Layered Compounds

A Layered Tin Bismuth Selenide with Three Different Building Blocks that Account for an Extremely Large Lattice Parameter of 283 Å

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Abstract: The layered compound Sn_{24}Bi_{20}Se_{27} exhibits an extraordinarily long-periodic 150R stacking sequence. The crystal structure contains three different building blocks, which form upon the addition of Sn to a Bi-rich bismuth selenide. Sn-doped Bi_{2} double (“2”) layers similar to those in elemental bismuth, Sn_{0.3}Bi_{0.7}Se_{q} quintuple (“5”) layers and Sn_{0.2}Bi_{0.8}Se_{(2q)} septuple (“7”) layers are arranged in a 7525757525 | 7525757525 | 7525757525 sequence, which corresponds to a structure with a = 4.1819(4) and c = 282.64(6) Å in space group R3m. The structure of a micro-crystal was determined using microfocused synchrotron radiation and refined as a formally commensurately modulated structure in (3 + 1)D superspace (superspace group R3m(m00|000)), with a trivial basic structure that contains just one atom. The stacking sequence as well as the cation distribution are confirmed by aberration-corrected scanning transmission electron microscopy (STEM) in combination with chemical mapping by X-ray spectroscopy with atomic resolution. Stacking faults are not typical but have been observed occasionally.

This can lead to compounds with large lattice parameters, which can be expected to be beneficial for thermoelectric properties as phonon scattering on the nanometer scale decreases thermal conductivity.[12] Compounds in the binary M/X systems with M = Sb, Bi and X = Se, Te form trigonal layered structures built up from M_{2} double layers (symbolized by “2”)—comparable to those in the element structures of Sb and Bi—and tetradymite-like M_{2}X_{3} quintuple blocks symbolized by “5”. Complex stacking results in large lattice parameters, for example, c = 103 Å for Bi_{3}Te_{3}, which features a 2555 | 2555 | 2555 sequence.[13] So far, no single-crystal X-ray data have been reported for such layered chalcogenides with long-periodic stacking sequences that exhibit lattice parameters larger than these 103 Å. Electron diffraction data and high-resolution transmission electron microscopy (HRTEM) of quenched samples, however, showed the presence of a rhombohedral bismuth telluride Bi_{12.7}Te_{3} with a 138R-type stacking sequence (d \approx 0.11–0.75, c \approx 275 Å) of 55525552552 | 55525552552 | 55525552552.[14] In ternary systems such as Bi_{x}Te_{y}(Bi_{2}Te_{3}), (Tl = Ge, Sn, Pb), the structural chemistry is extended by building blocks with septuple (“7”) TlBi_{2}Te_{3} slabs in addition to quintuple (“5”) Bi_{2}Te_{3} slabs.[15] The structure with the longest periodicity has been found in a 159R-type germanium bismuth telluride that exhibits a 5557575757 | 5557575757 | 5557575757 stacking sequence with c \approx 318 Å as deduced from electron diffraction patterns.[16] However, crystal structure refinements have not been reported for such extreme cases.

With respect to inorganic compounds, unit-cell dimensions of more than 100 Å are very unusual in general. They have been reported for a few binary compounds like the well-known polytypes of SiC,[17] ZnS,[18] CdI_{2},[19] and PbI_{2}.[20] Varying sequences and orientations of the same structural entities result in polytypes with huge lattice parameters of up to 990 Å in SiC.[21] Such crystallographic phenomena have usually been observed only in small domains by electron microscopy; and the structures were assigned by plausibility or trial and error methods in case diffraction data were available. Only very few actual structure refinements based on single-crystal data of structure models with very large lattice parameters do exist. In this respect, even lattice parameters of around 57 Å as recently observed for cesium rare-earth silicates Cs_{2}RESi_{2}O_{13} (RE = Dy, Lu, Y, In) have been reported as being unusually large,[22] although for example, for the mineral turtmannite with c = 204 Å, a full structure refinement has been carried out.[23] Hexaferrites are also prone to form anisotropic structures with large translation periods along the stacking direction of Ba-rich and Fe-rich slabs, which can be arranged with varying sequences that exhibit translation periods of up to 1577 Å for Ba_{2}Zn_{15}Fe_{44}O_{80}.[24] While this extraordinary layer stacking has only been identified by electron microscopy, Rosseinsky et al. fully refined the crystal structure of Ba/Fe/Zn oxide hexaferrite polytypes, for example, Ba_{10}Fe_{12}Zn_{12}O_{30} with c = 488 Å, from single-crystal synchrotron data.[25] Hexaferrites can be identified by the 00l reflections in electron diffraction patterns and described by a unified (3 + 1)D superspace model.[26] Similar descriptions have been reported for pervoskite-like compounds.[27] Lidin et al. developed a similar superspace formal-
ism for the system Bi/Se described above.\textsuperscript{[28]} Such superspace
descriptions are well known from modulated structures, but the
(3 + 1)D description of long-periodic layered structures
does not mean that a somehow simpler structure is modified
by wave-like displacements or occupation modulations. In fact,
the hypothetical basic structure would consist of just one or a
few atoms. Therefore, the superspace formalism focuses, on
the one hand, on a unified description of a series of com-
ponents. On the other hand, it gives access to elegant structure
refinements in cases where the reflections of extremely large
unit cells are too closely spaced to be integrated from area-de-
tector data based on a 3D periodic indexing.

