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Synthesis of Yb$_y$Co$_4$Sb$_{12}$/Yb$_2$O$_3$ composites and their thermoelectric properties

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Composites containing Yb-filled CoSb$_3$ and well-distributed Yb$_2$O$_3$ particles are synthesized by *in situ* reaction method. The structural, chemical, and transport properties of the composites are studied. Some Yb$_2$O$_3$ particles with microsize locate at the grain boundaries of matrix and others distribute within Yb$_y$Co$_4$Sb$_{12}$ grains as nanoscale inclusions. The combination of the "rattling" of Yb ions inside the voids of CoSb$_3$ and the phonon scattering of the oxide defects results in a remarkable reduction in the lattice thermal conductivity. The thermoelectric performance of the composites is significantly improved, and the maximum figures of merit reach 1.3 for the Yb$_{0.25}$Co$_4$Sb$_{12}$/Yb$_2$O$_3$ and 1.2 for the Yb$_{0.21}$Co$_4$Sb$_{12}$/Yb$_2$O$_3$ composites at 850 K. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2345249]

During the last decade, intensive effort has been made in searching for high performance thermoelectric materials. The performance of thermoelectric materials is characterized by the figure of merit $ZT = \alpha^2 \sigma T / \kappa$ where α, σ, κ ($\kappa = \kappa_E + \kappa_L$), and T are the Seebeck coefficient, the electrical conductivity, the total thermal conductivity of the material, and the absolute temperature, respectively. CoSb$_3$-based filled skutterudites have been attracting considerable attention for their potential thermoelectric applications.[1–3] A series of *p*- and *n*-type filled skutterudites with high ZT's have been reported.[1–5] Unfortunately, the lattice thermal conductivities (κ_L) of the filled skutterudites, especially for *n*-type partially filled CoSb$_3$ skutterudites, still remain relatively high as compared with the state-of-the-art thermoelectric materials, such as Bi$_2$Te$_3$-based alloys. Further reduction of κ_L for the filled skutterudites is an effective approach to improve the thermoelectric performance of the filled CoSb$_3$.

Experimentally, it was shown that the κ_L of CoSb$_3$-based materials could be depressed dramatically by introducing fullerene (C$_{60}$) large defects into matrix, and a significant enhancement of ZT was observed in a wide temperature range.[6] A marked reduction in κ_L was also obtained by adding a small amount of ZrO$_2$ nanoparticles into ZrNiSn-based matrix.[7] These extra defects are believed to be inertial to electrical transport and therefore have little influence on the electrical transport properties of the matrix.[6,7] Thus, it is reasonable to assume that oxides, especially rare-earth (RE) oxides which form simultaneously during the synthesis of filled CoSb$_3$ skutterudites, may be good candidates for the reduction of κ_L. Furthermore, both theoretical[8] and experimental[2,9–12] studies already showed that Yb had a relatively high filling fraction in CoSb$_3$. Experimental work also demonstrated that Yb-filled skutterudites with filling fraction of about 0.2 possessed ZT close to 1 at $600-750$ K.[2,9,10] Therefore, it is expected that composites containing the filled CoSb$_3$ with higher Yb filling fractions and distributed Yb$_2$O$_3$

defects should have higher thermoelectric performance. In this letter, we report the synthesis and the thermoelectric properties of the Yb$_y$Co$_4$Sb$_{12}$/Yb$_2$O$_3$ composites by an *in situ* reaction method.

Details on the preparation of filled skutterudite samples were described in our earlier paper.[5] To achieve the Yb oxide, an excessive Yb metal was used and a proper annealing time was adopted during the preparation process. The final solid products were ground into fine powders in the air above 30 min for oxidizing the remainder Yb metal. The obtained powders were then sintered by spark plasma sintering at 850 K for 15 min in a graphite die to form dense pellets. Structural and chemical compositions of the polycrystalline samples were characterized by x-ray diffraction (XRD) and electron microprobe analyses (EPMA). The compositions of the Yb-filled skutterudite phases were then obtained from EPMA normalized to the full occupancy of the cobalt sites. Experimental procedures for electrical and thermal transport measurements were described elsewhere.[5]

