The great improvement effect of pores on ZT in Co$_{1-x}$Ni$_x$Sb$_3$ system

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In this paper, the Co$_{1-x}$Ni$_x$Sb$_{3+y}$ system ($x=0.1,0.2; y=0,0.05$) has been prepared by direct current induced hot press and annealing. Pores were made by annealing pressed Co$_{1-x}$Ni$_x$Sb$_{3+y}$ pellets into Co$_{1-x}$Ni$_x$Sb$_3$ pellets during annealing. It was found that from room temperature to 500 °C, the pores with diameter larger than 1 μm has significantly increased the Seebeck coefficient, considerably decreased the thermal conductivity, almost maintained the electrical conductivity constant, and therefore markedly improved the dimensionless figure of merit (ZT) of Co$_{1-x}$Ni$_x$Sb$_3$ system. By comparing the samples, we conclude that inducing pores into skutterudites is an effective route to greatly improve the ZT. © 2008 American Institute of Physics. [DOI: 10.1063/1.2963476]

Because of their good electrical transport properties, skutterudites materials based on CoSb$_3$ have been widely studied as potential next-generation thermoelectric materials.$^{1,4}$ One of the main obstacles to further improving their thermoelectric performance has been reducing their relatively high thermal conductivity.$^{5,6}$ It is reported that filling atoms into the voids in CoSb$_3$ can effectively decrease the thermal conductivity.$^{4–8}$ In state-of-the-art skutterudites, a dimensionless figure of merit, $ZT=\frac{S^2T}{\rho\kappa}$, of 1.25 has been obtained at 627 °C for n-type Ba$_0.3$Ni$_0.05$Co$_3.95$Sb$_{12.9}$.$^9$ 1.1 has been obtained at 447 °C for p-type Co$_{0.28}$Co$_{0.48}$Fe$_{1.52}$Sb$_{12}$. Multifilling has proved effective on further improving ZT.$^{11,12}$ In this work, attempt has been done to find a new way to enhance the ZT of CoSb$_3$ based material.

It was reported that in bulk Silicon, pores are expected to theoretically decrease the thermal conductivity.$^{13,14}$ On the other hand, the high-density bulk is considered as higher thermoelectric ZT. In CoSb$_3$ based material there has been no attempt to investigate the effects of pores on thermal conductivity and thermoelectric properties of skutterudites. This study was aimed mainly at making pores in Co$_{1-x}$Ni$_x$Sb$_3$ ($x=0.1,0.2$), as example of CoSb$_3$ based system, by annealing Co$_{1-x}$Ni$_x$Sb$_{3+y}$ ($y=0,0.05$) into Co$_{1-x}$Ni$_x$Sb$_3$ to investigate the effects of pores on the thermal conductivity and thermoelectric properties of skutterudites.

We synthesized Co$_{0.9}$Ni$_{0.1}$Sb$_{3+y}$ with pores and its comparison Co$_{0.9}$Ni$_{0.1}$Sb$_3$ without pores as well as Co$_{0.8}$Ni$_{0.2}$Sb$_3$ with pores and its comparison Co$_{0.8}$Ni$_{0.2}$Sb$_3$ without pores. The starting materials of Co$_{0.9}$Ni$_{0.1}$Sb$_{3+y}$ with pores, Co$_{0.8}$Ni$_{0.2}$Sb$_{3+y}$ without pores, Co$_{0.8}$Ni$_{0.2}$Sb$_3$ with pores, and Co$_{0.8}$Ni$_{0.2}$Sb$_3$ without pores were designed according to Co$_{0.9}$Ni$_{0.1}$Sb$_{3+y}$ ($x=0.1, y=0.05$ in Co$_{1-x}$Ni$_x$Sb$_{3+y}$), Co$_{0.9}$Ni$_{0.1}$Sb$_3$ ($x=0.1, y=0$), Co$_{0.8}$Ni$_{0.2}$Sb$_{3+y}$ ($x=0.2, y=0.05$ in Co$_{1-x}$Ni$_x$Sb$_{3+y}$), Co$_{0.8}$Ni$_{0.2}$Sb$_3$ ($x=0.2, y=0$), respectively. The samples were prepared through in the following three steps: ballmilling to make nanoparticles, direct-current-induced hot pressing (dc hot press) to compact the powders with full density, and annealing in different conditions for different samples. In the first step, appropriate quantities of high purity Co (99.998%, Alfa Aesar), Ni (99.996%, Alfa Aesar), and Sb (99.999%, Chengdu Chemphys Chemical Industry, China) were loaded in a jar in an Ar-filled glovebox and then ball milled for 39 h. ZrO$_2$ balls were used in ballmilling according to the weight ratio of ball/powder = 1/1. In the second step, the powder was pressed into pellets by dc hot pressing at a pressure of 80–160 MPa and temperature of 680–780 °C for 1–5 min in a 12.7 mm diameter graphite die. In the third step, the pressed pellets were annealed at 550–660 °C for 0.5–5 h in a tube furnace under protection of flowing Ar atmosphere for the samples of $y=0.05$, and annealed at 500–550 °C with pressure of 5 MPa for 0.5 h for the pellets of $y=0$, respectively. Finally the annealed samples were polished to standard dimensions of 12.7 mm in diameter and 1 or 2 mm in thickness for thermal conductivity measurement (LFA457, Netzsch), as well as x-ray diffraction (D8, Bruker). After thermal conductivity ($k$) measurement, the discs were cut into bar shape with dimensions of $2 \times 2 \times 11.5$ mm$^3$ for Seebeck coefficient ($S$) and electrical conductivity ($\sigma$) measurements by a four-point transport technique using a commercial system (ZEM-3, ULVAC-RIKO). Fractured fresh surface was investigated by scanning electron microscope (SEM) (JEOL 6340F) to obtain the information of the grain size and pores.

