Solid-State Structures

Synthesis, Structure, Solid-State NMR Spectroscopy, and Electronic Structures of the Phosphidotrielates Li₃AlP₂ and Li₃GaP₂

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Introduction

Lithium ion solid electrolytes have been intensively studied for years due to the promising enhanced safety and electrochemical performances of all-solid-state-batteries.[1–3] Thus, many new materials with potentially high lithium ion conductivity have been discussed in the literature.[3,6–7] Recently, with Li₄SiP₄, Li₅SiP₄, and α/β-Li₄GeP₄, we introduced group 14 phosphido-based lithium ion conductors, which achieve ionic conductivities up to 1 mS cm⁻¹[8–10]. Their structures are built by group 14 phosphorus tetrahedra [TIP₄]³⁻ (T = Si, Ge). In the case of Li₄SiP₄ and α/β-Li₄GeP₄, isolated [TIP₄]³⁻ tetrahedra occur. At lower Li contents we found that the tetrahedra are connected in different ways and form dimers as in Li₄SiP₄ or two-dimensional slabs as in Li₅SiP₄, or three-dimensional networks as in Li₅SiP₄[8,11]. Interestingly, the phases Li₅SiP₄, Li₅SiP₃ (= Li₃SiP₃), Li₄SiP₄, and Li₃SiP₃ are connected by a formal reduction of the formula by units of Li₃P.[12] A lower Li₃P content leads to a higher connectivity of the tetrahedra.

Compared to the related sulfide-based lithium ion conductors,[3,6,7,12] the anionic substructure of phosphido-based conductors carry one additional charge (formal "P³⁻" versus a formal "S²⁻"), and thus the Li content that is required for charge balance is higher. Recently, we expanded this concept of highly charged tetrahedra to lithium phosphidoaluminates by replacing the central group 14 metal by aluminium.[13]

Li₃AlP₄ contains highly charged [TIP₄]³⁻ tetrahedra and reaches high ionic conductivities of ~3.0 mS cm⁻¹ at room temperature. Besides this first report of a structurally characterized lithium phosphidoaluminate, another compound of the composition Li₃AlP₄ was mentioned already in 1952 and described with an orthorhombic distorted CaF₂-type structure, in which the phosphorus atoms form a distorted cubic close packing, although without reliable crystallographic data.[14] Two years later, the corresponding gallium compound Li₃GaP₂ was also postulated.[15] Despite the poorly characterized structure model, quantum-chemical calculations of Li₃AlP₂ and Li₃GaP₂ were performed, anticipating the model of vertex-sharing Al₄P₄ tetrahedra.[16–18] As for lithium phosphidotetrelates, lithium phosphidoaluminates can also be connected on a line in a Gibbs composition triangle (Finetti diagram). Li₃AlP₂ is located on the line in the phase system Li-Al-P connecting Li₃P and AlP (Figure S7, Supporting Information) by reducing Li₃AlP₂ by two units of Li₃P (Li₃AlP₂ = Li₃AlP₄ − 2x Li₃P). Assuming a charge-balanced valence compound, the degree of connectivity of the Al₄P₄ tetrahedra in Li₃AlP₂ must be higher, and isolated tetrahedra as observed in Li₃AlP₄ cannot occur.

Here we report on the synthesis and structural characterization of Li₃AlP₂ and Li₃GaP₂ by a simple ball milling approach.

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Both compounds are characterized by Rietveld analysis and MAS-NMR spectroscopy. In addition, electronic band structure calculations are discussed.

**Experimental Section**

Syntheses and sample preparation and all sample manipulations were carried out inside an argon-filled glove box (MBraun, p(\text{H}_2\text{O}) < 0.1 ppm). Lithium (Li, rods, Rockwood Lithium, > 99.9%) was cleaned of oxide layers prior to use. Aluminium (Al, granules, ChemPur, 99.99%), gallium (Ga, pieces, ChemPur, 99.99%) and phosphorus (P, powder, Sigma-Aldrich, 97%) were used without any further purification.

