Polyanionic Frameworks in the Lithium Phosphidogermanates Li$_2$GeP$_2$ and LiGe$_3$P$_3$ – Synthesis, Structure, and Lithium Ion Mobility

Henrik Eickhoff,[a] Christian Sedlmeier,[a] Wilhelm Klein,[a] Gabriele Raudaschl-Sieber,[a] Hubert A. Gasteiger,[a] and Thomas F. Fässler*[a]

Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of his 75th Birthday

Abstract. Recently fast lithium ion conductors were discovered in compounds containing tetrahedral SiP$_4^{8–}$ and GeP$_4^{8–}$ units. In the context of material development for all solid state batteries the ternary Li/Ge/P phase system has been further investigated and two new lithium phosphidogermanates were discovered on the lithium poor side of the ternary composition diagram. Li$_2$GeP$_2$ crystallizes in space group $I4_1/acd$ with unit cell parameters of $a = 12.3069(1)$ Å and $c = 19.0306(4)$ Å, consists of a framework of Ge$_4$P$_{10}$ supratetrahedra, and exhibits an ionic conductivity of $1.5(3) \times 10^{-7} \text{ S cm}^{-1}$ at $27 \text{ °C}$. LiGe$_3$P$_3$ crystallizes in $Pbam$ with $a = 9.8459(5)$ Å, $b = 15.7489(7)$ Å, and $c = 3.5995(2)$ Å. In LiGe$_3$P$_3$ Ge and P atoms form a two dimensional polyanion. The slabs consist of five- and six-membered heteroatomic rings comprising Ge$_2$P and Ge(P$_2$Ge)$_2$ tetrahedra including homoatomic Ge–Ge bonds. A semiconducting behavior with an electronic conductivity of $\sim 10^{-4} \text{ S cm}^{-1}$ and a remarkable stability vs. air and moisture is observed.

Introduction

The ongoing research on all solid state batteries as a next generation battery type is accompanied by the development of new materials. Especially, for the application as solid electrolytes a broad spectrum of compounds has been investigated.[1,2] Oxide based ion conductors are one of the largest groups and show generally good electrochemical compatibility with electrodes but relatively low ionic conductivities.[3,4] To overcome this drawback oxide was substituted with the larger and softer sulfide leading to an increased charge carrier concentration. The phosphide ion exhibits a higher charge compared to oxide and phosphides have been investigated. The phosphide oxide exhibits a higher charge compared to oxide and sulfide leading to an increased charge carrier concentration. These efforts resulted in the development of lithium phosphidosilicates – named for their structural similarity to oxidosilicates – Li$_8$SiP$_4$, Li$_3$SiP$_2$, Li$_4$Si$_2$P$_3$, and α- and β-Li$_3$GeP$_4$, which show conduction values of up to $0.1 \text{ mS cm}^{-1}$.[7–9]

Despite the alternating composition, lithium phosphidosilicates consist of tetrahedral building blocks also found in conventional fast ion conductors. Therefore, a close relationship to the above mentioned conventional solid electrolytes containing PS$_4^{3–}$ and GeS$_4^{4–}$ is present. Recently, even the relationship to Deiseroth’s lithium argyrodites was established. In argyrodites S$^2–$ ions appear beside the tetrahedral PS$_4^{3–}$ units and in accordance the reported Li$_{10}$Si$_2$P$_6$ contains two P$^{3–}$ anions per SiP$_4^{8–}$ tetrahedral unit.[10]

With respect to structure chemistry can the SiP$_4^{8–}$ units in ortho phosphidosilicates Li$_2$SiP$_4$ undergo – in analogy to ortho oxo-silicate – formally condensation reactions resulting in vertex- or edge-sharing tetrahedra. In consequence dimeric units are observed in Li$_{10}$Si$_2$P$_6$[11] polyanionic layers in Li$_3$Si$_3$P$_7$[11] and three dimensional networks in Li$_2$Si$_2$P$_4$[12] and LiSi$_3$P$_3$.[8]

