



A lithium ion conductor in $\text{Li}_4\text{SiO}_4\text{-Li}_3\text{PO}_4\text{-LiBO}_2$ ternary system

Mahreen Aslam, Xiang Yang Kong*

Institute of Materials for Mobile Energy, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China



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ABSTRACT

We developed a lithium ion conductor in $\text{Li}_4\text{SiO}_4\text{-Li}_3\text{PO}_4\text{-LiBO}_2$ ternary ceramic system comprising of the mole ratio as $\text{Li}_4\text{SiO}_4\text{:Li}_3\text{PO}_4\text{:LiBO}_2 = 60\text{:}40\text{:}20$ (termed as 40LP + 20B), exhibiting the ion conductivity of 5.7×10^{-6} S/cm at room temperature. From the X-ray diffraction patterns, the ternary solid solution has the orthorhombic phase structure with the increased unit cell volume due to the substitution of boron in lattice. The SEM images show that the high densification of the 40LP + 20B samples sintered at 900 °C for 6 h, and EDS mappings illustrate that the incorporating boron is distributed homogeneously in the grains and no precipitated impurity was observed on grain surface or around grain boundaries. The data of electrochemical impedance spectroscopy (EIS) reveal the low resistance from grain boundary, giving rise to the high bulk ion conductivity. The lithium ion conductor in $\text{Li}_4\text{SiO}_4\text{-Li}_3\text{PO}_4\text{-LiBO}_2$ system is of great potential as practical solid electrolyte for all-solid-state battery.

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1. Introduction

It is of great challenge to find new electrolytes suitable for the use in lithium or lithium ion batteries [1]. Stable solid electrolytes with high lithium ion conductivity are expected to offer several advantages over the commercialized liquid electrolytes such as higher thermal stability, absence of leakage and pollution, and a large electrochemical stability window [2]. To date, solid lithium ion conductors are extensively investigated in the materials of crystalline, glassy and composites with wide range of chemical compositions and different crystal structures, typically, $\text{Li}_{3x}\text{Ln}_{2/3-x}\text{TiO}_3$ ($\text{Ln} = \text{La, Pr, Nd, Sm}$) with perovskite structure [3], $\text{Li}_{1+x}\text{Ti}_2-x\text{M}_x(\text{PO}_4)_3$ ($\text{M} = \text{Al, Sc, Y, La}$) with NASICON structure [4], glass ceramics ($\text{Li}_7\text{P}_3\text{S}_{11}$), composites ($\text{Li}_2\text{S-SiS}_2\text{-Li}_3\text{PO}_4$) [5], and notable $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ with orthorhombic structure [6]. All these materials exhibit ion conductivities of the order of $10^{-4}\text{-}10^{-2}$ S/cm, but those compounds are not favorable as an electrolyte material for all-solid-state batteries due to their low stability in direct contact with commonly used intercalation electrode materials for battery applications. Garnet-related compounds, especially cubic- $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ attract more attention due to their high lithium ion conductivity ($\sim 10^{-4}$ S/cm) [7,8]. Regards of their chemical stability against electrode materials, the dense garnet ceramics are considered as solid state electrolytes for all-solid-state batteries. However, it is difficult to synthesize the pure garnet materials as well as to obtain dense ceramics with cubic polymorph for high ionic conductivity [9]. In this communication, we address a lithium ion conductor in $\text{Li}_4\text{SiO}_4\text{-Li}_3\text{PO}_4\text{-LiBO}_2$

ternary system for its reasonable ion conductivity and good stability as well as easy fabrication, potential as practical solid electrolyte used in all-solid state battery.