Several Yb-filled CoSb$_3$ samples are prepared, and only two of them with relatively high filling fractions of Yb contain Yb$_2$O$_3$ particles in the matrix. Our XRD and EPMA show that the Yb$_{0.21}$Co$_4$Sb$_{12}$/Yb$_2$O$_3$ and Yb$_{0.25}$Co$_4$Sb$_{12}$/Yb$_2$O$_3$ composites are obtained with a trace amount of impurity phases of Sb, CoSb$_2$, and YbSb$_2$. Table I lists the chemical composition and some physical properties for all the samples at room temperature. The carrier concentrations for Yb$_y$Co$_4$Sb$_{12}$ with low Yb filling fractions ($y=0.10,0.15$) in this work and those for the reported Yb$_y$Co$_4$Sb$_{12}$ compounds[2] are nearly in a linear relation to the filling fraction of Yb in CoSb$_3$. The carrier concentrations of the two composite samples are relatively high, due to the high filling fraction and probably the existence of impurity phases (YbSb$_2$ and CoSb$_2$) in the samples. Our data also indicate that the maximum filling fraction of Yb in CoSb$_3$ is about 0.25 without any charge compensation, which is consistent with both the previous experimental[2,9–11] and the theoretical[8] results.

TABLE I. Summary of composition and some physical properties of Yb-filled skutterudites with and without oxide particles at room temperature. n, a, κ_L and ρ^* are the carrier concentration, lattice constant, the lattice thermal conductivity, and the relative density of the samples, respectively.

Systems	n (10^{20}/cm^{-3})	a (Å)	κ_L (W/m K)	ρ^* (%)
$Yb_{0.10}Co_4Sb_{12.77}$	1.0	9.043	3.49	98.5
$Yb_{0.15}Co_4Sb_{12.81}$	1.6	9.047	2.75	97.9
$Yb_{0.21}Co_4Sb_{12.65}/Yb_2O_3$	3.3	9.053	2.04	97.4
$Yb_{0.25}Co_4Sb_{12.69}/Yb_2O_3$	8.4	9.056	1.72	97
$Yb_{0.19}Co_4Sb_{12}$[a]	1.9	9.051	2.6	⋯
$Yb_{0.46}Co_4Ge_{0.79}Sb_{11.21}$[a]	2.0	⋯	2.2	⋯

[a]Reference 12.

Figure 1 shows the backscattered electron image (a), the x-ray maps of oxygen (b) and Yb (c), and the transmission electron microscopy (TEM) image (d) of a nano-oxide particle in the composites. The gray area in Fig. 1(a) is the $Yb_{0.25}Co_4Sb_{12}$ phase, and the white places are the defects. The x-ray maps of oxygen and Yb [Fig. 1(b) and 1(c)] identify that the defects are mainly Yb_2O_3. A small amount of $YbSb_2$ is also observed together with the appearance of Yb_2O_3. Yb_2O_3 agglomerates into irregular clusters of different sizes located at the grain boundaries of the matrix. The average size of Yb_2O_3 defects is normally large due to the high nominal Yb concentration in the preparation of samples. There is also a large number of small white areas in multiplicated EPMA pictures, indicating the existence of Yb_2O_3 defects with less than microsize in the matrix. The presence of many Yb_2O_3 inclusions is also detected inside individual matrix grains with the size of about 20 nm or more as shown in Fig. 1(d). The content of Yb_2O_3 in $Yb_{0.25}Co_4Sb_{12}/Yb_2O_3$ composite is higher than that in $Yb_{0.21}Co_4Sb_{12}/Yb_2O_3$ composite.

The temperature dependences of electrical conductivity (σ), Seebeck coefficient (α), and power factor ($\alpha^2\sigma$) for all samples between 300 and 850 K are shown in Fig. 2. σ shows a metallic behavior over the entire temperature range for all samples. The absolute value of α deceases with increasing Yb filling fraction, due to the increase of carrier
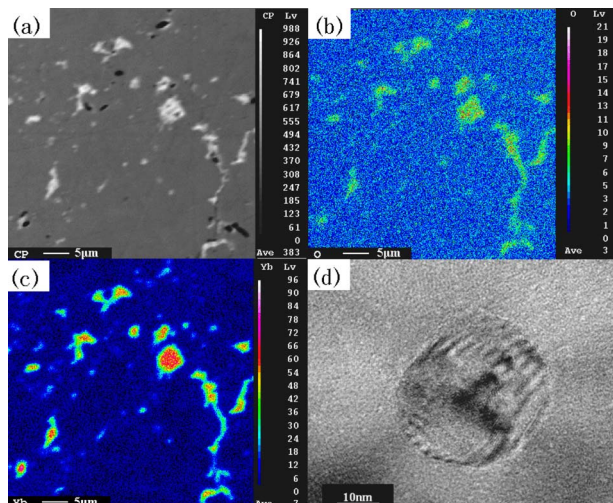

