

Seeded Growth of Type-II Na₂₄Si₁₃₆ Clathrate Single Crystals

Haruhiko Morito ^{1,*}, Hisanori Yamane ², Rie Y. Umetsu ¹ and Kozo Fujiwara ¹

¹ Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan; rieume@imr.tohoku.ac.jp (R.Y.U.); kozo@imr.tohoku.ac.jp (K.F.)

² Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan; hisanori.yamane.a1@tohoku.ac.jp

* Correspondence: morito@imr.tohoku.ac.jp

Abstract: Type-II Na₂₄Si₁₃₆ clathrate octahedral single crystals surrounded by {111} facets were grown by evaporating Na from a molten mixture of Na₄Si₄ and Na₉Sn₄ at 823 K for 12 h. One of the obtained single crystals was used as a seed for the following single crystal growth of the type-II clathrate using the same method. The single crystal grown on the seed maintained the octahedral shape. The weight of the crystal grown with the seed was increased from 0.6 to 30.4 mg by repeating the seeded growth and was proportional to the surface area of the seed crystal.

Keywords: clathrate; silicon; sodium; seed-crystal growth; single crystal



Citation: Morito, H.; Yamane, H.; Umetsu, R.Y.; Fujiwara, K. Seeded Growth of Type-II Na₂₄Si₁₃₆ Clathrate Single Crystals. *Crystals* **2021**, *11*, 808. <https://doi.org/10.3390/cryst11070808>

Academic Editor: Evgeniy N. Mokhov

Received: 22 June 2021
Accepted: 9 July 2021
Published: 12 July 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



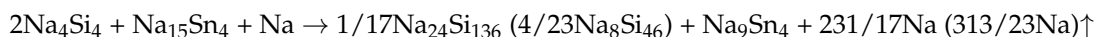
Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Clathrate compounds containing Na in Si cages are called Na–Si clathrates [1], and two types, type-I (Na₈Si₄₆) and type-II (Na_{*x*}Si₁₃₆, 0 < *x* ≤ 24), have been reported [2–5]. The electrical property of the type-II clathrate changes from metallic to semiconducting according to the amount of Na encapsulated in the cages [6]. Mott reported that the metal-insulator transition took place with decreasing *x* of the Na_{*x*}Si₁₃₆ clathrates [7]. Since a bandgap of 1.9 eV, which was shown for the Na-free type-II clathrate, Si₁₃₆, by experiments and first-principle calculation, is wider than that of 1.2 eV for diamond-type Si, it has attracted attention as a material for the next-generation solar cells [8–10].

Powders and polycrystalline samples of the Na–Si clathrates have been conventionally synthesized by thermal decomposition of a solid phase Zintl compound Na₄Si₄ [1–4]. It is difficult to prepare the bulk samples of the Na–Si clathrates by powder sintering because the clathrates have strong covalent Si–Si bonding and decompose into diamond-type Si (d–Si) at high temperature. Crystal growth of the type-II Na–Si clathrate was performed by thermal decomposition under pressure with spark plasma sintering (SPS) equipment [11]. The type-II single crystals of about 300 μm were also produced by another thermal decomposition method, in which Na was slowly removed from Na₄Si₄ heated at 938 K in a closed space surrounded with NaCl and graphite [12,13]. Recently, our research group achieved a solution growth of the Na–Si clathrate single crystals using a Na–Sn flux and obtained millimeter-sized single crystals [14,15]. In previous studies [15], single crystals of the type-I Na–Si clathrate with a size up to about 5 mm were prepared from a Na–Si–Sn solution at 773 K. Single crystals of type-II clathrate with {111} facets of about 2 mm on one side were grown at 873 K. Although the single crystals were formed by heating, they decomposed into d–Si during prolonged heating [15]. A more efficient crystal growth process without decomposition was necessary to obtain further large single crystals, furthering their application in devices.

