Crystal structure of $Ba_8Ga_{4.44}Ge_{39.14}\square_{2.42}$, $Ba_8Ga_{8.62}Ge_{36}\square_{1.38}$, and $Ba_8Ga_{12.35}Ge_{33.27}\square_{0.38}$, *three clathrate-I variants*

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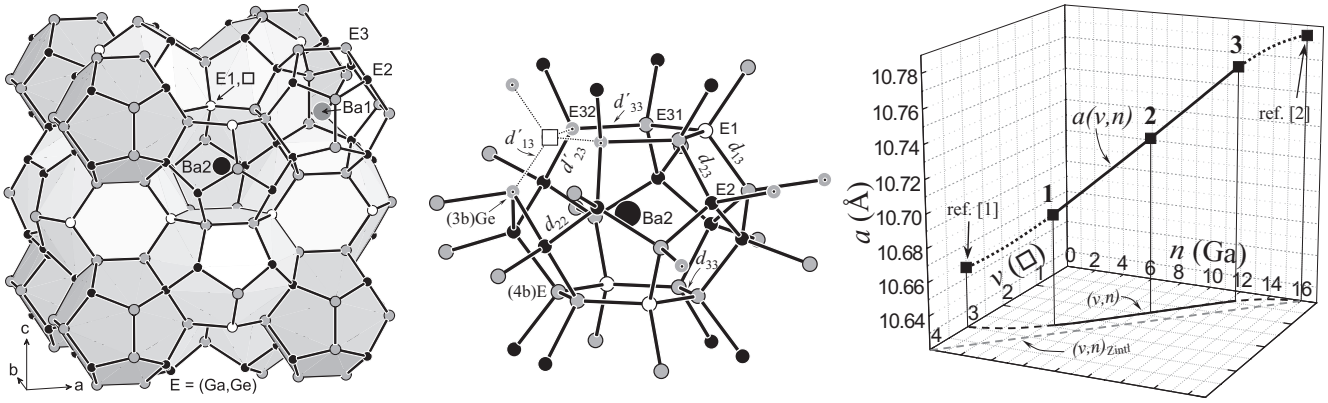
Received February 25, 2002, accepted and available on-line May 7, 2002; CSD-No. 409614, 409615 and 409616



Abstract

$Ba_8Ga_{4.44}Ge_{39.14}$ (**1**), cubic, $Pm\bar{3}n$ (No. 223), a = 10.6861(2) Å, V = 1220.3 Å^3, Z = 1, $R_{gt}(F)$ = 0.019, $wR_{ref}(F^2)$ = 0.037, T = 293 K.

$Ba_8Ga_{8.62}Ge_{36}$ (**2**), cubic, $Pm\bar{3}n$ (No. 223), a = 10.7274(2) Å, V = 1234.5 Å^3, Z = 1, $R_{gt}(F)$ = 0.022, $wR_{ref}(F^2)$ = 0.047, T = 293 K.

$Ba_8Ga_{12.35}Ge_{33.27}$ (**3**), cubic, $Pm\bar{3}n$ (No. 223), a = 10.7659(2) Å, V = 1247.8 Å^3, Z = 1, $R_{gt}(F)$ = 0.022, $wR_{ref}(F^2)$ = 0.046, T = 293 K.

Source of material

The samples with nominal composition $Ba_8Ga_4Ge_{39}$ (S-1), $Ba_8Ga_8Ge_{36}$ (S-2) and $Ba_8Ga_{12}Ge_{33}$ (S-3) were prepared by high--frequency induction melting of the elements (argon atmosphere, open glassy carbon crucible), and annealed at 1023 K for 9 days. The materials are grey metallic, brittle and stable in air. As shown by XRD and metallographic studies, the samples S-1, S-2 and S-3 contain minor amounts of Ba_6Ge_{25} (~3% – 9%).

Chemical composition of the majority phase determined by WDX analysis (CAMECA electron microprobe) was found to be $Ba_{8.02(1)}Ga_{4.44(1)}Ge_{39.12(2)}$ (S-1, **1**), $Ba_{7.95(3)}Ga_{8.62(3)}Ge_{36.05(4)}$ (S-2, **2**) and $Ba_{8.00(2)}Ga_{12.35(5)}Ge_{33.27(8)}$ (S-3, **3**), respectively.

Experimental details

The unit cell parameters were determined from the least-squares refinement of 2θ values of reflections in the range $18° < 2\theta < 120°$ [X ray powder data, λ(Cu $K_{\alpha 1}$) = 1.540598 Å; standards: LaB_6, a = 4.15695(6) Å, for **1** and **3** and Ge, a =5.65751(9) Å, for **2**]. For the reasons mentioned in the discussion, the occupancy (Occ) of the E(1) position was constrained in the refinements to that of E31 [Occ(E1) = Occ(E31) = 1 – Occ(E32)]. For **3** the splitting of the E3 position was not noticeable and a non-split model was refined. To obtain the composition found by the chemical analysis, Ga was positioned at the E1 and E2 sites.

