Precursor Routes to Quaternary Intermetallics: Synthesis, Crystal Structure, and Physical Properties of Clathrate-II $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$

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ABSTRACT

A new quaternary clathrate-II composition, $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$, was synthesized by kinetically controlled thermal decomposition (KCTD) employing both NaSi and NaAlSi as the precursors and CsCl as a reactive flux. The crystal structure and composition of $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$ were investigated using both Rietveld refinement and elemental analysis, and the temperature dependent transport properties were investigated. Our results indicate that KCTD with multiple precursors is an effective method for the synthesis of multinary inorganic phases that are not easily accessible by traditional solid-state synthesis or crystal growth techniques.

Keywords: quaternary clathrate-II, crystal synthesis, transport properties

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INTRODUCTION

Group 14 based intermetallic clathrates are of interest due to their unique structural and physical properties.[1-5] The crystal structure of binary compositions A_8E_{46} and $A_{24}E_{136}$ (where A is an alkali, alkaline earth, or lanthanide and E is Si, Ge, or Sn) can be thought of as a 3-dimensional framework of face sharing E_{20} dodecahedra and E_{24} tetrakaidecahedra, and E_{20} dodecahedra and E_{28} hexakaidecahedra, for the case of clathrate-I A_8E_{46} and clathrate-II $A_{24}E_{136}$, respectively, inside of which the A “guest” atoms reside.[1-5] Framework substitution by triel elements (group 13) or transition metals in clathrate-I compounds is readily possible and ternary clathrate-I compounds exhibit metallic, semiconducting, superconducting, or insulating behavior depending on the substitutional atom, the occupation fraction of the group 14 atoms and vacancies, if any, on the framework.[3-6] Clathrate-I compositions have been investigated as potential thermoelectric materials in addition to a variety of other technological applications including photovoltaics, magnetocalorics and superconductivity;[1,4,7-12] however, investigations on clathrate-II compositions are rare due to the difficulty in processing clathrate-II compositions in bulk form.[4] With few exceptions,[13-17] silicon clathrate-II compositions do not readily form by direct reaction of the elements. To overcome the limited access provided by conventional synthetic methods and obtain thermodynamically metastable, or otherwise difficult to access compositions, a variety of new synthetic techniques have been developed.[4] One such method, kinetically controlled thermal decomposition (KCTD), allows for the selective crystal growth of different clathrate structure types from appropriate alkali-metal precursors and reaction temperatures.[18,19] Another synthetic approach employs spark plasma sintering (SPS) whereby a pulsed DC current is the primary driver of the reaction.[20,21] A third approach

employs a cold plate in providing the lowest possible Na vapor pressure.[22] Very recently SPS was extended for the synthesis of ternary clathrates employing more than one precursor.[23]

In this study we employ KCTD to synthesize the quaternary clathrate-II composition $\text{Ca}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$ using NaSi and NaAlSi as precursors along with CsCl as the reaction flux. Although framework doped Si-based clathrate-I compositions have been investigated for thermoelectrics applications,[24-27] due to their lower weight and cost as compared to Ge-based clathrates for vehicle waste-heat recovery applications for example, this is the first report in which a clathrate-II composition is investigated with similar interests in mind. The structural and compositional characterization as well as transport properties of $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$ are discussed.

EXPERIMENTAL

All preparations were carried out in a N_2 -filled glove box to prevent oxidation of the elements. Elemental Al shot (99.999 %, Alfa Aesar) and Si in lump form (99.9999 %, Alfa Aesar) were first combined in the appropriate atomic ratio and arc melted in order to obtain an intimate mixture of the elements (and the resulting precursor phases). The resulting heterogeneous Al-Si mixture was ground into fine powder and loaded into a tungsten crucible together with Na (99.95 %, Aldrich) in the appropriate stoichiometric ratio ($24\text{Al}-112\text{Si} + 112\text{Na} \rightarrow 24\text{NaAlSi} + 22\text{Na}_4\text{Si}_4$). This crucible was then loaded into a sealed stainless steel canister, placed inside a quartz tube that was subsequently sealed under vacuum, and reacted at 923 K for 24 h. The resulting product was ground thoroughly and used as the precursor in KCTD reactions.

