

# Li<sub>5</sub>SnP<sub>3</sub> – a Member of the Series Li<sub>10+4x</sub>Sn<sub>2-x</sub>P<sub>6</sub> for x = 0 Comprising the Fast Lithium-Ion Conductors Li<sub>8</sub>SnP<sub>4</sub> (x = 0.5) and Li<sub>14</sub>SnP<sub>6</sub> (x = 1)

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Dedicated to Professor Richard Dronskowski 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<sub>5</sub>SnP<sub>3</sub> which completes with x=0 the series Li<sub>10+4x</sub>Sn<sub>2-x</sub>P<sub>6</sub> of the fast lithium-ion conductors α- and β-Li<sub>8</sub>SnP<sub>4</sub> (x = 0.5) and Li<sub>14</sub>SnP<sub>6</sub> (x = 1). Synthesis, crystal structure determination by single-

crystal and powder X-ray diffraction methods, as well as <sup>6</sup>Li, <sup>31</sup>P and <sup>119</sup>Sn MAS NMR and temperature-dependent <sup>7</sup>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.<sup>[1]</sup> 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.<sup>[2–4]</sup> 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.<sup>[5–8]</sup> Searching for high-performance ionic conductors, a large number of innovative SEs featuring ever increasing ionic conductivities has been reported over the last decades.<sup>[2–4,9,10]</sup> 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 phosphidotetrelates and the closely related lithium phosphidotrirelates 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  $3 \times 10^{-3} \text{ S cm}^{-1}$  have been reported<sup>[3,4,7]</sup> next to materials that feature a band gap of about 3 eV, indicative of semiconducting behavior.<sup>[11]</sup> In addition the compound LiGe<sub>3</sub>P<sub>3</sub> shows moderate electric conductivity and an unprecedented stability when exposed to water and air.<sup>[12]</sup> Apart from the latter and a few other exceptions, most of the so far discovered lithium phosphidotetrelates and -tri-relates are based on tetrahedral [TtP<sub>4</sub>] or [TtP<sub>4</sub>] units, which occur either as isolated [TtP<sub>4</sub>]<sup>8-</sup> or [TtP<sub>4</sub>]<sup>9-</sup> anions that are charge-compensated by the corresponding amount of Li<sup>+</sup> or they build frameworks of condensed tetrahedra and supertetrahedra, respectively.<sup>[8,11–15]</sup>

The compound Li<sub>10</sub>Si<sub>2</sub>P<sub>6</sub> comprises pairs of edge-sharing [SiP<sub>4</sub>] units resulting in the polyanion [Si<sub>2</sub>P<sub>6</sub>]<sup>10-</sup>.<sup>[16]</sup> Due to these building blocks, the formula is commonly given as Li<sub>10</sub>Si<sub>2</sub>P<sub>6</sub> rather than Li<sub>5</sub>SiP<sub>3</sub> to express the molecular-anionic character.

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Indeed, a compound with the composition  $\text{Li}_5\text{SiP}_3$  has been reported in the 1950s, and characterized by the determination of the cubic space group  $Fm\bar{3}m$  with a lattice parameter of  $a = 5.852 \text{ \AA}$ .<sup>[17]</sup> The structure is closely related to the antiferrotype or a defect variant of the  $\text{Li}_3\text{Bi}$  structure,<sup>[18]</sup> which can be described by a *ccp* of P atoms in which all tetrahedral voids are statistically occupied by  $\text{Li}^+$  and  $\text{Si}^{4+}$  in a mixing ratio of 5:1. So far, all attempts to reproduce these findings have failed.<sup>[13,16]</sup> However, about 20 years later the same structure was reported for the heavier homologue  $\text{Li}_5\text{SnP}_3$ <sup>[19]</sup> with identical cubic space group  $Fm\bar{3}m$  (no. 225) and a lattice parameter of  $a = 5.97 \text{ \AA}$ . Further investigations of the material's properties are still pending, whereas the lithium-rich phosphidostannates  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$  as well as  $\text{Li}_{14}\text{SnP}_6$  have been recently reported to show superionic lithium-ion conductivities of about  $1 \times 10^{-3} \text{ S cm}^{-1}$ . Interestingly in  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$ , the Li and Sn atoms are fully ordered in the tetrahedral voids of the *ccp* of P atoms, thus leading to polyanionic  $\text{SnP}_4^{8-}$  units. By contrast in  $\text{Li}_{14}\text{SnP}_6$ , the Li and Sn atoms are statistically distributed over the tetrahedral sites. Analysis of  $\text{Li}^+$  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.<sup>[7,8]</sup>

In the following we report on the systematic investigation of the system  $\text{Li}_{10+4x}\text{Sn}_{2-x}\text{P}_6$  ( $x = 0.0$  to  $1.0$ ) including the compounds  $\text{Li}_5\text{SnP}_3$ , ( $\alpha$ - and  $\beta$ -)  $\text{Li}_8\text{SnP}_4$  and  $\text{Li}_{14}\text{SnP}_6$  that arise for  $x = 0.0, 0.5$ , and  $1.0$ , respectively. Following a well-established synthesis route for lithium phosphidostannates including mechano-chemical milling allows for the first time the isolation and detailed characterization of the compound  $\text{Li}_5\text{SnP}_3$  by single-crystal and powder X-ray diffraction data completed by Rietveld refinement as well as  $^6\text{Li}$ ,  $^{31}\text{P}$  and  $^{119}\text{Sn}$  solid-state magic angle spinning (MAS) 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  $\text{Li}^+$  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 phosphidostannates  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$  and  $\text{Li}_{14}\text{SnP}_6$ , which allows for the formulation of new structure-property relationships regarding the ionic conductivity in solid-state  $\text{Li}^+$  conductors.

