

Article

Sodium Filling in Superadamantoide $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ and the Mixed Valent Arsenidosilicate-Silicide $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$

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Abstract: $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ and $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ were synthesized by heating mixtures of the elements at 950 °C. The crystal structures were determined by single crystal X-ray diffraction ($\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$: $I4_1/a$, $Z = 100$, $a = 19.8772(4)$ Å, $c = 37.652(1)$ Å; $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$: $C2/c$, $Z = 8$, $a = 10.8838(6)$ Å, $b = 10.8821(6)$ Å, $c = 13.1591(7)$ Å). $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ crystallizes similar to NaSi_2P_3 with interpenetrating networks of vertex-sharing T4 and T5 supertetrahedra. Gallium substitution at the silicon sites increases the charge of the cluster network, which is compensated for by a 36% higher sodium content. Since in contrast to NaSi_2P_3 , all sodium sites are now fully occupied, there is no significant ion mobility, as indicated by ^{23}Na -NMR. Consequently, the total sodium-ion conductivity of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ amounts to only $1.6(1) \times 10^{-7} \text{ S cm}^{-1}$ and is therefore three orders of magnitude lower than in NaSi_2P_3 . $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ crystallizes in a new structure type with layers of edge-sharing $(\text{Si}_{1-x}\text{Ga}_x)\text{As}_4$ tetrahedra alternating with layers that contain infinite Si_n zigzag chains. Lithium ions reside in channels between the chains, and thus, the structure does not provide three dimensional pathways for ion conduction and the measured total Li-ion conductivity amounts to only $1.3(1) \times 10^{-7} \text{ S cm}^{-1}$.

Keywords: superadamantoid; ion conduction; arsenidosilicate; crystal structures



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1. Introduction

Ion-conducting solids will play a key role as solid electrolytes in future all-solid-state batteries (ASSB) and are therefore the subject of intensive research [1–6]. The movement of ions in solids is determined by numerous factors, but the product of mobility and concentration of the ions in question is particularly important. However, these quantities are not independent of each other and are therefore difficult to optimize. During recent years, a series of ion-conducting phosphidosilicates have been published [7–12]. Conductivities up to $10^{-3} \text{ S cm}^{-1}$ [8], the easy availability of the constituting elements, and a rich structural chemistry make phosphidosilicates particularly interesting. Among these, we have discovered the compounds Asi_2P_3 ($A = \text{Li, Na, K}$) with interpenetrating networks of supertetrahedra up to T5 [10–12]. Alkali metal ions are mobile in spaces between these large units where they experience a significantly lower effective charge than in common phosphidosilicates with highly charged SiP_4^{8-} tetrahedra. This is one reason why these compounds are often good ionic conductors ($\sigma > 10^{-4} \text{ S cm}^{-1}$); although, they contain considerably fewer cations per unit volume than ion conducting phosphidosilicates with isolated tetrahedra. Nevertheless, the conductivity may be improved by incorporating more alkali metal ions. For this purpose, the negative charge of the supertetrahedra must be slightly increased, which could be achieved by partial substitution of Si^{4+} by Al^{3+} or Ga^{3+} . Our initial attempts to synthesize $\text{Na}_{1+2x}(\text{Si}_{1-x}\text{Tr}_x)_2\text{P}_3$ ($\text{Tr} = \text{Al, Ga}$) were not yet successful. However, since supertetrahedral clusters likewise occur in the gallium arsenides

$M_{15}Ga_{22}As_{32}$ and $M_3Ga_6As_8$ ($M = Sr, Eu$) [13], and also related Si/Ga mixed variants $M_4Ga_5SiAs_9$ and $MgaSiAs_3$ ($M = Sr, Eu$) exist [14], it seemed promising to prepare the homologous arsenides $Na_{1+2x}(Si_{1-x}Ga_x)_2As_3$. Here, we report on the synthesis, crystal structure and conductivity measurements of $Na_{1.36}(Si_{0.86}Ga_{0.14})_2As_{2.98}$ as well as about the new compound $Li_{1.5}Ga_{0.9}Si_{3.1}As_4$ with a previously unknown structure type containing infinite Si_n zigzag-chains.

2. Results and Discussion

The crystal structures of $Na_{1.36}(Si_{0.86}Ga_{0.14})_2As_{2.98}$ and $Li_{1.5}Ga_{0.9}Si_{3.1}As_4$ were determined from X-ray single crystal data. Table 1 shows the final parameters of the refinements, while the fractional atomic positions, equivalent and anisotropic displacement factors are listed in Tables S1–S6 in the Supporting Information. Starting from these crystallographic data, Rietveld refinements of the powder X-ray diffraction data confirmed the crystal structures and purity of the samples (Figure 1). Energy-dispersive X-ray spectra confirm the chemical compositions (Tables S7 and S8).