For compounds containing heavy A and Pn elements a larger number of crystal structures containing also homoatomic tetrel-tetrel bonds and formally negatively charged tetrel atoms are reported such as K$_3$Sn$_3$As$_3$ and KSnAs$_3$[12] which are so far not reported for ternary Li/Si/P compounds. A further frequently occurring composition is AT$_3$P$_n$ (A = Li, Na, K, Rb; $Tt = Si$, Ge, Sn; $Pn = P$, As)[13–15] whose structures consist of $Tt$–Pn slabs, which are separated by A atoms. In the cross section the slabs appear as columns of pentagonal rings bridged with attached Pn atoms (Figure 1). The rings represent tubes built from 9 atom cages or, from a different point of view, corner sharing $TtPn_3$ tetrahedra connected via $Tt_2$ dumbbells. Various stacking orders of the slabs lead to diverse structure types. The structural flexibility of this system is also exhibited by K$_3$Si$_3$As$_3$[16] in which certain $Tt$ and Pn positions are swapped, leading to a different connectivity of the tubes, and by Li$_3$NaSi$_6$[17] in which the slabs are solely built from Si.
distorted tetrahedral voids. As a result, every Ge atom is covalently bound to four P atoms, one P1 (Wyckoff pos. 16d), one P2 (16e) and two P3 (32g), forming tetrahedral GeP4 units. Ge–P distances are in the range of 2.3147(5) to 2.3445(4) Å, and are slightly shorter than the Ge–P bonds in α- and β-Li2GeP4 [dl(Ge–P) of 2.369–2.405 Å].

Four tetrahedra are condensed via common corners and formupertetrahedra which are further connected via shared corners to a hierarchical variant of a diamond structure. In the crystal structure two interpenetrating networks are present (Figure 2).

Table 1. Refinement data of the single crystal diffraction data of Li2GeP2 and LiGe3P3 at 120 K.

|                   | Li2GeP2            | LiGe3P3           |
|-------------------|--------------------|-------------------|
| Molar mass/g·mol−1| 148.458            | 317.751           |
| Crystal system    | tetragonal         | orthorhombic      |
| Space group       | I4/1/acd (142)     | Pbam (55)         |
| Radiation λ/Å     | 0.71073 (Mo-Kα)    | 0.71073 (Mo-Kα)   |
| Crystal size/Å³   | 0.40 × 0.21 × 0.19 | 0.55 × 0.07 × 0.01 |
| Crystal color, shape | red, block        | black, bar        |
| Cell parameters   |                    |                   |
| a/Å               | 12.30697(14)       | 9.8459(5)         |
| b/Å               | 12.30697(14)       | 15.7489(7)        |
| c/Å               | 19.0307(4)         | 3.5995(2)         |
| Cell volume/Å³    | 2882.42(9)         | 558.15(5)         |
| Z                 | 32                 | 4                 |
| ρ (calcd.)/g·cm−3 | 2.736              | 3.780             |
| μ/mm−1            | 9.109              | 16.750            |
| F(000)            | 2176               | 576               |
| Temperature /K     | 120                | 120               |
| Reflections collected | 22367              | 6903              |
| Independent reflections | 1057              | 927               |
| Reflections with I > 2σ(I) | 967               | 733               |
| Measuring range   | 3.17 / 29.99       | 3.31 / 30.00      |
| Goodness-of-fit on Fσ2 | 1.115             | 0.986             |
| Rσ = 0.0326 / 0.0123 | 0.0524 / 0.0362   |                   |
| R indices [Fσ2 ≥ 2σ(Fσ2)] | R1 = 0.0120       | R1 = 0.0306       |
| wR2 = 0.0283      | wR2 = 0.0757       |                   |
| R indices (all data) | R1 = 0.0141       | R1 = 0.0409       |
| wR2 = 0.0287      | wR2 = 0.0775       |                   |
| Largest diff. peak/ hole (e·Å−3) | 0.37 / −0.35 | 1.44 / −1.09     |

Results and Discussion

Li2GeP2

Almost single phase microcrystalline material of Li2GeP2 is obtained by ball milling and subsequent annealing at 600 °C. Single crystals of Li2GeP2 for crystal structure analysis are obtained from a stoichiometric reaction of the elements in a Ta ampoule at 700 °C. In the product mixture Li2GeP2 was found beside Ge and LiGe3P3. The new compound crystallizes with space group I41/acd and unit cell parameters a = b = 12.30697(14) Å and c = 19.0307(4) Å (120 K) (Table 1). Li2GeP2 is isotypic to known Li2SiP2. The structure contains one crystallographic position for Ge and three independent positions for P and Li, respectively. All P atoms form a strongly distorted cubic closed packing with Li and Ge atoms in slightly

While all Ge atoms are coordinated by 4 P atoms, all P atoms bridge Ge atoms (Table 2). Two-fold connected P atoms result in a formal charge of −1 per P atom. The negative charge is balanced by Li atoms that occupy the pseudo tetrahedral voids of the ccp of P atoms between the frameworks. The resulting coordination sphere for all P atoms consists of four Li+ beside the two Ge atoms. Li–P distances in Li2GeP2 are in the range of 2.548(4)–2.738(1) Å and are thus significantly longer than in Li2SiP2 [dl(Li–P) = 2.444(2)–2.763(2) Å; Table 3].

