Li$_5$SnP$_3$ – a Member of the Series Li$_{10+4x}$Sn$_{2-x}$P$_6$ for $x = 0$
Comprising the Fast Lithium-Ion Conductors Li$_8$SnP$_4$
($x = 0.5$) and Li$_{14}$SnP$_6$ ($x = 1$)

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Dedicated to Professor Richard Drönskowski on the occasion of his 60th birthday.

Abstract: The targeted search for suitable solid-state ionic conductors requires a certain understanding of the conduction mechanism and the correlation of the structures and the resulting properties of the material. Thus, the investigation of various ionic conductors with respect to their structural composition is crucial for the design of next-generation materials as demanded. We report here on Li$_5$SnP$_3$ which completes with $x = 0$ the series Li$_{10+4x}$Sn$_{2-x}$P$_6$ of the fast lithium-ion conductors $\alpha$- and $\beta$-Li$_8$SnP$_4$ ($x = 0.5$) and Li$_{14}$SnP$_6$ ($x = 1$). Synthesis, crystal structure determination by single-crystal and powder X-ray diffraction methods, as well as $^3$Li, $^{31}$P and $^{119}$Sn MAS NMR and temperature-dependent $^3$Li NMR spectroscopy together with electrochemical impedance studies are reported. The correlation between the ionic conductivity and the occupation of octahedral and tetrahedral sites in a close-packed array of P atoms in the series of compounds is discussed. We conclude from this series that in order to receive fast ion conductors a partial occupation of the octahedral vacancies seems to be crucial.

Introduction

Solid-state electrolytes (SE) are predicted to dominate mainly in electric vehicles and future lithium battery chemistry.$^{[1]}$ Therefore, extensive efforts are made aiming for the discovery of SE materials that are suitable to meet demanded properties for application in all-solid-state batteries.$^{[2–4]}$ Another approach focuses on a better understanding of the origin of materials’ properties, such as ionic conductivity. The elaboration of structure-property relationships by comparison of a variety of crystalline candidate materials that comprise diverse structural differences with respect to their electronic properties allows for designing and tailoring of materials’ properties as demanded.$^{[5–8]}$ Searching for high-performance ionic conductors, a large number of innovative SEs featuring ever increasing ionic conductivities has been reported over the last decades.$^{[2–4,9,10]}$ But a thorough investigation of structure-property relationships also demands the evaluation of less powerful materials in order to unveil the reasons for favorable or unfavorable properties.

The recently introduced family of lithium phosphidotetriates and the closely related lithium phosphidotetraiates are well-suited for further analyses of ionic conduction mechanisms as this class of materials offers a broad structural variety as well as a corresponding large variety of properties. For example, several compounds with a fast ionic conduction of up to $3 \times 10^{-5}$ S cm$^{-1}$ have been reported$^{[11–13]}$ next to materials that feature a band gap of about 3 eV, indicative of semiconducting behavior.$^{[11]}$ In addition the compound LiGe$_2$P$_3$ shows moderate electric conductivity and an unprecedented stability when exposed to water and air.$^{[12]}$ Apart from the latter and a few other exceptions, most of the so far discovered lithium phosphidotetraiates and -triates are based on tetrahedral [TrP$_x$] or [Tr$_2$P$_x$] units, which occur either as isolated [TrP$_x$]$^{6–}$ or [Tr$_2$P$_x$]$^{6–}$ anions that are charge-compensated by the corresponding amount of Li$^{+}$ or they build frameworks of condensed tetrahedra and supertetrahedra, respectively.$^{[13–15]}$

The compound Li$_5$Si$_4$P$_6$ comprises pairs of edge-sharing [SiP$_4$]$^{6–}$ units resulting in the polyanion [Si$_2$P$_4$]$_{10–}$.$^{[16]}$ Due to these building blocks, the formula is commonly given as Li$_{10}$Si$_4$P$_6$ rather than Li$_5$Si$_4$P$_6$ to express the molecular-anionic character.