**Synthesis of Li₃TrP₂ (Tr = Al, Ga):** Li₃TrP₂ was synthesized from the elements by ball milling and subsequent annealing. Li₃AlP₂: Lithium (388.0 mg, 55.3 mmol, 3 equiv), aluminium (498.1 mg, 18.5 mmol, 1 equiv) and phosphorus (1178.0 mg, 36.9 mmol, 2 equiv) were loaded in a WC milling set (50 mL jar, 3 balls with a diameter of 1.5 cm) and ball milled using a Retsch PM100 Planetary Ball Mill for 36 h at 350 rpm with resting periods (for 3 min every 10 min). For Li₃GaP₂: Lithium (350.8 mg, 50.0 mmol, 3 equiv), gallium (1163.0 mg, 16.7 mmol, 1 equiv) and phosphorus (1065.1 mg, 33.4 mmol, 2 equiv) were transferred to a WC milling set (45 mL jar, 7 balls with a diameter of 1.5 cm) and ball milled using a Fritsch Pulverisette 6 for 18 h at 350 rpm with resting periods (for 5 min every 10 min). For Li₃AlP₂, an ochre, and for Li₃GaP₂, a red powder is obtained. The powders were pressed into pellets with a diameter of 13 mm for 30 sec. at 5 kN using a hydraulic press (Specac Atlas 1ST). The fragmented pellets were filled into niobium ampoules (34 mm in diameter, 388.0 mg, 55.3 mmol, 3 equiv), aluminium (123.0 mg, 4.6 mmol, 1 equiv) and phosphorus (291.0 mg, 9.1 mmol, 2 equiv), and for Li₃GaP₂, lithium (34.5 mg, 4.9 mmol, 3 equiv), gallium (115.5 mg, 1.7 mmol, 1 equiv) and phosphorus (104.7 mg, 3.3 mmol, 2.0 equiv) were filled into a tantalum ampule. The ampules were sealed in an electric arc furnace (Edmund Bühlner MAM1), enclosed in a quartz reaction container under vacuum and subsequently heated at 5 K min⁻¹ up to 550 °C, dwelled for seven days, and then cooled at 0.075 K min⁻¹ to room temperature in a tube furnace (HTM Reetz Loba 1200-42-600-1-OW with a EURO- THERM S 14083 temperature controller), yielding Li₃AlP₂ (light ochre) and Li₃GaP₂ (red). In contrast to the ball mill synthesis, both products contain more impurities, with a few unknown reflections, accompanied by reflections of TaP (Li₃AlP₂) and GaP (Li₃GaP₂) (see Figure S4 and S5).

**Powder X-ray diffraction:** For powder X-ray diffraction (PXRD) measurements, the samples were grounded in an agate mortar and sealed inside 0.3 mm glass capillaries. PXRD measurements were performed at room temperature on a STOE Stadi P diffractometer equipped with a Ge(111) monochromator for CuKα radiation (λ = 1.54056 Å) and a Dectris MYTHEN DCS 1 K solid-state detector. The raw powder data were processed with the software package WinXPOW.[20]

**Structure determination and Rietveld refinement:** The structures of Li₃TrP₂ were determined by Rietveld refinements of the powder X-ray diffraction data using JANA2006.[20] The initial structure model was gained using the subprogram Superflip.[20] The space group Cmcn (no. 64) and the cell parameters were determined with the subprogram system evaluation of WinXPOW.[20] All cell parameters, all atom positions and the isotropic displacement parameters of Tr and P were refined freely. The isotropic displacement parameters of all Li atoms were refined coupled in Li₃AlP₂ and uncoupled in Li₃GaP₂.

CCDC 1979150 (Al) and 1979151 (Ga) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre through the CCDC/FIZ Karlsruhe deposition service.

**Energy-dispersive X-ray spectroscopy (EDX):** Pieces of Li₃TrP₂ were measured on a Hitachi TM-1000 Tabletop (15 kV) scanning electron microscope equipped with an energy dispersive X-ray an-
alyser (SWIFT-ED-TM). The samples were mounted onto an aluminium stub using graphite tape. To exclude aluminium impurities of the stub in the EDX spectra, measurements of the graphite tape on the aluminium stub without the samples were carried out, and no aluminium signal was registered. All samples were measured three times, and the values were averaged.

Differential scanning calorimetry (DSC). For thermal analysis samples of Li$_2$TrP$_2$, were sealed in niobium ampules and measured on a DSC instrument (Netzsch, DSC 404 Pegasus) under a constant gas flow of 75 mL min$^{-1}$. The samples were heated to 750 °C and then cooled to 150 °C twice at a rate of 10 °C min$^{-1}$. For the determination of the onset temperatures of the DSC signals, the PROTEUS Thermal Analysis software was used.[26]

Impedance spectroscopy: The electrochemical impedance spectroscopy for Li$_2$TrP$_2$ was performed in an in-house designed cell. The detailed setup and procedure are described in Restle et al.[11] Impedance spectra were recorded on a Bio-Logic potentiostat (SP-300) in a frequency range from 7 MHz to 50 mHz at a potentiostatic excitation of ±50 mV. Data were treated using the software EC-Lab (V 11.27). The measurements were performed in an Ar-filled glove box at 26 °C.