## Experimental Section

All syntheses were carried out under Ar atmosphere in glove boxes (MBraun, 200B) with moisture and oxygen levels below 0.1 ppm, or in containers, which were sealed under Ar atmosphere and vacuum ( $< 2 \cdot 10^{-2}$  mbar), respectively. Lithium phosphidostannates 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  $\text{Li}_{10+4x}\text{Sn}_{2-x}\text{P}_6$  with  $x = 0.00, 0.25, 0.50, 0.75, 1.00$  (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 ( $V = 50$  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:  $4 \text{ K min}^{-1}$ ) 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,  $\text{Cu}_{K\alpha 1}$  radiation,  $\lambda = 1.54056 \text{ \AA}$  or  $\text{Mo}_{K\alpha 1}$  radiation,  $\lambda = 0.70932 \text{ \AA}$ ) with a Dectris MYTHEN 1 K detector in Debye-Scherrer geometry. Samples were sealed in glass capillaries ( $\varnothing 0.3$  mm) for measurement. Raw data were processed with the WinXPOW<sup>[20]</sup> software prior to refinement.

The data analysis of  $\text{Li}_5\text{SnP}_3$  was performed using the full profile Rietveld method implemented in the FullProf program package.<sup>[21]</sup> 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 (Caglioti) 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  $\text{Li}_5\text{SnP}_3$  ( $Z = 1.33$ ) or  $\text{Li}_{6.67}\text{Sn}_{1.33}\text{P}_4$  ( $Z = 1$ ). 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  $\text{Li}_5\text{SnP}_3$  is assumed. All structures were visualized using DIAMOND.<sup>[22]</sup>

**Synthesis of powdery and single-crystalline  $\text{Li}_5\text{SnP}_3$ :**  $\text{Li}_5\text{SnP}_3$  is obtained as black powder on a gram scale and in high purity by annealing of the "reactive mixture" of the nominal composition " $\text{Li}_5\text{SnP}_3$ " ( $\text{Li}_{10+4x}\text{Sn}_{2-x}\text{P}_6$  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  $\beta$ -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 " $\text{Li}_5\text{SnP}_6$ ". The elements were annealed for 18 h at 873 K (heating

**Table 1.** Overview of the prepared "reactive mixtures" according to the formula  $\text{Li}_{10+4x}\text{Sn}_{2-x}\text{P}_6$  ( $x = 0.0$  to  $1.0$ ).

x	Composition
0.00	$\text{Li}_{10}\text{Sn}_2\text{P}_6 = \text{Li}_5\text{SnP}_3$
0.25	$\text{Li}_{11}\text{Sn}_{1.75}\text{P}_6$
0.50	$\text{Li}_{12}\text{Sn}_{1.5}\text{P}_6 = \text{Li}_8\text{SnP}_4$
0.75	$\text{Li}_{13}\text{Sn}_{1.25}\text{P}_6$
1.00	$\text{Li}_{14}\text{SnP}_6$

rate: 4 Kmin<sup>-1</sup>) in a sealed tantalum ampule and subsequently quenched in water.

**Single-crystal X-ray Diffraction Data Collection:** A single crystal of Li<sub>5</sub>SnP<sub>3</sub> was isolated and sealed in a glass capillary (0.1 mm). For diffraction data collection, the capillary was positioned in a 150 K cold N<sub>2</sub> gas stream. Data collection was performed with a STOE StadiVari (Mo<sub>Kα1</sub> 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 F<sup>2</sup> (SHELXL-2014).<sup>[23]</sup>

Further details of the crystal structure investigations may be obtained from the joint CCDC/FIZ Karlsruhe online deposition service: Deposition Number(s) CSD-2074706 (Li<sub>6.6667</sub>Sn<sub>1.33</sub>P<sub>4r</sub> single crystal), CSD-2074707 (Li<sub>6.6667</sub>Sn<sub>1.33</sub>P<sub>4r</sub> powder), CSD-2074709 (Li<sub>6.74</sub>Sn<sub>1.29</sub>P<sub>4r</sub> single crystal), and CSD-2074710 (Li<sub>6.70</sub>Sn<sub>1.30</sub>P<sub>4r</sub> 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 mLmin<sup>-1</sup> and a heating/cooling rate of 10 Kmin<sup>-1</sup>. Data collection and handling were carried out with the Proteus Thermal Analysis program,<sup>[24]</sup> and visualization was realized using OriginPro 2020.<sup>[25]</sup>

**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 ZrO<sub>2</sub> rotor. The resonance frequencies of the measured nuclei are 44.2, 121.5 and 111.9 MHz for <sup>6</sup>Li, <sup>31</sup>P and <sup>119</sup>Sn, respectively. The rotational frequency was set to 15 kHz. The MAS spectra were acquired at room temperature with recycle delays of 10 to 30 s and 1000 to 2736 scans. All <sup>6</sup>Li spectra were referenced to LiCl (1 M, aq) and LiCl (s) offering chemical shifts of 0.0 ppm and -1.15 ppm, respectively. The <sup>31</sup>P spectra were referred to (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub>(s) (ammonium dihydrogen phosphate) with a chemical shift of 1.11 ppm with respect to concentrated H<sub>3</sub>PO<sub>4</sub> (aq) (phosphoric acid). SnO<sub>2</sub> (s) (Cassiterite) was used as a secondary standard for the <sup>119</sup>Sn spectra, showing a chemical shift of -604.3 ppm<sup>[26,27]</sup> referred to (CH<sub>3</sub>)<sub>4</sub>Sn(l) (tetramethylstannane). All spectra were recorded using single-pulse excitation.

