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Refinement of the crystal structure of tetrasodium tetrasilicide, Na₄Si₄

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Received May 19, 2008, accepted and available on-line July 25, 2008; CSD no. 409953



Abstract

Na4Si4, monoclinic, C12/c1 (no. 15), a = 12.1536(5) Å, b = 6.5452(5) Å, c = 11.1323(6) Å, $\beta = 118.9(1)^{\circ}$, V = 775.3 Å³, Z = 4, $R_{gt}(F) = 0.028$, $wR_{ref}(F^2) = 0.064$, T = 293 K.

Source of material

The Zintl phase Na4Si4 was prepared from the elements with an excess of alkali metal (Na, ingot, 99.9 %, ChemPur; Si, pieces, 99.999 %, Alfa) in a closed Ta container which was sealed into an evacuated quartz glass ampoule. The reaction mixture was heated up to 750 °C within 1 hour, annealed for 3 hours and afterwards cooled down to ambient temperature within 4 days. Well shaped needle-like crystals were obtained by removing the excess of so-dium using vacuum distillation at 230 °C and 5×10^{-6} mbar [1,2]. Due to sensitivity of the compound to air and humidity, the investigated single crystal was sealed into a glass capillary under purified argon.

Experimental details

Lattice parameters were refined from synchrotron powder diffraction data ($\lambda = 0.39987$ Å), using 58 reflections between $4^{\circ} \le 2\theta \le 14.5^{\circ}$, and applying LaB₆ as internal standard (NIST, a = 4.15692 Å).

Discussion

The crystal structure of Na4Si4 was first determined by Witte, von Schnering and Klemm from Weißenberg film data on single crystals [1]. Na4Si4 was re-investigated in order to elucidate the chemical bonding by quantum chemical calculations as well as solid state nuclear magnetic resonance measurements. For these investigations, high quality crystallographic data are crucial. The present re-determination confirms structural information obtained in Ref. [1] and provides data of the crystal structure with higher accuracy. Two crystallographic non-equivalent sites for both Si and Na are occupied in the crystal structure. The Si atoms form distorted Si4⁴⁻ tetrahedranide anions. In comparison to the previous data the a- and c-axis are shortened by 0.036 Å and 0.048 Å, respectively. This results in a shortening of the distance d(Si1--Si1) = 2.466(1) Å by 0.045 Å, whereas the distance d(Si2-Si2) = 2.411(4) Å is elongated by 0.031 Å. The distances d(Si1-Si2) = 2.3797(7) Å and 2.4030(8) Å remain almost not affected thus the average distance of $d_{av} = 2.395(4)$ Å within the tetrahedranide anions is equal within the experimental error with the previous result ($d_{av} = 2.41(1) \text{ Å} [1]$). The tetrahedron faces Si2–Si2–Si1 and Si1–Si1–Si2 are μ_3 capped by Na1 with d_{av} = 3.2396(5) Å and by Na2 with $d_{av} = 3.5677(7)$ Å, respectively. Whereas the four tetrahedron edges Si1—Si2 are μ_2 bridged by Na1 with $d_{av} = 3.2914(7)$ Å, the two edges Si1—Si1 and Si2—Si2 are not coordinated by sodium. The Si2 atoms show two μ_1 contacts to Na2 with $d_{av} = 3.0641(8)$ Å and the Si1 atoms are μ_1 coordinated by Na1 (3.8382(8) Å) and by Na2 (3.203(1) Å).

Table 1. Data collection and handling.

Crystal:	silver block,
	size $0.045 \times 0.050 \times 0.060$ mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ:	8.79 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7, φ/ω
$2\theta_{\rm max}$:	63°
N(hkl) _{measured} , N(hkl) _{unique} :	2975, 1204
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	$I_{\rm obs} > 2 \sigma(I_{\rm obs}), 1139$
N(param)refined:	37
Programs:	WinCSD [3], SHELXL-97 [4],
6	DIAMOND [5]

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Atom	Site	x	y	Z	<i>U</i> ₁₁	U ₂₂	<i>U</i> 33	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Si(2)	8 <i>f</i>	0.09754(3)	0.03924(6)	0.35655(3)	0.0304(2)	0.0374(2)	0.0231(2)	0.0151(1)	0.0125(1)	0.0121(1)
Na(1)	8 <i>f</i>	0.35040(5)	0.3381(1)	0.35883(6)	0.0325(3)	0.0564(4)	0.0291(3)	-0.0028(2)	0.0148(2)	0.0047(2)
Na(2)	8 <i>f</i>	0.36871(5)	0.09411(9)	0.04668(6)	0.0295(3)	0.0331(3)	0.0462(3)	0.0064(2)	0.0149(2)	0.0044(2)

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Acknowledgment. We thank Aron Wosylus for synchrotron measurements.

References

- Witte, J.; von Schnering, H. G.; Klemm, W.: Die Kristallstruktur von NaSi und NaGe. Z. Anorg. Allg. Chem. 327 (1964) 260-273.
- Hohmann, E: Silicide und Germanide der Alkalimetalle. Z. Anorg. Allg. Chem. 257 (1948) 113-126.
- Akselrud, L. G.; Zavalii, P. Y.; Grin, Yu. N.; Pecharsky, V. K.; Baumgartner, B.; Wölfel, E.: Use of the CSD program package for structure determination from powder data. Mater. Sci. Forum 133-136 (1993) 335-340.
- 4. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
- Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 2.0f. Crystal Impact, Bonn, Germany 1998.