NMR spectroscopy: Magic-angle spinning (MAS) NMR spectra have been recorded on a Bruker Avance 300 NMR device operating at 7.04 T in a 4 mm ZrO$_2$ rotor. The resonance frequencies of the nuclei are 44.17, 78.21, 91.53, and 121.46 MHz for $^7$Li, $^{27}$Al, $^{11}$Ga, and $^{31}$P, respectively. The rotational frequency was set to 15 kHz for all nuclei. The MAS spectra have been obtained at room temperature with relaxation delays of 10 s ($^7$Li), 2 s ($^{27}$Al), 2 s ($^{11}$Ga), and 30 s ($^{31}$P), and 800 scans ($^7$Li), 280 scans ($^{27}$Al), 200 scans ($^{11}$Ga), and 720 scans ($^{31}$P). All $^7$Li spectra were referenced to LiCl (1 M,aq) and LiCl (s) with chemical shifts of 0.0 ppm and −1.15 ppm, respectively. The $^{27}$Al spectrum is referred to aluminium nitrate nonahydrate (s) with a chemical shift of −0.54 ppm with reference to Al(H$_2$O)$_6$ (s) in aqueous solution. The $^{27}$Ga spectrum is referred to gallium nitrate monohydrate (1 M,aq) with a chemical shift of 0 ppm. The $^{31}$P spectra were referred to ammonium dihydrogen phosphate (s) with a chemical shift of 1.11 ppm with reference to concentrated H$_3$PO$_4$. All spectra were recorded using single-pulse excitation.

Electronic structure calculations: The computational analysis for the structures Li$_2$AlP$_2$ and Li$_2$GaP$_2$ was performed using the Crystal17 program package and hybrid density functional methods.[23,24] A hybrid exchange correlation functional after Perdew, Burke and Ernzerhof (PBE0)[25,26] and triple-zeta valence + polarization level basis sets derived from the Karlsruhe basis sets for the elements Li, Al, Ga, and P were applied (further details are in the Supporting Information).[27–29] The starting geometry was taken from the experimental findings, and all structures were fully optimized within the constraints imposed by the space group symmetry. Band structures and density of states (DOS) were calculated for both structures. The nature of a stationary point on the potential energy surface was confirmed to be a minimum by a frequency calculation for each compound at Γ-point. No imaginary frequencies were observed. For data processing and visualization Jmol was used.[30]

Results and Discussion

Synthesis and characterization of Li$_2$TrP$_2$

Phase-pure Li$_2$AlP$_2$ and almost phase-pure Li$_2$GaP$_2$ were synthesized from the elements via a two steps procedure. Firstly, stoichiometric amounts of Li, Tr and P were ball milled resulting in reactive mixtures which showed the most intense reflections with large half width of the corresponding compound in the X-ray powder diffractionogram (see Figures S1 and S2 in Supporting Information). Subsequently, pellets of the reactive mixtures were annealed in niobium ampules at 700 °C for one day, yielding phase-pure Li$_2$AlP$_2$ and Li$_2$GaP$_2$, which contained small amounts of GaP as a side phase (see Figure 1). Powdered Li$_2$AlP$_2$ is yellow-ochre, powdered Li$_2$GaP$_2$ is brick-red (see Figure S3). Energy dispersive X-ray spectroscopy (EDX) investigations of the products show the absence of W and Nb and are in very good accordance with the Al/P and Ga/P ratios used in syntheses (see Table S1). Li$_2$AlP$_2$ and Li$_2$GaP$_2$ can also be synthesized by heating stoichiometric amounts of the respective elements at 550 °C for one week. However, an unknown phase accompanied by TaP remains as impurity in Li$_2$AlP$_2$, whereas the sample of Li$_2$GaP$_2$ contains GaP plus another unknown phase (see Figures S4 and S5). Due to the good quality of the powder diffractograms the structures of Li$_2$AlP$_2$ and Li$_2$GaP$_2$ could be solved and refined from the powder X-ray diffraction data. The results from the Rietveld refinement are shown in Figure 1, and parameters are listed in Table 1.

