

# Preparation and Structure of a New Germanium Clathrate, Ba<sub>24</sub>Ge<sub>100</sub>

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Single crystals of a new germanium clathrate, Ba<sub>24</sub>Ge<sub>100</sub>, were synthesized by the Czochralsky pulling method using a tetra-arc furnace under an Ar atmosphere. The crystal structure was studied by X-ray single-crystal analysis. The clathrate crystallized in the cubic space group *P4<sub>3</sub>32* with  $a = 14.5635(7)$  Å,  $V = 3088.9(2)$  Å<sup>3</sup>. The final refinement using 903 unique reflections converged at  $R = 0.032$  and  $R_w = 0.036$ . In the structure, germanium atoms are linked by  $sp^3$   $\sigma$ -bonds to form a three-dimensional network, in which barium atoms are enclosed. There are three sites for the barium atoms having different coordination environments. One site is in a Ge<sub>20</sub> dodecahedron and the others are coordinated with 20 Ge atoms and 8 Ge atoms, respectively.

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**Key Words:** germanium clathrate.

## INTRODUCTION

There are two types of silicon clathrate compounds,  $M_xSi_{46}$  and  $M_xSi_{136}$  ( $M = Na, K, Rb,$  and  $Cs$ ), which are isomorphous with the well-known gas hydrates, type I,  $G_x(H_2O)_{46}$ , and type II,  $G_x(H_2O)_{136}$  (1, 2), respectively. 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<sub>2</sub> are trapped. In the silicon clathrate compounds, the H–O...H hydrogen bonds of the gas hydrates are replaced with Si–Si covalent bonds. The type I silicon clathrate compounds,  $M_xSi_{46}$ , are composed of Si<sub>20</sub> dodecahedra and Si<sub>24</sub> tetrakaidecahedra. The Si polyhedra are connected by face sharing, alkali metals ( $M$ ) being placed in the center of the polyhedra. The type II silicon clathrates,  $M_xSi_{136}$ , are similarly composed of Si<sub>20</sub> dodecahedra and Si<sub>28</sub> 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,

( $M, Ba$ )<sub>x</sub>Si<sub>46</sub> ( $M = Na, K$ ) (4, 5), and have found that they showed superconductivity with a transition temperature of about 4 K (4–6). This is the first superconductor having an Si  $sp^3$  covalent network. Alkali metal-doped silicon clathrate compounds are prepared from Zintl monosilicides ( $MSi$ ) by partial removal of the alkali metals by thermal treatment. The Zintl monosilicides,  $MSi$  (or  $M_4Si_4$ ), consist of  $[Si_4]^{4-}$  Zintl anions (7–9), which would be linked together to form a silicon  $sp^3$  network by the removal of alkali metals, leaving part of the alkali atoms in the silicon cages. Barium-containing Zintl phase BaSi<sub>2</sub> (or Ba<sub>2</sub>Si<sub>4</sub>) also consists of Si<sub>4</sub> Zintl anions (10). It was expected that the removal of Ba atoms from BaSi<sub>2</sub> would result in Ba-containing silicon clathrate compounds. However, the removal of Ba from BaSi<sub>2</sub> required a very high temperature, and formed only a mixture of Si and BaSi<sub>2</sub>. In our synthesis of the Ba-containing silicon clathrate compound, we first prepared a solid solution between BaSi<sub>2</sub> and NaSi, and then Na atoms were removed at moderate temperatures (6). The resulting product contained BaSi<sub>2</sub> and a Ba-containing silicon clathrate compound, (Na, Ba)<sub>x</sub>Si<sub>46</sub>; BaSi<sub>2</sub> could be removed by washing with water. Silicon clathrate compounds thus prepared contained Na as well as Ba atoms in the silicon cages; the Na atoms mainly occupied the Si<sub>20</sub> cages, and the Ba atoms were in the Si<sub>24</sub> cages. The ideal composition should be Na<sub>2</sub>Ba<sub>6</sub>Si<sub>46</sub>. Recently, we have succeeded in the synthesis of Ba<sub>8</sub>Si<sub>46</sub> by using high-pressure and high-temperature conditions (11). Ba atoms occupy all of the Si<sub>20</sub> and Si<sub>24</sub> cages of the clathrate structure. The compound became a superconductor with a transition temperature of 8.0 K.

