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Enhanced thermoelectric figure of merit of $Co_4Sb_{11.5}Te_{0.5}$ via a two-pronged strategy combining grain refinement and nano-inclusions

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ABSTRACT

In this study, a strategy combining grain refinement and nano-inclusion is presented to enhance the thermoelectric figure of merit (*ZT*) of $Co_4Sb_{11.5}Te_{0.5}$. Homogeneously dispersed nano-TiN particles are introduced into the different grain-size skutterudite compounds $Co_4Sb_{11.5}Te_{0.5}$ through ball milling and spark plasma sintering. The phase purity, microstructures, and thermoelectric properties of all the samples are characterized. The results prove that the sample consisted of the finest grain (~220 nm) $Co_4Sb_{11.5}Te_{0.5}$ and nano-TiN demonstrates a much lower thermal conductivity of 2.34 $Wm^{-1} K^{-1}$ at room temperature and a highest *ZT* value of 1.07 at 800 K. Furthermore, annealing this sample at 500 °C for 50 h shows minor changes in structure and ZT value, indicating an excellent thermal stability.

1. Introduction

$CoSb_3$-based skutterudite compounds have been considered as promising medium temperature thermoelectric (TE) materials because of their high mobility, high atomic masses, low electrical resistivity and good Seebeck coefficients [1]. The binary $CoSb_3$ skutterudite, however, possesses a relative high thermal conductivity, which limits its thermoelectric performance governed by the so called dimensionless figure of merit (*ZT*) [2]. The *ZT* is given as $ZT = \frac{\alpha^2\sigma}{\kappa}T$, where α, σ, κ and T refer to the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. So far, Many efforts, such as filling [3,4], doping [5,6] and nanostructuring [7,8], have been made to suppress the thermal conductivity and improve the TE performance.

In previous studies, it has been found that Te substituting for Sb can effectively improve the *ZT* value of $CoSb_3$ skutterudite compounds. A. Moure [9] carried out an innovative synthesis of Skutterudite/oxide nanocomposites in air by high energy milling and sintering by Spark Plasma Sintering, which leads to *ZT* ca. 1 for Te-doped $CoSb_3$. Liu [10] has reported that the $CoSb_{2.85}Te_{0.15}$, fabricated by mechanical alloying combined with spark plasma sintering, has the highest ZT = 0.93 at 820 K. Deng [11] has reported that a maximum ZT value of 0.67 at 710 K was obtained for $Co_4Sb_{11.5}Te_{0.5}$ prepared by the high pressure and high temperature method. Nevertheless, for practice use, it is indispensable to pursue a higher ZT value of Te-doped $CoSb_3$ compounds.

In this work, we present a strategy combining grain refinement and nano-inclusions to further enhance the ZT of the Te-doped skutterudite $Co_4Sb_{11.5}Te_{0.5}$. Nano-TiN particles have been introduced into the different grain-size $Co_4Sb_{11.5}Te_{0.5}$ through ball milling (BM) and spark plasma sintering (SPS). In addition, an annealing treatment was carried out to investigate the thermal stability of some samples.

2. Experimental

The $Co_4Sb_{11.5}Te_{0.5}$ ingots were prepared as previously reported [12]. The obtained ingots were ground into powders in an agate mortar. The nano-TiN powders (20 nm, 1 vol%) were firstly dispersed in alcohol by ultrasonic dispersion, and then mixed with the as-received $Co_4Sb_{11.5}Te_{0.5}$ powders by different BM process (300 rpm for 50 h and 400 rpm for 20 min). For comparison, the $Co_4Sb_{11.5}Te_{0.5}$ powders without nano-TiN powders were also obtained by the same process. The milled powders were consolidated by SPS at 873 K for 7 min under 40 MPa. For convenience, the sintered bulks were named as S50H, ST50H, S20M and ST20M, where S denotes skutterudite $Co_4Sb_{11.5}Te_{0.5}$, T denotes TiN, 50H and 20 M denote the milling time is 50 h and 20 min, respectively. The S50H and ST50H were annealed at 773 K for 50 h in vacuum.

The constituent phases and microstructures were characterized by X-ray diffraction (XRD, Bruker: D8 Advance, Cu Kα), energy

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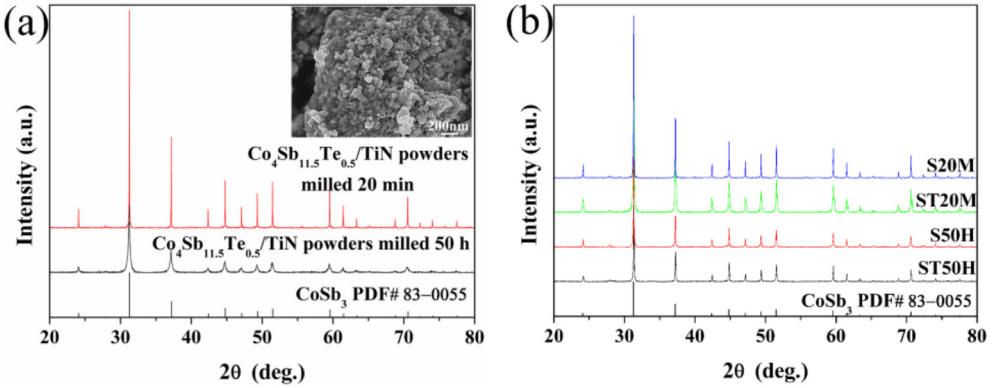

Fig. 1. (a) XRD patterns of the $Co_4Sb_{11.5}Te_{0.5}$/TiN powders milled different time, the FESEM image of the $Co_4Sb_{11.5}Te_{0.5}$/TiN powders milled 50 h (inset), (b) XRD patterns of the sintered bulks.