To confirm the crystal structure and purity, 31P-MAS-NMR spectra were recorded. The number and intensity of the observed signals agrees well with the crystallographic data. Three signals with a chemical shift of δ = −59.9, −164.8, −178.4 ppm and a relative intensity of 1:1:2 are assigned to the P positions.
Table 2. Atom coordinates of Li$_2$GeP$_2$ at 120 K from single crystal diffraction data.

| Atom | Wyck. | x         | y         | z          | $U_{iso}$ |
|------|-------|-----------|-----------|------------|----------|
| Ge1  | 32g   | 0.38142(2) | 0.33808(2)| 0.05570(2) | 0.00636(5) |
| P1   | 16d   | 0.5000    | 0.2500   | -0.02212(3)| 0.00768(10) |
| P2   | 16e   | 0.2500    | 0.44300(4)| 0.0000    | 0.00714(9)  |
| P3   | 32g   | 0.28249(3) | 0.22328(3)| 0.12775(2) | 0.00793(7)  |
| Li1  | 16f   | 0.0946(2)  | 0.1554(2) | 0.1250    | 0.0148(7)  |
| Li2  | 16f   | 0.1563(2)  | 0.4063(2) | 0.1250    | 0.0186(8)  |
| Li3  | 32g   | 0.3746(2)  | 0.0991(2) | 0.03521(13)| 0.0156(5)  |

Figure 2. Structural features of Li$_2$GeP$_2$. (a) A covalently bound Ge$_4$P$_{10}$ supertetrahedron with bond lengths. A single GeP$_4$ tetrahedron is highlighted in light blue. (b) The unit cell with the two independent diamond like frameworks of supertetrahedra depicted in dark blue and green.

P2, P1 and P3, respectively (Figure 3). The strong downfield chemical shift of P2 is attributed to the more different chemical environment. This atom represents the shared corner of condensed supertetrahedra, while P1 and P3 are situated on the edges of the supertetrahedra, therefore exhibiting a very similar chemical environment. All P atoms are surrounded by two Ge atoms and four Li atoms. While the coordination sphere of Li atoms within Li$_2$GeP$_2$ and Li$_2$SiP$_2$ through Ti atoms is very similar, a stronger deviation of Ti–P–Ti bond angles from the ideal tetrahedral angle is observed in Li$_2$GeP$_2$. The deviation in Li$_2$GeP$_2$, with a Ge–P–Ge angle of 101.7° at P1 and 105.0° at P3 is much larger than in Li$_2$SiP$_2$ (103.0° and 105.1°), respectively.

Along the four equivalent [111] directions of the cubic crystal system the tetrahedra framework bears large three-dimensionally connected channels that are occupied by Li$^+$. In combination with only two signals found in $^6$Li MAS NMR ($\delta = 2.4$ ppm, 3.6 ppm) for three different crystallographic Li sites. For an estimation of the ion conduction potential of Li$_2$GeP$_2$ geometric parameters are compared with those from the silicon containing compound. As expected the shortest Li–Li distances within the channels increase slightly with substitution of Si by Ge from a range of 2.916(9)–3.229(9) Å to 2.940(5)–3.290(5) Å, respectively. In contrast to the increasing Li-Li distances and unit cell parameters the bottleneck size, indicated by shortest P–P distances within the channel, shrinks, due to a rotation and distortion of the supertetrahedra. As a consequence two different occurring P–P distances decrease from 3.954(2) Å and 4.0012(9) Å to 3.9161(8) Å and 3.978(5) Å. Both effects might be responsible for the lower ionic conduc-
Table 3. Selected distances and angles in Li₂GeP₂ at 120 K from single crystal diffraction data.

| Atom 1 | Atom 2 | \(d_{1-2}/\text{Å} \) | Atom 1 | Atom 2 | Atom 3 | Angle |
|--------|--------|-----------------|--------|--------|--------|--------|
| Ge1    | P3     | 2.3147(5)       | P3     | Ge1    | P2     | 104.07(1) |
| Ge1    | P2     | 2.3258(4)       | P3     | Ge1    | P1     | 101.86(2) |
| Ge1    | P3     | 2.3280(5)       | P2     | Ge1    | P1     | 110.54(1) |
| Ge1    | Li3    | 3.083(3)        | P3     | Ge1    | P1     | 114.79(1) |
| Ge1    | Li3    | 3.124(4)        | P2     | Ge1    | Li3    | 110.97(1) |
| Ge1    | Li3    | 3.179(2)        | P3     | Ge1    | Li2    | 112.51(3) |
| P1     | Li1    | 2.557(3)        | 2\(\times\) | P1     | Li3    | 101.66(2) |
| P1     | Li3    | 2.653(3)        | 2\(\times\) | P3     | Li2    | 104.99(2) |
| P2     | Li3    | 2.548(4)        | 2\(\times\) | P3     | Li3    | 2.969(3) |
| P2     | Li2    | 2.679(2)        | 2\(\times\) | P3     | Li2    | 3.045(4) |
| P3     | Li1    | 2.460(2)        | 2\(\times\) | P3     | Li3    | 2.590(3) |
| P3     | Li3    | 2.548(4)        | 2\(\times\) | P3     | Li2    | 2.679(2) |
| P3     | Li3    | 2.738(1)        | 2\(\times\) | P3     | Li1    | 3.29(1) |
| Li1    | Li2    | 3.184(5)        | 2\(\times\) | Li1    | Li3    | 2.941(4) |
| Li1    | Li3    | 3.155(4)        | 2\(\times\) | Li2    | Li1    | 3.599(5) |
| Li2    | Li3    | 3.29(1)         |          | Li3    | Li1    | 3.599(5) |
| Li2    | Li3    | 2.941(4)        | 2\(\times\) | Li3    | Li3    | 3.353(7) |

