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Effects of Ge Dopant on Thermoelectric Properties of Barium and Indium Double-Filled *p*-Type Skutterudites

JIAN YU,[1] WEN-YU ZHAO,[1,2] BING LEI,[1] DING-GUO TANG,[1] and QING-JIE ZHANG[1,3]

1.—State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China. 2.—e-mail: wyzhao@whut.edu.cn. 3.—e-mail: zhangqj@whut.edu.cn

A series of Ge-doped and (Ba,In) double-filled *p*-type skutterudite materials with nominal composition $Ba_{0.3}In_{0.2}FeCo_3Sb_{12-x}Ge_x$ (x = 0 to 0.4, Δx = 0.1) have been prepared by melting, quenching, annealing, and spark plasma sintering methods. The effects of Ge dopant on the phase composition, microstructure, and thermoelectric properties of these materials were investigated in this work. A single-phase skutterudite material was obtained in the samples with $0 < x \leq 0.2$, and trace Fe_3Ge_2 was detected in the samples with $x \geq 0.3$. The electrical conductivity increased and Seebeck coefficient decreased with increasing x in the range of 0 to 0.2, while the inverse behaviors of electrical conductivity and Seebeck coefficient were observed in the samples with $x \geq 0.3$. The variations of electrical conductivity and Seebeck coefficient are attributed to the significant increase in the carrier concentration in the x range of 0 to 0.2 and the intensive impact of Fe_3Ge_2 when $x \geq 0.3$. The lattice thermal conductivity of all the Ge-doped samples was considerably reduced as compared with the undoped $Ba_{0.3}In_{0.2}FeCo_3Sb_{12}$ sample, and the lowest value of lattice thermal conductivity of the $Ba_{0.3}In_{0.2}FeCo_3Sb_{11.8}Ge_{0.2}$ sample reached 1.0 W m^{-1} K^{-1} at 700 K. The highest ZT value of 0.54 was obtained at 800 K for the $Ba_{0.3}In_{0.2}FeCo_3Sb_{11.7}Ge_{0.3}$ sample, increased by 10% as compared with that of $Ba_{0.3}In_{0.2}FeCo_3Sb_{12}$.

Key words: Filled skutterudite, *p*-type conduction, Ge dopant, thermoelectric properties

INTRODUCTION

Thermoelectricity has attracted much attention in the field of power generation and waste heat recovery.[1] The conversion efficiency of thermoelectric (TE) material is governed by the dimensionless figure of merit $ZT = \alpha^2\sigma T/\kappa$, where T is the absolute temperature, σ is the electrical conductivity, α is the Seebeck coefficient, and κ is the thermal conductivity ($\kappa = \kappa_C + \kappa_L$, where κ_C is the electronic contribution and κ_L is the lattice contribution). A good TE material should possess high power factor ($\alpha^2\sigma$) and low thermal conductivity.[2] In the past decade, skutterudite materials have received extensive interest due to their promising TE properties in the intermediate temperature range.[3,4]

Binary skutterudites crystallize in space group *Im-3* with chemical formula AB_3 (A = Co, Rh, or Ir; B = P, As, or Sb) and have two interstitial voids at the 2a positions of the unit cell. $CoSb_3$, one of the skutterudite family, has been extensively researched due to its narrow bandgap, high carrier mobility,[5] and cheap and environmentally friendly raw materials. However, the κ_L of binary $CoSb_3$ is almost ten times higher than that of other state-of-the-art TE materials, such as Bi_2Te_3, leading to a low ZT and thus poor conversion efficiency for TE devices based on skutterudites.[5–7] Many attempts have been made to decrease the κ_L, such as filling the interstitial voids to introduce resonant phonon scattering, and doping at the Co-site or Sb-site to create alloy scattering.

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