Refinement of the crystal structures of the *tetrahedro-*tetrasilicides K_4Si_4 , Rb_4Si_4 and Cs_4Si_4

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Abstract

K_4Si_4 , cubic, $P\bar{4}3n$ (no. 218), $a = 12.620(1)$ Å, $V = 2009.9$ Å³, $Z = 8$, $R_{gt}(F) = 0.017$, $wR_{ref}(F^2) = 0.041$, $T = 293$ K.

Rb_4Si_4 , cubic, $P\bar{4}3n$ (no. 218), $a = 13.042(1)$ Å, $V = 2218.4$ Å³, $Z = 8$, $R_{gt}(F) = 0.027$, $wR_{ref}(F^2) = 0.052$, $T = 293$ K.

Cs_4Si_4 , cubic, $P\bar{4}3n$ (no. 218), $a = 13.510(1)$ Å, $V = 2465.8$ Å³, $Z = 8$, $R_{gt}(F) = 0.022$, $wR_{ref}(F^2) = 0.053$, $T = 293$ K.

Source of material

The compounds, first characterized by Schäfer and Klemm [1] and by Busmann [2,3], were synthesized by Schwarz [4] from the elements in encapsulated Nb ampoules enclosed in evacuated quartz tubes (distilled alkali metal, silicon powder 100/100 and 60/60 and 40/40 mmol), heated up to 1173 K (K) and 1053 K (Rb) and 1023 K (Cs), respectively, within 4 h and annealed at these temperatures for 2 h and finally slowly cooled down to room temperature within 40 h. Well-shaped black crystals are formed with shiny faces of type {100} and {110} for K and dull faces for Rb. Red transparent polyhedra and platelets are formed for Cs. The compounds are very sensitive to oxidation and hydrolysis (Caution!) and have to be handled strictly under inert conditions.

Experimental details

Lattice parameters were determined from Guinier-Simon powder patterns [5] (Si standard, $a = 5.43102$ Å; $CuK\alpha_1$ radiation, $\lambda = 1.540598$ Å).

Discussion

The three silicides form the KGe structure type (*cP64*) as reported by Busmann [2,3]. The redetermination was done for higher accuracy parameters and the results are within the standard deviations of Busmann's film data. Dominant units are tetrahedrally distorted M_4Si_4 heterocubanes (*stellae quadrangulae*) formed by anionic Si_4^{4-} tetrahedra and completed by four μ^3 bridging cations, which furthermore interconnect the units via μ^1-M-Si *exo*-bonds [4,6,7]. About the relations to other structures see [6–9]. The M_4Si_4 units around 2a site have $\bar{4}3m$ symmetry with the homoatomic bond lengths $d(Si-Si) = 2.415(2)$ Å, $2.416(6)$ Å, $2.422(5)$ Å (after librational corrections: 2.429 Å, 2.429 Å, 2.437 Å) and with $d(\mu^3-M-Si) = 3.467(1)$ Å, $3.591(1)$ Å, $3.716(1)$ Å for $M = K, Rb, Cs$ respectively. The interconnecting distances are larger with $d(\mu^1-M-Si) = 3.616(1)$ Å, $3.656(2)$ Å, $3.932(2)$ Å. The Si_4^{4-} anions around 6c site are significantly flattened to $\bar{4}2m$ disphenoids with $d(Si-Si) = 2.410(1)$ Å (4×), $2.431(1)$ Å (2×) and $2.415(3)$ Å (4×), $2.435(4)$ Å (2×) and $2.412(3)$ Å (4×), $2.440(3)$ Å (2×) (mean values = $2.418(10)$ Å, $2.422(10)$ Å, and $2.426(13)$ Å). This deformation is also reflected in the $M-Si$ distances which are in the ranges of 3.332 Å – 3.485 Å, 3.454 Å – 3.633 Å and 3.581 Å – 3.756 Å for the μ^3 bridges (μ^1 connection range: 3.508 Å – 3.609 Å, 3.651 Å – 3.762 Å, 3.827 Å – 3.924 Å). Cs_4Si_4 is a semiconductor with $E_g = 2.06$ eV ($\epsilon_{mol} = 48 \times 10^{-6}$ cm³mol⁻¹) [4].