The second new compound, LiGe₃P₃, is prepared as almost single phase microcrystalline material via ball milling and subsequent annealing at 500 °C. Single crystals of LiGe₃P₃ are obtained through a stoichiometric reaction of the elements in a sealed Ta ampoule at 700 °C. The resulting product contained LiGe₃P₃, Ge, and Li₃P₇ as a result of the different chosen sample composition of Li₃Ge₃P₇ and the high melting point of Ge. LiGe₃P₃ crystallizes in the orthorhombic space group Pbam with the unit cell parameters of \(a = 9.8459(5)\) Å, \(b = 15.7489(7)\) Å, and \(c = 3.5995(2)\) Å (120 K) (Table 1). The second new compound, LiGe₃P₃ is isotypic to Li₀.₉Ge₂.₉As₃.₁[14] and comprises similar building blocks known from other compounds of the heavier homologues such as NaGe₃P₃.[13] Three crystallographic independent of each Ge and P atoms positions form a covalently connected two-dimensional polyanion that are separated in layers by Li (Table 4). As shown in Figure 4 Ge1 and all P sites form chains of corner-sharing Ge₄P₄ tetrahedra. These are a reoccurring structural motive in phosphidogermandates. The linear arrangement of Ge₄ tetrahedra along the \(c\) axis allows the formation of two six-membered rings between neighboring tetrahedra by the addition of two additional Ge atoms (Ge2 and Ge3) (\{P2–Ge1–P3–Ge2–P3’–Ge1’\} and \{P2–Ge1–P1–Ge3–P1’–Ge1’\}). The rings are further interconnected by a Ge2–Ge3 bond. As a consequence to further five-membered rings of the same atom sequence \{Ge1–P1–Ge3–Ge2–P3\} result. Additionally, this connectivity pattern leads to the formation of a second type of tetrahedra, Ge(P₃Ge), which is – due to the different atom types – strongly distorted. These tetrahedra are connected to Ge₄ tetrahedra by sharing a P vertex and forming oneexo-tetrahedral Ge2–P3 bond. This connectivity pattern leads to the formation of quasi pentagonal tubes parallel to the \(c\) axis. Further bonds between P2 atoms to Ge3 atoms of the neighboring tubes result in two dimensional sheets in the \(ac\) plane. Within these slabs, all P atoms are connected to three Ge atoms, leading to a formal charge of 0.

Table 4. Atom coordinates of LiGe₃P₃ at 120 K from single crystal diffraction data.

| Atom | Wyck. | x     | y     | z     | \(U_{iso}\) |
|------|-------|-------|-------|-------|------------|
| Ge1  | 4 \(g\) | 0.3836(2) | 0.1436(2) | 0.0000 | 0.0084(2) |
| Ge2  | 4 \(h\) | 0.05770(7) | 0.10283(4) | 0.5000 | 0.0121(2) |
| Ge3  | 4 \(h\) | 0.15069(7) | 0.25321(4) | 0.5000 | 0.0092(2) |
| P1   | 4 \(g\) | 0.3006(2) | 0.2878(10) | 0.0000 | 0.0093(3) |
| P2   | 4 \(h\) | 0.5277(2) | 0.11779(10) | 0.5000 | 0.0087(3) |
| P3   | 4 \(g\) | 0.1987(2) | 0.05294(10) | 0.0000 | 0.0100(3) |
| Li1  | 4 \(h\) | 0.7931(13) | 0.0699(9) | 0.5000 | 0.025(3) |
The atoms Ge1 and Ge3 form four covalent bonds to four P atoms or to three P atoms and one Ge atom, respectively. Since Ge2 is threefold connected to two P and one Ge atom a formal charge of −1 results. The negative charge of the polyanion is balanced by one Li ion per formula unit, thus LiGe3P3 is a charge balanced compound. Interestingly, LiGe3P3 is the first lithium phosphidotetrelate comprising formally charge neutral P atoms and a negatively charged Ge atom.