Discussion

Investigations on the clathrate-I phase in the system Ba–Ga–Ge showed the defect structure in the binary system ($Ba_8Ge_{43}\square_3$, a = 10.6565(2) Å [1]) and the fully occupied variant in the gallium-rich ternary region ($Ba_8Ga_{16}Ge_{30}$ [2-4], a = 10.7840(2) Å [2]). The clathrate-I type of structure (Pearson symbol *cP*54; figure left part) is characterized by a E_{46} net of four-bonded (4b)E atoms with guest atoms (Ba) inside the E_{20} and E_{24} cages.

The title gallium-poor ternary representatives of the clathrate-I phase are defect variants, $Ba_8Ga_nGe_{(46-\nu)-n}\square_\nu$ [Pearson symbol *cP*54-ν], and only the E1 site in the title structures is deficient in E atoms (this was also observed for $Ba_8Ge_{43}\square_3$ [1] and $Cs_8Sn_{44}\square_2$ [5]). As a consequence, the neighboring E3 position splits into E31 and E32 sites (E32 occurs only if E1 is empty).

A model for a short-range ordering with one vacancy at the E_{24-1} cage of Ba2 is shown in the central part of the figure, where the distances d(Ei—Ej) = d_{ij} are labelled (i, j = 1, 2, 3, 31, 32). Notice that E32 sites are three-fold (3b) bonded. For 50% vacancies at the E1 site, two E1 positions are empty around Ba2 (E_{24-2} cage) and the distances d(E31—E31) are not allowed, while the distances d(E31—E32) are allowed [1]. To compare split and non-split models, we consider d(E1—E31) ≡ d(E1—E3) = d_{13}, d(E2—E31) ≡ d(E2—E3) = d_{23} and d(E31—E31) ≡ d(E3—E3) = d_{33}. Among the bond distances in $Ba_8Ga_{16}Ge_{30}$ (**4**) [2], $Ba_8Ga_{12.35}Ge_{33.27}$ (**3**), $Ba_8Ga_{8.62}Ge_{36}$ (**2**), $Ba_8Ga_{4.44}Ge_{39.14}$ (**1**) and Ba_8Ge_{43} (**0**) [1], the mayor variations are observed for d_{23}/d'_{23} and d_{33}/d'_{33}. The d_{33} distance decreases continuously from 2.548(1) Å for ν = 0 (**4**) to 2.455(7) Å for ν = 2.42 (**1**); the value of d'_{33} increases from about 2.55 Å (= d_{33} for **4** and **3**) to about 2.60 Å (for **0**, **1** and **2**), and similarly the value of d'_{23} increases from about 2.48 Å to about 2.59 Å. The d'_{13} distance is nearly 2.22 Å for **0**, **1** and **2**.

Taking into account that in another analogous ternary structure with (4b)E and (3b)E atoms, $Ba_6In_4Ge_{21}$ [6], only germanium

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atoms were localized at the three-bonded (3b)E sites, we assume that the (3b)E sites in the title structures are only occupied by germanium. Thus, in terms of the Zintl concept, the title compounds can be formulated as:
$(Ba^{2+})_8((4b)Ga^{1-})_{4.44}((3b)Ge^{1-})_{9.68}((4b)Ge^{0})_{29.46}(1.88e^-)$ (**1**),
$(Ba^{2+})_8((4b)Ga^{1-})_{8.62}((3b)Ge^{1-})_{5.52}((4b)Ge^{0})_{30.48}(1.86e^-)$ (**2**)
$(Ba^{2+})_8((4b)Ga^{1-})_{12.35}((3b)Ge^{1-})_{1.52}((4b)Ge^{0})_{31.75}(2.13e^-)$ (**3**).
According to this, semimetallic- or metal-like properties are expected with electrons as charge carriers. In fact, the measurement of the electrical resistivity of sample S-3 (**3**) indicated a metal-like behaviour.
The value of the lattice parameter a for $Ba_8Ga_nGe_{(46-v)-n}\square_v$ (n = n(Ga), v = v(□)) decreases from 10.7840 Å for v = 0 (n =16) to 10.6565 Å for v = 3 (n = 0), figure right part. It is the quantity of vacancies that influence mostly $a(v,n)$, because the size of a Ga atom is similar to that of a Ge atom. Notice that the experimental (v,n) values deviate from the ideal ones $(v,n)_{Zintl}$ (gray dashed line; for ideal Zintl phases), and only for small values of v, the (v,n) curve can be approximated by the ideal line.

