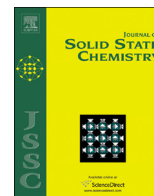




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Lithium-cation conductivity and crystal structure of lithium diphosphate

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ABSTRACT

The electrical conductivity of lithium diphosphate $\text{Li}_4\text{P}_2\text{O}_7$ has been measured and jump-like increasing of ionic conductivity at 913 K has been found. The crystal structure of $\text{Li}_4\text{P}_2\text{O}_7$ has been refined using high temperature neutron diffraction at 300–1050 K. At 913 K low temperature triclinic form of $\text{Li}_4\text{P}_2\text{O}_7$ transforms into high temperature monoclinic one, space group $P2_1/n$, $a=8.8261(4)$ Å, $b=5.2028(4)$ Å, $c=13.3119(2)$ Å, $\beta=104.372(6)^\circ$. The migration maps of Li^+ cations based on experimental data implemented into program package TOPOS have been explored. It was found that lithium cations in both low- and high temperature forms of $\text{Li}_4\text{P}_2\text{O}_7$ migrate in three dimensions. Cross sections of the migrations channels extend as the temperature rises, but at the phase transition point have a sharp growth showing a strong “crystal structure – ion conductivity” correlation.

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1. Introduction

Solid electrolytes with lithium ion conductivity are intensively investigated at present because their use in power sources with lithium or lithium alloys anodes holds much promise. A lot of lithium ion conducting materials with a large variety of structural types have been obtained by now [1,2]. In particular, lithium diphosphate $\text{Li}_4\text{P}_2\text{O}_7$ has rather high Li^+ conductivity ($\sim 10^{-1}$ S cm^{-1} at 925 K [3]) which furthermore may be enhanced by heterovalent substitutions [4]. To understand the conductivity mechanism of solid electrolytes the knowledge of their crystal structure peculiarities in the wide temperature range is necessary. Data on crystal structure of $\text{Li}_4\text{P}_2\text{O}_7$ at room temperature have been obtained by X-ray analysis of single crystals are controversial [5,6]. According to [5], the crystal lattice of $\text{Li}_4\text{P}_2\text{O}_7$ is monoclinic, space group $P2_1/n$, $a=5.190(2)$, $b=13.902(3)$, $c=7.901(3)$ Å, $\beta=89.97(3)^\circ$, $z=4$. Another model was proposed later: according to [6], the crystal structure of $\text{Li}_4\text{P}_2\text{O}_7$ at room temperature is interpreted as triclinic, space group $P-1$, $a=8.5613(4)$, $b=7.1100(3)$, $c=5.18510(10)$ Å, $\alpha=111.44(2)^\circ$, $\beta=89.986(3)^\circ$, $\gamma=103.065(4)^\circ$, $z=2$. This model was confirmed by data of the computer modeling of optimized crystal structures of several lithium phosphates and thio-phosphates, in particular, $\text{Li}_4\text{P}_2\text{O}_7$ [7]. The lattice parameters and coordinates of atoms conform rather well to the data [6]. The conclusion on triclinic lattice of low temperature form of $\text{Li}_4\text{P}_2\text{O}_7$ is confirmed by the investigation of the phase relations in the system

$\text{ZnO-Li}_2\text{O-P}_2\text{O}_5$ [8] too. Some discrepancy in the values of the structural parameters reported in different papers is probably the result of poor sensitivity of the X-rays to such light elements as lithium and oxygen. A lot of researchers of lithium compounds had to deal with this problem [9–13]. So neutron diffraction is the most preferable method for studying the structural peculiarities of the solid electrolytes containing light atoms.

In [7], the migration energy barrier for lithium vacancies at room temperature for one of the possible paths was evaluated based on the model of the crystal lattice of $\text{Li}_4\text{P}_2\text{O}_7$ using the computer modeling. However, the most detailed analysis of migration paths in solid electrolytes may be carried out using the program package TOPOS [14]. It permits to explore the migration maps based on the experimental structural parameters. This program package was successfully used for exploring migration maps of many solid electrolytes and, in particular, for low temperature form of KAlO_2 [15].