Static <sup>7</sup>Li NMR experiments were performed using a Bruker Avance III spectrometer operating at a magnetic field of 7 T employing a 4 mm WVT MAS probe. The resonance frequency of the <sup>7</sup>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 <sup>207</sup>Pb NMR shift of lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>) as chemical shift thermometer, which was also measured in a sealed glass tube. A saturation comb had been used prior to the <sup>7</sup>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 Li<sub>5</sub>SnP<sub>3</sub> (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.<sup>[3]</sup> The temperature was controlled via a Julabo Dyneo 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 phosphidostannates, mixtures with nominal compositions according to Table 1 were alloyed mechanically in a ball mill. The compositions were chosen according to the formula Li<sub>10+x</sub>Sn<sub>2-x</sub>P<sub>6</sub> (x=0.0 to 1.0) including also the compounds Li<sub>5</sub>SnP<sub>3</sub>,<sup>[19]</sup> α- and β-Li<sub>8</sub>SnP<sub>4r</sub>,<sup>[8]</sup> as well as Li<sub>14</sub>SnP<sub>6</sub>,<sup>[7]</sup> for x=0.0, 0.5 and 1.0, respectively.

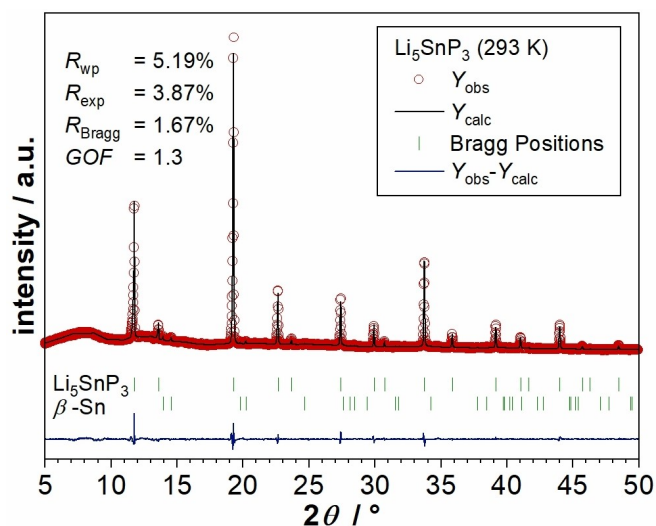
In order to detect further phases within this family of materials and to reveal existing phase widths of the compounds, the “reactive mixtures” were annealed at 673, 773 and 973 K, respectively. All “reactive mixtures” and products were analyzed using powder X-ray diffraction (PXRD) data for the identification of the occurring phases within the samples as well as for the determination of the cell parameters of the lithium phosphidostannates. The data showed the formation of the known compounds Li<sub>5</sub>SnP<sub>3</sub>,<sup>[19]</sup> α- and β-Li<sub>8</sub>SnP<sub>4r</sub>,<sup>[8]</sup> and Li<sub>14</sub>SnP<sub>6</sub>,<sup>[7]</sup> as well as the presence of Li<sub>3</sub>P and remaining β-Sn. Consequently, 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 Li<sub>5</sub>SnP<sub>3</sub> 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.

Differential scanning calorimetry, followed by PXRD measurements of the samples indicate the decomposition of Li<sub>5</sub>SnP<sub>3</sub> 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-Li<sub>8</sub>SnP<sub>4r</sub>. 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,<sup>[19]</sup> the single-crystal data of Li<sub>5</sub>SnP<sub>3</sub> indicate the cubic space group *Fm* $\bar{3}$ *m* (no. 225) and a lattice parameter of *a* = 5.9541(7) Å at 150 K (Figure 2 and Table 3).

The structure of Li<sub>5</sub>SnP<sub>3</sub> can be described as a *ccp* of P atoms (4*a* site) with the Sn and Li atoms statistically distributed in all tetrahedral voids (8*c* site) with a Sn:Li ratio of 1:5. The structure is thus closely related to the antiferroite structure with



**Figure 1.** Results of the Rietveld analysis of the powder X-ray diffraction pattern of  $\text{Li}_5\text{SnP}_3$  at 293 K. Red circles indicate observed intensities  $Y_{\text{obs}}$ , black lines show calculated intensities  $Y_{\text{calc}}$ , blue lines reveal the difference between observed and calculated intensities, and green marks indicate Bragg positions of  $\text{Li}_5\text{SnP}_3$  (weight fraction 99(1) %) and  $\beta\text{-Sn}$  (weight fraction 0.8(1) %), respectively.

