

Article

Caltech Library

Subscriber access provided by Caltech Library

Crystal growth conditions of type I and II Na-Si clathrates by evaporation of Na from a Na-Si-Sn solution

Haruhiko Morito, Masahi Shimoda, Hisanori Yamane, and Kozo Fujiwara

Cryst. Growth Des., Just Accepted Manuscript • DOI: 10.1021/acs.cgd.7b01342 • Publication Date (Web): 28 Nov 2017

Downloaded from http://pubs.acs.org on December 4, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



Crystal Growth & Design is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Crystal growth conditions of type I and II Na-Si clathrates by evaporation of Na from a Na-Si-Sn solution

Haruhiko Morito¹, Masashi Shimoda², Hisanori Yamane², and Kozo Fujiwara¹

1 Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.

2 Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.

KEYWORDS clathrate, single crystal, silicon, sodium

ABSTRACT

Single crystals of the type I clathrate Na₈Si₄₆ were synthesized by the evaporation of Na from a Na-Si-Sn solution (Na:Si:Sn = 6:2:1 molar ratio) at 723–873 K under an Ar atmosphere of 10^5 Pa. In the mixture of type I and type II clathrates prepared by heating at 773 K for 72 h, type I single crystals with sizes of up to 5 mm were found. A single phase of single crystals of the Na₂₄Si₁₃₆ type-II clathrate having a {111} crystal habit of about 2 mm on one side was obtained by heating at 873 K for 9 h.

1. INTRODUCTION

Sodium–silicon (Na-Si) clathrates, Na₈Si₄₆ (type I) and Na_xSi₁₃₆ $0 < x \le 24$ (type II), are open-framework compounds composed of polyhedral Si cages encapsulating Na atoms.^{1, 2} Type I Na-Si clathrate exhibits various characteristics, such as superconductivity,³ hydrogen storage,⁴ and thermoelectricity with a glasslike thermal conductitity,⁵ due to the unique open-framework structure. The electrical characteristics of stoichiometric type I clathrate Na₈Si₄₆ shows a metallic behavior, whereas those of type II clathrate Na_xSi₁₃₆ can be drastically changed from metallic to semiconductor as a function of x.^{6–9} The bandgap of the Na-free Si clathrate (Si₁₃₆) has been estimated to be 1.9 eV by first principles calculation, and this bandgap is larger than that of the diamond-type Si crystal.^{10, 11} Type II Na-Si clathrate could be of use in solar cell and optoelectronic devices.

The Na-Si clathrates have conventionally been synthesized by the thermal decomposition of a Zintl compound (Na₄Si₄) at temperatures of 673–823 K under a high vacuum ($< 10^{-2}$ Pa).^{1, 2} Using this method, the obtained samples are powdery solids with a grain size of micrometers because Na₄Si₄ (melting point 1071 K)¹² is solid at these temperatures. In addition, type I and II clathrates often coexist in the obtained samples, and it is difficult to prepare single-phase samples of each phase.¹³ For the study and practical application of the Na-Si clathrates, single crystals have been required.

Beekman *et al.* reported that type II clathrate $Na_{24}Si_{136}$ could be grown by heating Na_4Si_4 at 873 K under a load of 100 MPa using a spark-plasma sintering (SPS) apparatus.¹⁴ Furthermore, single crystals of type I and type II could be selectively prepared by a kinetically controlled thermal decomposition method in which Na_4Si_4 was sandwiched between graphite

Crystal Growth & Design

flakes with NaCl layers.^{15, 16} In this method, Na₄Si₄ was surrounded by a NaCl layer in a graphite mold to reduce Na evaporation. Na was gradually extracted from Na₄Si₄ via the reaction between the NaCl layer and graphite flakes, leading to slow crystal growth of the Na-Si clathrates. Type I and type II single crystals with sizes of about 200 and 250 μ m, respectively, were formed by heating at 858 and 938 K, respectively.¹⁶

Our group has succeeded in growing single crystals of the type I clathrate Na₈Si₄₆ with a size up to about 1.5 mm by the evaporation of Na from a Na-Si-Sn solution prepared by heating Na, Na₄Si₄, and Na₁₅Sn₄ at 723 K for 24 h.¹⁷ The crystal growth was performed under a reduced argon pressure of 10^4 Pa, which is higher than the pressures (< 10^{-2} Pa) used in conventional methods. A supersaturated condition for the flux growth of single crystal growth was realized by the reduction of the Na content in the solution. A mixture of polycrystalline type I and type II clathrates and Si was prepared by Na evaporation at 773 K for 12 h, but a single phase of the type II clathrate could not be obtained.

