Crystal structure of two tri(barium, calcium) tetragermanides, $\text{Ba}_{2.82}\text{Ca}_{0.18}\text{Ge}_4$ and $\text{Ba}_{2.89}\text{Ca}_{0.11}\text{Ge}_4$

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Abstract

$\text{Ba}_{2.82}\text{Ca}_{0.18}\text{Ge}_4$, orthorhombic, $Cmmm$ (No. 65),
 $a = 11.802(8) \text{ \AA}$, $b = 12.147(9) \text{ \AA}$, $c = 11.966(8) \text{ \AA}$,
 $V = 1715.4 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.047$, $wR(F^2) = 0.117$, $T = 298 \text{ K}$.

$\text{Ba}_{2.89}\text{Ca}_{0.11}\text{Ge}_4$, orthorhombic, $Cmmm$ (No. 65),
 $a = 11.7838(2) \text{ \AA}$, $b = 12.1818(2) \text{ \AA}$, $c = 12.0605(1) \text{ \AA}$,
 $V = 1731.3 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.034$, $wR(F^2) = 0.071$, $T = 298 \text{ K}$.

Source of material

$\text{Ba}_{2.82}\text{Ca}_{0.18}\text{Ge}_4$ and $\text{Ba}_{2.89}\text{Ca}_{0.11}\text{Ge}_4$ are prepared by heating at 1273 K a mixture of the elements with the Ba/Ca/Ge ratios of 2.25:0.75:4 and 2.5:0.5:4, respectively (12 h, cooling down within 5 h). Both compounds form grey-black, plate-like crystals with a metallic lustre.

The Ba/Ca3, Ba/Ca4, and Ba/Ca5 sites are occupied by different amounts of barium and strontium. The corresponding occupancy factors are also refined.

Discussion

$\text{Ba}_{2.82}\text{Ca}_{0.18}\text{Ge}_4$ and $\text{Ba}_{2.89}\text{Ca}_{0.11}\text{Ge}_4$ crystallize with the Ba_3Ge_4 structure type [1], which contains isolated Ge_4^{6-} and polymerized $[\text{Ge}_4^{6-}]_\infty$ butterfly anions. $\text{Ba}_{2.82}\text{Ca}_{0.18}\text{Ge}_4$ and $\text{Ba}_{2.89}\text{Ca}_{0.11}\text{Ge}_4$ can be described, according to the Zintl-Klemm concept, by the formulation $(\text{M}^{2+})_6[\text{Ge}_4^{6-}]_6[\text{Ge}_4^{6-}]_\infty$ ($\text{M} = \text{Ba}, \text{Ca}$). The Ba_3Ge_4 structure can be also described as (distorted) cubic close packing of Zintl anions with all tetrahedral and octahedral holes occupied by metal atoms. In $\text{Ba}_{2.82}\text{Ca}_{0.18}\text{Ge}_4$ and $\text{Ba}_{2.89}\text{Ca}_{0.11}\text{Ge}_4$, the larger octahedral positions M1 and M2 are exclusively occupied by barium, while the calcium amount on the smaller tetrahedral positions M3 to M5 is about 9% and 5%, respectively. The main characteristic of Ba_3Ge_4 is the presence of an unusually long intermolecular bond (2.87 Å). In $\text{Ba}_{2.82}\text{Ca}_{0.18}\text{Ge}_4$ and $\text{Ba}_{2.89}\text{Ca}_{0.11}\text{Ge}_4$, this bond is even more longer (2.92 Å and 2.89 Å, respectively) although, as expected, the cell volumes are smaller than in Ba_3Ge_4 .

1. Tri(barium, calcium) tetragermanide, $\text{Ba}_{2.82}\text{Ca}_{0.18}\text{Ge}_4$

Table 1. Data collection and handling.

