

Preparation of Guest Free Type II Si-Ge Clathrate using Ionic Liquid Method

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Guest free Type II Si-Ge alloy clathrate exhibits tunable band gap energy depending upon the composition ratio of Si and Ge. In an attempt to synthesize guest free type II Si-Ge alloy clathrates in various Si-Ge compositions, $\text{Na}_4(\text{Si}_{1-y}\text{Ge}_y)_4$ precursors were prepared with the variation of y from 0 to 1 and then annealed in a sealed glass tube together with ionic liquid. The obtained samples were characterized by powder XRD experiments and EDX measurements. The synthesis of Si-Ge clathrates were recognized as Si or Ge rich compositions. EDX data and Rietveld analyses of XRD data allowed us to verify the Si-Ge alloy clathrate with low Na content.

1. Introduction

Type II clathrates shows the crystalline structure with sp^3 bonding network [1] in which there are cage-like voids with 5 or 6 membered common ring windows. The network is typically made of group IV elements and usually contains guest atoms such as Na, resulting in the chemical formula of $\text{Na}_{24}\text{IV}_{136}$, if all of the voids are filled with Na (IV represents group IV elements). The Na could be removed from the Si or Ge type II clathrate, leading to “guest free” Si_{136} or Ge_{136} clathrate respectively. The guest free type II clathrates are expected as new semiconductor materials [2].

In 1965, Cros *et al.* synthesized type II Si clathrate by annealing the Zintl phase compound (Na_4Si_4) in inert gas [3] and Ge type II clathrates were synthesized in a similar method in 1970 [4]. Regarding the bandgap energy of these guest-free type II clathrates, the first principle calculation have predicted the band gap values as 1.8 to 1.9 eV for Si_{136} [5,6,7], 0.81 to 1.45 eV for Ge_{136} [8,9,10]. However, alloy clathrates expected to exhibit wide range of tunable band gap energy from 1.2 to 2.0 eV [11] with the variation of Si/Ge ratio. Recently, type II Si-Ge alloy clathrates $\text{Na}_x(\text{Si}_{1-y}\text{Ge}_y)_{136}$ were synthesized over the whole range of Si/Ge by heat treatment of $\text{Na}_4(\text{Si}_{1-y}\text{Ge}_y)_4$ precursor under vacuum [12]. However, the synthesized clathrates still contained Na inside the cages with $x = 1 - 5$ in $\text{Na}_x(\text{Si}_{1-y}\text{Ge}_y)_{136}$. Therefore, the synthesis of guest free Si-Ge alloy clathrate is essential for further application of these materials in the semiconductor devices. Guloy *et al.* [11] have proposed an effective method using ionic liquid to realize the guest free Ge clathrate.

The aim of this study includes the synthesis of type II guest free Si-Ge alloy clathrates by ionic liquid method and its characterization by powder X-ray diffraction (XRD) experiment, Rietveld analysis, EDX measurement etc.

2. Experimental details

Guest free type II Si-Ge alloy clathrate ($\text{Na}_x(\text{Si}_{1-y}\text{Ge}_y)_{136}$ ($x < 1$)) was produced by the following a three-step procedure. At first, a mixture of Si (Nilaco, 99.999%), Ge (Nilaco, 99.999%) and sodium



hydride (NaH) [14] powder (Sigma-Aldrich, 90%) was packed in a BN-crucible and sealed in a stainless container. This operation is carried out in a glove box filled with dry Ar. Then the container was heated at 650 °C for 48 h or 750 °C for 24 h, and the precursor ($\text{Na}_4(\text{Si}_{1-y}\text{Ge}_y)_4$ ($y = 0 - 1$)) was obtained.

In the second step, the prepared $\text{Na}_4(\text{Si}_{1-y}\text{Ge}_y)_4$ was transferred into a quartz tube (80 mm ϕ × 1200 mm) in the glove box. The quartz tube was pumped down to about 10^{-4} Pa, and set inside an electric furnace. Then the samples were annealed for 4–24 h in a temperature range of 300–400 °C. Thereafter, most of the samples were transformed into Na doped Si-Ge alloy clathrate ($\text{Na}_x(\text{Si}_{1-y}\text{Ge}_y)_{136}$ ($x > 1$)) by degassing of Na from $\text{Na}_4(\text{Si}_{1-y}\text{Ge}_y)_4$.

