High-Pressure Synthesis of a New Silicon Clathrate Superconductor, Ba_8Si_{46}

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A new silicon clathrate compound with a composition of Ba_8Si_{46} was prepared under high-pressure and high-temperature conditions. The compound was isomorphous with Na_8Si_{46} and became a superconductor with a transition temperature of 8.0 K. Barium atoms occupy all of the Si_{20} and Si_{24} cages of the clathrate structure. This is the first clathrate superconductor obtained as a bulk phase.

Introduction

Silicon clathrate compounds, M_xSi_{46} (M = Na, K, Rb, Cs), are isomorphous with the well-known type-I gas hydrates, $G_x(H_2O)_{46}$;[1] the H−O···H hydrogen bonds of the gas hydrates are replaced with the Si−Si covalent bonds, and the alkali metal atoms (M) are trapped in the silicon polyhedra, replacing gas molecules (G) such as Ar, methane, and CO_2. The silicon clathrates are composed of Si_{20} dodecahedra and Si_{24} tetrakaidecahedra, the two kinds of polyhedra being connected by sharing faces. The alkali metal containing silicon clathrate compounds were extensively studied by a French group in the late 1960s.[2] Recently, we have succeeded in the synthesis of a Ba-containing silicon clathrate, $(Na, Ba)_xSi_{46}$, and have found that it showed superconductivity with a transition temperature (T_c) of about 4 K.[3,4] This is the first superconductor having a Si-sp^3 covalent network. Here we report a new silicon clathrate superconductor, Ba_8Si_{46}, with $T_c = 8.0$ K, which has been prepared with the aid of high pressure. This is the first silicon clathrate that is obtained as a bulk phase and doped with only barium.

Experimental Section

Silicon and barium metal (purified by distillation in a vacuum) were mixed in an atomic ratio of 46:8 and 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 glovebox. The powdered melt was placed in a 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 multianvil 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, and then the sample was quenched to room temperature before the pressure was gradually released. The obtained sample was analyzed for magnetic properties by a SQUID magnetometer (Quantum Design MPMS-5) and electrical resistivity down to 2 K by a dc four-probe method. The X-ray powder diffraction (XRD) pattern was measured by using graphite monochromated Cu Kα radiation. The XRD data were collected at every 0.02° over the range 10−110° in 2θ by a continuous scan mode with a scan speed of 1°/min. The structure of the silicon clathrate was analyzed on the basis of the profile data using a RIETAN-94 X-ray powder Rietveld analysis program[5] included in the X-ray diffractometer (MAC Science, model M18XHF). The following three regions were excluded from the Rietveld refinement due to low diffraction angles and a trace of BN and Si: 16.00−22.0, 25.50−27.00, and 28.00−29.00° in 2θ.

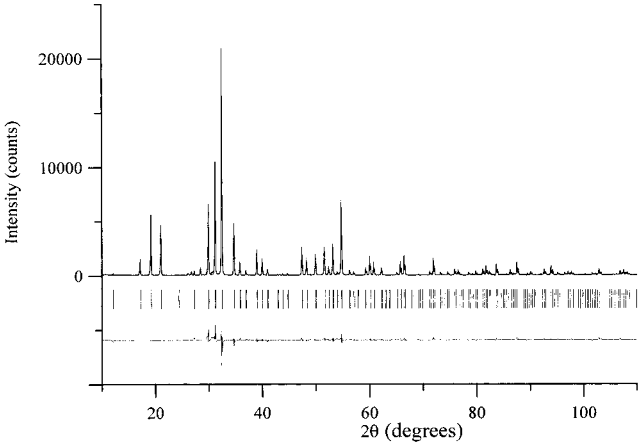

Figure 1. Observed (solid line) and final calculated (dotted line) profile plots, thick marks for the Bragg peak positions, and the difference profile plot from the Rietveld refinement of Ba_8Si_{46}.

