Fast Lithium Ion Conduction in Lithium Phosphidoaluminates

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 85th birthday
Abstract: Solid electrolyte materials are crucial for the development of high-energy-density all-solid-state batteries (ASSB) using a nonflammable electrolyte. In order to retain a low lithium-ion transfer resistance, fast lithium ion conducting solid electrolytes are required. We report on the novel superionic conductor Li$_4$AIP$_4$, which is easily synthesised from the elements via ball-milling and subsequent annealing at moderate temperatures and which is characterized by single-crystal and powder X-ray diffraction. This representative of the novel compound class of lithium phosphidoaluminates has, as an undoped material, a remarkable fast ionic conductivity of 3 mS cm$^{-1}$ and a low activation energy of 29 kJ mol$^{-1}$ as determined by impedance spectroscopy. Temperature-dependent $^7$Li NMR spectroscopy supports the fast lithium motion. In addition, Li$_4$AIP$_4$ combines a very high lithium content with a very low theoretical density of 1.703 g cm$^{-3}$. The distribution of the Li atoms over the diverse crystallographic positions between the [AIP]$_{1+}$ tetrahedra is analyzed by means of DFT calculations.

Introduction

The development of advanced energy-storage technologies plays a key role in realizing electric vehicles.$^{[1-4]}$ Next-generation high-energy-density storage systems require low flammability, good electrochemical stability, and fast charging times. Li-ion batteries based on organic electrolytes hinder the commercialization of long-range electric vehicles. All-solid-state batteries (ASSBs) are promising candidates to overcome safety concerns of currently used Li-ion batteries with flammable organic liquid electrolytes.$^{[5,6]}$ Replacing the organic liquid electrolyte by an inorganic solid-state electrolyte (SSE), ASSBs offer high energy and power density, mechanical stability, and safety benefits.$^{[9-14]}$ However, ASSBs are limited by the slow ionic mobility of the SSE.$^{[15]}$ Hence, the discovery, characterization, and optimization of lithium superionic conducting solid phases are among the main aspects of today’s battery material research.$^{[8,16-18]}$ Despite the clear advantage of ASSBs, achieving Li-ion conductivity in SSEs comparable to that in liquid electrolytes (> 10 mS cm$^{-1}$) is a demanding task.$^{[9]}$ In the last decades, different crystalline materials have been proven to act as lithium conductors such as perovskite-type structures,$^{[19-22]}$ lithium superionic conductor (LISICON)-type structures,$^{[23-26]}$ thio-LISICON-type structures and thiphasophates,$^{[27-32]}$ sodium superionic conductor (NASICON)-type structures,$^{[33,34]}$ garnet-type structures,$^{[35-37]}$ lithium arygoxides,$^{[38]}$ lithium borohydrides,$^{[39]}$ lithium nitrides,$^{[40-42]}$ lithium hydrides,$^{[43]}$ and lithium halides.$^{[44]}$ The best lithium ion conductors currently known are rather complex systems such as Li$_{6.5}$Si$_{1.5}$P$_{1.4}$S$_{0.6}$Cl$_{0.3}$ and Li$_{6.7}$M$_{1.5}$Sb$_{1.5}$I$_{0.5}$ (M = Si, Ge, Sn) with an ionic conductivity of 25 and 24 mS cm$^{-1}$, respectively, outperforming the conductivity of liquid-based electrolytes.$^{[45,46]}$ By increasing the carrier densities, changing the diffusion pathways of the mobile species, creating vacancies or increasing structural defects, the ionic conductivity can be further optimized.$^{[8,16]}$ An effective way to increase the carrier density is especially the aloivalent substitution of cations: for example, in Li$_5$PS$_4$ making a formal substitution of “P$^5^+$” with “Ge$^{4+}$” results in Li$_3$Ge$_2$P$_6$S$_4$, having a four times higher ionic conductivity.$^{[28]}$