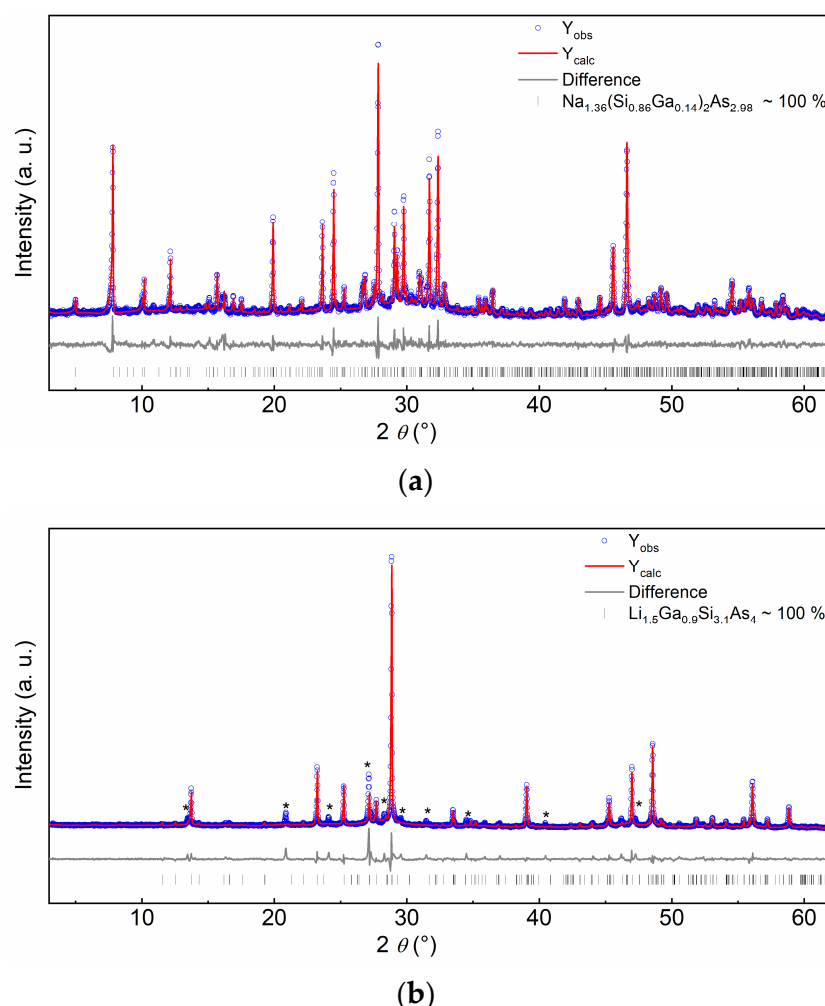
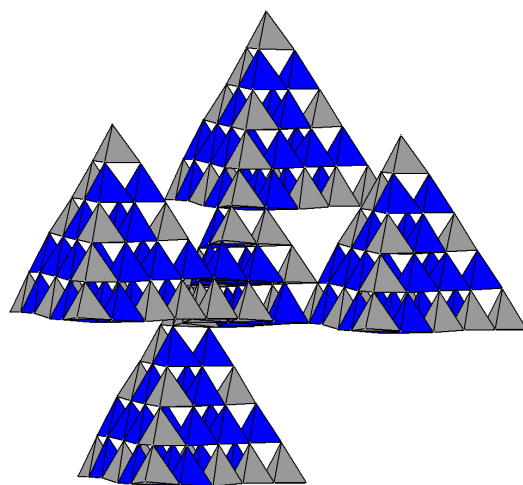


Figure 1. X-ray powder diffraction patterns (blue), refined profiles (red) and difference curves (grey) of $Na_{1.36}(Si_{0.86}Ga_{0.14})_2As_{2.98}$ (a) and $Li_{1.5}Ga_{0.9}Si_{3.1}As_4$ (b). Reflections who could not be assigned are marked with an asterisk.

$Na_{1.36}(Si_{0.86}Ga_{0.14})_2As_{2.98}$ crystallizes in the non-centrosymmetric tetragonal space group $I4_1/a$ (No. 88) and forms a diamond-analogue network of T4+T5 supertetrahedra. The structure is very similar to that of $NaSi_2P_3$ with each T4 cluster coordinated tetrahedrally by four T5 clusters and vice versa, via one common $SiAs_4$ tetrahedron (Figure 2).

Table 1. Crystallographic data of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ and $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$.

Formula	$\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$	$\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$
formula mass/g mol ^{−1}	322.59	460.00
space group	$I 4_1/a$ (No. 88)	$C2/c$ (No. 15)
$a/\text{\AA}$	19.8772(4)	10.8838(6)
$b/\text{\AA}$	a	10.8821(6)
$c/\text{\AA}$	37.652(1)	13.1591(7)
β/deg	90	101.904(3)
$V_{\text{cell}}/\text{\AA}^3$	14,876.3(7)	1525.0(1)
Z	100	8
$\rho_{\text{X-ray}}/\text{g cm}^{-3}$	3.601	4.007
μ/mm^{-1}	18.189	20.887
radiation	Mo-K α	Mo-K α
θ -range/ $^\circ$	2.35–30.50	5.36–29.39
reflections measured	157,235	13,182
independent reflections	11,375	13,182
refined parameters	373	98
R_σ	0.0498	
R_{int}	0.0235	0.0894
$R1$ ($F > 2\sigma(F)$ /all)	0.0243/0.0300	0.0530/0.0784
$wR2$ ($F^2 > 2\sigma(F^2)$ /all)	0.0543/0.0561	0.1597/0.1766
GooF	1.118	1.034
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}/\text{e \AA}^{-3}$	0.14/−0.99	2.63/−1.74
Twin volume fractions		0.499(7)/0.501(7)

**Figure 2.** Tetrahedral connectivity of a T4 with four T5 supertetrahedra in $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$. The T4/T5 units contain SiAs_4 (grey) and mixed occupied $(\text{Si}_{1-x}\text{Ga}_x)\text{As}_4$ (blue) tetrahedra.

Two symmetry-related diamond-like networks of clusters interpenetrate each other (Figure 3), as described for NaSi_2P_3 [11] and LiSi_2P_3 [10]. Likewise, the silicon atoms in the centers of the T5 units are missing. Such vacancies also occur in other supertetrahedral compounds like $[\text{In}_{34}\text{S}_{54}]^{6-}$ [15] and $\text{HP-B}_2\text{S}_3$ [16]. For NaSi_2P_3 , Haffner et al. explained the missing silicon atom with the necessity of charge neutrality inside the cluster [11]. In the present case, the arsenic atom at the center of the T4 clusters is only 60% occupied, which reduces the negative charge in the T4 cluster. The gallium atoms are not evenly distributed over the silicon sites within the clusters; instead, we find positions containing only silicon next to those with different fractions ranging from about 15% to 40% gallium (Figure 2). Without using charge constraints to the partial occupations, the composition is $\text{Na}_{1.360(1)}^+\text{Si}_{1.722(3)}^{4+}\text{Ga}_{0.278(3)}^{3+}\text{As}_{2.983(1)}^{3-}$, which deviates from charge neutrality by only 0.7% (0.13 electrons). Thus, we have increased the sodium content of NaSi_2P_3 by 36% while preserving the crystal structure. This shows that our concept of increasing the alkaline metal

concentration by increasing the cluster charge by doping the silicon sites with trivalent atoms works, in principle. The sodium atoms in $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ are located at the same positions as in NaSi_2P_3 except for one additional site with large displacements, which has to be described as split position with high uncertainty. Thus, the higher sodium content results from the complete occupation of the sodium positions in contrast to NaSi_2P_3 , in which all sodium sites are only partially occupied.

