Synthesis of the intermetallic clathrate Na₂Ba₆Si₄₆ by oxidation of Na₂BaSi₄ with HCl

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Abstract

A new preparation route to the intermetallic clathrate-I compound Na₂Ba₆Si₄₆ is introduced, which allows one to make large amounts of product with standard laboratory equipment. The precursor Na₂BaSi₄ is oxidized with gaseous HCl at 673 K to Na₂Ba₆Si₄₆, NaCl and BaCl₂. Full-profile refinement of the crystal structure from the X-ray powder diffraction data revealed a composition close to Na₂Ba₆Si₄₆ (Na₁.₉₄(1)Ba₆.₀₆(1)Si₄₆, space group Pm\(^{3}\)n, \(a = 10.281(1)\ \text{Å}\)). Differential scanning calorimetry showed an exothermic effect at 874 K, indicating that Na₂Ba₆Si₄₆ is metastable. The product was additionally characterized by scanning electron microscopy. The electronic structure of Na₂Ba₆Si₄₆ was investigated by a first-principles, all-electron full-potential method, predicting metallic conductivity. Na₂Ba₆Si₄₆ obtained by oxidation with HCl shows Pauli paramagnetism; no bulk superconductivity was found down to 1.8 K in a magnetic field of 20 Oe.

Keywords: Na₂Ba₆Si₄₆, Na₂BaSi₄; Crystal structure; Silicon clathrates; Oxidation; Superconductivity; Electronic structure

1. Introduction

The discovery of superconductivity in Na₂Ba₆Si₄₆ by Yamanaka et al. in 1995 has initiated new research activities on clathrate compounds [1,2]. Superconductivity for clathrates had not been known before, and the question arose whether \(T_c\) could be influenced by the kind or amount of metal atoms embedded in the Si₄₆ framework of the clathrate-I type (Fig. 1) [3–5].

A barrier to the further development of the chemistry and physics of silicon clathrates is difficulties in the synthesis. Direct formation from the elements or binary compounds has been only achieved with elaborate high-pressure synthesis techniques [6]. The thermal decomposition of precursor compounds under vacuum [7] can also be used in the synthesis of silicon clathrates, and Na₂Ba₆Si₄₆ was first obtained by Yamanaka et al. with this method from the precursor Na₂BaSi₄ [1]:

\[
17 \text{Na}_2\text{BaSi}_4 \xrightarrow{773 \text{ K}, 8 \text{ h}, 10^{-2} \text{ Pa}} \text{Na}_2\text{Ba}_6\text{Si}_{46} + 11\text{BaSi}_2 + 32\text{Na(g)}.
\]

The method is suitable for laboratory scale, but the metal content of the reaction product is easily affected by small variations of the actual reaction conditions.

A new promising synthesis route, which was applied to the synthesis of clathrate-II \(\square_{25}\text{Ge}_{136}\), is the oxidation of a precursor with protons in an ionic liquid [8]. More recently, the oxidation process has turned out to be notably simplified by gas–solid reactions, and the clathrate-I silicides Na₂₀₂Si₄₆ and K₇₇Si₄₆ could be obtained by oxidation of NaSi and KSi with HCl [9]. Here we report on the oxidation of Na₂BaSi₄ with gaseous HCl to Na₂Ba₆Si₄₆ with fully occupied metal sites.

2. Experimental

2.1. Preparation

The precursor for the oxidation reaction was obtained by annealing a compact pill of a 2:1 mixture of NaSi [10] and
BaSi₂ [11] powders at 873 K for 5 d in a closed Ta ampoule [1]. A single phase of Na₂BaSi₄ was only formed after a second heat treatment at 1073 K in a closed ampoule. For the synthesis of NaSi, a stoichiometric mixture of the elements was heated in a closed Ta ampoule under Ar in 4 h to 1073 K, kept at this temperature for 2 h and cooled down within 40 h to room temperature. For the synthesis of BaSi₂, a closed Ta ampoule with a stoichiometric mixture of the elements was first heated for 2 min at 1500 K in an induction furnace, ground, and subsequently annealed for 48 h at 1273 K.

