doi:10.1017/S1431927610062306
Microsc. Microanal. 16 (Suppl 2), 2010

Thermoelectric and Structural Characterization of $In_xRh_4Sb_{12}$ ($0 < x < 0.2$) Skutterudites

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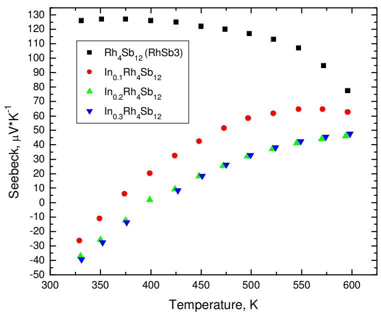
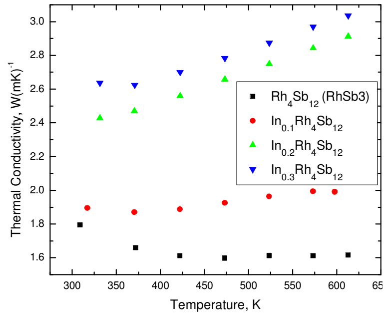
Thermoelectric materials play a unique and import role in the global effort toward energy diversification. Skutterudite-based materials have been extensively studied due to their highly tunable transport properties and show promise as a viable substitute for current thermoelectric (TE) materials. The skutterudite crystal (a naturally occurring mineral) exhibits a unique open crystal structure with two icosahedral void-sites per unit cell. Interstitial filling of the icosahedral void-sites has been a heavily exploited approach that reliably reduces the lattice thermal conductivity and produces a concomitant enhancement of the thermoelectric figure of merit (ZT). Partial indium-void-site filling of cobalt antimonide skutterudites has proven an effective strategy in achieving a ZT namely through a reduction in lattice thermal conductivity. As little work has been published on void-filled rhodium antimonide ($RhSb_3$) skutterudite compounds, a series of In-filled rhodium antimonides skutterudites ($In_xRh_4Sb_{12}$) were synthesized and their thermoelectric properties and microstructure characterized.
Polycrystalline samples of $In_xRh_4Sb_{12}$ ($0 < x < 0.3$) were prepared by solid-state reaction [1]. The crystal structure was characterized by powder X-Ray diffraction. The principle thermoelectric properties; Seebeck coefficient, electrical resistivity and thermal conductivity, were measured from 300–600K. Temperature dependence of the Seebeck coefficients and electrical resistivity of $In_xRh_4Sb_{12}$ are shown in Figs. 1 and 2, respectively. The unfilled $RhSb_3$ structure exhibits typical semiconducting behavior over the temperature range; however the In-filled compounds become increasingly degenerate with greater indium filling at high temperatures. Unexpectedly no reduction of lattice thermal conductivity was observed with indium filling (Fig. 3).
Microstructural studies were performed using SEM (Fig. 4) and TEM/HREM (Fig. 5) analysis in order to further understand the unexpected trend in thermal transport with indium filling as well as to verify the presence and distribution of indium within the sample. All samples exhibit a high degree of porosity with an increasing crystallite size with indium content. The bright contrast in STEM image may indicate a variation in composition, e.g on possible segregation of In. EDS spectra of local areas of $In_{0.2}Rh_4Sb_{12}$ sample (not shown) indicate that there are In-rich areas in the sample. The microstructural analysis reveals that the unusual increase in lattice thermal conductivity with indium filling can be correlated with an increasing grain size which results in fewer acoustic-phonon grain boundary scattering events.

Reference

[1] Tao He et.al., Chem. Mater. 18 (2006), 759-762





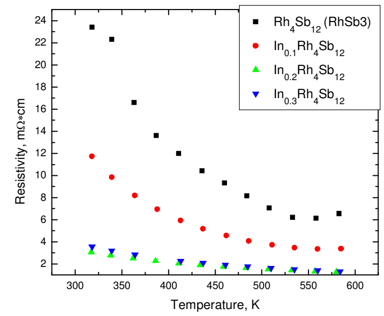


FIG. 1. The temperature dependence of the Seebeck coefficients $In_xRh_4Sb_{12}$ (0 <x< 0.2)

FIG. 2. Electrical resistivity of $In_xRh_4Sb_{12}$ (0 <x< 0.2)

FIG. 3. Thermal Conductivity of $In_xRh_4Sb_{12}$ (0 <x< 0.2)

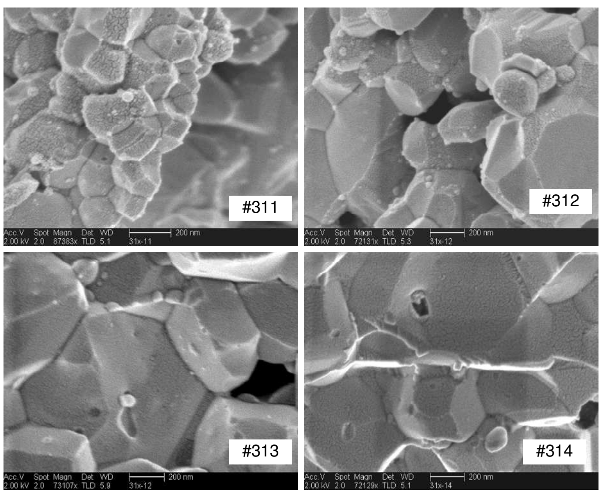
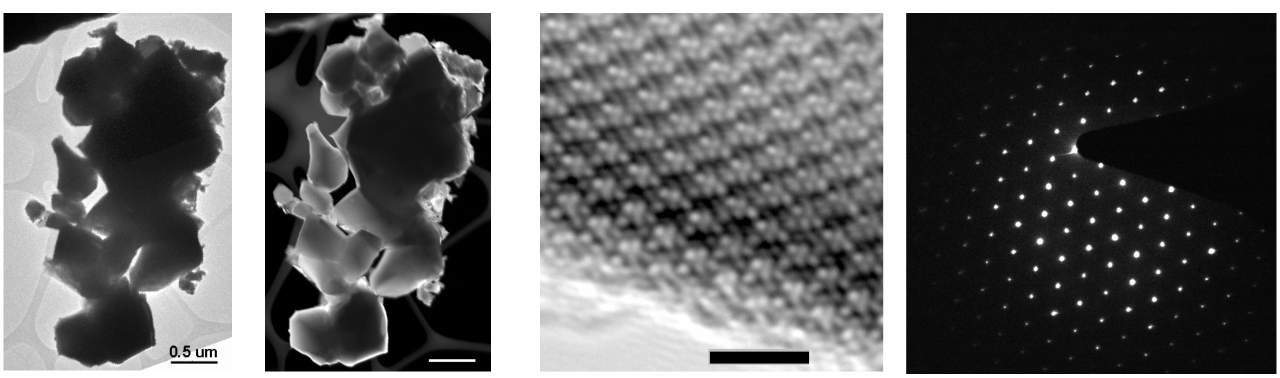


FIG. 4. SEM images of Rh_3Sb_4 (left) and $In_{0.1}Rh_4Sb_{12}$ (right) samples (#311 and #312, respectively)



a. b. c d.

FIG. 5. Low magnification bright –field TEM (a) and STEM (b) images of $In_{0.1}Rh_4Sb_{12}$ sample (#313) that contains many grains. HREM image (c) and corresponding diffraction pattern (d) of one of the crystallites.