Thermoelectric and Structural Characterization of In$_x$Rh$_4$Sb$_{12}$ (0 $<$ x $<$ 0.2) Skutterudites

J. Eilertsen*, S. Rouvimov**, P. Plachinda**, Terry J Hendricks III*, and Mas Subramanian*

*Department of Chemistry, Oregon State University, Corvallis, OR 97331
** Department of Physics, Portland State University, Portland, OR 97207-0751

Thermoelectric materials play a unique and important 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. Intersitial 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$_x$Rh$_4$Sb$_{12}$) were synthesized and their thermoelectric properties and microstructure characterized.

Polycrystalline samples of In$_x$Rh$_4$Sb$_{12}$ (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$_x$Rh$_4$Sb$_{12}$ 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$_4$Sb$_{12}$ 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
FIG. 1. The temperature dependence of the Seebeck coefficients $\text{In}_x\text{Rh}_4\text{Sb}_{12}$ ($0 < x < 0.2$)

FIG. 2. Electrical resistivity of $\text{In}_x\text{Rh}_4\text{Sb}_{12}$ ($0 < x < 0.2$)

FIG. 3. Thermal Conductivity of $\text{In}_x\text{Rh}_4\text{Sb}_{12}$ ($0 < x < 0.2$)

FIG. 4. SEM images of Rh$_3$Sb$_4$ (left) and In$_{0.1}$Rh$_4$Sb$_{12}$ (right) samples (#311 and #312, respectively)

FIG. 5. Low magnification bright–field TEM (a) and STEM (b) images of In$_{0.1}$Rh$_4$Sb$_{12}$ sample (#313) that contains many grains. HREM image (c) and corresponding diffraction pattern (d) of one of the crystallites.