Seeded Growth of Type-II Na\textsubscript{24}Si\textsubscript{136} Clathrate Single Crystals

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**Abstract:** Type-II Na\textsubscript{24}Si\textsubscript{136} clathrate octahedral single crystals surrounded by [111] facets were grown by evaporating Na from a molten mixture of Na\textsubscript{4}Si\textsubscript{4} and Na\textsubscript{4}Sn\textsubscript{4} 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

1. Introduction

Clathrate compounds containing Na in Si cages are called Na–Si clathrates \cite{1}, and two types, type-I (Na\textsubscript{4}Si\textsubscript{4}) and type-II (Na\textsubscript{24}Si\textsubscript{136} 0 < x ≤ 24), have been reported \cite{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 \cite{6}. Mott reported that the metal-insulator transition took place with decreasing x of the Na\textsubscript{24}Si\textsubscript{136} clathrates \cite{7}. Since a bandgap of 1.9 eV, which was shown for the Na-free type-II clathrate, Si\textsubscript{136}, 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 \cite{8–10}.

Powders and polycrystalline samples of the Na–Si clathrates have been conventionally synthesized by thermal decomposition of a solid phase Zintl compound Na\textsubscript{4}Si\textsubscript{4} \cite{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 \cite{11}. The type-II single crystals of about 300 \( \mu \)m were also produced by another thermal decomposition method, in which Na was slowly removed from Na\textsubscript{4}Si\textsubscript{4} heated at 938 K in a closed space surrounded with NaCl and graphite \cite{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 \cite{14,15}. In previous studies \cite{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 \cite{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, Na\textsubscript{4}Si\textsubscript{4}, and Na\textsubscript{15}Sn\textsubscript{4} were used as the starting materials \cite{14,15}. A Na–Si–Sn solution was formed by dissolving Na\textsubscript{4}Si\textsubscript{4} into the melt of Na\textsubscript{15}Sn\textsubscript{4}. The Na–Si clathrates were crystallized by evaporating Na from this solution. The formula for the formation of clathrates could be expressed as follows:
2Na₄Si₄ + Na₁₅Sn₄ + Na → 1/17Na₂₄Si₃₆ (4/2₃Na₉Si₄₀) + Na₉Sn₄ + 2/₃Na (3/2₃Na)↑

Since the Na–Si clathrates are also dissolved into the melt of Na₁₅Sn₄, 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 Na₉Sn₄ because the clathrates were obtained with Na₉Sn₄ after heating. In this study, single crystals of the Na–Si clathrates were prepared using a Na₉Sn₄ melt as a flux, and the seeded crystal growth was attempted to grow a large Na–Si clathrate single crystal.

2. Experimental

Na₄Si₄ and Na₉Sn₄ were used as starting materials. To prepare Na₄Si₄, 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 Na₉Sn₄, 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 Na₄Si₄ and Na₉Sn₄ were taken out from the BN crucibles. Each ingot was cut into pieces 1–2 mm in size with a nipper. Na₄Si₄ and Na₉Sn₄ in a molar ratio of 2:1 (Na₄Si₄: 0.500 g, Na₉Sn₄: 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 Na₄Si₄ (0.100 g) and Na₉Sn₄ (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, CuKα, 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$_4$Si$_4$ and Na$_9$Sn$_4$ 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$_4$Si$_4$ with a melting point (m.p.) of 1071 K [17] could be dissolved in the melt of Na$_9$Sn$_4$ (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, Na$_{24}$Si$_{136}$.

**Figure 1.** Optical micrographs of (a) type-I and (b) type-II Na–Si clathrate single crystals obtained by heating Na$_4$Si$_4$ and Na$_9$Sn$_4$ at 823 K for 12 h, followed by alcohol and acid treatments.

Type-I and type-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$_4$Si$_4$ and Na$_9$Sn$_4$ 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).
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 <100> and <111> were evaluated. Crystal growth along the <100> 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 <100> direction was calculated from this straight line, it was $0.0124 \pm 0.0006 \mu m/s$. Similarly, the crystal growth velocity along the <111> direction was $0.0072 \pm 0.0004 \mu m/s$ 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 <111> was slower than that of <100>. From this result, it was clarified that [111], which has slow crystal growth, is exposed on the surface of the single crystal.

![Figure 2](image)

**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.

![Figure 3](image)

**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 Na$_{24}$Si$_{136}$ were performed by heating Na$_4$Si$_4$ and Na$_8$Sn$_4$ 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 diffraction patterns of (a) type-I and (b) type-II Na–Si clathrate crystals obtained by heating Na$_4$Si$_4$ and Na$_8$Sn$_4$ 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.

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