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Structural and transport properties of lithium-conducting NASICON materials

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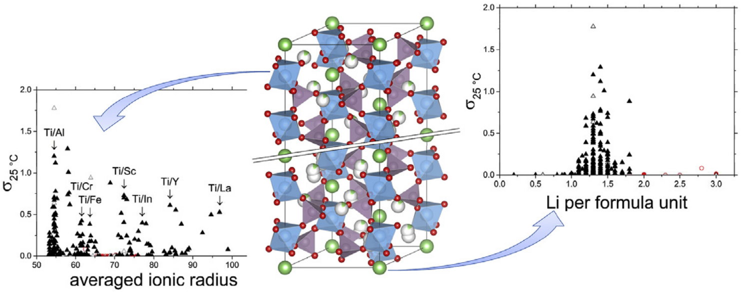
HIGHLIGHTS

- Comprehensive overview of Li-containing NASICON materials.
- In dept examination of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$.
- Maximum conductivity with 1.3 mol Li per formula unit and rhombohedral structure.
- Ideal size of metal cations is 50-60 pm favoring titanium based compositions.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium-containing NASICON-structured materials are a promising class of solid-state Li-ion conductors for application in electrochemical energy storage devices. Amongst the wide variety of possible compositions the highest conductivities are reported for materials according to the formula $Li_{1+x}M^{(III)}_xM^{(IV)}_{2-x}(PO_4)_3$, in which the substitution of tetravalent with trivalent metal cations leads to incorporation of additional lithium ions and a higher mobility of the charge carriers.

For this study, we surveyed more than 300 research articles about Li-NASICON materials. The relations between composition, structure and conductivity are evaluated to give a comprehensive overview of published data on synthesized compositions. A special focus is laid on $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ as the single most conductive and investigated material.

The collected conductivities show a wide scattering in a range of 10^{-10} S cm^{-1} up to 10^{-3} S cm^{-1}. The highest values are obtained for materials with M(III) to M(IV) cation ratios of x = 0.3–0.4. Further characteristics for high conductivity are evaluated and the rhombohedral structure as well as cation sizes of around 50–60 p.m. are identified as crucial prerequisites, favoring titanium-based compositions. Considering the evaluated data, selected compositions are suggested for further investigation to support future research.

1. Introduction

To improve the usability of fluctuating energy sources, application in portable consumer electronics and the development of electromobility, electrical energy storage must be improved. Among the commercially available batteries, lithium-ion cells provide the highest energy density and output voltage. Typically, these cells use lithium salts dissolved in propylene carbonate as liquid electrolytes. The main

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disadvantages involved in this concept are limited operating temperature and safety concerns due to the flammable electrolyte. One promising approach for improvement are solid-state batteries, as they could provide better safety aspects, longer lifespan and wider range of operation temperature. Combining the advantages of the solid-state battery concept and the lithium-ion charge carrier as an all-solid-state lithium-ion battery is desired. Advanced approaches aim to incorporate metallic lithium anodes and lithium-air batteries with a higher cell voltage and higher specific energy. The feasibility of these concepts depends on the applied solid-state electrolyte, for which a wide range of materials is being considered [1]. One of these materials are lithium-containing NASICON materials.

The term NASICON denotes a class of **Na**$^+$ **S**uper **I**onic **Con**ductors, and was first mentioned by *Hong* and *Goodenough* in 1976 [2,3] for the solid solution $Na_{1+x}Zr_2Si_xP_{3\text{-}x}O_{12}$. The material was developed to provide an ionic conductor, which is stable in air and allows migration of the charge carriers in all three dimensions. Today, the term is broadly applied to a group of phosphates with the general formula AMM′(PO$_4$)$_3$, where the A-site is usually occupied by alkali ions or alkaline-earth ions. The M and M′ sites are occupied by various transition metal ions with oxidation states between II and V. A review of a wide range of compositions is given in Ref. [4].

Shortly after the discovery of the NASICON structure, lithium was substituted for sodium as a charge carrier [5,6]. Over the last four decades, there has been extensive research on this class of materials, mostly because of its promising characteristics as an electrolyte in electrochemical applications. The present work therefore aims to provide a comprehensive overview of published data on synthesized compositions. The electrical and structural properties of these Li-NASICON materials and the relations between the relevant characteristics are evaluated to assist further research.

2. Structure

The most prevalent crystal structure for NASICON materials is the rhombohedral modification with space group $R\bar{3}c$, as shown in Fig. 1. Orthorhombic, monoclinic and rarely triclinic variations are reported, depending on composition, synthesis conditions and temperature. The authors regard only the rhombohedral and the closely related triclinic $C\bar{1}$ and monoclinic Cc structures as NASICON materials in the strict sense, because materials with different space groups, especially orthorhombic types, belong to the $Sc_2(WO_4)_3$-type structure [7,8].