Fine powders of the precursor (0.15 mmol, calculated for Na₂BaSi₄) and NH₄Cl (3.0 mmol) in separate glass crucibles were sealed in a Duran glass ampoule. The ampoule was placed for 1 h in a calibrated tube furnace at 673 K. The reaction product was washed with demineralized water to remove NaCl and BaCl₂.

2.2. Characterization

2.2.1. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed in closed Nb ampoules on a Netzsch DSC 404 C calorimeter under argon atmosphere from room temperature up to 1573 K with a 10 K min⁻¹ heating rate.

2.2.2. X-ray powder diffraction

Unit cell parameters were calculated from least-square refinement of X-ray Guinier powder diffraction (XRPD) data (Cu Kα₁ radiation, λ = 1.540598 Å, graphite monochromator, Huber 670 camera, 5° ≤ 2θ ≤ 100°, Δ2θ = 0.005°; LaB₆ NIST standard with a = 4.1569162(97) Å). The positions of the reflections were determined by single profile fit. The diffraction data for Rietveld refinement were collected with a STOE STADI P diffractometer (Ge (1 1 1) monochromator, zero-background holder, Bragg-Brentano geometry). All calculations were performed with the WinCSD program package [12]; structure drawings were made with the program ATOMS [13].

2.2.3. Magnetic susceptibility

Magnetization was measured at various external fields between 20 Oe (1.59 × 10⁻⁵ A m⁻¹) and 70 kOe (5.57 × 10⁻⁵ A m⁻¹) in a temperature range from 1.8 to 400 K in a SQUID magnetometer (MPMS XL-7, Quantum Design) on polycrystalline samples (m ≈ 20 mg). The contribution of the glass sample holder was subtracted.

2.2.4. Scanning electron microscope

The morphology of the sample was investigated with a Philips XL 30 scanning electron microscope (SEM) (LaB₆ cathode). Energy dispersive X-ray spectroscopy (EDXS) was performed with an attached EDAX Si(Li) detector for the determination of chemical composition.

2.3. Calculation procedure

The all-electron full-potential local orbital minimal basis method ([14,15]) was used in this study. The atomic orbital-like basis functions are obtained by solving an effective Schrödinger equation, which contains the spherically averaged crystal potential and a confining potential [16]. The confining potential forces the basis functions to be more localized than the genuine atomic orbitals. The accuracy with respect to the calculation of physical quantities is comparable to that of other all-electron full-potential methods. For the presented calculations, the density functional theory [17] with the local density approximation [18] was used. We have chosen Perdew-Wang parameterization [19] for the exchange-correlation potential. The basis set for Na and Si consisted of 3s, 3p and 3d states as valence, with 2s and 2p states treated as semicore. The basis set for Ba consisted of 6s, 6p and 5d states as valence, with 5s and 5p states treated as semicore. Convergence with respect to k-points was carefully checked. The structural parameters from single-crystal diffraction data [20] were used in the calculations.

3. Results and discussion

3.1. Investigations on Na₂BaSi₄

The crystal structure of Na₂BaSi₄ (Pearson symbol oI56, space group Ima2) consists of metal cations and isolated Si₄⁺ Zintl cluster anions. Single crystals were obtained from the elements by annealing at 1073 K [21]. On the other hand, a monoclinic unit cell and a homogeneity range (Na₄₋ₓBa₂ₓ)Si₄ with x = 0.4–0.6 was found by the reaction of NaSi and BaSi₂ at 873 K [1]. Our syntheses following the latter procedure always resulted in the formation of two phases. The powder diffraction pattern of the main phase is mostly consistent with the calculated one for Na₂BaSi₄ according to the crystal structure model [21]. However, the refined lattice parameters deviate from the literature data (Table 1) and the measured intensity of the reflection (1 1 0) is much lower than expected. This reflection mainly represents the scattering power of the Ba...
position (site 4b), indicating the lower Ba occupancy on this position. The second phase shows broad reflections of low intensity and has not been further investigated yet, but a silicide with appropriately higher Ba content can be assumed.