The Ge–P distances occurring in this compound of 2.314(2)–2.405(1) Å are in the range of typical Ge–P single bonds (Table 5). With a length of 2.5391(9) Å the Ge–Ge single bonds are longer than those in elemental Ge (2.450 Å)[19] and GeP (2.369, 2.393 Å)[20] but significantly shorter than in NaGe3P3 (2.627 Å).[13]

The Li atom is situated in a strongly distorted tetrahedral coordination of three P [d(Li–P) = 2.64(1)–2.94(1) Å] and one Ge [d(Li–Ge) = 2.66(1) Å]. In the second coordination sphere the distorted tetrahedron is supplemented by two P atoms and two Ge atoms to a two times capped, heavily distorted octahedron.

Impedance spectroscopy and polarization measurements hint for a dominant electronic conduction of approximately $10^{-4}$ S cm$^{-1}$ ($C = 0.40–0.49$ nF; $\omega_{\text{Apex}} = 160–300$ kHz; $a \geq 0.99$) and no ionic share could be detected. The value is the highest reported electronic conductivity of lithium phosphogermanates so far.

$^{31}$P MAS NMR spectra confirm the crystallographic results (Figure 5). Three signals occur within a small chemical shift range ($\delta = -59.5, -119.4, -126.3$ ppm) and an intensity ratio of 1:1:1. According to only one independent crystallographic site for Li, in the $^6$Li MAS NMR spectrum a single signal at $\delta = 2.4$ ppm is detected.

**Syntheses**

Almost single phase bulk material of Li$_2$GeP$_2$ and LiGe$_3$P$_3$ is prepared from a two-step synthesis route, including mechanochemical milling and subsequent annealing. The mechanical processing reduces grain sizes, improves the distribution of elements and, additionally, leads to the formation of precursor compounds in a reactive mixture. Temperatures of 600 °C and 500 °C, respectively, applied in the following annealing step are chosen based on DSC measurements. For Li$_2$GeP$_2$, an onset for melting and solidifying is observed between 684 °C and

---

**Table 5.** Selected distances and angles in LiGe$_3$P$_3$ at 120 K from single crystal diffraction data.

| Atom 1 | Atom 2 | $d_{1-2}$ /Å | Atom 1 | Atom 2 | Atom 3 | Angle |
|--------|--------|-------------|--------|--------|--------|-------|
| Ge1    | P3     | 2.314(2)    | P3     | –      | –      | 111.82(5) |
| Ge1    | P2     | 2.328(1)    | P2     | –      | –      | 101.29(7) |
| Ge1    | P1     | 2.339(2)    | P1     | –      | –      | 107.66(6) |
| Ge2    | P3     | 2.405(1)    | P2     | –      | –      | 112.13(5) |
| Ge2    | Ge3    | 2.539(1)    | P1     | –      | –      | 96.90(6) |
| Ge2    | Li1    | 2.66(1)     | P1     | –      | –      | 95.54(4) |
| Ge2    | Li2    | 3.09(1)     | P2     | –      | –      | 98.62(5) |
| Ge3    | P2     | 2.365(2)    | P2     | –      | –      | 98.62(5) |
| Ge3    | P1     | 2.374(1)    | P1     | –      | –      | 98.62(5) |
| Ge3    | Li1    | 3.12(1)     | P1     | –      | –      | 98.62(5) |
| P1     | Li1    | 2.94(1)     | P3     | –      | –      | 101.29(7) |
| P1     | Li2    | 2.72(1)     | Ge1    | –      | –      | 94.92(5) |
| P2     | Li1    | 2.64(1)     | Ge3    | –      | –      | 98.62(5) |
| P3     | Li1    | 2.64(1)     | Ge1    | –      | –      | 101.29(7) |
| P3     | P2     | 2.64(1)     | Ge1    | –      | –      | 94.92(5) |
| P3     | P3     | 2.64(1)     | Ge2    | –      | –      | 96.90(6) |

---

Figure 4. Structural features of LiGe$_3$P$_3$. (a) Detailed view of a Ge$_3$P$_3$ tube consisting of corner sharing GeP$_4$ tetrahedra (light blue) and GeP$_3$Ge tetrahedra (green). (b) Detailed view of a Ge$_3$P$_3$ tube without highlighted tetrahedra. (c) Expanded unit cell with slabs of Ge–P tubes. Tetrahedra are highlighted to emphasize the conductivity.
677 °C, respectively. In LiGe₃P₃ these thermal events are assigned to distinct peaks is observed with onsets of 701 °C and 647 °C. All samples were synthesized with an excess of 5–7% Li. Compared to stoichiometric mixtures this excess reduces the phase fraction of side phases, especially unreacted Ge, in the final product. Following that approach phase fractions can be determined via Rietveld refinement (Figure 6) to be 97% for LiGe₃P₃, containing 1% Ge and 2% Li₂GeP₂.

