

Preparation, microstructure and electrical properties of $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ nanoceramics

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Abstract NASICON-type $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ solid electrolytes were prepared by various processes, such as crystallization of glasses, spark plasma sintering (SPS) and conventional sintering process from nanosized precursor powders synthesized by a sol–gel route. The experimental results showed that grain size and relative density were the main factors determining the ionic conductivity of the bulk materials. The SPS technique produced ceramics with nearly 100% of the theoretical density. Maximum room temperature conductivities, $1.39 \times 10^{-3} \text{ S cm}^{-1}$ and $1.12 \times 10^{-3} \text{ S cm}^{-1}$ of grain boundary conductivity and total conductivity, respectively were obtained which were the highest values for Li^+ inorganic oxide conductors as reported. Crystallization of ceramics from a glass was also certified as a favorable route to fabricate a bulk material with high conductivity.

Keywords NASICON · $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ · Ceramics · Lithium ion conductivity

1 Introduction

Non aqueous solutions and polymers are at present used as the electrolytes for lithium ion batteries. However, these organic electrolytes cannot meet the requirements of size-compactness, safety, integration and stability at high temperatures [1]. Therefore, solid lithium superionic conductors exhibiting sufficient ionic conductivity at ambient temperature are expected. The NASICON-type structured

$\text{LiM}_2(\text{PO}_4)_3$ ($M = \text{Ti}, \text{Ge}, \text{etc.}$) has been found to possess favorable conducting tunnel for lithium ions. However, grain boundary effects and difficulties in obtaining dense products to great extent restricted their practical use [2]. Such materials were mainly prepared by solid state reaction process. The conventional ceramics exhibited ionic conductivity of 10^{-4} – 10^{-5} Scm^{-1} at room temperature [3, 4], which cannot meet the requirements of solid electrolytes for all solid state lithium batteries. Glass-ceramics is a category of materials of great potential as solid electrolytes because they can be made into desired shape and size easily, have favorable microstructure and exhibit good chemical stability. A few literatures have reported the improvement in electrical properties of NASICON-typed solid lithium ion conductors compared with their conventional ceramic analogues [5–9].

In this paper, we deal with the grain size and relative density of the bulk materials on their ionic conductivity of the $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ systems. Various processes were applied to fabricate the NASICON-type structured ceramics.

2 Experimental

The NASICON-type $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ glass-ceramics were prepared by crystallization from glasses (GC) and by spark plasma sintering (SPS) processes. The precursor powder was first prepared by a sol–gel process. Reagent-grade $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (AR), $\text{LiNO}_3 \cdot \text{H}_2\text{O}$ (AR), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR) and $\text{NH}_4\text{H}_2\text{PO}_4$ (AR) were used as the starting materials with citric acid as the polymer precursor and distilled water as the solvent. They were weighted at the same molar ratio of the components of $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$. After homogenization of the solution, a certain volume of

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glycol was added to promote polyesterification and polycondensation reactions. The metal ion concentration was adjusted to 0.20 mol l^{-1} and the pH value was adjusted in the range from 1.2 to 11. The molar ratio of citric acid/glycol was 1:1. The obtained powders were prepared by heat-treating the dry gel at $800 \text{ }^\circ\text{C}$ for 2 h. For GC process, the powder was melted at $1400\text{--}1500 \text{ }^\circ\text{C}$ for 1 h. The melts were poured onto stainless steel plates and the glasses formed were annealed at 500°C and finally cooled down naturally. SPS process was carried out with the powders as precursor and post heat treatment was taken at appropriate temperatures.

XRD were carried out to determine the phase of the powders and ceramics. The microstructure of the ceramics was observed by field emission scanning electron microscopy (SEM). Polished samples were prepared for ionic conductivity measurements with gold electrodes sputtered on both sides of the samples as blocking electrodes. Complex impedance measurements for ceramic samples were carried out over the frequency range of $10^{-1}\text{--}10^6 \text{ Hz}$.