There are also two types of alkali metal-containing germanium clathrate compounds, type I,  $M_xGe_{46}$ , and type II,  $M_xGe_{136}$  ( $M = Na, K,$  and  $Rb$ ) (1, 2, 12). In this study, an attempt has been made to prepare a Ba-containing germanium clathrate. In the first step, a solid solution of BaGe<sub>2</sub> (13, 14) and NaGe (9, 15) was prepared by a method similar to that used for the preparation of (Na, Ba)<sub>x</sub>Si<sub>46</sub>. A solid solution BaNa<sub>2</sub>Ge<sub>4</sub> was obtained and Na was removed by evaporation at elevated temperatures.

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However, all of the Na atoms were removed from the system to form a compound with a composition of  $\text{BaGe}_4$ . The presence of this compound was already reported (16, 17), but the structure was still unknown. In this study  $\text{BaGe}_4$  was prepared by the arc melting method. It was anticipated that determining the structure of  $\text{BaGe}_4$  would give important information about the intermediate product between Zintl phase and clathrate. Here we report the preparation of the single crystals of  $\text{BaGe}_4$  and the X-ray single-crystal analysis. It has been found that  $\text{BaGe}_4$  should have a composition of  $\text{Ba}_{24}\text{Ge}_{100}$ , and has a germanium clathrate network similar to  $\text{K}_8\text{Sn}_{25}$  (18),  $\text{K}_6\text{Sn}_{25}$  (19), and  $\text{Ba}_6\text{In}_4\text{Ge}_{21}$  (20, 21).

## EXPERIMENTAL

$\text{Ba}_{24}\text{Ge}_{100}$  was synthesized using arc furnaces. A mixture of barium and germanium in a mole ratio of 1 : 4 was melted in an arc furnace under an Ar atmosphere. The reaction immediately finished and a bulk product having a metallic luster was obtained. Single crystals were obtained by the Czochralsky pulling method using a tetra-arc furnace under an Ar atmosphere. The compositions of the product were determined by using an X-ray microanalyzer (JEOL JSM-840F).

A single crystal suitable for the structure analysis was selected from the pulled-up grown crystals. Intensity data

**TABLE 1**  
Crystallographic Data for  $\text{Ba}_{24}\text{Ge}_{100}$

Formula	$\text{Ba}_{24}\text{Ge}_{100}$
Formula weight	1319.39
Space group	$P4_132$ (No. 213)
$a$ (Å)	14.5635(7)
$V$ (Å <sup>3</sup> )	3088.9(2)
$Z$	1
$F_{000}$ electrons	4544
Linear absorption coefficient (cm <sup>-1</sup> )	313.8
$T$ (K) of data collection	293
Crystal size (mm)	0.35 × 0.15 × 0.05
Diffractometer	Bruker Smart 1000 CCD system
Radiation (graphite monochromated)	$\text{MoK}\alpha$ , 0.7107 Å
Collection region	$-14 \leq h \leq 14$ $0 \leq k \leq 20$ $0 \leq l \leq 20$
$2\theta$ limit	$4 \leq 2\theta \leq 61$
No. of measured reflections	4696
No. of used reflections (with $ F_o  > 3\sigma F_o $ )	903
No. of variable parameters	49
$R$ , $R_w^a$	0.0331, 0.0363
Goodness of fit, $S^b$	1.93
Residual density <sup>c</sup> (e Å <sup>-3</sup> )	2.2

$$^a R = \sum(|F_o| - |F_c|) / \sum|F_o|, R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} (w = 1/\sigma(F_o)^2).$$

$$^b S = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}.$$

<sup>c</sup> The highest residual electrons of the final difference Fourier map.

