

A single crystal X-ray and powder neutron diffraction study on NASICON-type $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($0 \leq x \leq 0.5$) crystals: Implications on ionic conductivity



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ARTICLE INFO

Article history:

Received 29 March 2016

Received in revised form

11 August 2016

Accepted 13 August 2016

Available online 16 August 2016

Keywords:

$\text{LiTi}_2(\text{PO}_4)_3$

Al^{3+} substitution

LATP

NASICON

Single crystal X-ray diffraction

Neutron diffraction

ABSTRACT

Single crystals of NASICON-type material $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ (LATP) with $0 \leq x \leq 0.5$ were successfully grown using long-term sintering techniques. Sample material was studied by chemical analysis, single crystal X-ray and neutron diffraction. The Ti^{4+} replacement scales very well with the Al^{3+} and Li^+ incorporation. The additional Li^+ thereby enters the M3 cavity of the NASICON framework at x, y, z ~ (0.07, 0.34, 0.09) and is regarded to be responsible for the enhanced Li^+ conduction of LATP as compared to Al-free LTP. Variations in structural parameters, associated with the Ti^{4+} substitution with $\text{Al}^{3+} + \text{Li}^+$ will be discussed in detail in this paper.

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1. Introduction

Lithium-based batteries, in particular Li-air concepts, have the highest theoretical energy densities among conventional batteries. Their specific energy density excluding oxygen of 11430 Wh kg^{-1} – similar to the energy density of fossil fuels – make them attractive as a possible energy source for electric vehicles even if only half of this energy density might be used in future [30]. In Li-air batteries, mainly water-based electrolytes are developed nowadays, which is problematic due to rapid corrosion of Li metal at low pH. Therefore solid electrolytes are under development, which are stable against water and Li metal. For this purpose garnets [23] or Li-based

NASICON materials are of special interest due to their high ionic conductivity, especially $\text{Li}_{1+x+y}(\text{M}, \text{Al}, \text{Ga})_x(\text{Ge}_{1-q}\text{Ti}_q)_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ and $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$. Both materials, however, are prone to reduction (Ge^{4+} to Ge^{2+} , Ti^{4+} to Ti^{3+}) and subsequent decomposition when the material is in contact with metallic Li. A solution for avoiding this reaction is the application of thin protective coatings of Li-conduction garnets or a polymer electrolyte or the use of Li alloys as anode material [30].

NASICON – type materials are skeleton structures, which were originally discovered by Ref. [18] and proposed for fast Na^+ ionic conductivity in the pioneering work of [16]. A skeleton structure is defined to consist of a rigid framework with interconnected interstitial space in which ions move in three dimensions [16]. They identified materials based on $\text{Na}_{1+x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$ to show high and fast Na^+ conductivity. A huge amount of work on many different NASICON and Li-based NASICON-type materials have been

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done since then.

LATP is among the most widely investigated solid electrolyte materials for Li-ion batteries because of its relatively high Li-ion conductivity, chemical stability and mechanical strength. Its Li-ion bulk conductivity is induced by partial substitution of Ti^{4+} with Al^{3+} , in combination with the incorporation of additional Li^+ into the structure (see Fig. 1 for structural details). The electrical conductivity therefore depends strongly on the substitution parameter x .

In order to better understand the transport properties from the crystal chemical point of view, highly accurate diffraction data are needed. Structural information on LATP is available from several studies, e.g. Refs. [4,5,7,8,12,29] and [10]. However, in most cases only lattice parameters are provided and the main focus of these studies is on synthesis and electrochemical property characterization of LTP with various substituents. More detailed structural data are only available from the recent studies of [5,12,24] and [22]. Considering the importance of LATP to enable new battery concepts, it is remarkable that up to now no single crystal diffraction studies are available, which is attributed to the difficulties in preparing single crystals from Li-conducting materials in general.

However, we succeeded to synthesize single crystals of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$, with $0 < x < 0.5$ and investigated these single crystals by means of single crystal X-ray diffraction (SC-XRD) combined with time-of-flight (*t.o.f.*) powder neutron diffraction (PND). This finally enables a detailed analysis of structural variation in LATP as a function of x , which is necessary to fully understand the structure-property relationships in this class of materials.