In the present study, the growth of larger crystals of the Na₈Si₄₆ type I clathrate was attempted by reducing the evaporation rate of Na from the Na-Si-Sn solution. To reduce the Na evaporation rate, we heated the solution at an Ar pressure of 10^5 Pa, which is close to atmospheric pressure and higher than that of the previous study (10^4 Pa). The higher pressure enabled us to grow type II single crystals at 873 K.

2. EXPERIMENTAL SECTION

A piece of Na metal (Nippon Soda, purity 99.95%, 171–187 mg), Si powder (Kojundo Chemical Laboratory, 4N, 70–76 mg), and Sn granules (Wako Pure Chemical Industries,

99.99%, 147–161 mg) were weighed in a mole ratio of Na:Si:Sn = 6:2:1 in an Ar-filled glove box ($O_2 < 1$ ppm, $H_2O < 1$ ppm). These starting materials were charged in a boron nitride crucible (Showa Denko, 99.5%, 6.5 mm inner diameter, 18 mm depth) and sealed in a stainlesssteel container (SUS316, 12.7 mm outer diameter, 80 mm height) with Ar gas. The container was heated in an electric furnace at 1173 K for 12 h and cooled to room temperature. After heating, a mixture of Na₁₅Sn₄, Na₄Si₄, and Na was obtained in the BN crucible. The BN crucible containing the mixture was transferred to another long stainless steel container with a different size (45 mm outer diameter, 200 mm height) in the Ar-filled glove box. A schematic of the container is shown in the Supplemental Data of Ref. 18. The sample in the crucible was placed in the lower part of the container, and this part was heated with an electric heater at 723–923 K. Na metal was evaporated from the sample and condensed at the upper cooler upper part of the container, which had a temperature gradient. After heating, the crucible was taken out from the container in the Ar-filled glove box. Air- and moisture-sensitive compounds such as Na₄Si₄ and Na-Sn binary compounds in the products were reacted with 2-propanol and ethanol in air, and the watersoluble reactants were removed by washing with water (alcohol treatment). Sn formed by this treatment was removed from the residues by dissolution in a dilute nitric acid aqueous solution (acid treatment).

The morphologies of the crystals in the residues were observed with an optical microscope (Olympus, SZX16) and a scanning electron microscope (SEM, Keyence, VE-8800). Some of the residues from the products were powdered in an agate mortar, and the powder X-ray diffraction (XRD) patterns were measured using an X-ray diffractometer (XRD, Rigaku, RINT 2200, Cu radiation) to identify the crystalline phases.

Crystal Growth & Design

The XRD intensity data of a type II clathrate single crystal were measured with a single crystal XRD diffractometer (Bruker AXS, D8QUEST/CP, Mo radiation) and analyzed with the APEX-III program.¹⁹ The structure refinement was performed using SHELXL97.²⁰ The facet planes of the type I and II single crystals were indexed with the XRD intensity data. The density of the type II single crystals was measured by the Archimedes method. Quantitative analysis of type II single crystals was carried out using an electron probe microanalyzer (EPMA, JEOL, JXA-8200). The software program VESTA²¹ was used for drawing the crystal structure.

3. RESULTS AND DISCUSSION

3.1 Crystal growth conditions of the Na-Si clathrates

Table 1 shows the synthesis conditions (heating temperature and time), the crystalline phases and weight of residues after the alcohol/acid treatments. The evaporated Na ratio (R_{Na} = (amount of Na evaporated)/(amount of Na in the starting sample) × 100 (%)) was calculated by postulating that the weight loss of the sample after heating corresponded to the amount of the evaporated Na. Figure 1 shows the relationship between the heating time, *t* (h), and the evaporated Na ratio, R_{Na} (%), together with the crystalline phases of the residues identified by powder XRD. Photographs of the whole residues obtained after the alcohol/acid treatments of the samples prepared at different conditions are shown in Fig. 2.

