Targeted Synthesis

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Telluride Misfit Layer Compounds: $[(PbTe)_{1.17}]_m(TiTe_2)_n$**

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Abstract: *Telluride misfit layer compounds are reported for the first time. These compounds were synthesized using a novel approach of structurally designing a precursor that would form the desired product upon low-temperature annealing, which allows the synthesis of kinetically stable products that do not appear on the equilibrium phase diagram. Four new compounds of the* $[(PbTe)_{1.17}]_m(TiTe_2)_n$ *family are reported, and their structures were examined by a variety of X-ray diffraction techniques.*

In 1990, DiSalvo highlighted how the concepts and basic principles that form the core of synthetic molecular chemistry had yet to be developed and applied towards the synthesis of new extended solids.[1] These principles include the ability to predict composition (stoichiometry), structure (the geometric arrangement of atoms), and reaction mechanism (an understanding of how reactants evolve into products). The relative lack of predictive power and detailed control over reaction mechanisms in synthetic solid-state chemistry has historically limited the number of ternary and higher-order compounds that have been prepared. Stein[2] and co-workers attributed this to the diffusion-limited, high-temperature reactions that are traditionally used to prepare new solid-state compounds, which yield the most thermodynamically stable products. To overcome slow solid-state diffusion rates, several synthesis approaches start with amorphous precursors and use composition as the experimental tool to direct nucleation; however, the nucleation of the desired products is not controlled.[3–6] Stein and co-workers also suggested that a key factor that enables the rational prediction of the composition and structure of products would be the retention of structural elements of the starting material in the product, which would require significantly reduced reaction temperatures.

Recently, we have shown that it is possible to prepare entire families of structurally related metastable compounds with designed compositions and structures, which are based on an existing thermodynamically stable prototype structure consisting of an intergrowth of two different structural motifs.[7] Vacuum deposition techniques were used to produce a layered precursor of alternating elemental constituents. By tuning the relative thickness of these individual elemental layers, the local composition can be systematically controlled. The local composition in the precursor(s) controls the identity of the structure(s) that nucleate. The presumably random nucleation events result in an unusual rotational disorder between layers, which is known as turbostratic disorder.[8] The nanoarchitecture of the precursor remains intact during the low-temperature self-assembly of products, and the essential structural framework of the products can be predicted based on the bonding motifs that are found in the binary compounds. To explore how general this approach might be, we attempted to use this synthesis approach to prepare a previously unknown family of compounds, $[(PbTe)_{1+\delta}]_m(TiTe_2)_n$, where δ represents the difference of in-plane packing density of the two constituents, which are structurally related to the so-called misfit layer compounds, which are described by the general formula $[(MX)_{1+\delta}]_m(TX_2)_n$. To the best of our knowledge, there are no known tellurides with this structure type, although the constituent binary compounds PbTe and $TiTe_2$ exist with structures that are similar to those found in misfit layer compounds.

Briefly, an initial series of five precursors was made with m:n values targeted at m:n = 1:1, 1:3, 1:5, 5:1, and 3:1 by depositing a Pb–Te bilayer m times and a Ti–Te bilayer n times, assuming that δ was the same as for the known selenide compound.[9] Based on the composition and thickness of these initial samples, the deposition parameters were iteratively adjusted to obtain the desired composition for each layer and to scale the individual layers to the correct thickness. The diffraction patterns of the optimized as-deposited samples suggest that some self-assembly occurred during the deposition process and the time for which the sample was kept at room temperature. An annealing study by X-ray diffraction is shown in Figure 1. The precursor used in this study was designed to form the $[(PbTe)_{1.17}]_3(TiTe_2)_1$ compound upon annealing. After annealing for 30 seconds at 200 °C, all expected 00l diffraction peaks in this scan range were visible and more intense. One minute of annealing at 200 °C slightly increased the diffraction intensities, but increasing the annealing temperature to 300 °C led to decomposition of the desired product. This low decomposition temperature explains why this compound has not been previously observed.

