

## Structure Refinement of AuSn<sub>2</sub>

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Well-shaped single crystals of binary AuSn<sub>2</sub> were obtained as a side product during the synthesis of LiAu<sub>3</sub>Sn<sub>4</sub>. The structure of AuSn<sub>2</sub> has been studied by X-ray diffractometer data: *Pbca*, *Z* = 8, *a* = 689.8(1), *b* = 701.1(1), *c* = 1177.3(2) pm, *wR*<sub>2</sub> = 0.0533, 1234 *F*<sup>2</sup> values, and 29 variables. The gold atoms show a distorted octahedral coordination by tin at Au–Sn distances ranging from 272 to 283 pm. The structure can be considered as an intergrowth of pyrite and marcasite related slabs. Consequently one observes Sn1–Sn2 dumb-bells with a Sn–Sn distance of 289 pm, while all other Sn–Sn distances are larger than 322 pm.

**Key words:** Stannide, Intermetallics, Crystal Chemistry

### Introduction

Due to its excellent wettability for many metals, tin is the main and most important component in most modern soft-solders. An overview of the various commercially used soft soldering alloys is given in the *Tin Handbook* [1]. During the soldering process, various metal stannides can form. Especially the stannides with the coinage metals have attracted considerable interest for various soldering applications for microelectronic assemblies [1]. They can occur at the solder/metal interfaces or as precipitations. The stannides are much more brittle than the solder alloys, and consequently they are responsible for the brittleness and fracture of solder joints. Today, many joints in microelectronic devices are made of gold, leading to the stannides AuSn, AuSn<sub>2</sub>, and AuSn<sub>4</sub> as potential candidates for precipitate formation.

AuSn (yuanjiangite) and AuSn<sub>2</sub> have also been observed in nature. Yuanjiangite most likely formed by *in situ* replacement of placer gold within tin-rich sed-

Table 1. Crystal data and structure refinement for AuSn<sub>2</sub>.

Empirical formula	AuSn <sub>2</sub>
Molar mass	434.35 g/mol
Unit cell dimensions	<i>a</i> = 689.8(1) pm <i>b</i> = 701.1(1) pm <i>c</i> = 1177.3(2) pm <i>V</i> = 0.5694 nm <sup>3</sup>
Space group	<i>Pbca</i>
Pearson symbol, <i>Z</i>	oP24, 8
Calculated density	10.13 g/cm <sup>3</sup>
Crystal size	20 × 50 × 60 μm <sup>3</sup>
Transmission ratio (max/min)	5.46
Absorption coefficient	68.5 mm <sup>-1</sup>
<i>F</i> (000)	1432
$\theta$ Range	3° to 35°
Range in <i>hkl</i>	±11, ±11, ±18
Total no. reflections	7854
Independent reflections	1234 ( <i>R</i> <sub>int</sub> = 0.0529)
Reflections with <i>I</i> > 2σ( <i>I</i> )	1166 ( <i>R</i> <sub>sigma</sub> = 0.0300)
Data/parameters	1234 / 29
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.230
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0272; <i>wR</i> <sub>2</sub> = 0.0523
<i>R</i> Indices (all data)	<i>R</i> <sub>1</sub> = 0.0303; <i>wR</i> <sub>2</sub> = 0.0533
Extinction coefficient	0.0053(2)
Largest diff. peak and hole	2.53 and -1.81 e/Å <sup>3</sup>

iments [2], and AuSn<sub>2</sub> was observed next to argentiferous native gold particles from the Le Boiron river in Western Switzerland [3].

AuSn<sub>2</sub> was first reported by Schubert *et al.* and the structure was refined on the basis of X-ray film data [4, 5]. An alternative description of the structure was given some time later by Kripyakevich [6]. During our systematic phase analytical investigations of the Li–Au–Sn system [7–10] when searching for novel battery anode materials, we obtained well-shaped single crystals of AuSn<sub>2</sub>. A redetermination of the AuSn<sub>2</sub> structure on the basis of precise single-crystal diffractometer data is reported herein.