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Indeed, a compound with the composition Li₅SnP₆ has been reported in the 1950s, and characterized by the determination of the cubic space group Fm3m with a lattice parameter of $a = 5.852 \text{ Å}$. The structure is closely related to the antifluorite type or a defect variant of the Li₅Bi structure, which can be described by a ccp of P atoms in which all tetrahedral voids are statistically occupied by Li⁺ and Si⁴⁺ in a mixing ratio of 5:1. So far, all attempts to reproduce these findings have failed. Furthermore, about 20 years later the same structure was reported for the heavier homologue Li₅SnP₆ with identical cubic space group Fm3m (no. 225) and a lattice parameter of $a = 5.97 \text{ Å}$. Further investigations of the material's properties are still pending, whereas the lithium-rich phosphostannates α- and β-Li₅SnP₆, as well as Li₅SnP₆, have been recently reported to show superionic lithium-ion conductivities of about $1 \times 10^{-3} \text{ S cm}^{-1}$. Interestingly in α- and β-Li₅SnP₆, the Li and Sn atoms are fully ordered in the tetrahedral voids of the ccp of P atoms, thus leading to polyanionic SnP₆⁶⁻ units. By contrast in Li₅SnP₆, the Li and Sn atoms are statistically distributed over the tetrahedral sites. Analysis of Li⁺ diffusion pathways based on powder neutron diffraction data unveiled structural variations, which were directly connected to the different values of the ionic conductivities of the three compounds.

In the following we report on the systematic investigation of the system Li₁₀₋₄Sn₂₋₄P₆ (x = 0.0 to 1.0) including the compounds Li₅SnP₆ (α- and β-) Li₅SnP₆ and Li₅SnP₆ that arise for $x = 0.0$, 0.5, and 1.0, respectively. Following a well-established synthesis route for lithium phosphidotetrelates including mechano-chemical milling provides for the first time the isolation and detailed characterization of the compound Li₅SnP₆ by single-crystal and powder X-ray diffraction data completed by Rietveld refinement as well as $^7\text{Li}$ NMR measurements. Differential scanning calorimetry (DSC) and isothermal annealing experiments of the reactive mixtures obtained via mechanical alloying were carried out to investigate the thermal properties of the materials. Furthermore, the Li⁺ mobility and its activation energy, as well as the ionic and electronic conductivity were determined via temperature-dependent $^7\text{Li}$ NMR spectroscopy and electrochemical impedance spectroscopy (EIS). Finally, all data and the associated properties are compared to that of the recently reported lithium phosphostannates α- and β-Li₅SnP₆ and Li₅SnP₆ which allows for the formulation of new structure-property relationships regarding the ionic conductivity in solid-state Li⁺ conductors.

### Experimental Section

All syntheses were carried out under Ar atmosphere in glove boxes (MBraun, 2008) with moisture and oxygen levels below 0.1 ppm, or in containers, which were sealed under Ar atmosphere and vacuum ($< 2 \times 10^{-7} \text{ mbar}$), respectively. Lithium phosphostannates are sensitive to oxygen and moisture; in particular, contact with water results in a vigorous reaction including the formation of flammable and toxic gases (e.g., phosphine). Therefore, disposal must be addressed in small amounts at a time and under proper ventilation.

#### Bulk Synthesis via Ball Milling and Annealing

All samples were prepared by a well-established synthesis route starting from the elements, lithium (Rockwood Lithium, 99%), tin (Merck, 99.9%) and red phosphorus (ChemPUR, 99.999%) in stoichiometric amounts aiming for compositions according to the formula $\text{Li}_{10-x} \text{Sn}_{2-x} \text{P}_6$ with $x = 0.0$, 0.25, 0.50, 0.75, 1.00 (Table 1), followed by annealing at moderate temperatures.

In the first step, a reactive mixture” (m = 5.0 g) was prepared by mechano-chemical milling using a Retsch PM100 Planetary Ball Mill (350 rpm, 18 h, 10 min interval, 3 min break) with a tungsten carbide milling jar ($V = 50 \text{ mL}$) and three balls with a diameter of 15 mm.

In the second step, the “reactive mixture” was pressed into pellets, sealed in batches of 0.3 to 1.0 g in carbon-coated silica glass ampules and heated in a muffle furnace (Nabertherm, L5/11/P330) to 673, 773 or 973 K (heating rate: 4 K min⁻¹) for 24 h, followed by quenching of the hot ampules in water.

#### Powder X-Ray Diffraction and Rietveld Refinement

Data were collected at room temperature on a STOE Stadi P diffractometer (Ge(111) monochromator, Cu Kα)), $\lambda = 1.54056 \text{ Å} \text{ and } \text{Mo Kα}}$, $\lambda = 0.70932 \text{ Å}$) with a Dectris MYTHEN 1 K detector in Debye-Scherrer geometry. Samples were sealed in glass capillaries (Ø 0.3 mm) for measurement. Raw data were processed with the WinXPOW software prior to refinement.

