Finite and Infinite Chains of Heavy-Atom Clusters

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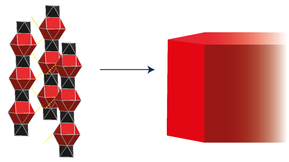
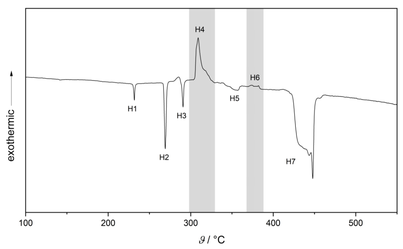
Motivation

Cuboctahedral clusters of type $[M_6X_{12}]$[1], occasionally filed with interstitial atoms[2], *Z*, are known to differ in chemical bonding despite their uniform shape, depending on the number of available valence electrons. In our ongoing search for new topological insulators[3] we decided to substitute three tin(II) cations for the two bismuth(III) counter ions in $Bi_2[PtBi_6I_{12}]_3$[4], as we had previously done with lead(II) cations[5]. This proved more difficult than with the lead(II) compound as the tin-deficient $(Bi_{2x}Sn_{1-3x})[PtBi_6I_{12}]$ also formed. This compound formed finite chain units as had previously been observed in $Bi_2[PtBi_6I_{12}]_3$. An in- depth thermal analysis revealed a synthetic pathway that allowed the targeted synthesis of the desired compound $Sn[PtBi_6I_{12}]$ to be achieved, wherein infinite chains could be observed, thereby giving rise to a quasi-3D material. Further investigations into the electronic structure also revealed an insight into the effect of spin-orbit-coupling (SOC) on the bandgap and its physical properties.

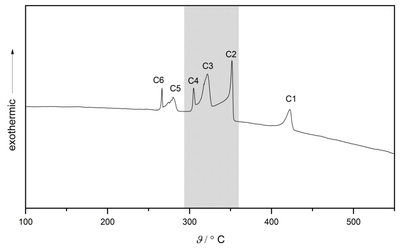


Thermal Analysis

- Stoichiometric amounts of Bi, Pt, Sn and BiI_3 (2:1:1:4) were prepared in an argon-filled glovebox and sealed in a silica ampoule.
- The sample was investigated via differential scanning calorimetry (DSC) by heating the sample to 800°C and cooling back down to room temperature at a rate of 2 K min⁻¹.
- Subsequent ex-situ experiments and values known from literature confirmed the individual phase transitions., wherein $(Bi_{2x}Sn_{1-x})[PtBi_6I_{12}]$ with $x = 0$ denotes the target phase with infinite chains.



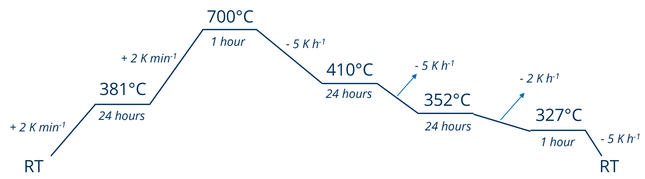
Signal	ϑ_{onset} / °C	ϑ_{peak} / °C	Effect	Allocation
H1	229	232	endothermic	melting of Sn
H2	265	269	endothermic	melting of Bi
H3	279	285/290	exothermic & endothermic	formation & decomposition of Bi_4I_4
H4	303	309–330	exothermic	formation of $(Bi_{2x}Sn_{1-3x})[PtBi_6I_{12}]$ $0 \le x \le 0.3$ and then $x = 0$
H5	337	354	endothermic	partial decomposition of $x \neq 0$
H6	369	374/381	exothermic	formation of $x = 0$
H7	413	443/447	endothermic	decomposition of $x \neq 0$ and then $x = 0$

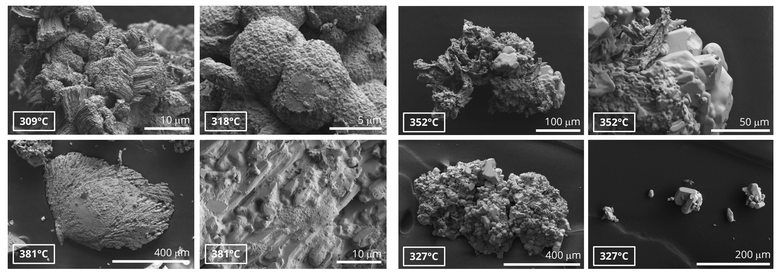


Signal	ϑ_{onset} / °C	ϑ_{peak} / °C	Effect	Allocation
C1	427	422	exothermic	solidification of BiI_3
C2	355	352	exothermic	formation of $(Bi_{2x}Sn_{1-3x})[PtBi_6I_{12}]$ with $0 \le x \le 0.3$
C3	327	321	exothermic	transformation to $x = 0$
C4	307	305	exothermic	partial re-transformation to $x = 0.3$
C5	286	280	exothermic	crystallization of Bi_2Pt (*o*P24)
C6	268	266	exothermic	solidification of Bi

