Crystal Structure and Properties of the Titanium Stannide Ti$_2$Sn$_3$

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Intermetallic Compounds, Electrical Conductivity, $^{119}$Sn Mössbauer Spectroscopy

The recently reported binary stannide Ti$_2$Sn$_3$ is confirmed. Its structure was determined from single-crystal X-ray diffractometer data: $\text{Cmca}$, $a = 596.7(4)$, $b = 1995(2)$, $c = 701.3(4)$ pm, $Z = 8$, $R = 0.027$ for 817 structure factors and 30 variable parameters. The crystal structure is compared to that of V$_2$GaSn$_2$, which has the same space group symmetry and atomic positions. The Ga atoms of V$_2$GaSn$_2$ occupy those Sn positions of Ti$_2$Sn$_3$ which have the smaller coordination number. The two different titanium atoms of Ti$_2$Sn$_3$ have 11 neighbors of which 3 and 4, respectively, are titanium atoms. The three different tin atoms have 5 titanium with 8 or 10 additional tin neighbors. They show only a slightly broadened but unresolved $^{119}$Sn Mössbauer signal with an isomer shift reflecting the high tin content of this intermetallic compound and a relatively large quadrupole splitting of 2.10 mm·s$^{-1}$. Ti$_2$Sn$_3$ is a good metallic conductor and a Pauli paramagnet.

**Introduction**

In the course of our investigations of transition metal stannides with a high content of tin we have reported on V$_2$Sn$_3$, NbSn$_2$, and CrSn$_2$ [1], on MoSn$_3$ [2], on two modifications of CoSn$_3$ [3], and on RhSn$_3$, RhSn$_4$, α-IrSn$_4$, and Os$_4$Sn$_{17}$ [4]. Recently the phase diagram of the binary system titanium-tin was reinvestigated and a new phase with a relatively high tin content, designated as “TiSn*”, was found, which is stable up to at least 700 °C [5]. This phase, characterized by its X-ray powder diagram, is formed by a peritectic reaction of Ti$_6$Sn$_5$ with the tin-rich melt and seems to be the titanium stannide with the highest tin content. The present report describes the crystal structure and some physical properties of this compound for which we found the composition Ti$_2$Sn$_3$, in agreement with the proposed phase diagram [5].

**Experimental**

**Sample Preparation**

The stannide Ti$_2$Sn$_3$ was prepared by reaction of the elemental components. Titanium was purchased as a sponge (Carl Roth, stated purity 99.999 %) and tin in the form of ingots (Heraeus, 99.999 %). The metals (~1 g with the ideal atomic ratio 2:3) were sealed into an evacuated tantalum tube, which was enclosed under vacuum in a silica tube. The sample was heated to 600 °C at a rate of 60 °C/h, held at that temperature for 2 weeks and slowly cooled (4 °C/h) to room temperature. The sample could easily be crushed. The surface of the grains showed silvery metallic luster. The powder is stable on air for a long time. An energy-dispersive X-ray fluorescence analysis of the sample in a scanning electron microscope did not reveal any impurity elements heavier than sodium. The X-ray powder diagram showed great similarity to that reported earlier [5].

**Physical Properties**

The temperature dependence of the electrical conductivity of Ti$_2$Sn$_3$ was measured with a four-probe technique [6] for a polycrystalline sample of approximate dimensions 1 x 1 x 2 mm$^3$. The sample was contacted with four copper filaments using a silver epoxy cement and cured at 125 °C for 2 min. The mounted sample was placed into a stainless steel lance which was slowly lowered into a helium containing Dewar vessel. The temperature was measured by an adhering calibrated germanium sensor.

As can be seen from Fig. 1, the electrical resistivity of Ti$_2$Sn$_3$ increases with increasing temper-
Fig. 1. Electrical conductivity of a compact polycrystalline sample of Ti$_2$Sn$_3$ as a function of temperature.

Fig. 2. Magnetic susceptibility of the Pauli paramagnet Ti$_2$Sn$_3$.

Fig. 3. $^{119}$Sn Mössbauer spectrum of a sample of Ti$_2$Sn$_3$ as measured at a temperature of 297 K. The isomer shifts are relative to CaSnO$_3$.

