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Ionic conduction and vibrational characteristics of Al^{3+} modified monoclinic $LiZr_2(PO_4)_3$

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ABSTRACT

Effects of Al^{3+} substitution for Zr^{4+} in $LiZr_2(PO_4)_3$ on its structure and lithium ion conduction are investigated. $Li_{1+x}Zr_{2-x}Al_x(PO_4)_3$ samples prepared via a sol-gel route and calcined at 900 °C crystallize in monoclinic structure with $P2_1/n$ space group and show a reduction in cell volume with an increase in x. Raman spectra showed an increase in broadening of higher frequency v_1 & v_3 vibrational modes and a spectral weight transfer between v_2 & v_4 bending modes of PO_4 tetrahedra with the increase in Al^{3+} doping. Analysis of Raman spectra further suggested that the renormalization of the mode frequencies in doped samples is controlled by Li-ion motion via strongly interacting with internal bending modes of PO_4 tetrahedra. A significant improvement in ionic conductivity was observed in Al-doped samples, and the highest conductivity of $1.83 \times 10^{-4}\ \Omega^{-1}m^{-1}$ and lithium diffusion coefficient of about $5.7 \times 10^{-19}\ m^2s^{-1}$ was observed for $Li_{1.25}Zr_{1.75}Al_{0.25}(PO_4)_3$ at room temperature. Li transference number suggested that the conductivity in $Li_{1.25}Zr_{1.75}Al_{0.25}(PO_4)_3$ is predominantly ionic. Activation energy was found to decrease from 0.58 eV for $LiZr_2(PO_4)_3$ to 0.47 eV for $Li_{1.25}Zr_{1.75}Al_{0.25}(PO_4)_3$.

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1. Introduction

Fast growing markets of mobile electronic devices, electric vehicles, and smart grids raised the demand for high energy density lithium batteries. Such high energy density batteries can be realized by utilizing the metallic lithium as an anode. However, the use of high capacity lithium anode is hampered by the serious safety issues related to the formation of dendrites during lithium deposition/dissolution cycles [1–5]. Replacing flammable and volatile liquid electrolytes with inorganic solid electrolytes in rechargeable lithium batteries could circumvent the safety issues to a large extent [1,2,6–10]. This has led to a renewed focus on fast lithium ion conducting materials in recent years. $Li_xM_2(PO_4)_3$ phases is one such group which is being widely investigated as the potential solid electrolytes for next-generation rechargeable lithium battery applications [11–24]. Structural framework of these materials consists of corner sharing MO_6 octahedra and PO_4 tetrahedra forming a 3D network of interstitial tunnels through which lithium ion movement is facilitated. Several compounds with M = Ti, Zr, Sn, Hf, Sc, etc. have been studied extensively for their structure and electrochemical behavior [21,24–29]. Rhombohedral $LiTi_2(PO_4)_3$ based compounds show highest Li^+ conductivity among various $Li_xM_2(PO_4)_3$. Electrochemical stability against lithium metal, high grain boundary resistance, high interfacial resistance, and difficulty in sintering remain serious issues with the effective use of these materials as a solid-electrolyte in lithium batteries [1,2,9,22,26,30–34].

$LiZr_2(PO4)_3$ (LZP) is another important compound in view of the high reduction potential against lithium metal which makes it an attractive candidate for use as an electrolyte in high energy density batteries. LZP crystallizes in monoclinic (β′ phase) or triclinic (α′ phase) structures at room temperature depending on the synthesis conditions [12–16,18,19,35–39]. While there have been some reports on the structure and lithium ion conduction in rhombohedral $LiZr_2(PO_4)_3$ (α phase), reports on monoclinic LZP are scarce [13,16,18,19,35,38]. An orthorhombic (β) to monoclinic (β′) phase transition around 300 °C on cooling has been reported in low temperature synthesized β-phase [35,40]. In the β′ structure (Fig. 1), fully ordered Li is located in a regular tetrahedral surrounding with no vacant neighboring site available for facile

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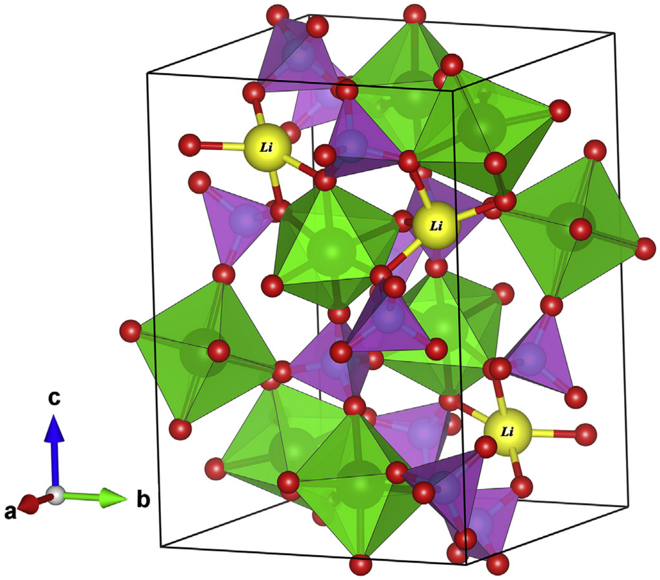

Fig. 1. Schematic representation of the $LiZr_2(PO_4)_3$ with monoclinic structure. Large spheres represent lithium ions; ZrO_6 octahedra and PO_4 tetrahedra are shown in green and violet colors, respectively. Red colour solid sphere represents oxygen atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

hopping; whereas, in β structure, Li was found to be distributed over two sites in 2:1 ratio. The short distance between partially occupied sites produces low energy barrier for Li ions between these sites in orthorhombic LZP [40]. As a result, relatively lower lithium ionic conductivity and higher activation energy is expected in β′-LZP as compared to β-LZP. One of the foremost prerequisites for a material to be used as a solid-electrolyte in batteries is the high ionic conductivity (>1 $mScm^{-1}$). The reported room temperature ionic conductivity for both α′ and β′ phases of LZP is much lower than desired for battery applications. Concerted efforts, therefore, have been exercised in this regard to improve the lithium ion conduction in LZP. Most of these studies have been on stabilizing the high conducting α-phase of LZP by aliovalent doping [13,15,16,19,36–38].