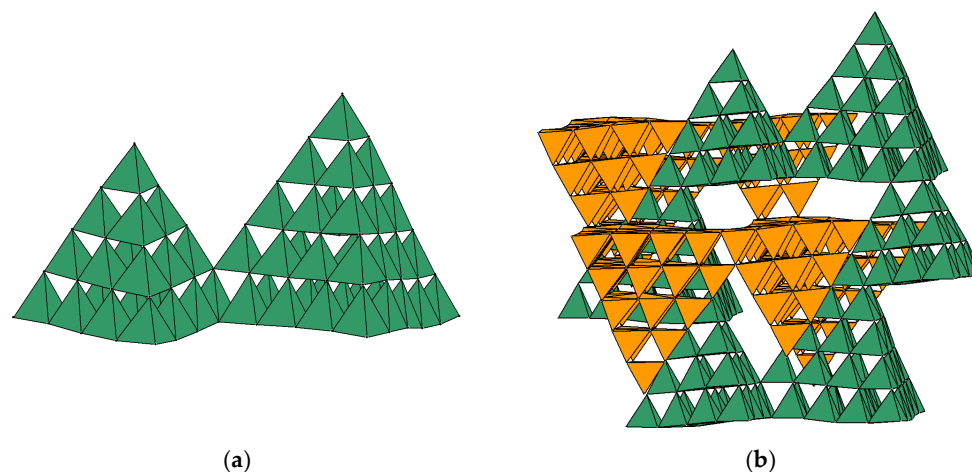


Figure 3. (a) The T4/T5 supertetrahedral units (green) consist of a T4 and T5 supertetrahedra, linked via a one common SiAs_4 tetrahedron. (b) Three of the T4/T5 units build a network of six-membered rings (green), which is interpenetrated by the second six-membered ring network (orange).

The sodium atoms between the clusters are coordinated in distorted NaAs_6 octahedral or trigonal prismatic polyhedra with Na-As distances from 2.93 to 3.64 Å. One sodium site shows significantly larger Na-As distances up to 4.2 Å without an apparent coordination polyhedron. It is located in the center of the gap between the networks which is not filled with sodium atoms in NaSi_2P_3 . Probably this position becomes populated after all other sodium sites are completely filled. We observe extremely elongated thermal displacement ellipsoids at this site (Figure 4) because of the substantial positional disorder. The ^{23}Na -MAS-NMR spectrum of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ shows one very broad signal with three maxima originating from several overlapping signals (Figure 5). Though we were not able to assign the signals to sodium sites, the fact that NMR distinguishes the sodium atoms at different sites suggests at best low or no mobility of the ions.

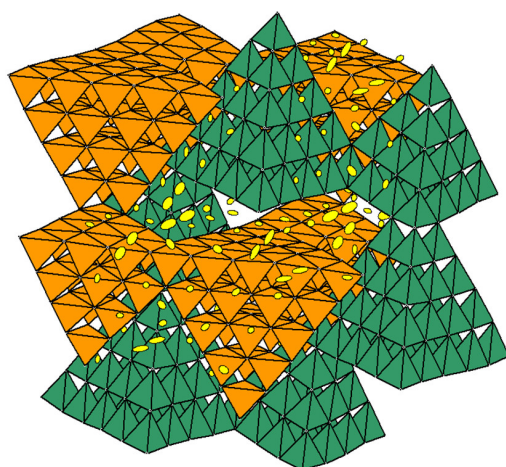


Figure 4. Interpenetrating networks (green and orange) of T4 and T5 clusters in $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$. The anisotropic thermal displacement ellipsoids of the sodium atoms in the gaps between the rings are visualized (yellow).

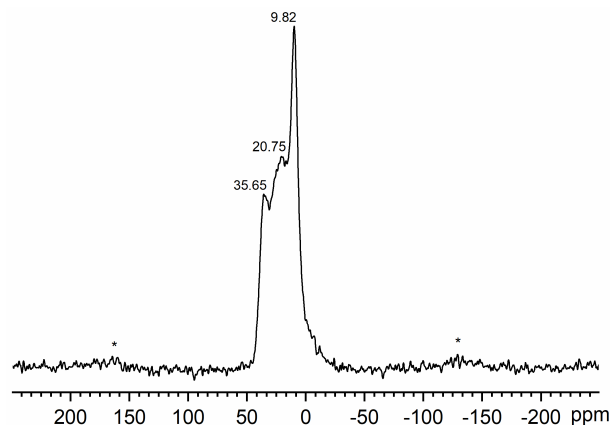


Figure 5. The ^{23}Na -MAS-NMR spectra ($\nu_{\text{rot}} = 10$ kHz) of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$. $(\nu - \nu_0)/\nu_0$ (^{23}Na) = 9.82, 20.75, 35.65 ppm, spinning side bands are denoted with asterisks.

$\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ crystallizes in a monoclinic space group ($C2/c$, no. 15). The structure contains two alternating layers along the c -axis (Figure 6).

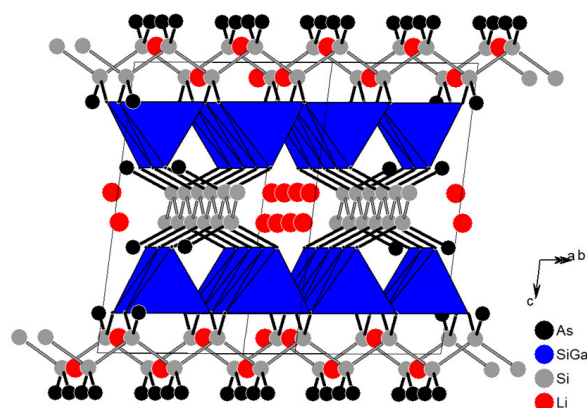


Figure 6. Crystal structure of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$. Besides the layers of $(\text{Si}_{1-x}\text{Ga}_x)\text{As}_4$ tetrahedra (blue), silicon forms zigzag-chains (grey). Lithium is located in channels between the zigzag-chains (red).

One layer is formed by corner-sharing $(\text{Si}_{1-x}\text{Ga}_x)\text{As}_4$ tetrahedra with the Si/Ga-As distances close to values in the literature [14]. The second layer contains Si-Si bonded zigzag-chains next to channels filled with lithium atoms. The channels run along $[1\ 1\ 0]$ and $[-1\ -1\ 0]$ directions. Silicon forms SiSi_2As_2 tetrahedra with Si-Si distances of 2.345–2.349 Å and an angle of 110.1° between three silicon atoms (Figure 7). Infinite zigzag-chains of silicon atoms are known from the Zintl-phase CaSi with the CrB-type structure and similar Si-Si distances (2.452 Å) [17]. Si_2 pairs occur more frequently, for example, in $\text{BaCuSi}_2\text{P}_3$ [18], $\text{Ca}_3\text{Si}_2\text{P}_4$, $\text{Ca}_3\text{Si}_8\text{P}_{14}$ [19], and $\text{Na}_{31}\text{Ba}_5\text{Si}_{52}\text{P}_{83}$ [20].

