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

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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 $x, y, z \sim (0.07, 0.34, 0.09)$ 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.

Keywords: $\text{LiTi}_2(\text{PO}_4)_3$, Al^{3+} substitution, LATP, NASICON, single crystal X-ray diffraction, neutron diffraction

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 (Zhang et al, 2008). 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 (Murugan et al., 2007) 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 (Zhang et al., 2008).

NASICON – type materials are skeleton structures, which were originally discovered by Hong (1976) and proposed for fast Na^+ ionic conductivity in the pioneering work of Goodenough et al. (1976). A skeleton structure is defined to consist of a rigid framework with interconnected interstitial space in which ions move in three dimensions (Goodenough et al., 1976). 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 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 Figure 1 for structural details). The electrical conductivity therefore depends strongly on the substitution parameter x .

Figure 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.

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.* (Wong et al., 1998), (Arbi et al., 2015; Arbi et al., 2013; Arbi et al., 2002; Arbi et al., 2007), Dashjav and Tietz (2014) and Bucharsky et al. (2015). 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 Arbi et al. (2013), Dashjav and Tietz (2014), (Perez-Estebanez et al., 2014) and (Monchak et al., 2016). 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 $(\text{NH}_4)\text{H}_2\text{PO}_4$ (Merck, 99 %), plus an excess of 20 wt% Li were mixed and homogenized in an agate 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 μm . Small single crystals were easily obtained after crushing the pellet and sieving the coarse powder with a mesh size of 64 μm . 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 mm in diameter). Intensity data were collected with graphite-monochromatized Mo K_α X-ray radiation (50 kV, 30 mA). The crystal-to-detector distance was 30 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 (Bruker, 2015). Structure solution using direct methods and subsequent weighted full-matrix least-squares refinements on F^2 were carried out with SHELX-2012 (Sheldrick, 2015) as implemented in the program suite WinGX 2014.1 (Farrugia, 2012).

Details on data collection and results of structure refinement of selected samples are given in Table 2, the fractional atomic coordinates, anisotropic and equivalent isotropic atomic displacement parameters are compiled in Table 3, while Table 4 gives selected bond lengths and additional secondary structural parameters, and the full set of data is available via the CIFs in the supplementary material.

2.3. Neutron diffraction

On LATP with $x = 0.4$, neutron powder diffraction measurements were performed on the time-of-flight powder diffractometer, POWGEN, located at the Spallation Neutron Source at Oak Ridge National Laboratory. The data were collected with neutrons of central wavelengths 1.333 Å and 2.665 Å, covering the d -spacing range of 0.45–6.2 Å and 1.15–10.5 Å, respectively. For the ND measurements approximately 2 g of powder was loaded in a vanadium can of 8 mm in diameter and data were collected at low temperature (10 K) and room temperature (300 K). Data were refined using the Fullprof-Suite of programs using pseudo-Voigt function with back-to-back exponential functions and using the profile function of POWGEN. The background was modelled with a polynomial function of 6th order. After achieving stable refinements, the powder neutron diffraction data were combined with the single crystal X-ray diffraction data and all atoms, except Li2, were modelled using anisotropic atomic displacement parameters. The results of the simultaneous refinement are included in Tables 3 and 4.

2.4. Electron microprobe analysis

The chemical composition of polycrystalline samples of LATP were determined by electron microprobe analysis (EMPA) using a field emission gun JEOL Superprobe JXA 8530F at the Natural History Museum, Vienna. Elements and X-ray lines used for the analysis are P ($K\alpha$), Ti ($K\alpha$) and Al ($L\alpha$). Operating conditions included an accelerating voltage of 15 kV and beam current of 20 nA with wavelength dispersive X-ray spectrometers (WDS). The electron beam was ~10 µm in diameter. Standard specimens used for calibration were Durango apatite (for P), synthetic TiO₂ (for Ti) and Al₂O₃ (for Al). Theoretical values for Li₂O, calculated for $x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5 from $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$, were added as fixed concentrations to the on-line ZAF correction procedure (Table 1).

3. Results and Discussion

3.1. Synthesis and mineral chemistry

High quality sample material could be obtained using the synthesis route described above, yielding coarse grained material with individual single crystals up to 150 μm in size. Individual crystals show well developed faces and idiomorphic cube-like habitus. In a recent investigation (Hupfer et al., 2016) noted rapid grain growth of individual LATP crystals at 1100°C in a matrix of fine grained sample material already after 30 minutes of sintering up to a size of 100 μm , however with distinct formation of cracks due to the stress induced by highly anisotropic thermal expansion, after 8 h of sintering these authors almost exclusively observed large grains > 100 μm in their samples with multiple cracks. It should be noted that the crystals in this study were free of any crack. As impurity phases orthorhombic LiTiPO_5 and small amounts of rutile TiO_2 (< 1.4 wt.%) and berlinite AlPO_4 (< 1 wt.%) were identified by X-ray powder diffraction methods and subsequent Rietveld refinements. These results are given in the supplement Table S1. The amount of LiTiPO_5 increases from 4 wt. % in Al free $\text{LiTi}_2(\text{PO}_4)_3$ to almost 18 wt. % for the samples richest in Al^{3+} ($x = 0.5$). In the electron microprobe analysis, the samples appear to be homogeneous in the backscattered electron images, both from grain to grain and from rim to core in individual grains. As an example, a part of the sample of LATP with $x = 0.5$, which shows the largest amounts of impurities, is depicted in Figure 2.

Figure 2: Backscattered electron image from electron microprobe analysis of embedded and polished crystals of LATP with $x = 0.5$. Impurity phases are readily seen from differences in grey scales. Green, red, and orange dots indicate LiTiPO_5 , LATP, and TiO_2 , respectively.