### Experimental Section

#### Synthesis

The crystals of AuSn<sub>2</sub> were obtained as a side product during the synthesis of LiAu<sub>3</sub>Sn<sub>4</sub> [7]. Starting materials were lithium rods (Merck, > 99%), gold wire (Degussa-Hüls, Ø1 mm, > 99.9%) and a tin bar (Heraeus, 99.9%). The elements were weighed in the 1:3:4 atomic ratio and sealed in an evacuated tantalum tube [11]. The latter was enclosed in an evacuated silica ampoule for protection against oxidation. The ampoule was then rapidly heated to 1070 K, annealed at 870 K for two days and finally cooled to room temperature by switching off the furnace. The light grey polycrystalline

Table 2. Atomic coordinates and anisotropic displacement parameters ( $\text{pm}^2$ ) for  $\text{AuSn}_2$ . All atoms lie on the general Wyckoff site 8c. The anisotropic displacement factor exponent takes the form:  $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]$ .  $U_{\text{eq}}$  is defined as a third of the trace of the orthogonalized  $U_{ij}$  tensor.

Atom	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{\text{eq}}$
Au	0.01177(3)	0.89185(3)	0.11650(2)	115(1)	112(1)	136(1)	-8(1)	4(1)	-1(1)	121(1)
Sn1	0.85258(5)	0.25116(6)	0.08937(4)	133(2)	132(2)	169(2)	-4(1)	14(1)	29(1)	144(1)
Sn2	0.12914(5)	0.52783(6)	0.17234(3)	142(2)	131(2)	134(2)	9(1)	12(1)	21(1)	136(1)

Table 3. Interatomic distances (pm) in  $\text{AuSn}_2$ . Standard deviation are all equal or smaller than 0.1 pm.

Au:	1	Sn1:	1	Au:	271.9
	1	Sn2:	1	Au:	276.7
	1		1	Au:	278.5
	1		1	Sn2:	289.1
	1		1	Sn2:	321.5
	1		1	Sn2:	345.1
	1	Sn2:	1	Au:	273.4
	1		1	Au:	275.7
	1		1	Au:	283.4
	1		1	Sn1:	289.1
	1		1	Sn1:	321.5
	1		1	Sn1:	345.1

sample is stable in air over months. For further details we refer to the original work on  $\text{LiAu}_3\text{Sn}_4$  and  $\text{LiAuSn}$  [7, 9].

#### X-ray imaging plate data and structure refinement

Irregularly shaped single crystals of  $\text{AuSn}_2$  were isolated from the annealed sample by mechanical fragmentation and examined by Laue photographs on a Buerger precession camera (equipped with an imaging plate system Fujifilm BAS-1800) in order to establish suitability for intensity data collection. Intensity data were collected at room temperature by use of a Stoe IPDS-II diffractometer with graphite monochromatized Mo- $K_\alpha$  radiation. A numerical absorption correction was applied to the data. All relevant crystallographic details are listed in Table 1. Our refined lattice parameters (Table 1) are in good agreement with the data originally reported by Schubert *et al.* [5], v. c.  $a = 690.9$ ,  $b = 703.7$ , and  $c = 1178.9$  pm.

The systematic extinctions of the data set were compatible with space group  $Pbca$ , in agreement with the previous investigation by Schubert *et al.* [5]. The atomic parameters determined from the X-ray film data were taken as starting values and the structure was refined using SHELXL-97 (full-matrix least-squares on  $F_o^2$ ) [12] with anisotropic atomic displacement parameters for all three sites. As a check for the correct composition, the occupancy parameters were refined in separate series of least-squares cycles. All sites were fully occupied within less than one standard uncertainty. In the final cycles the ideal occupancies were assumed again. A final difference Fourier synthesis revealed no significant residual peaks (see Table 1). The refined positional parameters and