The data analysis of Li₅SnP₆ was performed using the complete form Rietveld method implemented in the FullProf program package. To model the peak profile, the pseudo-Voigt function was chosen. The background contribution was determined using a linear interpolation between selected data points in non-overlapping regions. The scale factor, zero angular shift, profile shape parameters, resolution (Cagliotti) parameters, asymmetry and lattice parameters as well as fractional coordinates of atoms and their displacement parameters were varied during the fitting. Free refinement of the occupancy of the 8c site by Sn and Li exhibited only marginal deviations from the electron-precise formula Li₅SnP₆ (Z = 1.33) or Li₅SnP₆ (Z = 1). The corresponding data are given as Supporting Information. In addition, a second refinement was carried out with site occupancies set to the exact stoichiometry. Since the results of both refinements were in very good agreement, the electron precise stoichiometry Li₅SnP₆ is assumed. All structures were visualized using DIAMOND.

#### Synthesis of powdery and single-crystalline Li₅SnP₆

Li₅SnP₆ is obtained as black powder on a gram scale and in high purity by annealing of the reactive mixture” of the nominal composition “Li₁₀Sn₂P₆” $\text{Li}_{10-x} \text{Sn}_{2-x} \text{P}_6$ with $x = 0.0$) in carbon-coated silica glass ampules at 773 K for 24 h, followed by quenching of the hot ampule in water. The weight fraction of remaining β-Sn was determined via Rietveld refinement to 0.8(1) %.

Single crystals were obtained by a high-temperature reaction of lithium (Rockwood Lithium, 99%), tin (Merck, 99.9%) and red phosphorus (Sigma-Aldrich, 97 %) in a ratio corresponding to “Li₅SnP₆.” The elements were annealed for 18 h at 873 K (heating

| Table 1. Overview of the prepared “reactive mixtures” according to the formula $\text{Li}_{10-x} \text{Sn}_{2-x} \text{P}_6$ (x = 0.0 to 1.0). |
| --- |
| x    | Composition                      |
| 0.00 | Li₅SnP₆                         |
| 0.25 | Li₅SnP₆, P₆                   |
| 0.50 | Li₅SnP₆, P₆                   |
| 0.75 | Li₅SnP₆, P₆                   |
| 1.00 | Li₅SnP₆                        |
rate: 4 Kmin⁻¹) in a sealed tantalum ampule and subsequently quenched in water.

**Single-crystal X-ray Diffraction Data Collection:** A single crystal of Li₅SnP₄ was isolated and sealed in a glass capillary (0.1 mm). For diffraction data collection, the capillary was positioned in a 150 K cold N₂ gas stream. Data collection was performed with a STOE StadiVario (MoKα radiation) diffractometer equipped with a Dectris PILATUS 300 K detector. Structures were solved by Direct Methods (SHELXS-2014) and refined by full-matrix least-squares calculations against F² (SHELXL-2014).

Further details of the crystal structure investigations may be obtained from the joint CCDC/PIZ Karlsruhe online deposition service: Deposition Number(s) CSD-2074706 (Li₅SnP₄, single crystal), CSD-2074707 (Li₅Sn₁₃P₄, powder), CSD-2074709 (Li₅Sn₁₂P₄, single crystal), and CSD-2074710 (Li₅Sn₆P₄, powder) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

**Differential Scanning Calorimetry (DSC):** The thermal behavior of the compounds was studied with a Netzsch DSC 404 Pegasus device. Niobium crucibles were filled with the samples and sealed by arc-welding. Empty sealed crucibles served as a reference. Measurements were performed under an Ar flow of 75 mL min⁻¹ and a heating/cooling rate of 10 K min⁻¹. Data collection and handling were carried out with the Proteus Thermal Analysis program,[24] and visualization was realized using OriginPro 2020.[25]

