

Alkali Metals Extraction Reactions with the Silicides Li₁₅Si₄ and Li₃NaSi₆: Amorphous Si *versus allo*-Si

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Supporting Information



ABSTRACT: The silicides $Li_{15}Si_4$ and Li_3NaSi_6 were subjected to chemical extraction of the alkali metal component by liquid ammonia and ethanol, respectively, which after washing yielded black powders of amorphous silicon. The investigated reactions are interesting with respect to both the formation of novel Si modifications and the delithiation process in Si anode materials. The products termed *a*-Si (from $Li_{15}Si_4$) and *a-allo*-Si (from Li_3NaSi_6) were characterized by a combination of methodologies (X-ray diffraction, transmission electron microscopy, differential thermal analysis, Raman, atomic absorption, and energydispersive X-ray spectroscopy) which revealed (i) a porous microstructure for *a*-Si built from spherically shaped particles with sizes around 10 nm, (ii) partial surface oxidation of both materials and (iii) the presence of nanocrystalline Si in both materials. The result of the protic oxidation of Li_3NaSi_6 is at variance with earlier findings reporting the formation of a crystalline bulk allotrope of silicon (*allo*-Si) from the topotactic combination of silicon layers present as polyanions in Li_3NaSi_6 . Additionally, quantum chemical calculations show that silicon layers in Li_3NaSi_6 cannot combine to energetically favorable allotropic forms of Si. This is different from Li_7Ge_{12} , where polyanionic germanium layers topotactically convert to the germanium allotrope *m-allo*-Ge upon oxidation.

1. INTRODUCTION

The search for new forms of semiconducting silicon and germanium attracts increasing attention because novel or superior electronic transport and optical properties—being real or envisioned—will allow improving performance and scalability of devices based on established semiconductor technologies.^{1,2} Desired new crystalline forms range from nanomaterials (particles, wires, tubes),¹ nano- and mesostructures (e.g., nano- and mesoporous germanium)^{3–7} to new allotropes.^{8–13} Amorphous forms, which are widely used in thin film transistors and photovoltaic applications, are being tailored by impurity doping or by compositing with nanocrystalline particles.^{14,15}

Nanosilicon is also in the midpoint of the search for electrochemically active anode materials since silicon possesses

a ~10 times higher capacity in Li ion batteries when compared to commercially used graphite.^{16–18} Generally, Li₁₅Si₄ and amorphous Si phases are discussed during charging and discharging processes. Although there are numerous reports on the electrochemical lithiation of Si to form amorphous or crystalline Li–Si alloys and delithiation to form amorphous Si, a chemical delithiation of presynthesized Li₁₅Si₄ has not been reported.^{19–22}

In general, Zintl phases comprising alkali or alkaline earth metals and silicon or germanium represent versatile precursors toward new forms of silicon and germanium. Metal extraction

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from solid Zintl phases or the oxidation of Zintl anions in solution are established routes. Examples include the crystalline clathrate-II allotrope of silicon from simple thermal decomposition of NaSi into Na_xSi₁₃₆ and subsequent Na extraction with I₂,²³ the crystalline germanium clathrate from the oxidation of Ge₉^{4–} Zintl ions in ionic liquids,²⁴ and the isolation of silicon sheets with a two-dimensional graphitic structure by the redox assisted exfoliation of CaSi₂.^{25–27} Metal extraction allows also for bulk amorphous and nanocrystalline samples. This was shown by McMillan et al.²⁸ and Wang et al.,¹⁴ respectively, by applying a solid state metathesis (SSM) reaction between NaSi or NaGe and NH₄X (X = Cl, Br), where NaX is subsequently removed by washing with alcohol or water. NaSi may also be directly oxidized by alcohols to yield nanosized amorphous Si.²⁹

Zintl phases with layered polyanions are especially interesting for obtaining new allotropes because of their potential for topotactic reactions. Ideally, metal extraction will lead to a kinetically favored (low barrier) oxidative coupling of twodimensional polyanions, retaining (or only slightly rearranging) their topology. Deintercalation reactions with Li₇Ge₁₂ and Li₃NaSi₆, whose layered structures are shown in Figure 1, were



Figure 1. Zintl phases $\rm Li_7Ge_{12}$ and $\rm Li_3NaSi_6$ containing polyanionic layers (a) $^2_{\infty}[Ge_{12}]^{7-}$ and (b) $^2_{\infty}[Si_6]^{4-}$ (black) being separated by Li (red) and Na (yellow) atoms.

already performed in the 1980s and yielded new allotropic forms of Ge and Si, named *allo*-Ge and *allo*-Si, respectively.^{8–11} However, the structures of these *allo* forms eluded conclusive characterization. Only recently, a bulk synthesis strategy for microcrystalline *allo*-Ge (*m-allo*-Ge) was established and the structure of *allo*-Ge could be determined by a combination of experimental and quantum chemical methodologies.^{13,30} Indeed, the five-ring topology of the initial ${}^{2}_{\infty}$ [Ge₁₂]^{7–} layers is strictly retained in *m-allo*-Ge. From *m-allo*-Ge, another allotrope of Ge–hexagonal 4*H*-Ge–can be obtained which is exclusively built from six-rings.^{9,12} Subsequently, the thermochemistry and optical properties of these Ge allotropes were investigated in detail.³¹ The situation for *allo*-Si remains unclear. In 2002, Conesa suggested structure models for *allo*-Si based on the ${}^{2}_{\infty}$ [Si₆]^{4–} layers in Li₃NaSi₆,³² however, experimental validation is still missing.

Here, we describe metal extractions with Li_3NaSi_6 and $Li_{15}Si_4$. The former were aimed at renewed efforts into the synthesis and structural characterization of *allo-Si*, the latter to emulate by chemical means the delithiation process occurring electrochemically in silicon based lithium batteries (cycling Si against Li) where amorphous and crystalline $Li_{15}Si_4$ correspond to the fully lithiated (discharged) state.^{19,20} We solve the quarter-century old puzzle of *allo-Si* and show that *allo-Si* is not accessible from Li_3NaSi_6 . Instead, products essentially correspond to amorphous Si. Amorphous Si is also the product of

the chemical delithiation of $Li_{15}Si_{4}$. However, there are subtle differences between both materials, which are introduced by the simultaneous formation of nanocrystalline Si.