In previous studies on the crystal growth of the Na–Si clathrates, Na, Na₄Si₄, and Na₁₅Sn₄ were used as the starting materials [14,15]. A Na–Si–Sn solution was formed by dissolving Na₄Si₄ into the melt of Na₁₅Sn₄. The Na–Si clathrates were crystallized by evaporating Na from this solution. The formula for the formation of clathrates could be expressed as follows:



Since the Na–Si clathrates are also dissolved into the melt of $\text{Na}_{15}\text{Sn}_4$, the seeded crystal growth could not be applied. However, as suggested in the reaction formula, the Na–Si clathrates can coexist with the melt of Na_9Sn_4 because the clathrates were obtained with Na_9Sn_4 after heating. In this study, single crystals of the Na–Si clathrates were prepared using a Na_9Sn_4 melt as a flux, and the seeded crystal growth was attempted to grow a large Na–Si clathrate single crystal.

2. Experimental

Na_4Si_4 and Na_9Sn_4 were used as starting materials. To prepare Na_4Si_4 , the pieces of Na metal (Nippon Soda Ltd., Tokyo, Japan, purity 99.95%) and Si powder (Kojundo Chemical Laboratory Co., Saitama, Japan, purity 99.99%) were weighted so that the molar ratio was Na:Si = 1:1, and put in a BN crucible (Showa Denko KK, Tokyo, Japan, purity 99.5%, outer diameter Φ 8.5 mm, inner diameter Φ 6.5 mm, depth 18 mm) in an Ar gas-filled glove box. These samples were sealed in a reaction container made of stainless steel (SUS316: outer diameter Φ 12.7 mm, inner diameter Φ 10.7 mm, height 80 mm) with Ar gas. For the preparation of Na_9Sn_4 , a BN crucible containing Na and granular Sn (FUJIFILM Wako Pure Chemical Corporation, Ltd., Osaka, Japan, purity 4N) (molar ratio, Na:Sn = 9:4) were sealed in another SUS container, and heated at 973 K for 12 h. After heating, both containers were opened in the glove box, and the ingots of Na_4Si_4 and Na_9Sn_4 were taken out from the BN crucibles. Each ingot was cut into pieces 1–2 mm in size with a nipper. Na_4Si_4 and Na_9Sn_4 in a molar ratio of 2:1 (Na_4Si_4 ; 0.500 g, Na_9Sn_4 ; 0.835 g) was put in a BN crucible (Showa Denko KK, Tokyo, Japan, purity 99.5%, outer diameter Φ 20 mm, inner diameter Φ 18 mm, depth 29 mm), and sealed in a SUS316 container (outer diameter Φ 45 mm, inner diameter Φ 40 mm, 200 mm height) for crystal formation. The schematic diagrams of the containers are shown in the supplementary data and the details of the procedures were described in the previous studies [14–16]. The crucible was heated at 823 and 873 K for 12 and 3 h, respectively. After heating, the crucible was taken from the container in the glove box, and the sample weight was measured to evaluate the evaporated Na. Subsequently, the sample was transferred to the air and washed with 2-propanol, ethanol, and pure water in that order (alcohol treatment). Sn remained after this treatment was dissolved in dilute nitric acid water solution (nitric acid concentration of 10% or less) (acid treatment).

One of the obtained single crystals was picked up as a seed crystal, and it was placed in a BN crucible (outer diameter Φ 8.5 mm) with Na_4Si_4 (0.100 g) and Na_9Sn_4 (0.167 g) in a molar ratio of 2:1, where the total weight of the sample and the size of the crucible were reduced to easily distinguish the crystal grown on the seed from other crystals newly formed by spontaneous nucleation. The crucible containing the seed crystal was heated at 823 K for 12 h. The seeded-grown crystal was taken out by means of the alcohol and acid treatments and used as the seed for the next crystal growth. The seeded growth was repeated three times in the same conditions.

The morphology of the obtained crystals was observed with an optical microscope (Leica, Tokyo, Japan, WILD-M3Z) and a scanning microscope (SEM; JEOL, Tokyo, Japan, JSM-6610A). The crystalline phases of the products were identified by powder X-ray diffraction (XRD) using a powder diffractometer (Rigaku, Tokyo, Japan, RINT2200, $\text{CuK}\alpha$, 40 kV and 30 mA). To confirm the quality and crystal orientation of the single crystal, an XRD pattern was taken with a Laue camera and an X-ray generator (Rigaku, Tokyo, Japan, RASCO-II BLA, W target, 30 kV, and 30 mA). The composition of the crystal was determined with an energy dispersive X-ray spectrometer (EDS; JEOL, Tokyo, Japan, JED-2300 Series) which was attached with the SEM.