The binary system of $\text{Li}_3\text{PO}_4\text{-Li}_4\text{SiO}_4$ solid solution has been investigated extensively [10–14]. Li_4SiO_4 material has the structure generally described in terms of isolated $(\text{SiO}_4)^{4-}$ anionic clusters with ordered distribution of Li^+ ions over available cationic sites which are coordinated with 4, 5 or 6 oxygen atoms in a monoclinic unit cell ($P21/m$ space group). LiO_4 , LiO_5 and LiO_6 polyhedra are linked by edge- and corner-sharing. $\gamma\text{-Li}_3\text{PO}_4$ has a very similar orthorhombic structure ($Pmn2$ ~ space group) formed of isolated $(\text{PO}_4)^{3-}$ anionic clusters with lithium ions in tetrahedral coordination [10]. These two lithium-containing compounds have ordered structure concerning Li ions, resulting in very low ion conductivity. Fortunately, mixing of these two compounds can dissolve each other into solid solution up to 60 mol%, leading to the vacancies or interstitial sites in the lattice for the increase of conductivity [11]. The solid solution of $\text{Li}_{4-x}\text{Si}_1-x\text{P}_x\text{O}_4$ with the composition of $0 < x < 0.12$ is stable in the Li_4SiO_4 monoclinic structure, while the $\text{Li}_{4-x}\text{Si}_1-x\text{P}_x\text{O}_4$ with composition $0.12 < x < 0.6$ is metastable in the orthorhombic structure similar to $\gamma\text{-Li}_3\text{PO}_4$. The ion conductivities of the solid solutions are several orders of magnitude greater than those of either end group. For example, Li ion conductivity of the samples with the compositions of $x \sim 0.5$ to 0.6 can achieve at the level of 10^{-6} S/cm and the activation energies is about 0.51–0.52 eV¹³, while the ion conductivity for $x = 0.4$ is reported lower than that of the above compositions ($\sim 10^{-7}$ S/cm) [14]. It was noted that the doping amount of LiBO_2 from 0.5 to 5 wt.% as sintering agent into $\text{Li}_{4-x}\text{Si}_1-x\text{P}_x\text{O}_4$ ($x = 0.6$) solid solution could improve the ion conductivity due to the densification of ceramics [15]. Thus, it

* Corresponding author.

E-mail address: xykong@sjtu.edu.cn (X.Y. Kong).

is intriguing that the ternary system of $\text{Li}_4\text{SiO}_4\text{-Li}_3\text{PO}_4\text{-LiBO}_2$ ceramic could be novel lithium ion conductor. In this case, up to the amount of 20 mol% LiBO_2 incorporated into the $\text{Li}_{4-x}\text{Si}_{1-x}\text{P}_x\text{O}_4$ system ($x = 0.4$) were investigated for the increase of ion conductivity. The effects of incorporating boron on phase structure and grain boundary as well as the densification are also discussed.

2. Experimental

The ceramic pellet samples were prepared by solid state reaction and sintered for densification. Li_4SiO_4 (Aldrich, 99%), Li_3PO_4 (Aldrich, 99%), B_2O_3 (Aldrich, 99%) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (Aldrich, 99.9%) were used as the starting materials. The powders of the starting materials were mixed and formed into pellets by cold press under the pressure of 15–20 MPa for 2 min. The sample termed as 40LP was prepared with 60 mol% of Li_4SiO_4 and 40 mol% of Li_3PO_4 for $\text{Li}_{4-x}\text{Si}_{1-x}\text{P}_x\text{O}_4$ ($x = 0.4$); The sample termed as 40LP + 20B was prepared by mixing B_2O_3 , LiOH and 40LP sample according to the mole ratio of $\text{Li}_4\text{SiO}_4\text{:Li}_3\text{PO}_4\text{:LiBO}_2 = 60\text{:}40\text{:}20$. Regards of the solid state reaction and evaporating loss of lithium oxide at high temperature, the additional 10 mol% amount of LiOH was added for compensation of Li ion concentration in ternary system. To obtain homogenous solid solution, the mixture of starting materials were subjected to the solid state reaction at 900 °C and 2 h aging in the fluxing argon atmosphere for several times. For dense ceramic pellets, 40LP samples were sintered at 900 °C in fluxing argon atmosphere for 4 h, and the 40LP + 20B samples were sintered at 900 °C in fluxing argon atmosphere for 4 h and 6 h, respectively. The evaluated rate of increasing temperature was 10 °C/min, and cooling down naturally. The as-received ceramic pellets were termed as 40LP/4 h, 40LP + 20B/4 h and 40LP + 20B/6 h, respectively. Pellet dimensions and weights were measured before and after sintering. The relative density of as-received ceramic pellets was measured by the routine method based on Archimedes principle.

The phase structures were identified by X-ray diffraction method (XRD, Rigaku Ultima IV) using $\text{CuK}\alpha$ radiation ($\lambda = 1.54178\text{Å}$). Scanning electron microscopy (SEM) was conducted of as received pellets using Zeiss ultra 55 SEM to observe the grain morphology from the fresh fracture surface of sample. Energy dispersive X-ray spectroscopy (EDS) was done to map the spatial distribution of boron in the grain or grain boundary by means of Oxford INCA penta FETx3 detector. The

electrical performance was examined by electrochemical impedance spectroscopy (EIS) using modulab ECS Solartron Analytical System. For this purpose, the pellets were polished to make their surface smooth and Au thick films were deposited by evaporation method as the blocking electrode. Impedance was recorded in frequency range 0.01 Hz to 1 MHz. An AC perturbation was applied with amplitude (rms) 10 mV. Complex impedance spectra were analyzed to reveal the resistances of grain and grain boundary as well as their associated capacitances.