Figure 5. ³¹P MAS NMR spectrum of LiGe₃P₃ with inset for ⁶Li MAS NMR spectrum. Signals from side phase Li₂GeP₂ are indexed with grey colored chemical shifts and rotation side bands are marked with asterisks.

Since additional reflections occur in the diffraction pattern of Li₂GeP₂ which cannot be assigned to a known compound, an exact determination of the phase fractions is not possible. Comparison of the Li₂GeP₂ and Ge content leads to a ratio of 86:1. While Li₂GeP₂, similar to all other known lithium phosphidogermanates and lithium phosphidosilicates, shows vigorous reactions in contact with water, LiGe₃P₃ exhibits a remarkable stability. By deliberately exposing LiGe₃P₃ samples to air and water for 24 h each, followed by PXRD measurements, no change in crystallinity and ratio of LiGe₃P₃ and Ge is detected, while the Li₂GeP₂ side phase clearly degrades. This stability against moisture may be explained by structural features of LiGe₃P₃, as there are the low charge of the anionic partial structure together with a higher degree of condensation of GeP₄ units.

Conclusions

The new lithium phosphidogermanates Li₂GeP₂ and LiGe₃P₃ are the first compounds with large polyanions in the Li/Ge/P phase system and comprise three- and two-dimensional anionic substructure, respectively. The realized structure types are known for lighter and heavier homologues, respectively, and both contain GeP₄ units, which are a common building block for all lithium phosphidotetrelates. In Li₂GeP₂, which is isotypic to Li₂SiP₂, the tetrahedra form frameworks of GeP₄ₐ₈upertetrahedra and large channels for Li⁺. In contrast to the increasing unit cell parameters, compared to Li₂SiP₂, the channel size shrinks significantly due to rotation and warping of the supertetrahedra, leading to lower ionic conductivities of 1.5(3) x 10⁻⁷ S·cm⁻¹.

The compound LiGe₃P₃ is isotypic to Li₀.₆₇Ge₂.₉As₃.₁ and there consist identical polyanions as NaGe₃P₃. LiGe₃P₃ forms slabs of GeP₄ tetrahedra and Ge₂ dumbbells and is the first lithium phosphidotetrelate comprising formally negatively charged tetrel atoms. Although very similar polyanions are observed in various compounds they often realize different structure types. The cation size seems to have a particular effect on the structure type. The two Li containing compounds LiGe₃P₃ and Li₀.₆₇Ge₂.₉As₃.₁ crystallize in the same structure type containing two polyanionic slabs in the unit cell, but even by replacing Li with Na in NaGe₃P₃ a different structure type with only one slab within the unit cell is realized. The difference in the crystal structure of LiGe₃P₃ compared to the so far known lithium phosphidotetrelates is also indicated by an altering macroscopic behavior. While in LiGe₃P₃ the electric properties are dominated by electronic conduction, an unprecedented stability in contact with water is observed. The information about the broad set of properties found in the new phosphidogermanates can help designing new generations of ionic conductors.

Experimental Section

All syntheses were carried out in an argon atmosphere in Gloveboxes (MBraun, 200B) with moisture and oxygen level below 1 ppm or in containers, which were sealed under Ar atmosphere.
Bulk Synthesis via Ball Milling and Annealing: For both compounds the synthesis route includes two steps, using lithium (Rockwood Lithium, 99%), germanium (EVOCHEM GmbH, 99.99%) and red phosphorus (ChemPur, 99.99%). In the first step reactive mixtures (3 g) were prepared by mechanochemical milling using a Retsch PM100 planetary ball mill (350 rpm, 36 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 300 mg fractions of the reactive mixture were pressed to pellets, sealed in a carbon coated silica glass ampoules and were annealed. To reduce the amount of side phases such as Ge, a slight excess of Li was used for synthesis of both compounds.

Single crystals of Li$_2$GeP$_2$ and LiGe$_3$P$_3$ were obtained by a high temperature reaction of mixtures with the element ratios for Li, Ge and P of 2:1:2 and 3:3:7, respectively. The samples (300 mg) were heated in a tantalum ampoule to 700 °C for 24 h and slowly cooled to room temperature (rate: 1 K·min$^{-1}$). Li$_2$GeP$_2$ crystallizes as red transparent blocks and LiGe$_3$P$_3$ forms black bar-shaped crystals.

For Li$_2$GeP$_2$ 294.4 mg (42.4 mmol) Li, 1467.6 mg (20.2 mmol) Ge and 1251.6 mg (40.4 mmol) P were loaded into the ball mill and for the annealing process the sample was heated to 600 °C with a rate of 4 K·min$^{-1}$ and dwell for 24 h, afterwards slowly cooled for 24 h to 500 °C and finally cooled to room temperature with a rate of 1 K·min$^{-1}$.