2. EXPERIMENTAL SECTION

Solid-State Synthesis. Starting materials were lithium rods (99%, Rockwood-Lithium), sodium rods (99%, Chempur) and silicon powder (99.999%, Sigma-Aldrich). All steps of solid state synthesis and preparation of air- and moisture-sensitive samples were carried out in a glovebox (MBraun, Ar-atmosphere, H₂O and O₂ levels <0.1 ppm). Metal ampules (tantalum and niobium) for solid state synthesis were thoroughly cleaned, heated to 1000 °C under dynamic vacuum ($p < 1 \times 10^{-3}$ mbar) for at least 2 h and transferred to the glovebox. An all-glass Schlenk line supplied with Ar, which is dried over P₂O₅, molecular sieve and heated titanium sponge (T = 750 °C), was used for baking out ampules, encapsulating ampules in silica tubes, handling air- and moisture-sensitive materials, and reactions in inert atmosphere.

 $Li_{15}Si_4$. Bulk samples of $Li_{15}Si_4$ were synthesized according to ref 33 by mechanical ball-milling of stoichiometric mixtures of elemental Li and Si in a RETSCH PM 100 planetary ball mill. The procedure yields large quantities (up to several grams) of X-ray pure $Li_{15}Si_4$.

Li₃NaSi₆. Li₃NaSi₆ was typically synthesized according to

 $Li_{12}Si_7 + 4NaSi + 13 \alpha - Si \rightarrow 4Li_3NaSi_6$

Stoichiometric mixtures of reactants with a total mass of 0.5 g were homogenized in an agate mortar, pressed to a pellet and sealed in a metal ampule which was then encapsulated in a silica jacket under vacuum. Ampules were heated in a muffle furnace to 550 °C at a rate of 5 K min⁻¹ and annealed for 24 h. After slow cooling at 0.075 K min⁻¹ the samples were recovered inside the glovebox. The procedure yields X-ray pure samples of Li3NaSi6 (see Figure S1a in the Supporting Information). Li₃NaSi₆ may also be obtained from annealing ball-milled mixtures of $Li_{15}Si_4$, Na, and α -Si (RETSCH PM 100 planetary ball mill, duration: 70 min, 250 rpm, 10 min interval, 5 min break, direction reversal, ball charge 3, ball size 15 mm diameter) with molar ratios 1:5:26 at 600 °C (total mass, 2.0 g; heating rate, 4 K min⁻¹; dwell time, 7 days; cooling rate, 0.075 K min⁻¹ to room temperature) or from annealing ball-milled stoichiometric mixtures of the elements at 550 °C (total mass, 0.5–3.0 g; heating rate, 1-2 K min⁻¹; dwell time, 5-7 days; cooling rate, 0.1 K min⁻¹ to room temperature). These samples always contained small amounts of impurities (Li₁₂Si₇ and/or α -Si, cf. Figure S1b in the Supporting Information). It was later recognized that when using Nb ampules, Li₃NaSi₆ samples also contained small amounts of NbSi₂ although this impurity could not be detected in powder X-ray diffraction patterns.

 $Li_{12}Si_7$ and NaSi. The binary precursors for Li_3NaSi_6 were synthesized from stoichiometric mixtures of the elements with a total mass of 2.0 g each. The reactions were carried out in tantalum ampules which were encapsulated in silica jackets under vacuum. Sample annealing was done in a muffle furnace. For $Li_{12}Si_7$, the temperature was raised to 750 °C at 5 K min⁻¹, followed by 1 h dwelling, cooling to 400 °C at a rate of 0.5 K min⁻¹, dwelling for 6 h and subsequent quenching. For NaSi, the temperature was raised stepwise to 600 °C: 5 K min⁻¹ to 500 °C, 1 h dwelling, 5 K min⁻¹ to 600 °C. After a dwell time of 30 h a cooling rate of 5 K min⁻¹ was applied. Samples were recovered inside the glovebox.

Extraction Reactions. One half gram of $\text{Li}_{15}\text{Si}_4$ was loaded into a custom-built extractor for liquid ammonia (Westfalen AG; dried over sodium). The apparatus, shown in Figure 2, is connected to a high-vacuum glass line that is supplied with purified argon (see above). The extraction process (taking place at -78 °C by using an isopropanol dry ice bath) was stopped after the color of the liquid ammonia solution had turned from deep to light blue after approximately 40 extraction cycles. After evaporating ammonia from the extractor, the solid black product consisting of amorphous silicon and LiNH₂ was recovered in the glovebox. To remove LiNH₂, 157 mg of the mixture were filled into a Schlenk flask. The powder was suspended in 20 mL of dry toluene (dried over Na). Subsequently, 50 mL of ethanol (dried over



Figure 2. (a) Custom-built apparatus for extracting Li from $Li_{15}Si_4$ with liquid NH_3 . $Li_{15}Si_4$ powder is loaded onto the frit inside the glovebox. When NH_3 is condensed onto $Li_{15}Si_4$ (sample space is cooled, -78 °C), a deep blue color is observed. (b) By closing valve 1, the extract is transported into the cooled reservoir. (c) By opening valve 1, and cooling the sample space, NH_3 can be recondensed onto the solid. (c) Thereafter, $Li/LiNH_2$ remains in the reservoir. The color is characteristic for a concentrated metallic bronze solution of Li in NH_3 denoted as $Li(NH_3)_x^{-34}$

Na) was added slowly while stirring. After 5 min, the black suspension (pH ~8) was transferred into an Erlenmeyer flask followed by adding 50 mL ethanol and 1 mL acetic acid to adjust the pH value (pH ~5). After stirring shortly, the black solid was separated via centrifugation and washed three times with 20 mL ethanol. Finally, the powder was dried under vacuum while periodically heated to 150–200 °C with a heat gun. This procedure yielded 30–40 mg of a black product, thereafter termed *a*-Si.

Prior to subjecting Li₃NaSi₆ to extraction reactions, the material was ground in an agate mortar or ball-milled in a hermetically sealed stainless steel jar (RETSCH PM 100 planetary ball mill) for 8 h at 300 rpm (ball charge, 3; ball size, 15 mm diameter). A typical reaction with ball-milled starting material was carried out as follows: 135 mg of Li₃NaSi₆ were shortly (5–10 min) treated with 30 mL of ethanol under inert conditions. Subsequently, 4 mL of concentrated HCl solution were added. The solid product was separated by centrifugation, repeatedly washed (3–4 times) with 30 mL of a 1:1 ethanol–water mixture (V/V), dried under vacuum, and finally retained as a black fine powder (in the following termed *a-allo*-Si). The

reactions were modified using *i*-PrOH, air, H_2O , HNO₃, HOAc, and Ph₂CO instead of EtOH. For details, see ref 35 and Table 1.