When the starting Na-Si-Sn solution was heated at 723 K for 48 h, about 18.5% of the Na was evaporated ($R_{Na} = 18.5\%$). The product was completely dissolved by the alcohol/acid treatments, and there was no crystal. The Si in the Na-Si-Sn solution crystallized as Na₄Si₄, which was eluted during the alcohol treatment. R_{Na} increased with increasing heating time,

reaching 31.6% after heating for 96 h and to 57.7% after heating for 216 h, as shown in Fig. 1. The residues of 2.4 and 68 mg obtained by heating for 96 and 216 h, respectively, were single phases of the type I clathrate Na₈Si₄₆ (Table 1, Figs. 2 (a) and (b)). If all the amount of Si (71 mg) in the starting sample with Na:Si:Sn = 6:2:1 is used for clathrate formation, 81.1 mg of type I Na₈Si₄₆ would be formed. Thus, the yields of type I crystals prepared by heating at 723 K for 216 h were 84% based on the amount of Si in the starting sample. The size of the type I single crystals prepared at 723 K for 216 h was about several hundred micrometers, although the maximum was 1.5 mm (Fig. 2 (b)). In a previous study of type I single crystal formation,¹⁷ a Narich starting sample with a composition of Na:Si:Sn = 10:2:1 was heated at 723 K and 10⁴ Pa for 12 h, and 61% of the Na was evaporated. The Na concentration of the melt corresponded to that of the melt obtained after 35% Na evaporation from the starting melt with Na:Si:Sn = 6:2:1 by heating at 723 K and 10⁵ Pa for 216 h in the present study. Although the Na evaporation rate of the previous study was faster than that of the present study, the sizes of the type I crystals obtained by heating at 723 K are similar in both studies.

 R_{Na} was 23.9% after heating at 773 K and 10⁵ Pa for 24 h, and there was no crystal after the alcohol/acid treatment, and this was also the case after heating at 723 K and 10⁵ Pa for 48 h. After heating for 48 h, R_{Na} increased to 41.7% at 773 K, and 47 mg of the residue, including granular type I single crystals with a size of more than 2 mm, was obtained, as shown in Fig. 2 (c). R_{Na} was increased to 53.3% by heating for 72 h, and a type I single crystal of 5 × 3 × 3 mm³ with {110} habit planes and aggregates of a few millimeters of type I (Na₈Si₄₆) and type II (Na_xSi₁₃₆) single crystals were obtained (Fig. 2 (d)). A mixture of type II microcrystals (several micrometers to several tens of micrometers) and Si powder was formed by heating for 120 h with $R_{\text{Na}} = 72.9\%$.

ACS Paragon Plus Environment

Crystal Growth & Design

Photographs of the whole residues after the alcohol/acid treatments of the samples prepared by heating at 823 K for 12 h ($R_{Na} = 34.8\%$) and 24 h ($R_{Na} = 65.5\%$) are shown in Fig. 2 (e) and (f), respectively. The 33-mg residue formed after heating for 12 h comprised granular single crystals of the type I clathrate with a size of up to ~1 mm. Most of the single crystals with about 1 mm in size have {110} habits as shown in Fig. 3(a). The residue after 24 h heating was composed of a few granular single crystals of type I (size: < 1 mm) and type II (size: 0.5–1.5 mm). The total weight of these crystals was 65 mg. The triangular {111} and quadrangular {100} planes were developed for most of the type II crystals (Fig 3(b)). After heating for 36 h ($R_{Na} = 81.1\%$), the residue was a mixture of type II single crystals and Si grains.

Granular type I single crystals (maximum size: ~ 2 mm, total weight of the residue: 27 mg) were obtained by heating at 873 K for 6 h ($R_{Na} = 31.8\%$), as shown in Fig. 2 (g). Type II single crystals weighing 62 mg in total with a size of 2–3 mm and {111} triangular facets were obtained by heating for 9 h ($R_{Na} = 51.2\%$) (Fig. 2 (h)). The formation yields of type II crystals prepared at 873 K for 9 h were 76 % based on the amount of Si in the starting sample. The residue became a mixture of type II and Si after heating for 12 h ($R_{Na} = 65.3\%$).