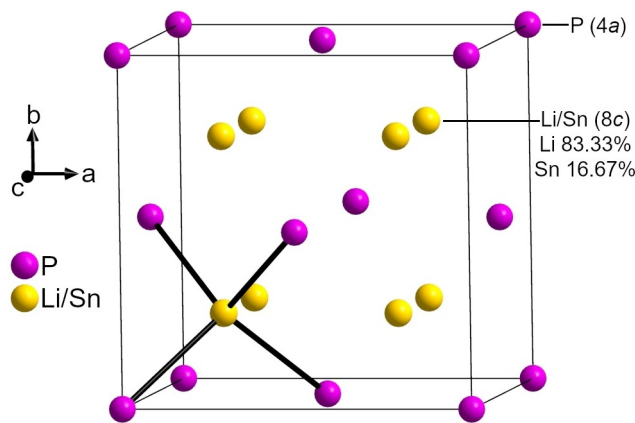
**Table 2.** Details of the Rietveld structure refinements of  $\text{Li}_5\text{SnP}_3$  ( $Z = 1.33$ ) at 293 K.

Empirical formula	$\text{Li}_{6.67}\text{Sn}_{1.33}\text{P}_4$
$T$ [K]	293
formula weight [ $\text{g mol}^{-1}$ ]	328.08
Group (no.)	$Fm\bar{3}m$ (225)
Unit cell parameters [ $\text{\AA}$ ]	$a = 5.98715(5)$
$Z$	1
$V$ [ $\text{\AA}^3$ ]	214.615(3)
$\rho_{\text{calc}}$ [ $\text{g cm}^{-3}$ ]	2.541
$2\theta$ range [deg]	5.000–49.9441
$R_p$	3.87 %
$R_{\text{wp}}$	5.19 %
$R_{\text{exp}}$	3.87 %
$\chi^2$	1.80
GOF	1.3
$R_{\text{Bragg}}$	1.67 %
$R_f$	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  $\text{Li}_{14}\text{SnP}_6$  is almost isotopic to that of  $\text{Li}_5\text{SnP}_3$ , but with a slightly larger lattice parameter ( $a = 6.01751(3) \text{ \AA}$ ) 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  $\text{Li}_3\text{Bi}$ -type structure was also observed for the lighter homologues  $\text{Li}_{14}\text{SiP}_6$  and  $\text{Li}_{14}\text{GeP}_6$ .<sup>[3,7]</sup>

All interatomic Li/Sn–P (2.5782(2)  $\text{\AA}$ ), Li/Sn–Li/Sn (2.9771(3)  $\text{\AA}$ ) and P–P distances (4.2102(3)  $\text{\AA}$ ) are within the



**Figure 2.** Structure of  $\text{Li}_5\text{SnP}_3$  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) $_4$  tetrahedra.

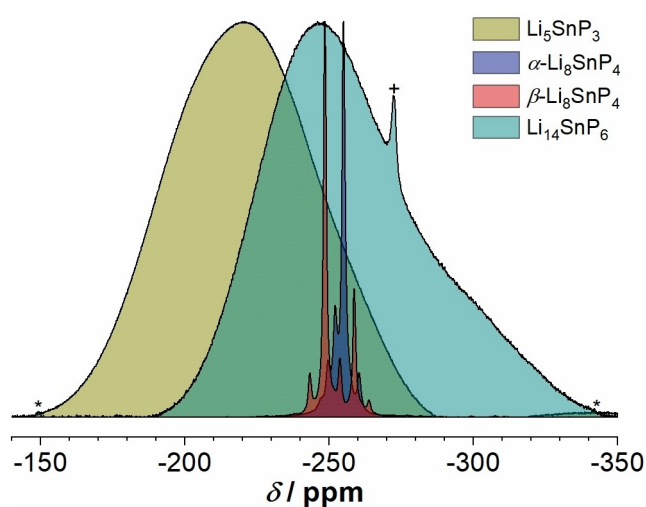
**Table 3.** Crystallographic data and refinement parameters of  $\text{Li}_5\text{SnP}_3$  ( $Z = 1.33$ ) or  $\text{Li}_{6.67}\text{Sn}_{1.33}\text{P}_4$  ( $Z = 1$ ) at 150 K with fixed site occupancy factors.

empirical formula	$\text{Li}_5\text{SnP}_3/\text{Li}_{6.67}\text{Sn}_{1.33}\text{P}_4$
Formula weight [ $\text{g mol}^{-1}$ ]	328.08
Crystal size [ $\text{mm}^3$ ]	$0.08 \times 0.08 \times 0.09$
Crystal color	black
$T$ [K]	150
Crystal system	cubic
Space group (no.)	$Fm\bar{3}m$ (225)
Unit cell parameter [ $\text{\AA}$ ]	$a = 5.9541(7)$
$Z$	0.75/1
$V$ [ $\text{\AA}^3$ ]	211.08(7)
$\rho_{\text{calc}}$ [ $\text{g cm}^{-3}$ ]	2.583
$\mu$ [ $\text{mm}^{-1}$ ]	4.644
$F(000)$ [e]	147
$\theta$ range [deg]	5.934–46.355
Index range ( $hkl$ )	$-7 \leq h \leq 11,$ $-10 \leq k \leq 11,$ $-11 \leq l \leq 4$
Reflections collected	348
Independent reflections	72
$R_{\text{int}}$	0.0101
Reflections with $I > 2\sigma(I)$	72
Absorption correction	multi-scan
Data/restraints/parameters	72/0/4
Goodness-of-fit on $F^2$	1.248
$R_1, wR_2$ (all data)	0.0231, 0.0231
$R_1, wR_2$ [ $I > 2\sigma(I)$ ]	0.0626, 0.0626
Largest diff. peak and hole [ $\text{e \AA}^{-3}$ ]	0.968/–0.497
Depository no.	CSD-2074706

