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Effect of Nanostructuring on the Thermoelectric Properties of $Co_{0.97}Pd_{0.03}Sb_3$

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We synthesized n-type $CeO_2/Co_{0.97}Pd_{0.03}Sb_3$ composites with nanometric grain sizes (200 nm to 300 nm) by spark plasma sintering in order to promote phonon scattering at grain boundaries. Powdered samples were initially obtained by ball milling $Co_{0.97}Pd_{0.03}Sb_3$ together with x vol.% (x = 0, 0.5, 1, 2) of CeO_2 nanoparticles. This additive slows down the grain size growth of the skutterudite matrix which occurs during sintering, thereby contributing to phonon scattering. The nanostructured samples display reduced Hall electron concentration compared with that of the reference $Co_{0.97}Pd_{0.03}Sb_3$ because of Fe contamination by the steel balls and vials. However, the electronic transport properties are nearly identical to those of $Co_{0.98}Pd_{0.02}Sb_3$, which allows for comparison with this latter compound. The lattice thermal conductivity is strongly decreased in nano-$Co_{0.97}Pd_{0.03}Sb_{12}$ (−40% at 300 K). This results in an enhanced (+32%) ZT value peaking at 0.65 at 650 K in nano-$Co_{0.97}Pd_{0.03}Sb_{12}$ + 2% CeO_2 when compared with micro-$Co_{0.98}Pd_{0.02}Sb_3$.

Key words: Thermoelectricity, skutterudite, composite, microstructure, figure of merit

INTRODUCTION

Strongly improved performance has been observed in the past few years by nanostructuring bulk thermoelectric materials. Increases of 50% for the figure of merit $ZT = \frac{\alpha^2 T}{\rho\lambda}$ (where α is the Seebeck coefficient, ρ is the resistivity, and λ is the thermal conductivity) were, for instance, observed in compacts of Si-Ge[1] and Bi_2Te_3[2] made of nanograins (~20 nm). In these cases, the lattice thermal conductivity is reduced by scattering of phonons on the very numerous grain boundaries of these very fine microstructures, leading to these improvements. $CoSb_3$ displays thermoelectric properties that make it suitable for nanostructuring. It is a very well-known semiconducting skutterudite[3–6] with a large power factor when properly doped (~3 mW m^{-1} K^{-2} at 300 K). However, $CoSb_3$ displays an overly large lattice thermal conductivity of ~8.5 W m^{-1} K^{-1} at 300 K, which must be reduced in order to reach high ZT values. Several studies deal with nanostructuring by the reduction of the grain size of $CoSb_3$ to nanometric sizes. By solvothermal synthesis followed by, respectively, hot uniaxial pressing (HUP) or spark plasma sintering (SPS), Toprak et al.[7] and Mi et al.[8] both obtained $CoSb_3$ compacts with grain size of 150 nm, leading to lattice thermal conductivity as small as 1.5 W m^{-1} K^{-1} at 300 K. By using a similar synthesis technique, Ji et al.[9] mixed micro and nano $CoSb_3$ grains and reduced the lattice thermal conductivity to 4 W m^{-1} K^{-1}. In previous work,[10] we used ball milling and SPS to synthesize $CoSb_3$ with grain size in the 300 nm range, and the thermal conductivity reduced to 6 W m^{-1} K^{-1}. However, in all these cases, "raw" $CoSb_3$ was synthesized and accurate control of the power factor was not performed, leading in most cases to rather low ZT values.[7,9,10] Only a few studies report ZT improvement

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