The results of electron microprobe analysis are compiled in Table 1. The Li_2O content was fixed to the theoretical value of the corresponding nominal compositions. LATP with $x = 0.5$ is the only sample where in some rare cases, there is a slightly lighter grey core part in some

crystals as compared to the rim. However, it was not possible to resolve any difference in chemical composition between the different regions, so – if ever – chemical inhomogeneity is very small. As can be seen from the results of electron microprobe analysis, the LATP crystals formed during synthesis are close to the composition of the starting material. The increasing amount of Al^{3+} almost ideally scales with the decreasing amount of Ti^{4+} , also the content of P^{5+} suggests full occupation of the tetrahedral sites and no admixture onto other positions in the structure. It is therefore concluded that during the long-term synthesis LATP crystals have been formed which can be describe indeed by the $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ substitutional mechanism.

3.2. Crystal structure refinement

For all collected data sets, intensity statistics and systematic extinctions agree with space group $R\bar{3}c$, which is the typical space group symmetry for the NASICON-type materials. The data set of the sample with nominal Al^{3+} contents of $x = 0.4$ was used to obtain a structure model. Structure solution with direct methods gave Ti/Al on $12c$, P1 on $18e$ and two oxygen atom positions O1 and O2, both on $36f$, which agree very well with the atomic positional parameters previously published for $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ compounds (*e.g.* Aatiq et al. (2002), Arbi et al. (2013), (Dashjav and Tietz, 2014)). The largest residual peak in the residual electron density map was located at position 0, 0, 0, corresponding to Li at the M1 site (Wyckoff position $6b$). After adding Li1 at $6b$ additional residual electron density was found at 0.07, 0.34, 0.09 (Wyckoff position $36f$), which is close to the M3 position in NASICON compounds (*e.g.* Catti et al. (2004)). A very similar position was determined by (Arbi et al., 2013) for Li in $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ with $x = 0.2$ and 0.4 using neutron diffraction data and for $\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ (Monchak et al., 2016). The Li content at M3 was refined freely without any constraints and correlates well with the Al^{3+} content.

To verify the Li distribution obtained from SC-XRD data, *t.o.f* PND data were collected and analyzed. As a starting point, only the $\text{Ti}_2(\text{PO}_4)_3$ framework was refined and the difference Fourier maps clearly showed negative densities, indicative for Li at 0, 0, 0 (M1 – $6b$ position). Including Li on the M1 site and inspection of the remaining residual nuclear densities after convergence of refinement revealed further negative nuclear densities close to 0.07, 0.34, 0.09, *i.e.* at identical position as obtained from the single crystal X-ray data. As shown in

Figure 3, a good agreement between observed and calculated neutron diffraction data with low residual factors ($R_{wp} = 4.02$, $R_B = 4.68$ %) could be obtained with this structural model. The data also revealed the presence of LiTiPO_5 as an impurity phase with mass fraction of 9.8(4) %, in perfect agreement with the amount obtained from powder X-ray diffraction. In a final step of the refinement, the neutron diffraction data were combined with the SC-XRD data and treated in a simultaneous X-ray/neutron (XN) refinement. The results of this refinement are included in Table 2. The XN refinements showed the P sites to be fully occupied with phosphorus, while the mixed refinement of the octahedral site with Ti + Al gave a composition of $[\text{Al}_{0.421(9)}\text{Ti}_{1.579(9)}]$ in good agreement with the composition from electron microprobe analysis and single crystal X-ray data $[\text{Al}_{0.407(9)}\text{Ti}_{1.593(9)}]$. The content of the Li on the M3 site in the XN refinement is 0.42(2) thus higher and closer to the Al^{3+} content than the one obtained by single crystal X-ray refinement. The results of the XN refinement can be regarded as a proof that a 1 : 1 substitution of $\text{Al}^{3+} + \text{Li}^+$ for Ti^{4+} indeed takes place.

Figure 3: Comparison of the experimental and calculated neutron diffraction data of $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$. Blue tick-marks correspond to the LATP phase, while red ones represent the Bragg – peaks of the impurity phase LiTiPO_5 .

Arbi et al. (2013) as well as (Perez-Estebanez et al., 2014) noted that the Li^+ content at M1 decreases with increasing Al^{3+} substitution. Within the solid solution series of this study, there is also a trend of a small decrease of Li^+ on M1 in the case of free refinement of the occupancy, with a Li^+ deficit of ~ 0.1 mol/formula unit for $x = 0.5$, thus supporting the observation of Arbi et al. (2013). However, the Li deficit is by far not as pronounced as found by (Perez-Estebanez et al., 2014). For $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$, (Monchak et al., 2016) also report almost full occupation of M1 with Li, however, they observed a decreasing occupation of M1 with increasing temperature, while the occupation with Li on M3 increases. The neutron diffraction data on LATP with $x = 0.4$ also indicate only a small vacancy concentration of ~ 0.03 mol/formula unit in free refinements at M1. However, as the occupation of Li^+ on M1 is highly correlated with the atomic displacement parameters in our single crystal X-ray data and Li is a very weakly scattering atom for X-rays, the M1 position was finally fixed to full occupancy to reduce correlations of parameters. Arbi et al. (2013) also found that the Al concentration in their material deviates from the nominal values, *i.e.* for $x_{\text{nom}} = 0.4$ they refined 0.27. In the single crystal data of this study, the observed Al content on the Ti sites is in excellent agreement with the nominally intended values. Dashjav and Tietz (2014) found Li both on the M1 position and on $0, 0, \frac{1}{4}$; however, considering the different preparation routes and the long-term annealing of the samples in the series of this study, there is no Li found at this position. With Li on M1 (anisotropic) and M3 and Al^{3+} substitution for Ti on the octahedral positions, the “largest” residual electron density peaks are below $+0.4 \text{ e}/\text{\AA}^3$. They are close to the O2 and O1 oxygen atoms, which could be a hint for very small positional disorder with increasing Al^{3+} contents.