On the way to new candidates with good lithium ion conducting abilities, we recently have investigated lithium phosphidosilicates and phosphidogermanates.$^{[47,48]}$ The idea of replacing S$^2^-$ by P$^5^-$ enables the accommodation of even more lithium ions in the structures. Since our first report in 2016 on the aristo-type Li$_5$SiP$_4$,$^{[47]}$ also Li$_5$SiP$_4$ was established as good lithium ion conductor.$^{[49]}$ Recently, we have also shown that the system can be extended to the heavier homologue germainan and that for Li$_3$GeP$_2$ two Li-ion conducting modifications exist which display ionic conductivities of up to $8.6 \times 10^{-5}$ S cm$^{-1}$ at 298 K.$^{[48]}$ Structurally, phosphidosilicates and phosphidogermanates are built up by [TP]$^{4-}$ tetrahedra, where T denotes the respective tetrel atom (Si, Ge). Relating to the building principles of oxidosilicates, thiosilicates, and thiphosphates, these tetra-
The tetrahedra can be formally condensed and covalently connected by sharing edges or corners; hence a large variety of structure motifs can be gained. The idea of phosphide-based structures as ionic conductors results from the aliovalent substitution of \([\text{TiS}_3]^{4-}\) tetrahedra, which are an key building block in sulfide-based electrolytes, leading to the analogous complex anions based on phosphorus. Due to the resulting higher charge, \([\text{TiP}_3]^{4-}\) tetrahedra allow for more lithium ions per formula unit for charge compensation when compared to \([\text{TiS}_3]^{4-}\). In addition, the more negatively charged \(\text{P}^{3-}\) is more polarizable than \(\text{S}^{2-}\).

The coincidence of a higher charge carrier density due to more Li ions for charge compensation together with a large number of vacancies is considered as an important prerequisite for a higher lithium ion conductivity. Certainly, this aspect must be in line with a low activation energy for lithium mobility as it occurs in structures with an effective polyhedral connectivity.\[^{[56]}\] An aliovalent substitution of formal “\(\text{Si}^{4+}\)” by “\(\text{Al}^{3+}\)” and formation of \([\text{AlP}_3]^{4-}\) instead of \([\text{SiP}_3]^{4-}\) tetrahedra allow for the presence of an even higher number of lithium ions and a strong influence on the Li occupation in voids. Ternary phases comprising the elements lithium, aluminum, and phosphorus were scarcely investigated. In the 1950s Juza et al. reported briefly the first lithium phosphidoaluminate, \(\text{Li}_4\text{AlP}_3\), and described its structure as a strongly distorted fluoride-type lattice in which P atoms form a close-packed atom arrangement and Al and Li atoms are randomly distributed over the tetrahedral sites.\[^{[51]}\] Occupation of Li ions in octahedral sites was, however, not considered. Two further publications on \(\text{Li}_4\text{AlP}_3\) were based on the poor structural characterization.\[^{[52,53]}\]

Here we report on the lithium-richer representative of the phosphidoaluminates, obtained by formal aliovalent substitution of “\(\text{Ti}^{4+}\)” by “\(\text{Al}^{3+}\)” in \(\text{Li}_4\text{TiP}_3\). The insertion of \(\text{Al}^{3+}\) leads to formally ninefold negatively charged \([\text{AlP}_3]^{-}\) tetrahedra, resulting in an even higher lithium density per formula unit and a change in the spatial extent of the diffusion pathways. Due to the nature of the structure in which P atoms form a cubic-close-packing arrangement, there are still a high number of unoccupied octahedral sites present. We expect that an increase of the carrier density will also lead to an increase of the ionic conductivity. Indeed, only recently, ab initio simulations suggested that doping of the moderate lithium-ion conductor \(\text{Li}_4\text{SiP}_3\) with Al could enhance the ionic conductivity.\[^{[47,54]}\]

**Results and Discussion**

**Synthesis and Crystal Structure of \(\text{Li}_4\text{AlP}_3\)**

\(\text{Li}_4\text{AlP}_3\) was synthesized from the elements by a two-step procedure. After ball-milling of stoichiometric amounts of Li, Al and P, the powder mixture was annealed at 973 K for one day yielding almost phase-pure \(\text{Li}_4\text{AlP}_3\) with 2.3(1) wt % LiP impurities (see Figure 1). Complete data of the Rietveld refinement are given in the Supporting Information (Tables S1 and S2). Single crystals of \(\text{Li}_4\text{AlP}_3\) were obtained by the direct reaction of the elements at 1073 K with a slight excess of P using a ratio of 9:1:4:2 (Li:Al:P). The resulting product contains besides \(\text{Li}_4\text{AlP}_3\) also \(\text{Li}_3\text{P}\) and TaP (see Figure S4). Energy-dispersive X-ray spectroscopy (EDX) investigations of single crystals show an Al/P ratio which is in very good agreement with the expected values (see Table S6). \(\text{Li}_4\text{AlP}_3\) can also be synthesized starting from \(\text{Li}_3\text{P}\). However, again unreacted \(\text{Li}_3\text{P}\) remains as a contamination (see Figure S5). According to EDX measurements, the single crystals were free of Ta. The details of the structure refinement of the single-crystal X-ray diffraction of \(\text{Li}_4\text{AlP}_3\) are listed in Table 1 (further data are given in Tables S3 and S4 in the Supporting Information).