1. $Ba_8Ga_{4.44}Ge_{39.14}$

Table 1. Data collection and handling.

Crystal:	grey block with metallic lustre, size 0.11 × 0.14 × 0.15 mm
Wavelength:	Ag K_α radiation (0.56086 Å)
μ:	170.22 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 225 exposures, $\Delta\varphi$ = 0.8°
$2\theta_{max}$:	51.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15955, 463
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 415
$N(param)_{refined}$:	22
Programs:	SHELXL-97 [7], ATOMS [8]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	2*a*		0	0	0	0.0087(1)	U_{11}	U_{11}	0	0	0
Ba(2)	6*d*		1/4	1/2	0	0.0160(2)	0.0357(2)	U_{22}	0	0	0
E(1) [a]	6*c*	0.596(4)	1/4	0	1/2	0.0096(5)	0.0083(4)	U_{22}	0	0	0
E(2) [b]	16*i*		0.18356(2)	x	x	0.00992(9)	U_{11}	U_{11}	–0.00178(7)	U_{12}	U_{12}
E(31) [c]	24*k*	0.596	0	0.3069(2)	0.1149(3)	0.0092(3)	0.0084(8)	0.0097(6)	0	0	–0.0007(5)
E(32) [c]	24*k*	0.404	0	0.3317(4)	0.1280(5)	0.0116(6)	0.013(1)	0.012(1)	0	0	0.0020(9)

a: E(1) = Ga
b: E(2) = 0.054Ga + 0.946Ge
c: E(31), E(32) = Ge

2. $Ba_8Ga_{8.62}Ge_{36}$

Table 3. Data collection and handling.

Crystal:	grey block with metallic lustre, size 0.12 × 0.19 × 0.20 mm
Wavelength:	Ag K_α radiation (0.56086 Å)
μ:	170.13 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 275 exposures, $\Delta\varphi$ = 0.8°
$2\theta_{max}$:	47.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15516, 376
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 329
$N(param)_{refined}$:	22
Programs:	SHELXL-97 [7], ATOMS [8]

Table 4. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	2*a*		0	0	0	0.0095(2)	U_{11}	U_{11}	0	0	0
Ba(2)	6*d*		1/4	1/2	0	0.0167(4)	0.0379(3)	U_{22}	0	0	0
E(1) [a]	6*c*	0.770(6)	1/4	0	1/2	0.0099(7)	0.0077(5)	U_{22}	0	0	0
E(2) [b]	16*i*		0.18401(3)	x	x	0.0091(2)	U_{11}	U_{11}	–0.0016(1)	U_{12}	U_{12}
E(31) [c]	24*k*	0.770	0	0.3076(4)	0.1171(6)	0.0095(5)	0.009(1)	0.0091(6)	0	0	–0.0003(8)
E(32) [c]	24*k*	0.230	0	0.332(1)	0.127(2)	0.012(2)	0.014(5)	0.015(4)	0	0	0.004(3)

a: E(1) = Ga
b: E(2) = 0.25Ga + 0.75Ge
c: E(31), E(32) = Ge

3. $Ba_8Ga_{12.35}Ge_{33.27}$

Table 5. Data collection and handling.

Crystal:	grey block with metallic luster, size 0.07 × 0.14 × 0.15 mm
Wavelength:	Ag K_α radiation (0.56086 Å)
μ:	170.19 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 275 exposures, $\Delta\varphi$ = 0.8°
$2\theta_{max}$:	47.38°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15917, 377
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 307
$N(param)_{refined}$:	16
Programs:	SHELXL-97 [7], ATOMS [8]

Table 6. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	2*a*		0	0	0	0.0092(2)	U_{11}	U_{11}	0	0	0
Ba(2)	6*d*		1/4	1/2	0	0.0160(4)	0.0392(3)	U_{22}	0	0	0
E(1) [a]	6*c*	0.936(7)	1/4	0	1/2	0.0094(6)	0.0075(5)	U_{22}	0	0	0
E(2) [b]	16*i*		0.18448(3)	*x*	*x*	0.0077(2)	U_{11}	U_{11}	–0.0013(1)	U_{12}	U_{12}
E(3) [c]	24*k*		0	0.30928(5)	0.11830(5)	0.0098(3)	0.0116(3)	0.0095(3)	0	0	0.0008(2)

a: E(1) = Ga
b: E(2) = 0.421Ga + 0.579Ge
c: E(3) = Ge

Acknowledgments. The work was supported by the Fonds der Chemischen Industrie. The authors thank Ms. K. Schulze and Mrs. M. Eckert for the WDX and EDX analyses.

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