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Crystal structure of the Tl_4PbSe_3 ternary compound

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Tl_4PbSe_3 was prepared by reaction of the elemental components in quartz ampoules at 850 K. Its crystal structure was solved and refined from X-ray single crystal data. Tl_4PbSe_3 is isotypic with Tl_4SnS_3 and crystallizes in the centrosymmetric space group *P*4/*ncc* (*a* = 8.5346(2) Å, *c* = 12.6871(7) Å), as a distorted derivative of the In_5Bi_3 type of structure.

Intermetallics / Crystal structure / X-ray diffraction

1. Introduction

In the systems Tl_2Y–XY (X = Sn, Pb; Y = S, Se, Te) Tl_4XY_3 ternaries were obtained [1-10] except for the pseudobinary system Tl_2Se–PbSe. The observed Tl_4XY_3 compounds crystallize in isotypic tetragonal crystal structures, however, the crystal structures of Tl_4PbS_3 and Tl_4PbSe_3 were not established. The ternary selenides and tellurides form from the tetragonal (space group *I*4/*mcm*) binary compounds Tl_5Se_3 and Tl_5Te_3. Both binary compounds are known with the Cr_5B_3 type structure. Nordell and Miller [10] propose the valence state Tl^{1+} for the 16*l* atoms and Tl^{2+} for the 4*c* site. This assignment is based on a comparison of bond distances, the coordination environments and Mulliken populations with other thallium compounds. The formula Tl_5Te_3 can thus be rewritten as $Tl_4^{1+}Tl^{2+}Te_3$. The thallium atoms on the 4*c* site can be fully replaced by other elements, resulting in a group of ternary compounds: Tl_4XY_3 (X = Sn, Pb; Y = S, Se, Te).

2. Experimental details

Tl_4PbSe_3 was prepared from proper amounts of high-purity elemental solids (Tl – 99.99 wt. %, Pb – 99.998 wt. %, Se – 99.9998 wt. %) by encapsulating them under vacuum in quartz ampoules. The samples were annealed at maximal synthesis temperature (850 K) for 24 hours and then at 573 K for one week. The obtained substance was investigated by difference thermal analysis (NTR-62) and X-ray powder diffraction (DRON-4, Cu *K*α radiation). Only one endothermic effect was observed at 792 K. The enthalpy and entropy of melting are 64 kJ/mol and 81 J/mol K, respectively. X-ray data of powder showed that Tl_4PbSe_3 can be crystallized in a tetragonal lattice isotypic to $Tl_4SnS_3(Se_3, Te_3)$, Tl_4PbTe_3. A Tl_4PbSe_3 single crystal was obtained by the Bridgman technique. A small irregularly shaped single crystal was selected from an alloy with nominal composition Tl_4PbSe_3. Single crystal data for Tl_4PbSe_3 were collected at room temperature on a four-circle diffractometer Xcalibur Oxford Diffraction with a CCD detector (graphite monochromatized Mo *K*α radiation, ω scan mode). The crystal structure of Tl_4PbSe_3 was successfully solved by direct methods and refined using SHELX-97 package programs [11,12].

3. Results and discussion

The Tl_4PbSe_3 compound crystallizes in the tetragonal system (centrosymmetric space group *P*4/*ncc*, *Z* = 4) and its structure, which is isotypic to that of Tl_4SnS_3, is built-up from sheets with strong Tl-Se interactions. The tin atom exhibits an undistorted octahedral surrounding. Table 1 contains the crystal data information, and details of the data collection and structure refinement. Atomic parameters and anisotropic displacement parameters are listed in

Table 1 Crystallographic data for the Tl_4PbSe_3 single crystal and experimental details of the structure determination.

Empirical formula	Tl_4PbSe_3
Structure type	Tl_4SnS_3
Formula weight (g/mol)	1682.07
Space group	*P4/ncc* (130)
Pearson symbol	*tP*32
Crystal dimensions (mm^3)	0.14×0.13×0.04
Unit cell dimensions:	
a (Å)	8.5346(2)
c (Å)	12.6871(7)
V ($Å^3$)	924.12(6)
Z	4
Calculated density ($D_{calc,}$ g/cm^3)	9.067
Absorption coefficient (μ, mm^{-1})	99.394
Scan mode	ω
Theta range for data collection (deg.)	3.21 ÷ 26.36
F(000)	2032
Range in *h k l*	$-10 \leq h \leq 9$, $-10 \leq k \leq 9$, $-15 \leq l \leq 8$
Total no. reflections	5004
Independent reflections	478 (R_{int}=0.0802)
Reflections with $I > 2\sigma(I)$	376 (R_{sigma}=0.0308)
Weighting scheme	$1/[\sigma(F_o)^2 + (0.0291\times P)^2 + 15.8895\times P]$
Data/parameters	478/22
Goodness-of-fit on F^2	1.280
Final *R* indices [$I > 2\sigma(I)$]	R_1=0.0287, wR_2=0.0624
R indices [all data]	R_1=0.0496, wR_2=0.0818
Extinction coefficient	0.0270(19)
Largest diff. peak and hole (e/$Å^3$)	1.751 and -2.188

Table 2 Atomic coordinates and displacement parameters for the Tl_4PbSe_3 single crystal.