According to single-crystal and powder X-ray structure determination and refinement, \(\text{Li}_4\text{AlP}_3\) crystallizes in the cubic space group \(\text{P}4\text{3}3\text{m}\) (no. 218). The structure of \(\text{Li}_4\text{AlP}_3\) is built up of isolated \([\text{AlP}_3]^{-}\) tetrahedra surrounded by \(\text{Li}^+\) ions (Figure 2 a). The \(\text{AlP}_3\) tetrahedra are slightly distorted with P-Al-P angles ranging from 110.89(2)° to 108.77(2)° in comparison to the ideal tetrahedron angle of 109.74°. The Al–P bonds at 2.425(1) and 2.433(1) Å are longer than the Al–P bonds observed in compounds with connected \(\text{AlP}_3\) tetrahedra like \(\text{AlP}_3\) (2.360(1) Å), \(\text{Na}_3\text{AlP}_2\) (2.376(4) Å), and \(\text{Sr}_2\text{AlP}_3\) (2.377(3)–2.417(2) Å).\[^{[55–57]}\]

For the discussion of the coordination polyhedra of Li atoms, the structure is considered as a distorted cubic-face-centered packing of P atoms with Li and Al atoms filling voids in between and Wyckoff positions giving the multiplicity of the site. With \(Z=8\), there are 32 P atoms per unit cell resulting in 64 tetrahedral and 32 octahedral voids. The atoms Al1 and Al2 occupy 1/8 of the tetrahedral voids on Wyckoff positions 2a and 6d, respectively. We like to point out that the Al atoms are fully ordered, and no mixed occupancy of Al and Li occurs, in contrast to the mixed Li/Si occupancy in the Li-rich phase \(\text{Li}_4\text{SiP}_3\).\[^{[90]}\] The remaining tetrahedral voids in the title compound are occupied by Li atoms as follows: Li1, Li4, and Li5 (on Wyckoff positions 6b, 12f, and 24i, respectively).
All Li atoms exhibit large displacement ellipsoids (Figure 2a) which points towards a static or thermal displacement indicative of a high lithium ion mobility. All atomic positions except Li1 were refined anisotropically. Interestingly, the octahedral positions Li6a and Li6b exhibit ellipsoids that point towards the center of the triangular faces of the neighboring tetrahedral voids that are only partially filled with Li2 and Li3 (Figure 2b).

The high structural diversity of the Li atoms including disorder and split positions reflects the possibility of high lithium ion mobility. Li–P distances in the tetrahedral voids range from 2.50(1) to 2.73(1) Å, and in the octahedral voids they range from 2.56(1) to 3.46(1) Å. The bond lengths are similar to those in other ternary phases containing Li and P, such as Li2SiP3, Li4SiP3, Li5SiP3, and Li6Si2P5.[47,60]

According to the valence rules, Li3AlP4 is an electron-neutral compound and can be described as (Li+)3[AlP4]–, with formally two negative charges for the P atoms and one negative charge for the Al atom, balanced by nine Li+ ions.

### DFT Calculations

DFT computations based on the experimentally derived structural information were performed to serve a double purpose: first, to corroborate the refined structural model obtained from experiments; second, to obtain information about stability trends and the coordination of individual atoms in the presence of crystallographic disorder. We constructed a series of discrete atomistic models which approximate the disordered structure (making simplifications as detailed in the Supporting Information). The energetic stability of the new compound as compared to competing phases is analyzed according to the line in the ternary composition (Gibbs) diagram. Since Li3AlP4 is located on the line between the binaries LiP and AlP (Figure S6), it is straightforward to inquire the formation energy according to 3LiP + AlP = Li3AlP4 and to assess whether the title compound is stable with regard to the constituent binaries. The computed energies of ten randomized structural models were compared to those of the competing binary phases (3LiP + AlP) which are set as energy zero. The formation of the ternary title compound from the binaries is energetically favored by approximately 30 kJ mol–1 (Figure 3a and the Supporting Information), even without taking configurational entropy into account (which will further stabilize the ternary phase, as there are no partially occupied crystallographic positions in either LiP or AlP).

