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A NEW SYSTEM OF LITHIUM FAST ION CONDUCTORS BASED ON $LiTi_2P_3O_{12}$ AND PYROPHYLLITE

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ABSTRACT

Pyrophyllite has been used as a starting material for the synthesis of Lithium fast ion conductors of the $Li_{1+3x}Al_xTi_{2-x}Si_{2x}P_{3-2x}O_{12}$ system by high temperature solid phase reaction. Most of the reactions completed at 1073-1423 K. X-ray diffraction analysis and an a.c. impedance technique were employed to characterize these fast ion conductors. The results showed that the lattice symmetry of most compositions in the system is R3c and the maximum ionic conductivity reaches up to the order of 10^{-2} S cm^{-1} at 573K. The highest conductivity corresponds to the initial composition x = 0.15.

1. INTRODUCTION

In the search for fast ion conductors to be used in the electrochemical devices, e.g., high energy or power density battery systems, one of the criteria for selecting starting materials is low cost and abundance in natural resources. In recent years scientists have paid attention to utilizing some natural mineral as a starting material to prepare so called mineral solid electrolytes. For example, montmorillonite solid electrolyte was prepared by using natural silicate mineral montmorillonite as a starting material and the montmorillonite electrolytes have been used in solid state batteries [1-3].

We have been working on a layered silicate mineral pyrophyllite $Al_2[Si_4O_{10}](OH)_2$ for several years and recently a new family of sodium fast ion conductors based on pyrophyllite have been prepared in our laboraroty[4]. This work led us to investigating a new series of lithium fast ion conductors that is based on pyrophyllite and $LiTi_2P_3O_{12}$. This paper deals with the preparation and the structural characterization and the electrical conductivity of $Li_{1+3x}Al_xTi_{2-x}Si_{2x}P_{3-2x}O_{12}$ fast ion conductors.

2. EXPERIMENTAL

2.1 *Materials*

The natural mineral pyrophyllite is from Fuzhou, China. The refined pyrophyllite (95% $Al_2[Si_4O_{10}](OH)_2$) was used as a starting material. At high temperature, the $Al_2[Si_4O_{10}](OH)_2$ was converted to to $Al_2Si_4O_{11}$ by the removal of water. A.R. grade TiO_2, Li_2CO_3 and $NH_4H_2PO_4$ (Shanghai Reagent Factory) were used as starting materials.

2.2 *Solid Phase Synthesis*

The Lithium fast ion conductors of $Li_{1+3x}Al_xTi_{2-x}Si_{2x}P_{3-2x}O_{12}$ system were prepared as follows:

$Al_2[Si_4O_{10}](OH)_2$ and other ingredients (TiO_2, Li_2CO_3) were dried in an ovèn at 573 K. $NH_4H_2PO_4$ was dried at 393 K just prior to use and kept in a desiccator. Exact mole ratios of the ingredients were weighed out and ground together in an agate mortar. The entire solid was then transfered to a platinum vessel which was heated at 443 K for 4 h. and at the temperature range 1073-1473 K for several more hours. Other samples were heated for up to 20 h. The vessels plus ingredients were also weighed before and after heating to check for any weight losses associated with heat treatment..

2.3 *X-ray Diffraction Analysis*

X-ray powder diffraction patterns were then taken with a computer-automated diffractometer(D/Max-ra) using CuK radiation (λ=1.5418Å). The lattice parameters were obtained by solving the simultaneous equations[5].

2.4 *Electrical Conductivity Measurements.*

Electrical conductivities were measured by an a.c. impedance technique on sintered discs (13mm diameter and about 2 mm thick) from 298-673 K in the frequency range 20 Hz to 200 KHz. The discs were prepared by pressing the powders in evacuable die at 4 ton/cm^2. They were sintered at 1073-1273 K for several hours. The discs were coated with silver paint, dried at 373 K and then heated at 873 K for 30 min. The sample discs were sandwiched between two silver plates to be sure of good electrode electrolyte contact. The entire cell assembly was placed in tubular furnace whose temperature could be controlled to ± 2 K by using a temperature controller (Model DRZ-4).