FIG. 1. (Color online) Backscattered electron image (a) and x-ray maps for oxygen (b) and Yb (c) in the $Yb_{0.25}Co_4Sb_{12}/Yb_2O_3$ composite. (d) shows the TEM image of a typical Yb_2O_3 nano-oxide particle in the $Yb_{0.21}Co_4Sb_{12}/Yb_2O_3$ composite.
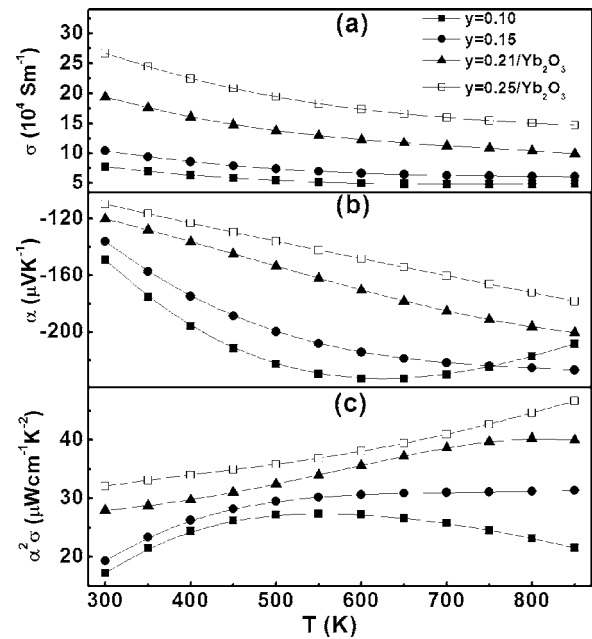

FIG. 2. Temperature dependences of the electrical conductivity (a), Seebeck coefficient (b), and power factor (c) for $Yb_yCo_4Sb_{12}$ compounds and $Yb_yCo_4Sb_{12}/Yb_2O_3$ composites.

concentration (Table I). α also increases with increasing temperature except for the $Yb_{0.10}Co_4Sb_{12}$ compound. Notice that all the samples exhibit relatively large α, similar to the reported data for $CoSb_3$-based n-type filled skutterudites.[2–5,9–12] High $\alpha^2\sigma$ for the composites are achieved [Fig. 2(c)], especially with a value of 47 μW/cm K^2 for $Yb_{0.25}Co_4Sb_{12}/Yb_2O_3$ at 850 K, identifying that these composites keep good electrical transport properties.

Figure 3 plots κ_L as a function of the Yb filling fraction at room temperature for all samples. κ_L values are estimated by subtracting the electronic contribution κ_E from the total thermal conductivity. The Weidemann-Franz relation with Lorentz constant of $L_0 = 2.0 \times 10^{-2}$ V/K^2 is applied to estimate $\kappa_E (= L_0 \sigma T)$. κ_L for single phased Yb-filled skutterudite compounds are close to the reported values with similar Yb filling fractions.[2,12] For both $Yb_{0.21}Co_4Sb_{12}/Yb_2O_3$ and $Yb_{0.25}Co_4Sb_{12}/Yb_2O_3$ composites, however, κ_L are much lower than those of the $Yb_yCo_4Sb_{12}$ compounds with the similar Yb filling fractions. The κ_L of the $Yb_{0.25}Co_4Sb_{12}/Yb_2O_3$ composite is about 1.72 W/m K at room temperature and decreases to 0.52 W/m K at 800 K (inset in Fig. 3), approaching the limit of the theoretical
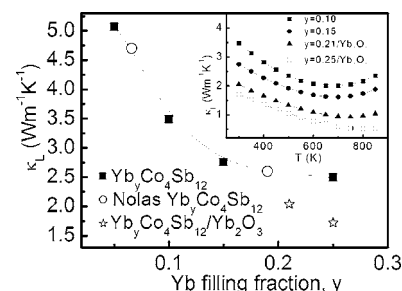

