Effects of Annealing on Microstructure and Thermoelectric Properties of Nanostructured CoSb₃

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Nanocrystallization of thermoelectric materials is an effective way to reduce their thermal conductivity, but so far the thermal stability of nanostructured thermoelectric materials has been little studied. Effects of annealing treatment on the microstructure and the thermoelectric properties of nanostructured $CoSb_3$ were investigated in this work. Samples with average grain size of 300 nm were prepared by spark plasma sintering of high-energy ball-milled nanosized $CoSb_3$ powders. The study shows that annealing has a very significant impact on the grain size of the samples. The grain size of the sample with 100 h annealing is three times greater than before annealing. The major phase in the 150-h-annealed sample is still skutterudite, except for a trace amount of Sb phase. With increasing annealing time, the density reduces slightly. In addition, the power factor of the sample decreases, thus resulting in a decrease of the thermoelectric figure of merit.

Key words: Nanostructured CoSb₃, annealing, thermoelectric properties

INTRODUCTION

Thermoelectricity is becoming increasingly important in the fields of cooling, heating, power generation, and waste heat recovery.¹ The efficiency of thermoelectric (TE) devices is mainly determined by the TE materials. Good TE materials must have a large dimensionless figure of merit $ZT = \alpha^2 \sigma T/\kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity ($\kappa = \kappa_{\rm el} + \kappa_{\rm lat}$, where $\kappa_{\rm el}$ is the electronic contribution and $\kappa_{\rm lat}$ is the lattice contribution), and *T* is the temperature. The *ZT* value of a TE material can be improved by either increasing the electrical power factor (PF) $\alpha^2 \sigma$, decreasing the thermal conductivity κ , or a combination of both for a given system.²

Skutterudite compounds have attracted much attention in the last decade as promising TE materials.³⁻⁶ One of the remarkable features of skutterudites is that guest atoms can be introduced into

their cage-like framework structure to form filled skutterudites, which are suggested as "phonon glass/electron crystal" materials. The rattling motion of such filler atoms can effectively scatter phonons and cause a significant decrease of the lattice thermal conductivity.⁶ In addition, nano-structuring of thermoelectric materials is another effective approach to achieve lower thermal conductivity. Many reports have shown that *ZT* can be improved by nanostructuring thermoelectric materials, mainly due to reduced thermal conductivity.^{7,8}

It is generally known that, when a TE material is used in practice, it inevitably suffers thermal loading, so a good TE device requires TE materials with excellent performance stability at the service temperatures. Therefore, it is equally important to research the evolution of the microstructure and properties of these materials at their service temperatures. Recently, research in this field has received more attention. Hara et al.⁹ studied the effects of aging on the thermoelectric properties of *n*-type CoSb₃ in ambient air. El-Genk et al.¹⁰ reported the experimental results of performance

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