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Thorium tin antimonide, $ThSn_{0.2}Sb_{1.8}$

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$ThSn_{0.2}Sb_{1.8}$ represents the upper limit of Sn substitution into $ThSb_2$. The Sn atoms enter the Sb site in the UAs_2-type or *anti*-Cu_2Sb-type (a binary variant of the PbFCl-type or ZrSiS-type) structure of $ThSb_2$, which is built up of layers of Th-centred monocapped square antiprisms.

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ() = 0.000 Å
Disorder in main residue
R factor = 0.025
wR factor = 0.066
Data-to-parameter ratio = 23.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The structures adopted by thorium distannide $ThSn_2$ ($ZrSi_2$-type, space group *Cmcm*, single-crystal X-ray data) (Cirafici *et al.*, 1983) and diantimonide $ThSb_2$ (UAs_2-type or *anti*-Cu_2Sb-type, space group *P*4/*nmm*, powder X-ray data) (Ferro, 1956; Chechernikov *et al.*, 1970) are closely related, but they are distinguished by the presence of an anionic zigzag chain in the former and its absence in the latter. The question is then raised whether an intermediate structure is possible in a mixed-anion phase $Th(Sn_xSb_{1-x})_2$. The formation of $ThSn_{0.2}Sb_{1.8}$, described here, in the presence of excess Sn, indicates that only phase segregation occurs, and that the maximum solubility of Sn into $ThSb_2$ is 10% [i.e. $Th(Sn_{0.1}Sb_{0.9})_2$].

$ThSn_{0.2}Sb_{1.8}$ adopts the same structure as the parent binary $ThSb_2$, with Sn and Sb atoms disordered over two anion sites (Fig. 1). Square nets of Th, *X*1, and *X*2 atoms are stacked along the *c*-axis direction, with the *X*2 net being twice as dense as the others. Each Th atom is surrounded by nine anions in a monocapped square antiprism (the squares having different sizes). The ternary PbFCl-type or ZrSiS-type structure is a very common one for compounds containing two differently sized anions that order (Tremel & Hoffmann, 1987; Wang & Hughbanks, 1995), but $ThSn_{0.2}Sb_{1.8}$ is perhaps better described as a binary UAs_2-type or *anti*-Cu_2Sb-type variant, given the anion disordering of the similarly sized Sn and Sb atoms. Nevertheless, the limited solid solubility in $Th(Sn_x$-$Sb_{1-x})_2$ suggests that there is a critical electron count beyond which the structure is no longer stable.

Experimental

Crystals of $ThSn_{0.2}Sb_{1.8}$ were obtained in a reaction of a 0.25 g mixture of Th, Hf, and Sb powders in a 3:1:5 molar ratio in the presence of a ten-fold excess of Sn, in an attempt to prepare Th_3HfSb_5. The reactants were placed in an alumina crucible and sealed within an evacuated fused-silica tube. The tube was heated at 1073 K for 5 d and allowed to cool to room temperature after the furnace was turned off. The crystal selected for structure determination was found by EDX analysis to contain 30% Th, 6% Sn, and 64% Sb, corresponding to a composition of $ThSn_{0.2}Sb_{1.8}$. Other crystals examined by EDX analysis had similar compositions.

Crystal data

$ThSn_{0.20}Sb_{1.80}$
M_r = 474.93
Tetragonal, $P4/nmm$
a = 4.3501 (3) Å
c = 9.2129 (6) Å
V = 174.34 (2) Å^3
Z = 2
D_x = 9.047 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 57.52 mm^{-1}
T = 295 (2) K
Prism, gray
0.38 × 0.19 × 0.04 mm

Data collection

Bruker Platform/SMART 1000 CCD diffractometer
φ and ω scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 2001)
T_{min} = 0.005, T_{max} = 0.109
2344 measured reflections
233 independent reflections
233 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 33.1°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.066
S = 1.53
233 reflections
10 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0244P)^2 + 2.4273P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.90 e Å^{-3}
$\Delta\rho_{min}$ = −4.13 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.022 (2)

Table 1
Selected bond lengths (Å).

Th—Sb1^{i}	3.2000 (4)	Th—Sb2^{ii}	3.3348 (4)
Th—Sb1	3.2752 (12)	Sb2—Sb2^{iii}	3.0760 (2)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $-x+1, -y, -z$.

Given their similar scattering factors, Sn and Sb are indistinguishable in the X-ray diffraction experiment. Thus the occupancies of the anion sites were fixed at 0.10 Sn and 0.90 Sb, in accordance with the composition determined by EDX analysis. Compared with an earlier refinement from powder diffraction data on $ThSb_2$ (Ferro, 1956), the present refinement on $ThSn_{0.2}Sb_{1.8}$ shows substantially decreased s.u. in interatomic distances (by two orders of magnitude). The maximum peak and deepest hole are located 0.74 and 1.50 Å, respectively, from Th and Sb1.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXTL*.

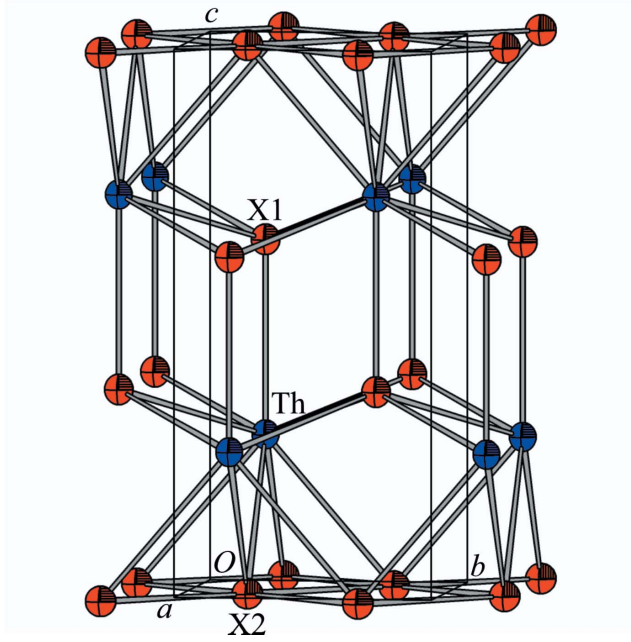

Figure 1
Projection of $ThSn_{0.2}Sb_{1.8}$ along the a axis. Displacement ellipsoids are drawn at the 90% probability level. Sites labeled as $X1$ and $X2$ each contain 0.10 Sn and 0.90 Sb.

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