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High-pressure synthesis and structure of a new silicon clathrate $Ba_{24}Si_{100}$

Hiroshi Fukuoka [a], Kengo Ueno [a], Shoji Yamanaka [a,b,]*

[a] *Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan*
[b] *CREST, Japan Science and Technology Corporation (JST), Kawaguchi 332-0012, Japan*

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Abstract

A new silicon clathrate $Ba_{24}Si_{100}$ was prepared from a stoichiometric mixture of 12 $BaSi_2$ and 76 Si in a molar ratio using a high pressure of 1.5 GPa at 800°C. The X-ray Rietveld analysis revealed that $Ba_{24}Si_{100}$ was isotypic with K_8Sn_{25}, consisting of Ba containing dodecahedral silicon cages, $Ba@Si_{20}$, which are linked by sharing the pentagonal faces. A chiral zeolite-like network was formed; the rest of Ba atoms occupied the resulting interstices of Si_{20} open-cages and Si_8 pseudo-cubic spaces. The synthesis using a pressure higher than 3 GPa at 800°C gave a mixture of the type I silicon clathrate Ba_8Si_{46} and Si. It should be noted that the germanium analog $Ba_{24}Ge_{100}$ was prepared by a simple arc-melting under Ar atmosphere, while the silicon analog required a moderately high pressure for the preparation. $Ba_{24}Si_{100}$ showed a metallic conductivity © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silicon clathrate; High-pressure synthesis; Barium; Si-sp^3 network

1. Introduction

There are two types of silicon clathrate compounds, M_xSi_{46} and M_xSi_{136} (M = Na, K, Rb, Cs), which are isotypic with the well known gas hydrates, type I, $G_x(H_2O)_{46}$ and type II, $G_x(H_2O)_{136}$, respectively [1,2]. In the gas hydrates, water molecules are linked by hydrogen bonds to form three-dimensional networks with cages, in which various gas molecules such as methane, Ar, and CO_2, are trapped. The silicon clathrate compounds are isotypic with these gas hydrates, the H–O···H hydrogen bonds of the gas hydrates are replaced with the Si–Si covalent bonds. The type I silicon clathrate compounds, M_xSi_{46} are composed of Si_{20} dodecahedra and Si_{24} tetrakaidecahedra. These Si polyhedra are connected by face sharing and alkali metals (M) are centered in the polyhedra. The type II silicon clathrates, M_xSi_{136} are similarly composed of Si_{20} dodecahedra and Si_{28} hexakaidecahedra. Alkali metal containing silicon clathrate compounds were extensively studied by a French group in the late 1960s [1–3].

Recently, we have succeeded in the synthesis of Ba containing silicon clathrate compounds, $(M, Ba)_xSi_{46}$ (M = Na, K) [4,5] and have found that it showed superconductivity with a transition temperature of about 4 K [6]. This is the first superconductor having Si-sp^3 covalent network. The Ba containing silicon clathrate was prepared from a ternary Zintl phase Na_2BaSi_4 by removing part of Na by thermal treatment. The Zintl phase was segregated into a mixture of $BaSi_2$ and $(Na, Ba)_xSi_{46}$; the $BaSi_2$ was removed by washing with water. The clathrate compound was therefore always obtained in a powder form. The silicon clathrate compound thus prepared contained Na as well as Ba atoms in the silicon cages; the Na atoms mainly occupy the Si_{20} cages, and the Ba atoms are in the Si_{24} cages. The ideal composition should be $Na_2Ba_6Si_{46}$. Very recently, we have succeeded in the synthesis of Ba_8Si_{46} as a bulk phase by using high pressure and high temperature conditions, where Ba atoms occupy all of the Si_{20} and Si_{24} cages of the clathrate structure as shown in Fig. 1 [7]. The com-

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* Corresponding author. Fax: + 81-824-247740.
E-mail address: syamana@ipc.hiroshma-u.ac.jp (S. Yamanaka).

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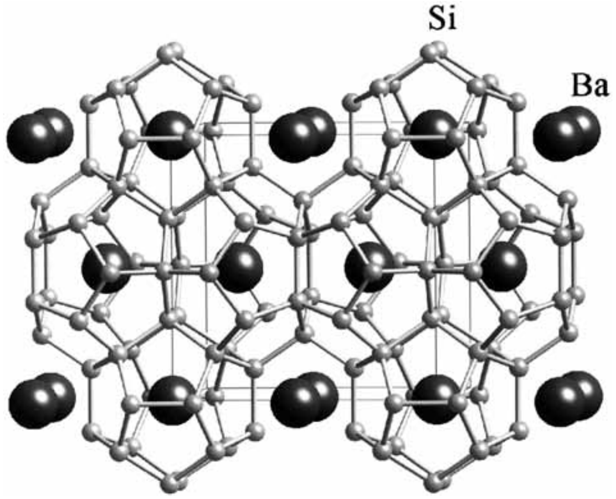

Fig. 1. Schematic structural model of a silicon clathrate compound Ba_8Si_{46}. The atoms behind the top are not shown for clarity.

pound became a superconductor with a transition temperature (*Tc*) of 8.0 K. This is the highest *Tc* ever obtained among silicon clathrate compounds.