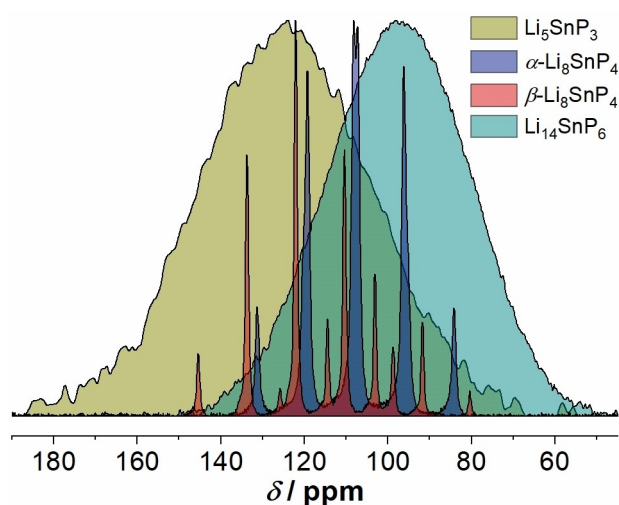
range of those found for related ternary or binary compounds like  $\text{Li}_{14}\text{TtP}_6$  ( $Tt = \text{Si, Ge, Sn}$ ),<sup>[3,7]</sup> ( $\alpha$ -/ $\beta$ -) $\text{Li}_8\text{TtP}_4$  ( $Tt = \text{Si, Ge, Sn}$ )<sup>[8,13,14]</sup> and  $\text{Li}_3\text{P}$ .<sup>[28]</sup>

The  $^{31}\text{P}$  MAS NMR spectrum of  $\text{Li}_5\text{SnP}_3$  shows one very broad resonance ( $\sim 17$  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  $\text{Li}_{14}\text{TtP}_6$  ( $Tt = \text{Si, Ge, Sn}$ ).<sup>[3,7,29]</sup> 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  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$ .<sup>[8]</sup> In

comparison to the resonances of the latter and of other closely related lithium phosphidostannates such as  $\text{Li}_{14}\text{SnP}_6$ ,<sup>[7]</sup> the maximum of the signal pertaining to  $\text{Li}_5\text{SnP}_3$  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  $\text{Li}_5\text{SnP}_3$  are covalently bound to at least one Sn atom, whereas in  $\text{Li}_{14}\text{TtP}_6$  also  $\text{P}^{3-}$  anions are present according to  $[(\text{Li}^+)_{14}(\text{TtP}_4)^{8-}(\text{P}^{3-})_2]$ . In analogy to the structures of  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$  and  $\text{Li}_{14}\text{SnP}_6$ , respectively, the Sn atoms are occupying tetrahedral voids, resulting in  $\text{SnP}_4$  units.<sup>[7,8]</sup> Regarding the electron-precise stoichiometry ( $\text{Li}_5\text{SnP}_3$  or  $\text{Li}_{6.67}\text{Sn}_{1.33}\text{P}_4$ ), each P atom is statistically coordinated by 1.33 Sn atoms. Thus, one would expect the coordination of 1/3 of all P atoms by two Sn atoms, and all the others coordinate to one



**Figure 3.** Overview of the  $^{31}\text{P}$  MAS NMR spectra of  $\text{Li}_5\text{SnP}_3$  (olive),  $\alpha$ - $\text{Li}_8\text{SnP}_4$  (blue),  $\beta$ - $\text{Li}_8\text{SnP}_4$  (red),<sup>[8]</sup> and  $\text{Li}_{14}\text{SnP}_6$  (teal).<sup>[7]</sup> Spinning sidebands and  $\text{Li}_3\text{P}$  (impurity) are indicated by \* and +, respectively.



**Figure 4.** Overview of the  $^{119}\text{Sn}$  MAS NMR spectra of  $\text{Li}_5\text{SnP}_3$  (olive),  $\alpha$ - $\text{Li}_8\text{SnP}_4$  (blue),  $\beta$ - $\text{Li}_8\text{SnP}_4$  (red),<sup>[8]</sup> and  $\text{Li}_{14}\text{SnP}_6$  (teal).<sup>[7]</sup>

Sn atom. In other words, two Sn atoms occupy adjacent tetrahedral voids and form edge-sharing tetrahedra with the formula  $[\text{Sn}_2\text{P}_6]^{10-}$ . Such units are also observed in the homologous lithium phosphidosilicate  $\text{Li}_{10}\text{Si}_2\text{P}_6$ .<sup>[16]</sup> However, the  $[\text{Sn}_2\text{P}_6]^{10-}$  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 ( $1b\text{-P}^{2-}$ ) and P atoms surrounded by two Sn atoms ( $2b\text{-P}^{1-}$ ) was not feasible. Possible reasons are given after the discussion of the  $^{119}\text{Sn}$  NMR spectrum.