In addition to the energetic stability, having an ensemble of computationally optimized structural models allows us to quantify the distribution of interatomic distances and to compare with experimental results. Smoothed histograms over all ten structures are given in Figure 3b. The computed Al–P distances in the relaxed structures are 2.44(4) Å, with a narrow distribution indicating the rigidity of the tetrahedral AlP4 units. The Li–P distributions peak at 2.6 Å, but include a substantial amount of larger distances, reflecting the more disordered nature of the Li atoms which are often shifted away from the centers of the octahedral voids. The distribu-

### Table 1: Crystallographic data and refinement parameters of the SC-XRD analysis of Li3AlP4

| Parameter                                      | Value             |
|------------------------------------------------|-------------------|
| Empirical formula                              | Li3AlP4           |
| Formula weight [g mol–1]                       | 210.93            |
| Crystal size [mm3]                             | 0.2 × 0.2 × 0.1   |
| Crystal color                                  | dark brown–golden |
| Crystal shape                                  | plate             |
| T [K]                                         | 150(1)            |
| Space group                                    | P43n (no. 218)    |
| Unit cell dimension [Å]                        | a = 11.852(1)     |
| V [Å3]                                        | 1664.7(6)         |
| Z                                              | 8                 |
| ρ (calc.) [g cm–3]                             | 1.703             |
| μ [mm–1]                                       | 0.908             |
| θ Range [°]                                    | 2.430–32.494      |
| Index range hkl                                | –17 ≤ h ≤ 17     |
| –17 ≤ k ≤ 16                                  |
| –17 ≤ l ≤ 12                                  |
| Reflections collected                          | 13214             |
| Independent reflections                       | 1013              |
| Rint                                          | 0.0498            |
| Reflections with θ > 2θ(θ)                    | 758               |
| Data/restraints/parameter                     | 1015/0/63         |
| Absorption correction                         | empirical         |
| Goodness-of-fit on F2                         | 1.277             |
| Final R indices [I > 2σ (I)]                  | R1 = 0.026        |
| wR2 = (Σ[w(Fo2 – Fc2)2]/Σ[w(Fo2)2])1/2       | 0.067             |
| R indices (all data) [k]                      | R1 = 0.041        |
| wR2 = (Σ[w(Fo2 – Fc2)2]/Σ[w(Fo2)2])1/2       | 0.080             |
| Largest diff. peak and hole[e Å–1]            | 0.362/–0.417      |
| Deposition no.                                  | CSD-1962473       |

[a] R1 = Σ [Fo] – |Fc||/ Σ |Fo|.
[b] wR2 = (Σ w(Fo2 – Fc2)2/ Σ w(Fo2)2)1/2.
tion of Li–Li distances in the relaxed structures spans a broad range, starting at ≈ 2.4 Å, peaking at ≈ 2.6 Å, and becoming significantly less pronounced beyond 3.0 Å, in good agreement with the experimental observations (Table S5).

Impedance Spectroscopy

The lithium ion conductivity of Li₉AlP₄ was determined from impedance measurements in a blocking electrode configuration. Impedance spectra at different temperatures (273, 298, 313, 333, and 353 K according to the temperature profile shown in the inset) are displayed in Figure 4a and feature a semicircle at high frequencies and a low-frequency tail. The semicircle can be described as parallel circuit element of a resistor and a constant phase element ($R/Q$), with $R$ representing both intragrain and grain boundary contributions to the lithium ion transport which could not be resolved, and thus only the total ionic resistance of the sample could be determined. For the constant phase element, the fit of the data acquired at 298 K resulted in $\alpha$ values of $\approx 0.87$ and $Q$ parameters with a value of $\approx 17 \times 10^{-9}$ F s$^{(\alpha-1)}$; the ionic conductivity was determined to be $\sigma_\alpha$(Li₉AlP₄) = $(3.03 \pm 0.16) \times 10^{-3}$ S cm$^{-1}$ at 298 K (obtained from three independently measured cells). The activation energy for lithium ion transport (Figure 4b) was investigated by temperature-dependent impedance measurements in the range from 273–353 K, yielding $E_A^{\text{PEIS}}$ of $28.5 \pm 0.8$ kJ mol$^{-1}$ (≈ 0.29 eV); this was determined from three independently measured cells, using the $\sigma_\alpha T$ values of only the first heating and cooling cycle of each sample. This activation energy is in very good agreement with the value obtained by NMR spectroscopy (shown below). The temperature ramp of a heating and cooling cycle is displayed in the inset of Figure 4a. Colored dots indicate at which temperatures PEIS measurements were performed. In this context it should be mentioned that conductivities (and thus the product $\sigma_\alpha T$) for heating and cooling differ by less than 6%. Error bars are calculated separately for heating and cooling steps by taking the mean of three independent measurements obtained from three cells.