Figure 4: Variation of lattice parameters in the $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ solid solution including literature data. Data of this study are plotted vs. the refined Al^{3+} content.

As displayed in Figure 4 the lattice parameters of $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ decrease with increasing substitution of Ti^{4+} ($r_{\text{VI}} = 0.61 \text{ \AA}$) by the smaller Al^{3+} ($r_{\text{VI}} = 0.54 \text{ \AA}$) in octahedral coordination (Shannon and Prewitt, 1970). The decrease is linear and data of single crystal and powder samples agree well and show the same trend. The slope of literature data of (Arbi et al., 2013) is similar to the one determined in this study. Between $x = 0.0$ and 0.5 the lattice parameters a and c decrease by 0.32% and 0.45% , respectively, *i.e.* the latter is more affected by the Ti^{4+} substitution.

3.3. Structural considerations

In brief, the crystal structure of $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ consists of $(\text{Ti,Al})\text{O}_6$ octahedra, which have their metal atoms located on the 3-fold axis of the unit cell. The octahedra share all of their corners with neighboring PO_4 tetrahedra, while the PO_4 tetrahedra vice versa share all their vertices with the octahedra, forming a poly-anionic $[(\text{Ti,Al})_2\text{P}_3\text{O}_{12}]$ three-dimensional framework (Figure 1). Two main cavities can be identified in the NASICON structure, the first one hosts the M1 site in octahedral coordination at $6b$ position with site symmetry $\bar{3}$. This position can be related to the empty octahedral sites in the related corundum structure (Catti et al., 2004). In the LATP samples of this study, this site host Li^+ with a Li1-O distance of $2.265(1) \text{ \AA}$, which remains almost constant with increasing Al^{3+} substitution. Also the polyhedral volume of the M1 site remains unaffected by the Al^{3+} substitution. The geometry of the oxygen coordination polyhedron around Li1 becomes more distorted, expressed by an increase of the octahedral quadratic elongation (OQE) and the octahedral angle variance (OAV). Also evident from the structure refinements is the large anisotropic atomic displacement of Li at this site. With increasing Al^{3+} content the equivalent isotropic atomic displacement U_{eq} increases from $\sim 0.05 \text{ \AA}^2$ in Al^{3+} -free to $U \sim 0.08 \text{ \AA}^2$ in samples richest in Al^{3+} (Fig. 5), indicative for higher mobility of Li at M1 in Al-rich samples. The U_{eq} values for all other atoms also increase, however, to a much lesser extent (cf. Table 3). The second largest U_{eq} values shown for the O1 oxygen atom, which is bonded to the Li2 site, thus is indirectly affected by the increasing displacement of the Li1 atom.

Figure 5: Variation of equivalent atomic displacement parameters of Li ions within the series $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$.

With increasing Al^{3+} content, the distance between Li1 and Ti/Al decrease linearly, and also a tendency of a decreasing Li1-Li2 interatomic distances can be deduced, even if the estimated standard deviations for the latter are large (Table 4).

The second cavity in NASICON-type materials surrounds the M3 site, which ideally is located at $[x, y, z = 0, \frac{1}{3}, \frac{1}{12}]$ in position $18e$ with site symmetry 2. Within the LATP series, Li2 is located in the M3 cavity, but is displaced from the $18e$ to a general $36f$ position. Li2 exhibits a distorted 6-fold coordination with Li-O bond lengths ranging from 2.10 to 2.67 Å, the average $\langle \text{Li2-O} \rangle$ bond length is rather constant at 2.32(5) Å throughout the solid solution series. Similar to Li1, U_{eq} increases with increasing Al^{3+} content. In general the volume of the Li2O_6 polyhedron is smaller than the one of the Li1 octahedron. Additionally, the volume of the Li2O_6 polyhedron is inversely correlated with the Al^{3+} content, it decreases distinctly towards Al^{3+} -rich compositions (Fig. 6). This reduction in volume goes along with an increase in polyhedral distortion, while for average and individual Li2-O distances no clear picture could be derived due to large estimated standard deviations, especially for the Li-poor crystals of the series.

Figure 6: Variation of the polyhedral volumes at the M1 and M3 Li sites in the series $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$.

The PO_4 tetrahedron is very regular, both in terms of angular and bond angle distortion; it shows an average bond length of $\langle 1.5294(12) \rangle$ in pure $\text{LiTi}_2(\text{PO}_4)_3$ which is in good agreement with literature data of Aatiq et al. (2002), but deviate to some extent from those of Pinus et al. (2012). Within the increasing substitution of Ti^{4+} by Al^{3+} , small adjustments in bond lengths, bond angles and distortional parameters take place: individual and average P-O distances slightly decrease, as does the tetrahedral volume; vice versa, the quadratic tetrahedral elongation and the tetrahedral angle variance increase, so that the PO_4 tetrahedron in Al^{3+} -rich samples is smaller but more distorted (Table 4). More distinct variations are observed for the $(\text{Ti},\text{Al})\text{O}_6$ octahedron. The incorporation of Al^{3+} decreases the average $\langle \text{Ti}/\text{Al}-\text{O} \rangle$ bond length from $1.9287(12) \text{ \AA}$ to $1.9127(12) \text{ \AA}$, the two symmetrically independent individual Ti-O bonds decrease with parallel uniform trends (Figure 7). Consequently, the polyhedral volume also decreases and the Al^{3+} substitution lets the OQE parameter unaffected, while the small OAV further decreases. This means that the octahedron becomes more ideal and regular towards Al^{3+} -rich compositions.