Powder X-ray Diffraction (PXRD). For examining the phase purity of precursor materials and phase analysis of products, laboratory PXRD patterns were recorded on a Stoe STADI P diffractometer (Ge(111) monochromator for Cu $K_{\alpha 1}$ radiation, $\lambda = 1.54056$ Å) equipped with a Dectris MYTHEN DCS 1K solid state detector. Samples were ground in agate mortar and sealed inside 0.3 mm glass capillaries. All measurements were performed in a 2θ range of 5–90° (PSD steps, 0.06-1.00°; time/step, 10-40 s). Rietveld refinements of crystalline samples were carried out with the TOPAS 4.0 software.³⁶ High-energy PXRD measurements for a-Si and a-allo-Si were carried out at the beamline P02.1, at PETRA III, DESY (Hamburg). This beamline operates at a fixed energy of approximately 60 keV. The wavelength has been determined to be 0.20727(6) Å by using a LaB₆ NIST standard. The beam size is approximately 0.8 mm in diameter. The materials were enclosed in 0.7 mm glass capillaries and placed in front of the detector. For both samples, 30 2D diffraction images, each obtained through the accumulation of 20 frames with an exposure time of one second per frame, were collected with a PerkinElmer amorphous silicon area detector (XRD1621) placed at 329 mm from the sample. The distance between the sample and the detector was determined with a LaB_6 NIST standard. The 2D diffraction images were then integrated into a linear scattering signal with the software Fit2D and averaged.³⁷ Pair distribution functions (PDFs) were extracted by using the PDFgetX3 software.³⁸ The different steps of the PDF extraction include the subtraction of the scattering signal from the container, the correction for Compton scattering, absorption effects, and multiple scattering, and normalization to obtain the function S(Q). Finally, the pair distribution function, G(r), is obtained by sine Fourier transformation of the normalized scattering intensity, F(Q) = Q[S(Q)-1], to a maximum Q-value, Q_{max} , of 22.0 Å⁻¹. In PDFgetX3, the Fourier transformation is executed using exponential damping so as to suppress termination ripples, at the cost of reduced spatial resolution.

Differential Thermal Analysis (DTA). Differential thermal analysis was carried out with a NETZSCH DSC 404 Pegasus apparatus equipped with a DTA carrier system. Custom-built niobium crucibles were thoroughly cleaned, heated to 1000 °C under dynamic vacuum ($p < 1 \times 10^{-3}$ mbar) for 2 h and transferred to an Ar-filled glovebox. Crucibles were loaded with 20–30 mg of sample. The open

Table 1. Summary of Alkali Metal Extraction Reactions with Li₃NaSi₆ Targeting the Synthesis of *allo*-Si; Crystalline Products That Were Identified by Powder X-ray Diffraction Are Specified

no.	Li ₃ NaSi ₆ (mg)	reagent	additional solvent (mL)	experimental details	crystalline phases identified by PXRD
1	135	(a) EtOH, 30 mL (dried over Na); (b) HCl, 4 mL		ball-milled $\rm Li_3NaSi_6$ and EtOH were stirred in a Schlenk flask (5–10 min), 4 mL of HCl was added, washed with EtOH, dried under vacuum	α -Si, Na ₈ Si ₄₆
2	600	EtOH (dried over Na), 15 mL/20 mL		stirred in a Schlenk flask for 14 days followed by decanting EtOH, stirred another day with 20 mL of EtOH, washed with EtOH, dried under vacuum b	Li ₃ NaSi ₆ , <i>α</i> -Si
3	100 ^{<i>a</i>}	<i>i</i> -PrOH, 0.5 mL	Et ₂ O, 5	stirred in a Schlenk flask, 3 months, washed with $\mathrm{Et_2O}$ (4×), dried under vacuum ^b	Li ₃ NaSi ₆ , NbSi ₂
4	400 ^{<i>a</i>}	<i>i</i> -PrOH, 1 mL	Et ₂ O, 9	stirred in a Schlenk flask, 6 weeks, washed with $Et_2O(3X)$, dried under vacuum ^b	α-Si
5	100 ^{<i>a</i>}	<i>i</i> -PrOH, 0.75 mL	Et ₂ O, 14	stirred in a vial, 2 weeks, washed with $Et_2O(3x)^c$	Li ₃ NaSi ₆
6	300 ^a	air		6 months ^c	Li ₃ NaSi ₆
7	50 ^a	H ₂ O, 5 mL		stirred in a vial, 2 weeks, washed with $H_2O(2x)^c$	
8	100 ^a	HNO ₃ (68%), 6 mL		stirred in a Schlenk flask, 4 days, washed with $H_2O(3x)$, dried under vacuum ^b	Li ₃ NaSi ₆
9	50 ^a	HOAc, 3 mL		stirred in a vial, 4 weeks, washed with $H_2O(3x)^c$	α-Si
10	30 ^{<i>a</i>}	buffer solution NaHPO ₄ /KHPO ₄ , 5 mL		stirred in a vial, 4 days, washed with H_2O^c	Li ₃ NaSi ₆
11a	1000 ^{<i>a</i>}	Ph ₂ CO 5 M, 3 mL	THF, 10	stirred in a Schlenk flask, 3 months, washed with THF (4×), dried under vacuum b	Li ₃ NaSi ₆ , NbSi ₂
11b	217 from 11a	H ₂ O, 5 mL		stirred in a vial, c 2 months, washed with H2O (3×)	SiO ₂ , NbSi ₂ , Li ₂ SiO ₃ , Na ₂ SiO ₂

^aLi₃NaSi₆ was synthesized in a Nb ampule ^bReacted, washed, and dried under inert conditions. ^cSample handling carried out in air.

end was closed by crimping and then sealed by arc-welding inside the glovebox under cooling. All measurements were performed under an Ar-flow rate of 60–70 mL min⁻¹ and a heating/cooling rate of 10 K min⁻¹. An empty niobium crucible served as reference. Samples were recovered after the measurement by opening the niobium crucibles inside the glovebox. The Proteus Thermal Analysis program was used for data handling.³⁹

Transmission Electron Microscopy (TEM). Transmission electron microscopy and selected-area electron diffraction (SAED) measurements were performed in a Tecnai F30 STwin microscope (300 kV, field emission gun (FEG) cathode, spherical aberration coefficient $C_s = 1.2$ mm). EDX nanoprobe analysis as part of the TEM examinations were carried out using a Si/Li detector (EDAX System). To prevent oxidation and contamination of the samples the entire procedure for TEM preparation was done in an Ar-filled glovebox. Ground samples of *a*-Si and *a-allo*-Si were placed onto a lacey-carbon grid and subsequently transferred to the TEM in an argon-filled bag. Heating experiments (cf. Figures S9 and S10 in the Supporting Information) were performed with a single-tilt heating stage to tentatively prove crystallization and morphology changes at elevated temperatures.