Li$_2$GeP$_2$ was prepared from 70.0 mg (101 mmol) Li, 2057.2 mg (28.3 mmol) Ge and 877.3 mg (28.3 mmol) P. The fractions used for annealing were heated to 500 °C with a rate of 4 K·min$^{-1}$, dwell for 48 h and cooled to room temperature with a rate of 1 K·min$^{-1}$.

Powder X-ray Diffraction: Data were collected at room temperature on a STOE Stadi P diffractometer equipped with a Ge(111) monochromator, a Cu-K$_\alpha$ radiation source (λ = 1.54056 Å) and a Dectris MYTHEN 1 K detector in Debye–Scherrer setup. Samples were sealed in glass capillaries (Ø 0.3 mm) for measurement. The sample of Li$_2$GeP$_2$ was diluted with diamond powder to reduce X-ray absorption and all diffraction patterns were referenced against a Si standard. Raw data were processed with WinXPOW[21] software and Rietveld refinement were executed with FullProf.[22] During Rietveld refinement Li displacement parameters were kept constant and the reflections of added diamond powder were refined by profile fitting.

Single Crystal X-ray Data Collection: Single crystal of Li$_2$GeP$_2$ and LiGe$_3$P$_3$ were isolated and sealed in a glass capillary (0.3 mm). For diffraction data collection, the capillary was mounted on a Xcalibur3 (Oxford Diffraction, Mo-K$_\alpha$ radiation, λ = 0.71073) diffractometer equipped with a Sapphire 3 CCD detector and a nitrogen jet cooling system for measurements at 120 K. Structures were solved by Direct Methods (SHELXS-2014) and refined by full-matrix least-squares calculations against F$^2$ (SHELXL-2014).[23] Detailed information on the single crystal data collection and structural refinements are listed in Tables 1–5, further details are given in the Supporting Information.

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD-1953470 (Li$_2$GeP$_2$, 120 K), CSD-1953471 (Li$_2$GeP$_2$, 293 K), CSD-1953472 (LiGe$_3$P$_3$, 120 K), and CSD-1953473 (LiGe$_3$P$_3$, 293 K).

Differential Scanning Calorimetry (DSC): For investigation of the thermal behavior of the compounds a Netzsch DSC 404 Pegasus device was used. Niobium crucibles were filled with 50 mg to 100 mg sample and sealed by arc-welding. Empty sealed crucibles served as reference. Measurements were performed in an argon flow of 75 mL·min$^{-1}$ and a heating/cooling rate of 10 K·min$^{-1}$ up to a temperature of 750 °C. Data collection and handling was carried out with the Proteus Thermal Analysis program.[24]

Solid State MAS NMR Spectroscopy: Magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded with a Bruker Avance 300 operating at 7.04 T. Resonance frequencies of 44.2 and 121.5 MHz and pulse widths of 6 and 1.33 μs were applied for $^6$Li and $^{31}$P measurements, respectively. For both nuclei relaxation delays of 30 s were set. Samples were diluted with Nb$_2$O$_5$ in a 1:2 ratio, packed in 4 mm ZrO$_2$ MAS NMR probes and rotated with frequencies of 15 kHz during the measurements. The spectra were referenced to 1 mol·L$^{-1}$ LiCl aqueous solution, solid LiCl and (NH$_4$)$_2$HPO$_4$. 

Electric Conductivity Measurements: The ionic and electronic conductivities of Li$_2$GeP$_2$ and LiGe$_3$P$_3$ at room temperature were determined by electrochemical impedance spectroscopy (EIS) in a custom build cell. The setup consisted of two stainless-steel current collectors, a stainless-steel casing, a PEEK tube, hardened stainless-steel dies and pistons comprising a gasket for tightening the cell as well as six screws for fixing the cell. Between the two 8 mm dies powdered samples (100 mg) were loaded and the screws were fastened with a torque of 30 Nm, compressing the samples to at least 93% of the crystal density. For the determination of the compressed pellet thickness, distances between six holes in the current collectors were measured using a precision caliper. Impedance spectra were recorded on a Bio-Logic potentiostat (SP-200) in a frequency range from 3 MHz to 50 mHz at a potentiostatic excitation of ±50 mV. Data were processed using the software EC-Lab (V 11.26). The measurements were performed in an Ar-filled glove box at 298 K. The electronic conductivity was determined with the same setup using a potentiostatic polarization applying voltages of 50, 100 and 150 mV for 16 h each. All measurements were conducted in a tempered glove box at 27(1) °C. Total conductivities obtained from impedance measurements were corrected for the electronic contribution to obtain the ionic conductivity.

