Crystal structure of the defect clathrate-I, $\text{Ba}_8\text{Ge}_{43}$

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Abstract

$\text{Ba}_8\text{Ge}_{43}$, cubic, $Pm\bar{3}n$ (No. 223), $a = 10.6565(2)$ Å, $V = 1210.2$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.036$, $wR_{\text{ref}}(F^2) = 0.055$, $T = 293$ K.

Source of material

$\text{Ba}_8\text{Ge}_{43}$ was prepared as single phase by melting the elements in an open glassy carbon crucible (HF furnace, argon atmosphere) and annealing at 1068 K (6 d). The single crystals were obtained from the as-cast sample. The substance is silvery metallic, brittle, relatively stable in air and moisture. EDX analysis of bulk samples resulted in the chemical composition $\text{Ba}_{8.0(1)}\text{Ge}_{42.9(1)}$.

Experimental details

The lattice parameters were determined from the least-squares refinement of the 2θ values of 54 reflections ($18^\circ < 2\theta < 100^\circ$, powder data). The X-ray powder data were obtained on the sample with nominal composition $\text{Ba}_8\text{Ge}_{43}$ ($\lambda(\text{CuK}\alpha_1) = 1.540598$ Å; LaB_6 standard, $a = 4.15695(6)$ Å).

Discussion

$\text{Ba}_8\text{Ge}_{43}$ was first obtained as a by-product of the decomposition of $\text{Ba}_3\text{Ge}_4\text{C}_2$ [1] at 1123 K (1 h) under high pressure (ca. 40 kb). The $\text{Ba}_8\text{Ge}_{43}$ structure (upper part of the figure) belongs to the clathrate-I type with Pearson symbol $cP(54-3)$. Refined occupancies of Ge(1), Ge(31) and Ge(32) positions resulted in the chemical composition $\text{Ba}_8\text{Ge}_{42.93(5)}$. Only the Ge(1) site is deficient in germanium. Consequently, the neighbouring Ge(3) position splits into the two near sites Ge(31) and Ge(32) (Table 2). The latter occurs only if Ge(1) is empty. Similar results were obtained for the $\text{A}_8\text{Sn}_{44}\square_2$ clathrates, $A = \text{K}, \text{Rb}, \text{Cs}$ [2, 3]. A short range ordered model of the vacancies ($\square$) in the germanium environment of Ba(2) atoms is shown in the lower part of the figure (atomic distances in Å). The investigation of the possible long range ordering in long time annealed samples is in progress. Per formula unit, 31 germanium atoms are fourfold bonded (4b) and 12 germanium atoms in the Ge(31) sites are threefold bonded (3b). The compound may be formulated as $(\text{Ba}^{2+})_8((3b)\text{Ge}^{1-})_{12}((4b)\text{Ge}^0)_{31}(4e^-)$. According to this, $\text{Ba}_8\text{Ge}_{43}\square_3$ is a Zintl phase with a few electrons in not localized antibonding states of the network or in conduction bands. Semimetallic or metallic properties are expected [4, 5].

Table 1. Data collection and handling.

Crystal:	silvery metallic, platelike, size $0.02 \times 0.15 \times 0.25$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	326.16 cm^{-1}
Diffractometer, scan mode:	Nicolet R3m/V, ω
$2\theta_{\text{max}}$:	55.04°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	1892, 273
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 209
$N(\text{param})_{\text{refined}}$:	19
Programs:	SHELXL-97 [6], ATOMS [7]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{iso}
Ge(31)	24k	0.505(4)	0	0.3073(3)	0.1124(3)	0.0133(8)
Ge(32)	24k	0.495	0	0.3332(3)	0.1314(3)	0.0190(9)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ba(1)	2a		0	0	0	0.0131(4)	U ₁₁	U ₁₁	0	0	0
Ba(2)	6d		1/4	1/2	0	0.0218(8)	0.0368(6)	U ₂₂	0	0	0
Ge(1)	6c	0.488(9)	1/4	0	1/2	0.013(2)	0.014(2)	U ₂₂	0	0	0
Ge(2)	16i		0.18364(6)	x	x	0.0157(3)	U ₁₁	U ₁₁	−0.0024(3)	U ₁₂	U ₁₂
Ge(3) ^a	24k		0	0.3196(1)	0.1213(1)	0.0165(6)	0.0373(7)	0.0267(6)	0	0	0.0166(6)

a: Ge(3) is the average position of Ge(31) and Ge(32), see Table 2.

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