Regarding the  $^{119}\text{Sn}$  NMR spectrum of  $\text{Li}_5\text{SnP}_3$ , the high level of cation disorder also results in only one very broad ( $\sim 13$  kHz) tin resonance at a chemical shift of 124.6 ppm (Figure S9). In analogy to the  $^{31}\text{P}$  NMR measurements, this effect has also been observed in the  $^{119}\text{Sn}$  spectrum of  $\text{Li}_{14}\text{SnP}_6$ .<sup>[7]</sup> In comparison to the latter, the maximum of the signal for  $\text{Li}_5\text{SnP}_3$  shows a downfield shift of 26.5 ppm, and the resonances of the lithium phosphidostannates  $\text{Li}_5\text{SnP}_3$ ,  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$  and  $\text{Li}_{14}\text{SnP}_6$  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.<sup>[7,8]</sup>

Regarding the electron-precise stoichiometry of the so far known lithium phosphidostannates the structure of  $\text{Li}_{14}\text{SnP}_6$  shows both,  $[\text{SnP}_4]^{8-}$  and  $\text{P}^{3-}$  units, whereas the two modifications of  $\text{Li}_8\text{SnP}_4$  only contain  $[\text{SnP}_4]^{8-}$  tetrahedra, and the basic structure of  $\text{Li}_5\text{SnP}_3$  consists of  $[\text{Sn}_2\text{P}_6]^{10-}$  units.<sup>[7,8]</sup> 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  $[\text{SnP}_4]$  tetrahedra in  $\text{Li}_5\text{SnP}_3$ , which are correspondingly reported for  $\text{Li}_{10}\text{Si}_2\text{P}_6$ . In contrast to the strongly covalent character of the Si–P bonds leading to molecule-like  $[\text{Si}_2\text{P}_6]$  units<sup>[16]</sup> the bonding situation in  $\text{Li}_5\text{SnP}_3$  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  $^6\text{Li}$  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  $^6\text{Li}$  resonances reported for lithium phosphidotetrelates and -trielates.<sup>[3,4,7,8,11–14,16]</sup>

### Lithium-ion mobility

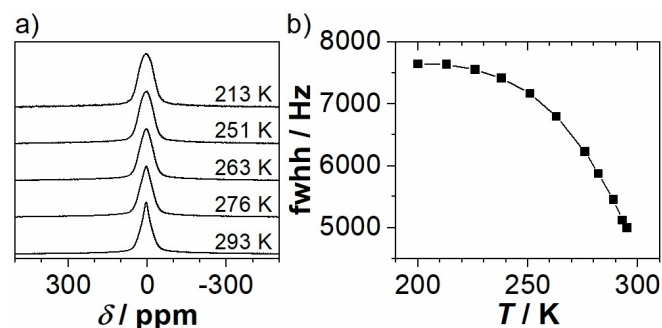
The  $\text{Li}^+$  mobility, the activation energy and the ionic as well as the electronic conductivity are evaluated and compared to recent results of the related compounds  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$  and  $\text{Li}_{14}\text{SnP}_6$ .

For a rough estimation of the activation barrier for  $\text{Li}^+$  mobility in crystalline  $\text{Li}_5\text{SnP}_3$  the dynamic behavior of  $\text{Li}^+$  was investigated by temperature-dependent evolution of the static  $^7\text{Li}$  NMR line width. Since the central transition of the  $I = 3/2$   $^7\text{Li}$  nucleus is broadened by homonuclear ( $^7\text{Li}$ – $^7\text{Li}$ ) and heteronuclear ( $^7\text{Li}$ – $^{31}\text{P}$ ) dipolar coupling, both of which scale with the second Legendrian ( $3 \cos^2 \beta - 1$ ), any dynamic process leads to a

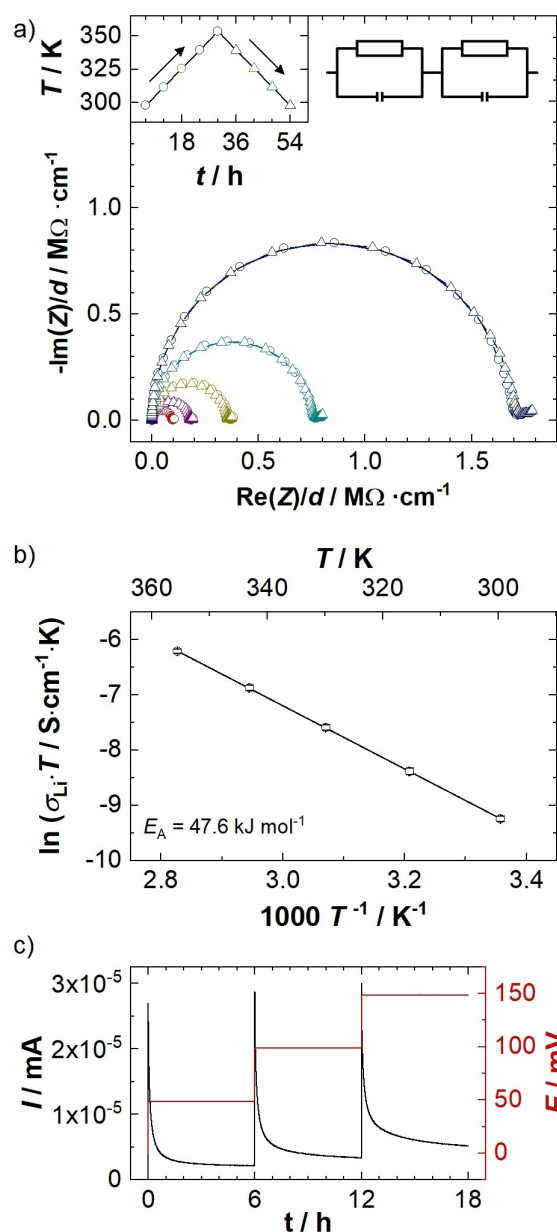
(partial) averaging of this orientational dependence and, thus, to a narrowing of the NMR line. The corresponding results are depicted in Figure 5. At 213 K a single Gaussian line was obtained at 3.9 ppm with a line width of about 7.6 kHz. At temperatures above 263 K the signal becomes more heterogeneous and increasingly Lorentz-shaped, combined with a stronger narrowing of the line. The resonance remains heterogeneous up to 300 K, with a line width of 5.0 kHz. Application of the empirical Waugh-Fedin relation,  $E_A^{\text{NMR}} = 0.156 \cdot T_{\text{onset}}^{[30]}$  allows for a rough estimation of the activation energy. Since the high-temperature plateau is not reached at 300 K an activation energy of  $E_A^{\text{NMR}} = 47 \text{ kJ mol}^{-1}$  or higher can be assumed.

