Redetermination of the crystal structure of tetrasodium *tetrahedro*-tetrastannide, Na_4Sn_4 and tetrapotassium *tetrahedro*-tetrastannide, K_4Sn_4

Yu. Grin^I, M. Baitinger^{II}, R. Kniep^{III} and H. G. von Schnering*^{II}

^I Max-Planck-Institut für Chemische Physik fester Stoffe, Pirnaer Landstr. 176, D-01257 Dresden, Germany

^{II} Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany

^{III} Technische Universität Darmstadt, Eduard-Zintl-Institut, Hochschulstraße 10, D-64289 Darmstadt, Germany

Received May 31, 1999, transferred to 2nd update of database ICSD in 1999, CSD-No. 409434 and CSD-No. 409435

Abstract

Na_4Sn_4 , tetragonal, $I4_1/acd$ (No. 142), $a = 10.475(1) \text{ \AA}$, $c = 17.412(2) \text{ \AA}$, $V = 1910.5 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.058$, $wR(F) = 0.058$, $T = 295 \text{ K}$.

K_4Sn_4 , tetragonal, $I4_1/acd$ (No. 142), $a = 11.409(1) \text{ \AA}$, $c = 18.649(2) \text{ \AA}$, $V = 2427.5 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.036$, $wR(F) = 0.036$, $T = 295 \text{ K}$.

Source of material

Stoichiometric mixtures of the elements were heated up to 1273 K for 1 day and annealed at 673 K for one week (Nb container welded at 30 kPa Ar). Single phases (by X-ray diffraction) with silvery grey crystals were formed. The compounds are very sensitive against oxidation and hydrolysis and have to be handled under inert conditions. Lattice parameters were determined from Guinier-Simon powder patterns [1] with Si standard ($\lambda(\text{CuK}\alpha_1) = 1.54051 \text{ \AA}$; $a(\text{Si}) = 5.4305 \text{ \AA}$).

Discussion

Both compounds form the $I4_1$ structure of NaPb [2] as shown by Hewaidy et al. [3] for K_4Sn_4 and by Müller et al. [4] for Na_4Sn_4 from single crystal structure analysis. In order to compare several NaPb-type structures in detail, both crystal structures were redetermined. The lattice parameters are slightly different to the former values while the c/a ratios are almost unchanged. Two interpenetrating 3D frameworks of condensed M_4Sn_4 ($\text{M} = \text{Na}, \text{K}$) *stellae quadrangulae* (distorted heterocubanes [5]) are formed, hierarchically related to the Cu_2O structure [6]. The tetrahedranide anions Sn_4^{4-} ($d(\text{Sn}-\text{Sn}) = 2.978(2) \text{ \AA}$ (Na_4Sn_4); $d(\text{Sn}-\text{Sn}) = 2.949(1) \text{ \AA}$ (K_4Sn_4)) are connected via twofold μ^3 -bridging M1 atoms to ${}^3_4(\text{M}_{14/2}[\text{Sn}_4])$ substructures which are interconnected by 'interstitial' μ^2 -bridging M2 atoms. In total, 16 M atoms form cages around the tetrahedra with $3.350(2) \text{ \AA} < d(\text{Na}-\text{Sn}) < 3.539(2) \text{ \AA}$ and $3.682(1) \text{ \AA} < d(\text{K}-\text{Sn}) < 3.850(2) \text{ \AA}$, respectively.

1. Tetrasodium *tetrahedro*-tetrastannide, Na_4Sn_4

Table 1. Data collection and handling.

