

Nanostructure-Assisted Phonon Scattering in Lead-Free Thermoelectric Materials: A TEM Investigation of the SnTe System

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We have used HRTEM and STEM EDX to determine the important roles of endotaxial nanostructures in a lead-free thermoelectric (TE) material, SnCd_{0.03}Te, with 2% CdS and 2% ZnS; where maximum *ZT*s of ~1.3 and ~1.1 are achieved at 873 K, respectively. TE materials convert wasted heat into electric energy. The conversion efficiency of TE materials is characterized by a dimensionless figure of merit $ZT = S^2 \sigma T / \kappa$, where *S* is the Seebeck coefficient, σ is the electrical conductivity, *T* is the absolute temperature and $\kappa = \kappa_e + \kappa_l$ is the total thermal conductivity, including both electronic (κ_e) and lattice (κ_l) contributions. The record-high *ZT* values resulting from nanoscale precipitates in p-type SnTe make SnTe-based materials ideal candidate for p-type lead chalcogenides [1-3] for high temperature thermoelectric power generation.

Figure 1 (a) and (b) show TEM images of nanostructured SnCd_{0.03}Te with 2% CdS and 2% ZnS, respectively. High-density nanoscale precipitates are found in both samples, presented by dark contrast in the images. These precipitates have two orthogonal symmetry variants, as schematically depicted in the inset in the upper right corner of Figure 1 (a). The SAD pattern along [001] orientation with an aperture that captures both the matrix and the precipitates shows only one set of Bragg reflection spots, indicating no notable difference in lattice spacing between the matrix and the precipitate because of their small lattice mismatch. We have also employed statistical analysis to obtain the size distribution of SnCd_{0.03}Te-2%CdS and SnCd_{0.03}Te-2%ZnS samples along [001] orientation based on Figure 1(a) and (b), respectively. In Figure 1 (c), the histograms of these two samples show notable difference. We found that for SnCd_{0.03}Te-2%CdS, most nanoscale precipitates range from 3 to 4 nm in size, but for SnCd_{0.03}Te-2%ZnS, the size of the majority precipitate falls within 4.5 to 7 nm range. Comparing ZnS and CdS cases, the larger size of ZnS nanostructures reduces interface area to the matrix, which in relative terms may result in reduced phonon scattering.

Figure 2 shows the HRTEM images and STEM EDX results of SnCd_{0.03}Te with 2% CdS and 2% ZnS, respectively. An HRTEM image in Figure 2 (a) depicts a coherent nanoscale CdS precipitate embedded in the SnCd_{0.03}Te matrix along [001] orientation. No line defects or discontinuities are observed at the matrix/precipitate interface, confirming coherently strained nanoscale endotaxial precipitates. The STEM-EDS results in Figure 2 (b) indicate that the nanoscale precipitates are rich in Cd and S, but the matrix is devoid of sulfur. Similar analysis were applied to SnCd_{0.03}Te with 2% ZnS. Zn and S signals present only in the nanoscale precipitates, but not in the matrix.

High *ZT* values of SnTe system with CdS and ZnS nanoscale precipitates are attributed to the enhanced phonon scattering at the nanoscale precipitates/matrix interfaces, which decreases the lattice conductivity κ_l without degrading σ . The *ZT* = 1.3 in SnCd_{0.03}Te-2%CdS is the record-high value for

the p-type SnTe system. SnTe therefore as an attractive lead-free chalcogenide system is promising for high temperature power generating thermoelectric material. [4]

References:

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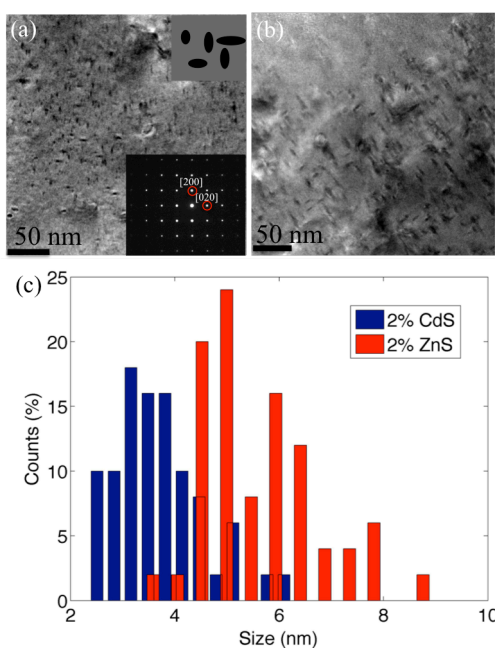


Figure 1 (a) and (b) are low magnification TEM images of SnCd_{0.03}Te-2%CdS and SnCd_{0.03}Te-2%ZnS, respectively. The inset of the upper right corner of (a) is a schematic show of nano precipitates (black) embedding in the matrix (gray). The inset of the lower right corner of (a) is the SAD pattern taken along [001] direction. (c) is the histograms of precipitate size for SnCd_{0.03}Te-2%CdS (blue) and SnCd_{0.03}Te-2%ZnS (red), respectively.

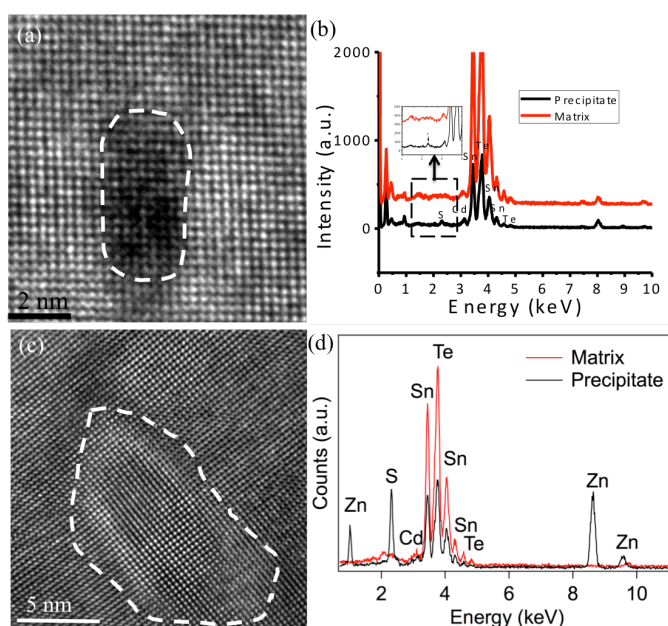


Figure 1 (a) HRTEM image of one nanoscale precipitate in SnCd_{0.03}Te-2%CdS, highlighted by the dashed white line. (b) is STEM EDS of the SnCd_{0.03}Te-2%CdS sample. The spectra were taken at the precipitate and the matrix respectively. The Sn, Te, Cd, and S peaks were detected at the precipitate as shown in the inset. The matrix is with Sn, Te and Cd. (c) HRTEM image of one nano precipitate in SnCd_{0.03}Te-2%ZnS highlighted by the dashed white line. (d) is STEM EDS of the SnCd_{0.03}Te-2%ZnS sample. The spectra were taken at the precipitate and the matrix respectively. The precipitate has Zn and S signal, but the matrix has none.