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Short communication

The preparation and lithium mobility of zinc based NASICON-type solid electrolyte $Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$

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Abstract

A series of Nasicon-type solid electrolytes $Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$ was synthesized by conventional solid state ceramic route. X-ray diffraction and Rietveld whole pattern refinement were applied to investigate the phase, structure and the unit cell parameters of those solid electrolytes. EIS complex impedance method was carried out to study the Li^+ conductivity. The results showed that $Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$ with $x=0.1$ $y=0.5$ presents highest ionic conductivity 7.2×10^{-5} S cm^{-1} at ambient temperature and 2.0×10^{-3} S cm^{-1} at 473 K. The activation energy of Li^+ migration was calculated to be ca. 20 kJ mol^{-1}. The influence of Zn^{2+} element on the structure and Li^+ mobility was preliminary explained.

Keywords: C. Ionic conductivity; Nasicon-type solid electrolyte; Ion doping; Rietveld refinement

1. Introduction

NASICON-type materials $LM_2(PO_4)_3$ (L=alkali metal ions like Li, Na, K; M=Ge, Ti, Sn, Hf, Zr) have attracted increasing research interest because of their high ionic conductivity and potential applications as solid electrolytes in all-solid-state lithium battery, fuel cells, sensors, etc. The typical structure of these compounds is rhombohedral (space group $R\bar{3}C$), which offers an open unit cell supporting L cation hopping in the channel connected by interstitial M1 sites and M2 sites based on the $M_2(PO_4)_3$ framework where two MO_6 octahedra and three PO_4 tetrahedra share oxygen atoms [1].

For the last 20 years, great efforts have been made for maximizing the Li^+ conductivity of $LM_2(PO_4)_3$ system, especially $LiTi_2(PO_4)_3$. Many attempts have been reported in the literature. The partial substitution of Ti^{4+} by trivalent elements and P^{5+} by tetravalent elements were proved to be effective ways for the following reasons: (1) charge balance dictates that inclusion of low valence ions incorporates greater concentrations of lithium ions in the solid phase. (2) The inclusion of doping ions with specific size and electronegativity tunes the size of the bottleneck in the diffusion passageway [2]. For example, $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ ($x=0.3$–0.4) and $Li_{1+2x+2y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$ ($x=0.3$, $y=0.2$) prepared by conventional solid state ceramic route both showed ionic conductivity as high as 10^{-4}–10^{-5} at room temperature [3]. Sol–gel method followed by melt-quenching can further improve the ionic conductivity one order of magnitude for greatly reducing the porosity of the solid electrolyte pellet [4,5]. However, high temperature above 1500 °C was needed for melt-quenching method. High-energy ball-milling is still a versatile method for the mass production of ceramics. Hence further exploring of the doping element and material composition is still urgently needed for achieving the required ionic conductivity at the lowest cost.

In this paper, a series of Nasicon-type electrolytes $Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$ was synthesized by means of conventional high energy ball milling. The compound was characterized by X-ray diffraction and micro-structure parameters

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were determined by Rietveld whole pattern refinement. The influence of Zn^{2+}, Al^{3+} and Si^{4+} concentration on the ionic conductivity was scrutinized.

2. Experiments

2.1. The preparation of $Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$

$Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$ (LAZTSP) was prepared by conventional solid-state reaction of a stoichiometric mixture of Li_2CO_3 (Aladdin, AR), NH_4H_2PO4 (Aladdin, AR), TiO_2 (Aladdin, AR), SiO_2 (Aladdin, AR),Al_2O_3 (Aladdin, AR) and ZnO (Aladdin, AR). The overall reaction for the formation of LAZTSP was given as follows:

$$\frac{1+2x+2y}{2}Li_2CO_3+\frac{x}{2}Al_2O_3+xSiO_2+(2-x-y)TiO_2+yZnO$$
$$+(3-x)NH_4H_2PO_4\overset{900\ ^\circ C}{\Longrightarrow}Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$$
$$+\frac{1+2x+2y}{2}CO_2\uparrow+(3-x)NH_3\uparrow+\frac{9-3x}{2}H_2O\uparrow$$