X-ray diffraction results indicate that the x-ray diffraction patterns of all samples after annealing step are all skutterudite phases. That means the additional Sb in the samples with $y=0.05$ has been volatized during annealing.

SEM investigation shows that there are two types of particles in the all samples, larger ones of about 1–1.2 μm in bar shape and smaller ones of about 0.3 μm in spherical shape. There are pores with diameter ranging from 1 to 1.5 μm in the samples as expected. The grain size is...
more homogeneous in the samples with pores than that in the samples without pores for both $x = 0.1$ and $x = 0.2$. Figure 1(a) shows the representative SEM image of the samples without pores and Fig. 1(b) shows the representative SEM image of the samples with pores. The density measurement indicates the sample without pores possesses full density and the sample with pores possesses 92% density. We guess that the larger ones grew from the alloyed powder during ballmilling, and grew faster than the smaller ones from unalloyed powder that needs additional nucleation energy. As expected, the pores were formed during annealing when additional Sb in Co$_{1-x}$Ni$_x$Sb$_{3.05}$ volatized. The pressure during annealing for Co$_{1-x}$Ni$_x$Sb$_3$ system is support for formation of full density. Appropriate annealing temperatures assure that the samples with the same $x$ values basically possess the same mean grain size.

Figure 2(a) shows the temperature dependence of $\sigma$ of the as-prepared samples. It is clearly shown that the $\sigma$ of Co$_{0.9}$Ni$_{0.1}$Sb$_3$ with pores is the same as that of Co$_{0.9}$Ni$_{0.9}$Sb$_3$ without pores, and the $\sigma$ of Co$_{0.8}$Ni$_{0.2}$Sb$_3$ with pores possess close $\sigma$ value, by only 5.7% difference. The probable reason is that pores increase carrier concentration, which keeps constant with increasing temperature. On the other hand, the relatively lower density results in lower carrier concentration, which increases as the temperature increases. The two effects compete with each other. The two factors basically balance in Co$_{0.9}$Ni$_{0.1}$Sb$_3$ with pores above 200 °C, whereas in Co$_{0.8}$Ni$_{0.9}$Sb$_3$ with pores the two factors imbalance at all measuring temperature scope. Between room and 400 °C the reducing effect owing to less density is less than the increasing effect owing to pores, between 400 °C and 500 °C the increasing effect is less than the reducing effect. The competition difference of the samples with different $x$ values is probably owing to the higher carrier concentration in Co$_{0.8}$Ni$_{0.1}$Sb$_3$ than that in Co$_{0.9}$Ni$_{0.1}$Sb$_3$; that is to say, in Co$_{0.8}$Ni$_{0.1}$Sb$_3$ the change in carrier concentration originating from temperature excitation is more than that in Co$_{0.9}$Ni$_{0.1}$Sb$_3$.

The temperature dependence of the $S$ of as-prepared samples is displayed in Fig. 2(b). All samples have negative Seebeck coefficients, indicating that the dominating carriers are electrons. Comparing the samples without pores, the samples with pore possess much higher $S$, probably due to the charges deposition at pores.

Thermal conductivity ($k$) is a crucial factor to the thermoelectric performance. The total $k$ of the samples is shown in Fig. 2(c). Co$_{0.9}$Ni$_{0.1}$Sb$_3$ with pores possesses much lower thermal conductivity than Co$_{0.9}$Ni$_{0.1}$Sb$_3$ without pores. The same case occurs in Co$_{0.8}$Ni$_{0.2}$Sb$_3$. We can conclude that the pores decrease the thermal conductivity by almost 1 W/mK. The behavior originates from the reduction in the channels.
for phonon transport and the increased phonon scattering at the pore surfaces,\(^{14}\) since the electronic thermal conductivity \(k_e = L_0/\sigma T\) has not changed due to unchanged \(\sigma\). Figure 2(d) shows the calculated dimensionless figures of merit (ZT) versus the temperature for all samples. It is obvious that the ZT of \(\text{Co}_{0.9}\text{Ni}_{0.1}\text{Sb}_3\) with pores is far larger than that of \(\text{Co}_{0.9}\text{Ni}_{0.1}\text{Sb}_3\) without pores, and the ZT of \(\text{Co}_{0.8}\text{Ni}_{0.2}\text{Sb}_3\) with pores is far larger than that of \(\text{Co}_{0.8}\text{Ni}_{0.2}\text{Sb}_3\) without pores. This encouraging result illustrates firmly the advantage of pores for ZT enhancement.

In summary, pores in CoSb\(_3\) based skutterudites can markedly increase the Seebeck coefficients, significantly reduce the thermal conductivity, almost not change the electrical conductivity, and consequently greatly improve the ZT. We can conclude that inducing pores into skutterudites can greatly improve the ZT.

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