3. Results and Discussion

After heating Na_4Si_4 and Na_9Sn_4 at 823 K for 12 h, a dome-shaped ingot (diameter; ~15 mm, height ~5 mm) was obtained. While the starting sample before heating was in the form of grains of about 1 to 2 mm, the solidified homogeneous sample including single crystals was obtained. This result suggests that Na_4Si_4 with a melting point (m.p.) of 1071 K [17] could be dissolved in the melt of Na_9Sn_4 (m.p. 751 K [18]) at 823 K. The weight of the sample was reduced from 1.335 g to 1.171 g by heating, which indicated that approximately 34% of Na in the starting sample was evaporated. After heating and alcohol and acid treatments, the granular crystals and octahedral crystals were obtained as shown in Figure 1a,b, respectively. The powder XRD pattern revealed that the granular and octahedral crystals were type-I and type-II clathrates, respectively (Supplementary Materials). The total weight of type-I and type-II clathrate crystals was 204 and 34 mg, respectively. In a previous study [15], the {110} and {111} facets were dominant in the crystals of the type-I and type-II clathrates grown at 823 K, respectively. The Na and Si contents analyzed by EDS analysis were 14.7 (2) and 85.3 (2) at.%, respectively, showing that the obtained type-II single crystals were fully Na-occupied type-II clathrate, $\text{Na}_{24}\text{Si}_{136}$.

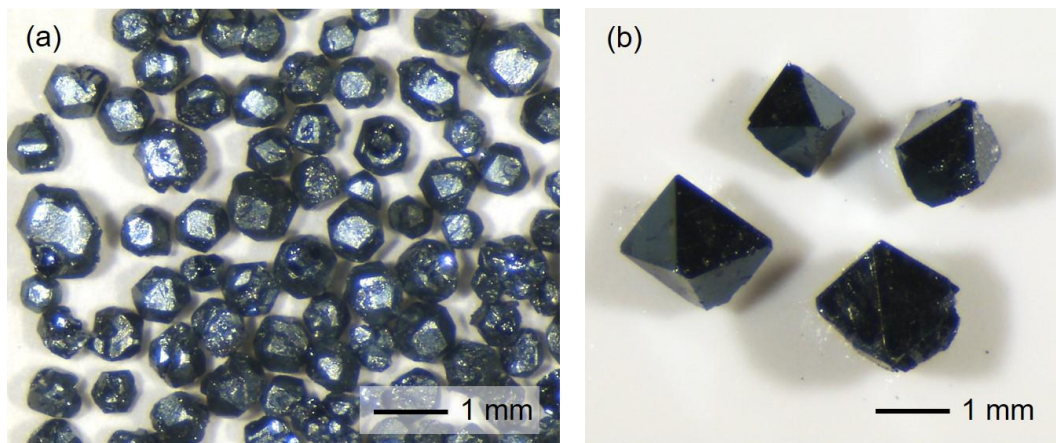


Figure 1. Optical micrographs of (a) type-I and (b) type-II Na-Si clathrate single crystals obtained by heating Na_4Si_4 and Na_9Sn_4 at 823 K for 12 h, followed by alcohol and acid treatments.

Type-I and -II crystals were also obtained by heating at 873 K for 3 h. The size of the type-II single crystals was slightly larger than that of crystals prepared at 823 K. However, the crystal surface was uneven and cracked, which might be due to an increased growth rate at a higher temperature. A part of the crystals was decomposed into d-Si.