It should be mentioned that until now the crystal structure of lithium diphosphate has only been studied at room temperature, while for exploration of ionic conductivity, an investigation of its structure at high temperature is necessary. So the goal of this work was an investigation of the conductivity mechanism of $\text{Li}_4\text{P}_2\text{O}_7$ based on the study of its crystal structure by means of powder neutron diffraction over a wide temperature range as well as on migration maps of Li^+ ions built with the program package TOPOS.

2. Materials and methods

Conventional solid-state reaction procedure was employed to prepare $\text{Li}_4\text{P}_2\text{O}_7$ compound. The starting materials were Li_2CO_3

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(reagent grade) and $\text{NH}_4\text{H}_2\text{PO}_4$ (analytical grade). Appropriate amounts of the starting materials were weighed within the accuracy of $\pm 10^{-4}$ g using an FX-40CJ analytical balance, mixed in a jasper mortar and sintered in an aluminum crucible at 500 K for 10–12 h. The resulting mass was reground and heated again. The final temperature was 1070 ± 10 K. The pellets for conductivity measurement were prepared by pressing fine powder in a steel die at ~ 300 MPa. The pressed pellets were sintered on Pt plate at 1110 ± 10 K. The open porosity of the sintered pellets did not exceed 5%. One pellet was ground for phase characterization employing X-ray powder diffraction (XRD) (Rigaku Dmax-2200, CuK α , Japan) at room temperature. Thermal analysis was performed using STA 449C Jupiter[®] thermal analyzer (NETZSCH, Germany). Conductivity was measured over the range of 650–1050 K with gold electrodes using P 5083 AC bridge. The frequency range was 100 Hz–100 kHz. The results were plotted as complex impedance plane plots Z'' vs. Z' .

Neutron diffraction experiments were carried out using the high resolution powder neutron diffractometer HRPT (SINQ Spallation source of Paul Scherrer Institute, Villigen, Switzerland) [16]. The sample $\text{Li}_4\text{P}_2\text{O}_7$ was placed in the evacuated vanadium container. Structural parameters were refined by Rietveld technique using Fullprof program [17].

To determine migration maps (i.e. sets of migration paths of mobile cation within the framework) from crystallographic data, we used Voronoi–Dirichlet approach [18] implemented into the program package TOPOS [19].

3. Results and discussion

3.1. Conductivity

According to [20] at 903 K (according to our data at 913 K) the low temperature phase of $\text{Li}_4\text{P}_2\text{O}_7$ transforms into the high temperature one. Over the interval of 720–890 K lithium ion conductivity is 5.6×10^{-3} – 3.2×10^{-2} S/cm, activation energy $E = 156 \pm 1$ kJ/mol. With increasing temperature to 920 K conductivity jumps by half an order of magnitude (Fig. 1) and reaches 10^{-1} S/cm, the activation energy decreases down to 80 ± 0.6 kJ/mol. An electronic conductivity over the whole temperature range studied does not exceed 0.1% of total conductivity.

3.2. Crystal structure

3.2.1. Low temperature form (room temperature)

An indexing of the room temperature X-ray pattern of the synthesized sample of $\text{Li}_4\text{P}_2\text{O}_7$ confirms triclinic symmetry (space

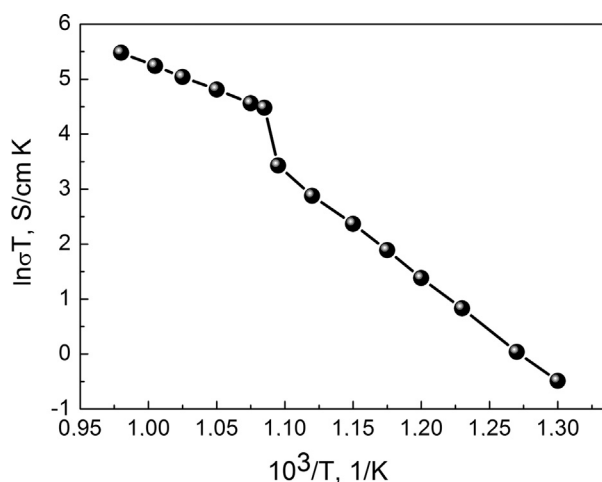


Fig. 1. Temperature dependence of the ionic conductivity for $\text{Li}_4\text{P}_2\text{O}_7$.

group P-1) proposed in [6]. At a later stage the structural parameters were refined using neutron diffraction data.