1. Tetrapotassium *tetrahedro*-tetrasilicide, K_4Si_4

Table 1. Data collection and handling.

Crystal:	black shiny {100} and {110} forms, size $0.5 \times 0.5 \times 0.5$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	21.65 cm ⁻¹
Diffractionmeter, scan mode:	Syntex P1, $\omega/2\theta$
$2\theta_{max}$:	55.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2042, 425
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 403
$N(param)_{refined}$:	25
Programs:	SHELXTL-plus [10], ATOMS [11]

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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
K(1)	8e	0.33221(5)	x	x	0.0386(2)	U ₁₁	U ₁₁	−0.0028(2)	U ₁₂	U ₁₂
K(2)	24i	0.33581(4)	0.14092(4)	0.06450(4)	0.0359(3)	0.0391(3)	0.0330(3)	0.0029(2)	−0.0032(2)	0.0020(3)
Si(1)	8e	0.06766(5)	x	x	0.0302(2)	U ₁₁	U ₁₁	−0.0041(3)	U ₁₂	U ₁₂
Si(2)	24i	0.06197(5)	0.31695(5)	0.42628(5)	0.0300(3)	0.0281(3)	0.0278(3)	−0.0028(3)	0.0040(3)	0.0028(3)

2. Tetrarubidium *tetrahedro*-tetrasilicide, Rb₄Si₄**Table 3.** Data collection and handling.

Crystal:	dull black polyhedron, size 0.4 × 0.4 × 0.4 mm
Wavelength:	Mo K _α radiation (0.71073 Å)
μ:	179.01 cm ^{−1}
Diffractometer, scan mode:	Syntex P1, ω/2θ
2θ _{max} :	54.88°
N(hkl) _{measured} , N(hkl) _{unique} :	1599, 398
Criterion for I _{obs} , N(hkl) _{gt} :	I _{obs} > 2 σ(I _{obs}), 338
N(param) _{refined} :	24
Programs:	SHELXTL-plus [10], ATOMS [11]

Table 4. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Rb(1)	8e	0.33167(6)	x	x	0.0382(3)	U ₁₁	U ₁₁	−0.0025(4)	U ₁₂	U ₁₂
Rb(2)	24i	0.33548(6)	0.14102(6)	0.06361(6)	0.0364(5)	0.0391(5)	0.0334(4)	0.0027(4)	−0.0031(4)	0.0009(4)
Si(1)	8e	0.0655(2)	x	x	0.0320(8)	U ₁₁	U ₁₁	−0.004(1)	U ₁₂	U ₁₂
Si(2)	24i	0.0603(2)	0.3149(2)	0.4287(2)	0.029(1)	0.027(1)	0.028(1)	−0.004(1)	0.004(1)	0.001(1)

3. Tetraesium *tetrahedro*-tetrasilicide, Cs₄Si₄**Table 5.** Data collection and handling.

Crystal:	transparent red polyhedron, size 0.6 × 0.6 × 0.6 mm
Wavelength:	Mo K _α radiation (0.71073 Å)
μ:	120.56 cm ^{−1}
Diffractometer, scan mode:	Syntex P1, ω/2θ
2θ _{max} :	54.98°
N(hkl) _{measured} , N(hkl) _{unique} :	2481, 500
Criterion for I _{obs} , N(hkl) _{gt} :	I _{obs} > 2 σ(I _{obs}), 493
N(param) _{refined} :	25
Programs:	SHELXTL-plus [10], ATOMS [11]

Table 6. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cs(1)	8e	0.33172(4)	x	x	0.0385(2)	U ₁₁	U ₁₁	−0.0016(2)	U ₁₂	U ₁₂
Cs(2)	24i	0.33610(4)	0.14229(3)	0.06493(4)	0.0399(3)	0.0408(3)	0.0373(2)	0.0032(2)	−0.0051(2)	0.0021(2)
Si(1)	8e	0.0634(1)	x	x	0.0327(7)	U ₁₁	U ₁₁	−0.0045(7)	U ₁₂	U ₁₂
Si(2)	24i	0.0591(2)	0.3124(1)	0.4317(1)	0.0311(9)	0.0292(9)	0.0290(9)	−0.0035(7)	0.0038(7)	0.0032(8)

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