After a second annealing in a closed Nb ampoule at 1073 K, which was also the reaction temperature in [21], the second phase was not detectable any more with XRPD. The lattice parameters are close to those previously reported (Table 1) and the Ba sites are estimated to be fully occupied, which is a further proof for the existence of a homogeneity range [1]. These findings are in accordance with a DSC experiment in a closed Nb ampoule, which showed two endothermic signals at 895 and 1314 K on heating. The signal at 895 K is weak and may be assigned to the second phase.

3.2. Oxidation of Na2BaSi4 to Na2Ba6Si46

The preparation of Na2Ba6Si46 follows a method that was recently reported for the syntheses of Na6.2Si46 and K7.0Si46 [9]. The precursor Na2BaSi4 was reacted in a closed glass reactor with gaseous HCl to Na2Ba6Si46 and metal chlorides:

\[11.5\text{Na}_2\text{BaSi}_4 + 32\text{HCl} \xrightarrow{1\text{h}, 673\text{K}} \text{Na}_2\text{Ba}_6\text{Si}_{46} + 21\text{NaCl} + 5.5\text{BaCl}_2 + 16\text{H}_2.\]

Gaseous HCl was obtained from NH4Cl, which is completely decomposed to HCl and NH3 under reaction conditions [22,23]. Gaseous NH3 and H2 have no significant influence on the oxidation of the precursor (see also [9]).

For the oxidation route, the homogeneity range of (Na,Ba)xSi4 was found to have no influence on the composition of the final product according to XRPD data. In contrast to the thermal decomposition of Na2BaSi4, no BaSi2 is formed [1]. During the thermal decomposition of Na2BaSi4 mainly Na is evaporated so that the Ba content in the precursor (Ba:Si = 1:4) is too high to form a single-phase clathrate Na2Ba6Si46 (Ba:Si = 1:7.7) and as a result BaSi2 is always formed as a by-product.

After dissolving NaCl and BaCl2 with water, Na2Ba6Si46 was obtained as gray, fine crystalline powder with particle sizes between 1 and 100 μm (Fig. 2). Characterization by EDXS showed besides Na, Ba and Si small impurities of Cl and N (or O), which could be due to NH4Cl or metal chloride residuals. A complete quantitative analysis was not possible on unoriented powder particles. In addition, the XRPD patterns showed a small amount of a clathrate-II silicide (Na,Ba)xSi136 as a by-product together with the main-phase Na2Ba6Si46 (Fig. 3).
3.3. Crystal structure determination

The atomic parameters of the clathrate-I structure (Pearson symbol cP54, space group Pn\bar{3}m) and the composition Na1.94(1)Ba6.06(1)Si46 have been obtained from XRPD data by Rietveld analysis (Tables 2 and 3). The profile fit was affected by the small amount of the by-product (Na,Ba)Si136 with clathrate-II structure (Fig. 3).

The structure refinement revealed fully occupied Si sites and regular atomic displacement parameters. The sites of the metal atoms are fully occupied as well. A stable structure refinement could only be achieved with a mixed occupancy of the metal site in the pentagonal dodecahedral Si20 cage (SOF(Na) = 0.970(6); SOF(Ba) = 0.030).

The refined composition is equal to the ideal one within 5 e.s.d. We consider the composition of the compound as Na2Ba6Si46.

3.4. Crystal structure of Na2Ba6Si46

The clathrate-I structure type of Na2Ba6Si46 is related to the Cr3Si type, in which the Na atoms occupy the vertices, the Ba atoms the faces and the Si atoms all tetrahedral voids of the cubic unit cell [20,24]. The Na atoms are located in pentagonal dodecahedra [Na@Si20] and the Ba atoms in tetrakaidecahedra [Ba@Si24] of the framework formed by four-bonded Si atoms (Fig. 4).