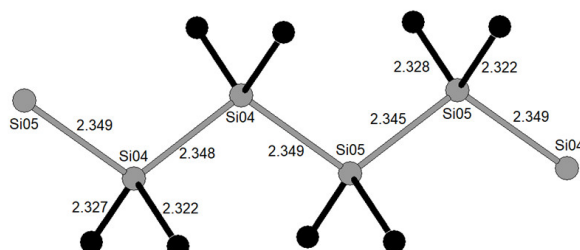


Figure 7. Silicon zigzag-chains with the bond lengths between the silicon (grey) and arsenide atoms (black).

Besides the layer-based structure, there are also T3 supertetrahedral clusters visible, forming an intertwining network with lithium between the clusters (Figure 8). The T3 supertetrahedral units are connected by corner-sharing SiSi_2As_2 tetrahedrons, resulting in an overlap of the clusters along the edges.

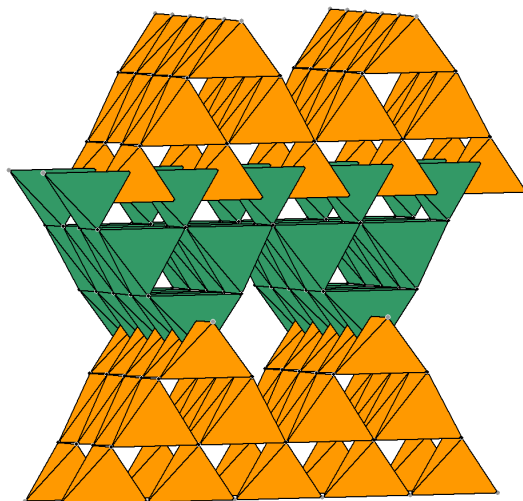


Figure 8. Illustration of the T3 cluster network in $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$. The T3 units are lined up in chains (green and orange) which form a network of inter-twining cluster-chains.

The lithium atoms are located in channels between the silicon chains and coordinated in a trigonal prismatic fashion with typical Li-As distances (2.10–2.11 Å). The ^7Li -MAS-NMR-measurement shows one slightly broadened signal (Figure 9). This signal is presumably a superposition of two signals with similar chemical shifts. The relatively broad signal suggests a weak ion mobility, significantly smaller than in LiSi_2P_3 [10] and more comparable to $\text{Ca}_2\text{Li}_4\text{SiP}_4$ [21].

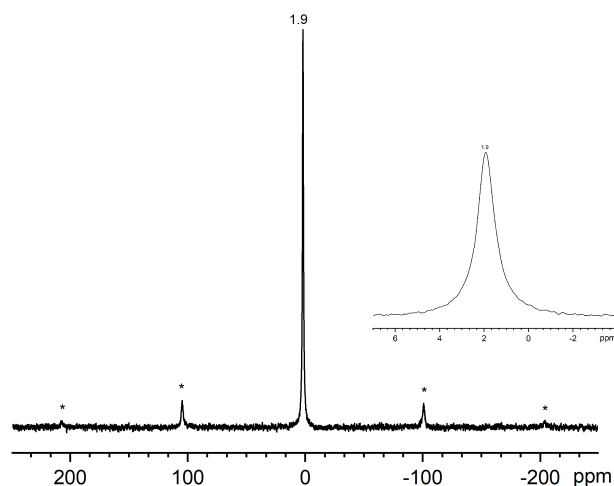


Figure 9. The ^7Li MAS NMR spectra ($\nu_{\text{rot}} = 20$ kHz) of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$. $(\nu - \nu_0)/\nu_0$ (^7Li) = 1.9 ppm, spinning side bands are denoted with asterisks.

Besides the main phase $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$, the Rietveld refinement (Figure 1) shows additional reflections, which could not be assigned. Table S4 lists the parameters of the Rietveld refinement. Scanning transmission electron microscopy (STEM) visualizes well the different layers in the structure of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ (Figure 10). The brighter spots can be assigned to the $(\text{Si}_{1-x}\text{Ga}_x)\text{As}_4$ tetrahedra. The Si-Si bonded zigzag-chains perpendicular to the viewing plane are recognizable as very weak spots. These spots alternate with dark sections, which stand for the channels filled with Li atoms. The weak spots of the silicon

atoms of the zigzag-chains parallel to the viewing plane are next to the corresponding slightly brighter spots of the arsenic atoms.

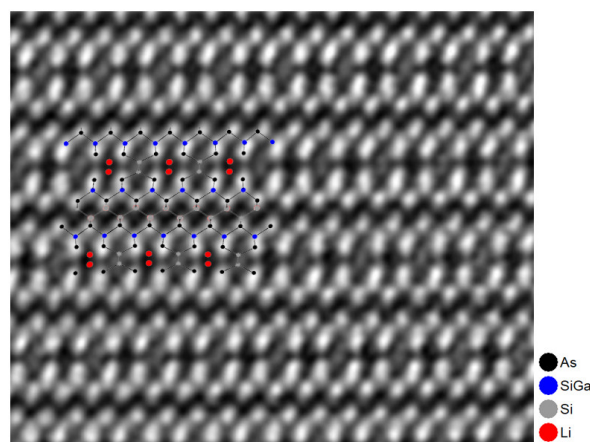


Figure 10. STEM measurement of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$. The arsenic and gallium atoms are visible as bright spots. In addition, the location of the silicon chains perpendicular to the viewing plane are recognizable.

Electrochemical impedance spectroscopy (EIS) was used to determine the ionic conductivity of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ and $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$. All EIS data were fitted using equivalent circuit models containing resistors (R), capacitors (C), and constant phase elements (CPE). Resistors and CPEs were used to model partial ionic and electronic conductivities, and polarization. CPEs were used to account for non-ideal sample behavior [22,23]. Capacitors were used to model stray capacities, which were determined at 25 °C and then kept constant for all other spectra [24]. Figure 11 shows impedance data for $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$.