3. Results and discussion

In Fig. 1, XRD pattern data are shown for entire range of solid solutions along with standard data for Li_4SiO_4 (PDF No. 37-1472) and $\gamma\text{-Li}_3\text{PO}_4$ (PDF No. 15-0760). From Fig. 1c, it is clear that the reflection peaks shift left from the original pattern of $\gamma\text{-Li}_3\text{PO}_4$, typically marked in the planes (020), (021) and (002) respectively. It indicates that the as-received sample is the typical single solid solution phase of $\text{Li}_{3.6}\text{Si}_{0.6}\text{P}_{0.4}\text{O}_4$ with the orthorhombic structure similar to $\gamma\text{-Li}_3\text{PO}_4$ [10], and both the b-axis (010) and c-axis (001) are expanded dramatically from the original lattice structure while a-axis (100) is changed little. In Fig. 1d, it is observed that there are two set patterns, one representing the solid solution phase with orthorhombic structure, another representing the impurity (\blacklozenge) indexed as LiPO_3 according to PDF No.26-1177. Nevertheless, in Fig. 1e, the reflection peaks of as LiPO_3 impurity are almost disappeared, the dominate peaks are represented for the single solid solution phase. The occurrence of LiPO_3 impurity in the 40LP + 20B/4 h sample is responsible from the incorporation of boron into $\text{Li}_{3.6}\text{Si}_{0.6}\text{P}_{0.4}\text{O}_4$ and a little phosphate is precipitated from ternary solid solution system. In the ref. [15], the impurity of Li_2SiO_3 appeared in the additive of 5 wt.% LiBO_2 into $\text{Li}_{3.4}\text{Si}_{0.4}\text{P}_{0.6}\text{O}_4$ sample, resulted from extraction of lithia from the Li_4SiO_4 by reaction with LiBO_2 . However, regards of the longer sintering time from 4 h to 6 h, the LiPO_3 impurity was dissolved again for the complete ternary solid solution. It is also obvious that the reflection peaks of the 40LP + 20B sample sintering for 4 h and 6 h are left shifting from those of the original 40LP sample, specifically the peak indexed as (002) reflection shifting dramatically. It means that the lattice constant of solid solution is dilated due to the incorporation of boron to form the ternary solid solution system. It was assumed that increase of lattice constant upon

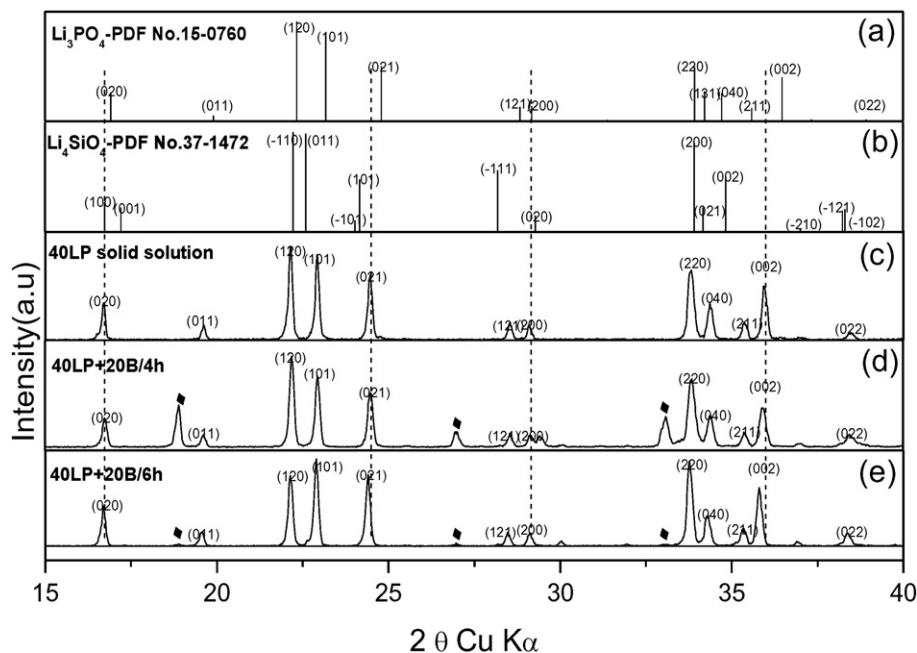


Fig. 1. XRD patterns corresponding to the standard data for Li_3PO_4 (a) and Li_4SiO_4 (b), 40LP/4 h (c), 40LP + 20B/4 h (d), and 40LP + 20B/6 h (e), respectively.

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