Figure 7: Variation of the average and individual Ti-O bond lengths in the series $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$.

The decrease in $(\text{Ti,Al})\text{O}_6$ octahedral bond lengths and volume is the main reason for the distinct decrease of the lattice parameter c . Besides the change in polyhedral geometry, also changes in the tilting between octahedral and tetrahedral interconnections of the poly-anionic framework can be detected. The angle between Ti1-O1-P1 amounts to $157.50(14)^\circ$ in $\text{LiTi}_2(\text{PO}_4)_3$ and decreases with increasing Al^{3+} content down to $156.34(14)^\circ$ (Figure 8). This decrease in polyhedral tilt angle is a necessity for the decreasing size of the TiO_6 octahedron and also contributes to the decrease in the lattice parameter c . By decreasing of the Ti1-O1-P1 angle, additionally the size of the M3 cavity becomes smaller, which is expressed by the decreasing size of the M3 polyhedral volume. On the contrary, the Ti1-O2-P1 tilt angle increases from $138.08(13)^\circ$ to $139.09(14)^\circ$, which contributes to the smaller decrease of the lattice parameter a and to the fact that the volume of the M1 cavity remains almost constant.

Figure 8: Variation in $\text{TiO}_6 - \text{PO}_4$ tilt angles within the series $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$.

3.5. Lithium mobility pathways

A huge amount of investigations were performed in order to understand the enhanced Li-ion conduction in LTP materials caused by the substitution of Ti^{4+} by Al^{3+} . Lang et al. (2015) found that bulk diffusion is only slightly changed by substitution using DFT calculations. Other possible reasons for the enhanced conductivity are the different thermal expansions or the anharmonic behavior of oxygen atoms. These possible reasons, however, can be excluded today due the almost same thermal expansion behavior of LTP and LATP as shown by Arbi et al. (2014).

In the present study an almost linear behavior in the lattice parameters, polyhedral volumes, jump distances between the M1 and M3 sites, and their Li site occupation is observed. Nevertheless, there is a huge increase of three orders of magnitude after incorporating Al into LTP. Duluard et al. (2013) suggested a relation between the strong increase in conductivity and microstructure. Indeed, (Aono et al., 1990; Aono et al., 1991) found such a significant decrease in the electrical resistance in bulk and grain boundary as a function of density. However, very recently (Rettenwander et al., 2016), conductivity measurements on LTP and LATP single crystals showed that microstructure and density can be excluded as reasons for the enhanced Li-ion conduction. The authors finally conclude that the increase in Li-ion bulk conductivity is intrinsic in nature and is based only on the incorporation of the additional Li-ions as highly mobile charge carriers within the fast – diffusion pathways in the NASICON structure, as discussed by Lang et al. (2015). These authors provide a theoretical evidence that the substitution of Ti^{4+} with Al^{3+} leads to additional Li ions in the energetically favored M3 sites associated with the displacement of next neighbored Li (M1) towards the next M3 site. Also very recently Epp et al. (2015) were able to fully support the theoretical findings by investigating the underlying diffusion mechanism in LATP by NMR spectroscopy. They revealed several distinct diffusion processes with activation energies in excellent agreement with the calculated values. Additionally (Monchak et al., 2016) provide a detailed study of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ in which they were able to fully describe experimentally the possible diffusion pathways using neutron diffraction by – among others – the difference bond valence method and the maximum – entropy method (MEM). In full agreement with the present study, they verified the occupation of the M3 position with Li and constructed a 3D diffusion pathway along a M1 – M3 – M3 – M1 zig-zag chain, which best is viewed in a two dimensional (0 1 -4) section (Monchak et al., 2016).

In the present study, SC-XRD combined with *t.o.f.* PND provide a detailed experimental evidence for the proposed diffusion mechanism. A linear increase of Li occupancy at M3 and the Li1-Li2 distance with increasing Al content (see Table 4) is observed accompanied with an almost linear increase in the isotropic displacement parameter (see Figure 5), which clearly indicates higher mobility of Li within the Li-ion sub-lattice. The initial introduction of 0.1 mol Al per formula unit, however, leads to a strong (non-linear) increase in the Li-ion bulk conductivity by three orders of magnitudes (Rettenwander et al., 2016). Finally, based on all the theoretical and experimental evidences, we are able to conclude that the additional Li occupying M3 sites is necessary to induce high Li ion motion, *i.e.*, a Li ion from an M1 site

moves only if the vacant site is immediately filled by a Li^+ ion from an adjacent M3 site. Therefore, conductivity increases rapidly as soon as M3 sites are populated and ion transport is enabled, while further population of the M3 sites only leads to a minor increase in conductivity.