A residue of 18 mg was obtained from the sample prepared by heating at 923 K for 3 h $(R_{Na} = 32.8\%)$, and this was the single phase of diamond-type Si. Figures 4 (a) and (b) show SEM images of a fragment of the residue, which was covered with aggregated Si spheres of 20–50 µm in diameter. The surface of the spheres consisted of petal-like streaky grains. No pores were observed on the fracture surface of the fragment. This result indicates that the fragment under the aggregates of spheres was a bulk Si crystal.

3.2 Discussion of the crystal growth of Na-Si clathrates in the Na-Si-Sn solution

In the present study, the single phase of type I clathrate was obtained at 723 K, and the type II clathrate was formed at 773–873 K. Type I crystals were also formed by heating at 823 K for 12 h and 873 K for 6 h, and the single phase product of type II clathrate was prepared by heating at 973 K for 9 h. In the sample prepared at 923 K, the only diamond-type Si was formed and the crystallization of clathrate was not confirmed. Horie *et al.* reported that multiphase samples of type I and type II clathrates could be synthesized by the general method in which Na₄Si₄ compound was heated at 723–793 K under a high vacuum (10⁻² Pa).¹³ In this synthesis, the ratio of type I contained in the sample was increased with increasing synthesis temperature. However, type I crystals thermally decomposed into Si and the sample changed to a mixture of type II and Si above 823 K.¹³ In the kinetic thermal decomposition method using SPS, a single phase of type I, a mixture of type I and type II, a single phase of type II, and diamond-type Si were obtained at 723, 823, 873, and 923 K, respectively.¹⁶ As similar to the case of these previous studies, the type II clathrate crystallizes at temperature higher than that of the type I clathrate crystallization, and the clathrates could not be formed over 923 K in the present study.

The evaporation rate of Na from the Na-Si-Sn solution and supersaturation of the clathrate crystals could be reduced by increasing the Ar pressure from 10⁴ Pa in the previous study¹⁷ to 10⁵ Pa. As a result, the Na-Si clathrates crystals could grow from a smaller number of crystal nuclei in the Na-Si-Sn solution and crystal growth of type I clathrate could continue for 72 h at 773 K, resulting in growing a type I single crystal with a size over 3 mm. Furthermore, the reducing of Na evaporation rate realized the crystal growth of the Na-Si clathrates at higher temperatures of 823–873 K.

Crystal Growth & Design

The amounts of single-phase type I crystals obtained at 723 K for 96 h ($R_{Na} = 31.6\%$), 823 K for 12 h ($R_{Na} = 34.8\%$), and 873 K for 6 h ($R_{Na} = 31.8\%$) were 2.4, 33 and 27 mg, respectively. Under these conditions, R_{Na} was around 32–35%, but the number of crystals obtained at 723 K was about one-tenth of those prepared under other conditions. The size of the crystals increased from less than 1 mm to about 2 mm with increasing temperature. These results may give an explanation of the crystal growth during cooling, based on the temperature dependence of solubility. However, diamond-type Si crystals (18 mg) were formed by heating at 923 K for 3 h ($R_{Na} = 32.8\%$), and no clathrate crystallized. The formation of Si at 923 K indicates that the Na-Si clathrate crystals did not grow during the present cooling process.

Form the present results, the type I clathrate was first crystallized by Na evaporation, and, then, the type II clathrate was crystallized at 773–873 K and $R_{\text{Na}} \ge \sim 50\%$. From the morphology and the developed habit planes of the single crystals as shown Fig 3 (a) and (b), it is conceivable that the type I clathrates dissolved into the solution again and the type II clathrates crystallized during the process. Further heating led to the decomposition of the clathrates to Si.

3.3 Crystal structure analysis of type II single crystal

The composition of type II single crystals obtained by heating at 823 K for 24 h was analyzed by EPMA, revealing a Na: Si ratio of (15.0 ± 0.2) : (85.0 ± 0.2) (at.%), which agrees with the composition x = 24 of Na_xSi₁₃₆ ($0 < x \le 24$), indicating the full occupation of the Na atoms in the Si₂₈ and Si₂₀ cages in the structure. Other impurity elements such as Sn were not detected. The density of the type II single crystals measured by the Archimedes method was 2.28 ± 0.02 Mg/m³.