There are two types of alkali metal containing germanium clathrate compounds, Type I, M_xGe_{46} and Type II, M_xGe_{136} (M = Na, K, Rb) [1,2]. There is also a Ba containing germanium clathrate compound with a composition of Ba_8Ge_{43} [8], which has vacancies in the network. It is a semiconductor, and does not show superconductivity. We have prepared a new germanium clathrate compound with a composition $Ba_{24}Ge_{100}$ [9]. This clathrate compound was prepared by a simple arc-melting under Ar atmosphere, and the single crystal X-ray analysis revealed that it was isotypic with K_8Sn_{25}, which is also isotypic with $K_6Sn_{23}Bi_2$, $Ba_6In_4Ge_{21}$ [10,11], and K_6Sn_{25} [12]. The presence of the corresponding isotypic silicon compound has been anticipated, and in this report, we have succeeded in preparing a new silicon clathrate compound $Ba_{24}Si_{100}$ using high-pressure.

2. Experimental

2.1. Synthesis

Silicon and barium metal (purified by distillation in vacuum) were mixed in atomic ratios 46/8 and 25/6. Each mixture was arc-melted in a water-cooled copper crucible under Ar atmosphere. The resulting melt was found to be a mixture of Si and $BaSi_2$, which was ground in an Ar filled glove-box. The powdered melt was placed in an h-BN cell (6 mm in inner diameter and 5 mm in length) which was in turn placed in a carbon tube heater, and in a pyrophyllite cube as a pressure media. A cubic multi anvil press (Riken model CP-10) was used. The BN cell was heated by the carbon heater and the temperature was monitored by a thermocouple placed under the cell. The pressure applied was in a range of 1–5 GPa at 800°C, and maintained for 1 h, then the sample was quenched to room temperature before the pressure was gradually released.

2.2. X-ray Rietveld analysis

The X-ray powder diffraction (XRD) pattern was measured using graphite monochromated Cu Kα radiation. The XRD data were collected at every 0.03° over the range of 10 to 120° in 2θ. The structure of the silicon clathrate was analyzed on the basis of the profile data over the range of 25 to 120° using a RIETAN-94 X-ray powder Rietveld analysis program [13] included in the X-ray diffractometer (MAC Science, model M18XHF).

2.3. Electric conductivity

Electric conductivity of the clathrate sample was measured on the compressed disk sample (6 mm in diameter and 0.8 mm in thickness) by van der Pauw method [14] in a temperature range of 2–250 K using a cryostat of a SQUID magnetometer (Quantum Design MPMS-5).

3. Results and discussion

Although $Ba_{24}Ge_{100}$ was prepared by a simple melting of a mixture of Ba and Ge under Ar atmosphere, similar arc-melting of Ba and Si gave a mixture of $BaSi_2$ and Si. As shown in a previous study [7], if such mixture of a composition of $8BaSi_2 + 30Si$ (Ba/Si = 8/46) was treated under a pressure of 3 GPa at 800°C, a clathrate compound Ba_8Si_{46} was obtained. In this study, the applied pressure was decreased down to 1.5 GPa at 800°C. Then, we could not obtain the clathrate, but a mixture of an unknown phase and Si. The unknown phase was found to be very similar to $Ba_{24}Ge_{100}$ with respect to the XRD patterns [9]. When a mixture of 24 $BaSi_2$ and 52 Si (Ba/Si = 24/100) was treated under the same condition of 1.5 GPa at 800°C, the same unknown phase was obtained as a single phase;

$$24BaSi_2 + 52Si \xrightarrow{\text{1.5 GPa at 800°C}} Ba_{24}Si_{100}$$

The XRD diffraction peaks could be indexed on the basis of a cubic unit cell with $a = 14.0685(2)$ Å. The Rietveld analysis was performed on the XRD pattern shown in Fig. 2, and the structural parameters were successfully refined on the basis of the structure of $Ba_{24}Ge_{100}$. The crystallographic data are listed in Table 1.