2. Experimental

2.1. Synthesis

Polycrystalline samples of LATP with $0 < x < 0.5$ were

synthesized using conventional solid state reaction. The stoichiometric amounts of Li_2CO_3 (VWR International, Belgium, 99%), TiO_2 (VWR International, Belgium, 99%), Al_2O_3 (Alfa Aesar, 99.99%) and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ (Merck, 99%), plus an excess of 20 wt% Li were mixed and homogenized in an agar mortar. Before use, the TiO_2 was dried at 600°C for 6 h; all other reagents were used directly as received. Then, the mixture of the powder were put into a Pt crucible and slowly heated up with 120°C/h heating rate up to 1000°C and kept there for 6 h in air and cooled down to room temperature with 300°C/h . After this calcination step, the powder sample was crushed, homogenized in a mortar and pressed to pellets. During a second heat treatment, the pellets were sintered at 1000°C for 720 h (1 month) in a corundum crucible on a powder bed of LATP. During this period the powder particles grew to irregularly formed grains with crystal edges of up to $150\ \mu\text{m}$. Small single crystals were easily obtained after crushing the pellet and sieving the coarse powder with a mesh size of $64\ \mu\text{m}$. Nearly cubic shaped crystals were chosen for the single crystal measurements.

2.2. Single crystal X-ray diffraction

Single crystal X-ray diffraction data were collected on a Bruker SMART APEX CCD-diffractometer. A single crystal was selected on the basis of its optical properties (sharp extinctions, regular shape and homogeneity in colour) and glued on top of a glass capillary ($0.1\ \text{mm}$ in diameter). Intensity data were collected with graphite-monochromatized Mo K_α X-ray radiation ($50\ \text{kV}$, $30\ \text{mA}$). The crystal-to-detector distance was $30\ \text{mm}$ and the detector positioned at $-28^\circ 2\theta$ using an ω -scan mode strategy at four different ϕ positions (0° , 90° , 180° and 270°). 630 frames with $\Delta\omega = 0.3^\circ$ were acquired for each run. Three-dimensional data were integrated and corrected for Lorentz-, polarization and background effects using the APEX3 software [9]. Structure solution using direct methods and subsequent weighted full-matrix least-squares refinements on

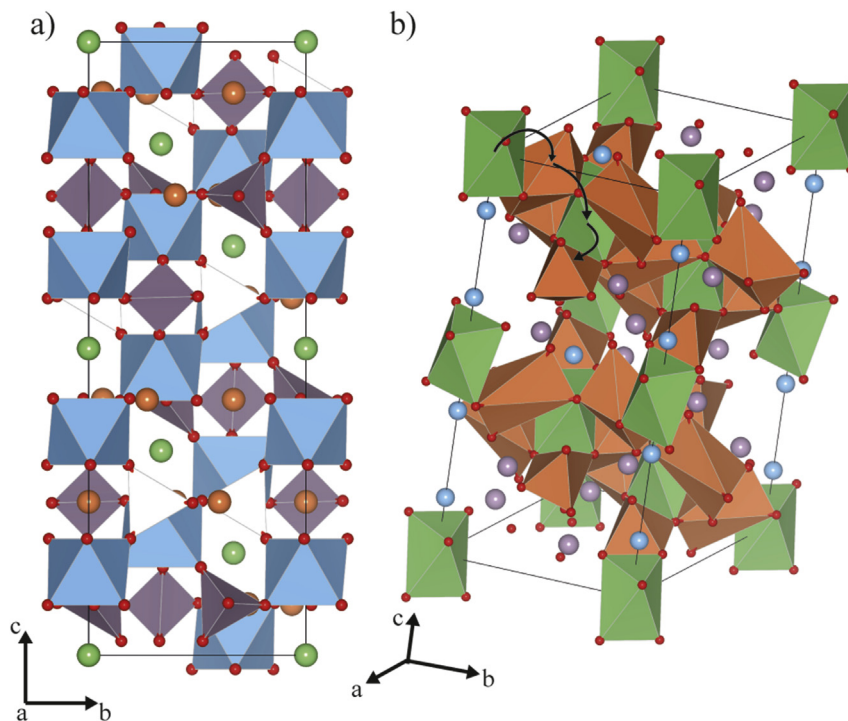


Fig. 1. (a) Crystal structure (space group $R\bar{3}c$) of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$. Green (M1/6b) and orange (M3/36f) spheres correspond to Li^+ in octahedral sites. Blue octahedra (12c) are occupied by Ti^{4+} or Al^{3+} . The purple tetrahedra are occupied by P^{5+} (18e). O^{2-} are located at the corners of the polyhedra (red spheres - 36f). (b) Li^+ connectivity within the NASICON structure formed by M1 and M3 polyhedra. Black arrows indicate a possible diffusion process. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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