Synthesis and Structural Properties of Type I Potassium SiGe Alloy Clathrates

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We report on the synthesis and structural characterization of type I SiGe alloy clathrates, with potassium as the guest species, synthesized by thermal decomposition and kinetically controlled thermal decomposition from $K_4(\text{Si}_{1-x}\text{Ge}_x)_4$ precursor phases with $x = 0.1, 0.3$, and 0.75 . The $K_8(\text{Si}_{1-x}\text{Ge}_x)_{46}$ clathrates were structurally characterized by X-ray diffraction. Rietveld refinement on the XRD data indicated that Ge preferentially occupies the $24k$ and $6c$ sites for $x < 0.5$ but preferentially occupies the $16i$ and $24k$ sites for $x > 0.5$.

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1. Introduction

Inorganic clathrate compounds have open-framework crystal structures wherein the host framework encapsulates “guest” species. Typically, the framework is made up of Group 14 elements (X) with interstitial elements (A) made up of alkali, alkaline earth, rare-earth, tellurium, and halogen elements [1]. Due to their chemical diversity and structural features clathrates are of interest for a diverse range of potential applications, including thermoelectrics [2], superconductors [3], photovoltaics [4,5], and lithium-ion batteries [6].

The type I clathrate unit cell can be thought of as being formed by two different types of polyhedra, two 24 atom and six 20 atom polyhedron, resulting in an A_8X_{46} stoichiometric composition. Type I Si and Ge clathrates encapsulating potassium guest atoms, K_8Si_{46} and K_8Ge_{44} , are most commonly synthesized by thermal decomposition of the precursor phase K_4Si_4 and Ke_4Ge_4 , respectively [7-9]. Recently Stefanoski *et al.* reported the single crystal growth of both type I and II silicon clathrates with potassium guest atoms by kinetically controlled thermal decomposition [10,11]. In this technique the alkali metal vapor formed during the thermal decomposition process is absorbed by a graphite layer that modifies the local vapor pressure to control the reaction kinetics. Oxidation of the precursor K_4Ge_9 was also used to synthesize type II Ge clathrates [12]. Alloyed SiGe clathrates are of fundamental interest as they allow for (a) modifying the band structure and that could result in tuning the electrical properties [13] and (b) enhancement of thermoelectric properties [14]. Synthesis of alloyed SiGe clathrates encapsulating alkali or alkaline earth guest have been reported [1, 4, 15, 16]. Prior work on type I alloyed SiGe clathrates has investigated variation in thermoelectric performance as a result of framework alloying [14, 16-18], however, the SiGe alloying fraction was varied only over a narrow range. Ramachandran et al. reported on synthesis of 50 at.% SiGe alloyed clathrate with

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4 potassium guest via thermal decomposition of Zintl precursor phase but the resulting clathrate
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6 had poor crystallinity [15] . In this work we report on the synthesis of three new compositions of
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8 alloyed SiGe type I clathrates ($K_8(Si_{1-x}Ge_x)_{46}$ with $x=0.1, 0.3$ and 0.75) from Zintl precursor
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10 phases $K_4(Si_{1-x}Ge_x)_4$ by thermal decomposition and kinetically controlled thermal decomposition
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12 process and perform structural characterization. The Si-Ge tetrahedrons in these precursors
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14 presumably allow for clathrate formation [16] as is the case of $[Si_4]^{4-}$ in Na_4Si_4 for silicon
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16 clathrate formation [1].
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25 The $Si_{1-x}Ge_x$ diamond phase alloys were synthesized by mechanical alloying stoichiometric
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27 amounts of silicon (Alfa, 99.9999 %) and germanium (Alfa, 99.9999%) as described in
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29 Baranowski *et al* [4]. For the preparation of the Zintl precursors, $K_4(Si_{1-x}Ge_x)_4$, elemental
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31 potassium and ball milled $Si_{1-x}Ge_x$ alloys were weighed in 1.4: 1 molar ratio, placed in a ceramic
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33 crucible, covered with aluminum foil and subsequently placed in a quartz tube before heated to
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35 395 °C for 24 h under flowing Ar. The precursor synthesis technique employed in this work was
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37 relatively simple and achieved without need of sealing the crucible (typically tantalum or
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39 niobium) containing the potassium plus $Si_{1-x}Ge_x$ mixtures. Extreme care should be taken while
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41 handling elemental potassium and the precursors as they are air and moisture sensitive. The
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43 thermal decomposition of the precursor, to the clathrate phase, was accomplished by heating at
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45 395 °C for 48 h under dynamic vacuum (~ 1 m Torr). Details of the kinetically controlled thermal
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47 decomposition technique can be found in Ref. 10. In this technique, the precursor ($K_4(Si_{1-x}Ge_x)_4$)
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49 is sandwiched between two layers of graphite flakes, subjected to uniaxial pressure and heated to
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51 undergo thermal decomposition to clathrate phase. NaCl is used between the precursor and the
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53 graphite flake to prevent adhesion of the clathrate crystals to the flake and to allow alkali metal
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4 to be transported in the vapor phase [10]. Here $K_4(Si_{1-x}Ge_x)_4$ with $x = 0.1, 0.3$, and 0.75 were
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6 heated to 550°C for 8h, 530°C for 8h, and 485°C for 5h, respectively, to obtain the type I alloy
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8 clathrates. After decomposition process, all the samples were washed with ethanol to remove any
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10 residual potassium. Extreme caution should be taken while washing the sample with ethanol and
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12 this process should be carried out in an inert atmosphere. The final clathrate compounds are
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14 stable in air.
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20 The phase purity and crystal structure of the specimens were determined by powder X-ray
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22 diffraction (XRD) at room temperature by a Bruker D8 Focus diffractometer in Bragg-Brentano
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24 geometry using $\text{Cu K}\alpha$ radiation and a graphite monochromator. The XRD patterns were
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26 obtained between 10° and 100° in steps of 0.01° with a counting rate of 1° per minute. Rietveld
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28 refinement was accomplished using the GSAS suite of programs [21]. The initial positional
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30 parameters were obtained from the data previously reported for K_8Si_{46} [22]. For refinement of
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32 the SiGe alloy clathrates, the Si plus Ge occupancy was constrained to 1 for each of the three
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34 framework sites ($6c$, $16i$, $24k$).
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41 **3. Results and Discussion**

