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Thermoelectric Properties of Multifilled Skutterudites with La as the Main Filler

HUIYUAN GENG,[1,2,3] TAKAHIRO OCHI,[2] SHOGO SUZUKI,[2] MASAAKI KIKUCHI,[2] SATORU ITO,[2] and JUNQING GUO[2]

1.—State Key Laboratory of Advanced Welding & Joining, Harbin Institute of Technology, Harbin 150001, China. 2.—Materials Research Laboratory, R&D Division Furukawa Co., Ltd., 1-25-13 Kannondai, Tsukuba, Ibaraki 305-0856, Japan. 3.—e-mail: genghuiyuan@hit.edu.cn

Bulk multifilled *n*- and *p*-type skutterudites with La as the main filler were fabricated using the spark plasma sintering (SPS) method. The thermoelectric properties and thermal stability of these skutterudites were investigated. It was found that the interactions among the filling atoms also play a vital role in reducing the lattice thermal conductivity of the multifilled skutterudites. $ZT = 0.76$ for *p*-type $La_{0.8}Ba_{0.01}Ga_{0.1}Ti_{0.1}Fe_3CoSb_{12}$ and $ZT = 1.0$ for *n*-type $La_{0.3}Ca_{0.1}Al_{0.1}Ga_{0.1}In_{0.2}Co_{3.75}Fe_{0.25}Sb_{12}$ skutterudites have been achieved. Furthermore, the differential scanning calorimetry (DSC) results show that there is no skutterudite phase decomposition till 750°C for the $La_{0.8}Ba_{0.01}Ga_{0.1}Ti_{0.1}Fe_3CoSb_{12}$ sample. The thermal stability of the $La_{0.8}Ba_{0.01}Ga_{0.1}Ti_{0.1}Fe_3CoSb_{12}$ skutterudite is greatly improved. Using the developed multifilled skutterudites, the fabricated module with size of 50 mm × 50 mm × 7.6 mm possesses maximum output power of 32 W under the condition of hot/cold sides = 600°C/50°C.

Key words: Skutterudite, multiple filling, thermoelectric material, thermoelectric module

INTRODUCTION

Thermoelectric materials have attracted much attention in recent years because of their ability to directly convert heat into electricity. Among the identified thermoelectric materials, filled skutterudites[1–4] are considered as some of the most promising materials for commercial intermediate-temperature power generation because of their outstanding thermoelectric and mechanical properties.

The efficiency of thermoelectric materials is governed by the dimensionless figure of merit, ZT. ZT is defined as $ZT = \alpha^2 T/\rho\kappa$, where α, ρ, κ, and T indicate the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively. To further improve the ZT of filled skutterudites, double,[5–8] triple,[9–11] and multiple[12] filling approaches have been proposed based on the "rattling in the oversized cage" concept. One of the main ideas of multiple filling is to use different atoms to serve as "rattlers" to scatter phonons with different frequencies. Since the Yb filling atom possesses low vibration frequency,[5,13] Yb is believed to be effective in scattering low-frequency phonons, which dominate the thermal conduction in crystals. Despite its high price, Yb is usually used as one of the main fillers in multifilled skutterudites, such as $Ba_uLa_vYb_wCo_4Sb_{12}$,[9] $Ce_{0.1}In_xYb_yCo_4Sb_{12}$,[10] $(Sr,Ba,Yb)_yCo_4Sb_{12}$,[11] etc. In our previous work,[12] $ZT = 1.0$ for *n*-type $Yb_{0.3}Ca_{0.1}Al_{0.1}Ga_{0.1}In_{0.1}Co_{3.75}Fe_{0.25}Sb_{12}$ skutterudite was achieved. In addition, $ZT = 0.75$ for *p*-type multifilled $La_{0.7}Ba_{0.01}Ga_{0.1}Ti_{0.1}Fe_3CoSb_{12}$ skutterudite has also been realized. Based on the developed multifilled skutterudites, the fabricated module with size of 50 mm × 50 mm × 7.6 mm has generation performance with power output of 32 W and conversion efficiency of 8% under the condition of hot/cold sides = 600°C/50°C.

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