Li$_2$AlP$_2$ and Li$_2$GaP$_2$ crystallize in the orthorhombic space group Cmce (no. 64) with five independent crystallographic positions (P1, P2, Trl, L1, and L2) (Table S2). Compared to the earlier reported cell (a = 11.47, b = 11.61 and c = 11.73 Å), which corresponds to a 2×2×2 orthorhombic distorted supercell of the anti-CaF$_2$ structure type,[14] we observe a corresponding 2×1 orthorhombic supercell. A 3×1×1 unit cell of the orthorhombic crystal structure is displayed in Figure 2a. The crystal structure is built up by an orthorhombic distorted cubic close packing of P atoms. The Tr atoms occupy one quarter of the tetrahedral voids, forming AlP$_2$, tetrahedra. The occupation occurs in a fully ordered manner and is found only in every second layer. Within the layer the Tr atoms occupy 50% of the tetrahedral voids. Pairs of the resulting AlP$_2$, tetrahedra are connected by sharing edges through P1, and the resulting dimers share corners through P2, resulting in a two-dimensional

| Table 1. Crystallographic data of Li$_2$AlP$_2$ and Li$_2$GaP$_2$ obtained by Rietveld analysis of the powder diffraction data. |
|------------------|------------------|
| empirical formula | Li$_2$AlP$_2$     | Li$_2$GaP$_2$ |
| formula weight (g mol$^{-1}$) | 109.75          | 152.49       |
| T [K]             | 300              | 300          |
| radiation wavelength λ [Å] | 1.5406 Å      | 1.5406 Å    |
| Colour            | yellow ochre     | brick red    |
| crystal system    | orthorhombic     | orthorhombic |
| space group       | Cmce (no. 64)    | Cmce (no. 64) |
| unit cell dimension |                  |              |
| a [Å]             | 11.5138(2)       | 11.5839(2)  |
| b [Å]             | 11.7634(2)       | 11.7899(2)  |
| c [Å]             | 9.8302(1)        | 9.8129(2)   |
| V [Å$^3$]         | 798.292(2)       | 793.28(2)   |
| Z                 | 2                | 2            |
| p (calc.) [g cm$^{-3}$] | 1.8496         | 2.5336       |
| θ range [°]       | 5.062−110.002    | 5.029−109.999 |
| R$_p$             | 0.0287           | 0.0533       |
| R$_w$             | 0.0381           | 0.0710       |
| R$_{wp}$          | 0.0320           | 0.0364       |
| goodness-of-fit   | 1.19             | 1.95         |
| deposition no.    | 1979150          | 1979151      |
tetrahedra. However, in the tetrahedra of LiNaAlP2, range from 2.51(1) to 2.61(1) Å and from 2.50(1) to 2.65(1) Å in Li3GaP2. Overall, these distances are in good agreement compared to other binary or ternary phases containing Li and P.\(^{[8-11]}\) Considering three positively charged lithium atoms and the threefold negatively charged \(\text{AlP}_4\) layers, the first ternary alkali metal-based phosphido-gallate with trigonal planar GaP3 triangles are reported (Na3GaP3\(_4\), K3GaP3\(_4\), Rb3GaP3\(_4\), Cs3GaP3\(_4\)).\(^{[37-40]}\) and \(\text{Li3GaP2}\) represents the first ternary alkali metal-based phosphido-gallate with gallium in a tetrahedral coordination environment. Further, in quaternary mixed-alkali metal phosphido-gallate, such GaP3 tetrahedra already exist, for example, in K3NaGaP2 and Cs3NaGaP2.\(^{[41]}\) As observed for phosphidoaluminates derivatives with larger alkali metals like Na3AlP2, in K3NaGaP2 and Cs3NaGaP2, the GaP3 tetrahedra are arranged in edge-sharing 1D chains. Related alkaline earth metal phosphido-gallates contain the same polyanion \(\text{AlP}_4\).\(^{[3]}\) Formally three Li ions are replaced by one and a half alkaline earth metal, such as in Ca3AlP6, Ca3GaP6, Sr3GaP6, and Ba3AlP6.\(^{[34,42]}\) A structural change depending on the size of the alkaline earth metal atom can also be observed in these species. In the case of the smaller Ca and Sr atoms the structures contain distorted 2D layers of edge- and corner-sharing \(\text{TrP}_4\) tetrahedra. However, in Ba3AlP6, the larger Ba atoms lead to a segregation into twisted chains with only edge-sharing AlP4 tetrahedra.