In the pseudobinary system (SnSe)\textsubscript{2},Bi\textsubscript{2}Se\textsubscript{3}, compounds with
very diverse structures are formed.\textsuperscript{[29]} Besides cubic SnBi\textsubscript{2}Se\textsubscript{7},
\((x = 4)\) with defect NaCl-type structure, and layered SnBi\textsubscript{2}Se\textsubscript{7},
\((x = 0.5)\) with defect GeS\textsubscript{2}Te\textsubscript{2}-type structure, at least four com-
ponents \((0.8 \leq x \leq 3)\) with structures derived from lillianite
\((\text{Pb,Bi})\textsubscript{2}S\textsubscript{2}\textsubscript{3}\textsubscript{3}[30]\) have been discovered. Here we report the single-

Crystallographic data

Crystal structure of SnBi\textsubscript{2}Se\textsubscript{5}.

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ters are given in Tables S5 and S6 (note that R values for some “satellite orders” are affected by adjacent very strong reflections of other orders and that the intensity does not decrease with increasing “satellite order” as there is no wave-like modulation).

The long-periodic trigonal structure of Sn₃Bi₂_4Se₂₇ with a 150R stacking sequence is built up from three different kinds of slabs: double and quintuple layers known from the system Bi/Te, an additional septime layers obtained by the introduction of Sn. The 7525757525 sequence corresponds to an extremely large lattice parameter of the 3D-periodic structure, which amounts to 282.6 Å. This is the first layered chalcogenide with three different building blocks, and it features by far the longest translation period found in the system Sn/Bi/Se. Taking into account the slabs, the lattice parameter is given as Sn₃Bi₂_4Se₂₇. Assuming Bi⁰ and Sn⁰ in the double layers and Sn²⁻, Bi¹⁻, and Se⁰ in the quintuple and septime slabs, the overall charge of the compound is neutral within standard deviations. Sn/Bi cation disorder in septime slabs has also nicely been confirmed by X-ray diffraction and Mössbauer spectroscopy of SnBi₂Se₇.[24]

A structure model in 3D derived from the description in superspace (Figure 1) can be only be refined tentatively (Table S7) using a 3D dataset. Since such a 3D dataset corresponds to a (3 + 1)D one with satellite reflections up to the 3⁰ order, the model has too many parameters without a reasonable amount of observed data. Thus, the commensurately modulated description is inevitable although there is no wave-like modulation as known from typical modulated structures. However, the refined atom positions of such a 3D model do not deviate much from those directly derived from the (3 + 1)D superspace model (Table S8). Referring to the superspace description of bismuth selenides by Lidin et al.,[28] the q-vector of 87/50 = 1.74 can be correlated to the stacking sequence and the resulting number of atom layers in the unit cell (Table S9). STEM-HAADF images (Figure 2) confirm the long-periodic stacking sequence of Sn₃Bi₂_4Se₂₇ as derived from the single crystal data. The presence of Sn on all metal atom sites as indicated by the X-ray data corresponds well with aberration-corrected STEM-HAADF and chemical mapping by atomic-resolution EDX. Figure 3 shows a 52S stacking sequence with a double layer in the center (a–d) and a 57 stacking sequence with a van der Waals gap between the two blocks (e–h). Intensities in STEM images and their projection perpendicular [001] further confirm the atom distribution along the sequence (Figure S10). Selected-area electron diffraction (SAED) patterns and Fourier transforms of STEM images along [210] match the diffraction pattern calculated from the 3D model derived from the (3 + 1)D structure refinement (Figure 4) and thus additionally confirm the lattice parameter of 286.6(6) Å. A further SAED pattern along [100] with the corresponding simulation is shown in Figure S11.