Since the above process is not sufficient for realizing guest free clathrate, an additional treatment using the ionic liquid (a mixture of dodecyl trimethyl ammonium chloride and AlCl_3) [11,14] was carried out as the third step. In this step, the Si-Ge alloy clathrate obtained in the above was put in a glass vessel, which was then sealed together with the ionic liquid. The samples were heated at 320 °C for 48 h. The gaseous HCl generated from the ionic liquid plays an important role in removing the sodium atoms from the clathrate, resulting in the guest free Si-Ge alloy clathrate ($\text{Na}_x(\text{Si}_{1-y}\text{Ge}_y)_{136}$ where $x < 1$). The prepared samples were washed with acetone and pure water. The samples were characterized by XRD measurements with Cu $K\alpha$ radiation (Smartlab, Rigaku Corporation) and energy dispersive X-ray (EDX) analysis (EMAX EX-220, Horiba) with acceleration voltage of 15 kV. Crystal structure information was estimated by Rietveld analysis method.

3. Results and Discussion

XRD measurements were performed for various nominal Si-Ge ratio of $\text{Na}_4(\text{Si}_{1-y}\text{Ge}_y)_4$ precursors and the resulting lattice volume as a function of Ge nominal composition ratio has been shown in Fig. 1. For comparison, the previous single crystalline data [15] are also plotted as a function of Ge composition derived from the

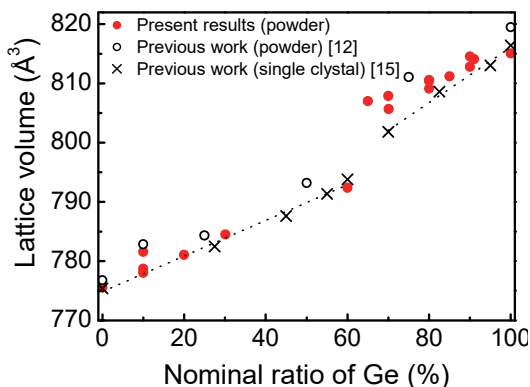


Fig. 1. The variation of cell volumes of $\text{Na}_4(\text{Si}_{1-y}\text{Ge}_y)_4$ ($y = 0 - 1$) versus Ge nominal ratio. The values reported by L. Baranowski [12] and H. Morito [15] are represented by \times and \circ , respectively. The dashed line in the inset is the result of a linear fitting of the single crystal data.

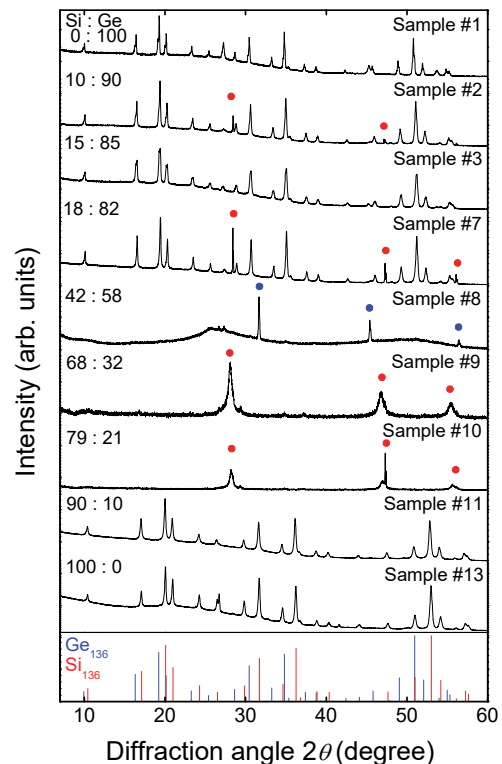


Fig. 2. Powder X-ray diffraction patterns measured for various Si-Ge composition samples. The values of Si-Ge composition ratio for each sample are denoted on the left side. Red and blue circles correspond to the peaks from diamond structures of Si and/or Ge. The calculated diffraction peak intensities of Si_{136} , Ge_{136} are represented in the bottom of this figure for reference.