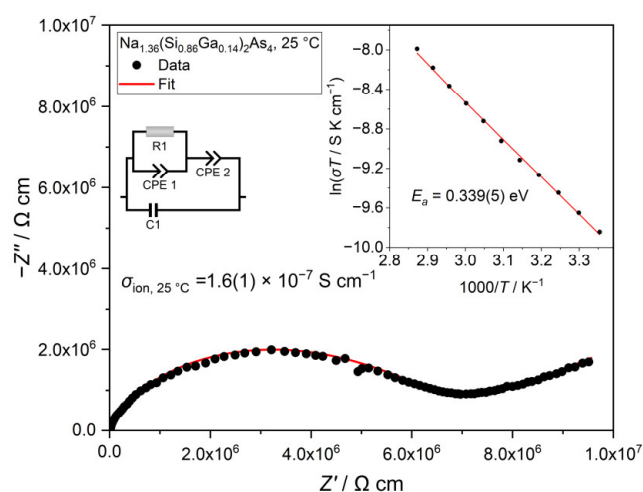


Figure 11. Impedance data of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$. Shown are the collected data points (black) and the corresponding equivalent circuit fit (red). The equivalent circuit used to fit the data is also shown. The inset shows an Arrhenius plot to determine the activation energy using temperature-dependent data, resulting in an activation energy of 0.339(5) eV.

The EIS data $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ show a depressed semicircle with a spike in the low frequency region. Hence, the data were fitted using an equivalent circuit with a resistor and a CPE in parallel (R1/CPE1) to model a single semicircle and a CPE in series (CPE2) to model polarization at the electrodes. In addition, a capacitor (C1) was used in series to the other circuit elements to account for stray capacity, which was fitted to 4×10^{-12} F. To calculate the capacity of CPE1 , the Brug formula was used [23,25]. The capacity of CPE1 at

25 °C is 1.42×10^{-11} F, which is of the order of magnitude for both bulk and grain boundary processes [26]. Since an unambiguous assignment is hence not possible, only total conductivities are reported. The total Na^+ ionic conductivity of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ at 25 °C is $1.6(1) \times 10^{-7} \text{ S cm}^{-1}$. The inset in Figure 11 shows an Arrhenius plot used for the determination of the activation energy E_a for the Na^+ transport, yielding 0.339(5) eV. To determine the partial electronic conductivity of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$, potentiostatic polarization measurements were carried out. The respective I/t and I/U curves are shown in Figures S1 and S2. Additional information on polarization measurements is also given in the Supporting Information. The partial electronic conductivity determined from polarization measurements of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ is $2.1(5) \times 10^{-8} \text{ S cm}^{-1}$. The reported partial electronic conductivity can be seen as a maximum, since the system might not have fully equilibrated after 6 h of polarization. To set the partial ionic σ_{ion} and electronic conductivities σ_{eon} in relation, the ionic transference number $\tau_{\text{ion}} = \sigma_{\text{ion}} / (\sigma_{\text{ion}} + \sigma_{\text{eon}})$ can be calculated [27]. For $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$, τ_{ion} is 0.88. For an ideal ion conductor, τ should be as close to unity as possible; hence, $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ can be classified as a mixed ionic–electronic conductor [27].

The EIS data of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ are shown in Figure 12. Again, a depressed semi-circle with a barely visible spike in the low frequency region is visible. In contrast to $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$, the low frequency spike is significantly flatter indicating a relatively large influence of a partial electronic conductivity. To model the EIS data of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$, the same equivalent circuit like for $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ was used, but in addition another resistor in parallel to the other circuit, element R2 was added in order to account for the apparent partial electronic conductivity [27]. The capacity of the capacitor C1 was again determined at 25 °C and fixed at 6×10^{-12} F for all fits. The Brug capacity of CPE1 is 3.54×10^{-11} F at 25 °C; hence again, an unambiguous assignment of the process is not possible [23,25,26]. Calculated solely from R1, the total Li^+ ion conductivity of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ at 25 °C is $1.3(1) \times 10^{-7} \text{ S cm}^{-1}$. The E_a for the Li^+ ion transport in $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ determined from an Arrhenius fit is 0.405(5) eV. The corresponding Arrhenius fit is shown in the inset of Figure 12. The partial electronic conductivity determined from EIS $\sigma_{\text{eon,EIS}}$ using R2 is $3.28(5) \times 10^{-8} \text{ S cm}^{-1}$ at 25 °C, which is in good agreement with the partial electronic conductivity determined from direct current polarization measurements $\sigma_{\text{eon,DC}}$, which is $1.7(1) \times 10^{-8} \text{ S cm}^{-1}$ at 25 °C. The respective I/t and I/U curves are shown in Figures S3 and S4. The respective ionic transference numbers τ_{ion} for $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ range from 0.88 to 0.80. Taking the partial equilibration of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ into account, $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ is showing a stronger influence of electronic leakage compared to $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$.

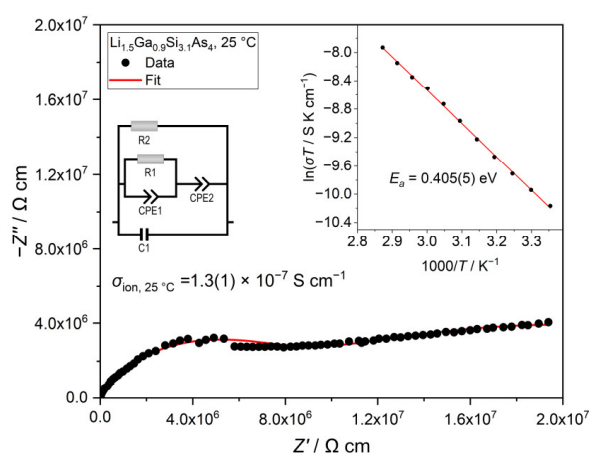


Figure 12. Impedance data of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$. Shown are the collected data points (black) and the corresponding equivalent circuit fit (red). The equivalent circuit used to fit the data is also shown. The inset shows an Arrhenius plot to determine the activation energy using temperature-dependent data, resulting in an activation energy of 0.405(5) eV.

3. Materials and Methods

3.1. Synthesis

The compounds were prepared using solid-state reactions. Samples were handled under inert conditions in an argon-filled glovebox with concentrations of O₂ and H₂O < 0.1 ppm. A stoichiometric ratio of metallic sodium (Alfa Aesar: Haverhill, MA, USA, 99.8%) or lithium (Sigma-Aldrich: Taufkirchen, Germany, 99.99%) were filled with metallic gallium (Alfa Aesar, 99.999%) in an alumina crucible. Silicon powder (Alfa Aesar, 99.999%) and arsenic powder (Alfa Aesar, 99.999%) were grounded and added to the crucible. The crucible was sealed in a silica ampoule and the ampoule was sealed in another silica ampoule. The reaction mixture was heated to 950 °C and temperature was maintained for 60 h. After cooling slowly to 750 °C, the furnace was shut off. The sample was grounded and reheated with the same procedure, yielding a dark grey, moisture-sensitive powder.