Attenuated Total Reflectance Fourier Transformed Infrared Spectroscopy. ATR-FT-IR spectra were recorded on a Varian 670 IR FT-IR spectrometer equipped with a Pike GladiATR ATR accessory and using a diamond ATR element. All measurements were performed at room temperature. The Varian Resolution Pro software was used for data handling.⁴⁰

Raman Spectroscopy. Raman spectra for a-Si and a-allo-Si were measured using a LabRAM HR 800 spectrometer. The instrument is equipped with an 800 mm focal length spectrograph and an air-cooled (-70 °C), back thinned CCD detector. Samples were sealed in 0.7 mm glass capillaries. The capillaries were placed on a glass slide and samples were excited with an air-cooled double frequency Nd:YAG laser (532 nm). The laser was focused onto the sample using a 50X superlong working distance (WD = 20.5 mm) Mitutoyo objective. Measurements were performed in two steps. The samples were excited at 0.56 mW laser power (corresponding to a low power density of 5.5 $\times 10^{-6}$ mW μ m⁻²) and spectra were recorded at different spots of the sample. Next the samples were heated with the laser for 1 min by increasing the power to 14 mW and a spectrum was measured at this laser power and another one at the low laser power used in the initial examination (0.56 mW). The laser power was adjusted by a software controlled filter wheel with 6 ND filters. Spectra were collected with an exposure time of 60 s (10 accumulations) and using a grating of 600 lines mm⁻¹. All spectra were calibrated and normalized. The spatial resolution of the instrument is specified as 1 μ m in diameter.

Elemental Analysis. A JEOL-JSM 7500F scanning electron microscope (SEM) equipped with an Oxford X-Max EDX (energy-dispersive X-ray spectroscopy) analyzer with Mn as internal standard was used to determine elements with atomic numbers larger than four. Samples were handled inside an Ar-filled glovebox or outside if not air-sensitive and fixed on a graphite platelet which was attached to an aluminum stub. The lithium content determination was carried out by atomic absorption spectroscopy using a Varian AA280FS device. C, H, N contents were determined by a Hekatech Euro EA CHNSO-Analyzer.

Computational Details. Quantum chemical calculations with the Perdew–Burke–Ernzerhof hybrid density functional method (DFT-PBE0)^{41,42} were performed using the CRYSTAL09 software package.⁴³ Split-valence + polarization (SVP) quality basis sets were employed for Si, Na, and Li. The basis set for Si was taken from ref 44. For the alkali metals they were derived from the molecular def-SVP basis set (see the Supporting Information).

Both the lattice and the atomic parameters of Si trial structures (according to Conesa)³² were allowed to relax within the constraints imposed by the space group symmetry for structural optimization. The shrinking factor (SHRINK) used for the generation of a Monkhorst–Pack-type grid of *k*-points in reciprocal space was 4 for lattice sizes larger 10 Å, 8 for lattices smaller or equal 10 Å, but larger than 5 Å and 16 for smaller lattice parameters. Tight tolerance factors of 8, 8, 8, 8,

and 16 were used for the evaluation of the Coulomb and exchange integrals (TOLINTEG). Default optimization convergence thresholds and an extra-large integration grid (XLGRID) for the densityfunctional part were applied in all calculations. Another computational study concerned the full structural relaxation of the Si substructure of Li₃NaSi₆. Here the experimental structure of Li₃NaSi₆¹¹ was first fully optimized and the obtained lattice and Si atomic parameters used as a starting model for subsequent relaxation of an elemental Si structure. This step was performed without any symmetry constraints at DFT-PBE⁴¹/SVP level of theory. At this point the system was metallic and the Fermi surface was smeared with a width of 0.02 au. For the evaluation of the tolerance and exchange integrals (TOLINTEG), tight criteria of 7, 7, 7, 7, and 14 were used and for the densityfunctional part, a large integration grid (LGRID) was applied. The geometry optimization starting from the Si substructure in Li₃NaSi₆ naturally resulted in large changes in the geometry. Therefore, the optimization process had to be carried out carefully and was manually restarted several times to enable the reclassification of the two-electron integrals as the geometry became very different from the original geometry. Between the steps, the symmetry had to be lowered to space group P1 (1) and too big displacements from one point of the potential surface to the next had to be avoided by the keyword MAXTRADIUS. The resulting minimum structure was subsequently optimized at the DFT-PBE0/SVP level of theory and its space group determined with FINDSYM.⁴⁵ Stationary points were confirmed to be minima for all optimized structures by applying frequency calculations.^{46,47}

3. RESULTS AND DISCUSSION

Chemical Extraction Experiments with Li₁₅Si₄ (Synthesis of *a*-Si). Because the structure of the highly air- and moisture-sensitive silicide $Li_{15}Si_4$ comprises isolated Si atoms that are embedded in a Li matrix,³³ nanoparticulate forms of Si could be obtained by a soft extraction of Li. Hence, chemical delithiation of Li₁₅Si₄ was realized using liquid ammonia. The extraction apparatus is shown and described in Figure 2. The blue color of liquid ammonia when condensed onto Li15Si4 powder clearly indicates the formation of solvated electrons (Figure 2b). The formation of a metallic bronze solution,³⁴ as shown in Figure 2c, typically indicates that Li is extracted. After several extraction cycles solely LiNH₂ was identified as crystalline phase in the PXRD pattern of the product (see Figure S2 in the Supporting Information; residual Li content: 21.9(1) wt % Li vs 48.1 wt % in $Li_{15}Si_4$). The IR spectrum essentially only shows NH stretching and HNH deformation modes at 3259 and 1560 cm⁻¹/1538 cm⁻¹, respectively (see Figure S3 in the Supporting Information).⁴⁸ Si–O vibrational bands that typically occur at around 800–1100 cm⁻¹ and would indicate O impurities are not observed.¹⁴ As the last step, LiNH₂ is removed by slowly reacting it with ethanol in a toluene suspension. Acetic acid was used to adjust to acidity as silicon dissolves under alkaline conditions. Alternatively, a buffered solution can be used to remove LiNH₂. The delithiation of Li₁₅Si₄ is formulated as follows

$$\text{Li}_{15}\text{Si}_4 \xrightarrow{\text{NH}_3} 15(1-x)\text{Li}_{\text{NH}_3} + 4\text{Si} + 15x\text{Li}\text{NH}_2 + 7.5x\text{H}_2$$

As can be seen from the PXRD pattern in Figure S2 in the Supporting Information, the dried black product is amorphous and will be termed *a*-Si in the following.