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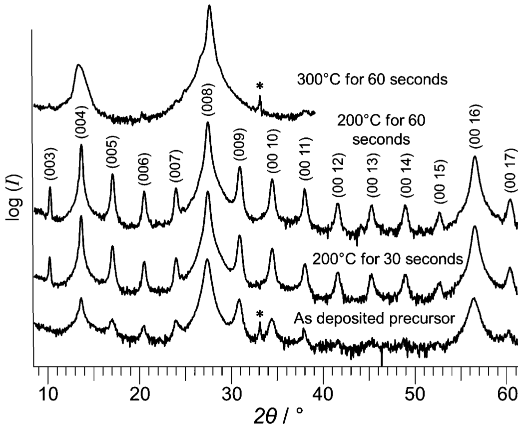

Figure 1. Specular X-ray diffraction patterns collected after annealing of the precursor that was designed to form $[(PbTe)_{1+\delta}]_3(TiTe_2)_1$. The annealing time and the annealing temperature are indicated above each diffraction scan. The 00*l* indices are given above the pattern of the sample that was annealed at 200 °C for 60 seconds. The sharp reflection at approximately 33°, which is marked with an *, is due to the silicon substrate.

Additional optimized precursors targeting ratios of m:n = 1:1, 1:2, 3:1, and 5:1 were annealed for one minute at 200 °C, and the diffraction patterns of the successfully synthesized $[(PbTe)_{1.17}]_m(TiTe_2)_n$ compounds are shown in Figure 2. All of the diffraction patterns contain only the 00*l* diffraction peaks for the targeted compounds, indicating that the samples are highly textured. The *c* axis lattice parameters changed by 6.47 Å for each additional PbTe structural unit that was added to the structure and by 6.73 Å between the 1:1 and the 1:2 compounds, suggesting that this is the thickness of a $TiTe_2$ structural unit in the unit cell. The thicknesses of the corresponding structural units of the binary compounds are 6.454 Å[10] for PbTe and 6.491 Å[11] for $TiTe_2$, which supports this interpretation. The retention of the nanoarchitecture of the precursor as the products self-assemble enables the rational design of precursors for a specific product.

More detailed structural information was obtained through high-resolution X-ray diffraction scans in the *hk*0 direction. Analysis of the *hk*0 reflection series according to the Le Bail approach for the $[(PbTe)_{1+\delta}]_3(TiTe_2)_1$ compound yielded the in-plane lattice parameters of the binary constituents; PbTe displays a tetragonal lattice constant of a = 6.526(2) Å and $TiTe_2$ a hexagonal lattice constant of a = 3.799(4) Å. The reflection positions that correspond to both PbTe and $TiTe_2$ do not change significantly as m and n are varied, whereas the relative scattering intensities change as expected as the m:n ratio is varied. These lattice parameters are close to those reported for bulk PbTe (6.454 Å[10]) and $TiTe_2$ (3.777 Å[11]). From the determined in-plane cell parameters, the misfit of the compound was calculated to be 0.174. This is close to the assumed value of 0.16, which was taken from the selenide compound that was used as the target for this synthesis.

The analysis of the 00*l* reflection series of the compound $[(PbTe)_{1+l}]_3(TiTe_2)_1$ yielded a lattice parameter of c = 26.044(1) Å, and Rietveld refinement gave the positions of the atomic planes along this axis (Figure 3). The Ti–Te atomic plane distance of 1.66(1) Å is in good agreement with that of the bulk material (1.7 Å[11]). In contrast, the atomic plane distances in the PbTe layers deviate strongly from those of the bulk compound. Instead of a constant distance between the