Results and Discussion

The X-ray diffraction pattern of the arc-melted sample was a mixture of $BaSi_2$ and Si. The mixture was converted into a single phase of Ba_8Si_{46} by the treatment under a pressure of 3 GPa at 800 °C for 1 h. If the applied pressure was lower than 2 GPa, the conversion was not completed. The clathrate Ba_8Si_{46} is isomorphous with Na_8Si_{46} ($a = 10.19$ Å).[1] All of the peaks of the diffraction pattern were indexed on the basis of a cubic unit cell of $a = 10.328(2)$ Å. The Rietveld refinement pattern is shown in Figure 1. In Table 1 the crystallographic

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Table 1. Crystallographic Data for Ba_8Si_{46} Obtained by Rietveld Refinement

Atomic Coordinates and Isotropic Thermal Parameters

atoms	posn	x	y	z	B, Å^2
6 Si(1)	6*c*	0.25	0	0.5	0.26(32)
16 Si(2)	16*i*	0.1864(6)	0.1864(6)	0.1864(6)	0.38(25)
24 Si(3)	24*k*	0	0.3055(9)	0.1199(10)	0.35(21)
2 Ba(1)	2*a*	0	0	0	2.05(19)
6 Ba(2)	6*d*	0.25	0.5	0	0.71(10)

Other Crystallographic Data

space group $Pm\bar{3}n$; lattice param $a = 10.328(2)$ Å; reliability factors (%)[a]

$R_{wp} = 14.88$, $R_e = 6.31$, $R_f = 4.39$; goodness-of-fit S (R_{wp}/R_e) = 2.36

[a] R_{wp}, R-weighted pattern; R_e, R-expected; R_f, R-structure factor.

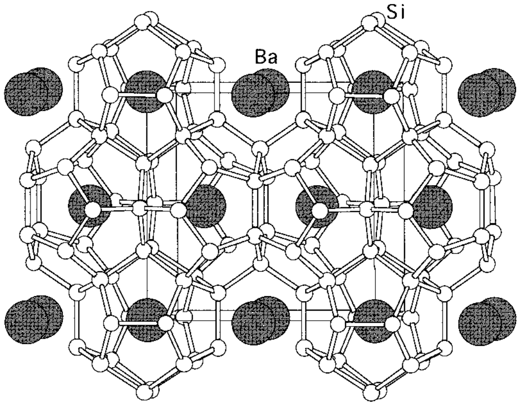

Figure 2. Schematic structural model of Ba_8Si_{46}. The atoms behind the top are not shown for clarity.

Table 2. Selected Interatomic Distances and Bond Angles in Ba_8Si_{46} Shown in Figure 3

Distances (Å)

Si(1)−Si(3)	2.415(9)	Ba(2)−Si(1)	3.651(7)
Si(2)−Si(3)	2.386(7)	Ba(2)−Si(2)	3.824(3)
Si(3)−Si(3)	2.477(21)	Ba(2)−Si(3)	3.497(7)
Si(2)−Si(2)	2.274(24)	Ba(1)−Ba(2)	5.773(1)
Ba(1)−Si(2)	3.335(12)	Ba(2)−Ba(2)	5.164(1)
Ba(1)−Si(3)	3.390(8)		

Angles (deg)

α, Si(3)−Si(3)−Si(2)	106.7(2)	ϵ, Si(3)−Si(1)−Si(3)	108.0(2)
β, Si(3)−Si(2)−Si(3)	109.4(3)	φ, Si(1)−Si(3)−Si(2)	105.5(4)
γ, Si(3)−Si(1)−Si(3)	112.4(5)	υ, Si(3)−Si(2)−Si(2)	109.5(3)
δ, Si(1)−Si(3)−Si(3)	123.7(2)		

data for Ba_8Si_{46} determined by the Rietveld refinement are summarized. The coordinates given in the table agreed well with those of (Ba, Na)$_x$Si$_{46}$.[3] A schematic structural model of Ba_8Si_{46} is shown in Figure 2. The Ba atoms in Ba_8Si_{46} occupy all of the silicon cages. The selected interatomic distances and bond angles in Ba_8Si_{46} are listed in Table 2 for the two types of silicon cages (Si_{20} and Si_{24}) linked by sharing a pentagonal face shown in Figure 3.