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43 The measured and simulated XRD patterns and the difference profiles for the clathrates
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45 prepared by thermal decomposition are shown in Fig. 1 and the refinement parameters are listed
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47 in Table 1. XRD patterns for the alloyed precursors are provided in the supplementary section.
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49 Alloys synthesized by conventional thermal decomposition and kinetically controlled thermal
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51 decomposition process are labelled a to e and a1 to c1, respectively. Phase pure $K_8Si_{17.6}Ge_{28.4}$ (d)
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53 was obtained, K_8Si_{46} (a) and $K_8Si_{41.3}Ge_{4.7}$ (b) contained trace amounts of α -Si, $K_{6.9}Si_{28.5}Ge_{17.5}$ (c)
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55 contained $\sim 10\text{wt}\%$ α -Si plus a trace amount of an unidentified phase, and K_8Ge_{44} (e) contained
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amorphous phase. All atomic positions are fully occupied for K_8Si_{46} (a) while vacancies exist on the framework 6c site for K_8Ge_{44} (e), consistent with that of previous reports [9, 23]. Rietveld refinements were carried out to investigate the presence of Ge framework vacancies in alloyed SiGe clathrates. But this could not be definitely answered from the conventional XRD data. Hence we constricted the Si plus Ge occupancy to be one. For $\text{K}_8\text{Si}_{41.3}\text{Ge}_{4.7}$ (b), the Si-to-Ge ratio was close to that of the precursor while $\text{K}_{6.9}\text{Si}_{28.5}\text{Ge}_{17.5}$ (c) and $\text{K}_8\text{Si}_{17.6}\text{Ge}_{28.4}$ (d) had a higher and lower Ge content, respectively, than that of the precursors. As in other clathrate compounds [24-26], preferential site occupancy was observed. The refinement results indicate that germanium preferentially occupies the 24k and 6c sites when the Ge content was below 50% and the 16i and 24k site when the Ge content was above 50%. We also note vacancies at the 2a site for $\text{K}_{6.9}\text{Si}_{28.5}\text{Ge}_{17.5}$, as previously reported for other potassium-containing clathrates [23, 27]. The SiGe alloy clathrates were also synthesized by kinetically controlled thermal decomposition. The XRD patterns and refinement results are shown in Fig. 2 and Table 1, respectively. The Si-to-Ge ratios of the clathrate phases are closer to that of the precursors and the site occupancy for the Si/Ge framework follows the same trend as that exhibited by the clathrates prepared by thermal decomposition (Table 1). The $\text{K}_{7.6}\text{Si}_{14.9}\text{Ge}_{31.1}$ (c1) specimen also contained amorphous phase. The lattice constants with Ge concentration for all clathrates compounds are shown in Fig. 3 and obey Vegard's law, exhibiting a linear increase with increasing germanium content. The two compounds with vacancies on the K 2a site deviate slightly from Vegard's law (Fig. 3). Note that in order to investigate the presence of framework vacancies on alloyed clathrates further experimental characterization is warranted.

4. Conclusions

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4 A relatively low temperature, high-yield synthesis technique to synthesize $K_4(Si_{1-x}Ge_x)_4$
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6 precursors from elemental K and $Si_{1-x}Ge_x$ was used to synthesize SiGe alloy type I clathrates.
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8 Thermal decomposition and kinetically controlled thermal decomposition were used to
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10 synthesize K containing SiGe type I clathrates. The alloy clathrate compositions have lattice
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12 parameters in between that of the pure silicon and germanium clathrate phases and generally
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14 obey Vegard's law with slight deviations in the case of potassium vacancies. Germanium shows
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16 preferential framework site occupancy. When the Ge concentration was less than 50 %, 24*k* and
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18 6*c* sites are preferred and when greater than 50 %, the 16*i* and 24*k* sites are preferred. The
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20 kinetically controlled thermal decomposition yields alloy clathrates with Si-to-Ge ratios closer to
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22 that of the precursors.
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39 structural refinement, and synthesis employing kinetically controlled thermal decomposition.
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Table 1. Rietveld refinement results for the type I $K_8(Si_{1-x}Ge_x)_{46}$ clathrates synthesized for this study.