Crystal:	grey-black platelet, size $0.05 \times 0.10 \times 0.40 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71073 \text{ \AA}$)
μ :	265.37 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 120 exposures, $\Delta\varphi = 1.5^\circ$
$2\theta_{\text{max}}$:	47.9°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	4792, 769
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 718
$N(\text{param})_{\text{refined}}$:	49
Programs:	SHELXS-96 [2], SHELXL-96 [3], COLTURE [4]

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Table 2. 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)	4j		0	0.1608(2)	1/2	0.028(1)	0.022(1)	0.030(1)	0	0	0
Ba(2)	4g		0.6628(2)	0	0	0.025(1)	0.0216(9)	0.031(1)	0	0	0
Ba(3)	4k	0.92(2)	0	0	0.1610(2)	0.027(1)	0.021(1)	0.020(1)	0	0	0
Ca(3)	4k	0.08	0	0	0.1610	0.027	0.021	0.020	0	0	0
Ba(4)	4l	0.91(2)	0	1/2	0.3256(2)	0.024(1)	0.021(1)	0.020(1)	0	0	0
Ca(4)	4l	0.09	0	1/2	0.3256	0.024	0.021	0.020	0	0	0
Ba(5)	8m	0.91(2)	1/4	1/4	0.2553(1)	0.0281(9)	0.0203(8)	0.0214(9)	0.0004(6)	0	0
Ca(5)	8m	0.09	1/4	1/4	0.2553	0.0281	0.0203	0.0214	0.0004	0	0
Ge(1)	8q		0.1944(2)	0.3936(2)	1/2	0.030(1)	0.023(1)	0.022(1)	−0.003(1)	0	0
Ge(2)	8p		0.1366(2)	0.2016(2)	0	0.033(1)	0.022(1)	0.021(1)	0.002(1)	0	0
Ge(3)	8n		0	0.2935(2)	0.1425(2)	0.028(1)	0.025(1)	0.032(2)	0	0	−0.004(1)
Ge(4)	8o		0.1986(2)	0	0.3478(2)	0.031(1)	0.025(1)	0.029(2)	0	−0.009(1)	0

2. Tri(barium, calcium) tetragermanide, Ba_{2.89}Ca_{0.11}Ge₄**Table 3.** Data collection and handling.

Crystal:	grey-black plate, size 0.10 × 0.15 × 0.20 mm
Wavelength:	Mo K _α radiation (0.71073 Å)
μ:	266.32 cm ^{−1}
Diffraction, scan mode:	Siemens Platform CCD, 3500 exposures, Δω = 0.15°
2θ _{max} :	78.92°
N(hkl) _{measured} , N(hkl) _{unique} :	2767, 2767
Criterion for I _{obs} , N(hkl) _{gt} :	I _{obs} > 2 σ(I _{obs}), 2329
N(param) _{refined} :	50
Programs:	SHELXS-96 [2], SHELXL-96 [3], COLTURE [4]

Table 4. 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)	4j		0	0.16052(4)	1/2	0.0133(2)	0.0150(2)	0.0243(2)	0	0	0
Ba(2)	4g		0.66274(4)	0	0	0.0113(2)	0.0134(2)	0.0247(2)	0	0	0
Ba(3)	4k	0.957(5)	0	0	0.16013(4)	0.0131(2)	0.0134(2)	0.0137(2)	0	0	0
Ca(3)	4k	0.053	0	0	0.16013	0.0131	0.0134	0.0137	0	0	0
Ba(4)	4l	0.939(5)	0	1/2	0.32506(4)	0.0115(2)	0.0152(2)	0.0127(2)	0	0	0
Ca(4)	4l	0.061	0	1/2	0.32506	0.0115	0.0152	0.0127	0	0	0
Ba(5)	8m	0.951(4)	1/4	1/4	0.25565(3)	0.0143(2)	0.0150(2)	0.0144(2)	0.0003(1)	0	0
Ca(5)	8m	0.049	1/4	1/4	0.25565	0.0143	0.0150	0.0144	0.0003	0	0
Ge(1)	8q		0.19429(6)	0.39403(5)	1/2	0.0149(3)	0.0147(3)	0.0160(3)	−0.0016(2)	0	0
Ge(2)	8p		0.13796(6)	0.20182(5)	0	0.0161(3)	0.0136(3)	0.0147(3)	0.0012(2)	0	0
Ge(3)	8n		0	0.29337(6)	0.14108(6)	0.0116(2)	0.0167(3)	0.0218(3)	0	0	−0.0044(2)
Ge(4)	8o		0.19819(6)	0	0.34816(6)	0.0155(3)	0.0173(3)	0.0202(3)	0	−0.0050(2)	0

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