Crystal structure of tri(barium, strontium) tetragermanide, $\text{Ba}_{2.62}\text{Sr}_{0.38}\text{Ge}_4$

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Abstract

$\text{Ba}_{2.62}\text{Ge}_4\text{Sr}_{0.38}$, orthorhombic, $Cmmm$ (No. 65), $a = 11.773(8) \text{ \AA}$, $b = 12.126(8) \text{ \AA}$, $c = 11.950(8) \text{ \AA}$, $V = 1706.0 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.027$, $wR(F^2) = 0.070$, $T = 298 \text{ K}$.

Source of material

$\text{Ba}_{2.62}\text{Sr}_{0.38}\text{Ge}_4$ is prepared by heating a mixture of the elements with a Ba/Sr/Ge ratio of 2.5:0.5:4 at 1273 K (12 h, cooling down within 5 h). $\text{Ba}_{2.62}\text{Sr}_{0.38}\text{Ge}_4$ forms grey-black, plate-like crystals with a metallic lustre.

The Ba/Sr3, Ba/Sr4, and Ba/Sr5 sites are occupied by different amounts of barium and strontium. The corresponding occupancy factors are also refined.

Discussion

$\text{Ba}_{2.62}\text{Sr}_{0.38}\text{Ge}_4$ crystallises with the Ba_3Ge_4 structure type [1]. It contains isolated Ge_4^{6-} and polymerized $[\text{Ge}_4^{6-}]_\infty$ butterfly anions. $\text{Ba}_{2.62}\text{Sr}_{0.38}\text{Ge}_4$ can be described, according to the Zintl-Klemm concept, by the formulation $(\text{M}^{2+})_6[\text{Ge}_4^{6-}]_1[\text{Ge}_4^{6-}]$ ($\text{M} = \text{Ba}, \text{Sr}$). 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 $\text{Ba}_{2.62}\text{Sr}_{0.38}\text{Ge}_4$, the larger octahedral positions M1 and M2 are exclusively occupied by barium, while the strontium amount on the smaller tetrahedral positions M3 to M5 is 18%, 21%, and 18%, respectively. The main characteristic of Ba_3Ge_4 is the presence of an unusually long intermolecular bond ($2.87 \text{ \AA}$). In $\text{Ba}_{2.62}\text{Sr}_{0.38}\text{Ge}_4$, this bond is even more longer ($2.91 \text{ \AA}$) although, as expected, the cell volume is smaller than in Ba_3Ge_4 .

Table 1. Data collection and handling.

Crystal:	black plate, size $0.10 \times 0.20 \times 0.25 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71073 \text{ \AA}$)
μ :	280.64 cm^{-1}
Diffractionmeter, scan mode:	Stoe IPDS, 181 exposures, $\Delta\phi = 1.0^\circ$
$2\theta_{\text{max}}$:	48°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4872, 769
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 736
$N(\text{param})_{\text{refined}}$:	50
Programs:	SHELXS-96 [2], SHELXL-96 [3], COLTURE [4]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	4j		0	0.16057(8)	1/2	0.0194(5)	0.0223(5)	0.0270(6)	0	0	0
Ba(2)	8g		0.66281(8)	0	0	0.0166(5)	0.0208(5)	0.0274(6)	0	0	0
Ba(3)	4k	0.82(2)	0	0	0.16059(8)	0.0186(6)	0.0213(6)	0.0173(6)	0	0	0
Sr(3)	4k	0.18	0	0	0.16059	0.0186	0.0213	0.0173	0	0	0
Ba(4)	4l	0.79(2)	0	1/2	0.32525(8)	0.0162(6)	0.0227(6)	0.0158(7)	0	0	0
Sr(4)	4l	0.21	0	1/2	0.3252	0.0162	0.0227	0.0158	0	0	0
Ba(5)	8m	0.82(1)	1/4	1/4	0.25556(6)	0.0189(5)	0.0218(5)	0.0180(5)	0.0003(3)	0	0
Sr(5)	8m	0.18	1/4	1/4	0.25556	0.0189	0.0218	0.0180	0.0003	0	0
Ge(1)	8q		0.1938(1)	0.39389(9)	1/2	0.0201(7)	0.0208(7)	0.0194(6)	-0.0019(4)	0	0
Ge(2)	8p		0.1370(1)	0.20163(9)	0	0.0215(7)	0.0203(6)	0.0184(6)	0.0008(5)	0	0
Ge(3)	8n		0	0.29310(9)	0.1427(1)	0.0167(6)	0.0240(6)	0.0245(7)	0	0	-0.0042(5)
Ge(4)	8o		0.1986(1)	0	0.3471(1)	0.0213(7)	0.0228(6)	0.0236(7)	0	-0.0059(5)	0

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