Refinement of the crystal structure of dibarium tetrasilicide, Ba₂Si₄

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Abstract

Ba₂Si₄, orthorhombic, *Pnma* (no. 62), $a = 8.9326(4)$ Å, $b = 6.7262(2)$ Å, $c = 11.5335(5)$ Å, $V = 693.0$ Å³, $Z = 4$, $r_{\text{ref}}(F) = 0.025$, $wR_{\text{ref}}(F^2) = 0.044$, $T = 295$ K.

Source of material

Three samples, Ba₂Si_{3.8}, Ba₂Si₄ and Ba₂Si_{4.4} were prepared by arc melting of appropriate amounts of the elements (Ba, dendritic, 99.9 % Alfa Aesar; Si, pieces, 99.999 % Alfa). The reguli were sealed in Ta ampoules enclosed in evacuated quartz glass tubes. After subsequent annealing at 800 °C for one week, the samples were quenched in ice water.

Experimental details

Due to sensitivity to air and humidity, the investigated single-crystal was sealed into a glass capillary under purified argon. Lattice parameters were refined from powder diffraction data (CuKα₁, $\lambda = 1.540562$ Å), using 50–70 non-overlapping reflections between $18^\circ \leq 2\theta \leq 80^\circ$ applying LaB₆ as internal standard (NIST, $a = 4.15692$ Å). The formation of a significant homo-

geneity range was excluded by investigation of two- and single-phase samples. The lattice parameters of Ba₂Si₄ of these samples and those reported in [1] are equal within 3σ of the standard deviation.

Discussion

The crystal structure of Ba₂Si₄ was first determined by Janzon and Schäfer from Weissenberg film data on single crystals [2,3]. In Ref. 4 and 5 lattice parameters and atomic positions of Ba₂Si₄ are given on the basis of LDA and GGA calculations. Taking the intrinsic mismatch of structure data obtained from experimental and theoretical methods into account, the following discussion will focus on latest experimental structure determination [3]. Ba₂Si₄ was re-investigated in order to study the chemical bonding by quantum chemical calculations as well as by solid state NMR. The present study confirms the basic structural informations of Ref. 3 and provides data of the crystal structure with higher accuracy, being crucial for the further investigations.

Two crystallographic non-equivalent sites for Ba and three for Si are occupied in the crystal structure. The parameters of all atomic positions, except the x parameter of Ba2, are equal within 3σ of the standard deviation of the data reported in Ref. 3. Compared to the previous data the a axis is longer by 0.01 Å, the b and c axes are shorter by 0.02 and 0.04 Å, respectively. This results in a 0.4 Å shorter distance Si2–Ba2 (3.771(1) Å), which is now closer to the average Ba–Si distance ($d_{\text{av}} = 3.489(1)$ Å). The Si atoms form distorted, tetrahedron-like Si₄^{4–} anions also found in the tetraalkalimetal-tetrasilicides $M_4\text{Si}_4$ ($M = \text{Na, K, Rb, Cs}$) [6–10]. The coordination of the anions with Ba²⁺ in Ba₂Si₄ is different from the anion coordination with M^+ in the tetraalkalimetal-tetrasilicides $M_4\text{Si}_4$. Where in the later compounds the Si₄^{4–} anions are coordinated by 16 M^+ cations, only 11 Ba²⁺ cations coordinate to the anions in Ba₂Si₄. No heterocubane units (stellae quadrangulae) being a prominent feature in $M_4\text{Si}_4$ are formed in Ba₂Si₄. Only the faces Si1–Si3–Si3 and Si2–Si3–Si3 are μ_3 capped by Ba2 with an average distance of $d_{\text{av}}(\text{Ba}–\text{Si}) = 3.458(1)$ and $3.527(1)$ Å, respectively. Where the edges Si1–Si3 are μ_2 bridged by Ba2 with an average distance of $3.455(1)$ Å, the edges Si2–Si3 and Si1–Si2 are μ_3 coordinated by Ba1 with an average distance of $3.582(1)$ Å and $3.379(1)$ Å, respectively. The Si1 and Si3 atoms are μ_1 coordinated by Ba1 ($3.539(1)$ Å and $3.412(1)$ Å), Si2 is μ_1 coordinated by Ba2 with a distance of $3.771(1)$ Å. The homoatomic bond lengths within the anion are $d(\text{Si3}–\text{Si3}) = 2.395(2)$ Å, $d(\text{Si1}–\text{Si3}) = 2.393(2)$ Å and $d(\text{Si1}–\text{Si2}) = 2.434(2)$ Å. This is compared to Ref. 3 longer by 0.06, 0.02 and 0.02 Å. Only the distance $d(\text{Si2}–\text{Si3}) = 2.408(1)$ Å is shorter by 0.07 Å. Thus the average distance of $2.403(1)$ Å within the anion is equal within the experimental error with the previous data ($2.41(2)$ Å [3]).

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Table 1. Data collection and handling.

Crystal:	black irregular shaped, size 0.045 × 0.050 × 0.120 mm
Wavelength:	Mo K α radiation (0.7107 Å)
μ :	118.6 cm ⁻¹
Diffraction, scan mode:	Rigaku AFC7, ϕ/ω
$2\theta_{\max}$:	63°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	6791, 1234
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1178
$N(\text{param})_{\text{refined}}$:	34
Programs:	WinCSD [11], SHELXL-97 [12], DIAMOND [13]

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

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ba(1)	4c	0.01462(3)	¼	0.69300(2)	0.0134(1)	0.0135(1)	0.0125(1)	0	-0.00009(9)	0
Ba(2)	4c	0.83871(3)	¼	0.09466(3)	0.0176(1)	0.0127(1)	0.0135(1)	0	0.0003(1)	0
Si(1)	4c	0.1968(2)	¼	0.9655(1)	0.0180(6)	0.0147(6)	0.0103(6)	0	-0.0001(5)	0
Si(2)	4c	0.4166(2)	¼	0.0901(1)	0.0131(6)	0.0206(7)	0.0158(6)	0	0.0010(5)	0
Si(3)	8d	0.1938(1)	0.0719(2)	0.14505(8)	0.0184(4)	0.0126(4)	0.0147(4)	-0.0014(3)	0.0006(3)	0.0028(3)

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