**Solid-State NMR Spectroscopy:** Magic angle spinning (MAS) NMR spectra were recorded on a Bruker Avance 300 NMR device operating at 7.04 T by the use of a 4 mm ZrO₂ rotor. The resonance frequencies of the measured nuclei are 44.2, 121.5 and 111.9 MHz for Li[31]P, and Sn, respectively. The rotational frequency was set to 15.0 kHz. The MAS spectra were acquired at room temperature with recycle delays of 10 to 30 s and 1000 to 2736 scans. All Li[31]P spectra were referenced to LiCl (1 mm, aq) and LiCl (s) offering chemical shifts of 0.0 ppm and −1.15 ppm, respectively. The[31]P spectra were referenced to (NH₄)H₂PO₄(s) (ammonium dihydrogen phosphate) with a chemical shift of 1.11 ppm with respect to concentrated H₃PO₄(aq) (phosphoric acid). SnO₂(s) (Cassiterite) was used as a secondary standard for the[61]Sn spectra, showing a chemical shift of −604.3 ppm[26,27] referred to (CH₃)₂Sn(II) (tetramethylstannane). All spectra were recorded using single-pulse excitation.

Static[7]Li NMR experiments were performed using a Bruker Avance III spectrometer operating at a magnetic field of 7 T employing a 4 mm WWT MAS probe. The resonance frequency of the[7]Li nucleus is 116.6 MHz. The sample was sealed in a 4 mm glass tube to avoid contact with air and moisture. The temperature calibration for the measurements was performed using the temperature-dependent [20]Pb NMR shift of lead nitrate (Pb(NO₃)₂) as chemical shift thermometer, which was also measured in a sealed glass tube. A saturation comb had been used prior to the[7]Li data acquisition. The spectra were recorded in the temperature range from room temperature to 200 K with recycle delays of 60 s and 4 scans. All spectra were referenced to LiCl (9.7 M, aq).

**Impedance Spectroscopy and DC Conductivity Measurements:** Potentiostatic impedance spectroscopy was carried out using a Biologic SP-300 potentiostat in a frequency range of 7 MHz to 100 MHz with an excitation amplitude of ±10 mV. All measurements were conducted in an argon-filled glove box. Powder samples of Li₅SnP₄ (300 mg) were measured in a custom-built symmetric cell (Ø = 8 mm) with hardened steel electrodes under blocking conditions. Pressure was applied by six M14 screws, fastened with a defined torque of 30 Nm each, translating to proximately 480 MPa, so that the sample was compressed to 88% of its crystallographic density. A more detailed description can be found in the literature.[10] The temperature was controlled via a Julabo Dynoe DD 1000 Thermostat feeding an aluminum heating block, which enclosed the measurement cell. The electric conductivity was measured in the same cell setup with three polarization steps of 50, 100 and 150 mV, each held for 6 h to ensure equilibrium conditions.

**Results**

**Syntheses:**

For the systematic investigation of lithium-rich ternary lithium phosphostannates, mixtures with nominal compositions according to Table 1 were alloyed mechanically in a ball mill. The compositions were chosen according to the formula Li₁₀xSn₉P₄(α- or β-)Li₅SnP₄[19] and Li₁₃Sn₇P₄[20] as well as Li₅SnP₄ for x = 0.0, 0.5 and 1.0, respectively.

In order to detect further phases within this family of materials and to reveal existing phase widths of the compounds, the “reactive mixtures” were annealed at 673, 773 and 973 K, respectively. All “reactive mixtures” and products were analyzed using powder X-ray diffraction (PXRD) data for the identification of the occurring phases within the samples as well as for the determination of the cell parameters of the lithium phosphostannates. The data showed the formation of the known compounds Li₅SnP₄[19] and β-Li₅SnP₄[20] as well as Li₅SnP₄ as the presence of Li₅P and remaining β-Sn. No phase widths were observed for these compounds. Details of the results and all PXRD patterns are given as Supporting Information.

For the structural reinvestigation of Li₅SnP₄, the corresponding “reactive mixture” obtained by ball milling of the elements in stoichiometric amounts was annealed at 773 K for 24 h, followed by quenching of the hot ampule in water. By this method, the material is accessible on a gram scale and in high purity as indicated by Rietveld analysis (Figure 1). Details of the refinement are shown in Table 2.

Diffential scanning calorimetry, followed by PXRD measurements of the samples indicate the decomposition of Li₅SnP₄ at high temperatures, resulting in a mixture of β-Sn and another cubic phase, indicated by additional reflections assignable to a superstructure as observed for the ordered structures of α- and/or β-Li₅SnP₄. Since the additional reflections are broadened, a partial ordering of the cations is assumed. The corresponding thermograms and PXRD patterns as well as a detailed discussion of the results is given as Supporting Information.