FIG. 3. Lattice thermal conductivity (κ_L) at room temperature as a function of the Yb filling fraction for $Yb_yCo_4Sb_{12}$ compounds and $Yb_yCo_4Sb_{12}/Yb_2O_3$ composites. Insert: Temperature dependence of κ_L for $Yb_yCo_4Sb_{12}$ compounds and $Yb_yCo_4Sb_{12}/Yb_2O_3$ composites.
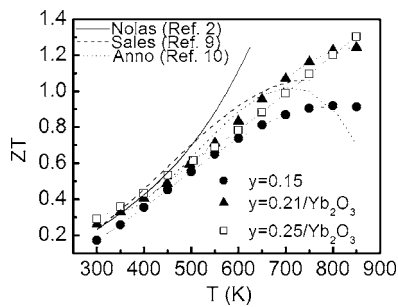
FIG. 4. Temperature dependence of *ZT* for $Yb_yCo_4Sb_{12}$ compounds and $Yb_yCo_4Sb_{12}/Yb_2O_3$ composites. *ZT* from others are also indicated in the figure.

minimum value, 0.3 W/m K.[13] The κ_L of the $Yb_{0.21}Co_4Sb_{12}/Yb_2O_3$ composite at room temperature is about 22% lower than that of $Yb_{0.19}Co_4Sb_{12}$ reported by No-las and co-workers,[2,12] although the Yb filling fractions for them are close to each other. The decrease of κ_L in the composites should be attributed to the oxide defects, which provide additional phonon scattering. Unlike the $CoSb_3/C_{60}$ composites where lattice phonons are mainly scattered by the large defects of fullerene,[6] both the large oxide defects located at grain boundaries and the nanoscale inclusions distributed in matrix grains give rise to phonon scattering and lower κ_L for the $Yb_yCo_4Sb_{12}/Yb_2O_3$ composites.[7,14] For now, we could not quantitatively estimate the different contributions from either the large oxide defects or the nanoscale inclusions to the reduction of κ_L. But, because the size of the large oxide defects is well beyond the mean free path of phonons in $CoSb_3$,[6] we believe that the significant reduction of κ_L could be mainly attributed to the phonon scattering by the nanoscale Yb_2O_3 inclusions in matrix grains.

Figure 4 displays the calculated dimensionless figures of merit (*ZT*) versus the temperature for all samples. The data from Nolas *et al.*, Sales *et al.*, and Anno *et al.* are also included in Fig. 4 for comparison. It is obvious that the *ZT* values of the composites are enhanced in comparison with the reported values of $Yb_yCo_4Sb_{12}$ compounds. *ZT*=1.3 is achieved for $Yb_{0.25}Co_4Sb_{12}/Yb_2O_3$ composite at 850 K and ranks as one of the highest *ZT* values reported so far for *n*-type skutterudites. This encouraging result illustrates firmly the potential of filled skutterudite composites as an advanced thermoelectric material in the intermediate temperature range.

In summary, Yb_2O_3 particles with different sizes were introduced into the Yb-filled skutterudites to form composite materials by *in situ* reaction method, and the effect of the oxide particles on the thermoelectric properties of the composites was investigated. The Yb_2O_3 particles depress the κ_L of the composites to come close to the minimum thermal conductivity of filled $CoSb_3$ and are essential to achieve a high *ZT* for the composites. Our study implies that introducing RE oxide additions into the matrix through methods such as *in situ* reaction is helpful in essentially improving *ZT* for conventional filled skutterudites, even though they already have good thermoelectric performance. We also like to address that the extra RE oxide particles are formed simultaneously during the synthesis of the filled $CoSb_3$ and that the $RE_yCo_4Sb_{12}/RE$ oxide composites are thermodynamically stable at elevated temperature in comparison with many other nanocomposite materials containing only the nanoparticles of $CoSb_3$ itself, and therefore they should have many practical applications.

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