The Si20 atoms (site 16i, Schläfli symbol 56) contribute only to Si5 rings and the Si24 tetrahedra show ideal tetrahedral angles. The tetrahedra centered on Si1 atoms (6c, 562) and Si3 atoms (24k, 56) contribute also to planar Si6 rings of the Ba@Si24 polyhedra and therefore show distinct deviations from the ideal tetrahedral angle.

The valence electrons of the metal atoms in silicon clathrates are mostly transferred to antibonding states of the Si46 net. The reduced bond order is indicated by the expansion of the Si–Si bond lengths, which are for Na2Ba6Si46 in the range of \( d(Si–Si) = 2.317(6)–2.499(9) \) Å with a mean value \( \bar{d}(Si–Si) = 2.385(3) \). For all clathrate-I silicides, the distances within the planar Si6 rings \( d(Si1–Si3) \) and \( d(Si3–Si3) \) are larger than \( d(Si–Si) = 2.35149(7) \) Å [25] in \( a\)-Si (Table 4). Especially the 12 \( d(Si3–Si3) \) bonds per unit cell are unusually long. Compared with electronic influence, the volume of the filling metal atoms has a minor influence because of the large cavity volume of the Si20 and Si24 cages.

The lattice parameter of 10.281(1) Å is close to the value determined for a single crystal of the composition Na2.0Ba6.0Si46 (\( a = 10.275(1) \) Å) [20]. However, both values are larger than \( a = 10.26(1) \) Å, which was found for Na2Ba6Si46 obtained by thermal decomposition [1,2]. In order to explain these different results, the product from the oxidation reaction was exposed to a static vacuum of...
10^{-2} \text{ mbar for 2 h at 753 K. Sodium evaporated and the lattice parameter decreased substantially from 10.281(1) to 10.265(1) Å. This is within standard deviation the value obtained for the product in [1], which might also have a lower content of Na as it was reported for compounds Na_{x}Ba_{6}Si_{46} (0.2 < x < 1.5) [3].

3.5. Electronic structure of Na_{2}Ba_{6}Si_{46}

The starting point for the analyses of the electronic structure of Na_{2}Ba_{6}Si_{46} was calculations on an empty clathrate $\square_8$Si_{46} [26–28]. We used a $k$-mesh of 12 $\times$ 12 $\times$ 12 in the full Brillouin zone (which gives 84 irreducible $k$-points). The band gap of $\square_8$Si_{46} was found to be 1.63 eV.

In a rigid band approach for Na_{2}Ba_{6}Si_{46} based on this calculation, the conduction bands of $\square_8$Si_{46} would be filled by 14 electrons of 2 Na and 6 Ba atoms. The density of states (DOS) at the Fermi level would then have a value of $N(E_F) = 35 \text{ states/eV}$. It was reported [29] that the DOS at the Fermi level for Na_{2}Ba_{6}Si_{46}, $N(E_F) = 47.9 \text{ states/eV}$, was notably larger than the value obtained from a rigid band approach. This high value was supposed to play an important role for the superconductivity in Na_{2}Ba_{6}Si_{46} [3,29].

Our calculations on Na_{2}Ba_{6}Si_{46} are based on structure parameters from single crystal structure data [20]. Both 12 $\times$ 12 $\times$ 12 and 16 $\times$ 16 $\times$ 16 meshes (165 irreducible $k$-points) were used to make sure that features in DOS are well converged. $N(E_F)$ has values of 24.5 and 24.8 states/eV, respectively, for 12$^3$ and 16$^3$ meshes. This is approximately two-thirds of the value expected from the rigid band approach and roughly half of the value reported in [29]. Our value is in good agreement with the estimate ($N(E_F) = 18 \text{ states/eV}$) based on NMR data [30].