The temperature dependence of the resistivity of a Ba_8Si_{46} disk is shown in Figure 4. The sample showed a very sharp superconducting transition at 8.0 K. The 10%−90% transition width was <0.1 K. Figure 5 shows the magnetic susceptibility of Ba_8Si_{46} as a function of temperature at 50 Oe. The sample showed a superconducting transition due to the occurrence of Meissner shielding at 8 K. This temperature is in good agreement with the transition temperature obtained by the resistivity measurement. The existence of the hysteresis between the two magnetization curves for the zero-field cooling (ZFC) and the field cooling (FC) modes indicates that the compound is a type-II superconductor. The volume susceptibility at 2 K was determined to be −0.092 on the basis of the ZFC data and the theoretical density of 3.60 g cm^{-3} estimated from the XRD data. This value is ~110% of the theoretical value ($-1/4\pi$) for perfect diamagnetism, indicating that this is a bulk superconductivity. The upper critical field (H_{c2}) for superconductivity was determined to be ca. 6 T at 2 K. This corresponds to a small coherence length of 74 Å.[6]

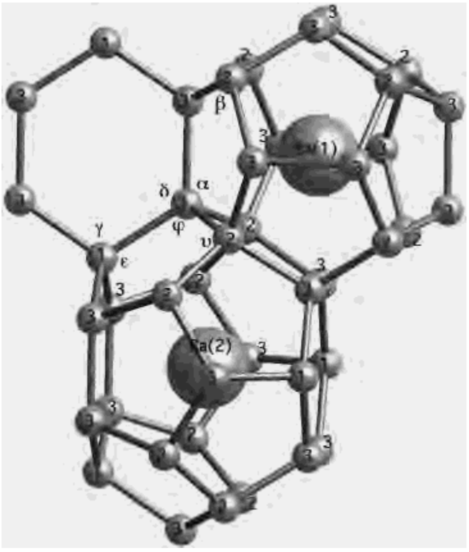

Figure 3. Schematic illustration of the two types of silicon polyhedra (Si_{20} and Si_{24}) linked by sharing a pentagonal face in Ba_8Si_{46}. The numbers on the Si atoms designate the positions assigned in Table 1.

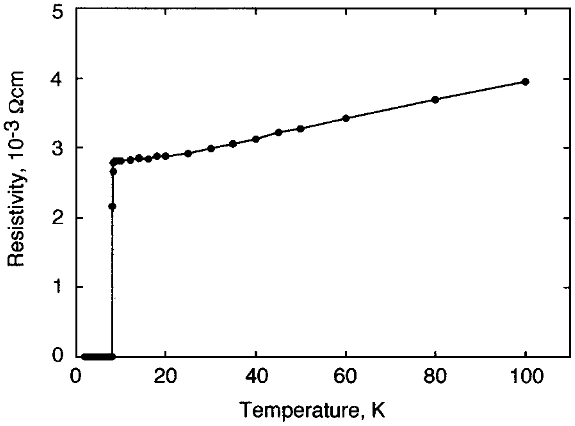

Figure 4. Temperature dependence of the resitivity of Ba_8Si_{46}.

So far the alkali metal containing silicon clathrate compounds have been prepared by the partial removal of alkali metal from Zintl phases, MSi (M = Na, K, Rb, Cs), at elevated temperatures in a vacuum.[2] The barium-containing silicon clathrates (M, Ba)$_x$Si$_{46}$ (M = Na, K) were also prepared in a similar method by removing alkali metals from the ternary Zintl phases of (M_2-Ba)Si_4 (M = Na, K).[3,7] Upon the removal of the alkali metals, the Zintl phases were segregated into $BaSi_2$ and the barium-containing silicon clathrate compounds. The $BaSi_2$ could be removed by dissolving with water. Therefore the resulting clathrates were all obtained in fine powder form. Those samples are not suitable for the study of physical properties due to the