Calculated amounts of starting materials soaked in anhydrous ethanol were ground in a planetary ball mill operated at 400 rpm for 12 h. The mixture was then dried overnight at 120 °C, sintered at 690 °C for 5 h in order to ensure total decomposition of reagents, and finally calcinated at 900 °C for 5 h. After cooling to room temperature, the mixture was again ground for 20 min in a agate mortar and made into pellets of 15 mm in diameter and 1.2–1.5 mm in thickness by cold pressing (200 MPa). These pellets were calcinated at 900 °C in air for 6 h. Four kinds of samples, namely $x=0.1$, $y=0.1$; $x=0.1$, $y=0.3$; $x=0.1$, $y=0.5$; $x=0.1$, $y=0.7$, were designated as LAZTSP0.1-0.1, LAZTSP0.1-0.3, LAZTSP0.1-0.5, and LAZTSP0.1-0.7, respectively.

3. Characterization

X-ray powder diffraction patterns were recorded at room temperature with a Bruker D8 Advance diffractometer operated at 36 kV and 20 mA using Cu Kα1 radiation. The patterns were obtained with a 0.02° step size and 5 s scan time in the range 10–90°. The whole X-ray pattern was fitted by GSAS (General Structure Analysis System) [6], a free software created by Allen C. Larson and Robert B. Von Dreele of American Los Alamos National Laboratory for the Rietveld refinement of structural models to both X-ray and neutron diffraction data. For ionic conductivity measurements, silver paint was applied to both sides of polished pellet, which was sandwiched between two silver electrodes. The complex impedance measurements were then performed on a Bio-logic vmp3 Multichannel potentiostats/galvanostats over the frequency range 1 to 1.0×10^5 Hz at decreasing temperatures from 473 K to 283 K.

4. Results and discussions

4.1. Phase analysis

Fig. 1 shows the X-ray diffraction patterns of the powders calcinated at 900 °C for 5 h in air. All the diffraction positions for all compositions can be indexed to the rhombohedral structure (space group $R\bar{3}C$) without the evidence of impurity phase. This also suggests the full substitution of Ti^{4+} by Zn^{2+} and Al^{3+}, of P^{5+} by Si^{4+}, respectively.

Fu [4] and Birke et al. [7] have reported impurity $AlPO_4$ phase was usually inevitable in all their products. Lakshmi Vijayan [8] also pointed out that trace amount of TiP_2O_7 was always identified at low 2θ range up to 29 °C due to Li loss at high calcinating temperature. Here the partial substitution of Ti^{4+} by Zn^{2+} seems to stabilize the Nasicon structure. Parameters including cell parameters, background, scaling, profile parameters GU, GV, GW, LX, LY, S/L, H/L, trans, shft, preferential orientation are refined. Appropriate refinement sequence is selected and after some cycles of refinement, the convergence is achieved. The ultimate Rietveld refinement result of LAZTSP0.1-0.5 is shown in Fig. 2. The calculated

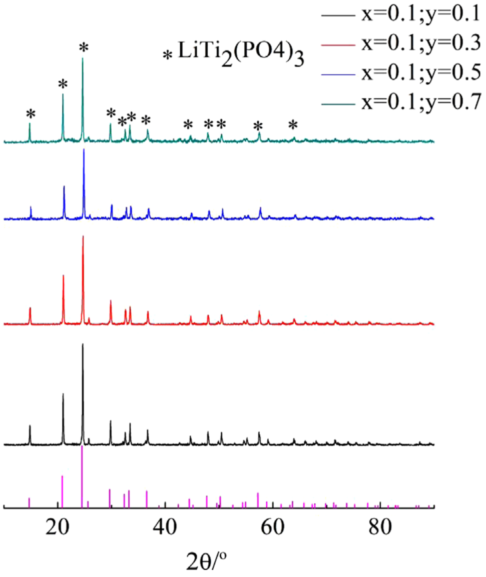

Fig. 1. X-ray diffraction patterns of $Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$ heat-treated at 900 °C for 5 h in air.