In comparison with the corresponding values determined for the lithium-rich phosphidostannates  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$  ( $E_A^{\text{NMR}} = 34$  and  $28 \text{ kJ mol}^{-1}$ , respectively) and  $\text{Li}_{14}\text{SnP}_6$  ( $E_A^{\text{NMR}} = 28 \text{ kJ mol}^{-1}$ ) the estimated activation energy for  $\text{Li}_5\text{SnP}_3$  is by far the highest. Moreover, since the onset temperature  $T_{\text{onset}}$  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  $\text{Li}_5\text{SnP}_3$  was determined by electrochemical impedance spectroscopy (EIS) in a blocking electrode configuration. The results obtained at temperatures between 298 and 353 K  $\pm 0.5 \text{ K}$  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  $3(5) \cdot 10^{-10} \text{ F}$  and a minor process with a capacitance of  $5(1) \cdot 10^{-7} \text{ F}$ . The first process can be assigned, according to Irvine et al.,<sup>[31]</sup> 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  $3.2(2) \cdot 10^{-7} \text{ S cm}^{-1}$ . Calculated from the slope of the Arrhenius plot in Figure 6b, the activation energy of the ionic mobility was determined to  $E_A^{\text{PEIS}} = 47.6(6) \text{ kJ mol}^{-1}$  ( $\sim 0.49 \text{ eV}$ ). 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



**Figure 5.** a) Static  $^7\text{Li}$  spectra of  $\text{Li}_5\text{SnP}_3$  at various temperatures; b) evolution of the  $^7\text{Li}$  line width in the temperature range from 200 K to room temperature for  $\text{Li}_5\text{SnP}_3$ . The solid line only serves as a guide to the eye.



**Figure 6.** a) Nyquist plot of  $\text{Li}_5\text{SnP}_3$  measured under blocking conditions, with spectra recorded at temperatures between 298 and 353 K according to the color code of the inset. Circles and triangles indicate data collection during heating and cooling, respectively. The equivalent circuit used for fitting is also shown; b) Arrhenius plot of the product of conductivity and temperature ( $\sigma_{\text{Li}} T$ ) obtained in one heating-cooling cycle, with error bars for each temperature based on the standard deviation from independent measurements with three cells; the shown linear fit was used to obtain the activation energy  $E_A^{\text{PEIS}}$ ; c) polarization curves of  $\text{Li}_5\text{SnP}_3$  for the determination of the electronic conductivity. The black line referring to the left y axis shows the recorded current, while the red line (right y axis) shows the applied potential steps.

as for impedance spectroscopy (Figure 6c). Application of Ohm's law results in an electronic conductivity of  $2.1(9) \cdot 10^{-8} \text{ S cm}^{-1}$ , which is approximately one order of magnitude lower than the ionic conductivity.

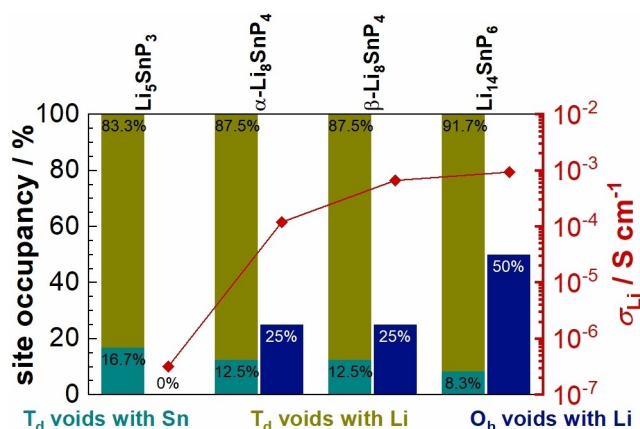
## Discussion and Conclusion

The straightforward synthesis of single crystals and phase-pure microcrystalline powders finally allows for a comparison of the structure and properties of  $\text{Li}_5\text{SnP}_3$  with that of the recently reported compounds  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$  and  $\text{Li}_{14}\text{SnP}_6$ , which contain an increasing percentage of  $\text{Li}^+$ .<sup>[7,8]</sup> 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  $\text{Li}^+$  because the exchange of one  $\text{Sn}^{4+}$  requires the insertion of four  $\text{Li}^+$  to keep the electronic preciseness of the structures. The relatively small amount of  $\text{Li}^+$  in  $\text{Li}_5\text{SnP}_3$  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  $\text{Li}^+$  content, however, also the octahedral voids are progressively filled reaching an occupancy of 25% in  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$  and of 50% in  $\text{Li}_{14}\text{SnP}_6$ .