3 Results and discussion

Figure 1 showed the X-ray diffraction patterns of the powders heat-treated at $800 \text{ }^\circ\text{C}$ for 2 h in air from the gels

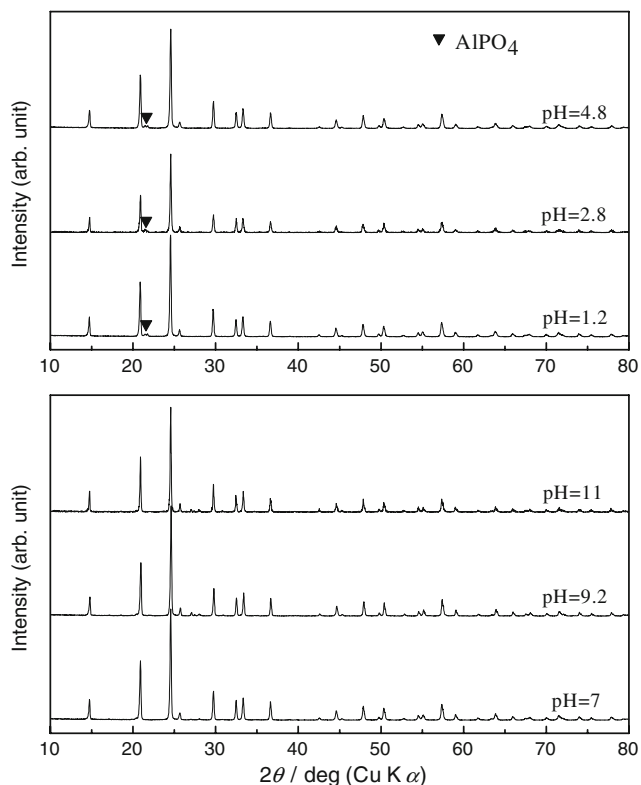


Fig. 1 XRD patterns of the powders prepared by a sol-gel process with different pH value of the solutions

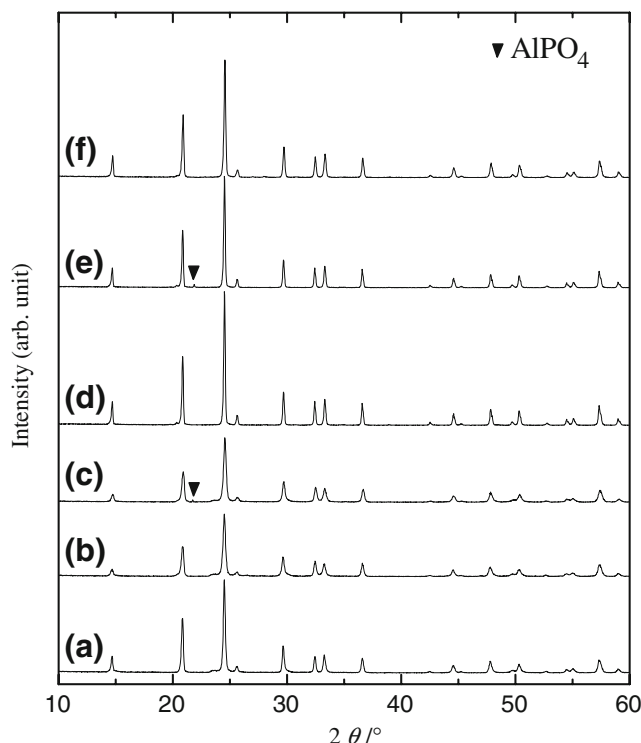


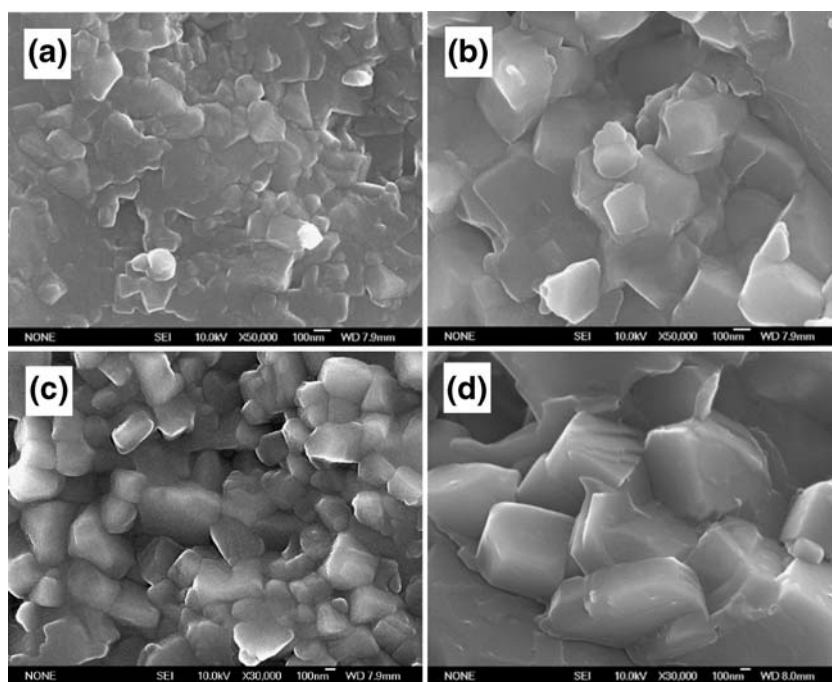
Fig. 2 X-ray diffraction patterns of various samples: (a) as-prepared powder; (b) ceramics sintered by SPS at $650 \text{ }^\circ\text{C}$ (SPS650); (c) ceramics sintered by SPS at $700 \text{ }^\circ\text{C}$ (SPS700); (d) SPS650 with post annealing; (e) SPS700 with post annealing; (f) conventional solid state sintering at $850 \text{ }^\circ\text{C}$