single crystalline analysis. The volume jump found around 65 % in Fig. 1, could be attributed to the structural change in $\text{Na}_4(\text{Si}_{1-y}\text{Ge}_y)_4$ precursor which transforms from Si-rich structure with $C2/c$ space group to Ge-rich one with $P2_1/c$ space group. The discrepancy of the present data from single crystalline data has been observed around 70–80% of Ge composition. This discrepancy is likely to be because the actual Ge composition was shifted from the nominal composition, due to precipitation of diamond structure Ge. Thus, in this work, we estimate the actual Si-Ge ratio on the basis of comparison of cell volumes of our sample and previous single crystal sample reported by Morito *et al.* [15]. The present cell volume was calculated from lattice constants derived by Rietveld analysis of the precursors.

Figure 2 shows the XRD results of the samples synthesized from precursors having various Si-Ge ratios. The Si-Ge ratio denoted on each data is approximately the same as the precursor estimated in the above. Although it is not clear whether the Si-Ge ratio in $\text{Na}_x(\text{Si}_{1-y}\text{Ge}_y)_{136}$ is conserved from $\text{Na}_4(\text{Si}_{1-y}\text{Ge}_y)_4$ or not. XRD peaks attributed to the $\text{Na}_x(\text{Si}_{1-y}\text{Ge}_y)_{136}$ were observed only from the samples of which the composition is Si-rich or Ge-rich. On the other hand, the samples with middle range of Si-Ge composition show no clathrate peaks, but the peaks of diamond structure or amorphous phase of Si and/or Ge.

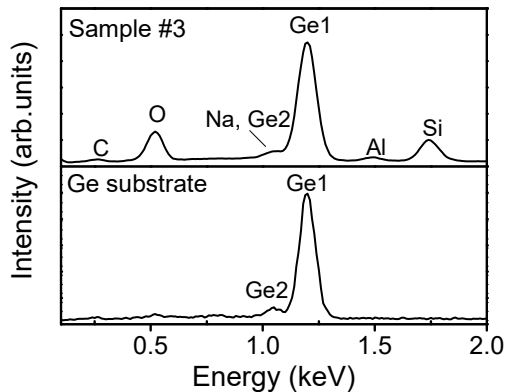


Fig. 3. EDX results measured for a sample of precursor's ratio with Si:Ge = 15:85 and Ge substrate.

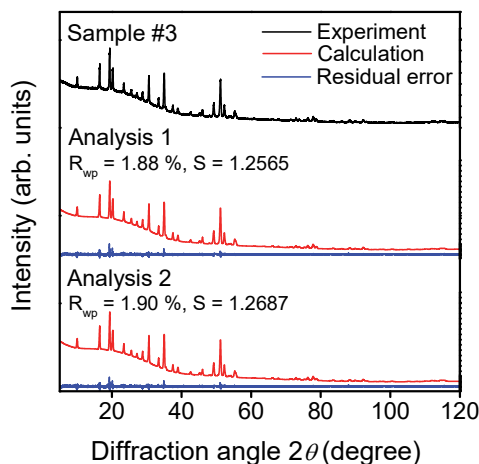


Fig. 4. Results of XRD measurement for sample #3 with a ratio of Si:Ge = 15:85 and its Rietveld analyses. The values of R_{wp} and S are denoted on the left side.

Figure 3 shows EDX spectrum of $\text{Na}_x(\text{Si}_{1-y}\text{Ge}_y)_{136}$ (sample #3) with a ratio of Si:Ge = 15:85. The data of Ge substrate are also shown for comparison. In the spectrum of the sample #3, Na related peak seems to appear around 1 keV. However, as compared to the Ge substrate, this peak can actually be seen as the peak of Ge origin. This shows that Na content is very small in clathrates which were synthesized by using ionic liquid. The Al and O peaks are likely to have originated from the ionic liquid and its oxidation.