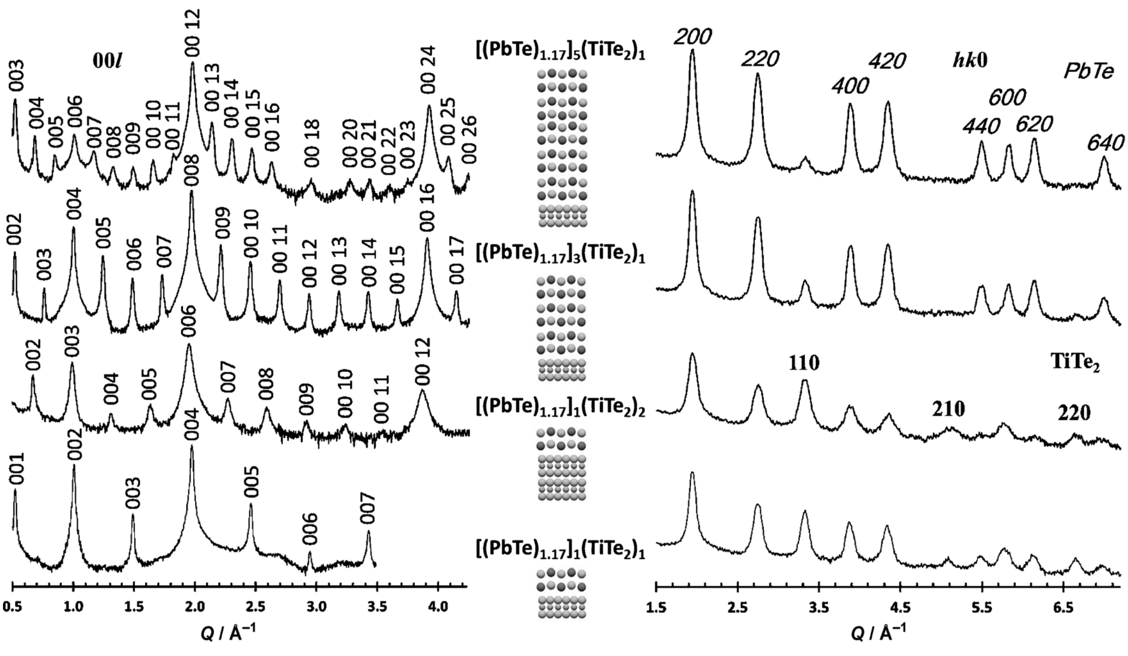

Figure 2. The out-of-plane diffraction patterns (left) and in-plane diffraction patterns (right) that contain the 00*l* and *hk*0 reflections, respectively, for some of the samples that were made in this study. Both sets of diffraction patterns are plotted on a logarithmic scale and offset to separate the patterns. The numbers above the Bragg peaks are the Miller indices of the reflections. Schematic unit cells for each compound are depicted in the center. For simplicity, these schematic representations do not show turbostratic disorder and are therefore only accurate for the *c* direction.

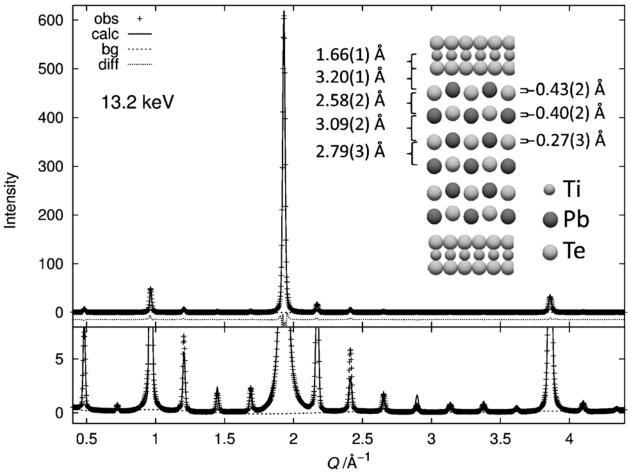

Figure 3. Results of the Rietveld refinement for the (00*l*) reflection series of $[(\mathrm{PbTe})_3]_{1.17}(\mathrm{TiTe}_2)_1$ with observed, calculated, and difference intensities. The arrangement of the atomic planes in the *c* direction and the atomic distances are shown in the inset.

