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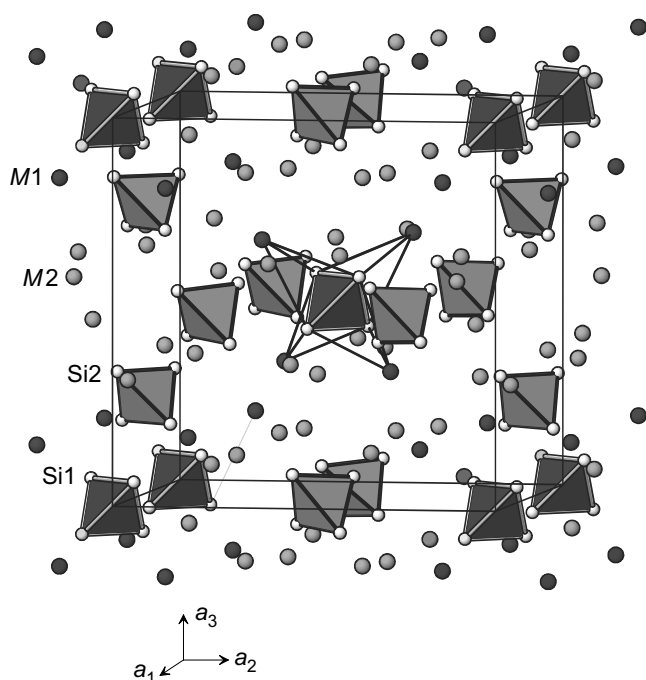
# Refinement of the crystal structures of the *tetrahedro-*tetrasilicides $K_4Si_4$ , $Rb_4Si_4$ and $Cs_4Si_4$

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## Abstract

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

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

$Cs_4Si_4$ , cubic,  $P\bar{4}3n$  (no. 218),  $a = 13.510(1)$  Å,  $V = 2465.8$  Å<sup>3</sup>,  $Z = 8$ ,  $R_{gt}(F) = 0.022$ ,  $wR_{ref}(F^2) = 0.053$ ,  $T = 293$  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  $\mu^3$  bridging cations, which furthermore interconnect the units via  $\mu^1$ -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 ( $4\times$ ),  $2.431(1)$  Å ( $2\times$ ) and  $2.415(3)$  Å ( $4\times$ ),  $2.435(4)$  Å ( $2\times$ ) and  $2.412(3)$  Å ( $4\times$ ),  $2.440(3)$  Å ( $2\times$ ) (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  $\mu^3$  bridges ( $\mu^1$  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 ( $\xi_{mol} = 48 \times 10^{-6}$  cm<sup>3</sup>mol<sup>-1</sup>) [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)                                     |
| $\mu$ :                                   | $21.65$ cm <sup>-1</sup>   |
| Diffractometer, scan mode:                | Syntex P1, $\omega/2\theta$  |
| $2\theta_{max}$ :                         | $55.02^\circ$  |
| $N(hkl)_{measured}$ , $N(hkl)_{unique}$ : | 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]  |

\* Correspondence author

**Table 2.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

| Atom  | Site        | <i>x</i>   | <i>y</i>   | <i>z</i>   | <i>U</i> <sub>11</sub> | <i>U</i> <sub>22</sub> | <i>U</i> <sub>33</sub> | <i>U</i> <sub>12</sub> | <i>U</i> <sub>13</sub> | <i>U</i> <sub>23</sub> |
|-------|-------------|------------|------------|------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| K(1)  | 8 <i>e</i>  | 0.33221(5) | <i>x</i>   | <i>x</i>   | 0.0386(2)              | <i>U</i> <sub>11</sub> | <i>U</i> <sub>11</sub> | −0.0028(2)             | <i>U</i> <sub>12</sub> | <i>U</i> <sub>12</sub> |
| K(2)  | 24 <i>i</i> | 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) | 8 <i>e</i>  | 0.06766(5) | <i>x</i>   | <i>x</i>   | 0.0302(2)              | <i>U</i> <sub>11</sub> | <i>U</i> <sub>11</sub> | −0.0041(3)             | <i>U</i> <sub>12</sub> | <i>U</i> <sub>12</sub> |
| Si(2) | 24 <i>i</i> | 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, Rb<sub>4</sub>Si<sub>4</sub>****Table 3.** Data collection and handling.