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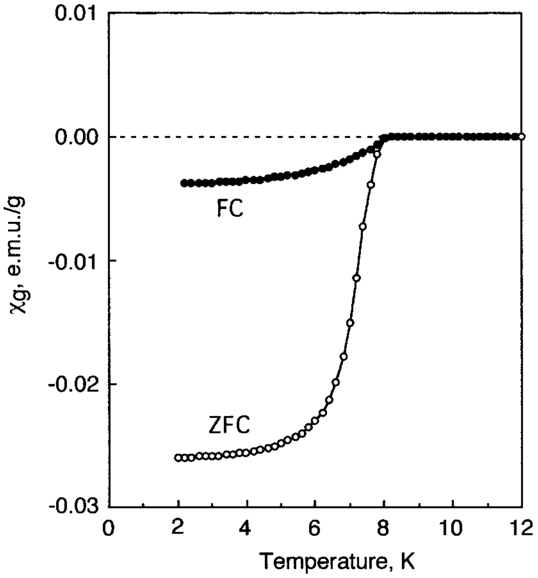

Figure 5. Temperature dependence of the magnetic susceptibility of Ba_8Si_{46} observed in a magnetic field of 50 Oe: (○) zero-field cooled (ZFC); (●) field cooled (FC).

presence of oxidized grain boundaries. Note that Ba_8Si_{46} is the first silicon clathrate sample prepared under high pressure and obtained in bulk form. Barium-containing ternary silicon clathrate compounds $Ba_8T_xSi_{46-x}$ (T = Au, Ag, Ni, Cu, Pt; $x \approx 6$) were prepared by Cordier et al.,[8] where transition metals (T) replaced part of the silicon atoms at 6*c* sites connecting Si_{20} polyhedra in the clathrate network. The ternary silicon clathrates can be synthesized by simple melting of the constituent elements at high temperatures. Those are metallic but not superconductors. Note that the binary compound Ba_8Si_{46} cannot be obtained by a simple melting of Ba and Si; the arc-melting gave only a mixture of $BaSi_2$ and Si. The total volume of 8 $BaSi_2$ (ref 9) and 30 Si is calculated to be 778.2 cm^3/mol, and the volume of Ba_8Si_{46} is 663.6 cm^3/mol, about 15% smaller than the reactant mixture. Therefore high-pressure conditions should favor the formation of Ba_8Si_{46}. Although the clathrate structure appears to be loosely packed, the volume change is favorable for the formation as the system.

The T_c determined for Ba_8Si_{46} is much higher than those of solid solutions $Na_xBa_6Si_{46}$ ($x \leq 2$) prepared by the decomposition of the Zintl phase in our previous study,[10] where Na atoms occupy the Si_{20} cages and Ba atoms the Si_{24} cages. It was shown that the removal of Na raised the T_c from 2.6 to 4.8 K for $x =$ 1.5 to 0.2 in $Na_xBa_6Si_{46}$. Saito and Oshiyama[11] showed by theoretical calculation of the band structure of a barium-containing silicon clathrate that the barium can engage in hybridization with silicon orbitals to form a new band, which is partially filled with electrons of Ba to realize a high density of states favorable for superconductivity. Their theoretical approach was supported by the ^{29}Si and ^{137}Ba NMR study by Shimizu et al.[12] The role of the Na atoms in the Si_{20} cavities is not clear; the increase of the Na concentration decreases T_c, whereas the removal of Na or replacement with Ba increases T_c.

It is well-known that silicon of the diamond structure is transformed to the β-Sn structure with octahedrally coordinated silicon.[13] High-pressure transformations of Zintl silicides were extensively studied by Evers et al.[14,15] They showed that the silicon subnetworks were easily transformed under the application of a moderate range of high pressure. Recently, Imai et al.[16,17] showed that layered $BaSi_2$ prepared under high pressure exhibited superconductivity at 6 K. A missed silicon Zintl phase, LiSi, has recently been prepared by using high pressure.[18] High-pressure synthesis of silicon compounds will be a very promising field to develop new silicon chemistry.

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