synthesized at various pH values. All patterns showed the peaks corresponding to the lithium-analogue of NASICON, viz. $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$. It was seen that impurity peaks due to AlPO_4 were only evident in samples prepared under acid conditions (pH 1–5). Under basic conditions a crystalline $\text{LiTi}_2(\text{PO}_4)_3$ -type phase appeared with no evidence for impurity phases. The average particle size of the powder determined by TEM analysis was about 60 nm and the size distribution was favorable.

The hexagonal lattice parameters of the $\text{LiTi}_2(\text{PO}_4)_3$ -type phase were obtained by a least-squares fit. The a - and c -parameters for the specimen prepared at pH=7 were determined to be $8.483 \pm 0.002 \text{ \AA}$ and $20.826 \pm 0.005 \text{ \AA}$, respectively. These values were slightly smaller than those reported for the sintered $\text{LiTi}_2(\text{PO}_4)_3$ ($a=8.513 \text{ \AA}$ and $c=20.878 \text{ \AA}$) [10], which certified the structural modifications resulted from the replacement of Ti^{4+} by Al^{3+} in $\text{LiTi}_2(\text{PO}_4)_3$.

Figure 2 showed the XRD patterns of all ceramics sintered by different routes. It was indicated that the peaks corresponding to NASICON structure were appeared in all samples. Pure crystalline $\text{LiTi}_2(\text{PO}_4)_3$ phase was obtained as seen in Figs. 2(a), (b), (d) and (f). However, peaks indexed to AlPO_4 were detected for LATP ceramics by annealing at $650 \text{ }^\circ\text{C}$ for 6 h after SPS at $700 \text{ }^\circ\text{C}$ and the

Fig. 3 Microstructure of the fracture section of different samples (a) SPS sintering with post annealing at 650 °C; (b) SPS sintering at 700 °C with post annealing at 650 °C; (c) by crystallization from glass at 950 °C for 24 h and (d) conventional solid state sintering in air at 850 °C for 6 h



specimen prepared by SPS at 700 °C, indicating possible loss of lithium content during the process. After annealing at 650 °C for 6 h, the intensity of the peaks due to $\text{LiTi}_2(\text{PO}_4)_3$ increased (d and e), indicating gradual growth of $\text{LiTi}_2(\text{PO}_4)_3$ phase. It was noticed, the impurity crystalline AlPO_4 phase was usually inevitable as shown in the references [5, 11].

Figure 3 demonstrated the microstructure of the fractured surface of various bulk samples. As seen, the SPS technique made it possible to make real nanoceramics. The ceramics sintered at 650 °C with a post heat treatment at the same temperature resulted in the grain size about 100 nm. The increase of the sintering temperature to 700 °C led to obvious growth of the grains to the average size of

about 400 nm. However, the conventional solid state sintering (SSS) process made a ceramic sample remarkably big grain size, e.g., about 1.5 μm , although the sintering temperature was as low as 850 °C. For comparison, the microstructure of the glass ceramics crystallized at 950 °C for 24 h from a glass with the same composition was also shown. Its grains were sized about 0.6 μm , comparable to the SPS sintered sample at 700 °C.