The NASICON structure consists of a skeleton of vertex-sharing PO$_4$ tetrahedra and MO$_6$ octahedra, which provide a network of three-dimensional pathways for the lithium ions. This skeleton allows for the high degree of stability and flexibility of NASICON materials and a multitude of compositions [9]. There are two main cavities for lithium in the structures labelled M1 and M2. The M1 site is coordinated by six oxygen ions between two MO$_6$ octahedra along the *c*-axis. It lies at Wyckoff position 6b (0 0 0) with site symmetry $\bar{3}$ and is the most stable and most commonly occupied position. The larger eightfold-coordinated M2 site lies between two M1 sites at Wyckoff position 18*e* (*x* 0 ¼) with site symmetry 2. Six M2 sites concurrently surround each M1 site, and, accordingly, the multiplicity of the M2 site is three times that of M1.

For most stoichiometric LiM$_2$(PO$_4$)$_3$ compounds, lithium is located exactly at the M1 site, while LiZr$_2$(PO$_4$)$_3$ shows a very distorted tetrahedral coordination around the center of the M1 site [12]. Substitution with trivalent metal ions according to the formula $Li_{1+x}M^{(III)}_xM^{(IV)}_{2-x}(PO_4)_3$ generally leads to additional occupation of further positions by lithium. These positions were first assumed to be identical to those in the original NASICON with Wyckoff position 18e, although the M2 cavity is very large in size compared to the ionic radius of Li$^+$. Current research, however, found a new position to be in better agreement with the measured data for most compositions. A splitting of the M2 position into two new positions surrounding the original site results in the M3 site at Wyckoff position 36*f* within the M2 cavity [10,13]. In the endmembers of $M^{(III)}/M^{(IV)}$-substitution series with $x = 2$, i.e. the fully Li-intercalated phases with three lithium atoms per formula unit, only the M3 site was found to be populated [14,15].

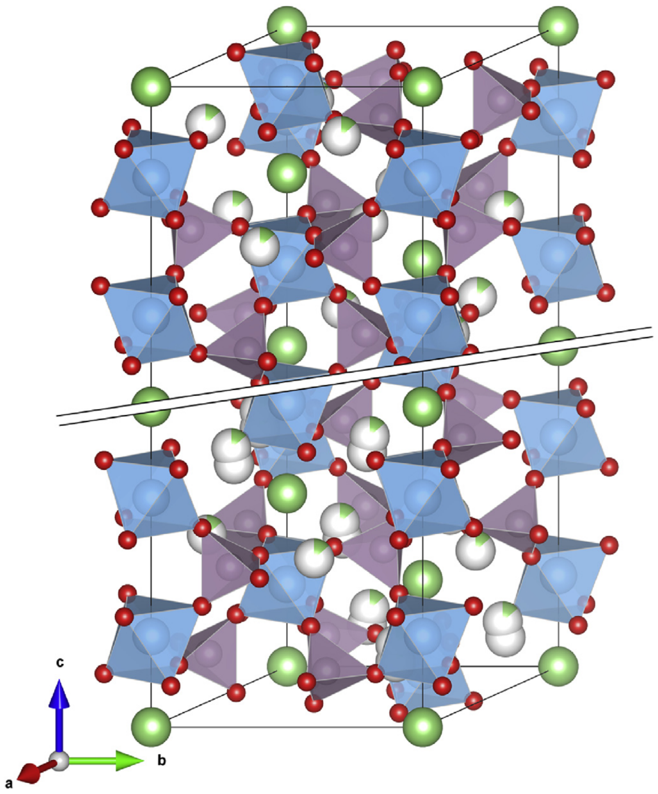

Fig. 1. Rhombohedral $R\bar{3}c$ structure of $Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$ [10]. The oxygen is shown in red, blue octahedra and purple tetrahedra correspond to (Al/Ti)O$_6$ and PO$_4$ units, respectively. Lithium ions are shown in green at the M1 position with Wyckoff position 6b (Occ. = 1). The top half shows the additional lithium at the M2 site in 18*e* position (Occ. = 0.14), the bottom half at M3 in 36*f* position (Occ. = 0.07). The illustration was generated with VESTA 3 [11]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3. Conductivity

This review includes a total of 181 different compositions from 78 references over a timespan of more than 30 years. All materials correspond to the general formula $Li_{1+2x+y-z}M^{(II)}_xM^{(III)}_yM^{(IV)}_{2-x-y-z}M^{(V)}_z(PO_4)_3$. Compositions employing substitution of Si for P or Na and Mg for Li, materials with additional binders like lithium salts as well as amorphous materials were excluded, as they are quite rare and would only obstruct the comparative analysis of the data. The conductivities at room temperature range from insulating $1 \cdot 10^{-10}$ S cm^{-1} to $1.32 \cdot 10^{-3}$ S cm^{-1}.

Fig. 2 gives an overview of the most investigated subgroup with the formula $Li_{1+x}M^{(III)}_xM^{(IV)}_{2-x}(PO_4)_3$. Here, trivalent M cations are substituted for the tetravalent cation, introducing additional lithium ions and modifying the skeleton structure.

In addition to the ionic radii, the figure shows the maximum total conductivity reported at room temperature as well as the number of references for each combination and the number of different $M^{(III)}/M^{(IV)}$ ratios found in literature. Conductivities at higher temperatures were extrapolated to room temperature using the Arrhenius equation:

$$\sigma T = Ae^{\frac{-E_a}{RT}} \tag{1}$$