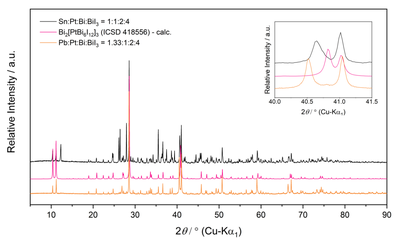
Synthesis & Crystal Structure

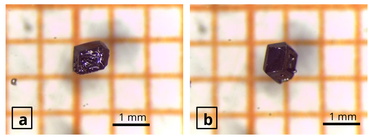
- Stoichiometric amounts of Bi, Pt, Sn and BiI_3 (2:1:1.33:4) were prepared by grinding the reactants together in an argon-filled glovebox and sealing them in a silica ampoule. This was then heated according to the following temperature profile:

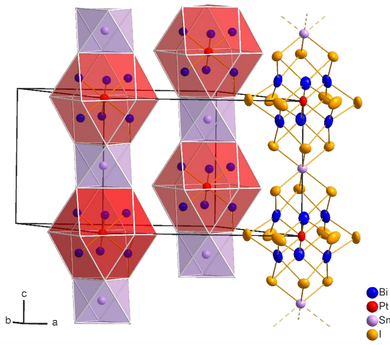




- Powder X-ray diffraction (PXRD) showcased that the change at the cation site between the clusters can be observed, especially between 40° and 41° 2θ(Cu-Kα_1).
- Single crystal X-ray diffraction (SCXRD), as well as energy dispersive X-ray spectroscopy (EDX) confirmed the composition of the crystals obtained as $Sn[PtBi_6I_{12}]$ from the optimized synthesis.
- The crystals obtained had an edge length of up to 1 mm (a and b).
- $(Bi_{2x}Sn_{1-x})[PtBi_6I_{12}]$ with $x = 0$ formed infinite chains and with $x = 0.205$ formed finite chains.



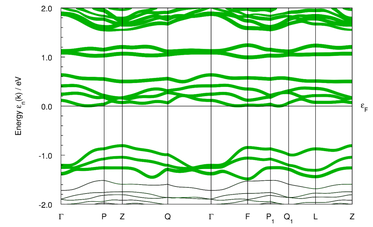


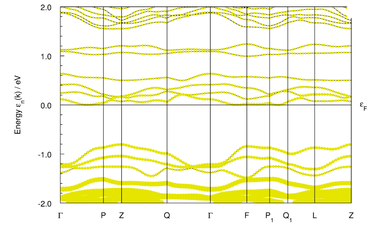


	Sn[PtBi$_6$I$_{12}$]	(Bi$_{2x}$Sn$_{1-3x}$)[PtBi$_6$I$_{12}$], x = 0.205(1)
R(int)	0.047	0.054
Parameters	33	35 (1 restraint)
$R_1[F_o > 4\sigma(F_o)]$	0.019	0.027
R_1[all F_o]	0.024	0.046
wR_2 (same weighting scheme)	0.035	0.022
U_{eq}(Sn) /pm²	246.7(9)	294.9(20)
d(Sn–I) /pm	315.66(3)	311.05(3)
Residual density /e·Å^{-3}	–2.30 to 1.90	–1.75 to 1.89

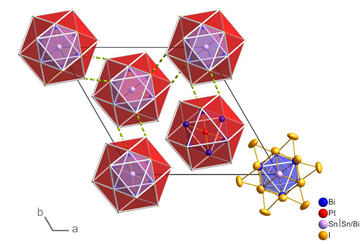
Electronic Properties

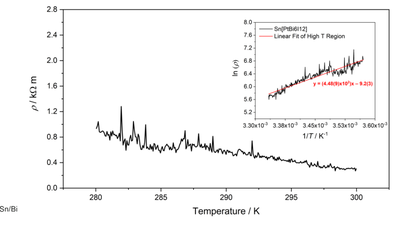
- Fully relativistic density functional theory calculations including an implementation of the bifunctional formalism[6] in combination with Hohenber-Kohn theorems for the exchange energy indicate a bandgap of 0.81 eV between bands that are dominated by contributions of bismuth (left) and iodine (below).





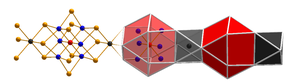
- Despite relatively strong inter cluster bridges of type I^{i-a} (shown below) and the presence of only heavy elements, the Z_2 invariant is (0;000) and therefore $Sn[PtBi_6I_{12}]$ is topologically trivial.
- A four-point measurement allowed a bandgap of 0.81 eV to be derived via an Arrhenius plot of the data, despite high ohmic resistance at lower temperatures.





Outlook

The field of Bi-based cuboctahedral clusters offers many possibilities due to the effect that SOC and the ionic radii of the substituted cations have on the chemical bonding, as well as the variability of this system for potentially topologically materials. Especially if magnetic cations can be substituted in successfully, materials with interesting physical properties may be found.



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Mitglied im Netzwerk von:

DRESDEN concept

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