Typical complex impedance plots were illustrated in Fig. 4 for $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ ceramics prepared by SPS sintering at 650 °C with a post heat treatment. Only one semicircle was observed at all testing temperatures. These semicircles were ascribed to the correspondence of the bulk impedance of the samples. The disappearance of the bulk impedance semicircle at 105 °C could be ascribed to the low resistance of the bulk at the enhanced temperature. The total resistance (R_t) and the bulk resistance (R_b) of the sample were obtained from the right and left intercept of the semicircle with the real axis in the plots respectively. The value of the grain boundary resistance (R_{gb}) was

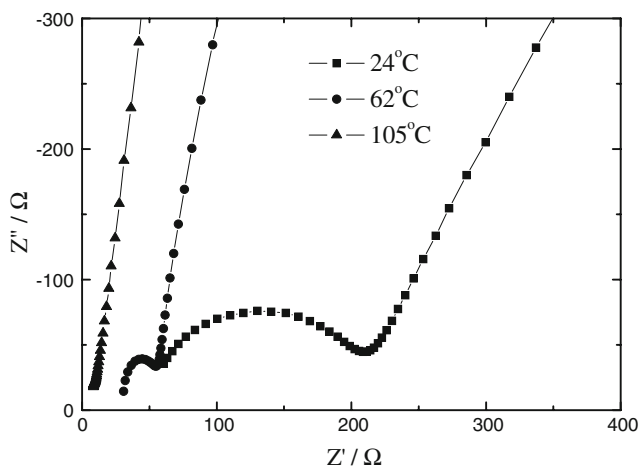


Fig. 4 Typical complex impedance of the $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ ceramics

Table 1 The average particle size and basic properties of different samples.

Sample	Grain size (nm)	Relative density (%)	Grain boundary conductivity (S cm^{-1})	Total conductivity (S cm^{-1})
SPS650	<100	100	1.39×10^{-3}	1.12×10^{-3}
SPS700	~400	99	1.02×10^{-3}	0.78×10^{-3}
GCS950	~600	97	0.93×10^{-3}	0.49×10^{-3}
SSS850	~1,500	95	0.79×10^{-3}	0.36×10^{-3}

therefore the difference between R_t and R_b . The R_b , R_{gb} and R_t were used to calculate the corresponding values of σ_b (bulk conductivity), σ_{gb} (grain boundary conductivity) and σ_t (total conductivity), respectively. The results were listed in Table 1 for all the samples. In order to understand deeply the factors determining the ionic conductivity, the relative density of all the samples was tested by the Archimedes' method with ethanol as a medium. As listed, the ceramics prepared by SPS gave rise to the highest density, nearly fully condensed sample was obtained at 650 °C. It seemed that the relative density had more close relationship with the grain boundary. Since all the samples had the same chemical composition, their bulk conductivity should be comparable, therefore, the higher the grain boundary conductivity, the higher the total conductivity. From Table 1, we found that the total conductivity was proportional to the relative density of the sample. Similar predominant effect of interfacial/grain boundary on the total conductance of ceramics was also presented by Balaya et al. [12]. The ceramic sample prepared by conventional solid state sintering process had the biggest grain size, nearly 1.5 μm . It was also indicated by the table that the grain size of the sample was reversely proportional to the relative density, the overgrowth of the grains would remarkably cause the decrease in the relative density of the sample and therefore reduce its ionic conductivity. It was reasonable to suggest that a decrease in grain size even to nanoscale and at the same time a high bulk density are imperative to the high conductivity of inorganic lithium ion conductors.

4 Conclusions

Pure NASICON structured $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ ceramics were prepared by different processes with a nano precursor powder synthesized by a sol–gel method. The SPS technique produced dense conductors with nearly 100%

of the theoretical density at 650 °C. Their maximum room temperature conductivity, $1.39 \times 10^{-3} \text{ S cm}^{-1}$ and $1.12 \times 10^{-3} \text{ S cm}^{-1}$ of grain boundary and total conductivity, respectively reached the highest values for inorganic oxide Li^+ conductors as reported. The grain size of the samples was reversely proportional to their relative densities. The overgrowth of the grains would cause remarkable decrease in the relative density of the samples and therefore the decline of their ionic conductivity. It was reasonable to suggest that a decrease in grain size even to nanoscale and high bulk density are imperative to the high conductivity of inorganic lithium ion conductors.

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