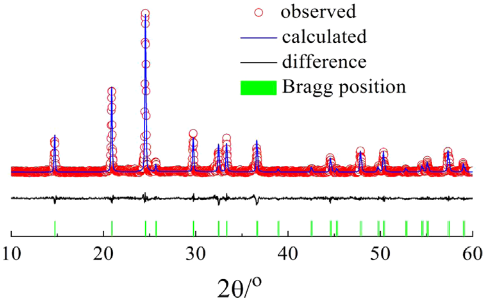

Fig. 2. Rietveld refinement of LAZTSP0.1-0.5.

pattern matches the observed pattern well. Refined cell parameters are listed in Table 1 together with the data of ionic conductivity. Considering the ionic radius of Al^{3+} 53 pm, Ti^{4+} 68 pm and Zn^{2+} 74 pm, the inclusion of Al^{3+} causes the shrinkage of unit cell parameter a and c. This is supposed to facilitate Li^{+} mobility by regulating the size of ion conducting passageway and matching the size of the charge carrier Li^{+}.

However, at the same time, it may narrow the triangular windows that relate M1 and M2 sites and enlarge the Li^{+} diffusion activation energy at this bottleneck [2]. The introduction of Zn^{2+} slightly enlarges the unit cell parameters, especially parameter a by modifying the orientation of part of ZnO_6 octahedra, thus lowers the energy barrier at the triangle bottleneck. Surely, an excess amount of Zn^{2+} will expand the cell overmuch and offset the favorable effects brought by the inclusion of Al^{3+} in the matrix, as in the case of $x=0.1$, $y=0.7$. The detailed calculations of structural changes with the introduction of Al^{3+} and Zn^{2+} will be discussed in a forthcoming paper.

4.2. Li mobility

Fig. 3 shows the complex impedance plots, which reflect the ion conducting behaviors, of $Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$ solid electrolyte pellets for 4 kinds of samples at 283 K. A typical plot consists of a semi-circle associated with the grain-boundary contribution at high frequency and a spike characteristic of blocking effects at electrode/electrolyte interface at low frequency. Similar to Ref. [9], only one semicircle can be distinguished for all the specimens.

Since it is not possible to distinguish between the grain-boundary resistance and grain-interior resistance in all instances. Only total ionic conductivities σ_t are listed in Table 1. Values of σ_t in the table are calculated by Zview software using the equivalent circuit model $(Q_{gb}R_{gb})(C_bR_b)Qt$. The parallel combination C_bR_b represents the grain-interior resistance for the bulk of crystalline $Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$; the constant phase element Q_{gb} and the resistor R_{gb} in parallel represent the resistance of the grain boundaries while the constant phase

Table 1
The ionic conductivities of $Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$ at tested temperatures and unit cell parameters.

Composition	σ (S cm^{-1})					E_a (kJ mol^{-1})	a (Å)	c (Å)
	283 K	323 K	373 K	423 K	473 K		8.513[a]	20.878[a]
$x=0.1$, $y=0.1$	9.0×10^{-6}	2.1×10^{-5}	6.2×10^{-5}	1.1×10^{-4}	2.1×10^{-4}	18.6	8.496	20.819
$x=0.1$, $y=0.3$	2.2×10^{-5}	5.0×10^{-5}	5.0×10^{-5}	9.9×10^{-5}	5.1×10^{-4}	17.8	8.502	20.832
$x=0.1$, $y=0.5$	7.2×10^{-5}	1.8×10^{-4}	4.3×10^{-4}	9.1×10^{-4}	2.0×10^{-3}	19.2	8.509	20.850
$x=0.1$, $y=0.7$	3.2×10^{-5}	9.8×10^{-5}	3.2×10^{-4}	7.0×10^{-4}	1.2×10^{-3}	21.5	8.518	20.882

[a] Denotes the unit cell parameters of $LiTi_2P_3O_{12}$.