In addition, Figure 7 reveals a correlation between the occupancy of the octahedral voids and the ionic conductivity, and the latter increases from  $\text{Li}_5\text{SnP}_3$  to  $\text{Li}_{14}\text{SnP}_6$  by more than three orders of magnitude. The relatively low ionic conductivity of  $\text{Li}_5\text{SnP}_3$  is attributed to the absence of occupied octahedral voids and corroborates the assumption that these vacancies are

**Table 4.** Comparison of the cell parameter  $a$ , the ionic and electronic conductivities  $\sigma_{\text{Li}}$  and  $\sigma_{\text{el}}$  and the activation energy  $E_{\text{A}}^{\text{PEIS}}$  of the lithium phosphidostannates  $\text{Li}_5\text{SnP}_3$ ,  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$  and  $\text{Li}_{14}\text{SnP}_6$  at ambient temperature.

empirical formula	$\text{Li}_5\text{SnP}_3$	$\alpha$ - $\text{Li}_8\text{SnP}_4$	$\beta$ - $\text{Li}_8\text{SnP}_4$	$\text{Li}_{14}\text{SnP}_6$
$a$ [Å]	5.98715	11.97626	11.99307	6.01751
$\left(\frac{a}{2}\right)$ [Å]		(5.98813 Å)	(5.996535 Å)	
$\sigma_{\text{Li}}$ [ $\text{S cm}^{-1}$ ]	$3.2 \cdot 10^{-7}$	$1.2 \cdot 10^{-4}$	$6.6 \cdot 10^{-4}$	$9.3 \cdot 10^{-4}$
$\sigma_{\text{el}}$ [ $\text{S cm}^{-1}$ ]	$2.1 \cdot 10^{-8}$	$1.4 \cdot 10^{-7}$	$6.1 \cdot 10^{-7}$	$4.1 \cdot 10^{-7}$
$E_{\text{A}}^{\text{PEIS}}$ [ $\text{kJ mol}^{-1}$ ]	47.6	36.0	32.4	33.8



**Figure 7.** Correlation between the occupation of the tetrahedral and octahedral voids and the resulting ionic conductivity of the phases  $\text{Li}_5\text{SnP}_3$ ,  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$  and  $\text{Li}_{14}\text{SnP}_6$ . The percentages of Sn and Li in the tetrahedral voids are shown in teal and olive, respectively, and the partial occupation of the octahedral voids is indicated in blue. The corresponding ionic conductivity at room temperature is shown in red according to the scale on the right.

energetically less favored. As a consequence,  $\text{Li}^+$  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  $\text{Li}^+$  diffusion pathways in  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$  and  $\text{Li}_{14}\text{SnP}_6$ .

The systematic investigation of the ternary Li/Sn/P system within the formula  $\text{Li}_{10+4x}\text{Sn}_{2-x}\text{P}_6$  ( $x=0.0$  to 1.0) did not lead to compounds with other Li/Sn ratios than that of the previously reported phases  $\text{Li}_5\text{SnP}_3$ ,<sup>[19]</sup>  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$ <sup>[8]</sup> and  $\text{Li}_{14}\text{SnP}_6$ .<sup>[7]</sup> Interestingly, no ordered structure is observed for  $\text{Li}_5\text{SnP}_3$  and  $\text{Li}_{14}\text{SnP}_6$ , whereas two polymorphs with distinctly ordered cation positions are found for the  $\text{Li}_8\text{SnP}_4$ . In addition, there is no evidence of a phase width of the compounds. The disorder in  $\text{Li}_5\text{SnP}_3$  and  $\text{Li}_{14}\text{SnP}_6$  is in accordance with the recorded  $^{31}\text{P}$  and  $^{119}\text{Sn}$  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  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$ , indicating the presence of  $[\text{SnP}_4]$  tetrahedra in  $\text{Li}_5\text{SnP}_3$ , which in accordance with the charge are expected to form edge-sharing  $[\text{Sn}_2\text{P}_6]^{10-}$  dimers as found as ordered variant in  $\text{Li}_{10}\text{Si}_2\text{P}_6$ .<sup>[16]</sup>

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  $\sigma_{\text{Li}}=3.2(2) \cdot 10^{-7} \text{ S cm}^{-1}$  of  $\text{Li}_5\text{SnP}_3$  in combination with vacant octahedral sites on the one hand, and the high ionic conductivity of  $\alpha$ - and  $\beta$ - $\text{Li}_8\text{SnP}_4$  as well as of  $\text{Li}_{14}\text{SnP}_6$  with partially filled octahedral sites on the other unequivocally proof 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  $\text{Li}^+$  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 phosphidostannates corresponds to the latter case and leads to an overall flattening of the energy landscape. In this context the investigation of less promising  $\text{Li}^+$ -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  $\text{Li}_5\text{SnP}_3$ , details on the investigation of the system  $\text{Li}_{8-4x}\text{Sn}_{1+x}\text{P}_4$  ( $x=-0.333$  to  $+0.333$ ), differential scanning calorimetry (DSC),  $^6\text{Li}$ ,  $^{119}\text{Sn}$ , and  $^{31}\text{P}$  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.

**Keywords:** ball milling · lithium-ion conductors · NMR spectroscopy · phosphidotetrelates · X-ray diffraction

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