**TABLE 2**  
Atomic Parameters for  $\text{Ba}_{24}\text{Ge}_{100}$  with Standard Deviations in Parentheses

Atom	Wyckoff site	$x$	$y$	$z$	$U_{\text{iso}}$ (Å <sup>2</sup> )
Ge(1)	8c	0.03046(12)	0.03046(12)	0.03046(12)	0.0284(7)
Ge(2)	24e	0.20297(11)	0.04252(10)	0.00014(10)	0.0195(8)
Ge(3)	12d	$\frac{1}{8}$	0.16907(10)	0.41907(10)	0.0204(8)
Ge(4)	24e	0.23965(10)	0.93497(11)	0.87355(11)	0.0191(8)
Ge(5)	24e	0.41558(11)	0.85259(11)	0.08346(10)	0.0207(8)
Ge(6)	8c	0.32523(10)	0.32523(10)	0.32523(10)	0.0176(5)
Ba(1)	8c	0.18988(6)	0.18988(6)	0.18988(6)	0.0211(3)
Ba(2)	4b	$\frac{7}{8}$	$\frac{7}{8}$	$\frac{7}{8}$	0.0265(5)
Ba(3)	12d	$\frac{1}{8}$	0.81026(9)	0.06026(9)	0.0597(9)

were collected on the SMART 1000 CCD-equipped diffractometer (Bruker Japan) using monochromated  $\text{MoK}\alpha$  radiation. The structure was determined using the software SHELXS97 (22). The final refinement was performed by the full-matrix least-squares method using the program ANYBLK (23).

## RESULTS AND DISCUSSIONS

The composition of the crystals obtained by the Czochralsky method was determined to be  $\text{BaGe}_{3.94}$  by X-ray microanalysis. This compound crystallized in the cubic space group  $P4_132$  (No. 213) with  $a = 14.5635(7)$  Å. X-ray single-crystal analysis revealed that the composition was  $\text{Ba}_{24}\text{Ge}_{100}$  ( $\text{BaGe}_{4.17}$ ), which was slightly different from the nominal composition determined by X-ray microanalysis. This difference was probably caused by a contamination of  $\text{BaGe}_2$  and Ge in the samples used for the microanalysis, in addition to the standard deviation of the experimental data. The crystallographic data for  $\text{Ba}_{24}\text{Ge}_{100}$  are listed in Table 1. The atomic parameters and thermal vibrational parameters are given in Tables 2 and 3.

**TABLE 3**  
Thermal Vibrational Parameters for  $\text{Ba}_{24}\text{Ge}_{100}$  with Standard Deviations in Parentheses

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ge(1)	0.0284(7)	0.0284(7)	0.0284(7)	0.0014(7)	0.0014(7)	0.0014(7)
Ge(2)	0.0202(8)	0.0194(8)	0.0189(8)	0.0012(6)	0.0013(6)	-0.0014(6)
Ge(3)	0.0216(11)	0.0198(7)	0.0198(7)	-0.0012(7)	0.0012(7)	0.0035(9)
Ge(4)	0.0184(8)	0.0197(7)	0.0193(8)	-0.0007(6)	0.0008(6)	-0.0025(6)
Ge(5)	0.0247(8)	0.0198(8)	0.0177(8)	-0.0017(7)	0.0006(7)	0.0008(6)
Ge(6)	0.0176(5)	0.0176(5)	0.0176(5)	-0.0020(6)	-0.0020(6)	-0.0020(6)
Ba(1)	0.0211(3)	0.0211(3)	0.0211(3)	0.0009(4)	0.0009(4)	0.0009(4)
Ba(2)	0.0265(5)	0.0265(5)	0.0265(5)	0.0063(6)	0.0063(6)	0.0063(6)
Ba(3)	0.113(2)	0.0329(6)	0.0329(6)	0.0025(7)	-0.0025(7)	0.0060(8)

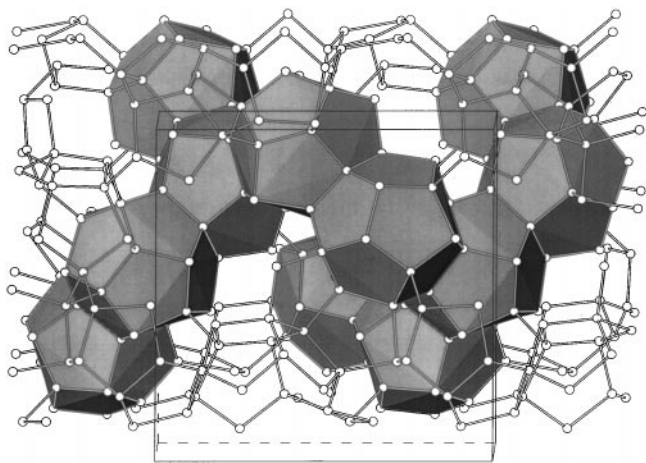


FIG. 1. Structure of Ba<sub>24</sub>Ge<sub>100</sub> illustrating a helical array of Ge<sub>20</sub> dodecahedral units.