In Figure 9 the bulk conductivity $\sigma_{\text{b,Li}}$ of single crystals (Rettenwander et al., 2016) is shown in dependence of the analytical Li content listed in Table 1. The dome-shaped curve can be derived as the molar fraction of charge carriers (Kawai and Kuwano, 1994), assuming that only the M3-sublattice composed of Li ions and vacancies is contributing to the charge transport. In the case of LATP this seems to be justified, because all compositions investigated here show full occupancy of the M1 site. The molar fraction of charge carriers can be expressed as

$$F_{\text{Li,V}} = \frac{c_{\text{Li}} \times c_{\text{V}}}{c_{\text{Li}} + c_{\text{V}}} \quad \text{Eq. (1)}$$

in which c_{Li} and c_{V} are the Li ions and vacancies located in M3. Since the number of Li ions in M1 site is assumed as constant (1 mole per formula unit), the abscissa spans from 1 to 2 Li ions per formula unit. The maximum of $F_{\text{Li,V}}$ is obtained at 1.5 and matches very well with the measured ionic conductivity of the materials showing the highest value at 1.4. The similar dependence of $F_{\text{Li,V}}$ and $\sigma_{\text{b,Li}}$ on the Li content supports misleadingly the assumption made above that the ionic transport in LATP is only governed by the hopping of Li ions from one M3 site to the next.

Figure 9: Theoretical dependence of concentrations of mobile Li ions, c_{Li} , (straight line) and vacancies, c_V , (dashed line) on M3 sites for the compositions $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ and resulting molar fraction of charge carriers, $F_{Li,V}$, (dash-dotted line) according to eq. (1). The open diamonds show the analytical Li content (Table 1) along the $F_{Li,V}$ curve, the gray diamond shows the Li content after refinement of the neutron diffraction data indicating the excellent agreement with the analytical result for $x = 0.4$. The bulk conductivities (filled squares) were taken from (Rettenwander et al., 2016).

However, ionic transport can only take place, when Li ions jump along the sites M3-M1-M3) and therefore Li1 at the M1 sites seem to contribute in a cooperative way. When a Li ion on M3 tries to move forward, it has to push a Li ion from a M1 site to a M3 site. After one combined hopping of the two Li ions the occupancy is the same as before and the observed full occupancy of M1 with Li(1) just reflects an apparent static situation. In this theoretical assumption only the Li ions on M3 sites trigger the ionic transport and Figure 9 reflects the dominating role of charge carriers on M3 sites. It is important to note that 1) a recent NMR study revealed an addition diffusion-induced rate peak and maybe a change of the conduction mechanism above 300 °C (Epp et al., 2015). It is possible that at elevated temperatures the occupancy of the M1 sites is reduced and a de-coupled diffusion of Li ions occur. 2) The occupancy of the 6*b*-site in Na ion conductors is often reduced resulting in the classical ion transport via vacancies. Since there are no restraining mobile ions and the fact that more charge carriers are present, the ionic conduction is much higher than in Li ion conductors (Guin et al., 2016).

Acknowledgment

This research was supported by the Austrian Science Fund (FWF): project number P25702. The authors gratefully acknowledge the financial support provided by JCNS to perform the neutron scattering measurements at the Spallation Neutron Source (SNS), Oak Ridge, USA. Part of the research conducted at SNS was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy (DOE).

References

- Aatiq, A., Menetrier, M., Croguennec, L., Suard, E., and Delmas, C. (2002) On the structure of $\text{Li}_3\text{Ti}_2(\text{PO}_4)_3$. *Journal of Materials Chemistry*, 12(10), 2971-2978.
- Aono, H., Sugimoto, E., Sadaoka, Y., Imanaka, N., and Adachi, G. (1990) IONIC-CONDUCTIVITY OF SOLID ELECTROLYTES BASED ON LITHIUM TITANIUM PHOSPHATE. *Journal of the Electrochemical Society*, 137(4), 1023-1027.
- . (1991) ELECTRICAL PROPERTY AND SINTERABILITY OF $\text{LiTi}_2(\text{PO}_4)_3$ MIXED WITH LITHIUM SALT (Li_3PO_4 OR Li_3BO_3). *Solid State Ionics*, 47(3-4), 257-264.
- Arbi, K., Bucheli, W., Jimenez, R., and Sanz, J. (2015) High lithium ion conducting solid electrolytes based on NASICON $\text{Li}_{1+x}\text{Al}_x\text{M}_{2-x}(\text{PO}_4)_3$ materials (M = Ti, Ge and $0 \leq x \leq 0.5$). *Journal of the European Ceramic Society*, 35(5), 1477-1484.
- Arbi, K., Hoelzel, M., Kuhn, A., Garcia-Alvarado, F., and Sanz, J. (2013) Structural Factors That Enhance Lithium Mobility in Fast-Ion $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ ($0 \leq x \leq 0.4$) Conductors Investigated by Neutron Diffraction in the Temperature Range 100-500 K. *Inorganic Chemistry*, 52(16), 9290-9296.
- . (2014) Local structure and lithium mobility in intercalated $\text{Li}_3\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ NASICON type materials: a combined neutron diffraction and NMR study. *Physical Chemistry Chemical Physics*, 16(34), 18397-18405.
- Arbi, K., Mandal, S., Rojo, J.M., and Sanz, J. (2002) Dependence of ionic conductivity on composition of fast ionic conductors $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$, $0 \leq x \leq 0.7$. A parallel NMR and electric impedance study. *Chemistry of Materials*, 14(3), 1091-1097.
- Arbi, K., Rojo, J.M., and Sanz, J. (2007) Lithium mobility in titanium based Nasicon $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ and $\text{LiTi}_{2-x}\text{Zr}_x(\text{PO}_4)_3$ materials followed by NMR and impedance spectroscopy. *Journal of the European Ceramic Society*, 27(13-15), 4215-4218.
- Bruker. (2015) APEX3 (Version 2015. 10-0), Bruker AXS Inc, Madison, Wisconsin, USA.
- Bucharsky, E.C., Schell, K.G., Hintennach, A., and Hoffmann, M.J. (2015) Preparation and characterization of sol-gel derived high lithium ion conductive NZP-type ceramics $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$. *Solid State Ionics*, 274, 77-82.
- Catti, M., Comotti, A., Di Blas, S., and Ibberson, R.M. (2004) Extensive lithium disorder in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ Nasicon by neutron diffraction, and the $\text{Li}_{1+x}\text{Fe}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ phase diagram. *Journal of Materials Chemistry*, 14(5), 835-839.
- Dashjav, E., and Tietz, F. (2014) Neutron Diffraction Analysis of NASICON-type $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}\text{P}_3\text{O}_{12}$. *Zeitschrift für anorganische und allgemeine Chemie*, 640(15), 3070-3073.
- Duluard, S., Paillassa, A., Puech, L., Vinatier, P., Turq, V., Rozier, P., Lenormand, P., Taberna, P.-L., Simon, P., and Ansart, F. (2013) Lithium conducting solid electrolyte $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ obtained via solution chemistry. *Journal of the European Ceramic Society*, 33(6), 1145-1153.
- Epp, V., Ma, Q.L., Hammer, E.M., Tietz, F., and Wilkening, M. (2015) Very fast bulk Li ion diffusivity in crystalline $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ as seen using NMR relaxometry. *Physical Chemistry Chemical Physics*, 17(48), 32115-32121.
- Farrugia, L. (2012) WinGX and ORTEP for Windows: an update. *Journal of Applied Crystallography*, 45(4), 849-854.
- Goodenough, J.B., Hong, H.Y.P., and Kafalas, J.A. (1976) Fast Na^{+} -ion transport in skeleton structures. *Materials Research Bulletin*, 11(2), 203-220.