An octahedral single crystal of type-II clathrate with no surface irregularities or cracks was used as a seed crystal (Figure 2a). It was placed at the bottom of the BN crucible, and Na_4Si_4 and Na_9Sn_4 grains were added. The crucible was heated at 823 K for 12 h in the container filled with Ar. The sample obtained after heating was ingot-like, and no crystals were exposed above the surface. After alcohol and acid treatments, the seeded grown octahedral single crystal with a size over 1 mm and other small crystals were separated. The SEM photo of the seeded grown single crystals is shown in Figure 2b. This octahedral crystal was used as the seed crystal for the second-seeded growth by the same procedure as the first one. The single crystal isotropically grown on the seed, maintaining the octahedral morphology, was obtained as shown in Figure 2c. The SEM photo of the octahedral single crystal with a size of about 3 mm obtained by the third growth is shown in Figure 2d. The equilateral triangle facets of the octahedral crystal were confirmed as being the {111} plane of the cubic type-II clathrate by Laue XRD (Supplemental Data).

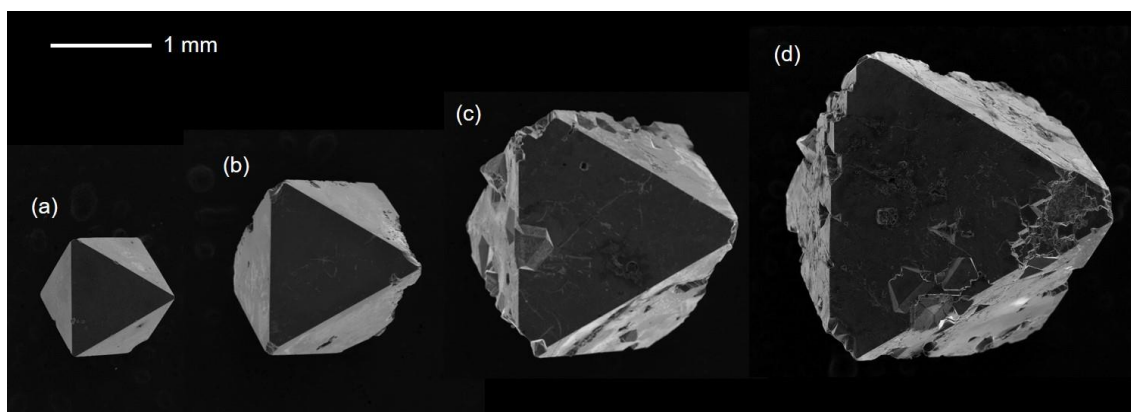


Figure 2. SEM images of (a) the seed crystal prepared by heating Na_4Si_4 and Na_9Sn_4 at 823 K for 12 h, seeded grown single crystals by heating at 823 K for the total heating time of (b) 12, (c) 24, and (d) 36 h.

The weight of the crystals obtained at each heating time is plotted in Figure 3. The weight of the seed crystal prepared by heating the Na–Si–Sn solution at 823 K for 12 h was 1.9 mg. The weight of the crystal increased to 6.3 mg after the first seeded growth (the total heating time was 24 h). By repeating the seeded crystal growth while increasing the total heating time to 36 and 48 h, the weight of the crystal was changed to 16.0 and 30.4 mg, respectively. The weight of the seeded-grown crystals was in proportion to the surface area of the seed crystal as shown in the inset graph of Figure 3. The surface area was calculated with the length of one side of the octahedron. The result shows that the growth rate per unit area of the crystal was constant at each seeded growth. Since the crystals grew isotropically while maintaining the orientation of the single crystal, the crystal growth velocities along $\langle 100 \rangle$ and $\langle 111 \rangle$ were evaluated. Crystal growth along the $\langle 100 \rangle$ direction was considered as the distance from the center position of the octahedron to the apex of the octahedron. When this distance was plotted against the crystal growth time, it tended to increase linearly. Thus, when the crystal growth velocity along the $\langle 100 \rangle$ direction was calculated from this straight line, it was $0.0124 \pm 0.0006 \mu\text{m/s}$. Similarly, the crystal growth velocity along the $\langle 111 \rangle$ direction was $0.0072 \pm 0.0004 \mu\text{m/s}$ as a result of calculating from the distance from the center of the octahedron to the center of gravity of the $\{111\}$ plane. The crystal growth velocity of $\langle 111 \rangle$ was slower than that of $\langle 100 \rangle$. From this result, it was clarified that $\{111\}$, which has slow crystal growth, is exposed on the surface of the single crystal.