The size of the alkali-metal atom has a strong impact on the connectivity of the AlP4 tetrahedra. In LiNaAlP2, the identical 2D \(\text{AlP}_4\) layers of AlP4 tetrahedra exist like in Li3AlP2, although with larger distances between the layers due to the larger Na ions that are located between the layers. The same applies to LiKAlP2. Interestingly, in Na3AlP2, a one-dimensional \(\text{AlP}_4\) chain with exclusively edge-sharing tetrahedra is observed. The reason might be that the large Na atoms do not allow a filling of the tetrahedra. More space is provided, when the Na atoms are located between the chains.\(^{[33]}\) In the case of Cs3AlP2, a different structure is adopted.\(^{[36]}\) The Al atoms are coordinated in a trigonal planar manner by phosphorus atoms, leading to dimers of edge-sharing triangles. In the case of related gallium compounds, only ternary alkali metal phosphido-gallates with trigonal planar GaP3 triangles are reported. As expected, the Al–P bonds are slightly shorter in the Ga–P P3 bond lengths are in the narrow range between 2.398(3) and 2.410(3) Å for the Al1–P1 and Al1–P2 distances, respectively, and between 2.404(2) and 2.419(2) Å for the Ga1–P1 and Ga1–P2 distances, respectively. As expected, the Al–P bonds are shorter than in the Al–P bonds. The Al–P bond lengths are very similar to those in \(\text{LiNaAlP2}\) (2.410(3)–2.426(3) Å) and are in the range of other known compounds with strong Al–P interactions like in \(\text{AlP2}\) (2.360 Å), \(\text{NaAlP2}\) (2.376(4) Å) or in \(\text{SrAlP4}\) (2.377(3)–2.417(2) Å) and weaker Al–P interactions like in \(\text{Li3AlP2}\) (2.423(2)–2.434(1) Å).\(^{[33-34]}\) In the case of \(\text{GaP2}\), the Ga–P bonds are longer than in \(\text{GaP2}\) (2.360(1) Å) and slightly shorter than in \(\text{Ba3GaP6}\) (2.43(1) Å), where \(\text{GaP2}\) dimers occur.\(^{[50]}\) Due to the edge- and corner-sharing situation of the \(\text{TrP}_4\) tetra-

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**Figure 2.** a) 3 x 1 x 1 Unit cell of the crystal structure of \(\text{Li}_{12}\text{TrP}_{26}\). b) 3 x 3 on top view of one layer in \(\text{Li}_{12}\text{TrP}_{26}\). c) \(\text{Li}, \text{Tr}\) and \(\text{P}\) are depicted in grey, orange and purple, respectively (displacement ellipsoids are set at 90% at room temperature).
Differential scanning calorimetry

DSC measurements of both compounds were performed (Figures S9 and S10) and show that Li₃AlP₂ is stable up to 750°C, whereas Li₃GaP₂ is stable only up to about 710°C. Above this temperature Li₃GaP₂ might melt or decompose into other unknown phases, as also supported by the PXRD data after the measurement (Figures S11 and S12).

Impedance spectroscopy

The Nyquist-plots for Li₃AlP₂ and Li₃GaP₂ are shown in Figure S17 and Figure S18. The Nyquist-plots display only the behaviour of a capacitor. Hence, no lithium diffusion was observed by electrochemical impedance spectroscopy.

MAS-NMR spectroscopy

For Li₃AlP₂ and Li₃GaP₂, ⁶Li, ⁷¹Ga, and ³¹P MAS-NMR measurements were performed (see Figure 3). In agreement with the crystallographic multiplicity, two independent ⁶Li signals occur in the expected ratio of 1:2 (4.00 and 2.96 ppm in Li₃AlP₂ and 4.14 and 3.39 ppm in Li₃GaP₂). The lithium atoms inside the ₂[TrP₃] layers are shifted more downfield than the others. In comparison to the signals of the aluminium phase, the resonances of both lithium signals in the gallium phase are shifted to lower fields. Hence, the layer itself and the more