This is the third type of silicon clathrate isotypic with $Ba_{24}Ge_{100}$ and K_8Sn_{25},which crystallize into the cubic space group $P4_132$ (or $P4_332$). The structure consists of

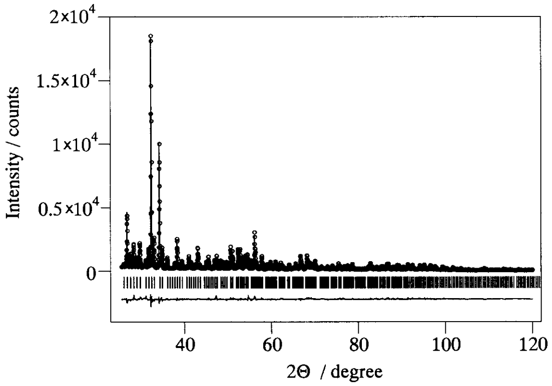

Fig. 2. Observed (open circles) and final calculated (line) profile plots, thick marks for the Bragg peak positions, and the difference profile plot from the Rietveld refinement of $Ba_{24}Si_{100}$.

one kind of Ba containing distorted pentagonal silicon dodecahedron $Ba@Si_{20}$, which shares its three pentagonal faces and one external bond to four different dodecahedra. As a result, a chiral zeolite-like network is formed as shown in Fig. 3. Ba atoms in sites 12*d* and 4*b* are located in the channels surrounded by the linked dodecahedral network, and centered in Si_{20} open cages and Si_8 distorted cubes formed in the channels, respectively (Fig. 4). There are two types of Si atoms, 32 three-bonded (in sites 8*c* and 24*c*) and 68 four-bonded (in sites 24*c*, 12*d*, 24*e*, and 8*c*) Si atoms. The three-bonded Si atoms form distorted cubes and co-ordinate to the Ba atoms in 4*b* sites located in the center of the cubes (Fig. 4). The averaged bond lengths of Si–Si, and Si–Ba atoms are 2.415 and 3.571 Å, respectively, which are in good agreement with those of Type I and II clathrate compounds.

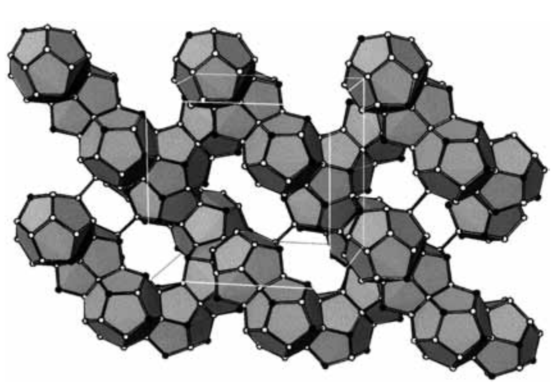

Fig. 3. Zeolitic network formed by face sharing of $Ba@Si_{20}$ dodecahedra of $Ba_{24}Si_{100}$. Closed and open circles are three- and four-bonded Si atoms, respectively.

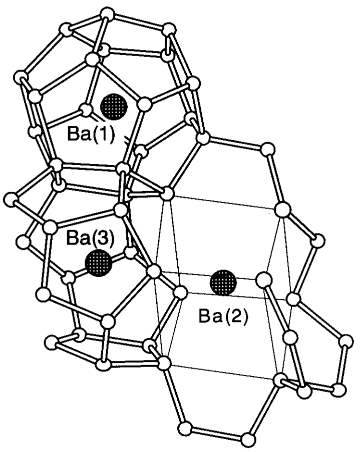

Fig. 4. Environments of Ba atoms in sites 8*c* (Ba(1)), 4*b* (Ba(2)), and 12*d* (Ba(3)) in Si_{20} dodecahedron, Si_8 distorted cubes, and Si_{20} open cages, respectively.

Table 1
Crystallographic data and atomic coordinates for $Ba_{24}Si_{100}$

Atom	Wyckoff site	*x*	*y*	*z*	*B* (Å^2)
Si(1)	8*c*	0.0362(6)	0.0362(6)	0.0362(6)	1.3(3)
Si(2)	24*e*	0.2038(5)	0.0427(5)	−0.0000(6)	0.7(2)
Si(3)	12*d*	0.125	0.1696(6)	0.4196(6)	2.7(3)
Si(4)	24*e*	0.2387(5)	0.9394(7)	0.8752(6)	1.1(2)
Si(5)	24*e*	0.4156(5)	0.8605(5)	0.0769(5)	0.7(2)
Si(6)	8*c*	0.3256(6)	0.3256(6)	0.3256(6)	2.8(4)
Ba(1)	8*c*	0.1887(2)	0.1887(2)	0.1887(2)	1.37(7)
Ba(2)	4*b*	0.875	0.875	0.875	1.7(1)
Ba(3)	12*d*	0.125	0.8072(1)	0.0572(1)	2.34(7)
Composition	$Ba_{24}Si_{100}$				
Space group	$P4_132$ (No. 213)				
Lattice constant (Å)	$a = 14.0685(2)$				
R values (%) [a]	$R_{WP} = 9.56$, $R_E = 5.26$, $R_P = 6.69$, $R_I = 5.08$, $R_F = 3.50$				