The crystal structure of Ba<sub>24</sub>Ge<sub>100</sub> is given in Fig. 1, where only the network of germanium atoms is shown. The germanium network can be characterized as the interconnection of Ba-containing Ge<sub>20</sub> dodecahedra Ba@Ge<sub>20</sub>, which are illustrated as shaded polyhedra in Fig. 1. These

polyhedra share their three pentagonal faces with each other to form a complicated three-dimensional network like a “jungle gym.” In the projection along a unit cell axis, a helical array of Ge<sub>20</sub> dodecahedra can be seen (Fig. 1). The Ge<sub>20</sub> dodecahedron is almost regular (Fig. 2a). The Ge<sub>20</sub> dodecahedral units alone cannot fill all spaces; therefore, this structure has two types of interstices. The shapes of the interstices are shown in Figs. 2b and 2c. One is a Ge<sub>20</sub> open cage composed of six pentagonal faces and two open square windows (Fig. 2c). The other is a pseudo-cubic space surrounded by eight Ge atoms (Fig. 2b). The germanium network of Ba<sub>24</sub>Ge<sub>100</sub> is composed of these three structural units; the Ge<sub>20</sub> pentagonal dodecahedron with the Ba(1) atom, the Ge<sub>20</sub> open cage with the Ba(3) atom, and the pseudo-cubic space with the Ba(2) atom.

Selected bond distances and angles for Ba<sub>24</sub>Ge<sub>100</sub> are listed in Table 4. The average bond distance for the Ge–Ge bonds is 2.538 Å, which is 0.09 Å longer than that in the element, 2.450 Å. In Ba<sub>24</sub>Ge<sub>100</sub>, all germanium atoms have *sp*<sup>3</sup>-hybridized orbitals, but 32 out of 100 of germanium atoms have only three  $\sigma$ -bonds with three different germanium atoms. Each of the remaining 68 germanium atoms has four  $\sigma$ -bonds. The chemical formula of Ba<sub>24</sub>Ge<sub>100</sub> is, therefore, described as Ba<sub>24</sub>[(3*b*-Ge)<sub>32</sub>(4*b*-Ge)<sub>68</sub>]. In this

