MS15 Mineralogical and inorganic crystallography

MS15-03

Design of High-Temperature Syntheses for Cluster Compounds $(Bi_{2x}A_{1-3x})[PtBi_6I_{12}]$ with A = Mn, Fe, Sn, Pb

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Abstract

During the search for new topological insulators[1][2], we discovered pseudo one-dimensional compounds $(Bi_{2x}A_{1-3x})[PtBi_6I_{12}]$ with $0 \leq x \leq 1/3$. Reacting Bi with Pt, BiI_3 and a divalent metal A = Mn, Fe, Sn[3], Pb[4] above 300 °C yielded shiny, black, air insensitive crystals of these subiodides. Synthesis of pure samples and growth of single-crystals with x = 0 was achieved through extensive investigations into the synthetic pathways with the help of differential scanning calorimetry and phase analysis of samples annealed at the temperatures of the identified thermal effects.

The isostructural title compounds crystallize in the rhombohedral space group –R . The crystal structures contain cuboctahedral $[PtBi_6I_{12}]^{2-}$ cluster anions. A^{2+} cations in octahedral voids between trigonal faces of two adjacent cuboctahedra concatenate them into infinite linear chains. If x is not equal to 0, the higher charge of the Bi^{3+} cations in the octahedral voids is compensated by vacancies that break the chain into finite strands. In $Bi_2[PtBi_6I_{12}]3$[5], i.e. for x = 1/3, these are cluster triples. The crystals' cube-like morphology originates from six Bi···I inter-cluster bridges per cluster connecting the chains.

The heavy elements show strong spin-orbit coupling, which, if it exceeds the width of the chemical band gap, would be expected to result in a nontrivial topology. In the case of magnetic cations, spin polarization could lead to surface states that all share the same chirality. The full-relativistic electronic band structures and the topological invariants are presented.

References

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Fig.1 The different analytical methods involved.