In accordance with previous reports,[19] the single-crystal data of Li₅SnP₄ indicate the cubic space group Fm̅3m (no. 225) and a lattice parameter of a = 5.9541(7) Å at 150 K (Figure 2 and Table 3).

The structure of Li₅SnP₄ can be described as a ccc of P atoms (4a site) with the Sn and Li atoms statistically distributed in tetrahedral voids (8c site) with a Sn:Li ratio of 1:5. The structure is thus closely related to the antifluorite structure with...
Table 2. Details of the Rietveld structure refinements of Li₄Sn₃P₃ (Z = 1.33) at 293 K.

| Empirical formula | Li₄Sn₃P₃ |
|-------------------|---------|
| T [K]             | 293     |
| formula weight (g mol⁻¹) | 328.08 |
| Group (no.)       | Fm3m (225) |
| Unit cell parameters [Å] | a = 5.98715(5) |
| Z                 | 1       |
| V [Å³]           | 214.615(3) |
| ρ[obs] [g cm⁻³]  | 2.541   |
| 2θ range [deg]   | 5.000−49.9441 |
| R_p              | 3.19%   |
| Rwp              | 3.87%   |
| Rexp             | 1.67%   |
| GOF              | 1.3     |
| R_Bragg          | 1.67%   |
| R_L              | 1.48%   |
| Depository no.   | CSD-2074707 |

P and Li/Sn on Ca and F atom positions, respectively. The structure was also confirmed by powder X-ray diffraction and Rietveld refinement at 293 K. Atomic coordinates and anisotropic displacement parameters as well as the results from the powder X-ray diffraction at 293 K and the single-crystal X-ray diffraction at 150 K are given in the Supporting Information.

The structure of the lithium-rich compound Li₄Sn₃P₃ is almost isotypic to that of Li₄Sn₃P₆ but with a slightly larger lattice parameter (a = 6.01751(3) Å) and a different occupation of the mixed Li/Sn positions in the tetrahedral voids and – due to the higher Li amount – partially occupied octahedral sites (4b). The same Li₂Bi-type structure was also observed for the lighter homologues Li₃Si₃P₆ and Li₃GeP₆.¹³

All interatomic Li/Sn−P (2.5782(2) Å), Li/Sn−Li/Sn (2.9771(3) Å) and P−P distances (4.2102(3) Å) are within the range of those found for related ternary or binary compounds like Li₆TiP₆ (Tt = Si, Ge, Sn),¹³,¹⁴ (α− and β−) Li₄Si₂P₄ (Tt = Si, Ge, Sn),¹³,¹⁴ and Li₁₆P₄.²⁰

The ³¹P MAS NMR spectrum of Li₄Sn₃P₃ shows one very broad resonance (~ 17 kHz) at a chemical shift of ~220.3 ppm (Figure S8). A comparable broadening was also observed in case of the structurally related and highly disordered compounds Li₄Sn₃P₃ (Tt = Si, Ge, Sn).¹³,²⁰ Furthermore, it is assumed that the in some extend very complex coupling of Sn and P atoms also leads to a merging of signals with a related chemical shift as recently reported for example, for α− and β−Li₄Sn₃P₃.²⁰

**Table 3. Crystallographic data and refinement parameters of Li₄Sn₃P₃ (Z = 1.33) or Li₄Sn₃P₆ (Z = 1) at 150 K with fixed site occupancy factors.**

| empirical formula | Li₄Sn₃P₃/Li₄Sn₃P₆ |
|-------------------|------------------|
| Formula weight (g mol⁻¹) | 328.08 |
| Crystal size [mm³] | 0.08×0.08×0.09 |
| Crystal color       | black            |
| T [K]              | 150              |
| Crystal system      | cubic             |
| Space group (no.)  | Fm3m (225)        |
| Unit cell parameter [Å] | a = 5.9541(7) |
| Z                  | 1                |
| V [Å³]             | 211.08(7)        |
| ρ[obs] [g cm⁻³]    | 2.583            |
| μ [mm⁻¹]           | 4.644            |
| F(000) [e]         | 147              |
| d range (deg)      | 5.934−46.355     |
| Index range (hkl)  | −7 ≤ h ≤ 11, −10 ≤ k ≤ 11, −11 ≤ l ≤ 4 |
| Reflections collected | 348              |
| Independent reflections | 72               |
| Rwp                | 0.0101           |
| Reflections with I > 2σ(I) | 72               |
| Absorption correction | multi-scan      |
| Data/restraints/parameters | 72/4/4        |
| Goodness-of-fit on F² | 1.248           |
| R_p, wR_p (all data) | 0.0231, 0.0231 |
| R_p, wR_p (I > 2σ(I)) | 0.0626, 0.0626 |
| Largest diff. peak and hole (e Å⁻³) | 0.968/−0.497 |
| Depository no.     | CSD-2074706      |