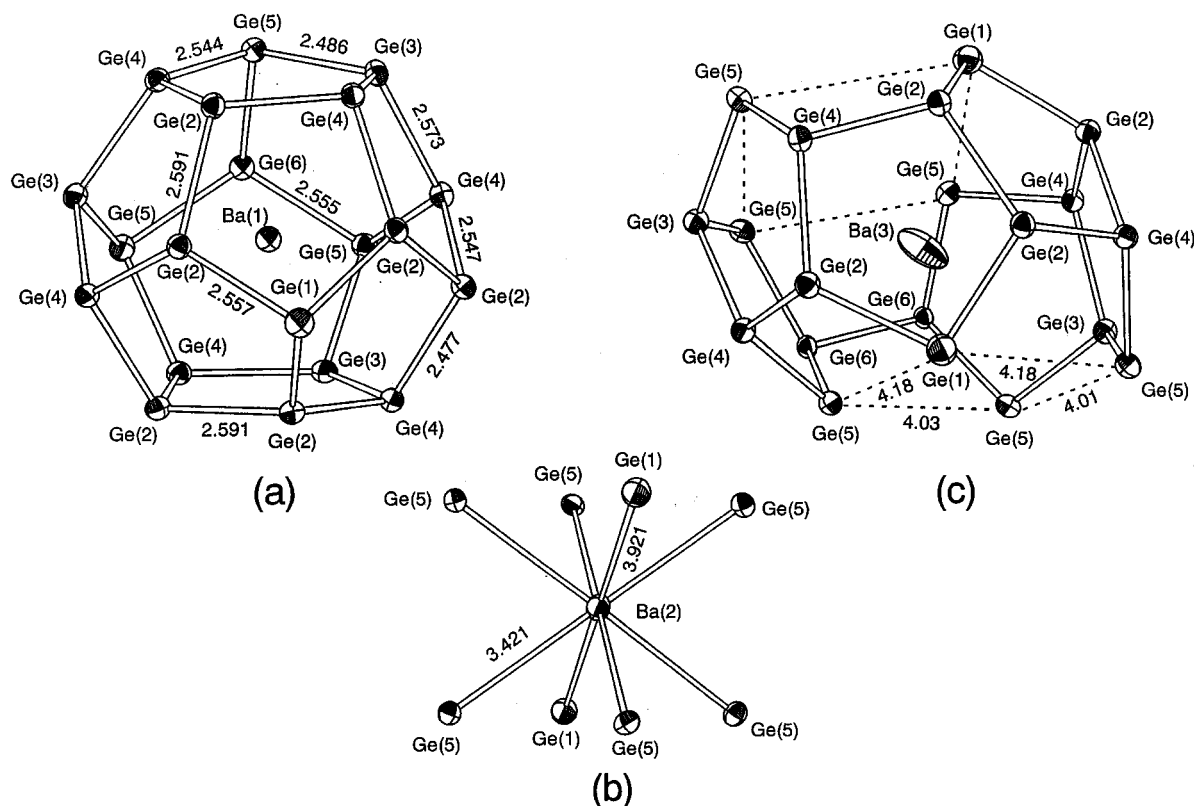


FIG. 2. ORTEP drawings for the three structural units of Ba<sub>24</sub>Ge<sub>100</sub>: (a) Ba(1)@Ge<sub>20</sub> dodecahedron, (b) Ba(2)Ge<sub>8</sub> pseudo-cubic, and (c) Ba(3) Ge<sub>20</sub> open cage with 50% probability.

formation, 16 electrons are excessively donated to the germanium host network. Ge(1) and Ge(5) in Table 2 are bonded to three germanium atoms and one Ba(2) atom forming the  $\text{Ge}_8$  pseudo-cubic spaces (Fig. 2b). Bond angles for normal germanium atoms having four  $\sigma$ -bonds are  $101.3\text{--}119.1^\circ$ , while the three  $\sigma$ -bonded germanium atoms have smaller angles of  $96.6\text{--}102.9^\circ$ .

The structure of this germanium network is isotypic with those of  $\text{K}_8\text{Sn}_{25}$  ( $\text{K}_{32}\text{Sn}_{100}$ ) (18) and  $\text{K}_6\text{Sn}_{25}$  ( $\text{K}_{24}\text{Sn}_{100}$ ) (19). In  $\text{Ba}_{24}\text{Ge}_{100}$  and  $\text{K}_6\text{Sn}_{25}$ , the Ba(3) and the corresponding K atom are on 12*d* special positions which are at the center of the  $\text{Ge}_{20}$  open cages, respectively. On the other hand, in  $\text{K}_8\text{Sn}_{25}$  the K atoms are placed on 24*e* general positions near the center of the  $\text{Sn}_{20}$  open cages. The number of the guest metal atoms in the unit cell is, therefore, different between these two  $\text{Sn}_{25}$  compounds. In the reported  $\text{K}_8\text{Sn}_{25}$  structure, two K atoms on the 24*e* site are very close with a distance of 2.9 Å. In our refinement, the thermal vibrational parameters for the all atoms sites are well defined on the reasonable values. The residual density also showed no excess atoms in the unit cell. We, therefore, concluded that the composition of our germanium clathrate was  $\text{Ba}_{24}\text{Ge}_{100}$ , in accordance with  $\text{K}_6\text{Sn}_{25}$ . Recently, the crystal structure of  $\text{Ba}_6\text{In}_4\text{Ge}_{21}$  (21) was reported. This compound is isotypic with  $\text{Ba}_{24}\text{Ge}_{100}$  and all indium atoms participate in the germanium network as (4*b*-) atoms.