The single crystal of Na₂₄Si₁₃₆ prepared by the kinetic thermal decomposition method was analyzed by XRD (cubic, space group $Fd\bar{3}m$ (No. 227) a = 1.47121(1) nm).¹⁵ The atomic displacement parameter of the Na2 site in the Si₂₈ cage of Na_xSi₁₃₆ was extremely large compared to that of the Na1 site in the Si₂₀ cage. Similar results have been reported in previous studies of other researchers.^{6, 7, 9, 11} In the structural model of Na₂₄Si₁₃₆ determined in the previous study, the Na2 site was divided to an off-center site (48f).¹⁵ In the present study, the crystal structure of a single crystal of the type II clathrate obtained after heating at 823 K for 24 h was analyzed with this model, and the *R*1 value of the refinement was 0.8% for all data (*R*1 = $\Sigma ||F_0| - |F_c|| / \Sigma |F_0|$, where F_0 and F_c are observed and calculated structure factors, respectively). The results of the analysis are shown in Tables S1–S3 and Fig. S1. The cubic lattice constant a =1.47088(3) nm is consistent with the literature value, and the refinement of the occupancies for the two Na sites showed no deficiency. The density of 2.281 Mg/m³ calculated with the formula of Na₂₄Si₁₃₆ agreed with that from measurement.

4. Conclusions

Single crystals of type I clathrate Na₈Si₄₆ were obtained by Na evaporation from a Na-Si-Sn solution (Na:Si:Sn = 6:2:1 molar ratio) at 723–873 K under an Ar atmosphere of 10^5 Pa, where the evaporated Na ratio (R_{Na}) was over 30%. The type II clathrate crystallized with R_{Na} of about 50% or more at 773–873 K. In a mixture of type I and type II clathrates prepared by heating at 773 K for 72 h, type I single crystals with a size up to about 5 mm were found. A single phase of type II crystals having a {111} crystal habit of about 2 mm on one side was obtained by heating at 873 K for 9 h. Single crystal X-ray analysis revealed that the type II

ACS Paragon Plus Environment

1				
2		I O' 1 41	NT '4 ' 41	6.6. 4
4	clathrate crystallized at 823 K was F	$x_{24}S_{136}$, where the	Na sites in the cage	s of S1 atoms were
5	fully occupied			
6 7	Turiy occupicu.			
8				
9				
10				
11				
12				
14				
15				
16				
1/				
18				
20				
21				
22				
25 24				
25				
26				
27				
28 29				
30				
31				
32				
33 34				
35				
36				
37				
38 39				
40				
41				
42				
43 44				
45				
46				
47				
48				
50				
51				
52				
53				
54 55				
56				
57				
58				
59 60	AC	S Paragon Plus Environ	iment	
		<u> </u>		

Crystal Growth & Design

FIGURES



Figure 1. Heating time dependence of the evaporated Na ratio, R_{Na} , and the crystalline phases at 723, 773, 823, and 873 K.





Figure 2. Photographs of the crystals prepared by heating a Na-Si-Sn solution at 723 K for 96 h (a) and 216 h (b), at 773 K for 48 h (c) and 72 h (d), at 823 K for 12 h (e) and 24 h (f), and at 873 K for 6 h (g) and 9 h (h).



Figure 3. SEM images of the type I single crystal prepared at 823 K for 12 h (a) and type II sigle crystal prepared at 823 K for 24 h (b).





h.





Figure S1. Crystal structure of Si28 and Si20 cages in Type II clathrate prepared by heating a Na-Si-Sn solution at 823 K for 24 h.

Crystal Growth & Design

Table 1. The heating temperature and time, Na evaporation ratio against the initial Na in the starting materials, R_{Na} (%), and the products obtained by the alcohol/acid treatments.

Heating conditions		Na evaporation ratio, R_{Na} (%)	Products	Mass of products (mg)	
Temp. (K)	Time (h)				
723	48	18.5	-	0	
	96	31.6	type I	2.4	
	216	57.7	type I	68	
773	24	23.9	-	0	
	48	41.7	type I	47	
	72	53.3	type I, II	65	
	120	72.9	type II, Si	72	
823	12	34.8	type I	33	
	24	65.5	type I, II	65	
	36	81.1	type II, Si	70	
873	6	31.8	type I	27	
	9	51.2	type II	62	
	12	65.3	type II, Si	65	
923	3	32.8	Si	18	

ACS Paragon Plus Environment

3
4
5
0
/
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
20
27
20
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
<u>10</u>
50
50
57
52 52
55
54
55
56
57
58
59
60

ASSOCIATED CONTENT

Supporting Information.