Lithium motion in inorganic solid electrolytes is primarily via thermally activated hopping of Li ions between vacant (Schottky defects) and/or interstitial (Frenkel defects) sites. Amount of these intrinsic defects determine the ionic conductivity in a given material [6,22,41,42]. In addition, polarizability and size of the constituent ions affect the ionic conductivity as these determine the nature of conduction pathways for ions in the material [43]. Extrinsic interstitials and vacancies can also be induced by the substitution of aliovalent cations. Accordingly, ionic conduction in solids can be tailored by the appropriate doping. For instance, doping of Al^{3+} for M^{4+} in $Li_xM_2(PO_4)_3$ (where M = Ti, Ge, Sc, Hf, etc.) ceramics is known to increase the lithium ion conductivity significantly [1,6,20–22,34]. For instance, optimum Al^{3+} doping in $LiTi_2(PO_4)_3$ and $LiGe_2(PO_4)_3$ was reported to increase the room temperature ionic conductivity by 3 orders of magnitude [29,44]. Such phenomenal enhancement in conductivity has been attributed to the increased Li^+ concentration, change in the size of the bottleneck of Li^+ transport pathways, and improved sintering behaviour. However, it was shown recently that additional Li (to compensate the charge imbalance due to the substitution of tetravalent Ti^{4+} by Al^{3+}) influences the ionic mobility only marginally. This opening of the bottleneck results in a decrease of the activation energy by a mere 0.02 eV and does not explain the 3 orders of magnitude increase in conductivity [22]. Arbi et al. linked improved Li mobility in Al^{3+} doped $LiTi_2(PO_4)_3$ to the local distortions arising from vibrational motion of O ions [21].

Raman spectroscopy is very sensitive to any small change in the unit cell; therefore, any change in the unit cell will be reflected via a change in the phonon self-energy parameters such as phonon frequency. In this system Zr and lithium ions are linked with PO_4 tetrahedra via Zr—O—P bonds, therefore any change in the Zr—O and Li—O interaction will be directly reflected as a change in mode frequency associated with the internal modes of PO_4 tetrahedra. Gaining an understanding of the structure – composition – property relationship is crucial to advance the fundamental knowledge about the Li-ion conduction in these materials. This motivated us to perform a detailed Raman analysis of $LiZr_2(PO_4)_3$ as a function of doping and understand the effect of doping on the phonon modes which may result from the change in lattice parameter as well as increase in Li ion concentration with doping.

In the present work, we focus on the effects of Al^{+3} substitution in low temperature synthesized monoclinic LZP on its crystal structure, microstructure, vibrational characteristics, and lithium conductivity. Direct current polarization study to estimate the contribution of ionic conductivity to the total conductivity in the selected composition is also reported.

2. Experimental

$Li_{1+x}Zr_{2-x}Al_x(PO_4)_3$ [$x = 0$, 0.1, 0.2, 0.25, 0.3, 0.4, and 0.5] powders were synthesized *via* a sol-gel method using citric acid as chelating agent. Starting precursors (of purity >99.5%) $LiNO_3$, $ZrOCl_2.8H_2O$, $Al(NO_3)_3$, and $NH_4H_2PO_4$ were dissolved in doubly deionized water in separate beakers. Except for $LiNO_3$, which was taken in 10% excess of desired stoichiometry, all precursors were used in the stoichiometric ratio. These solutions were mixed in an aqueous solution of citric acid and ethylene glycol (molar ratio of ethylene glycol:citric acid = 1:1) under continuous stirring. After vigorous stirring at 80 °C for 6 h, the solution was heated at 150 °C to obtain a semi-transparent gel. This gel was further calcined at 500 °C for 12 h to obtain a white powder. This powder was then pressed uniaxially under a pressure of 200 MPa into cylindrical pellets with the thickness of 1–2 mm and diameter of 10 mm. The pressed pellets were then sintered at 900 °C for 12 h at a heating rate of 3 °C/min for varying durations in air. During the final sintering, pellets were buried in the sacrificial powder of the same composition to minimize volatilization of lithium and to avoid the contamination from alumina boat.

To confirm the phase purity, sintered pellets were crushed into powders and X-ray diffraction patterns were recorded using a Bruker-D2 Phaser diffractometer with Cu-Kα radiation in the 2θ range of 10–80° at a step size of 0.02°. Archimedes' method was used to calculate the densities of the sintered pellets by using the Xylene (density ~ 0.86 g/cm^3) as the liquid medium. Unpolarised micro Raman measurements were performed by Raman spectrometer (LabRam HR-Evolution) in the backscattering configuration. Under ambient environment, the Raman spectra were recorded through collecting scattered light dispersed by spectrometer with 1800 lines/mm grating with Peltier cooled CCD detector in the frequency range from 50 to 1200 cm^{-1}. The obtained Raman spectra were excited by 532 nm laser with 50x LWD objective. Laser power was kept low (~1 mW) at the sample surface in order to avoid any heating effect.

Field emission scanning electron microscope (SUPRA 55) equipped with an Oxford Link-Isis energy dispersive X-ray spectroscopy (EDS) detector was used for compositional and microstructural analyses. For impedance and chronoamperometry measurements, polished surfaces of pellets were painted with

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