Figure 1. Results of the Rietveld analysis of the powder X-ray diffraction pattern of Li₄Sn₃P₃ at 293 K. Red circles indicate observed intensities Y_obs black lines show calculated intensities Y_calc, blue lines reveal the difference between observed and calculated intensities, and green marks indicate Bragg positions of Li₄Sn₃P₃ (weight fraction 99(1)%) and β−P (weight fraction 0.8(1) %), respectively.

Figure 2. Structure of Li₄Sn₃P₃ from single-crystal data at 150 K. P atoms (4a), and mixed Li/Sn sites (8c, Li 83.33% and Sn 16.67%) are depicted as pink and gold displacement ellipsoids, respectively, all set at 90% probability. Black lines mark (Li/Sn)−P bonds, resulting in (Li/Sn)₃P₃ tetrahedra.

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comparison to the resonances of the latter and of other closely related lithium phosphidotetrelates such as Li$_3$SnP$_6$[7] the maximum of the signal appertaining to Li$_3$SnP$_3$ shows a downfield shift of about 20 to 40 ppm. This indicates a lower shielding of the P atoms and hints for a lower formal charge (< 2) and to a higher coordination number of P by Sn atoms (Figure 3). At the local level, all P atoms in Li$_3$SnP$_3$ are covalently bound to at least one Sn atom, whereas in Li$_4$SnP$_4$, also P$^-$ anions are present according to $[\text{Li}_4^+\text{SnP}_4^-$] (P$^-$)]. In analogy to the structures of α- and β-Li$_3$SnP$_4$ and Li$_3$SnP$_6$, respectively, the Sn atoms are occupying tetrahedral voids, resulting in SnP$_4$ units.[7,8] Regarding the electron-precise stoichiometry (Li$_3$SnP$_3$ or Li$_{30}$Sn$_{122}$P$_5$), each P atom is statistically coordinated by 1.33 Sn atoms by two Sn atoms, and all the others coordinate to one Sn atom. In other words, two Sn atoms occupy adjacent tetrahedral voids and form edge-sharing tetrahedra with the formula [Sn$_2$P$_4$]$_{10}^{-}$. Such units are also observed in the homologous lithium phosphidosilicate Li$_3$SiP$_4$.[16] However, the [Sn$_2$P$_4$]$_{10}^{-}$ units are not ordered, and thus, the chemically different P atoms do not appear with a distinct difference in the chemical environment. A further resolution of the broad signal in order to distinguish P atoms located next to only one Sn atom (1b-P$^-$) and P atoms surrounded by two Sn atoms (2b-P$^-$) was not possible. Possible reasons are given after the discussion of the $^{119}$Sn NMR spectrum.

Regarding the $^{119}$Sn NMR spectrum of Li$_3$SnP$_3$, the high level of cation disorder also results in only one very broad (~13 kHz) tin resonance at a chemical shift of 124.6 ppm (Figure S9). In analogy to the $^{31}$P NMR measurements, this effect has also been observed in the $^{119}$Sn spectrum of Li$_3$SnP$_6$.[7] In comparison to the latter, the maximum of the signal for Li$_3$SnP$_3$ shows a downfield shift of 26.5 ppm, and the resonances of the lithium phosphidotannates Li$_3$SnP$_6$ α- and β-Li$_3$SnP$_4$ and Li$_3$SnP$_6$, shown in Figure 4 are upfield shifted depending on the Sn to P ratio indicating the slightly different bonding situations within the compounds discussed above.[7,8]