Figure 3. ⁶Li (a, b), ⁷¹Ga (c), ³¹P (e, f) MAS-NMR spectra of Li₃AlP₂ (left) and Li₃GaP₂ (right). Spinning sidebands are marked with an asterisk.
electronegative metal gallium lead to a higher deshielding of the signals. For both compounds the chemical shift of the Li atoms are in the same range as those for related phosphidosilicates like Li₈SiP₄ and Li₃Si₃P₇.[8, 11] The ⁷¹Al, respectively ⁷¹Ga NMR spectra show only one signal in accordance with the crystal structure. The Al shift of 137 ppm utterly fits to the one of tetrahedral aluminium phosphines in solution and matches almost perfectly to the tetrahedrally coordinated Al in Al₃P (142 ppm).[44, 45] The chemical shift of 304 ppm of Ga also is in good agreement with the tetrahedral environment of Ga in Ga₃P (307 ppm).[46] The shape of the ⁷¹Ga signal is slightly asymmetric due to small GaP impurities at 307 ppm. Li₃AlP₂ shows two singlets in the ³¹P MAS-NMR spectrum. Both signals can be integrated with a value of one. Their chemical shifts are in the range of isolated P³⁻ in Li₃P and tetrahedrally coordinated P in Li₃SiP₄.[8, 46] For Li₃GaP₂ two main signals occur with almost the same integrated intensity. The ³¹P signals are shifted slightly more to lower fields than in Li₃AlP₂. The small signal at −143 ppm can be assigned to GaP.[47] Summing up, the NMR measurements are in very good agreement with the crystal structure evaluation on the basis of the Rietveld analyses.

**Electronic structures**

For Li₃AlP₂ and Li₃GaP₂ a computational analysis was carried out at a DFT-PBE0/TZVP level of theory. The optimized structure for Li₃AlP₂ and Li₃GaP₂ exhibit a maximum deviation of 1.95% for all parameters and average atomic distances, which reassures the experimental findings (Table 2). Band structure calculations show that both compounds are semiconductors with direct band gaps (Figure 4). Due to the usage of hybrid functional the calculated band gaps are typically in good agreement with the experiment. The calculated band gap of Li₃GaP₂ of 2.8 eV is significantly smaller than the one of Li₃AlP₂ (3.1 eV). This divergence is in accordance with the two different colours of the phases: Li₃AlP₂ with a larger band gap is of

![Figure 4. Density of states (DOS) (left) and Band structure (right) of a) Li₃AlP₂ exhibiting a direct band gap of 3.1 eV and b) Li₃GaP₂ exhibiting a direct band gap of 2.8 eV. The Fermi level is located at 0 eV. Blue points in the band structure diagram correspond to the top and bottom of the valence and conduction band, respectively.]
Table 2. Atomic distances (d) and cell parameters a, b and c for Li₄AlP₄ and Li₄GaP₄ as well as deviation (Δd) from experimental data in percentages.

|        | Li₄AlP₄ d [Å] | Li₄AlP₄ Δd [%] | Li₄GaP₄ d [Å] | Li₄GaP₄ Δd [%] |
|--------|--------------|----------------|--------------|----------------|
| a      | 11.5388      | 0.22           | 11.5910      | 0.02           |
| b      | 11.7560      | 0.06           | 11.7834      | 0.02           |
| c      | 5.8267       | 0.11           | 5.8289       | 0.24           |
| Av. Al/Ga-P | 2.41      | 0              | 2.43         | 0.62           |
| Al/Ga-Al/Ga | 3.05      | 0.66           | 3.10         | 0              |
| Li–Li  | 2.89         | 0.35           | 2.88         | 1.95           |
| Al/Ga–Li | 2.92      | 1.85           | 2.92         | 0              |

Conclusions

Li₄AlP₄ is a new representative of lithium phosphidoaluminates. It is the first lithium phosphidoaluminate with interconnected Al₄P₄ tetrahedra. In the orthorhombic distorted lattice, the Al₄P₄ tetrahedra are connected via edges and corners to give \( \text{[TrP}_2\text{]} \) 2D layers. The lithium atoms are located between and within these layers. Li₄GaP₄ represents the first lithium phosphogallinate. Both phases are easily accessible through ball milling of the elements and subsequent annealing and show thermal stability up to 700 °C. In the respective MAS-NMR spectra all different positions can be assigned individually. Though both compounds are poor ion conductors, band structure calculations reveal that Li₄AlP₄ and Li₄GaP₄ are direct band gap semiconductors with band gaps of 3.1 and 2.8 eV, respectively. These results demonstrate that lithium phosphidoaluminates can—depending on the content of Li₃P—also exhibit structures with connected TrP₄ tetrahedra.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aluminum · gallium · NMR spectroscopy · phosphorous · semiconductors

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