Occasionally, stacking faults and different stacking sequences have locally been observed during extensive electron microscopy studies (Figure S12). Yet, the presented structure is by far the predominant stacking sequence.

In conclusion, repeated annealing afforded Sn₃Bi₂_4Se₂₇, a new compound in the system Sn/Bi/Se with an extraordinarily long-periodic 150R stacking sequence 7525757525, resulting in a lattice parameter of c = 282.6(6) Å. The structure is built up from three different types of slabs, which significantly expands the plethora of known structure models for layered chalcogenides. In Sn₃Bi₂_4Se₂₇, the structural features of binary pnictogen-rich chalcogenides, that is, double and quintuple layers and those of ternary tetradymite-like chalcogenides, that is, quintuple and septime layers, are combined and lead to the unusual long-range ordering. It remains, however, an open and very intriguing question, why such structures form and why they are seemingly thermodynamically stable. The large unit cell and the mixed occupancies impede theoretical calculations as alternative models with different arrangements of the same building blocks will show only tiny differences in the strength of van der Waals interactions between the slabs. For example, in the related compound Ge₅Sb₄Te₂, which features much smaller translation periods, activation energies for transitions between ordered and disordered models, which differ by ca. 1 eV in energy, have been calculated to be as low as 0.005 eV.[28] The structure model was obtained by means of X-ray diffraction using a microfocused synchrotron beam and confirmed by

![Figure 2. Fourier-filtered STEM-HAADF image (300 kV) along [210] with an image of the crystal structure of Sn₃Bi₂_4Se₂₇ in the corresponding projection as an overlay; the asymmetric unit (7525757525 sequence, cf. text) is shown on the right in an enlarged image. In the HAADF images, brighter contrast corresponds to Bi/Sn atom columns and darker contrast to Se atom columns. Se atoms are displayed as gray circles and Bi/Sn as white circles.](image-url)
STEM-HAADF measurements with atomic resolution and EDX mappings. The synergism of these methods enables unprecedented accuracy of structure determination of microcrystalline compounds and promotes the discovery of numerous new related layered compounds with mixed site occupancies. These may exhibit intriguing physical properties such as thermoelectricity or non-trivial topological behavior.

Experimental Section

\( \text{Sn}_{2.8(4)}\text{Bi}_{20.2(4)}\text{Se}_{27} \) was formed during the decomposition of a quenched sample of \( \text{SnBi}_{4}\text{Te}_{7} \) upon repeated heating. For TEM measurements, the powdered sample was drop-cast on a copper grid coated with a holey carbon film. This grid was fixed on a glass capillary for single crystal data collection at the European Synchrotron Radiation Facility (ESRF). For STEM measurements, polycrystalline pieces were embedded in epoxy resin and mechanically cut and thinned to a thickness of \( \approx 20 \mu\text{m} \) in the center using a dimple grinder. Electron transparency was achieved by polishing a hole in the center of the disc by Ar-ion milling (Figure S13). Further details are given in the Supporting Information.
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Conflict of interest

The authors declare no conflict of interest.

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[21] Superspace group space group P3m1(001) = a = 4.1819(4), c = 6.56528(5) Å, V = 85.61(1) Å³, Z = 3, pw = 7.7857 g/cm³, R1 (all data) = 0.0451, R1 ([> 2σ]) = 0.0446, wR1 (all) = 0.0969, wR1 ([> 2σ]) = 0.0678, R2 = 0.0310, R2 = 0.054, 12 parameters for 6375 reflections (41 independent). 3D model: space group P3m1, a = 4.1819(4), c = 282.64(6) Å. Further details of the crystal structure investigations are given in the Supporting Information. Deposition number 1949450 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
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