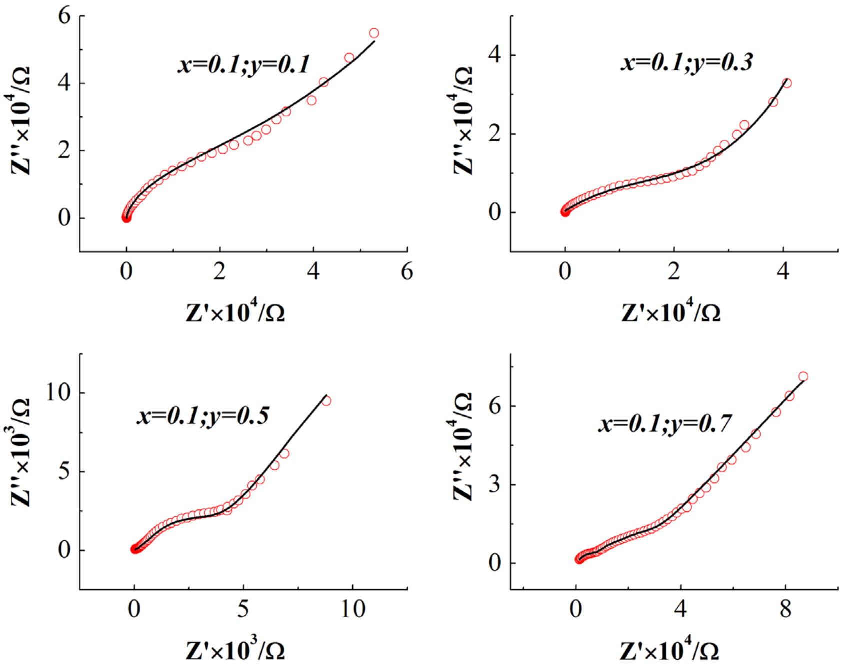

Fig. 3. The complex impedance plots of $Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$ solid electrolyte pellets for 4 kinds of samples at 283 K.

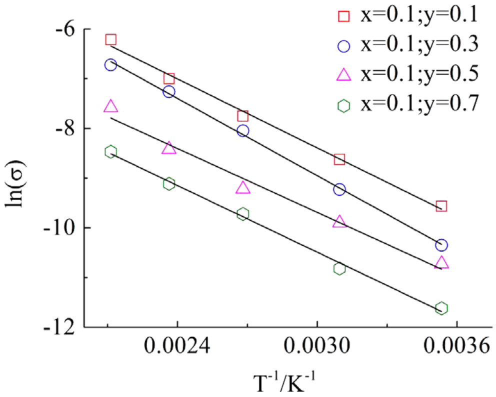

Fig. 4. Arrhenius plots of $Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$ (ln σ vs. 1/T).

element Q_t represents the blocking effect at electrolyte/Ag electrode interface. From the figure, the Li^+ mobility is highly dependent on Zn^{2+} concentration. With the increasing of Zn^{2+} concentration, Li^+ conductivity increases gradually, reaches a maximum value of $7.2\times10^{-5}\,S\cdot cm^{-1}$ at $y=0.5$ and then decreases. Fig. 4 shows the relationship between ionic conductivity and testing temperatures. The total conductivities fit the Arrhenius equation: $\sigma=A\exp(-E_a/RT)$ well, where A is the pre-exponential parameter and R is the gas constant. Good linear relationships are observed for the whole testing temperature range involved. From the slopes of the lines, The typical value of E_a is around 20 kJ mol^{-1}.

5. Conclusion

Nasicon-type solid electrolyte $Li_{1+2x+2y}Al_xZn_yTi_{2-x-y}Si_xP_{3-x}O_{12}$ with $x=0.1$ $y=0.5$ presents highest ionic conductivity 7.2×10^{-5} S cm^{-1} at 283 K and 2.0×10^{-3} S cm^{-1} at 473 K. The activation energies of Li^+ migration are calculated to be about 20 kJ mol^{-1}. The introduction of Zinc element possibly reliefs the contraction of triangle bottleneck that relates M1 and M2 interstitial sites by the inclusion of Al^{3+}. Therefore, appropriate amount Zn^{2+} in the octahedral sites facilitates the Li^+ migration in the ion conduction channel.

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