Chemical extraction experiments with Li₃NaSi₆ (synthesis of *a-allo-Si*). As described in the introduction section, the Zintl phase Li₃NaSi₆ consists of polyanionic layers ${}^{2}_{\infty}$ [Si₆]⁴⁻ which are separated by Li and Na ions.¹¹ Previous attempts to deintercalate Li₃NaSi₆ and combine the Si layers topotactically employed protic solvents according to

$Li_3NaSi_6 + 4ROH \rightarrow 6 allo-Si + 2H_2 + 3LiOR + NaOR$

With water, an almost complete conversion (97%) to *allo*-Si was reported.^{10,11} Crystallites of α -Si were found concomitantly.^{10,11} Tentative unit-cell parameters for *allo*-Si were reported as orthorhombic, a = 13.29 Å, b = 3.79 Å, c = 12.63 Å.¹⁰ However, the reflection positions calculated from those parameters differ substantially from the diffraction pattern of *allo*-Si compiled in the Powder Diffraction File (PDF 41–1111).

We diligently tried to reproduce the reaction of Li₃NaSi₆ with protic solvents to allo-Si. Generally, we found that the reactivity of Li₃NaSi₆ strongly depends on the degree of crystallization (consistent with ref 11). For instance, a thoroughly powdered crystalline sample of Li₃NaSi₆ (see Figure S4a in the Supporting Information) was allowed to react with ethanol for 15 days (Table 1, reaction 2). Thereafter, reflections from Li₃NaSi₆ are still recognizable in the PXRD pattern and the increased background with maxima at $2\theta \approx 28^{\circ}$ and $\approx 53^{\circ}$ indicates the presence of an amorphous phase (see Figure S4b in the Supporting Information). In contrast, when using ball-milled Li₃NaSi₆ as starting material (see Figure S5b in the Supporting Information) reactions were completed within several minutes (Table 1, reaction 1). The PXRD pattern of the product shows an amorphous background as well as Bragg reflections of α -Si and Na₈Si₄₆ (see Figure S5c in the Supporting Information). This product is termed a-allo-Si in the following. The small clathrate impurity may have already been introduced in the synthesis of Li₃NaSi₆ although it is not recognizable in the PXRD pattern of the starting material (overlap of Bragg reflections). It may also be that ball-milling induces a partial decomposition of Li₃NaSi₆ leading to the formation of NaSi, which could be oxidized to form Na₈Si₄₆ when treated with protic reagents.

Extraction reactions employing mixtures of 2-propanol and diethyl ether (Table 1, reactions 3-5) yielded amorphous products beside α -Si and unreacted Li₃NaSi₆. In the case of reaction 3 the Li₃NaSi₆ starting material was synthesized in Nb ampules and contained a marginal NbSi₂ impurity (confirmed by EDX analysis). Crystalline NbSi₂ could not be observed in the PXRD pattern of the starting material but is clearly identified in the PXRD pattern of the oxidation product.

In contrast to alcohols, H_2O and acids rapidly oxidize Li_3NaSi_6 under formation of an amorphous phase. In some cases α -Si and unreacted Li_3NaSi_6 are identified as crystalline phases (Table 1, reactions 7-9). Because all reactions employing protic solvents as oxidative reagents are accompanied by the formation of LiOH and NaOH, the pH value is critical regarding the dissolution of Si. In reaction 10 a NaHPO₄/KHPO₄ buffer solution was employed to compensate for the pH increase. We also tried to oxidize Li_3NaSi_6 using a solution of benzophenone in THF. After three months the PXRD pattern of the product showed an increased background and Bragg reflections of NbSi₂ and residual Li_3NaSi_6 (Table 1, reaction 11a). Further oxidation of residual Li_3NaSi_6 with H_2O yielded Li_2SiO_3 , Na₂SiO₃, and SiO₂ (11b).

In summary, deintercalation of Li_3NaSi_6 with protic solvents leads inevitably to the formation of amorphous products. In most cases, significant amounts of Li_3NaSi_6 remained unreacted. Complete reactions were only achieved with ballmilled starting material. Regardless of reaction conditions for the deintercalation of Li_3NaSi_6 , we never observed the reflections reported for *allo*-Si (PDF 41–1111). Also, annealing partially oxidized samples of Li_3NaSi_6 at 300 °C for 2 weeks did not give rise to any new reflections. A closer inspection of the PXRD pattern of *allo*-Si reported in ref 11 and the database entry PDF 41–1111 reveals strong analogies to NbSi₂ (see Figure S6 in the Supporting Information). Li_3NaSi_6 employed in ref 11 was synthesized in Nb ampules at temperatures up to 800 °C, which readily explains the formation of NbSi₂. According to our experience, the presence of minor concentrations of NbSi₂ may not be recognizable in the diffraction pattern of crystalline Li_3NaSi_6 but will uncover in the PXRD pattern of the amorphous product after alkali metal extraction (i.e., reactions **3** and **11a**, Table 1).

Characterization of a-Si and *a-allo-Si. Elemental Analysis, FT-IR.* IR spectroscopic investigations clearly reveal Si–O vibrational modes for *a-Si*, in particular the Si–O stretching band at around 1069 cm⁻¹ (Figure 3), indicating a



Figure 3. ATR-FT-IR spectra of a-Si and a-allo-Si.

slight partial surface oxidation.¹⁴ This is additionally strengthened by SEM EDX examinations (see Figure S7 in the Supporting Information) and nanoprobe EDX analysis in the TEM (described below). The oxidation occurs during the removal of LiNH₂ with ethanol. According to SEM EDX, the average O content of *a*-Si samples is 12.8 ± 1.9 at. %. A slightly visible band at around 2100 cm⁻¹ may indicate the presence of Si-H. However, this band is significantly weaker than observed for hydrogen-capped silicon nanoparticles.⁴⁹ Furthermore, traces of Na (<1 at. %) were detected by SEM EDX. The residual Li content in a-Si (~1 wt %) was determined by atomic absorption spectroscopy. C, H, N impurities of a-Si samples are marginal (C, H, N < 1.2 wt %). In contrast to a-Si, the IR spectrum of a-allo-Si is essentially featureless. Si-O bands are barely visible. However, according to SEM EDX analysis *a-allo-Si* samples contain 7.4 \pm 1.9 at. % O.