Fig. 2 shows the room temperature neutron diffraction pattern of $\text{Li}_4\text{P}_2\text{O}_7$. For preliminary analysis we used the crystallographic data reported in [6]. According to the difference curve, experimental and calculated data are in good agreement. Table 1 lists the crystallographic data and details of the structure refinements of $\text{Li}_4\text{P}_2\text{O}_7$. Using the experimental atom coordinates and lattice parameters we calculated interatomic distances. Data for P and Li are shown in Table 2.

Fig. 3 represents the crystal lattice of $\text{Li}_4\text{P}_2\text{O}_7$. The structure consists of diphosphate groups P_2O_7 arranged by two PO_4 tetrahedra having a common corner. In the PO_4 tetrahedra there is one long P–O distance which corresponds to P–O–P bridge while the other three distances are shorter (Table 2). Li atoms are distributed over 4 nonequivalent positions and form distorted tetrahedra LiO_4 (Table 2). Lithium tetrahedra are linked to each other and to P_2O_7 groups by a common vertex or edge and form a continuous framework containing large voids, available for Li^+ ions transport.

Brown's phenomenological Bond Valence Model [21] can help to estimate the correctness of the refined crystal lattice. We calculated valence sums of cations and anions using the experimental bond lengths as $V_i = \sum (s_{ij})$ where $s_{ij} = \exp [(r_o - r_{ij})/B]$, r_o and B are empirical constants determined for each pair of atoms. Table 2 shows that at room temperature the obtained values of V_i are in good agreement with the oxidation state of the ion considered. As empirical constants for bond valence sums calculation are available only at room temperature, calculations at elevated temperatures were not carried out. Some deviation of the valence sums from theoretical values may be the result of the different degree of lithium tetrahedra distortion [22]. The degrees of distortion were calculated as

$$\delta = \sqrt{\sum_{i=1}^N \left| 1 - \frac{R_i}{\sum_{i=1}^N R_i/N} \right|^2}$$

where R_i is the distance for i pair, $N=4$ for a tetrahedron. The maximum value of δ is observed for Li_2O_4 tetrahedron, furthermore the average distance $\text{Li}_2\text{–O}$ (1.99 Å) also exceeds the average distances for other tetrahedra (Table 2). This suggests that the migration of Li^{2+} ions in the low temperature form of $\text{Li}_4\text{P}_2\text{O}_7$ is highly probable. A more detailed description of lithium ions migration will be provided below.

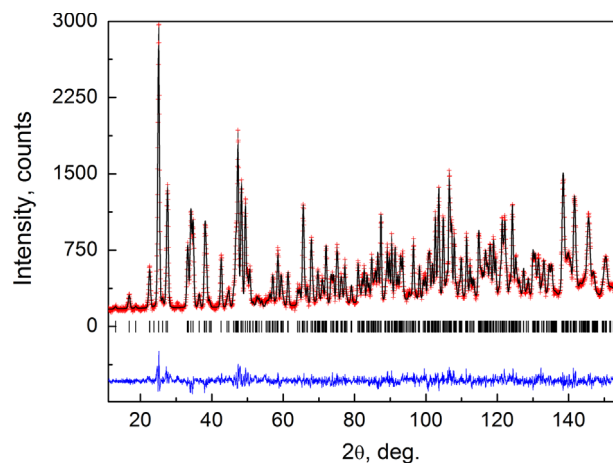


Fig. 2. Fitted powder neutron diffraction profile for $\text{Li}_4\text{P}_2\text{O}_7$ at room temperature, with observed (dots), calculated (solid line) and difference plots. Dashes designate angular positions of reflexes.

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