3.2. Single-Crystal X-ray Diffraction

Single crystals were selected from the polycrystalline sample in an argon-filled glovebox and sealed in glass capillaries (Hilgenberg GmbH, Marsfeld, Germany, 1.0 mm diameter). X-ray intensity data were obtained using a Bruker D8 Quest diffractometer (Bruker AXS Inc.: Madison, WI, USA, Mo-K α radiation, Göbel mirror optics, Photon-II CPAD detector). For intensity integration, data reduction and adsorption correction the software APEX3 v2016.5-0 ed [28] and SADABS v2012/1 [29] were used. Based on systematically absent reflections, the space group determination was carried out with XPREP v2008/2 [30]. The structure solution and refinement were carried out with OLEX2 v1.5 [31]. The final structure was visualized with the DIAMOND v3.2k software [32].

3.3. Powder X-ray Diffraction

The polycrystalline samples were grounded and filled in glass capillaries to avoid hydrolysis (Hilgenberg GmbH: Marsfeld, Germany, 0.3 mm diameter). The powder patterns were measured at an STOE Stadi-P diffractometer (STOE & Cie GmbH: Darmstadt, Germany, Cu-K α ₁ radiation, Ge(111)-monochromator, Mythen 1k detector (Dectris: Baden, Switzerland)) and the Rietveld refinements of the powder diffraction data were carried out using the single-crystal data as starting parameters using the TOPAS v4.1 software [33].

3.4. Solid-State MAS-NMR

The samples were filled into a commercial 2.5 mm zirconium rotor in an argon-filled glovebox. The ²³Na- and ⁷Li-NMR-spectra were measured on a Bruker Avance III 500 (Bruker AXS Inc.: Madison, WI, USA) with a field of 11.74 T under MAS conditions (ν_{rot} = 20 kHz) and Larmor frequencies of $\nu_0(^{23}\text{Na})$ = 132.33 Mhz and $\nu_0(^7\text{Li})$ = 194.42 MHz. The spectra were indirectly referenced to ¹H in 100% TMS at −0.124 ppm.

3.5. Energy-Dispersive X-ray Spectroscopy

Scanning electron microscopy was carried out with a Carl Zeiss EVO-MA 10 instrument with SE and BSE detector (Carl Zeiss: Oberkochen, Germany), controlled by the SmartSEM v5.07 Beta software [34]. The energy-dispersive X-ray spectroscopy (EDX) measurement was performed with a Bruker Nano EDX detector (Bruker AXS Inc.: Madison, WI, USA), X-Flash detector 410-M) using the QUANTAX 200 v1.9.4.3448 software package [35]. Samples were prepared on carbon pads, oxygen from partial hydrolysis was disregarded.

3.6. Scanning Transmission Electron Microscopy

In an argon-filled glovebox the polycrystalline sample were grounded, and the powder was placed on a copper grid covered with a carbon film (Plano GmbH: Wetzlar, Germany) and mounted on a single-tilt vacuum transfer holder. The sample was transferred to a FEI Titan Themis 300 (Thermo Fischer Scientific: Waltham, MA, USA) transmission electron microscope equipped with an X-FEG electron source, a Cs DCOR probe corrector, a US1000XP/FT camera system (Gatan: Unterschleissheim, Germany), and a windowless

4-quadrant Super-X energy dispersive X-ray spectroscopy detector. The measurements were performed at an acceleration voltage of 300 kV. For transmission electron microscopy (TEM) images, a $4k \times 4k$ FEI Ceta CMOS camera (Thermo Fischer Scientific: Waltheim, MA, USA) was utilized. Data processing and Fourier filtering were executed with JEMS v3.3.425 (SAED simulations) [36] and Velox v3.0 (STEM images, EDX maps) [37]. After test images and crystal X-ray diffraction scans were acquired, the sample was transferred to a double-tilt holder under air. After the sample was implemented in the transmission electron microscope, the measurement procedure was started.

3.7. Electrochemical Measurements

Electrochemical measurements were carried out under inert conditions in an argon-filled glovebox (O_2 and $H_2O < 0.1$ ppm). Before measurements, samples were ground in an agate mortar and compacted into pellets with a thickness of about 0.2–0.8 mm and a diameter of 3 mm using uniaxial cold-pressing with a pressure of ~ 0.75 t. The pellets had relative densities spanning from 74 to 91% for $Na_{1.36}(Si_{0.86}Ga_{0.14})_2As_{2.98}$ and 71–78% for $Li_{1.5}Ga_{0.9}Si_{3.1}As_4$. The pellets were measured in an RHD Instruments TSC SW closed measuring cell on an RHD Instruments Microcell HC cell stand using an Ivium compactstat.h (24 bit instrument) potentiostat. All measurements were carried out using stainless steel electrodes in a two-electrode, ion-blocking setup. The pressure in the measurement cell was about 700 kPa during measurements. The ionic conductivity σ was determined using EIS. Impedance was measured between 1 MHz and 1 Hz with an excitation voltage of 100 mV. The activation energy was determined from temperature-dependent EIS measurements between 25 and 75 °C in 5 °C steps and an equilibration time of 1 h. The activation energy E_a was extracted by fitting the temperature-dependent data to a linear, modified Arrhenius-type behavior using the equation $\sigma T = \sigma_0 e^{(-\frac{E_a}{k_B T})}$ with the temperature T , the pre-exponential factor σ_0 and the Boltzmann constant k_B [38]. Data processing and fitting procedures were carried out using the program RelaxIS 3 (RHD Instruments, Darmstadt Germany). The electronic conductivity was determined by potentiostatic polarization measurements. For potentiostatic measurements, voltages of either 0.10, 0.20, 0.30, 0.40 and 0.50 V ($Na_{1.36}(Si_{0.86}Ga_{0.14})_2As_{2.98}$) or 0.05, 0.10, 0.15, 0.20 and 0.25 V ($Li_{1.5}Ga_{0.9}Si_{3.1}As_4$) were applied for 6 h each with the ohmic drop of the resulting current measured. The resistance was calculated on the basis of Ohm's law using the current at equilibrium.