TEM Analysis. Representative results of the TEM investigations are shown in Figures 4 and 5. The morphology of *a*-Si and *a*-allo-Si samples differs remarkably. Samples *a*-Si show a highly porous microstructure built of agglomerated particles with sizes around 10 nm (Figure 4a). The electron diffraction pattern (Figure 4b) corresponds to faint rings of diffuse intensity which indicates marginal sizes of coherently scattering domains and thus short-range ordering. The diameters of these rings correlate with the d-values of α -Si nanocrystallites with sizes below 5 nm within the thin and electron transparent areas. The oxygen content as determined by nanoprobe EDX was



Figure 4. (a) Bright-field micrograph of *a*-Si particles, (b) electron diffraction pattern from *a*-Si sample containing diffuse concentric rings matching with nanocrystalline α -Si, (c) high-resolution micrograph showing crystalline nanoparticle (circled) in amorphous matrix and respective FFT-image showing sharp 111 reflections.



Figure 5. (a) Bright-field micrograph of *a-allo-Si*, (b) electron diffraction pattern from the circled area showing microcrystalline nature of the sample, (c) high-resolution micrograph showing crystalline nanoparticles (circled) in amorphous matrix.

about 8 at. % on average and up to 40 at. % in thin areas close to the boundary of particles. This agrees roughly with the result of the SEM EDX analysis. The oxygen containing areas do not show any structural ordering, thus, they are not indicated by any prominent intensity within the electron diffraction patterns.

Samples *a-allo*-Si consist of larger particles with minimum sizes of 50 nm (see Figure 5a). These particles contain crystallites of α -Si with sizes large enough to yield coherent scattering (cf. the fully indexed diffraction pattern in Figure 5b). Consequently, the width of the diffraction circles is considerably lower compared to *a*-Si (cf. Figure 4b). Moreover, the diffuse intensities clearly segregate into Bragg intensities as expected for rotationally disordered microcrystals of α -Si. Indeed, HRTEM confirms the presence of α -Si crystallites with sizes up to 10 nm in *a-allo*-Si (Figure 5c). For *a-allo*-Si the average oxygen content as established by nanoprobe EDX was comparable to *a*-Si (ca. 10 at. %), but the maximum value determined on the edges was only 15 at. %.

PXRD Investigations. The high energy diffraction patterns and PDFs for *a*-Si and *a-allo*-Si are compiled in Figure 6. In agreement with the TEM investigations the diffraction pattern of *a*-Si is void of sharp Bragg peaks. Broad maxima are located around $2\theta = 4$, 7, and 10.5° corresponding to d = 3.28, 1.75, and 1.19 Å, respectively.

The amorphous contribution to the pattern of *a-allo*-Si is modulated by the Bragg peaks of crystalline Si, which again reflects the finding from the TEM analysis. The minimum crystallite size yielding sharp Bragg peaks in X-ray diffraction is 4-5 nm.⁵⁰ The diffraction pattern of *a-allo*-Si contains also Bragg peaks from the Na₈Si₄₆ impurity. The positions of the peaks in the PDF for *a-allo*-Si closely correspond to the separation of atom pairs in crystalline Si. The PDF for *a*-Si resembles amorphous Si with a sharp first neighbor peak at 2.35 Å and a broad second neighbor peak at 3.8 Å.^{51,52} In contrast with amorphous Si this peak is clearly asymmetric. This



Figure 6. (a) High-energy X-ray diffraction patterns and (b) PDFs for the *a*-Si and *a-allo*-Si materials ($\lambda = 0.20727(6)$ Å, $Q_{max} = 21.0$ Å⁻¹).

asymmetry is robust with respect to variations of Qmax and indicates that the second peak is actually split. An analogous phenomenon has been recently observed and analyzed for amorphous Ge and attributed to a fraction of third neighbors being closer than some second ones, indicating structural relaxation (i.e., deviation from a continuous random network).⁵³ This interpretation is not applicable for our a-Si material which-according to the TEM analysis-represents a mixture of nanocrystalline Si embedded in an amorphous environment. Rather, the PDF for *a*-Si appears as a convolution of amorphous Si and sub-Bragg sized crystallites (2-4 nm). The contribution from the latter dominates the medium range of r (4–8 Å). Indeed the third peak centered at 5.7 Å for amorphous Si^{51,52} is clearly split according to crystalline Si (5.47 and 5.86 Å), whereas the faint fourth peak (centered at around 7 Å for amorphous Si)^{51,52} may indicate fine structure, mirroring distances from the center of crystallites to their (relaxed) interface with amorphous environment. It is tempting to interpret a-Si as paracrystalline Si where the crystallite size is large enough to express with distinct pairs in the PDF.⁵⁴ However, because of the partial oxidation of a-Si such conclusions remain highly ambiguous. The peaks in the PDF for a-allo-Si essentially correspond to crystalline Si, which is expected from the presence of crystallites larger than 5 nm.

Raman Spectroscopy. Figure 7 shows Raman spectra for *a*-Si and *a*-allo Si, respectively. Focusing first on *a*-Si (Figure 7a), the majority of observed spectra correspond to amorphous Si characterized by a broad maximum at 460–470 cm⁻¹ (the TO₁ band), weaker bands at 380 and 300 cm⁻¹ assigned to LO and LA, respectively, and a pronounced TA like band at low wavenumbers. Occasionally spectra characteristic of nanocrystalline (*nc*) Si (2–4 nm crystallite size) could also be obtained. Those display a sharp and asymmetric TO₂ peak at 500 cm^{-1.55} It is important to note that spectra of amorphous and *nc*-Si can only be observed when applying the lowest



Figure 7. Raman spectra for (a) *a*-Si and (b) *a*-allo-Si. The spectra in the upper panel in a) were obtained from different parts of the a-Si sample after increasing the laser power.

possible power density (0.56 W/5.5 × 10^{-6} mW μ m⁻²). Amorphous spectra did not change with time whereas *nc*-Si spectra showed well-known variations attributed to temperature increase. ^{56,57} When increasing laser power, amorphous and *nc*-Si spectra convert into a spectrum characteristic for (bulk) crystalline Si. The sharp and symmetric peak of the TO₂ band shifts to 519–521 cm⁻¹ and only varies slightly with temperature. The two phonon contributions at lower wavenumbers are absent.

