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Effect of doping of trivalent cations Ga^{3+}, Sc^{3+}, Y^{3+} in $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) system on Li^+ ion conductivity

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ABSTRACT

We report the effect of trivalent cations dopants in the $Li_{1.3}Al_{0.3-x}R_xTi_{1.7}(PO_4)_3$ ($R=Ga^{3+}$, Sc^{3+}, Y^{3+}) NASICON ceramic system in the concentration range $x=0.01,0.03,0.05,0.07$, on the Li^+ ion conducting properties using impedance spectroscopy. The samples were prepared by solid state reaction method and characterized by X-Ray Diffraction and density measurements. The electrical properties were studied using impedance spectroscopy in frequency range 10 Hz to 20 MHz and temperature range 303 K to 423 K. Although the porosity of the material decreased with doping, the overall Li^+ ion conductivity of the system did not improve with doping. Ionic radii of the dopant cations was found to be an important factor in formation of impurity phases and low Li^+ ion conductivity. Gallium doped samples exhibited a higher Li^+ ion conductivity compared to its scandium and yttrium doped counterparts.

1. Introduction

The necessity for compact electrical sources in the areas like transportation, medicine, defence and electronic equipments like mobile phones and laptops has placed an increased demand to look for sources of electrical energy like batteries, supercapacitors and fuel cells. Lithium batteries have emerged as promising candidates due to their higher energy density. Amongst lithium ion conducting materials, NASICON (Na like Super Ionic Conductors) compound $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) has been a widely studied system for its high Li^+ conductivity of $\sim10^{-3}$ S/cm [1,2,3,4,5] and its application as electrode and electrolyte material in the Lithium ion batteries. LATP compound has a rhombohedral ($R\bar{3}c$) symmetry with mutually facing alternate arrangement of TiO_6 octahedra [4,7]. The corner oxygen atoms of the octahedra are shared with PO_4tetrahedra. **M1** cation vacancies are formed between PO_4 tetrahedra amidst the ribbons while **M2** vacancies are formed between adjoining TiO_6 octahedra. Li^+ ions diffuse along the pathways (also called bottlenecks) which interconnect the **M1–M2** vacancies, in a robust 3-D NASICON network. From ^{27}Al NMR studies it was found that aluminum in the LATP NASICON compound is located at two positions – at tetrahedral (denoted as $\mathbf{Al_T}$) and octahedral (denoted as $\mathbf{Al_O}$) sites [3]. One of the primary reasons of higher Li^+ ion conductivity is the large size of the LATP lattice which provides broad enough passage for the Li^+ ions. In the present study we modify the LATP lattice by doping oxides of trivalent cations. The host Al^{3+}cation is replaced in the system $Li_{1.3}Al_{0.3-x}R_xTi_{1.7}(PO_4)_3$ ($R=Ga^{3+}$, Sc^{3+} and Y^{3+}) by other trivalent cations of larger ionic radii, which may further increase the lattice volume, but retain the charge neutrality of the lattice leading to higher values of Li^+ ion conductivity.

However the ion conducting oxide ceramic materials prepared using solid state reaction method in general suffer from porosity. Pores and cracks formed at grain boundaries inhibit a smooth passage of Li^+ ions across grain boundaries. Hence grain boundary conductivities in Li^+ ion conducting NASICON materials is an order or two lesser than in bulk (grain) and is an important limitation in using these compounds in commercial Li-ion batteries today [10,11]. Non conducting phases like $AlPO_4$ are an unavoidable by-product during the synthesis of LATP system [3,9] which may segregate towards grain boundaries. Although they reduce porosity within the material, they do not contribute towards improving Li^+ ion conductivity. Hence, inspite of presence of $AlPO_4$ the overall Li^+ ion conductivity in LATP NASICON compounds is reported to be of the order $\sim10^{-3}$ S/cm [3,5]. Hence it is interesting to investigate if doping of trivalent cations to replace Al^{3+} in the LATP would also form similar phases and affect the Li^+ ion conductivity as in case of their parent system LATP.