4. Conclusions

With $Na_{1.36}(Si_{0.86}Ga_{0.14})_2As_{2.98}$, we show that it is possible to increase the concentration of alkali metal ions in superadamantoid compounds with $NaSi_2P_3$ type structure. This is achieved when the charge of the supertetrahedra is increased by partial substitution of silicon by gallium. In $Na_{1.36}(Si_{0.86}Ga_{0.14})_2As_{2.98}$, the sodium concentration is increased by 36%, and all sites that are partially occupied in $NaSi_2P_3$ are now completely filled. This limits the mobility of the sodium ions, and therefore, we measure only low ionic conductivity. However, this approach can potentially lead to a higher ionic conductivity if it is possible to increase the concentration by only 5–10%, so that enough free sites remain for ionic movement. $Li_{1.5}Ga_{0.9}Si_{3.1}As_4$ is a mixed-valence arsenidosilicate-silicide which contains $(Si_{1-x}Ga_x)As_4$ tetrahedra with Si^{4+}/Ga^{3+} and Si_n zigzag-chains with divalent silicon. Lithium ions reside in channels, and 7Li -MAS-NMR indicates possible mobility; however, the channels do not provide three-dimensional migration pathways and the ion conduction is likewise low.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics12060166/s1>. Table S1. Crystallographic data for the Rietveld refinement of $Na_{1.36}(Si_{0.86}Ga_{0.14})_2As_{2.98}$. Table S2. Fractional atomic coordinates and equivalent displacement parameters of $Na_{1.36}(Si_{0.86}Ga_{0.14})_2As_{2.98}$. Table S3. Anisotropic displacement parameters of $Na_{1.36}(Si_{0.86}Ga_{0.14})_2As_{2.98}$. Table S4. Crystallographic data for the Rietveld refinement of $Li_{1.5}Ga_{0.9}Si_{3.1}As_4$. Table S5. Fractional atomic coordinates and equivalent displacement parameters

of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$. Table S6. Anisotropic displacement parameters of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$. Table S7. Elemental analysis of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ by EDX; signals of oxygen were not taken into account. Table S8. Elemental analysis of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ by EDX; signals of oxygen were not taken into account. Figure S1. I/t curve for the determination of the electronic conductivity of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$. Voltages of 0.1, 0.2, 0.3, 0.4, and 0.5 V were applied for 6 h each, with the current being recorded. Figure S2. I/U curve for the determination of the electronic conductivity of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$. The current was taken from potentiostatic polarization measurements after equilibrium. The resistance was calculated using Ohm's law, leading to a partial electronic conductivity of $2.1(5) \times 10^{-8} \text{ S cm}^{-1}$. Figure S3. I/t curve for the determination of the electronic conductivity of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$. Voltages of 0.05, 0.10, 0.15, 0.20, and 0.25 V were applied for 6 h each, with the current being recorded. Figure S4. I/U curve for the determination of the electronic conductivity of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$. The current was taken from potentiostatic polarization measurements after equilibrium. The resistance was calculated using Ohm's law, leading to a partial electronic conductivity of $1.7(1) \times 10^{-8} \text{ S cm}^{-1}$.

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Data Availability Statement: The supplementary crystallographic data are available under the deposition numbers CSD-2354473 ($\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$) and CSD-2354474 ($\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$) and can be accessed free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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References

1. Wang, L.; Li, J.; Lu, G.; Li, W.; Tao, Q.; Shi, C.; Jin, H.; Chen, G.; Wang, S. Fundamentals of electrolytes for solid-state batteries: Challenges and perspectives. *Front. Mater.* **2020**, *7*, 111. [[CrossRef](#)]
2. Sun, Y.-K. Promising all-solid-state batteries for future electric vehicles. *ACS Energy Lett.* **2020**, *5*, 3221–3223. [[CrossRef](#)]
3. Gao, Z.; Sun, H.; Fu, L.; Ye, F.; Zhang, Y.; Luo, W.; Huang, Y. Promises, challenges, and recent progress of inorganic solid-state electrolytes for all-solid-state lithium batteries. *Adv. Mater.* **2018**, *30*, e1705702. [[CrossRef](#)] [[PubMed](#)]
4. Lim, H.-D.; Park, J.-H.; Shin, H.-J.; Jeong, J.; Kim, J.T.; Nam, K.-W.; Jung, H.-G.; Chung, K.Y. A review of challenges and issues concerning interfaces for all-solid-state batteries. *Energy Storage Mater.* **2020**, *25*, 224–250. [[CrossRef](#)]
5. Zaman, W.; Hatzell, K.B. Processing and manufacturing of next generation lithium-based all solid-state batteries. *Curr. Opin. Solid State Mater. Sci.* **2022**, *26*, 101003. [[CrossRef](#)]
6. Banerjee, A.; Wang, X.; Fang, C.; Wu, E.A.; Meng, Y.S. Interfaces and interphases in all-solid-state batteries with inorganic solid electrolytes. *Chem. Rev.* **2020**, *120*, 6878–6933. [[CrossRef](#)]
7. Toffoletti, L.; Kirchhain, H.; Landesfeind, J.; Klein, W.; van Wullen, L.; Gasteiger, H.A.; Fassler, T.F. Lithium ion mobility in lithium phosphidosilicates: Crystal structure, ^7Li , ^{29}Si , and ^{31}P mas nmr spectroscopy, and impedance spectroscopy of Li_8SiP_4 and Li_2SiP_2 . *Chemistry* **2016**, *22*, 17635–17645. [[CrossRef](#)] [[PubMed](#)]
8. Strangmüller, S.; Eickhoff, H.; Müller, D.; Klein, W.; Raudaschl-Sieber, G.; Kirchhain, H.; Sedlmeier, C.; Baran, V.; Senyshyn, A.; Deringer, V.L.; et al. Fast ionic conductivity in the most lithium-rich phosphidosilicate $\text{Li}_{14}\text{SiP}_6$. *J. Am. Chem. Soc.* **2019**, *141*, 14200–14209. [[CrossRef](#)] [[PubMed](#)]
9. Eickhoff, H.; Strangmüller, S.; Klein, W.; Kirchhain, H.; Dietrich, C.; Zeier, W.G.; van Wullen, L.; Fässler, T.F. Lithium phosphidogermanates α - and β - Li_8GeP_4 —A novel compound class with mixed Li^+ ionic and electronic conductivity. *Chem. Mater.* **2018**, *30*, 6440–6448. [[CrossRef](#)]
10. Haffner, A.; Brauniger, T.; Johrendt, D. Supertetrahedral Networks and Lithium-Ion Mobility in Li_2SiP_2 and LiSi_2P_3 . *Angew. Chem. Int. Ed. Engl.* **2016**, *55*, 13585–13588. [[CrossRef](#)]