- Guin, M., Tietz, F., and Guillon, O. (2016) New promising NASICON material as solid electrolyte for sodium-ion batteries: Correlation between composition, crystal structure and ionic conductivity of $\text{Na}_3 + x\text{Sc}_2\text{SixP}_3 - x\text{O}_{12}$. *Solid State Ionics*, 293, 18-26.
- Hong, H.Y.P. (1976) Crystal structures and crystal chemistry in the system $\text{Na}_{1+x}\text{Zr}_2\text{SixP}_3 - x\text{O}_{12}$. *Materials Research Bulletin*, 11(2), 173-182.
- Hupfer, T., Bucharsky, E.C., Schell, K.G., Senyshyn, A., Monchak, M., Hoffmann, M.J., and Ehrenberg, H. (2016) Evolution of microstructure and its relation to ionic conductivity in $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$. *Solid State Ionics*, 288, 235-239.
- Kawai, H., and Kuwano, J. (1994) LITHIUM ION CONDUCTIVITY OF A-SITE DEFICIENT PEROVSKITE SOLID-SOLUTION $\text{La}_{0.67}\text{XLi}_3\text{XTiO}_3$. *Journal of the Electrochemical Society*, 141(7), L78-L79.
- Lang, B., Ziebarth, B., and Elsässer, C. (2015) Lithium Ion Conduction in $\text{LiTi}_2(\text{PO}_4)_3$ and Related Compounds Based on the NASICON Structure: A First-Principles Study. *Chemistry of Materials*, 27(14), 5040-5048.
- Monchak, M., Hupfer, T., Senyshyn, A., Boysen, H., Chernyshov, D., Hansen, T., Schell, K.G., Bucharsky, E.C., Hoffmann, M.J., and Ehrenberg, H. (2016) Lithium Diffusion Pathway in $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) Superionic Conductor. *Inorganic Chemistry*, 55(6), 2941-2945.
- Murugan, R., Thangadurai, V., and Weppner, W. (2007) Fast lithium ion conduction in garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *Angewandte Chemie-International Edition*, 46(41), 7778-7781.
- Perez-Estebanez, M., Isasi-Marin, J., Toebbens, D.M., Rivera-Calzada, A., and Leon, C. (2014) A systematic study of Nasicon-type $\text{Li}_i + \text{XMXTi}_2 - x(\text{PO}_4)_3$ (M: Cr, Al, Fe) by neutron diffraction and impedance spectroscopy. *Solid State Ionics*, 266, 1-8.
- Pinus, I.Y., Khoroshilov, A.V., Gavrichev, K.S., Tarasov, V.P., and Yaroslavl'tsev, A.B. (2012) On cationic mobility in Nasicon phosphates $\text{LiTi}_2(\text{PO}_4)_3$ and $\text{Li}_{0.9}\text{Ti}_{1.9}\text{Nb}_{0.1}(\text{PO}_4)_3$. *Solid State Ionics*, 212, 112-116.
- Rettenwander, D., Welzl, A., Pristat, S., Tietz, F., Taibl, S., Redhammer, G.J., and Fleig, J. (2016) A microcontact impedance study on NASICON-type $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($0 \leq x \leq 0.5$) single crystals. *Journal of Materials Chemistry A*, 4(4), 1506-1513.
- Shannon, R.D., and Prewitt, C.T. (1970) Revised values of effective ionic radii. *Acta Crystallographica Section B*, 26(7), 1046-1048.
- Sheldrick, G. (2015) Crystal structure refinement with SHELXL. *Acta Crystallographica Section C*, 71(1), 3-8.
- Wong, S., J. Newman, P., S. Best, A., M. Nairn, K., R. Macfarlane, D., and Forsyth, M. (1998) Towards elucidating microscopic structural changes in Li-ion conductors $\text{Li}_{1+x}\text{Ti}_2\text{-Al}[\text{PO}_4]_3$ and $\text{Li}_{1+x}\text{Ti}_2\text{-Al}[\text{PO}_4]_3\text{-}[\text{MO}_4]_3$ (M=V and Nb): X-ray and ^{27}Al and ^{31}P NMR studies. *Journal of Materials Chemistry*, 8(10), 2199-2203.
- Zhang, T., Imanishi, N., Hasegawa, S., Hirano, A., Xie, J., Takeda, Y., Yamamoto, O., and Sammes, N. (2008) Li/Polymer Electrolyte/Water Stable Lithium-Conducting Glass Ceramics Composite for Lithium-Air Secondary Batteries with an Aqueous Electrolyte. *Journal of the Electrochemical Society*, 155(12), A965-A969.