Table 1
The density and porosity of the samples.

Samples	S20M	ST20M	S50H	ST50H
d (g cm^{-3})	7.55	7.46	6.75	6.54
Porosity (%)	1.2	2.4	11.7	14.4
Average grain size (nm)	~220	~270	~1300	~1300

dispersive x-ray spectroscopy (EDS) and field-emission scanning electron microscopy (FESEM; Zeiss Ultra plus). The electrical conductivity and Seebeck coefficient were measured synchronously with the standard four-probe method (Sinkuriko: ZEM-3). The thermal conductivity was calculated from the measured thermal diffusivity (λ), heat capacity (Cp), and density (d) by the relationship of $\kappa = Cp\lambda d$. Cp and λ were measured by the differential

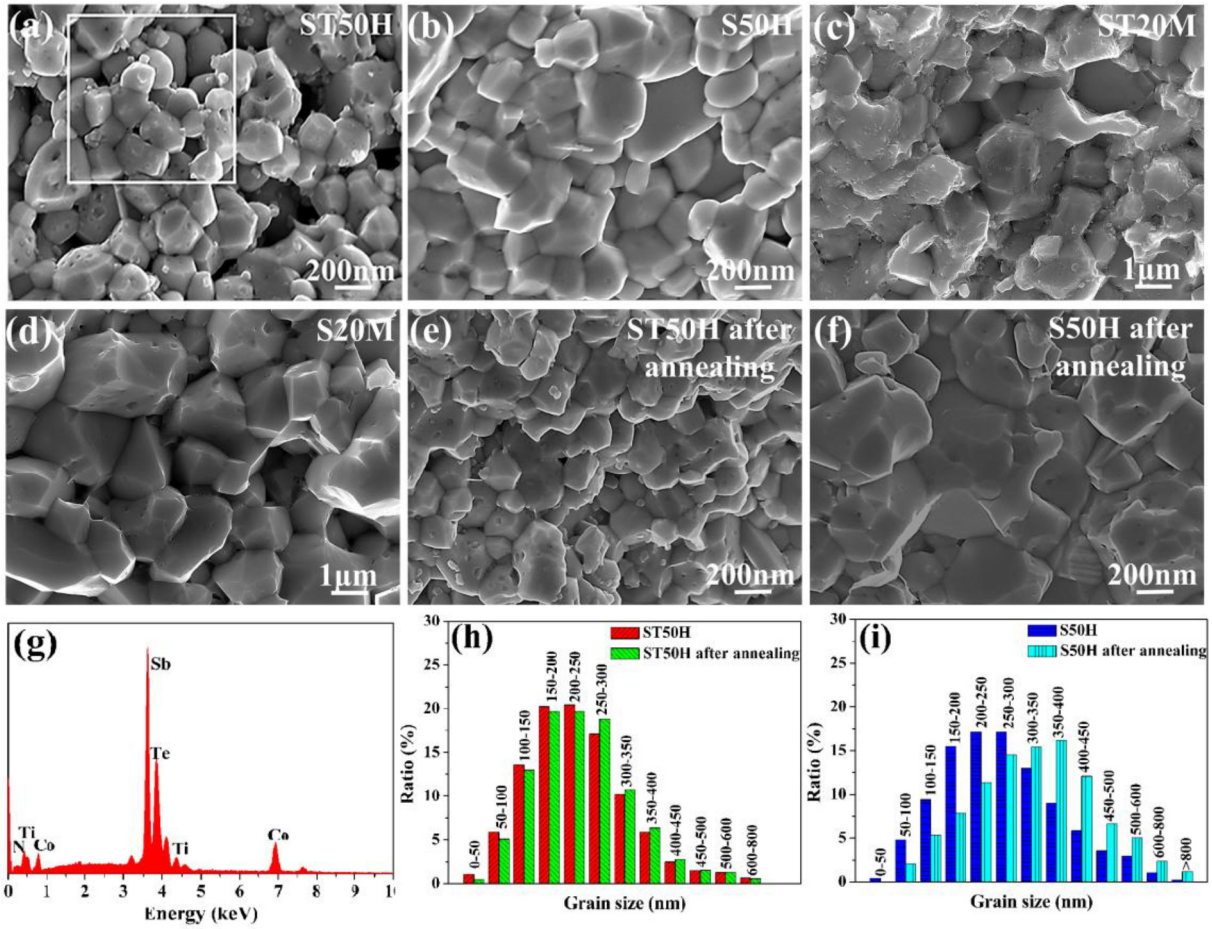

Fig. 2. FESEM images of the fracture surfaces of (a) ST50H (b) S50H (c) ST20M (d) S20M (e) ST50H after annealing and (f) S50H after annealing, (g) EDS analysis of the square area in (a), the grain size distribution of ST50H (h) and S50H (i) before and after annealing.