Note that the barium-containing pentagonal dodecahedra ( $\text{Ba@Ge}_{20}$ ) are the fundamental structural units in  $\text{Ba}_{24}\text{Ge}_{100}$  as well as in the type I and type II clathrates. The chemical formulas of type I and type II germanium clathrates are  $M_8\text{Ge}_{46-x}$  and  $M_x\text{Ge}_{136}$ , respectively. All three germanium clathrates belong to the cubic system with different ways of packing of the  $\text{Ge}_{20}$  dodecahedra. In  $\text{Ba}_{24}\text{Ge}_{100}$  and the type II clathrate, face-sharing dodecahedra are found in their structures, while in the type I clathrate the dodecahedra are isolated and are mutually connected through  $\text{Ge}_{24}$  tetrakaidecahedra by face sharing. A remarkable similarity between  $\text{Ba}_{24}\text{Ge}_{100}$  and the type I clathrate can be found in their local structures. The type I clathrate structure is composed of  $\text{Ge}_{20}$  dodecahedra and  $\text{Ge}_{24}$  tetrakaidecahedral cages, while the  $\text{Ba}_{24}\text{Ge}_{100}$  structure is composed of  $\text{Ge}_{20}$  dodecahedra and  $\text{Ge}_{20}$  open cages. Figure 3 compares the local connections of these cages in the two structures. Here, if the four germanium atoms (closed spheres in Fig. 3a) are removed from the  $\text{Ge}_{24}$  cage of the type I clathrate, the arrangement of the remaining pentagonal faces is almost the same as that in  $\text{Ba}_{24}\text{Ge}_{100}$  (Fig. 3b). On removal of the four germanium atoms, each of the eight atoms marked with an asterisk in Fig. 3a loses one bond and becomes a three  $\sigma$ -bonded atom. In  $\text{Ba}_{24}\text{Ge}_{100}$ , these atoms coordinate to the Ba(2) atoms to form the  $\text{Ba(2)Ge}_8$  pseudo-cubic structural units.

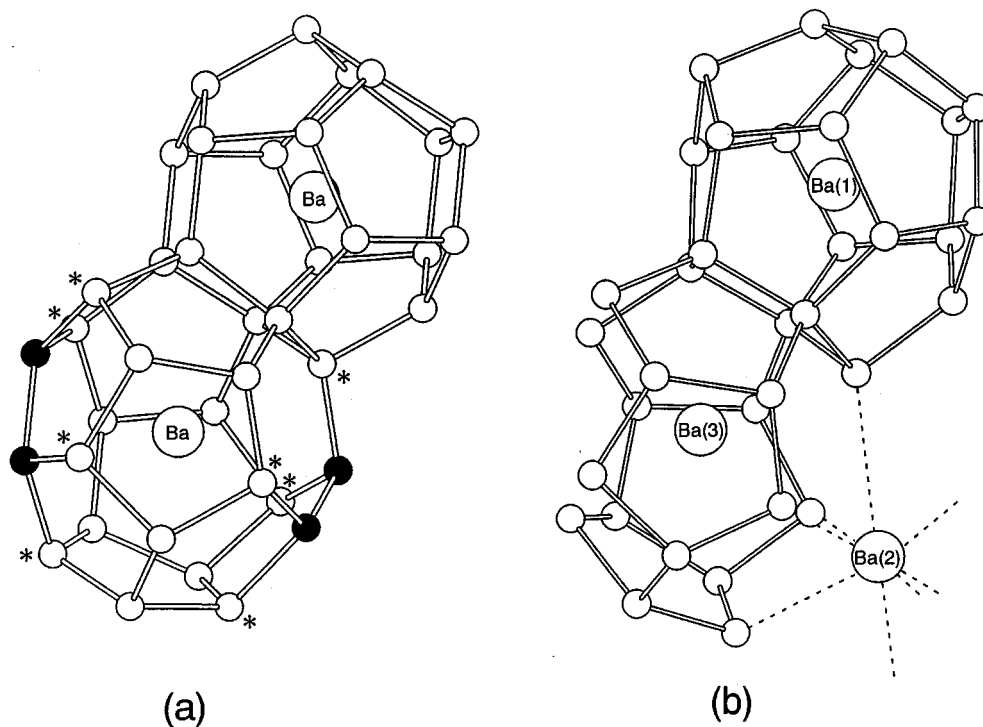


FIG. 3. Comparison of the local structure between (a) the type I clathrate and (b)  $\text{Ba}_{24}\text{Ge}_{100}$ .