DC polarization measurements in the range from 50–150 mV reveal an electronic conductivity of $(2.0 \pm 0.8) \times 10^{-7}$ S cm$^{-1}$ at 298 K (based on the standard deviation of two cells).

$^6$Li and $^7$Li NMR Spectroscopy

The $^6$Li MAS NMR spectrum at room temperature shows one signal at a chemical shift of 4.19 ppm (Figure 5). The fitting of a generalized Lorentzian function to the experimental data proves the presence of only one signal as observed before for related compounds.$^{[47,48]}$ Since the shifts...
of Li atoms in tetrahedral and octahedral voids are not distinguishable, it can be assumed that all lithium ions are mobile at room temperature.

Static $^7$Li NMR spectra were recorded as a function of temperature to study the dynamic behavior of the lithium ions. The central transition of the $I=3/2$ nucleus $^7$Li experiences a broadening only from the homo- ($^{7}$Li$-^{7}$Li) and heteronuclear (here: $^{7}$Li–$^{31}$P) dipolar couplings. Since both types of interactions scale with the second Legendrian $(3\cos^2\beta-1)$, any dynamic process should produce a (partial) averaging of the orientational dependence and hence entail a narrowing of the NMR signal.

At 290 K, the static $^7$Li spectrum (Figure 6a top) displays a homogeneous Lorentzian shape with a linewidth of 640 Hz. Upon cooling, the signal gradually broadens, developing a Gaussian line shape with a linewidth of 10.1 kHz (Figure 6a bottom). At intermediate temperatures (166 K and 200 K), the line shape indicates some heterogeneity, which may be related to a distribution of activation energies for the Li ions occupying eight distinct crystallographic positions. Individual contributions from the different Li sites in the crystal lattice could not be resolved. For temperatures $>234$ K, a homogeneous line shape is observed, indicating all Li ions are mobile.

The temperature-dependent evolution of the linewidth (FWHH; full width at half height) of the $^7$Li NMR signal is shown in Figure 6b. A rough estimation of the activation energy of lithium motion is possible employing the empirical Waugh–Fedin relation $E_A$ (kJ mol$^{-1}$) = 0.156 $T_{\text{onset}}$ (K)$^{[61]}$. As the onset temperature, we identified the temperature at which the linewidth is given by ($\nu_{\text{rigid lattice}} - \nu_{\text{mot. narrowing}}$)/2. This leads to an approximate onset temperature of 160 K which translates to an activation energy of 25 kJ mol$^{-1}$.

**Conclusion**

Recently, we reported the synthesis and characterization of Li$_8$SiP$_4$, for which we had optimized the ionic conductivity ($\approx 1$ mS cm$^{-1}$) in lithium phosphidotetrelates by increasing the amount of lithium compared to Li$_7$SiP$_4$.$^{[49]}$ With Li$_7$AlP$_4$, we now show that these materials can be further optimized, namely by full aliovalent replacement of the tetrelate atom. Compared to the ionic conductivities in Li$_7$SiP$_4$ (4.5 x 10$^{-5}$ S cm$^{-1}$) and $\alpha$-Li$_6$GeP$_4$ (1.8 x 10$^{-5}$ S cm$^{-1}$), via aliovalent substitution by aluminum and the associated higher lithium content in the structure alongside with a change in the distribution of vacancies (Table 2), the conductivity in Li$_7$AlP$_4$ is strongly increased up to 3.0(2) mS cm$^{-1}$ at room temperature. Concomitantly, the activation energy determined by impedance measurements drops significantly from 42 ($\alpha$-Li$_6$GeP$_4$), 39 (Li$_7$SiP$_4$), and 38 kJ mol$^{-1}$ ($\beta$-Li$_6$GeP$_4$) to 29 kJ mol$^{-1}$ in Li$_7$AlP$_4$.