A comparison of the DOS of Na_{2}Ba_{6}Si_{46} and $\square_8$Si_{46} shows that the fully occupied states are the same in both clathrates (Fig. 5). For both cases, the highest-lying fully occupied valence band has a bandwidth of 3.2 eV, the lower one 7.1 eV and the gap between the two is about 0.65 eV. Even the pseudo-gap inside the lower band at around $-7.5 \text{ eV}$ is preserved.

The hybridization between the states of the filler atoms and the Si_{46} framework modifies mainly the conduction bands. In Na_{2}Ba_{6}Si_{46}, the gap below the partially filled conduction band is only 0.64 eV. Thus, the hybridizations in Na_{2}Ba_{6}Si_{46} reduce the gap by approximately 1.0 eV compared with $\square_8$Si_{46} (Fig. 5). Analyses of the compositions of the electron energy bands reveal that in addition to already reported contributions of Ba $5d$ states [29], Na $3s$ basis functions contribute to various bands in the energy range $-1$ to 1 eV, including some of the bands crossing the Fermi level. This finding is in agreement with the analyses based on NMR experiments [3,30–32].

3.6. Physical properties of Na_{2}Ba_{6}Si_{46}

Magnetic susceptibility measurements of Na_{2}Ba_{6}Si_{46} obtained by oxidation with HCl revealed a temperature-independent Pauli-paramagnetic behavior with $\gamma_0 \approx 1.2 \times 10^{-3} \text{ emu mol}^{-1}$, as it is expected for a metallic compound (Fig. 6). A ferromagnetic impurity of less than 4 ppm was detected (calculated for elemental Fe). Only a negligibly small part (less than 0.1%) of the sample shows superconductivity in a field of 20 Oe (1.592 $\times$ 10^{5} A m^{-1}) at
$T_c = 3.3 \text{K}$, in both field-cooling and zero-field cooling runs. Superconductivity is therefore not the intrinsic property of Na$_2$Ba$_6$Si$_{46}$ obtained by oxidation with HCl and may be caused by impurity phases. This is in contradiction to the results of Kawaji et al. [2,3], who found bulk superconductivity for (Na,Ba)$_6$Si$_{46}$.

Since $T_c$ of Na$_{3.2}$Ba$_6$Si$_{46}$ has been reported to decrease with increasing Na content [3], the critical temperature of the composition Na$_2$Ba$_6$Si$_{46}$ might be out of the measurement range ($T_{\text{min}} = 1.8 \text{K}$). Further investigations on the different magnetic behavior of samples obtained by oxidation with HCl and by thermal decomposition are required.

3.7. Thermal behavior of Na$_2$Ba$_6$Si$_{46}$

DSC measurements in closed Nb ampoules revealed the metastable character of Na$_2$Ba$_6$Si$_{46}$. An exothermic effect runs. Superconductivity is therefore not the intrinsic property of Na$_2$Ba$_6$Si$_{46}$ obtained by oxidation with HCl and by thermal decomposition are required.

4. Conclusions

Na$_2$Ba$_6$Si$_{46}$ was synthesized in high yield by oxidation of Na$_3$BaSi$_4$ with gaseous HCl. Precursors of slightly different compositions always lead to the same reaction product. The novel synthesis route, first applied for the binaries Na$_6.2$Si$_{46}$ and K$_7.0$Si$_{46}$, was extended to a ternary compound, demonstrating the general applicability of the method. The short reaction times and the scalability to large amounts of material make a production of intermetallic clathrates for technical application conceivable.

Na$_2$Ba$_6$Si$_{46}$ obtained by oxidation with HCl shows no structural defects in the Si framework, and the cages are completely filled with Na and Ba atoms. The metastable compound decomposes at 874 K in a closed Nb ampoule. Differently from previously obtained products from thermal decomposition, we found Na$_2$Ba$_6$Si$_{46}$ obtained by oxidation with HCl not to be superconducting. The origin of this difference will be further investigated.

Band structure calculations have shown that besides Ba 5$d$ states Na 3$s$ states also contribute to bands in the vicinity of the Fermi level. The calculated value of DOS at Fermi level is about 25 states/eV.

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