It has been observed that if the values of ionic radii of the dopant cations are significantly larger than that of the host cations, the dopant cation cannot get fully substituted in the host lattice

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because the elastic strain energy developed due to size difference of the two cations acts to drive the dopant out of the lattice [14–17]. Such oversized dopants form oxide phases and get segregated towards grain boundaries. The thermal energy during synthesis assists the migration of such impurity phases [18–20]. Hence although there are reports [6–9] about Li^+ ion conductivity in inorganic ternary systems of $Li_{1.3}Al_{0.3-x}R_xTi_{1.7}(PO_4)_3$ type, a comparative study of the electrical properties for the dopants with increasing ionic radii as an important parameter has not been undertaken to the best of our knowledge.

2. Experimental

2.1. Sample preparation

Pellets of $Li_{1.3}Al_{0.3-x}R_xTi_{1.7}(PO_4)_3$ compound were prepared by mixing the powders of laboratory grade reagents Li_2CO_3, TiO_2, Al_2O_3, Ga_2O_3, Y_2O_3, Sc_2O_3,$(NH_4)_2H_2PO_4$ according to their stoichiometric proportions for the different concentrations ($x=0.01$, 0.03, 0.05, 0.07). The mixture was wet ground thoroughly and heated in open ampoules for 30 min at 573 K in an electrical furnace. After cooling, the mixture was ground to a fine white powder and heated to 1073 K for about 30 min and again left to cool slowly in the furnace. The fine powder was ground again for 30 min and uniaxially cold pressed at 70 MPa pressure, to form pellets of 10 mm diameter and 3 mm thickness. The pellets were then sintered at 1373 K for 5 h and left in the furnace to cool slowly. The samples of $Li_{1.3}Al_{0.3-x}R_xTi_{1.7}(PO_4)_3$ where $0.01 \le x \le 0.07$ were obtained the details of which are enlisted in Table 1. In the prepared samples, those doped with scandium and yttrium have a better structural stability and ruggedness compared gallium doped samples. Their surface is smooth and does not deteriorate for a long time.

2.2. Sample characterization

X-ray Diffraction (XRD) patterns were recorded at room temperature using Rigaku MiniFlex Cu Kα1 in a continuous scan mode in the 2θ range of 10° to 70°. Structure parameters were deduced by indexing the x-ray patterns, using POWDERX package (see Table 1). Density was measured using Archimedes method. Digital weighing balance (*A&D* Japan) with 0.01 mg accuracy was used to weigh the samples in air and in methanol, from which the density values were derived. Two probe impedance measurements using Solartron SI 1260 were performed to study the electrical properties of material. A very thin layer of silver paint was applied on both flat surfaces of the cylindrical pellet to work as electrodes for the impedance study. The frequency dependent impedance measurement were carried out in temperature range of 303 K to 423 K and in the frequency window of 10 Hz to 20 MHz.

3. Results and discussion

X-ray diffraction (XRD) was performed to determine the crystalline structure of samples. XRD patterns of gallium, scandium and yttrium doped samples of $x=0.03$ concentration along with those of the parent LATP system is presented in Fig. 1. Peaks corresponding to $LiTi_2(PO_4)_3$ (LTP) phase for rhombohedral $R\bar{3}c$ symmetry [1,2,3,5] are shown with symbols in Fig. 1. Few peaks corresponding to $AlPO_4$, $GaPO_4$, $ScPO_4$, YPO_4 are marked in the Fig. 1. These impurity phases contribute to less than 10% of the total phases and are generally unavoidable in ternary systems [6–10]. The values of lattice parameters (***a*** and ***c***) and the lattice volume increase as cations of larger ionic radii size (Ga^{3+}, Sc^{3+}, Y^{3+}) substitute in the lattice [12,13] in the LATP lattice. The values are similar to the reported ones [6–8].