Raman spectra for the *a-allo*-Si sample (Figure 7b) mirror the three constituents of this sample. First there are spectra reflecting a solely amorphous state. However, these spectra were frequently convoluted with contribution from *nc*-Si. Note that the shape of such spectra has been considered to be typical of paracrystalline Si.⁵⁰ Vice versa, spectra of *nc*-Si with a pronounced asymmetry stemming from an amorphous silicon contribution were recorded. Finally, we also obtained spectra corresponding to bulk crystalline Si. Those spectra are attributed to Si crystallites with a size larger than 5 nm. Accordingly, *a-allo*-Si contains α -Si crystallites with a large size variation (2 to ~10 nm), whereas α -Si crystallites in *a*-Si have sub-Bragg size (2–4 nm).

DTA Investigations. The amorphous-to-crystalline phase transition of *a*-Si and *a*-allo-Si was investigated by differential thermal analysis. Figure 8 shows the first heating traces for (i) Li_3NaSi_6 , (ii) partially deintercalated Li_3NaSi_6 (i.e., a mixture of Li_3NaSi_6 and *a*-allo-Si), (iii) *a*-allo-Si, and (iv) *a*-Si. Li_3NaSi_6 decomposes at around 600 °C (effect 2) into $Li_{12}Si_7$, NaSi, and α -Si (see Figure S8 in the Supporting Information). For the Li_3NaSi_6/a -allo-Si mixture, an additional exothermic effect is observed at 487 °C (effect 1). Comparing the PXRD patterns of the pure Li_3NaSi_6 sample and the Li_3NaSi_6/a -allo-Si mixture



Figure 8. First DTA heating traces of thermograms recorded for Li_3NaSi_6 , partially oxidized Li_3NaSi_6 (Li_3NaSi_6/a -allo-Si mixture), a-allo-Si, and a-Si ($T_{max} = 750$ °C, ± 10 K min⁻¹ heating/cooling rate, heat effects marked with * could not be assigned).

after DTA investigations (see Figures S4c and S8 in the Supporting Information), the latter clearly reveals larger portions of α -Si. The heating trace of the *a-allo*-Si sample only contains an irreversible exothermic effect that is markedly shifted to higher temperatures (effect 3 at 565 °C). The subsequently recorded PXRD pattern corresponds to α -Si (see Figure S5d in the Supporting Information). Thus, effect 1 and 3 are attributed to the amorphous-to-crystalline transition of *a-allo*-Si sample embrace the reported phase transition of *allo*-Si at ~527 °C.¹¹

The variation in temperature is ascribed to different concentrations of sub-Bragg sized nanocrystals (2-4 nm), that is the presence of different concentrations of crystallization nuclei in both samples. We assume that in a-Si the concentration of sub-Bragg sized crystallites is considerably smaller than in *a-allo-Si*. The phase transition of *a-Si* occurs at 658 °C (effect 4) which is similar to amorphous silicon obtained from ball milling at a heating rate of 40 K min⁻¹, but lower than the crystallization temperature for ion-implanted amorphous silicon (around 690 °C).^{58,59} Thus, for *a*-Si, nucleation (i.e., the formation of a critical concentration of critically sized nuclei) has to be induced prior to the transition, which explains the shift to higher temperatures. It is interesting to note that when heating individual particles of both a-Si and a-allo-Si in the TEM, crystallization is not observed below 700 °C (cf. Supporting Information, Figures S9 and S10).

Allotropism of Si (Or How Feasible is *allo*-Si?). As described above, the existence of a crystalline allotropic form of silicon obtained from Li₃NaSi₆ through oxidation is highly questionable. This is in contrast to *m*-allo-Ge, which is readily prepared from delithiating Li₇Ge₁₂. Both Li₇Ge₁₂ and Li₃NaSi₆ possess two-dimensional polyanions with five-membered rings, yet their topotactic combination leads to different branches of three-dimensional structures. According to Conesa, the

The two-dimensional slabs ${}^{2}_{\infty}$ [Si₆]⁴⁻ in Li₃NaSi₆ are built of four (4b), three (3b), and two (2b) bonded Si atoms, respectively (cf. Figure 9). Based on this structure, Conesa's



Figure 9. Si substructure in the phase Li_3NaSi_6 . The four (Si⁰), three (Si⁻), and two (Si²⁻) connected Si atoms are shown in black, light/ dark blue, and red, respectively. For the four different groups of *allo*-Si networks derived from this layered structure, the charged atoms are connected differently.

S group follows, which can be divided into four smaller structure groups. The **SA** group is built by connecting 2b-Si atoms (red) of neighboring layers and bonding them to 3b-Si atoms of their own layers (dark blue). The light blue 3b-Si atoms are bonded to the light blue ones of the neighboring layer. **SB** is a connection of red Si^{2–} atoms (2b) with light blue Si[–] atoms (3b) of the neighboring layer and dark blue Si[–] atoms (3b) of their own layer. For structures **SC**, the 2b-Si^{2–} atoms are connected to dark blue 3b-Si[–] atoms and to the red Si^{2–} of the neighboring layer. The 3b-Si[–] atoms (light blue) are connected to the same kind of the next layer. For each of these

types four structure variations exist. The fourth group **SD** is built by connecting red Si^{2-} atoms (2b) to both Si^{-} atoms (3b) of the next layer. For such a network, only one structure type is possible, the **TON** zeolite-type network (ZSM-22).

A comparison of total energies of the computationally relaxed Conesa S-type Si structures (Figure 10) shows that SD is the favored structure with an energy difference to α -Si of 13.7 kJ (mol Si)⁻¹ (Si–Si distances, 2.34–2.40 Å; angles, 90.7–142.9°; crystallographic density, 2.011 g cm⁻³, Figure 11a). Its



Figure 11. (a) Most stable network (**SD**) derived from the Si substructure of Li_3NaSi_6 with view along the *c*-direction emphasizing the one-dimensional channel structure built from 10-, 6-, and 5-membered rings; (b) network of the structure **SC1** with view along the *a*-direction. It is built of 6- and 5-membered rings.

structure has the lowest density of all **G** and **S** group networks and is equivalent to the zeolite network **TON**. As shown in Figure 11a it contains 10-, 6-, and 5-membered rings which form parallel channels proceeding along the *c*-axis. The diameter of the largest channel ranges from 6.6 to 7.4 Å. In energy, this framework is followed by **SC1** (Figure 11b) with a relative energy of 14.0 kJ (mol Si)⁻¹. Si–Si distances vary from 2.31 to 2.43 Å and angles range from 92.0 to 128.4°. The crystallographic density of this structure is 2.292 g cm⁻³ which is close to that of α -Si (2.290 g cm⁻³). **SC1** also displays onedimensional channels, which run along the *a* direction and are based on 6- and 5-membered rings (Figure 11b).