In order to prepare the silicon clathrate-II compound with nominal composition $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$, the NaSi + NaAlSi precursor mixture was ground together with CsCl (99.999 %, Acros) and synthesized by KCTD [18] at 1023 K for 9h under a dynamic vacuum of

10^{-6} Torr to obtain the pure Si quaternary clathrate-II compound in microcrystalline form. After reaction the product was washed with ethanol and distilled water before drying in air (CAUTION: NaSi can react violently with water).[21] Consolidation of the microcrystalline powders was accomplished at 623 K and 400 MPa for 10 minutes under vacuum (10^{-3} Torr) by SPS using a custom-designed WC die assembly with a pulsed DC current on : off ratio of 4:1. After densification the current and pressure were released and the WC tooling was cooled to room temperature under vacuum. The density of the polycrystalline pellet was approximately 80 % of the theoretical density from measurement of its dimensions and weight after polishing the surfaces of the pellet.

Powder X-ray diffraction (PXRD) data were collected with a Bruker D8 Advance diffractometer equipped with a Lynxeye detector using Cu K_{α} radiation. Structure refinements were accomplished by the Rietveld method using the GSAS suite of programs.[28,29] Energy dispersive X-ray (EDX) analysis was accomplished with an Oxford INCA X-Sight 7582 M equipped scanning electron microscope (SEM, JEOL JSM-6390LV). PXRD and EDX were used to examine the purity and chemical composition of the specimen. Optical diffuse reflectance measurements were performed at room temperature using a JASCO V-670 UV-Vis double beam spectrophotometer equipped with a 60 mm diameter integrating sphere. Reflectance data were collected in the wavelength range of 200 ~ 2700 nm. Thermal Gravimetric (TG) and Differential Thermal Analyses (DTA) measurements were carried out with a SDT Q600 (TA instruments) under N_2 flow with the specimen heated from 293 K to 1073 K at a rate of 10 K/min.

The densified $Cs_8Na_{16}Al_{24}Si_{112}$ specimen was cut into 2 mm $\times$ 2 mm $\times$ 5 mm parallelepipeds using a wire saw for temperature dependent four-probe ρ , S (gradient sweep method), and steady-state κ measurements from 300 K to 12 K. The measurements were conducted in a

custom radiation-shielded vacuum probe with uncertainties of 4%, 6%, and 8% for ρ , S , and κ measurements, respectively.[30] Electrical contacts to the specimens were made by soldering directly to nickel-coated surfaces using standard techniques, and thermal contacts were made using Stycast epoxy. All measurements were performed perpendicular to the pressing direction.

RESULTS AND DISCUSSION

KCTD reactions of NaAlSi + NaSi with CsCl were investigated at different temperatures, from 773 K to 1073 K, in order to obtain the temperature for optimal yield and purity. Clathrate-II forms at all temperatures, however, NaAlSi was an impurity at lower reaction temperatures (from 773 K to 973 K), the amount of the impurity decreasing with increasing temperature. For KCTD reactions over 1073 K the product decomposed to α -Si. Phase-pure Cs₈Na₁₆Al₂₄Si₁₁₂ was obtained at 1073 K. Figure 1 shows the PXRD of Cs₈Na₁₆Al₂₄Si₁₁₂ together with those of Na₂₄Si₁₃₆ [18] and Cs₈Na₁₆Si₁₃₆ [23] for comparison. Figure 2 shows the Rietveld analysis of Cs₈Na₁₆Al₂₄Si₁₁₂, the partial crystal structure is illustrated in Figure 3, and the crystallographic details are given in Table 1. The refined unit cell of Cs₈Na₁₆Al₂₄Si₁₁₂ ($a = 14.915(3)$ Å) is larger than that of Na₂₄Si₁₃₆ ($a = 14.7121(1)$ Å) [18] and Cs₈Na₁₆Si₁₃₆ ($a = 14.7564(4)$ Å) [23], as expected when Al is incorporated into the framework. Cs₈Na₁₆Al₂₄Si₁₁₂ is cubic (space group $Fd\bar{3}m$) with Cs and Na atoms occupying the crystallographic $8b$ and $16c$ sites, respectively. It is difficult to quantify the exact location of Al on the framework from PXRD data however our refinement results indicate Al to be on all three framework crystallographic sites. Site occupancy refinements for both the alkali and framework indicate full occupancy of all crystallographic sites, with good refinement results obtained for Al / Si ratio values of 0.2 / 0.8 for $8a$, 0.1 / 0.9 for $32e$, and 0.2 / 0.8 for $96g$ site. The bond distances between framework atoms are very close