Thermal Decomposition					
Precursor	KS _i	KS _i _{0.9} Ge _{0.1}	KS _i _{0.7} Ge _{0.3}	KS _i _{0.25} Ge _{0.75}	KGe
Nominal composition	K ₈ Si ₄₆	K ₈ Si _{41.4} Ge _{4.6}	K ₈ Si _{32.2} Ge _{13.8}	K ₈ Si _{11.5} Ge _{34.4}	K ₈ Ge ₄₆
Refined composition	K ₈ Si ₄₆	K ₈ Si _{41.3} Ge _{4.7}	K _{6.9} Si _{28.5} Ge _{17.5}	K ₈ Si _{17.6} Ge _{28.4}	K ₈ Ge ₄₄
<i>a</i> (Å)	10.2830(1)	10.3149(2)	10.3540(1)	10.5546(6)	10.6715(1)
<i>V</i> (Å ³)	1087.34(3)	1097.46(5)	1110.00(5)	1175.8(2)	1215.31(3)
Occup. K (2 <i>a</i>)	1	1	0.462(9)	1	1
Occup. K (6 <i>d</i>)	1	1	1	1	1
Occup. Si/Ge(6 <i>c</i>)	1/0	0.882(5)/0.118(5)	0.428(5)/0.572(5)	0.608(4)/0.392(4)	0/0.674(4)
Occup. Si/Ge (16 <i>i</i>)	1/0	0.985(5)/0.015(5)	0.764(5)/0.236(5)	0.505(5)/0.495(5)	0/1
Occup. Si/Ge (24 <i>k</i>)	1/0	0.843(4)/0.157(4)	0.571(5)/0.429(5)	0.246(5)/0.754(5)	0/1
R _p (%)	3.57	3.08	2.58	3.06	1.77
wR _p (%)	5.89	4.54	3.79	4.10	2.32
χ ²	5.644	4.048	3.241	4.683	1.6
Kinetically Controlled Thermal Decomposition					
Precursor	KS _i _{0.9} Ge _{0.1}	KS _i _{0.7} Ge _{0.3}	KS _i _{0.25} Ge _{0.75}		
Nominal composition	K ₈ Si _{41.4} Ge _{4.6}	K ₈ Si _{32.2} Ge _{13.8}	K ₈ Si _{11.5} Ge _{34.4}		
Refined composition	K ₈ Si _{41.4} Ge _{4.6}	K ₈ Si _{34.8} Ge _{11.2}	K _{7.59} Si _{14.9} Ge _{31.1}		
<i>a</i> (Å)	10.2935(1)	10.3598(1)	10.4680(6)		
<i>V</i> (Å ³)	1090.66(4)	1111.87(4)	1147.1(2)		
Occup. K (2 <i>a</i>)	1	1	0.80(4)		
Occup. K (6 <i>d</i>)	1	1	1		
Occup. Si/Ge(6 <i>c</i>)	0.887(4)/0.113(4)	0.642(5)/0.358(5)	0.59(2)/0.41(1)		
Occup. Si/Ge (16 <i>i</i>)	0.946(5)/0.054(5)	0.883(6)/0.117(6)	0.43(3)/0.57(3)		
Occup. Si/Ge (24 <i>k</i>)	0.871(4)/0.129(4)	0.701(4)/0.299(4)	0.19(3)/0.81(1)		
R _p (%)	2.88	2.81	2.27		
wR _p (%)	3.90	3.67	3.01		
χ ²	2.278	2.224	1.671

Fig. 1. Measured (empty circles) and simulated (solid red lines) powder XRD patterns for clathrates (a) K_8Si_{46} , (b) $\text{K}_8\text{Si}_{41.3}\text{Ge}_{4.7}$, (c) $\text{K}_{6.92}\text{Si}_{28.5}\text{Ge}_{17.5}$, (d) $\text{K}_8\text{Si}_{17.6}\text{Ge}_{28.4}$, and (e) K_8Ge_{44} synthesized by thermal decomposition. The difference between the observed and simulated plots is shown at the bottom of each pattern. Vertical tick marks represent allowed reflections. The cyan tick marks in (c) indicate peaks from α -Si.

Fig. 2. Measured (empty circles) and simulated (solid red lines) powder XRD patterns for (a1) $\text{K}_8\text{Si}_{41.4}\text{Ge}_{4.6}$, (b1) $\text{K}_8\text{Si}_{34.8}\text{Ge}_{11.2}$, and (c1) $\text{K}_{7.6}\text{Si}_{14.9}\text{Ge}_{31.1}$ synthesized by kinetically controlled thermal decomposition.

Fig. 3. Lattice constant as a function of Ge concentration for the clathrates prepared by thermal decomposition (red) and kinetically controlled thermal decomposition (blue).

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