Tables:

Table 1: Analytical compositions of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ crystals investigated in this study by electron microprobe analysis.

[illegible]

Table 2: Crystal data and structure refinement of selected compounds in the series $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ as determined from SC-XRD data, all data according to the trigonal crystal system, space group $R\bar{3}c$: H, Mo K_α ($\lambda = 0.71073 \text{ \AA}$), data collection at 298 K.

	x = 0	x = 0.1	x = 0.2	x = 0.3	x = 0.4	x = 0.5
a (Å)	8.5173(3)	8.5118(5)	8.5066(7)	8.5014(5)	8.4964(5)	8.4897(5)
c (Å)	20.8595(15)	20.8423(13)	20.8259(17)	20.8086(11)	20.7863(11)	20.7635(11)
V (Å ³)	1310.5(2)	1307.73(17)	1305.1(2)	1302.28(17)	1299.50(17)	1296.03(17)
Z	6	6	6	6	6	6
D _x (Mg/m ³)	2.947	2.943	2.937	2.936	2.929	2.925
μ (mm ⁻¹)	2.446	2.376	2.303	2.250	2.161	2.088
F(000)	1128	1124	1121	1118	1113	1109
Crystal Size (mm ³)	0.12 x 0.11 x 0.11	0.11 x 0.10 x 0.10	0.12 x 0.11 x 0.10	0.11 x 0.09 x 0.08	0.13 x 0.12 x 0.12	0.14 x 0.13 x 0.13
θ _{min} (°)	3.383	3.385	3.388	3.390	3.392	3.395
θ _{max} (°)	28.884°	29.786	29.805	29.836	29.866	29.900
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -27 ≤ l ≤ 28	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -27 ≤ l ≤ 28	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -27 ≤ l ≤ 28	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -27 ≤ l ≤ 28	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -27 ≤ l ≤ 29	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -27 ≤ l ≤ 28
Reflections collected	4648	5350	5368	5397	5346	5335
Indep. Reflections	387	420	420	419	419	420
R _{int} (%)	5.17	2.38	3.15	2.82	3.61	2.85
Completeness (%)	98.1	100	100	100	100	100
GooF on F ²	1.013	1.210	1.201	1.169	1.213	1.224
R ₁ all (%)	2.29	1.92	1.99	1.95	2.37	2.60
wR ₂ all (%)	5.24	4.92	4.68	4.88	5.38	5.94
Extinction	0.0000(3)	0.0059(5)	0.0038(4)	0.0070(5)	0.0022(4)	0.009(4)
Largest diff. peak and hole e.Å ⁻³	0.392/ -0.393	0.324/ -0.515	0.325/ -0.484	0.281/ -0.502	0.338/ -0.0538	0.412 -0.535

Table 3: Fractional atomic coordinates, anisotropic and equivalent isotropic atomic displacement parameters for selected samples of the series $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ as determined from SC-XRD data except data for $x = 0.4$, written in italics, which are determined from combined PND data and SC-XRD data.

ATOM	X	y	z	sof	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
x = 0											
Ti1	0	0	0.14174(2)	$\frac{1}{3}$	0.0045(2)	0.0045(2)	0.0047(3)	0	0	0.00225(12)	0.0046(2)
P1	0.29058(7)	0	0.25	$\frac{1}{2}$	0.0051(3)	0.0063(3)	0.0069(3)	0.0015(2)	0.0008(1)	0.00316(16)	0.0060(2)
O1	0.18477(17)	0.99565(17)	0.19014(6)	1	0.0109(6)	0.0136(6)	0.0135(7)	0.0027(5)	-0.0033(5)	0.0062(5)	0.0126(3)
O2	0.18834(17)	0.16444(17)	0.08097(6)	1	0.0076(6)	0.0102(6)	0.0099(6)	0.0016(5)	0.0007(4)	0.0022(5)	0.0102(3)
Li1	0	0	0	$\frac{1}{6}$	0.060(5)	0.060(5)	0.013(5)	0	0	0.030(3)	0.044(3)
x = 0.1											
Ti1	0	0	0.14176(2)	0.3165(9)	0.00525(19)	0.00525(19)	0.0049(2)	0	0	0.00262(9)	0.00513(17)
Al1	0	0	0.14176(2)	0.0168(9)	0.00525(19)	0.00525(19)	0.0049(2)	0	0	0.00262(9)	0.00513(17)
P1	0.29024(6)	0	0.25	$\frac{1}{2}$	0.0064(2)	0.0076(3)	0.0082(3)	0.00204(17)	0.00102(8)	0.00380(13)	0.00726(17)
O1	0.18450(16)	0.99500(16)	0.19003(5)	1	0.0127(5)	0.0160(6)	0.0141(5)	0.0024(4)	-0.0042(4)	0.0076(5)	0.0141(3)
O2	0.18804(15)	0.16394(16)	0.08115(5)	1	0.0088(5)	0.0112(5)	0.0106(5)	0.0022(4)	0.0011(4)	0.0018(4)	0.0116(3)
Li1	0	0	0	$\frac{1}{6}$	0.07698	0.07698	0.01916	0	0	0.03849	0.0577
Li2	0.067(19)	0.344(27)	0.074(8)	0.019(8)	--	--	--	--	--	--	0.015(2)
x = 0.2											
Ti1	0	0	0.14174(2)	0.2992(9)	0.00489(18)	0.00489(18)	0.0050(2)	0	0	0.00245(9)	0.00493(16)
Al1	0	0	0.14174(2)	0.0341(9)	0.00489(18)	0.00489(18)	0.0050(2)	0	0	0.00245(9)	0.00493(16)
P1	0.28989(6)	0	0.25	$\frac{1}{2}$	0.0062(2)	0.0077(3)	0.0088(3)	0.00242(18)	0.00121(9)	0.00386(14)	0.00740(17)
O1	0.18409(16)	0.99422(16)	0.18990(6)	1	0.0131(6)	0.0168(6)	0.0150(6)	0.0032(5)	-0.0046(4)	0.0077(5)	0.0149(3)

