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Creation of Yb_2O_3 Nanoprecipitates Through an Oxidation Process in Bulk Yb-Filled Skutterudites

JUAN DING,[1,2] HUI GU,[1] PENGFEI QIU,[3] XIHONG CHEN,[3] ZHEN XIONG,[3] QIANG ZHENG,[1] XUN SHI,[3] and LIDONG CHEN[3,4]

1.—State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China. 2.—University of Chinese Academy of Sciences, Beijing 100049, China. 3.—CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, China. 4.—e-mail: cld@mail.sic.ac.cn

An approach to introduce *in situ* nanoprecipitates into bulk filled skutterudites is developed through controlling the oxidation process of the fillers. $Yb_{0.3}Co_4Sb_{12}$ is selected as the base material, and prolonged oxidation at high temperatures in sealed quartz tubes under a low pressure of oxygen leads to the formation of Yb_2O_3 nanoinclusions. Transmission electron microscopy shows that the Yb_2O_3 nanoprecipitates are created within the skutterudite crystal grains through an internal oxidation mechanism. With increased time of oxidation, the amount of Yb_2O_3 nanoprecipitates is increased and the nanoprecipitates are more uniformly distributed in the matrix. For the samples oxidized for 10 days, the lattice thermal conductivity is reduced by about 19% at 850 K compared with the $Yb_{0.3}Co_4Sb_{12}$ matrix. The reduction in the lattice thermal conductivity originates from additional phonon scattering by the Yb_2O_3 nanoprecipitates, leading to a maximum ZT of 1.3.

Key words: Thermoelectric, filled skutterudite, nanocomposites

INTRODUCTION

Co_4Sb_{12}-based filled skutterudites have received great attention as promising thermoelectric materials due to their low lattice thermal conductivity (κ_L) and excellent electrical transport properties.[1–6] There are two large voids in the unit cell of skutterudites, and they can be filled by foreign species.[1,2] The filler atoms are loosely bonded with the neighboring Sb atoms, and their vibrations strongly scatter low-frequency thermal phonons and thereby greatly suppress κ_L, which, in turn, leads to an improvement in the dimensionless thermoelectric figure of merit (ZT).[1,2] Currently, rare-earth,[7–12] alkaline-earth,[13,14] and alkaline-metal[15] filled skutterudites have been systematically studied, and ZT values above unity have been reported, showing great potential in applications as mid- to high-temperature thermoelectric generators. Among these filled skutterudites, $Yb_xCo_4Sb_{12}$ is regarded as one of the best *n*-type single-filled skutterudites with excellent thermoelectric performance. In YbxCo$_4$Sb$_{12}$, the highest filling fraction x is estimated to be about 0.2,[7,16] within the range 0.15 to 0.35 of x values for fillers with charge state +2.[3–5] It is well known that nanoparticles or nanophases inside the crystal grains are believed to greatly reduce the lattice thermal conductivity and thereby further enhance the thermoelectric performance by introducing additional phonon defect scattering.[17–25] Zhao et al.[21] successfully introduced Yb_2O_3 nanoparticles into $Yb_xCo_4Sb_{12}$ using an *in situ* reaction method to show a significantly improved thermoelectric performance. This work suggests a new possibility of obtaining high ZT values in skutterudites by a cooperative effect of the fillers in the skutterudite voids and finely dispersed nanoinclusions in grains or at grain boundaries. In reality, most of the Yb oxide particles are aggregated at grain boundaries and only a very small amount of oxide particles are observed inside the grains of

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