**TABLE 4**  
Selected Bond Distances and Angles for Ba<sub>24</sub>Ge<sub>100</sub> with Standard Deviations in Parentheses

Ge(1)–Ge(2)	2.557(2) Å × 3	Ge(4)–Ge(2)	2.477(2) Å
		–Ge(2)	2.547(2) Å
Ge(2)–Ge(1)	2.557(2) Å	–Ge(3)	2.573(2) Å
–Ge(2)	2.591(3) Å	–Ge(5)	2.544(2) Å
–Ge(4)	2.477(2) Å		
–Ge(4)	2.547(2) Å	Ge(5)–Ge(3)	2.486(2) Å
		–Ge(4)	2.544(2) Å
Ge(3)–Ge(4)	2.573(2) Å × 2	–Ge(6)	2.555(2) Å
–Ge(5)	2.486(2) Å × 2		
		Ge(6)–Ge(5)	2.555(2) Å × 2
		–Ge(6)	2.511(5) Å × 2
Ba(1)–Ge(1)	4.021(4) Å	Ba(3)–Ge(1)	3.517(1) Å × 2
–Ge(2)	3.504(2) Å × 3	–Ge(2)	3.674(2) Å × 2
–Ge(2)	3.569(2) Å × 3	–Ge(2)	3.662(2) Å × 2
–Ge(3)	3.482(1) Å × 3	–Ge(3)	4.192(1) Å × 2
–Ge(4)	3.393(2) Å × 3	–Ge(4)	3.672(2) Å × 2
–Ge(4)	3.572(2) Å × 3	–Ge(4)	3.916(2) Å × 2
–Ge(5)	3.692(2) Å × 3	–Ge(5)	4.290(2) Å × 2
–Ge(6)	3.414(3) Å	–Ge(5)	4.394(2) Å × 2
Average	3.554 Å	–Ge(5)	3.338(2) Å × 2
		–Ge(6)	4.017(2) Å × 2
Ba(2)–Ge(1)	3.921(3) Å × 2	Average	3.867 Å
–Ge(5)	3.421(2) Å × 6		
Average	3.546 Å		
Ge(2)–Ge(1)–Ge(2)	96.55(9)°	Ge(2)–Ge(4)–Ge(2)	100.67(6)°
Ge(1)–Ge(2)–Ge(4)	107.27(9)°	Ge(2)–Ge(4)–Ge(3)	110.23(6)°
Ge(1)–Ge(2)–Ge(2)	111.71(7)°	Ge(2)–Ge(4)–Ge(5)	111.44(7)°
Ge(1)–Ge(2)–Ge(4)	119.14(7)°	Ge(2)–Ge(4)–Ge(3)	109.12(7)°
Ge(2)–Ge(2)–Ge(4)	109.37(8)°	Ge(2)–Ge(4)–Ge(5)	116.37(7)°
Ge(2)–Ge(2)–Ge(4)	107.31(4)°	Ge(3)–Ge(4)–Ge(5)	108.74(7)°
Ge(4)–Ge(2)–Ge(4)	101.30(6)°	Ge(3)–Ge(5)–Ge(4)	100.59(6)°
Ge(4)–Ge(3)–Ge(4)	106.46(10)°	Ge(3)–Ge(5)–Ge(6)	102.91(6)°
Ge(4)–Ge(3)–Ge(5)	110.82(4)°	Ge(4)–Ge(5)–Ge(6)	102.23(7)°
Ge(4)–Ge(3)–Ge(5)	110.63(4)°	Ge(5)–Ge(6)–Ge(5)	113.45(5)°
Ge(5)–Ge(3)–Ge(5)	107.51(11)°	Ge(5)–Ge(6)–Ge(6)	105.12(6)°

## CONCLUSION

Single crystals with a composition of Ba<sub>24</sub>Ge<sub>100</sub> were grown from a melt with a nominal composition of BaGe<sub>4</sub>. X-ray structural analysis has revealed that the crystal has a clathrate structure very similar to that of K<sub>6</sub>Sn<sub>25</sub>. Although the structure appears to be very complicated, the local structure can be derived from the type I clathrate structure, M<sub>x</sub>Ge<sub>46</sub>, by removing four Ge atoms from the Ge<sub>24</sub> cage in the type I structure.

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