doi:10.1017/S1431927616007182
Microsc. Microanal. 22 (Suppl 3), 2016

Microstructure Evolution in Nanostructured High-Performance Thermoelectrics: The case of p-type $Pb_{1-x}Na_xTe$-SrTe

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Thermoelectric (TE) materials, which convert waste heat to useful electricity, have had their widespread deployment limited by low energy conversion efficiencies. Recent collaborative work has introduced an innovative *all-scale hierarchical architecturing* approach[1]. In this approach, structural features across multiple length scales are introduced, ranging from point defects to nanoscale precipitates to microscale grain boundaries, which effectively scatter phonons across these disparate length-scales to achieve low thermal conductivity without significantly increasing charge carrier scattering. However, predictive control over synthesis and processing is required to control the microstructural constituents, especially the size, number and distribution of nanoscale precipitates, to achieve the targeted TE performance.

We present ongoing work that is focused on studying the correlation between materials processing and TE performance of lead chalcogenides (PbQ, Q=Te, Se, S), which have been proven to serve as efficient mid-temperature (500-900K) thermoelectrics. Among these, p-type $Pb_{1-x}Na_xTe$-SrTe system achieves the record ZT performance of ~2.2 at 915 K via hierarchical architecturing of microstructure. HREM and STEM-HAADF techniques are the most direct and reliable approach to determine the nature of nanoscale precipitates in order to reveal the processing-performance correlation in this system, and to provide a comprehensive blueprint for all lead chalcogenide systems.

$Pb_{0.98}Na_{0.02}Te$-8%SrTe was synthesized by mixing elemental precursors in the desired stoichiometric ratios, slowly heated to 1150 °C, soaked for 6 hours and then quenched to room temperature to 'lock-in' the solid solution structure. These samples were then annealed at 600 °C for 5, 10, 15, 20, and 25 days, separately, then crushed into fine powders and densified by the spark plasma sintering (SPS) method. The Sr-rich nanoscale precipitates were observed to grow with increasing annealing time, as expected. Figure 1 shows HREM images of $Pb_{0.98}Na_{0.02}Te$-8%SrTe that were (a) not annealed and (b) annealed for 25 days. Nanoscale precipitates are indicated by the dashed circles and arrows. Only one set of Bragg reflections were observed in the SAD patterns, suggesting a coherent interface of the matrix and precipitates due to the small (0.12%) lattice mismatch. Statistical analysis was also employed to obtain size distribution of these two samples based on HREM images taken along [110] directions. For the not annealed sample, most nanoscale precipitates range from 3-5 nm in size and the size distribution is narrow, while the majority of precipitates in the sample annealed for 25 days have sizes ranging from 8 to 16 nm with a wider size distribution relative to the sample without annealing (Figure 1(c)). Significant reduction in average lattice thermal conductivity as well as improvement in ZT were observed with increasing annealing time, indicating that the annealing process contributes to improved TE performance in this system. The presentation will also cover ongoing strain analysis, spatial distribution of dopant, and the determination of activation energy of the coarsening process based on the Lifshitz-Slyozov-Wagner theory.

References:

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[3] This work is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award Number DE-SC0014520.This work made use of the EPIC facilities of the NUANCE Center at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF NNCI-1542205); the MRSEC program (NSF DMR-1121262) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN.

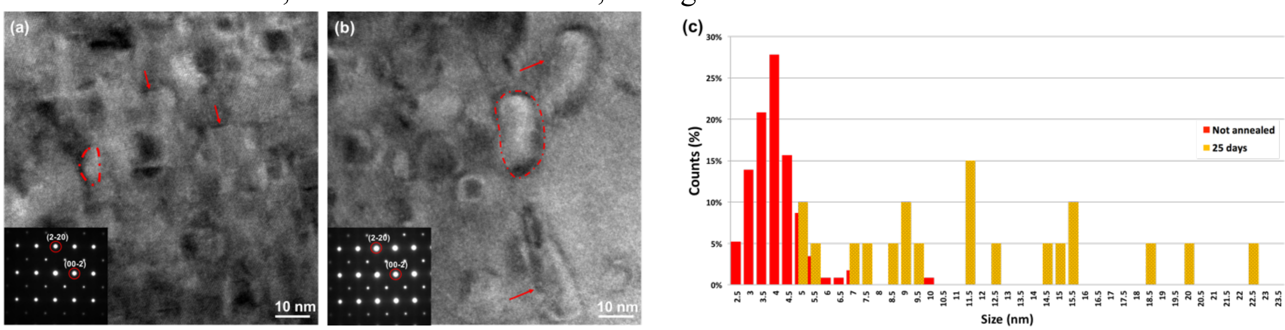

Figure 1 (a) and (b) are HREM images of $Pb_{0.98}Na_{0.02}Te$-8%SrTe annealed for 0 days and 25 days, respectively. Nanoscale precipitates are indicated by arrows and circles. The inset in the lower left corner of (a) and (b) are the SAD patterns taken along the [110] direction. (c) is the histogram of precipitate size for as-received (red) and 25 annealed (yellow) $Pb_{0.98}Na_{0.02}Te$-8%SrTe, respectively.

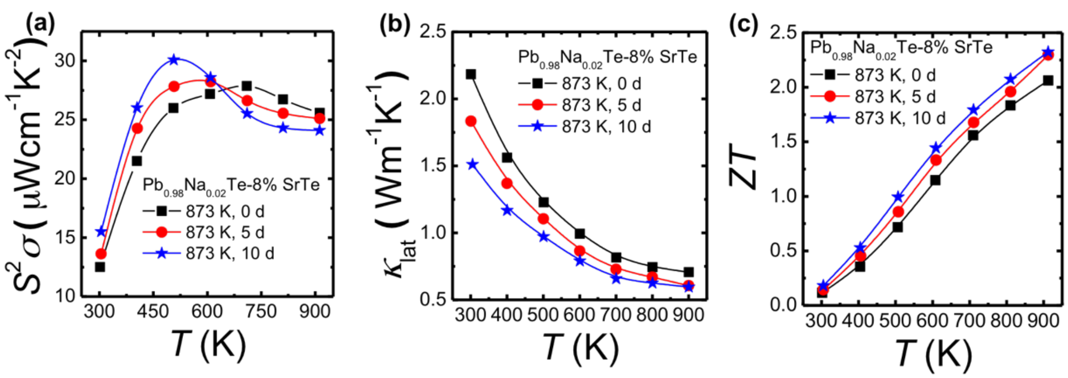

Figure 2 Thermoelectric properties as a function of temperature for as-received $Pb_{0.98}Na_{0.02}Te$-8%SrTe, 5 days annealed, and 10 days annealed: (a) power factor, (b) lattice thermal conductivity and (c) ZT.