x = 0.5											
Ti1	0	0	0.14180(3)	0.2481(9)	0.0057(2)	0.0057(2)	0.0067(3)	0	0	0.00286(12)	0.0061(2)
Al1	0	0	0.14180(3)	0.0852(9)	0.0057(2)	0.0057(2)	0.0067(3)	0	0	0.00286(12)	0.0061(2)
P1	0.28889(8)	0	0.25	$\frac{1}{2}$	0.0077(3)	0.0102(3)	0.0114(3)	0.0041(2)	0.00205(12)	0.00508(17)	0.0095(2)
O1	0.1829(2)	0.9919(2)	0.18969(8)	1	0.0163(7)	0.0213(8)	0.0193(8)	0.0052(6)	-0.0046(6)	0.0096(7)	0.0189(4)
O2	0.1882(2)	0.1640(2)	0.08172(7)	1	0.0099(7)	0.0161(7)	0.0141(7)	0.0040(6)	0.0017(5)	0.0014(6)	0.0156(3)
Li1	0	0	0	$\frac{1}{6}$	0.104(11)	0.104(11)	0.029(7)	0	0	0.052(5)	0.079(6)
Li2	0.070(8)	0.340(9)	0.096(2)	0.069(11)	--	--	--	--	--	--	0.018(3)

Table 4: Selected bond lengths and distortional parameters for selected samples of the series $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ as determined from SC-XRD data.

	x = 0	x = 0.1	x = 0.2	x = 0.3	x = 0.4	x = 0.5
Ti-O1 (Å)	1.8858(12)	1.8833(11)	1.8808(12)	1.8784(12)	1.8759(14)	1.8701(16)
Ti-O2 (Å)	1.9715(12)	1.9675(11)	1.9656(11)	1.9622(11)	1.9587(14)	1.9552(15)
⟨Ti-O⟩ (Å)	1.9287	1.9254	1.9232	1.9203	1.9173	1.9127
Vol.(TiO ₆) (Å ³)	9.47	9.43	9.40	9.36	9.32	9.28
OQE ^(a)	1.0077	1.0070	1.0068	1.0066	1.0063	1.0062
OAV ^(b)	23.19	23.05	22.32	21.60	20.84	20.44
P-O1 (Å)	1.5260(13)	1.5282(11)	1.5281(12)	1.5268(12)	1.5251(14)	1.5233(15)
P-O2 (Å)	1.5293(13)	1.5299(11)	1.5294(12)	1.5289(12)	1.5299(12)	1.5312(15)
⟨P-O⟩ (Å)	1.5277	1.5291	1.5288	1.5279	1.5275	1.5273
Vol. (PO ₄) (Å ³)	1.83	1.83	1.83	1.83	1.82	1.82
TQE ^(c)	1.0014	1.0015	1.0016	1.0017	1.0018	1.0020
TAV ^(d)	5.60	5.75	6.30	6.55	6.95	7.87
Li1-O2 (Å)	2.2674(12)	2.2663(11)	2.2674(11)	2.2681(11)	2.2694(14)	2.2684(15)
Li1-Ti1 (Å)	2.9567(5)	2.9546(5)	2.9574(5)	2.9497(5)	2.9575(6)	2.9443(7)
Vol (Li1O ₆) (Å ³)	13.39	13.33	13.35	13.35	13.35	13.32
Li1-Li2 (Å)	--	3.10(10)	2.96(16)	2.99(11)	2.97(7)	2.94(6)
Li2-O2 (Å)	--	2.16(12)	2.12(9)	2.10(11)	2.14(6)	2.13(5)
Li2-O2 (Å)	--	2.24(12)	2.16(9)	2.17(11)	2.20(6)	2.20(5)
Li2-O1 (Å)	--	2.25(12)	2.24(9)	2.33(11)	2.27(6)	2.24(5)
Li2-O2 (Å)	--	2.30(12)	2.37(9)	2.33(11)	2.34(6)	2.32(5)
Li2-O2 (Å)	--	2.44(12)	2.42(9)	2.43(11)	2.42(6)	2.43(5)
Li2-O1 (Å)	--	2.68(12)	2.67(9)	2.59(11)	2.64(6)	2.67(5)
⟨Li2-O⟩ (Å)	--	2.344	2.331	2.323	2.339	2.332
Vol. (Li2O ₆) (Å ³)	--	12.71	12.67	12.62	12.58	12.52

(a) octahedral quadratic elongation, (b) octahedral angle variance, (c) = tetrahedral quadratic elongation, (d) tetrahedral angle variance.