...ature as is typical for metallic conductors. A specific resistivity of 22(±5) Ωcm was obtained at room temperature. This value is in between the values of 11 Ωcm for β-tin (at 0 °C) and 42 Ωcm for titanium (at 20 °C) [7], which is somewhat surprising, since usually the electrical resistivities of intermetallic compounds are higher than those of their constituent metals. The electrical resistivity of Ti$_2$Sn$_3$ increases linearly between 70 and 300 K and is represented by the function $\rho = 0.11(±0.02) \text{Ωcm} + T \cdot 0.0735(±0.0001) \text{Ωcm K}^{-1}$, where $T$ is the temperature in K. The temperature coefficient of 0.0735 Ωcm K$^{-1}$ is considerably higher than that of elemental tin, which has a value of 0.0047 Ωcm K$^{-1}$ [7].

The magnetic susceptibility of Ti$_2$Sn$_3$ was determined with a SQUID magnetometer with a magnetic flux density of 3 T in the temperature range between 4 and 300 K as described earlier [8]. The compound shows nearly temperature independent Pauli paramagnetism down to 100 K (Fig. 2). The upturn of the magnetic susceptibility at lower temperatures may be ascribed to paramagnetic impurities or surface states. This is evident from the fit of the experimental susceptibility values to a modified Curie-Weiss law, where a temperature-independent part of the susceptibility $\chi_0 = 3.0 ± 0.2 \times 10^{-9} \text{m}^3\text{mol}^{-1}$ was obtained and the low value of $\chi_{\text{exp}} = 0.15(±0.02) \chi_B$ per formula unit for the magnetic moment. A value of 1.73 $\mu_B$ could be expected for one unpaired spin per formula unit.

A $^{119}$Sn Mössbauer spectrum of Ti$_2$Sn$_3$ was measured at room temperature using a Ca$^{119}$SnO$_3$ source and a palladium foil of 0.05 mm thickness to reduce the tin $\text{K}$ radiation emitted by the source (Fig. 3). Inspite of the fact that there are three different tin sites in Ti$_2$Sn$_3$, the spectrum could be fitted to one (albeit slightly broadened) signal with an isomer shift of 2.15(±0.02) mm s$^{-1}$ relative to CaSnO$_3$, a quadrupole splitting of $A'' = 2.10(±0.02) \text{mm s}^{-1}$, and a line width of $\Gamma = 0.84(±0.09) \text{mm s}^{-1}$, which is nearly identical with the expected natural line width. The sample contained a small amount of an impurity, perhaps β-tin, which was not fitted.

The isomer shift of 2.15 mm s$^{-1}$ is relatively high, which is in agreement with the relatively high tin content of Ti$_2$Sn$_3$ and the many Sn-Sn interactions. It may be compared to the isomer shifts of 2.52 mm s$^{-1}$ for elemental β-tin [9], 2.23 mm s$^{-1}$ for PtSn$_3$ [9], 2.00(±0.08) mm s$^{-1}$ for CeRu$_4$Sn$_6$ [10], 1.96(±0.04) mm s$^{-1}$ and 1.84(±0.02) mm s$^{-1}$ for the tin atoms in β- and α-YbPdSn [11], respectively, and 1.59(±0.01) mm s$^{-1}$ in Hf$_2$Ni$_3$Sn [12].
Structure determination

Single-crystals of Ti2Sn3 were selected from the crushed sample and investigated on a Buerger precession camera. They showed orthorhombic symmetry. For the intensity data collection a crystal of dimensions $20 \times 20 \times 10 \text{ mm}^3$ was used with a four-circle diffractometer (Enraf-Nonius, CAD4), graphite-monochromated MoKα radiation, a scintillation counter with pulse-height discrimination, and $\omega/2\omega$ scans on both ends of each scan. An empirical absorption correction was applied on the basis of psi-scan data. The ratio of the lowest to the highest transmission was 1.28.

The structure was solved and refined by the program package SHELXL-97 [13]. The space group $Cmca$ (No. 64) was suggested and confirmed during the structure refinement. The lattice constants of $a = 595.41(7)$, $b = 1994.8(3)$, $c = 702.1(1)$ pm were refined from the four-circle diffractometer data. These compare well with those of $a = 596.7(4)$, $b = 1995(2)$, $c = 701.3(4)$ pm, $V = 0.8346 \text{ nm}^3$, obtained from Guinier powder data using α-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. We consider the latter to be more accurate, because the data from the diffractometer tend to be affected by systematic errors due to absorption.

