Nanoscale Structural Features, Phase Relationships and Thermoelectric Properties of Melt Spun and Spark Plasma Sintered Filled Skutterudites

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The reduction of thermal conductivity remains a main approach to improvement of figure-of-merit of most state-of-the-art thermoelectric materials. In thermoelectric skutterudites it is achieved either by multiple filling of large lattice voids [1] or by developing of nanoscale spatial features in the material's structure. Nanostructuring by means of melt spinning (MS) combined with spark plasma sintering (SPS) has been shown to be prospective for rapid fabrication of fine-grained skutterudites with greatly reduced thermal conductivity and improved thermoelectric performance [2]. However, upon such non-equilibrium high-temperature processing the $CoSb_3$-based skutterudites, in particular, Fe-substituted p-type compounds, are prone to decompose into multiple phases, including lower antimonides and pure Sb, which may further deteriorate their thermoelectric performance. In this research we used X-ray diffractometry (XRD) and scanning electron microscopy (SEM) in order to evaluate the phase and microstructural relationships in the melt-spun filled Co_4Sb_{12} and $Fe_{4-x}Co_xSb_{12}$, as well as their change upon subsequent SPS. Our studies have shown that upon melt-spinning the skutterudites of both types decompose into multi-phase polycrystalline compounds and the nominal major phase is weakly preserved in them after rapid solidification. Surprisingly, larger amounts of skutterudite phase were found in melt-spun filled $Fe_{4-x}Co_xSb_{12}$ p-type materials as compared to their iron-free n-type counterparts. Whole profile fitting of XRDs, including Rietveld refinement and Williamson-Hall plot method, and SEM studies indicated in substantial reduction of grains to sizes below 100 nm for all phases developed upon MS. Furthermore, SPS of both conventional and melt spun skutterudites resulted in even further reduction of crystallites. Upon short annealing and sintering directly in SPS the multi-phase n-type materials were easily restored into single-phase filled $CoSb_3$ with nanoscale features preserved. Abundant secondary phases of $FeSb_2$ and pure Sb remained in the MS-SPS filled $Fe_{4-x}Co_xSb_{12}$ though. Relatively high and improved figure-of-merit ZT_{max} reaching 0.9 at $T \approx 700K$ has been gained in n-type $Yb_xCo_4Sb_{12}$ as compared to a conventional material with same nominal composition. However, the reduction in lattice thermal conductivity was not significant and comparable to that gained via multiple-filling approach. Development of abundant impurity phases in filled $Fe_{4-x}Co_xSb_{12}$ has unfortunately led to drastic drop in their thermoelectric performances, which even further deteriorated upon thermal cycling. In addition to these insights, some effects of filler atoms on phase relationships and nanoscale features in $CoSb_3$ and $Fe_{4-x}Co_xSb_{12}$ skutterudites are considered in the paper.

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