Atom	Ox.	Wyckoff	S.O.F.	*x/a*	*y/b*	*z/c*	U_{eq} ($Å^2$)
Tl1	+1	16*g*	1.00	0.12639(9)	0.57852(9)	0.09574(5)	0.0368(3)
Pb2	+2	4*c*	1.00	1/4	1/4	0.28456(11)	0.0320(4)
Se3	-2	4*c*	1.00	1/4	1/4	0.0223(3)	0.0334(8)
Se4	-2	8*f*	1.00	0.4149(2)	0.5851(2)	1/4	0.356(6)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl1	0.0383(5)	0.0396(5)	0.0326(5)	-0.0045(3)	0.0015(3)	0.0070(3)
Pb2	0.0318(5)	0.0318(5)	0.0323(7)	0	0	0
Se3	0.0318(11)	0.0318(11)	0.0366(19)	0	0	0
Se4	0.0377(9)	0.0377(9)	0.0313(13)	0.0115(12)	-0.0075(8)	-0.0075(8)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2klb^*c^*U_{23}]$.

Table 2. A projection of the structure of Tl_4PbSe_3 is shown in Fig. 1 together with the packing of $[PbSe_6]$ octahedra. The Tl_4PbSe_3 compound may be described as a distorted derivative of the In_5Bi_3 type of structure, which itself should be considered as a subfamily of the Cr_5B_3 type of structure.

The interatomic distances (Table 3) do not show considerable deviation from the sums of radii of the components. The coordination polyhedron of the Tl atom is a non-coplanar triangle Se_3. The coordination number of the Se atoms oscillates from 6 (octahedron Tl_4Sn_2) to 8 (distorted square anti-prism Tl_6Sn_2).

Table 3 Interatomic distances for Tl_4PbSe_3 (in Å).

Tl1	Se4	3.0064	Se3	Pb2	3.0162
	Se3	3.1372		Tl1	3.1372
	Se4	3.1459		Tl1	3.1372
	Se4	3.4923		Tl1	3.1372
	Tl1	3.5146		Tl1	3.1372
	Tl1	3.5230		Pb2	3.3273
	Tl1	3.5230			
	Tl1	3.6082			
Pb2	Se3	3.0162	Se4	Tl1	3.0064
	Se4	3.2175		Tl1	3.0064
	Se4	3.2175		Tl1	3.1459
	Se4	3.2175		Tl1	3.1459
	Se4	3.2175		Pb2	3.2175
	Se3	3.3273		Pb2	3.2175
				Tl1	3.4923
				Tl1	3.4923

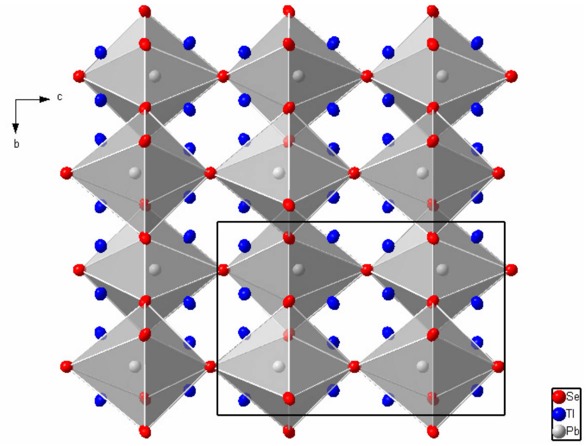

Fig. 1 Projection of the structure of Tl_4PbSe_3 showing the packing of $[PbSe_6]$ octahedra.

4. Conclusions

The new ternary compound of Tl_4PbSe_3 was prepared by solid-state reaction from the elements at 850 K in an evacuated silica tube.

The enthalpy and entropy of melting are 64 kJ/mol and 81 J/mol K, respectively

$Tl_4PbSe_3$was found to crystallize in the Tl_4SnS_3 structure type, space group *P*4/*ncc*.

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