Experimental details, crystallographic data; Figures S1; Table S1-S3. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

morito@imr.tohoku.ac.jp

Present Addresses

[†]If an author's address is different than the one given in the affiliation line, this information may be included here.

Author Contributions

*‡*These authors contributed equally.

ACKNOWLEDGMENT

This work was supported by JSPS KAKENHI Grant Number JP16H06123.

REFERENCES

- (1) Kasper, J. S.; Hagenmuller, P.; Pouchard M.; Cros C. Science 1965, 150, 1713.
- (2) Cros, C.; Pouchard M.; Hagenmuller P. J. Solid State Chem. 1970, 2, 570.
- (3) Kawaji, H.; Horie, H.; Yamanaka, S.; Ishikawa, M. Phys. Rev. Lett. 1995, 74, 1427.
- (4) Neiner, D.; Okamoto, N. L.; Condron, C. L.; Ramasse, Q. M.; Yu, P.; Browning, N. D.;
 Kauzlarich, S. M. J. Am. Chem. Soc. 2007, 129, 13857.

- (5) Tse, J. S.; Uehara, K.; Rousseau, R.; Ker, A.; Ratcliffe, C. I.; White, M. A.; MacKay, G.; *Phys. Rev. Lett.* 2000, *85*, 114.
- (6) Reny E.; Gravereau P.; Cros C.; Pouchard M. J. Mater. Chem. 1998, 8, 2839.
- (7) Ramachandran G. K.; Dong J.; Diefenbacher J.; Gryko J.; Marzke, R. F.; Sankey, O. F.;
 McMillan, P. F. J. *Solid State Chem.* 1999, *145*, 716.
- (8) Beekman, M.; Nolas, G. S. Physica B 2006, 383, 111.

- (9) Stefanoski, S.; Malliakas, C. D.; Kanatzidis, M. G.; Nolas, G. S. Inorg. Chem. 2012, 51, 8686.
- (10) Adams, G. B.; O'Keeffe, M. Phys. Rev. B 1994, 49, 8048.
- (11) Gryko, J; McMillan, P. F.; Marzke, R. F.; Ramachandran, G. K.; Patton, D.; Deb, S. K.;
 Sankey, O. F. *Phys. Rev. B* 2000, *62*, R7707.
- (12) Morito, H.; Yamada, T.; Ikeda, T.; Yamane, H. J. Alloys Compd. 2009, 480, 723.
- (13) Horie, H.; Kikudome, T.; Teramura, K.; Yamanaka, S. J. Solid State Chem. 2009, 182, 129.
- (14) Beekman, M.; Baitinger, M.; Borrmann, H.; Schnelle, W.; Meier, K.; Nolas, G. S.; Grin,
 Y. J. Am. Chem. Soc. 2009, 131, 9642.
- (15) Stefanoski, S.; Beekman, M.; Wong-Ng, W.; Zavalij, P.; Nolas, G. S. Chem. Mater.
 2011, 23, 1491.
- (16) Stefanoski, S.; Martin, J.; Nolas, G. S. J. Phys.: Condens. Matter 2010, 22, 485404.
- (17) Morito, H.; Shimoda, M.; Yamane, H. J. Cryst. Growth 2016, 450, 164.
- (18) Morito, H.; Yamane, H. Angew. Chem., Int. Ed. 2010, 49, 3638.
- (19) Bruker (2016). APEX3. Bruker AXS, Inc. Madison, Wisconsin, USA.
- (20) Sheldrick, G. M. Acta Cryst. A 2008, 64, 112.

(21)	Momma	K · Izumi	FΙ	Annl	Crust	2008	11	653
(21)	Momma,	, n ., izuiiii,	Г. Ј.	Аррі.	Crysi.	2008,	41,	033.

For Table of Contents Use Only

Crystal growth conditions of type I and II Na-Si clathrates by evaporation of Na from a Na-Si-Sn solution

Haruhiko Morito, Masashi Shimoda, Hisanori Yamane, and Kozo Fujiwara



Single crystals of type I clathrate Na_8Si_{46} and type II clathrate $Na_{24}Si_{136}$ were obtained by Na evaporation from a Na-Si-Sn solution.