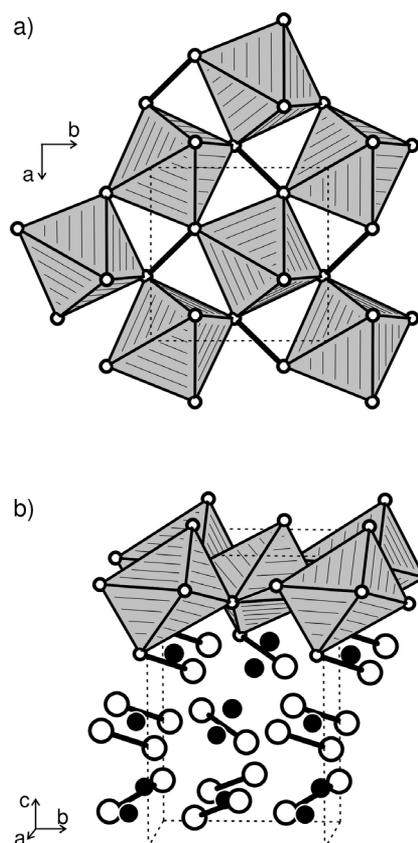


Fig. 1. Crystal structure of  $\text{AuSn}_2$ : a) one layer of slightly distorted corner-sharing  $\text{AuSn}_6$  octahedra; b) unit cell of  $\text{AuSn}_2$ . Gold and tin atoms are drawn as filled and open circles, respectively. The Sn1–Sn2 dumb-bells are emphasized in both drawings by bold lines. For details see text.

interatomic distances are listed in Tables 2 and 3. Further details on the structure refinement are available\*.

The single crystal (mounted on a quartz fibre) was coated with a thin carbon film and analyzed by EDX using a LEICA 420 I scanning electron microscope with elemental gold and tin as standards. The EDX analyses ( $35 \pm 2$  at.-% Au:

\*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD-415968.

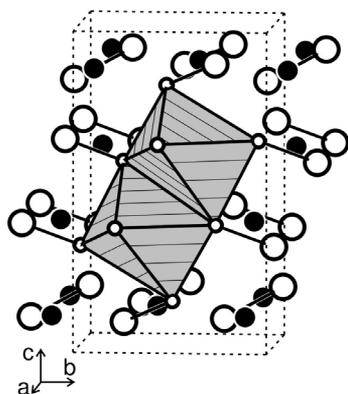


Fig. 2. Edge-sharing  $\text{AuSn}_6$  octahedra in the structure of  $\text{AuSn}_2$ .

$65 \pm 2$  at.-% Sn) revealed no impurity elements and was in agreement with the ideal composition.

### Discussion

The structure of  $\text{AuSn}_2$  has been refined from single crystal X-ray diffractometer data. The present experiment fully confirms the structural model reported by Schubert *et al.* [5], but the atomic positions and the occupancy parameters have been determined with much higher precision. In Fig. 1 we present the unit cell of  $\text{AuSn}_2$ . The gold atoms have a slightly distorted octahedral tin coordination at Au–Sn distances ranging from 272 to 283 pm, comparable to the sum of the covalent radii of 274 pm [13]. Similar Au–Sn distances have recently also been observed in  $\text{LiAuSn}$  (270 pm) [7],  $\text{Li}_2\text{AuSn}_2$  (273 pm) [10], and  $\text{SrAuSn}$

(279–286 pm) [14]. The  $\text{AuSn}_6$  octahedra are condensed *via* common corners in the *a*, *b* and *c* direction.

The gold atoms show an arrangement that resembles half of a face-centered cubic cell. The octahedral voids left by this arrangement are filled by Sn1–Sn2 dumbbells with a Sn–Sn distance of 289 pm, similar to the pyrite structure type. These Sn–Sn distances are close to the Sn–Sn single bond distance of 281 pm in the diamond modification of  $\alpha$ -Sn [15]. All other Sn–Sn distances are longer than 322 pm (Table 3), and thus even longer than in  $\beta$ -Sn ( $4 \times 302$  and  $2 \times 318$  pm) [15]. Chemical bonding in  $\text{AuSn}_2$  is thus governed by both the covalent Au–Sn and Sn1–Sn2 interactions.

A very distinct description of the  $\text{AuSn}_2$  structure was given by Kripyakevich [6].  $\text{AuSn}_2$  can be considered as an intergrowth structure of slightly orthorhombically distorted pyrite and marcasite related slabs. Within the pyrite slabs the distorted  $\text{AuSn}_6$  octahedra are condensed *via* common corners (Fig. 1), while the octahedra show edge-sharing in the marcasite related slabs (Fig. 2). This strongly influences the Au–Au distances. In the marcasite slab we observe a smaller Au–Au distance of 314 pm, while the shortest Au–Au distance in the pyrite slab is 467 pm. The short Au–Au distance of 314 pm, however, is more a geometrical constraint of the intergrowth procedure (edge-sharing octahedra) rather than an aurophilic interaction.

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