Figure 4 shows the experimental XRD pattern of the sample with the Si-Ge ratio of 15:85 and theoretical patterns optimized by Rietveld analysis conducted individually with different sets of initial parameters. Table I indicates the

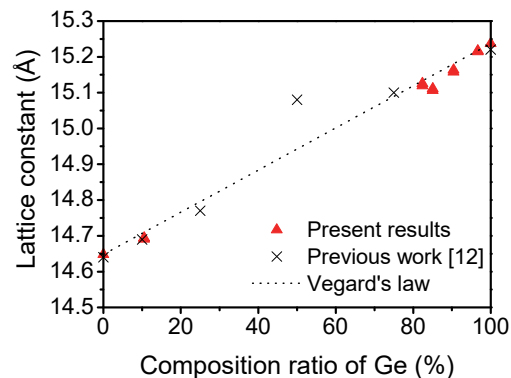


Fig. 5. The lattice parameters of $\text{Na}_x(\text{Si}_{1-y}\text{Ge}_y)_{136}$ versus Ge composition ratio. The dashed line in the inset is the Vegard's law. See text for the composition ratio of Ge.

Table I. Results of Rietveld analysis of sample #3 with precursor's ratio of Si:Ge = 15:85. The analyses were carried out under the assumption of type II clathrate with $Fd\bar{3}m$ space group.

	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	V (Å ³)
Analysis 1	15.1150(6)	15.1150(6)	15.1150(6)	90	90	90	3453.2(2)
Analysis 2	15.1108(2)	15.1108(2)	15.1108(2)	90	90	90	3450.36(8)

	Element	Wyckoff position	x	y	z	Occupancy	B (Å ²)
Analysis 1	Ge/Si	8a	0.875	0.875	0.875	0.79(9)/0.21(9)	0.97(9)
	Ge/Si	32e	0.78265(6)	0.78265(6)	0.78265(6)	0.863(9)/0.137(9)	1.21(6)
	Ge/Si	96g	0.81710(3)	0.81710(3)	0.62923(6)	0.908(7)/0.092(7)	1.35(3)
	Na	8b	0.375	0.375	0.375	0.000(9)	0.042
	Na	16c	0	0	0	0.000(6)	1
Analysis 2	Ge/Si	8a	0.875	0.875	0.875	0.666(6)/0.334(6)	0.50(9)
	Ge/Si	32e	0.78271(6)	0.78271(6)	0.78271(6)	0.723(4)/0.277(4)	0.66(5)
	Ge/Si	96g	0.81704(3)	0.81704(3)	0.62913(6)	0.77(5)/0.23(5)	0.96(2)
	Na	8b	0.375	0.375	0.375	0.000(8)	0.042
	Na	16c	0	0	0	0.000(8)	18.538

optimized structural parameters. Two sets of parameters were presented as optimized ones with sufficiently good S values of 1.2565 (Analysis 1) and 1.2446 (Analysis 2). Both analyses give identical values for the lattice constant, atomic position, and Na occupancy within 3 significant digits. On the other hand, Si-Ge occupancy and thermal parameter B show large discrepancies. This is likely to be observed because of a strong correlation between the occupancy and B parameter and hence, we have not emphasized the estimation of Si/Ge ratio from the Rietveld analysis. Nevertheless, the lattice constant, the atomic position, and Na occupancy are still worth discussing.

Figure 5 shows the lattice constant of $\text{Na}_x(\text{Si}_{1-y}\text{Ge}_y)_{136}$ as a function of Ge composition which was estimated for the precursor, as mentioned earlier. The previous data reported in Ref. [12] are also plotted for comparison purpose. Since, the data were shown as a function of the ratio of the initial Si-Ge mixture, there is no meaning in the strict comparison. At present, the lattice parameters are likely to follow Vegard's law, except for the data of middle range reported by Baranowski *et al.*[12]. According to them, the sample in the middle range largely included amorphous phase. The Si/Ge ratio possibly deviated from the initial one. Because of the lack of reliable data in the middle range in Si-Ge ratio, it is still not clear whether or not the Vegard's law holds in the whole range of Si/Ge ratios. The syntheses of Si/Ge clathrate in the middle Si-Ge ratio are highly required to clarify it.

4. Conclusions

We have successfully synthesized the guest free type II Si-Ge alloy clathrates in composition ranges of the Si rich or Ge rich, by using ionic liquid method. The Rietveld analysis results suggest that the Si-Ge alloy clathrates have very low Na concentrations, which are also consistent with EDX analysis. The present results suggest that the Si-Ge alloyed clathrate meet Vegard's law.

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