to those of $A_8Al_8Si_{38}$ ($A = Na, K, Rb, Cs$) [27,31] and longer than those of $Na_{24}Si_{136}$ ($2.3578(3) \sim 2.3976(6) \text{ \AA}$), [18] $Cs_8Na_{16}Si_{136}$ ($2.360(1) \sim 2.393(1) \text{ \AA}$), [23] and elemental Si ($2.368 \text{ \AA}$). This is an indication that the larger Al atoms (CN=4 and an effective ionic radius of $0.53 \text{ \AA}$, as compared to Si with CN=4 and an effective ionic radius of $0.40 \text{ \AA}$) [32] are on the framework. Table 2 gives the values of the atomic coordinates, equivalent isotropic parameters (U_{eq}) and selected bond distances are given in Tables 3. From TG/DTA analyses $Cs_8Na_{16}Al_{24}Si_{112}$ decomposes to $CsAlSiO_4$ and α -Si above 773 K. The UV-Vis diffuse reflectance spectrum does not show any absorption edge in the entire measured range, from 200 to 2700 nm, indicating that either the band gap is small or that the compound is metallic.

Figure 4 shows SEM images and EDX elemental mapping images of $Cs_8Na_{16}Al_{24}Si_{112}$. Elemental analysis (Figures 4(b) and 4(c)) of a cross section of the polycrystalline densified pellet (Figure 4(a)) shows uniform distribution of each element. The composition obtained by EDX analysis gives a Cs/Na/Al/Si atomic percent ratio of 4.9(1):12.5(5):13.0(3):69.6(8) (averaging data acquisitions from eight different points on the specimen), close to the target composition $Cs_8Na_{16}Al_{24}Si_{112}$ (5:10:15:70).

The temperature dependent ρ , S , and κ are shown in Figure 5. The modulus of S increases linearly with increasing temperature throughout the measured temperature range while the ρ values increase with increasing temperature above 75 K. The measured room temperature S ($-32 \mu V / K$) is smaller than that of $A_8Al_8Si_{38}$ ($A = K, Rb, Cs$) [31] but comparable to that of other Al containing clathrate-I compounds such as $Na_8Al_8Si_{38}$ ($-22 \mu V / K$), [20] $Ba_8Al_{14}Si_{31}$ ($-21 \mu V / K$) [33] and $Ba_8Al_{16}Si_{30}$ ($-48 \mu V / K$). [34] The relatively low density of our polycrystalline specimen, resulting in relatively high ρ values throughout the measured temperature range, illustrates the difficulty in densifying alkali-encapsulated Si-based clathrates, as is the case for

alkali-encapsulated Si-based clathrate-I compositions. [26,27] Although our refinement and EDX results do not allow us to quantify the aluminum content precisely, our electrical transport data suggest that the Al content is less than the target $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$ content. Semiconducting behavior is expected for $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$, from simple crystal chemistry arguments, however deviation from this stoichiometry will result in a metallic S and ρ temperature dependence, as shown in Figure 5. The measured κ values are shown in Figure 5 and increase up to 200 K after which point they decrease with increasing temperature. This behavior is similar to that of $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ [35] and $\text{Na}_{24}\text{Si}_{136}$, [36] however, our κ values are much smaller than that of these two compositions. Using the measured ρ values and the Wiedemann-Franz relation ($\kappa_E = L_0 \sigma T$ where $L_0 = 2.45 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$ and $\sigma = 1/\rho$), the electronic contribution, κ_E , to κ was estimated to be relatively small.

