c = 12.2833(4)$ Å $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$ and $V = 617.014$ (Å^3).

3.2. Structural description

The structure of $LiNa_3P_2O_7$ is reported in the literature [11]. Fig. 2 show that the compound is formed by one unique Lithium atom, two unique Sodium atoms, one unique Phosphor atom and four unique Oxygen atoms in the asymmetric unit of $LiNa_3P_2O_7$. The $[P_2O_7]^{4-}$ group is linked to three different LiO_4 tetrahedra through its terminal O atoms, while every LiO_4 tetrahedron shares its four vertices with three neighboring $[P_2O_7]^{4-}$ groups to form two-dimensional (2D) $\infty[LiP_2O_7]^{3-}$ layers extending in the (1 0 0) plane. In addition, the $\infty[LiP_2O_7]^{3-}$ layers are connected together by sharing O atoms with Na(1) and Na(2) cations located between these layers to generate a three-dimensional network .

3.3. IR spectroscopy investigation

The infrared (IR) spectra of $LiNa_3P_2O_7$ are shown in Fig. 3. The frequencies of the (P_2O_7) groups are assigned on the basis of the characteristic vibrations of the P—O—P bridge and PO_3 groups [12–15]. The assignment of different entities is based on a comparison with structurally related compounds [16] with the following sequence of diphosphate vibrations in the order of decreasing frequency:

$$\upsilon_{as}(PO_3) \succ \upsilon_s(PO_3) \succ \upsilon_{as}(P-O-P) \succ \upsilon_s(P-O-P) \succ \delta(PO_3) \succ \delta(P-O-P)$$

υ_{ac} and υ_s refer respectively to asymmetric and symmetric stretching vibrations of P—O bonds in (PO_3) groups or in (P—O—P) bridge; δ refers to deformation modes of (O—P—O) angles.

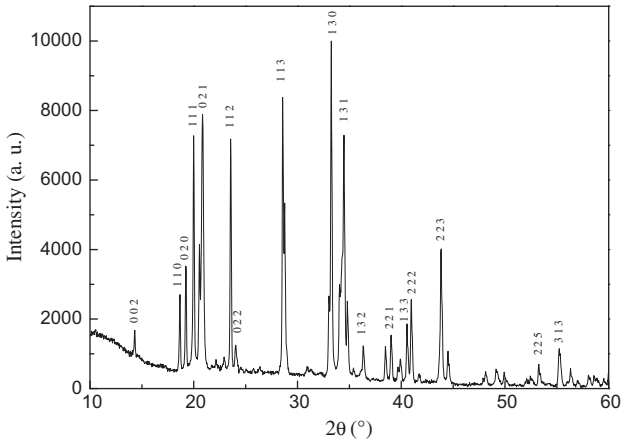

Fig. 1. Powder X-ray diffraction pattern of $LiNa_3P_2O_7$.

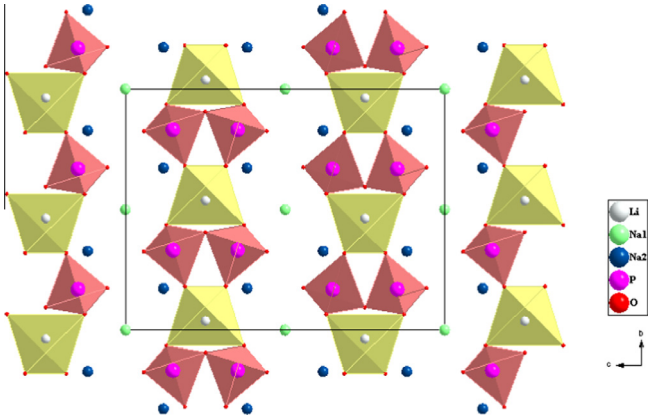

Fig. 2. Infrared analysis spectrum of $LiNa_3P_2O_7$.

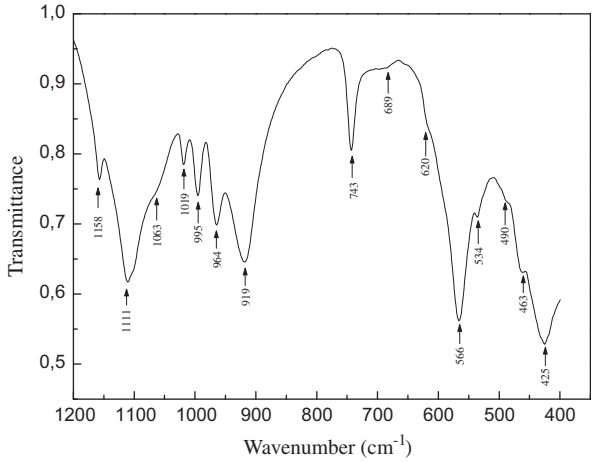

Fig. 3. The crystal structure of $LiNa_3P_2O_7$.

In these conditions, the infrared bands for $LiNa_3P_2O_7$ are distributed in four distinct wave number ranges, 400–675 cm^{-1}, 720–800 cm^{-1}, 850–990 cm^{-1}, and 990–1400 cm^{-1}.

Band assignments for the fundamental modes of this compound are given in Table 1 confirms the presence of the diphosphate groups in the title compound [17].

3.4. Impedance spectroscopy analysis

The impedance in its standard definition means quotient of vector voltage and vector current calculated from small single sinusoidal measurement. When an ac signal is applied to a system, the impedance of the system obeys Ohm's law, as ratio of voltage to current in the time domain [18].

The impedance is a complex quantity, having both magnitude $|Z|$ and phase angle ϕ expressed are:

$$Z(\omega) = |Z| \exp(-j\phi) \quad (1)$$

Table 1
Band assignment (cm^{-1}) for LiNa3P2O7.

Bands (cm^{-1})	Assignment
1158, 1111, 1063, 1019	υ_{as} (P—O) in PO_3
919, 964, 995	υ_s (P—O) in PO_3, υ_{as} (P—O—P) in P_2O_7
743	υ_s (P—O—P) in P_2O_7
689, 620, 566, 534	υ_{as} (P—O—P) in PO_3
490, 463, 425	υ_s (P—O—P) in PO_3