3. RESULTS AND DISCUSSION

3.1 *Phase Relationship and Unit-cell Parameters*

X-ray diffraction analysis was used to identify the phase relationship of lithium fast ion conductors of $Li_{1+3x}Al_xTi_{2-x}Si_{2x}P_{3-2x}O_{12}$ system based on pyrophyllite and $LiTi_2P_3O_{12}$. The results show that a solid solution with R$\bar{3}$c can be formed in the composition range x 0.2. At still higher values of x the phase relationship became more complicated. A second phase began at x = 0.25 and a glass phase started to appear for x >0.3.

The unit-cell parameters of R$\bar{3}$ c solid solutions in the $Li_{1+3x}Al_xTi_{2-x}Si_{2x}P_{3-2x}O_{12}$ system were completed by solving the simultaneous equations and listed in Table 1. The data in the Table I indicate the changes in structure upon the substitution of (TiO_6) octahedra by (AlO_6) and PO_4) tetrahedra by (SiO_4). The volume of the cell in the solid solution region decreased with increasing x.

Table 1. The phase relationship and unit-cell parameters of $Li_{1+3x}Al_xTi_{2-x}Si_{2x}P_{3-2x}O_{12}$ system

X	Observed Phase	Unit-cell parameters a(Å)	c(Å)	V(Å^3)
0	R3c	8.517	20.891	1312.26
0.10	R3c	8.516	20.891	1312.11
0.15	R3c	8.511	20.892	1310.69
0.20	R3c	8.509	20.894	1310.09
0.25	R3c	8.511	20.872	1309.34

3.2 *Electrical Conductivity*

Pyrophyllite is a layed silicate mineral[6]. Unlike the montmorillonite, it doesn't have any exchangeable ions[5], so it is not an ionic conductor. Also the $LiTi_2P_3O_{12}$ is not a good donductor[6] due to structural reasons. However, the electrical measurements showed that some compositions of the $Li_{1+3x}Al_xTi_{2-x}Si_{2x}P_{3-2x}O_{12}$ system are good fast ion conductors. The data for both conductivity and activation energy are presented in Table 2. The highest conductivity corresponds to the initial composition x = 0.15. The conductivity for this composition reaches 1.49×10^{-2} s/cm at 575 K.

$LiTi_2P_3O_{12}$ possesses three dimensional networks in space group $R\bar{3}c$[7]. The structure consistsof TiO_6 octahedra and PO_4 tetrahedra that are linked by corners. Every oxygen thus belongs simultaneously to a PO_4 group and a TiO_6 group. Like Na+ in the $NaZr_2P_3O_{12}$[8], Li+ ions fill a unique set of sites in a three-dimensional space. While the substitution of $LiTi_2P_3O_{12}$ by $Al_2[Si_4O_{10}](OH)_2$, i.e., Al^{3+} and Si^{4+} replace Ti^{4+} and P^{5+} simultaneously in the $Li_{1+3x}Al_xTi_{2-x}Si_{2x}P_{3-2x}O_{12}$ system, in order to maintain the charge balance, proper amount of Li+ ions would be introduced into other positions of the interstitial space which plays the role of the transport ions. For this reason, some compositions in the system would have correct Li+/vacancy ratio for optimum conductivity and behave like fast ion conductors.

Table 2. The conductivities and activation energies of $Li_{1+3x}Al_xTi_{2-x}Si_{2x}P_{3-2x}O_{12}$ system

X	Conductivities(S/cm) R.T.	473K	523K	573K	Ea(kJ/mol)
0.10	2.02×10^{-4}	2.45×10^{-3}	4.50×10^{-3}	6.51×10^{-3}	29.36
0.15	1.61×10^{-4}	4.66×10^{-3}	8.13×10^{-3}	1.49×10^{-2}	31.42
0.20	1.54×10^{-4}	2.79×10^{-3}	5.91×10^{-3}	1.03×10^{-2}	35.08
0.25	6.30×10^{-5}	9.60×10^{-4}	2.52×10^{-3}	4.39×10^{-3}	38.02

4. SUMMARY

The natural silicate mineral pyrophyllite can be introduced into $LiTi_2P_3O_{12}$ to form a $R\bar{3}c$ solid solution system which exhibits very promising properties as fast ion conductors.

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