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Thermoelectric Performance of Multiple-Doped $Co_4Sb_{12-x-y-z}Ge_xTe_yS_z$ Skutterudite Compounds

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$CoSb_3$ skutterudites multiply doped with Ge, Te, and S were synthesized by solid-state reaction and spark plasma sintering. x-Ray diffraction studies revealed that Ge, Te, and S entered the lattice of the $CoSb_3$ compounds, and while Te increased the lattice volume, Ge and S decreased it. Compared with the undoped and single-doped $CoSb_3$ compounds, the thermal conductivity and lattice thermal conductivity are significantly suppressed due to greatly increased point defect scattering. It is found that S is more effective for decreasing the lattice thermal conductivity than Te and Ge. The highest thermoelectric figure of merit, ZT, exceeds 1.1 for the $Co_4Sb_{11.25}Ge_{0.05}Te_{0.63}S_{0.07}$ compound at 800 K.

Key words: Skutterudite, doping, thermal conductivity

INTRODUCTION

The efficiency of a thermoelectric material is determined by its dimensionless figure of merit, $ZT = \alpha^2\sigma T/\kappa$, where T is the absolute temperature and α, σ, and κ are the Seebeck coefficient and the electrical and thermal conductivity of the material, respectively. Therefore, good thermoelectric materials have large α, high σ, and low κ.[1]

Skutterudite materials based on $CoSb_3$ are promising thermoelectric materials for applications in refrigeration and power generation.[2,3] Unfortunately, the thermal conductivity of binary skutterudites is relatively high compared with other thermoelectric materials;[3,4] Caillat et al.[5] reported that the room-temperature thermal conductivity of $CoSb_3$ was as high as 11 W m^{-1} K^{-1}. Therefore, much research has been focused on reducing the thermal conductivity of skutterudites. It has been demonstrated that filling the Sb-dodecahedron voids in $CoSb_3$ with atoms, such as rare earth elements, alkalines, and alkaline earth metals, can effectively decrease the thermal conductivity and enhance the ZT values.[6–9] Shi et al.[7] introduced three elements (Ba, La, and Yb) into the nanocages of $CoSb_3$ and found that the electrical and thermal transport can be optimized in a relatively independent way, leading to a continual increase of the ZT values. Formation of solid solutions between isostructural compounds is another effective approach for reducing the thermal conductivity by increasing point defect scattering.[10] So far, many studies have reported on synthesis and characterization of $CoSb_3$-based skutterudites substituted at Sb-site with semimetal, such as Te, Se, Ge, etc. Among all the single-substituted skutterudites reported to date, $Co_4Sb_{12-x}Te_x$ compounds show the highest thermoelectric performance due to the extremely enhanced power factors ($\alpha^2\sigma$) and the reduced thermal conductivity.[11,12] In Ge-Te or Sn-Te codoping, Ge and Sn elements, with fewer valence electrons than the host element, can extend the solubility of Te in $Co_4Sb_{12-x}Te_x$ compounds as charge-compensating elements and decrease the thermal conductivity more significantly than the electrical conductivity.[13–15] In our previous study,[16] we found that S could also enter the lattice of $CoSb_3$ when codoped with element Te, and that the thermal conductivity was reduced significantly and a maximum ZT ~1.08 was also achieved for the $Co_4Sb_{11.3}Te_{0.6}S_{0.1}$ compound.

In this work, we investigate the effects of multiple doping on the thermoelectric properties of

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