Li$_7$AlP$_4$ is easily accessible via ball-milling and crystallizes in the cubic space group $P43n$ (no. 218). First-principles computations suggest that Li$_7$AlP$_4$ is approximately 30 kJ mol$^{-1}$ more stable than the constituent binary phosphides. The structure of Li$_7$AlP$_4$ shows a close resemblance to the recently characterized lithium ion conductors Li$_7$SiP$_4$, $\alpha$-Li$_6$GeP$_4$, and $\beta$-Li$_6$GeP$_4$. However, in Li$_7$AlP$_4$, the highly negatively charged, isolated [AlP$_4]^-$ tetrahedra make it possible to accommodate a higher number of lithium ions per formula unit than in the phosphidotetrelates and therefore the new compound shows a much better Li ion conductivity. Whereas Li$_7$GeP$_4$ adopts both the $\alpha$ modification (space group $Pa\bar{3}$, no. 205) at lower temperature and the $\beta$ modification at higher temperatures (space group $P43n$, no. 218), Li$_7$AlP$_4$ crystallizes exclusively in analogy to the $\beta$ modification. These phosphidosilicides, -germanates, and -aluminates can be described as a close packing of P atoms with four octahedral and eight tetrahedral voids per formula unit. Consequently, Al, Si, and Ge atoms occupy 1/8 of the tetrahedral voids forming covalently connected Al–P, Si–P, and Ge–P bonds, respectively, and are located on fixed fully occupied positions in the structure. The series of compounds now give insight into the occupancy of the lithium atoms which varies according to Table 2. By comparing the lithium
content, tetrahedral voids are slightly less occupied, whereas in the octahedral voids more lithium is found in Li\textsubscript{9}AlP\textsubscript{4} compared to the situation in Li\textsubscript{8}GeP\textsubscript{4}. At a higher lithium content, the lithium ions are more evenly distributed over the tetrahedral and octahedral voids which might mainly result from a lower average electrostatic repulsion. The here observed decrease of lithium content in the tetrahedral and the increase of lithium content in the octahedral voids in the presence of more lithium is in accordance with the observation made by aliovalent substitution in garnets and was well investigated by Cussen.

Moreover, this increased population of octahedral voids contributes likely to the energy landscape flattening, as also seen in further electrolytes like in Li\textsubscript{10}GeP\textsubscript{2}S\textsubscript{12} and argyrodites. We found that the displacement of the Li\textsuperscript{+} position from the center of the octahedral voids increases with an increasing lithium content per formula unit. And, as also observed in garnets, this stronger displacement correlates with a higher ion mobility. In Li\textsubscript{9}AlP\textsubscript{4}, we found, for the first time in a phosphide-based material, a split position in the octahedral voids. Both positions are close to a triangular plane of the octahedra, supporting the hypothesis of lithium diffusion via face-sharing tetrahedra and octahedra. Lithium migration network analysis in phosphide-based materials like Li\textsubscript{8}GeP\textsubscript{4}, has already suggested that lithium diffusion is favored via face-sharing tetrahedra and octahedra. Interestingly, the split lithium positions in an octahedral environment, as observed here, has also been found in other fast ion conductors such as sulfide-based electrolytes and garnets: In Li\textsubscript{10}GeP\textsubscript{2}S\textsubscript{12} (LGPS), one Li atom (Wyckoff position 8g) exhibits a split position in a slightly distorted S\textsubscript{octahedron}, and in Li\textsubscript{10}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} (LLZO), one Li atom (Wyckoff position 96h) located in a strongly distorted O\textsubscript{octahedron} appears with a split position as well.

A change of the metal atom and a higher lithium concentration compared to the previously known compounds...
(Table 2) results in an extraordinarily high ionic conductivity of 3 mScm\(^{-1}\) at room temperature, a very low activation energy of 29 kJmol\(^{-1}\) (\(\approx 0.29\) eV), and a roughly 4 orders of magnitude lower electronic conductivity of 2.0 \(\times 10^{-7}\) Scm\(^{-1}\) at room temperature for the title compound. This high ionic conductivity is achieved by the accommodation of more lithium ions in the octahedral voids. One further benefit of Li\(_9\)AlP\(_4\) is its very low density of 1.7 gcm\(^{-3}\), which makes the compound very attractive for applications in all-solid-state batteries. Even though the Li content itself is not a decisive parameter for increasing the Li mobility, the possibility of aliovalent substitution of either Li\(_9\)\(\rightarrow\)Tr\(_1\)\(\rightarrow\)Tr\(_2\)P\(_4\) (Tr = triel element) allows for manifold optimization possibilities. Therefore, we will further investigate the tetrahedral and octahedral occupancy in solid solutions Li\(_9\)\(\rightarrow\)Tr\(_1\)\(\rightarrow\)Tr\(_2\)P\(_4\). Further studies will also focus on the thermal behavior and the electrochemical stability of this material. For Li\(_9\)AlP\(_4\), temperature-dependent powder neutron diffraction measurements in combination with MEM calculations are scheduled to localize the diffusion pathways.

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