Evaluation of the data using the computer software suggested the positions of the tin atoms on the basis of a Patterson synthesis, the titanium positions were located from difference Fourier analyses. The structure was refined by a full-matrix least-squares program using atomic scattering factors as provided by the program. The weighting scheme accounted for the counting statistics and a parameter correcting for isotropic secondary extinction was optimized as a least-squares parameter. To check for deviations from the ideal composition the occupancy parameters were refined together with the thermal parameters during one series of least-squares cycles, with the exception of the Sn3 position to hold the scale factor. No significant deviations from full occupancies were observed (Table 1) and in the final least-squares cycles we resumed to the ideal occupancies.

The $C$ centered cell contains $Z = 8$ formula units. The calculated density is $7.19 \text{ g cm}^{-3}$. The 3098 intensity values measured in one half of the reciprocal sphere up to $2\theta = 80^\circ$ were reduced to 817 by the data averaging (internal residual on $F^2$ values $R_i = 0.069$). A conventional residual of $R = 0.027$ was obtained for 556 structure factors greater than two standard deviations and 30 variable parameters. The weighted residual for all 817 $F^2$ values is 0.061. The highest and lowest residual electron densities are 2.0 and $-2.5 \text{ eÅ}^{-3}$. Finally, the positional parameters were standardized with the program STRUCTURE TIDY [14]. The atomic parameters and interatomic distances are listed in the Tables 1 and 2. Listings of the observed and calculated structure factors and the anisotropic displacement parameters are available*.

Discussion

The structure of Ti2Sn3 has the Pearson symbol oC40 [15] or oS40 [16], respectively. Using the TYPiX compilation [16] we readily found Ti2Sn3 to be isotypic with the ternary compound $V_2GaSn_2$ [17]. The positions of the gallium atoms in $V_2GaSn_2$ correspond to the Sn3 positions of Ti2Sn3. As could be expected, the vanadium positions correspond to the titanium positions. By accident the atom labels also correspond, i.e. the labels Ti1, Ti2, Sn1, Sn2, and Sn3 correspond to the labels V1, V2, Sn1, Sn2, and Ga.

Table I. Atomic parameters of Ti2Sn3. Standard deviations in the place values of the last listed digits are given in parentheses for all crystallographic data throughout the paper. The third column contains occupancy parameters which have been obtained in a separate series of least-squares cycles. In the final cycles the ideal occupancy parameters (100%) were assumed. The last column contains the equivalent isotropic thermal parameters ($\times 10^3 \text{ nm}^2$).

<table>
<thead>
<tr>
<th>Atom</th>
<th>$Cmca$</th>
<th>Occupancy</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{eq}$</th>
</tr>
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<tr>
<td>Ti1</td>
<td>8f</td>
<td>0.994(9)</td>
<td>0</td>
<td>0.08038(8)</td>
<td>0.0482(2)</td>
<td>0.51(2)</td>
</tr>
<tr>
<td>Ti2</td>
<td>8e</td>
<td>0.992(9)</td>
<td>1/4</td>
<td>0.33575(7)</td>
<td>1/4</td>
<td>0.46(2)</td>
</tr>
<tr>
<td>Sn1</td>
<td>8f</td>
<td>0.985(5)</td>
<td>0</td>
<td>0.12139(3)</td>
<td>0.42665(10)</td>
<td>0.60(1)</td>
</tr>
<tr>
<td>Sn2</td>
<td>8f</td>
<td>0.995(5)</td>
<td>0</td>
<td>0.22393(3)</td>
<td>0.07449(10)</td>
<td>0.69(1)</td>
</tr>
<tr>
<td>Sn3</td>
<td>8e</td>
<td>1</td>
<td>1/4</td>
<td>0.47928(3)</td>
<td>1/4</td>
<td>0.60(1)</td>
</tr>
</tbody>
</table>

* They may be obtained from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, by quoting the registry number CSD-411192. E-mail: crysdata@fiz-karlsruhe.de
Table II. Interatomic distances in the structure of Ti₂Sn₃. All distances shorter than 410 pm are listed. The standard deviations are all smaller than 0.2 pm with the exception of the Ti1-Ti1 distance, where it is 0.3 pm.

