Poster Presentation

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Unusual crystal structures in the system (SnSe)nBi2Se3

P. Urban[1], C. Fraunhofer[2], F. Fahrnbauer[1], G. Wagner[1], O. Oeckler[1]

[1]Leipzig University, Faculty of Chemistry and Mineralogy, Leipzig, Germany, [2]LMU Munich, Department of Chemistry, Munich, Germany

As intermediates between layered tellurides and chain-like sulfides, selenides exhibit a huge variety of structures and are promising candidates for thermoelectrics. The compounds (SnSe)nBi2Se3 cover the whole range of compound classes. (SnSe)0.5Bi2Se3 exhibits the 21R-GeSb2Te4 structure type (R-3m, a = 4.172Å, c = 38.86 Å, R1(obs) = 0.0246) [1] instead of the 12P stacking expected for this stoichiometry, HRTEM indicates the presence of stacking disorder. This phase coexists with "phase X" [2]. From such samples, e.g. (SnSe)~2Bi2Se3, single crystals of new compounds could be retrieved. Their structures resemble those of minerals of the lillianite series. Slowly cooled samples near the dystectic composition [2] in the phase diagram yielded lillianite-type (SnxBi1-x)5Se6 (x ≈ 2, Cmcm, a = 4.196 Å, b = 13.83 Å, c = 21.19 Å, R1(obs) = 0.0347) mixed with (SnxBi1-x)11Se13 (x ≈ 3, C2/m, a = 13.85 Å, b = 4.205 Å, c = 23.33 Å, β = 98.7°, R1(obs) = 0.0594), which is isotypic to KSn5Bi5Se13 [3]. Further a new phase (SnxBi1-x)8Se9 with heyrovskite-type structure (x ≈ 3, Cmcm, a = 4.193 Å, b = 13.87Å, c = 32.01 Å, R1(obs) = 0.0392) was obtained. These new structures consist of tropochemically twinned slabs that represent distorted cutouts of the rocksalt type. They are interconnected via cations in trigonal prisms. They are members of a homologous series that differ concerning the thickness of the slabs. The cubic high-temperature phase (SnSe)nBi2Se3 (~2.5 < n < 4) yields a metastable pseudocubic disordered rocksalt-type material (Fm-3m, a = 5.936 Å, R1(obs) = 0.0473) upon quenching. For n = 4, it contains homogeneously distributed nanoscale SnSe precipitates. Such a heterostructure might explain the low thermal conductivity (0.83 Wm-1K-1 at room temperature). The rather low electrical conductivity might be further tuned by substitution, which promises an intriguing approach for new nanostructured thermoelectrics easily accessible by partial phase transitions and exsolution effects.

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