11. Haffner, A.; Hatz, A.K.; Moudrakovski, I.; Lotsch, B.V.; Johrendt, D. Fast sodium-ion conductivity in supertetrahedral phosphidosilicates. *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 6155–6160. [\[CrossRef\]](#)
12. Haffner, A.; Hatz, A.K.; Zeman, O.E.O.; Hoch, C.; Lotsch, B.V.; Johrendt, D. Polymorphism and fast potassium-ion conduction in the T5 supertetrahedral phosphidosilicate KSi_2P_3 . *Angew. Chem. Int. Ed. Engl.* **2021**, *60*, 13641–13646. [\[CrossRef\]](#)
13. Weippert, V.; Haffner, A.; Stamatopoulos, A.; Johrendt, D. Supertetrahedral layers based on GaAs or InAs. *J. Am. Chem. Soc.* **2019**, *141*, 11245–11252. [\[CrossRef\]](#)
14. Weippert, V.; Haffner, A.; Johrendt, D. New layered supertetrahedral compounds T2-MSiAs₂, T3-MGaSiAs₃ and polytypic T4-M₄Ga₅SiAs₉ (M = Sr, Eu). *Z. Naturforschung B* **2020**, *75*, 983–989. [\[CrossRef\]](#)
15. Wang, C.; Bu, X.; Zheng, N.; Feng, P. Nanocluster with one missing core atom: A three-dimensional hybrid superlattice built from dual-sized supertetrahedral clusters. *J. Am. Chem. Soc.* **2002**, *124*, 10268–10269. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Sasaki, T.; Takizawa, H.; Uheda, K.; Yamashita, T.; Endo, T. High-pressure synthesis and crystal structure of B_2S_3 . *J. Solid State Chem.* **2002**, *166*, 164–170. [\[CrossRef\]](#)
17. Perrier, C.; Kreisel, J.; Vincent, H.; Chaix-Pluchery, O.; Madar, R. Synthesis, crystal structure, physical properties and Raman spectroscopy of transition metal phospho-silicides MSixPy (M = Fe, Co, Ru, Rh, Pd, Os, Ir, Pt). *J. Alloys Compd.* **1997**, *262–263*, 71–77. [\[CrossRef\]](#)
18. Yox, P.; Lee, S.J.; Wang, L.L.; Jing, D.; Kovnir, K. Crystal structure and properties of layered pnictides $\text{BaCuSi}_2\text{Pn}_3$ (Pn = P, As). *Inorg. Chem.* **2021**, *60*, 5627–5634. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Zhang, X.; Yu, T.; Li, C.; Wang, S.; Tao, X. Synthesis and crystal structures of the calcium silicon phosphides $\text{Ca}_2\text{Si}_2\text{P}_4$, $\text{Ca}_3\text{Si}_8\text{P}_{14}$ and $\text{Ca}_3\text{Si}_2\text{P}_4$. *Z. Für Anorg. Und Allg. Chem.* **2015**, *641*, 1545–1549. [\[CrossRef\]](#)
20. Haffner, A.; Zeman, O.E.O.; Brauniger, T.; Johrendt, D. Supertetrahedral anions in the phosphidosilicates $\text{Na}_{1.25}\text{Ba}_{0.875}\text{Si}_3\text{P}_5$ and $\text{Na}_{31}\text{Ba}_5\text{Si}_{52}\text{P}_{83}$. *Dalton Trans.* **2021**, *50*, 9123–9128. [\[CrossRef\]](#)
21. Weidemann, M.L.; Calaminus, R.; Menzel, N.; Johrendt, D. The phosphidosilicates $\text{AE}_2\text{Li}_4\text{SiP}_4$ (AE = Ca, Sr, Eu) $\text{Ba}_4\text{Li}_{16}\text{Si}_3\text{P}_{12}$. *Chemistry* **2024**, *30*, e202303696. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Macdonald, J.R.; Johnson, W.B. *Impedance Spectroscopy: Theory, Experiment, Applications*, 2nd ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2005.
23. Lasia, A. The origin of the constant phase element. *J. Phys. Chem. Lett.* **2022**, *13*, 580–589. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Kuhn, A.; Gerbig, O.; Zhu, C.; Falkenberg, F.; Maier, J.; Lotsch, B.V. A new ultrafast superionic Li-conductor: Ion dynamics in $\text{Li}_{11}\text{Si}_2\text{PS}_{12}$ and comparison with other tetragonal LGPS-type electrolytes. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14669–14674. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Brug, G.J.; van den Eeden, A.L.G.; Sluyters-Rehbach, M.; Sluyters, J.H. The analysis of electrode impedances complicated by the presence of a constant phase element. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *176*, 275–295. [\[CrossRef\]](#)
26. Irvine, J.T.S.; Sinclair, D.C.; West, A.R. Electroceramics: Characterization by impedance spectroscopy. *Adv. Mater.* **1990**, *2*, 132–138. [\[CrossRef\]](#)
27. Huggins, R.A. Simple method to determine electronic and ionic components of the conductivity in mixed conductors a review. *Ionics* **2002**, *8*, 300–313. [\[CrossRef\]](#)
28. *APEX III*, v2016.5-0 ed.; Bruker AXS Inc.: Madison, WI, USA, 2016.
29. *SADABS*, Version 2012/1; Bruker AXS Inc.: Madison, WI, USA, 2001.
30. *XPRep—Reciprocal Space Exploration*, Version 2008/2; Bruker AXS Inc.: Madison, WI, USA, 2008.
31. Dolomanov, O.; Bourhis, L.; Gildea, R.; Howard, J.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341. [\[CrossRef\]](#)
32. Brandenburg, K. *Diamond*, Version 3.2k; Crystal Impact: Bonn, Germany, 2014.
33. Coelho, A. *TOPAS-Academic*, Version 4.1; Coelho Software: Brisbane, Australia, 2007.
34. *SmartSEM*, Version 5.07; Beta; Carl Zeiss Microscopy Ltd.: Cambridge, UK, 2014.
35. *QUANTAX 200*, Version 1.9.4.3448; Bruker Nano GmbH: Berlin, Germany, 2013.
36. *JEMs*, Version 3.3.425; JEOL: Freising, Germany, 2008.
37. *Velox*, Version 3.0.0.815; ThermoFischer Scientific: Waltham, MA, USA, 2021.
38. Nuernberg, R.B. Numerical comparison of usual Arrhenius-type equations for modeling ionic transport in solids. *Ionics* **2019**, *26*, 2405–2412. [\[CrossRef\]](#)

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