Regarding the electron-precise stoichiometry of the so far known lithium phosphidotannates the structure of Li$_3$SnP$_3$ shows both, [SnP$_4$]$^{10-}$ and P$^-$ units, whereas the two modifications of Li$_3$SnP$_4$ only contain [SnP$_4$]$^{10-}$ tetrahedra, and the basic structure of Li$_3$SnP$_6$ consists of [Sn$_2$P$_4$]$^{10-}$ units.[7,8] This, in combination with the crystal structures and the just discussed NMR data, at first appears counterintuitively since neither the NMR data nor the crystallographic data clearly resolve the presence of edge-sharing [SnP$_4$] tetrahedra in Li$_3$SnP$_3$, which are correspondingly reported for Li$_3$SiP$_4$. In contrast to the strongly covalent character of the Si–P bonds leading to molecule-like [SiP$_4$] units[16] the bonding situation in Li$_3$SnP$_3$ is assumed to be mainly dominated by the ionic character of the Sn–P bonds resulting in much weaker bonds and, thus, in more uniform chemical environments.

The $^7$Li MAS NMR spectrum shows only one signal corresponding to the one Li site in the structure. The chemical shift of $\delta = 4.2$ ppm occurs within the characteristic range of $^7$Li resonances reported for lithium phosphidotetrelates and -triolates.[5,4,7,8,11–14,16]

### Lithium-ion mobility

The Li$^+$ mobility, the activation energy and the ionic as well as the electronic conductivity are evaluated and compared to recent results of the related compounds α- and β-Li$_3$SnP$_4$ and Li$_3$SnP$_6$.

For a rough estimation of the activation barrier for Li$^+$ mobility in crystalline Li$_3$SnP$_3$, the dynamic behavior of Li$^+$ was investigated by temperature-dependent evolution of the static $^7$Li NMR line width. Since the central transition of the $I = 3/2$ $^7$Li nucleus is broadened by homonuclear ($^7$Li–$^7$Li) and heteronuclear ($^7$Li–$^{31}$P) dipolar coupling, both of which scale with the second Legendrian (3 cos$^2$ β-1), any dynamic process leads to a

**Figure 3.** Overview of the $^{31}$P MAS NMR spectra of Li$_3$SnP$_3$ (olive), α-Li$_3$SnP$_4$ (blue), β-Li$_3$SnP$_4$ (red),[10] and Li$_3$SnP$_6$ (teal).[7] Spinning sidebands and Li$^+$ (impurity) are indicated by * and +, respectively.

**Figure 4.** Overview of the $^{119}$Sn MAS NMR spectra of Li$_3$SnP$_3$ (olive), α-Li$_3$SnP$_4$ (blue), β-Li$_3$SnP$_4$ (red),[10] and Li$_3$SnP$_6$ (teal).[7]
were approached, monitoring the current in the same cell setup of 50, 100 and 150 mV, each held until stationary conditions by polarization of the sample in three different potential steps (~0.49 eV). The electric conductivity of the sample was studied is by far the highest. Moreover, since the onset temperature \( T_{\text{onset}} \) is not reached at 300 K an activation energy allows for a rough estimation of the activation energy. Since the energy of the empirical Waugh-Fedin relation, \( E_{\text{a}}^{\text{Waugh-Fedin}} \), is estimated to be at 300 K or higher, no or only an extremely low conductivity is expected in electrochemical impedance measurements.

The ionic conductivity of \( \text{Li}_2\text{SnP}_3 \) was determined by electrochemical impedance spectroscopy (EIS) in a blocking electrode configuration. The results obtained at temperatures between 298 and 353 K ± 0.5 K are shown in Figure 6a. The Nyquist plots exhibit well resolved but slightly broadened semicircles and the onset of a branch at low frequencies. For the evaluation of the ionic conductivity only the high-frequency semicircle was fitted, using two serial R/C elements, revealing two processes involved in the ionic conduction mechanism, that is, a dominant process with a capacity of \( 3(5) \times 10^{-5} \) F and a minor process with a capacitance of \( 5(1) \times 10^{-5} \) F. The first process can be assigned, according to Irvine et al.\([31]\) to grain boundary-controlled ionic conductivity, while the latter resembles the contribution of a surface layer. The overall ionic conductivity at 298 K was determined to \( 3.2(2) \times 10^{-7} \) S cm\(^{-1}\). Calculated from the slope of the Arrhenius plot in Figure 6b, the activation energy of the ionic mobility was determined to \( E_{\text{a}}^{\text{PEIS}} = 47.6(6) \) kJ mol\(^{-1}\) (~0.49 eV). The electric conductivity of the sample was studied by polarization of the sample in three different potential steps of 50, 100 and 150 mV, each held until stationary conditions were approached, monitoring the current in the same cell setup as for impedance spectroscopy (Figure 6c). Application of Ohm’s law results in an electronic conductivity of \( 2.1(9) \times 10^{-8} \) S cm\(^{-1}\), which is approximately one order of magnitude lower than the ionic conductivity.
Discussion and Conclusion