Crystal:	silvery grey, irregular, size $0.1 \times 0.1 \times 0.1 \text{ mm}$
Wavelength:	Mo $K\alpha$ radiation ($0.71069 \text{ \AA}$)
μ :	52.3 cm^{-1}
Diffractometer, scan mode:	Stoe STADI4, $\omega/2\theta$
$2\theta_{\text{max}}$:	65°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	1793, 872
Criterion for $F_{\text{obs}}, N(hkl)_{\text{gt}}$:	$F_{\text{obs}} > 6 \sigma(F_{\text{obs}})$, 395
$N(\text{param})_{\text{refined}}$:	20
Programs:	CSD [7], ATOMS [8]

* Correspondence author
(e-mail: baiti@vsibml.mpi-stuttgart.mpg.de)

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

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Na(1)	16e	0.875(2)	0	1/4	0.034(7)	0.030(7)	0.044(7)	0	0	−0.007(7)
Na(2)	16f	0.375(1)	<i>x</i> +1/4	1/8	0.039(5)	<i>U</i> ₁₁	0.043(8)	−0.001(9)	−0.005(5)	− <i>U</i> ₁₃
Sn	32g	0.0695(2)	0.1261(2)	0.93525(9)	0.0263(8)	0.0302(9)	0.0276(7)	−0.0007(8)	−0.0088(8)	0.0114(8)

2. Tetrapotassium *tetrahedro*-tetrastannide, K₄Sn₄**Table 3.** Data collection and handling.

Crystal:	silvery grey, irregular, size 0.1 × 0.1 × 0.1 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71069 Å)
μ:	94.2 cm ^{−1}
Diffractionmeter, scan mode:	Stoe STADI4, ω/2θ
2θ _{max} :	60°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	1852, 897
Criterion for <i>F</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>F</i> _{obs} > 4 σ(<i>F</i> _{obs}), 682
<i>N</i> (<i>param</i>) _{refined} :	20
Programs:	CSD [7], ATOMS [8]

Table 4. Atomic coordinates and displacement parameters (in Å², origin choice 2).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
K(1)	16e	0.8621(3)	0	1/4	0.030(1)	0.036(2)	0.035(1)	0	0	−0.005(1)
K(2)	16f	0.3784(2)	<i>x</i> +1/4	1/8	0.037(1)	<i>U</i> ₁₁	0.037(2)	0.002(1)	−0.0009(9)	− <i>U</i> ₁₃
Sn	32g	0.06468(6)	0.13783(6)	0.93072(3)	0.0266(3)	0.0276(3)	0.0261(3)	−0.0002(3)	−0.0061(2)	0.0084(3)

References

- Simon, A.: Eine Methode zur Untersuchung extrem luftempfindlicher Substanzen mit der Guinier-Methode. *J. Appl. Crystallogr.* **3** (1970) 11–18.
- Marsh, R. E.; Shoemaker, D. P.: The Crystal Structure of NaPb. *Acta Crystallogr.* **6** (1953) 197–205.
- Hewaidy, I. F.; Busmann, E.; Klemm, W.: Die Struktur der AB-Verbindungen der schweren Alkalimetalle mit Zinn und Blei. *Z. Anorg. Allg. Chem.* **328** (1964) 283–293.
- Müller, W.; Volk, K.: Die Struktur des β-NaSn. *Z. Naturforsch.* **32b** (1977) 709–710.
- von Schnering, H. G.; Nesper, R.: Zusammenhänge der Strukturen von I–IV Zintl-Phasen mit einfachen AB-Strukturen. *Z. Kristallogr.* **162** (1983) 202–204.
- Carrillo-Cabrera, W.; Somer, M.; Peters, K.; von Schnering, H. G.: Single-crystal structure refinement of CsPb. VIth Conference on Solid State Chemistry, Zürich, 1997, Abstract PA122.
- Akselrud, L. G.; Grin, Y. N.; Zavalii, P. Y.; Pecharskii, V. K.; Fundamenskii, V. S.: CSD - universal program package for single crystal and/or powder structure data treatment - 12. European Crystallogr. Meeting, Collected Abstracts, Moscow, **3** (1989) 155.
- Dowty, E.: Atoms 4.1, A Complete Program for Displaying Atomic Structures. By Shape software, 521 Hidden Valley Road, Kingsport, TN 37663, USA 1998.