

## The Precipitation of $\text{Sb}_2\text{Te}_3$ via Intermediate Phases in the Thermoelectric Ag-Sb-Te System

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Interfaces can enhance thermoelectric materials properties both through phonon scattering to reduce the thermal conductivity and energy filtering to increase the Seebeck coefficient [1, 2]. As a result, the thermoelectrics community has developed fabrication techniques to obtain nanostructured materials with enhanced properties. One method to nanostructure bulk thermoelectric materials is to use controlled solid-state phase transformations to embed nanoscale second phases. This approach to nanostructuring requires an understanding of the microstructural evolution so that second phases can be optimized for phonon scattering (size, number density, composition, etc.), charge-carrier scattering, or both. This study focuses on phase transformations between rocksalt and tetradymite-structured compounds, which are also relevant in other thermoelectric systems (Pb-Sb-Te) [3].

A rocksalt-structured solid solution was prepared with the nominal composition  $\text{Ag}_{17}\text{Sb}_{30}\text{Te}_{53}$ . Upon annealing at  $500^\circ\text{C}$ , the tetradymite-structured compound,  $\text{Sb}_2\text{Te}_3$ , precipitated from solution. Detailed microscopic investigations of the precipitation reaction showed that the transformation proceeds through a series of compositional changes involving metastable states. First, double-Te stacking faults initially accommodate the Te-rich stoichiometry of the matrix phase. These stacking faults lie on  $\{111\}$  planes and serve as precursors to the formation of the precipitate phases. At intermediate times, the formation of  $\text{Sb}_2\text{Te}_3$  advances by first forming  $\sim 100$ -nm-thick plates of a metastable compound with an intermediate composition,  $(\text{Ag,Sb})_3\text{Te}_4$ . Eventually, the  $(\text{Ag,Sb})_3\text{Te}_4$  phase coarsens, agglomerates, and undergoes a compositional change to produce large,  $\mu\text{m}$ -wide  $\text{Sb}_2\text{Te}_3$  plates consistent with a Widmanstätten pattern. The intermediate seven-layer  $(\text{Ag,Sb})_3\text{Te}_4$  structure and composition was verified with simulations of electron diffraction patterns, high-resolution TEM images, and compositional measurements from EDS data. These intermediate phases are similar to the layered structures in the Bi(Sb)-Te(Se) system that can accommodate a range of metal/chalcogenide ratios by altering the periodicity of the double-Te layers [4, 5].

### References

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- [6] Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US-DOE-NNSA, under Contract DE-AC04-94AL85000. Support was provided in part by the USDOE-OBES-DMS, and the Sandia LDRD Office.

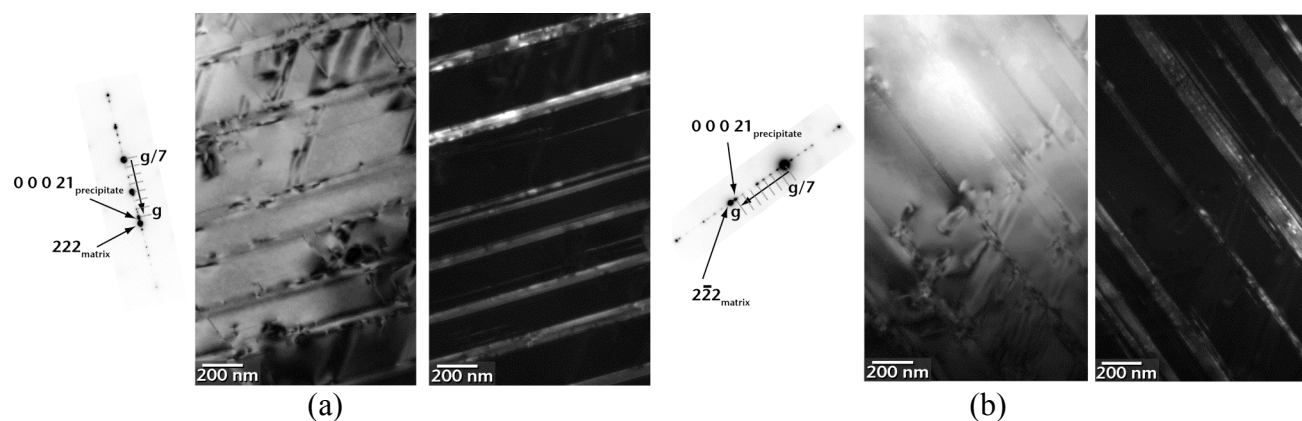


FIG. 1. Bright-field and dark-field image pairs for two orientation variants of the precipitates in the matrix, which are always parallel to the  $\{111\}$  planes in the rocksalt structure. In (a) the  $(222)$  planes of the matrix are parallel with the  $\{0\ 0\ 0\ 21\}$  planes of the precipitate, while in (b), the  $(2\bar{2}\bar{2})$  matrix planes are parallel to  $\{0\ 0\ 0\ 21\}$ . The superlattice reflections that occur at intervals of  $g/7$  are characteristic of a seven-layered structure expected for the metastable  $(\text{Ag,Sb})_3\text{Te}_4$  phase.

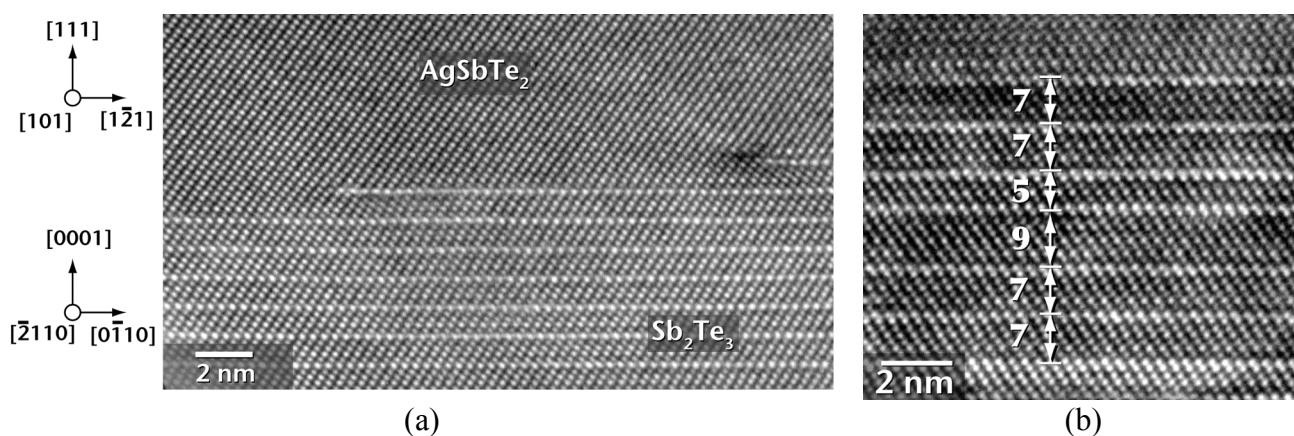


FIG. 2. (a) HRTEM image of the matrix ( $\approx\text{AgSbTe}_2$ )/precipitate ( $\text{Sb}_2\text{Te}_3$ ) interface. The bright fringes in the image are consistent with the spacings between double-Te layers, which occur at regular intervals of 5 close-packed planes in the  $\text{Sb}_2\text{Te}_3$  structure. The metastable intermediate phase is shown in (b), in which double-Te layers can be seen at intervals of 5, 7, and 9 close-packed planes. The variation in double-Te layer separation creates a structure that accommodates compositions between  $\text{AgSbTe}_2$  and  $\text{Sb}_2\text{Te}_3$ .