The straightforward synthesis of single crystals and phase-pure microcrystalline powders finally allows for a comparison of the structure and properties of LiSnP₃ with that of the recently reported compounds α- and β-LiSnP₃ and Li₂SnP₆ which contain an increasing percentage of Li⁺.⁷,8 On both the Li-poor and Li-rich sides, mixed Li/Sn positions in a small cubic unit cell occur. The cell parameters shown in Table 4 increase with a higher content of Li⁺ because the exchange of one Sn⁴⁺ requires the insertion of four Li⁺ to keep the electronic preciseness of the structures. The relatively small amount of Li⁺ in Li₂SnP₆ is found to occupy all tetrahedral voids, whereas the octahedral voids remain completely empty, and thus, the octahedral voids must be regarded as energetically less favored. With increasing Li⁺ content, however, also the octahedral voids are progressively filled reaching an occupancy of 25% in α- and β-LiSnP₃ and of 50% in Li₂SnP₆.

In addition, Figure 7 reveals a correlation between the occupancy of the octahedral voids and the ionic conductivity, and the latter increases from Li₂SnP₆ to Li₃SnP₄ by more than three orders of magnitude. The relatively low ionic conductivity of LiSnP₃ is attributed to the absence of occupied octahedral voids and corroborates the assumption that these vacancies are energetically less favored. As a consequence, Li⁺ diffusion does not occur via octahedral sites but through edge-sharing tetrahedral voids that require a higher activation energy if compared to the diffusion along face-sharing tetrahedral and octahedral voids, as recently shown by the investigation of Li⁺ diffusion pathways in α- and β-LiSnP₃ and Li₂SnP₆.

The systematic investigation of the ternary Li/Sn/P system within the formula LiₓSn₃Pₓ (x = 0.0 to 1.0) did not lead to compounds with other Li/Sn ratios than that of the previously reported phases Li₂SnP₆ (α-) and β-LiSnP₃ (β-). Interestingly, no ordered structure is observed for Li₂SnP₆ and Li₃SnP₄ whereas two polymorphs with distinctly ordered cation positions are found for the Li₃SnP₄. In addition, there is no evidence of a phase width of the compounds. The disorder in Li₂SnP₆ and Li₃SnP₄ is in accordance with the recorded 31P and 119Sn MAS NMR spectra, which exhibit extremely broad resonances. Such broad resonances hint for a vague chemical environment of the P and Sn atoms. Nevertheless, the chemical shift of the signals is within the range of the resonances reported for the ordered structures of α- and β-LiSnP₃ indicating the presence of [SnP₆] tetrahedra in Li₃SnP₄ which in accordance with the charge are expected to form edge-sharing [SnP₆]₄ dimers as found as ordered variant in Li₃SnP₆.⁵⁷

A two-step synthesis route, including mechanical alloying and subsequent annealing of the samples, yields all four compounds in high purity and on a gram scale allowing for a profound determination of the properties.

The low ionic conductivity of αLiSnP₃ = 3.2(2)·10⁻⁷ S cm⁻¹ of Li₂SnP₆ in combination with vacant octahedral sites on the one hand, and the high ionic conductivity of α- and β-LiSnP₃ as well as of Li₃SnP₄ with partially filled octahedral sites on the other unequivocally prove the importance of the participation of the octahedral voids in ion motion. In order to lower the activation energy one can either lower the energy barrier for Li⁺ motion between neighboring sites or raise the energy level of the respective sites. The partial occupation of the energetically unfavorable octahedral voids in the Li-rich phosphidotetrelates corresponds to the latter case and leads to an overall flattening of the energy landscape. In this context the investigation of less promising Li⁺-conducting materials with insufficient ionic conductivities for application, plays a key role in the understanding of the criteria to design and tailor next-generation ionic conductors.

Supporting Information Summary

Details of crystal structure determination of Li₂SnP₆, details on the investigation of the system LiₓSn₃Pₓ (x = 0.333 to +0.333), differential scanning calorimetry (DSC), ⁶Li, ¹¹⁹Sn, and ³¹P MAS NMR spectroscopy.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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