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

**Table 4.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

| Atom  | Site        | <i>x</i>   | <i>y</i>   | <i>z</i>   | <i>U</i> <sub>11</sub> | <i>U</i> <sub>22</sub> | <i>U</i> <sub>33</sub> | <i>U</i> <sub>12</sub> | <i>U</i> <sub>13</sub> | <i>U</i> <sub>23</sub> |
|-------|-------------|------------|------------|------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Rb(1) | 8 <i>e</i>  | 0.33167(6) | <i>x</i>   | <i>x</i>   | 0.0382(3)              | <i>U</i> <sub>11</sub> | <i>U</i> <sub>11</sub> | −0.0025(4)             | <i>U</i> <sub>12</sub> | <i>U</i> <sub>12</sub> |
| Rb(2) | 24 <i>i</i> | 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) | 8 <i>e</i>  | 0.0655(2)  | <i>x</i>   | <i>x</i>   | 0.0320(8)              | <i>U</i> <sub>11</sub> | <i>U</i> <sub>11</sub> | −0.004(1)              | <i>U</i> <sub>12</sub> | <i>U</i> <sub>12</sub> |
| Si(2) | 24 <i>i</i> | 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. Tetracesium tetrahedro-tetrasilicide, Cs<sub>4</sub>Si<sub>4</sub>****Table 5.** Data collection and handling.

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

**Table 6.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

| Atom  | Site        | <i>x</i>   | <i>y</i>   | <i>z</i>   | <i>U</i> <sub>11</sub> | <i>U</i> <sub>22</sub> | <i>U</i> <sub>33</sub> | <i>U</i> <sub>12</sub> | <i>U</i> <sub>13</sub> | <i>U</i> <sub>23</sub> |
|-------|-------------|------------|------------|------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Cs(1) | 8 <i>e</i>  | 0.33172(4) | <i>x</i>   | <i>x</i>   | 0.0385(2)              | <i>U</i> <sub>11</sub> | <i>U</i> <sub>11</sub> | −0.0016(2)             | <i>U</i> <sub>12</sub> | <i>U</i> <sub>12</sub> |
| Cs(2) | 24 <i>i</i> | 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) | 8 <i>e</i>  | 0.0634(1)  | <i>x</i>   | <i>x</i>   | 0.0327(7)              | <i>U</i> <sub>11</sub> | <i>U</i> <sub>11</sub> | −0.0045(7)             | <i>U</i> <sub>12</sub> | <i>U</i> <sub>12</sub> |
| Si(2) | 24 <i>i</i> | 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)              |

## References

1. Schäfer, R.; Klemm, W.: Das Verhalten der Alkalimetalle zu Halbmatalen. IX. Weitere Beiträge zur Kenntnis der Silicide und Germanide der Alkalimetalle. *Z. Anorg. Allg. Chem.* **312** (1961) 214-220.
2. Busmann, E.: Die Kristallstruktur von KGe und isotypen Germaniden und Siliciden. *Naturwissenschaften* **47** (1960) 82.
3. Busmann, E.: Die Kristallstrukturen von KSi, RbSi, CsSi, KGe, RbGe und CsGe. *Z. Anorg. Allg. Chem.* **327** (1964) 260-273.
4. Schwarz, M.: Rote, transparente Alkalimetallsilicide und über die Bindung einer neuen, metastabilen Silicium-Modifikation. Dissertation, Universität Stuttgart 1987.
5. Simon, A.: Eine Methode zur Untersuchung extrem luftempfindlicher Substanzen mit der Guinier-Methode. *J. Appl. Crystallogr.* **3** (1970) 11-18.
6. von Schnering, H. G.; Nesper, R.: Zusammenhänge der Strukturen von I-IV-Zintlphasen mit einfachen AB-Strukturtypen. *Z. Kristallogr.* **162** (1983) 202-204.
7. Nesper, R.: Structure and chemical bonding in Zintl-Phases containing lithium. *Progr. Solid State Chem.* **20** (1990) 1-45.
8. Nuss, J.; Hönle, W.; Peters, K.; von Schnering, H. G.: Tetrapnictido-titanate(IV)  $M_4TiX_4$  ( $M = Sr, Ba; X = P, As$ ), hierarchische Derivate der KGe-Struktur K<sub>4</sub>Ge<sub>4</sub>. *Z. Anorg. Allg. Chem.* **622** (1996) 1879-1885.
9. von Schnering, H. G.; Llanos, J.; Chang, J.-H.; Peters, K.; Peters, E.-M.; Nesper, R.: Refinement of the crystal structures of the *tetrahedro*-tetragermanides K<sub>4</sub>Ge<sub>4</sub>, Rb<sub>4</sub>Ge<sub>4</sub> and Cs<sub>4</sub>Ge<sub>4</sub>. *Z. Kristallogr. NCS* **220** (2005) 324-326.
10. Sheldrick, G. M.: SHELXTL-plus. Structure Determination Software Suite. Release 4.1. Siemens Analytical X-Ray Instruments, Madison, Wisconsin, USA 1990.
11. Dowty, E.: ATOMS. A Complete Program for Displaying Atomic Structures. Version 6.0. Shape Software, Kingsport, Tennessee, USA 2002.