To simulate computationally the topotactic recombination of Si layers in Li_3NaSi_6 (cf. Figure 9) to *allo-Si*, we carried out a full relaxation of the Si substructure in Li_3NaSi_6 without any symmetry restrictions. This resulted in a true local minimum with *Cmcm* space group symmetry being the **TON** (SD)



Figure 10. Energies relative to α -Si for Conesa's S-type structures (derived from the Si substructure of Li₃NaSi₆). The four different network classes are colored differently; SA in red, SB in green, SC in orange, and SD in blue. The energy difference to well-known open tetrahedral frameworks⁶⁰ is depicted as well (violet). All relative energies are also listed in Table S1 in the Supporting Information.

structure, which was also the favored of all "handmade" structures of Conesa, highlighting the key role of this network. Furthermore, the structure with the smallest density is favored in the present structural relaxation without any initial specification of Si–Si bonds.

Importantly, the most favorable structures that follow from the combination of two-dimensional slabs ${}^{2}_{\infty}$ [Si₆]^{4–} are rather high in energy, around 14 kJ (mol Si)⁻¹ with respect to the ground state structure of Si (α -Si). Several clathratic and zeolitic open tetrahedral frameworks have a considerably lower energy and are only by about 7 kJ (mol Si)⁻¹ less stable than α -Si. Such frameworks are also included in Figure 10. As already shown earlier the clathrate-II framework mtn and the chiral uni framework appear most favorable as Si allotropes.^{61,62} The crystallographic densities of those frameworks are lower compared to the "S" structures and range from 1.979 g cm⁻³ (mtn) to 2.180 g cm⁻³ (tum) (see Table S1 in the Supporting Information). In contrast the total energies of Conesa "G" structures (derived from Li₇Ge₁₂ layers) compare closely with the clathratic and zeolitic frameworks (cf. Figure S11, Table S1 in the Supporting Information) and are favored over the "S" structures derived from Li₃NaSi₆. This strongly supports the experimental observation that Li₃NaSi₆ is not a suitable precursor for topotactic formation of allo-Si, whereas allo-Ge is readily obtained from Li₇Ge₁₂.

CONCLUSION

Alkali metal extraction reactions with the silicides $Li_{15}Si_4$ and Li_3NaSi_6 lead to amorphous products termed *a*-Si and *a-allo-Si*, respectively. *a-Si* possesses a porous microstructure which is built from spherically shaped particles with a diameter of around 10 nm. The amorphous particles contain sub-Bragg sized (below 5 nm) Si crystallites which are revealed in TEM investigations and Raman spectroscopy. They have a partially oxidized surface, which is introduced in the purification process of *a-Si*. Extraction reactions with $Li_{15}Si_4$ chemically emulate the delibilitation process occurring in silicon-based lithium batteries. The porous microstructure of *a-Si* might bear close resemblance with electrochemically obtained amorphous Si.

a-allo-Si does not display a distinguished microstructure but consists of irregularly shaped particles with sizes larger than 50 nm. These particles contain sub-Bragg-sized and Bragg-sized crystallites with sizes up to 10 nm. The considerably lower crystallization temperature of *a-allo-Si* (around 570 °C) compared to a-Si (around 660 °C) suggests that the concentration of sub-Bragg-sized particles (acting as crystallization nuclei) is significantly larger in the former material. The formation of a-allo-Si from Li₃NaSi₆ contradicts earlier findings, reporting the formation of a crystalline bulk allotrope of silicon (allo-Si) from the topotactic combination of silicon layers present as polyanions in Li₃NaSi₆. Quantum chemical calculations show that the combination of Li3NaSi6 silicon layers does not lead to energetically favorable allotropic forms of Si. This is different to Li₇Ge₁₂, where polyanionic germanium layers topotactically convert to the germanium allotrope *m-allo-*Ge upon oxidation.

The alkali metal extraction reactions reported herein expand the methods for the fabrication of small nanoparticles. Further examples include the first commonly recognized successful production of Si nanoclusters capped with alkyl groups⁶³ via SiCl₄ + RSiCl₃ + Na \rightarrow Si + NaCl and the magnesiothermic reduction of silica⁶⁴ to form porous nanostructured Si, which was investigated as potential anode material.⁶⁵ In addition, small uncapped Si nanoparticles of 5–20 nm can be obtained without aggregation using a reverse micelles technique also showing a SiO₂ coverage. The decreased particle size of Si enhances the cycling stability of Si anodes. Using conductive additives, reversible capacities above 2000 mAh g⁻¹ were achieved with particles in the range of 5 to 20 nm. Smaller particles, however, increase the irreversible capacity losses.⁶⁶

ASSOCIATED CONTENT

Supporting Information

PXRD patterns of Li₃NaSi₆ samples from different reactions (Figure S1), PXRD patterns of (a) Li₁₅Si₄ bulk material, the sequential products after (b) Li-extraction with liquid ammonia, (c) subsequent treatment with ethanol, and (d) differential thermal analysis (Figure S2), ATR-FT-IR spectra of the a-Si/ LiNH₂ mixture obtained after Li extraction from Li₁₅Si₄ (Figure S3), PXRD patterns of Li₃NaSi₆, the product after partial oxidation with ethanol and subsequent DTA-investigation (Figure S4), PXRD patterns of Li₃NaSi₆ before and after ballmilling, the product after treatment with ethanol/HCl and subsequent DTA investigation (Figure S5), PXRD pattern of a NbSi₂ sample referenced with the database entry for allo-Si and NbSi₂ (Figure S6), results from EDX investigations of a-Si (Figure S7), Rietveld fit to the PXRD pattern of Li₃NaSi₆ after DTA (Figure S8), results from TEM heating experiments of a-Si and a-allo-Si (Figures S9 and S10), comparison of the total energies of networks optimized on the basis of Conesa's G-type structures (Figure S11), DFT-PBE0 results in tabular format (Table S1), and basis sets for Na and Li employed in the theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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