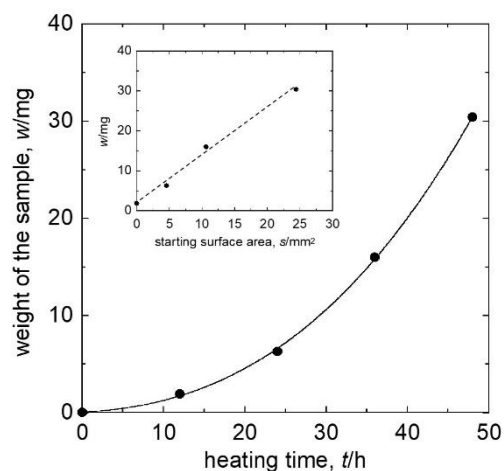


Figure 3. Weight of the seeded grown type-II Na–Si clathrate crystal plotted against the total heating time. The insert shows the relationship between the weight and surface area of the seed crystal.

The total weight of the single crystals except for the seeded grown crystal after the first seeded growth was 41.4 mg (total heating time 24 h). The weight was decreased to 33.8 and 27.6 mg by increasing the repeating time of the seeded growth. The crystal growth selectively occurred on the seed crystals and the crystal growth via spontaneous nucleation was suppressed by increasing the size of the seed crystal.

4. ConclusionS

Crystal growth of Na–Si clathrates and seeded growth of type-II clathrate $\text{Na}_{24}\text{Si}_{136}$ were performed by heating Na_4Si_4 and Na_9Sn_4 at 823 K for 12 h. The octahedral single crystals surrounded by {111} facets with a size of 3 mm were obtained on a seed crystal. By repeating the seed growth, the weight of the crystal was increased in proportion to the surface area of the seed crystal. These results pave the way for the production of Na–Si clathrate single crystals large enough for application in new devices and solar cells using efficient crystal growth methods with seed crystals, such as crystal pulling and top-seeded methods.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/cryst11070808/s1>, Figure S1: Schematic diagram of containers for (a) the preparation of the seed crystal and (b) the crystal growth of the Na–Si clathrate, Figure S2: Powder X-ray doffraction patterns of (a) type-I and (b) type-II Na–Si clathrate crystals obtained by heating Na_4Si_4 and Na_9Sn_4 at 823 K for 12 h, followed by alcohol and acid treatment, Figure S3: Photograph and Laue pattern of seeded grown single crystal by heating at 823 K for total heating time of 36 h.