Nyquist $Z' - Z''$ plots are shown for samples containing gallium, scandium and yttrium at $x=0.03$ concentrations in Figs. 2–4 respectively. Two semi circular arcs are formed for all three systems under study. A very small arc shown in the inset of Figs. 3 and 4 and formed in the frequency range of more than 10^5 Hz represents the grain region. The capacitance at higher frequencies is of the order of 10 pF which corresponds typically grain region [5,22,23]. The impedance values are fitted by using a parallel combination of **R** and **CPE** (Constant Phase Element) using equivalent circuit. The secondary (larger) arc formed at intermediate and low frequencies, represents higher values of impedance and corresponds to grain boundary and interfacial region between electrode and electrolyte. The impedance values in grain boundary and interfacial regions are affected by irregular boundaries, space charges and impurity phases [11] – and the impedance plot is fitted using a parallel combination of **R**, **C**, **CPE** in the subcircuit. The usage of extra capacitance **C** (marked with red and blue circles) can be noted in the inset of Figs. 3 and 4, for scandium and yttrium doped samples respectively which represent the grain boundary and interfacial regions. A plot of grain boundary capacitance for increasing concentration across three dopants at 353 K is seen in Fig. 5. With increasing segregation of dopant phases the grain boundary effects can be clearly seen for yttrium which is the largest among the doped cations.

Arrhenius plots of doped samples for grain and grain boundary regions are shown in Figs. 6 and 7 respectively. It can be seen that the Li^+ ion conductivity (order of 10^{-4} S/cm) for doped samples is

Table 1
Nomenclature, chemical formula, lattice parameters, lattice volume and porosity for samples LTP, LATP and doped samples.

Samples	**Chemical formula**	***a,b*** **(Å)**	***c*** **(Å)**	***Lattice Volume*** ($Å^3$)	***Porosity %***
LTP	$LiTi_2(PO_4)_3$	**8.5129**[a]	**20.878**[a]	1310.3[a]	–
LATP	$Li_{1.3}\ Al_{0.3}Ti_{1.7}(PO_4)_3$	**8.5039**	**20.5208**	1305.023	22
G1	$Li_{1.3}\ Al_{0.29}Ga_{0.01}Ti_{1.7}(PO_4)_3$	**8.51**	**20.75**	1303.965	15
G2	$Li_{1.3}Al_{0.27}Ga_{0.03}Ti_{1.7}(PO_4)_3$	**8.54**	**20.8**	1315.064	13
G3	$Li_{1.3}Al_{0.25}Ga_{0.05}Ti_{1.7}(PO_4)_3$	**8.555**	**20.85**	1306.428	13
G4	$Li_{1.3}Al_{0.23}Ga_{0.07}Ti_{1.7}(PO_4)_3$	**8.565**	**20.895**	1349.922	6
N1	$Li_{1.3}\ Al_{0.29}Sc_{0.01}Ti_{1.7}(PO_4)_3$	**8.5084**	**20.5245**	1288.741	19
N2	$Li_{1.3}Al_{0.27}Sc_{0.03}Ti_{1.7}(PO_4)_3$	**8.5192**	**20.6712**	1311.495	13
N3	$Li_{1.3}Al_{0.25}Sc_{0.05}Ti_{1.7}(PO_4)_3$	**8.485**	**21.0297**	1323.431	10
N4	$Li_{1.3}Al_{0.23}Sc_{0.07}Ti_{1.7}(PO_4)_3$	**8.624**	**20.7182**	1333.862	6
T1	$Li_{1.3}\ Al_{0.29}Y_{0.01}Ti_{1.7}(PO_4)_3$	**8.3**	**20.85**	1243.921	25
T2	$Li_{1.3}Al_{0.27}Y_{0.03}Ti_{1.7}(PO_4)_3$	**8.358**	**20.457**	1244.796	24
T3	$Li_{1.3}Al_{0.25}Y_{0.05}Ti_{1.7}(PO_4)_3$	**8.505**	**20.458**	1286.248	15
T4	$Li_{1.3}Al_{0.23}Y_{0.07}Ti_{1.7}(PO_4)_3$	**8.507**	**20.463**	1306.126	12

[a] From Ref. [6] (a).