Supporting Information (see footnote on the first page of this article): Details of the single crystal structure determinations at 120K and 293K, of the Rietveld refinements, of the stability experiments, and of the conductivity and DSC measurements.

Acknowledgements

The work was carried out as part of the research project ASSB coordinated by ZAE Bayern. The project is funded by the Bavarian Ministry of Economic Affairs, Regional Development and Energy. The authors greatly acknowledge Tassilo Restle for DSC measurements, and Johannes Landesfeind and Tanja Zünd for the design of the conductivity measurement cell.

Keywords: Ball milling; Lithium phosphidogermanates; Solid-state structures; Conducting materials; Ion conductor

References

[1] J. Janek, W. G. Zeier, Nat. Energy 2016, 1, 1.
[2] B. V. Lutsch, J. Maier, J. Electroceram. 2017, 38, 128.
[3] Z. Zhang, Y. Shao, B. V. Lotsch, Y.-S. Hu, H. Li, J. Janek, L. F. Nazar, C.-W. Nan, J. Maier, M. Armand, L. Chen, *Energy Environ. Sci.* **2018**, *11*, 1945.

[4] Y. Zhu, X. He, Y. Mo, *ACS Appl. Mater. Interfaces* **2015**, *7*, 23685.

[5] Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, R. Kanno, *Nat. Energy* **2016**, *1*, 16030.

[6] H.-J. Deiseroth, S.-T. Kong, H. Eckert, J. Vannahme, C. Reiner, T. Zaiß, M. Schlosser, *Angew. Chem.* **2008**, *120*, 767; *Angew. Chem. Int. Ed.* **2008**, *47*, 755.

[7] L. Toffoletti, H. Kirchhain, J. Landesfeind, W. Klein, L. van Wüllen, H. A. Gasteiger, T. F. Fässler, *Chem. Eur. J.* **2016**, *22*, 17635.

[8] A. Haffner, A.-K. Hatz, I. Moudrakovski, B. V. Lotsch, D. Johrendt, *Angew. Chem.** 2018**, *130*, 6263; *Angew. Chem. Int. Ed.* **2018**, *57*, 6155.

[9] H. Eickhoff, S. Strangmüller, W. Klein, H. Kirchhain, C. Dietrich, W. G. Zeier, L. van Wüllen, T. F. Fässler, *Chem. Mater.* **2018**, *30*, 6440.

[10] S. Strangmüller, H. Eickhoff, D. Müller, W. Klein, G. Raudaschl-Sieber, H. Kirchhain, C. Sedlmeier, V. Baran, A. Senyschyn, V. L. Deringer, L. van Wüllen, H. A. Gasteiger, T. F. Fässler, *J. Am. Chem. Soc.* **2019**, *141*, 14200–14209.

[11] H. Eickhoff, L. Toffoletti, W. Klein, G. Raudaschl-Sieber, T. F. Fässler, *Inorg. Chem.* **2017**, *56*, 6688.

[12] J. Klein, B. Eisenmann, *Mater. Res. Bull.* **1988**, *23*, 587.

[13] K. Feng, W. Yin, R. He, Z. Lin, S. Jin, J. Yao, P. Fu, Y. Wu, *Dalton Trans.* **2012**, *41*, 484.

[14] J. Mark, M. P. Hanrahan, K. E. Woo, S. Lee, A. J. Rossini, K. Kovnir, *Chem. Eur. J.* **2019**, *25*, 6392.

[15] M. Khatun, S. S. Siyoko, A. Mar, *J. Solid State Chem.* **2016**, *238*, 229.

[16] W.-M. Hurng, J. D. Corbett, S.-L. Wang, R. A. Jacobson, *Inorg. Chem.* **1987**, *26*, 2392.

[17] H.-G. von Schnering, M. Schwarz, R. Nesper, *J. Less-Common Met.* **1988**, *137*, 297.

[18] R. Juza, W. Schulz, Z. Anorg. Allg. Chem. **1954**, *275*, 65.

[19] M. E. Straumanis, E. Z. Aka, *J. Appl. Phys.* **1952**, *23*, 330.

[20] T. Wadsten, *Acta Chem. Scand.* **1967**, *21*, 593.

[21] WinXPOW V3.0.2.1.; STOE & Cie GmbH: Darmstadt, Germany, 2011.

[22] J. Rodriguez-Carvajal, J. Gonzales-Platas, *FullProf Suite* 2.05, Institute Laue-Langevin Grenoble: France, 2011.

[23] G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3.

[24] Proteus Thermal Analysis V4.8.2, Netzsch-Gerätebau GmbH: Selb, 2006.

Received: September 13, 2019
Published Online: November 21, 2019