[a] $R_{WP} = [\Sigma_i w_i(y_i - y_{ci})^2/\Sigma_i w_i y_i^2]^{1/2}$, $R_P = \Sigma_i(y_i - y_{ci})^2/\Sigma_i y_i^2$, $R_E = [(N_P - N_r - N_c)/\Sigma_i w_i y_i^2]^{1/2}$, $R_I = \Sigma_k|I_k(\text{'obs.'}) - I_k(\text{calc.})|/\Sigma_k I_k(\text{'obs'})$, $R_F = \Sigma_k|[I_k(\text{'obs.'})]^{1/2} - [I_k(\text{calc.})]^{1/2}|/\Sigma_k[I_k(\text{'obs'})]^{1/2}$, $w_i = 1/y_i$, y_i = observed intensity at the *i*th step. y_{ci} = calculated intensity at the *i*th step. I_k = intensity assigned to the *k*th Bragg reflection.

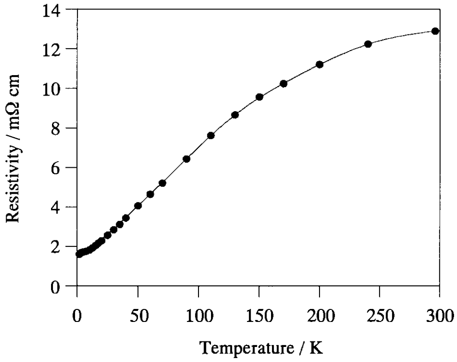

Fig. 5. Electrical resistivity of $Ba_{24}Si_{100}$ as a function of temperature.

Fig. 5 shows the electric resistivity of $Ba_{24}Si_{100}$ as a function of temperature in a range of 280 to 2 K. The resistivity decreases with the decreased temperature. Note that this is the first metallic compound among the clathrate compounds isotypic with the K_8Sn_{25} structure. The 32 electrons out of 48 electrons from 24 Ba atoms are bound at the 32 three-bonded Si atoms as lone pairs. The 16 excess electrons will remain in the conduction band of the Si network, which will give a metallic behavior to the clathrate. The band structures of the isotypic compounds $K_6Sn_{23}Bi_2$ and K_6Sn_{25} were calculated by Fässler [11]. There are no excess electrons in these compounds; all are trapped as lone pairs at the three-bonded atoms.

Saito and Oshiyama [15] calculated the band structure of the Ba containing silicon clathrate $Ba_6Na_2Si_{46}$, and revealed that Ba states showed strong hybridization with Si_{46} states, giving very high density of states at the Fermi level. Moriguchi et al. [16] also showed that the conduction band of Ba_8Si_{46} was strongly modified by the Ba state, having a strong peak of the density of states at the conduction edge. Such high density of states at the Fermi level must be favorable for the superconductivity observed for the Ba containing silicon clathrate compounds, $(Ba, Na)_xSi_{46}$. Although the metallic and Ba containing silicon clathrate $Ba_{24}Si_{100}$ was expected to become a superconductor, superconductivity was not observed in a temperature range down to 2 K.

The volume changes associated in the formation of Ba_8Si_{46} can be estimated from the molar volumes of Si (12.06), $BaSi_2$ (52.4) [17], $Ba_{24}Si_{100}$ (1676.8), and Ba_8Si_{46} (663.6 $cm^3\ mol^{-1}$) [7];

$$24BaSi_2 + 90Si \xrightarrow{\Delta V_1} Ba_{24}Si_{100} + 38Si \xrightarrow{\Delta V_2} 3Ba_8Si_{48}$$

The volume changes ΔV_1 and ΔV_2 are calculated to be -208 and -144 $cm^3\ mol^{-1}$, respectively. Therefore, high-pressure conditions favor the formation of $Ba_{24}Si_{100}$ and Ba_8Si_{46}. $Ba_{24}Si_{100}$ was obtained in the pressure region on 1.5–3 GPa at 800°C. The pressure higher than 3 GPa should favor the clathrate Ba_8Si_{46} of a more dense form.

It is interesting to note that the application of high pressure is very effective and required in the synthesis of Si clathrate compounds, whereas the Ge analogs can be prepared by simple melting without pressure.

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