CONCLUSION

A quaternary intermetallic silicon clathrate-II compound was synthesized by KCTD by employing a precursor that was a mixture of NaSi and NaAlSi together with the alkali metal halide CsCl. This is the first time a clathrate-II Al-Si framework composition is reported. Structural refinement indicates full occupancy of the framework and that Cs and Na reside at the crystallographic $8b$ and $16c$ sites, respectively. The framework bond distances, as well as PXRD refinement and elemental analysis, indicate that Al atoms are present on the framework sites. Transport and solid state UV-Vis diffuse reflectance measurements show semimetallic behavior with electron conduction. Our results indicate that the KCTD synthetic method can be employed for the synthesis of multinary inorganic clathrate phases that cannot be accessible by traditional crystal growth techniques.

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Table 1. Crystallographic details.

Space group, Z	$Fd \bar{3} m$ (#227), 1
a, Å	14.915 (3)
V, Å ³	3328 (2)
Diffractometer	Bruker D8 Advance
Radiation	Cu K α (1.54056 Å)
T (K)	298
D _{calc.} , g/cm ³	2.615
θ limits, deg.	7.5 to 50
Reduced χ^2	3.34
R _p , wR _p	0.0577, 0.0795
Goodness-of-fit on F ²	1.83

$$wR_p = ((\sum w(I_o - I_c)^2 / \sum w I_o^2)^{1/2} \text{ and } R_p = \sum |I_o - I_c| / \sum I_o$$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å²).

Atoms	Wyckoff sites	x	y	z	occupancy	U _{iso}
Cs	8b	0.3750	0.3750	0.3750	1	0.028 (4)
Na	16c	0	0	0	1	0.040 (5)
Si1/Al1	96g	0.0670 (1)	0.0670 (1)	0.3706 (2)	0.8 / 0.2	0.016 (4)
Si2/Al2	32e	0.2185 (2)	0.2185 (2)	0.2185 (2)	0.9 / 0.1	0.005 (4)
Si3/Al3	8a	0.1250	0.1250	0.1250	0.8 / 0.2	0.007 (4)

Table 3. Selected bond distances (Å).

Cs – Si1 / Al1	3.987 (3) x 12	Na – Si1 / Al1	3.418 (2) x 12
Cs – Si1 / Al1	4.051 (2) x 12	Na – Si2 / Al2	3.326 (3) x 6
Cs – Si2 / Al2	4.043 (6) x 4	Na – Si3 / Al3	3.229 (1) x 2
Si1 / Al1 – Si1 / Al1	2.398 (3) x 2	Si2 / Al2 – Si1/Al1	2.389 (4) x 3
	2.445 (4)	Si2 / Al2 – Si3/Al3	2.415 (6)
Si1 / Al1 – Si2 / Al2	2.389 (4)	Si3 / Al3 – Si2 / Al2	2.415 (6) x 4

Figure Captions

Figure 1. PXRD pattern for $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$ compared with simulated patterns of $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$ and $\text{Na}_{24}\text{Si}_{136}$. The red vertical line is intended to illustrate shift in the $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$ peaks relative to $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$ and $\text{Na}_{24}\text{Si}_{136}$.

Figure 2. PXRD data for $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$ including profile fit (black cross mark), profile difference (red line), profile residuals (blue line), and Bragg positions (purple ticks) from Rietveld refinement.

Figure 3. Partial crystal structure of $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$ illustrating all the crystallographic sites and their local environments. Cs (8b) and Na (16c) reside at the center of dodecahedron and hexakaidecahedron, respectively. Si and Al are on all three framework sites (8a, cyan; 32e, red; and 96g, blue). Atomic displacement parameters are shown for 90% probability.

Figure 4. (a) SEM image of a cross section and (b) elemental analysis from this cross sectional area with the magnified SEM image of the area represented by a red square in (a) as the inset. (c) EDS elemental mapping images of the SEM image in (a).

Figure 5. Temperature dependent (a) ρ and (b) S , and (c) κ .

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

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Quaternary $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$ clathrate-II was synthesized for the first time by kinetically controlled thermal decomposition (KCTD) employing a $\text{NaSi} + \text{NaAlSi}$ precursor mixture with CsCl as the reactive flux, and the structural and transport properties were investigated. Our approach demonstrates a new synthetic pathway for the synthesis of multinary inorganic compounds. This work reports the exploration of a new clathrate composition as this class of materials continues to be of interest for thermoelectrics and other energy-related applications.

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