<table>
<thead>
<tr>
<th></th>
<th>Ti1:</th>
<th>Sn1:</th>
<th>Ti2:</th>
<th>Sn2:</th>
<th>Sn3:</th>
</tr>
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<td>1Sn1</td>
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<td>277.8</td>
<td>277.8</td>
<td>287.0</td>
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<td>283.1</td>
<td></td>
<td>284.6</td>
<td>295.2</td>
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<tr>
<td>2Sn2</td>
<td>287.0</td>
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<tr>
<td>2Sn3</td>
<td>288.1</td>
<td></td>
<td>320.7</td>
<td>320.7</td>
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</tr>
<tr>
<td>2Sn1</td>
<td>309.9</td>
<td></td>
<td>325.5</td>
<td>325.5</td>
<td></td>
</tr>
<tr>
<td>2Ti2</td>
<td>306.6</td>
<td></td>
<td>337.7</td>
<td>332.8</td>
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</tr>
<tr>
<td>1Ti1</td>
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<td></td>
<td>343.5</td>
<td>361.8</td>
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<tr>
<td>Ti2:</td>
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<td>284.6</td>
<td></td>
<td>286.8</td>
<td>309.9</td>
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<td></td>
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<td>297.0</td>
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<td>2Sn3</td>
</tr>
</tbody>
</table>

As is usually the case for intermetallic compounds, all atoms have high coordination numbers (CN). The two different titanium atoms of Ti₂Sn₃ have 11 neighbors of which three (in the coordination polyhedron of the Ti1 atoms) and four (Ti2), respectively, are titanium atoms. The coordination polyhedra of the two titanium atoms in Ti₂Sn₃ (Fig. 4) are similar to the coordination polyhedra of the transition metal (T) atoms in Ti₆Sn₅ [18] and NbSn₂ [1]. In agreement with the larger size of the tin atoms (the “metallic” radii for CN 12 are 146.2 (Ti), 146.8 (Nb), and 162 pm (Sn) [19, 20]), the

Fig. 4. Coordination polyhedra in the structure of Ti₂Sn₃. The Wyckoff positions and the site symmetries are indicated in parentheses.

Fig. 5. Crystal structure of Ti₂Sn₃. The structure may formally be visualized as consisting of atomic layers which are shown in projections along the b axis in the right-hand part of the figure. Single-digit numbers correspond to the atom designations.
The average CN for the $T$ atoms decreases from 11.5 in Ti$_6$Sn$_5$ via 11 in Ti$_2$Sn$_3$ to 10 in NbSn$_2$. Interestingly, the number of the $T$ atoms in the coordination shell of a $T$ atom does not seem to be very important. This can be concluded from the coordination shells of the two different titanium atoms in Ti$_6$Sn$_5$ which have 6Ti + 6Sn (an almost perfect icosahedron) and 4Ti + 7Sn neighbors, respectively. Hence, both $T$–$T$ and $T$–Sn bonding is important.

The three different tin atoms of Ti$_2$Sn$_3$ all have five titanium neighbors with ten (Sn1 and Sn2) or eight additional tin neighbors (Sn3), resulting in CNs of 15 and 13, respectively. The fact that only one unresolved $^{119}$Sn Mössbauer resonance is obtained for the three tin sites shows that the differences of the environments are not very important. Yet, the different CNs are well reflected by the average interatomic distances. They amount to 293.4, 294.3, and 285.7 pm for the Sn–Ti interactions in the coordination polyhedra of the Sn1, Sn2, and Sn3 atoms, and 350.8, 354.1, and 335.0 pm, for the Sn–Sn interactions, respectively. As expected, the CNs of the tin atoms in Ti$_6$Sn$_5$ and NbSn$_2$ are comparably large with CNs of 14, 14, and 15 for the three tin sites in Ti$_6$Sn$_5$ and 15 for both tin sites in NbSn$_2$.

Relatively broad bands can be expected for the electronic structure of Ti$_2$Sn$_3$ from the high coordination numbers of all atoms. The difference in the electronegativity [21] of the titanium (1.4) and tin atoms (1.8) is small, in agreement with the fact that Ti–Ti, Ti–Sn, as well as Sn–Sn bonding is present. Hence, the metallic conductivity of this compound was to be expected. The Pauli paramagnetism shows that the magnetic spins of most electrons are well compensated.

As is frequently the case with intermetallic compounds with their interpenetrating coordination polyhedra and high coordination numbers, the total structure of Ti$_2$Sn$_3$ is difficult to visualize. In Fig. 5 we have somewhat arbitrarily cut the structure in atomic layers. It has to be emphasized that chemical bonding within and between the layers is expected to be of comparable strength. As can be seen, three kinds of layers can be discerned; one kind contains all the titanium and the Sn1 atoms. These are interleaved by layers formed only by Sn2 and Sn3 atoms. The layers of the first kind contain four Ti and two Sn1 atoms per unit mesh. The other layers are less densely packed and contain only four Sn2 or Sn3 atoms each. The whole structure can be visualized by positioning the layers on top of each other using the indicated cell edges for guidance.

Acknowledgements

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