Author Contributions: Conceptualization, H.M.; Data curation, H.Y.; Formal analysis, H.M., H.Y. and R.Y.U.; Investigation, H.M. and K.F.; Project administration, H.M.; Writing—Original draft, H.M.; Writing—Review and editing, H.Y. and K.F. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by JSPS KAKENHI grants (JP18H01887) and Japan Science and Technology Agency (JST) CREST (JPMJCR19J1).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Nolas, G.S. (Ed.) *The Physics and Chemistry of Inorganic Clathrates*; Springer: Berlin, Germany, 2014.
2. Kasper, J.S.; Hagenmuller, P.; Pouchard, M.; Cros, C. Clathrate Structure of Silicon $\text{Na}_8\text{Si}_{46}$ and $\text{Na}_x\text{Si}_{136}$ ($x < 11$). *Science* **1965**, *150*, 1713–1714. [[PubMed](#)]
3. Cros, C.; Pouchard, M.; Hagenmuller, P. Sur une nouvelle famille de clathrates minéraux isotopes des hydrates de gaz et de liquides. Interprétation des résultats obtenus. *J. Solid State Chem.* **1971**, *2*, 570–581. [[CrossRef](#)]
4. Reny, E.; Gravereau, P.; Cros, C.; Pouchard, M. Structural characterisations of the $\text{Na}_x\text{Si}_{136}$ and $\text{Na}_8\text{Si}_{46}$ silicon clathrates using the Rietveld method. *J. Mater. Chem.* **1998**, *8*, 2839–2844. [[CrossRef](#)]
5. Ramachandran, G.K.; Dong, J.; Diefenbacher, J.; Gryko, J.; Marzke, R.F.; Sankey, O.F.; McMillan, P.F. Synthesis and X-ray Characterization of Silicon Clathrates. *J. Solid State Chem.* **1999**, *145*, 716–730. [[CrossRef](#)]
6. Stefanoski, S.; Malliakas, C.D.; Kanatzidis, M.G.; Nolas, G.S. Synthesis and Structural Characterization of $\text{Na}_x\text{Si}_{136}$ ($0 < x \leq 24$) Single Crystals and Low-Temperature Transport of Polycrystalline Specimens. *Inorg. Chem.* **2012**, *51*, 8686–8692. [[PubMed](#)]
7. Mott, N.F. Properties of compounds of type $\text{Na}_x\text{Si}_{46}$ and $\text{Na}_x\text{Si}_{136}$. *J. Solid State Chem.* **1973**, *6*, 348–351. [[CrossRef](#)]
8. Adams, G.B.; O’Keeffe, M.; Demkov, A.A.; Sankey, O.F.; Huang, Y.-M. Wide-band-gap Si in open fourfold-coordinated clathrate structures. *Phys. Rev. B* **1994**, *49*, 8048–8053. [[CrossRef](#)] [[PubMed](#)]
9. Moriguchi, K.; Munetoh, S.; Shintani, A. First-principles study of $\text{Si}_{34-x}\text{Ge}_x$ clathrates: Direct wide-gap semiconductors in Si-Ge alloys. *Phys. Rev. B* **2000**, *62*, 7138–7143. [[CrossRef](#)]
10. Gryko, J.; McMillan, P.F.; Marzke, R.F.; Ramachandran, G.K.; Patton, D.; Deb, S.K.; Sankey, O.F. Low-density framework form of crystalline silicon with a wide optical band gap. *Phys. Rev. B* **2000**, *62*, R7707–R7710. [[CrossRef](#)]
11. Beekman, M.; Baitinger, M.; Borrmann, H.; Schnelle, W.; Meier, K.; Nolas, G.S.; Grin, Y. Preparation and Crystal Growth of $\text{Na}_{24}\text{Si}_{136}$. *J. Am. Chem. Soc.* **2009**, *131*, 9642–9643. [[CrossRef](#)] [[PubMed](#)]
12. Stefanoski, S.; Beekman, M.; Wong-Ng, W.; Zavalij, P.; Nolas, G.S. Simple Approach for Selective Crystal Growth of Intermetallic Clathrates. *Chem. Mater.* **2011**, *23*, 1491–1495. [[CrossRef](#)]

13. Stefanoski, S.; Martin, J.; Nolas, G.S. Low temperature transport properties and heat capacity of single-crystal $\text{Na}_8\text{Si}_{46}$. *J. Phys. Condens. Matter* **2010**, *22*, 485404. [[CrossRef](#)] [[PubMed](#)]
14. Morito, H.; Shimoda, M.; Yamane, H. Single crystal growth of type I Na–Si clathrate by using Na–Sn flux. *J. Cryst. Growth* **2016**, *450*, 164–167. [[CrossRef](#)]
15. Morito, H.; Shimoda, M.; Yamane, H.; Fujiwara, K. Crystal Growth Conditions of Types I and II Na–Si Clathrates by Evaporation of Na from a Na–Si–Sn Solution. *Cryst. Growth Des.* **2017**, *18*, 351–355. [[CrossRef](#)]
16. Morito, H.; Yamane, H. Double-Helical Silicon Microtubes. *Angew. Chem. Int. Ed.* **2010**, *49*, 3638–3641. [[CrossRef](#)] [[PubMed](#)]
17. Morito, H.; Yamada, T.; Ikeda, T.; Yamane, H. Na–Si binary phase diagram and solution growth of silicon crystals. *J. Alloy. Compd.* **2009**, *480*, 723–726. [[CrossRef](#)]
18. Sangster, J.; Bale, C.W. The Na–Sn (Sodium–Tin) System. *J. Phase Equilibria* **1998**, *19*, 76–81. [[CrossRef](#)]