(001) PbTe planes along the *c* axis, the six PbTe layers segregate into three PbTe double layers with a significantly larger distance between the double layers, as reported previously for $[(\mathrm{PbSe})_{1+\delta}]_m(T\mathrm{Se}_2)_n$, where T is either molybdenum or tungsten.[12] Furthermore, the individual PbTe atomic layers distort with Pb and Te moving in alternate directions, so that the outermost Pb atoms approach the neighboring dichalcogenide layers. The distances between the Pb and Te atomic planes of 0.27(3) to 0.43(2) Å are in the range of the puckering distances that have previously been observed for misfit layer compounds.[13–16] This effect is more pronounced close to the TiTe_2 layer and decreases toward the center of the PbTe stack, which is likely due to the finite thickness of the PbTe layers.

The TEM images in Figure 4 confirm the layered nature of the structure. There are six PbTe planes between the single Te–Ti–Te trilayers of TiTe_2. Each PbTe layer appears to have a single crystallographic orientation between the TiTe_2 trilayers, and the crystallographic orientation of the PbTe and TiTe_2 layers changes from layer to layer, confirming the turbostratic disorder that was indicated by our diffraction results.

The diffraction and TEM data attest to our ability to prepare targeted metastable compounds for which the structure of the designed precursor is preserved in the final products. The structure of the PbTe layers was observed to undergo a distortion, presumably as a consequence of competition between surface/interface and volume free-energy contributions to the total free energy of the system. The low decomposition temperature explains why these compounds have not been previously observed. There are many other metastable compounds that probably cannot be accessed by high-temperature synthesis routes, and accessing them and their potential properties requires further developments of the approach presented herein and other low-temperature synthesis approaches to extended solids.

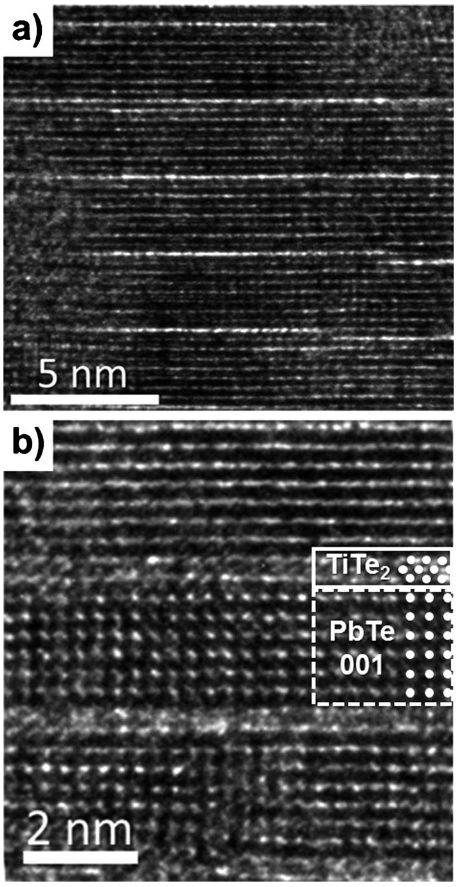

Figure 4. a) Representative TEM image of the $[(\mathrm{PbTe})_{1.17}]_3(\mathrm{TiTe}_2)_1$ compound. b) Higher-magnification image, containing a region with a [100] zone axis of PbTe.

Experimental Section

Samples were synthesized using a custom-built physical vapor deposition system.[9] High-resolution X-ray diffraction using a point detector was measured at the 33-BM-C beamline of the APS. For the *hk*0 reflection series, an incident X-ray energy of 13.1 keV was selected, whereas for the 00*l* reflection series, X-ray energies of 12.5 keV and 13.2 keV (i.e., above and below the Pb L3 edge) were chosen. Refinements according to the Le Bail[17] and Rietveld[18] approaches have been carried out using the GSAS program package.[19,20]

Cross-sections for the high-resolution transmission electron microscopy (HRTEM) investigations were prepared with an FEI Helios Nanolab D600. The in situ lift-out was done using an Omniprobe 200. HRTEM and electron diffraction studies were performed on an FEI aberration-corrected Titan 80–300 equipped with an objective lens C_s corrector.

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