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Dramatic thermal conductivity reduction by nanostructures for large increase in thermoelectric figure-of-merit of FeSb$_2$

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In this report, thermal conductivity reduction by more than three orders of magnitude over its single crystal counterpart for the strongly correlated system FeSb$_2$ through a nanostructure approach was presented, leading to a significant increase of thermoelectric figure-of-merit ($ZT$). For the samples processed with the optimal parameters, the thermal conductivity reached 0.34 Wm$^{-1}$ K$^{-1}$ at 50 K, leading to a $ZT$ peak of about 0.013, compared to 0.005 for single crystal FeSb$_2$, an increase of about 160%. This work suggests that nanostructure method is effective and can be possibly extended to other strongly correlated low temperature thermoelectric materials, paving the way for future cryogenic temperature cooling applications. © 2011 American Institute of Physics. [doi:10.1063/1.3651757]

Of the several strongly correlated semiconductors including FeSi,$^1$ Ce$_3$Bi$_4$Pt$_3$,$^2$ and FeGa$_3$,$^3$ FeSb$_2$ has recently stimulated extensive research efforts due to its colossal thermopower (Seebeck coefficient, $S$) at 10 K.$^4$ The thermopower of FeSb$_2$ single crystals is on the order of tens of mV K$^{-1}$ which contributes to the very large power factor (PF) of 0.23 Wm$^{-1}$ K$^{-2}$.$^{4,5}$ About 40 times of the best thermoelectric materials (Bi$_2$Te$_3$-based high-performance alloy ingots$^6,7$). However, it is the figure of merit, $Z = S^2\sigma/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ the electrical conductivity, and $\kappa$ the thermal conductivity, which determines the overall efficiency. To be practically useful, materials should have a dimensionless figure-of-merit ($ZT$) around 1. However, FeSb$_2$ single crystals have a peak $ZT$ of around 0.005 at 12 K due to a large value of thermal conductivity of about 500 Wm$^{-1}$ K$^{-1}$. In order for FeSb$_2$ to be a useful material for thermoelectric cooling, $ZT$ must be increased to a meaningful value.

The large lattice thermal conductivity of strongly correlated materials such as FeSb$_2$ at low temperatures limits their $ZT$. Zhang et al.$^8$ predicted that phonon size effects in nanostructured strongly correlated materials can be exploited to reduce phonon thermal conductivity while maintaining electron transport due to the long phonon mean free path and short electron mean free path. For example, it was estimated that single crystal FeSb$_2$ has an electron mean free path of less than 10 nm at all temperatures with a phonon mean free path around $40 \mu$m at 15 K.$^9$ This large difference of mean free paths allows the opportunity to tune the electrical and thermal properties almost independently by either doping$^{10,11}$ or nano-engineering the grain size.$^{11}$ In principle, thermal conductivity suppression can be realized through several different methods such as the introduction of impurities, defects, or grain boundaries. Although substantial thermal conductivity reduction was achieved by doping, no improvements in $ZT$ were reported due to altered electron transport properties in FeSb$_2$.$^{10,11}$

Nanostructure approach has proven to be a very efficient way to reduce the lattice contribution to the thermal conductivity in many thermoelectric material systems.$^{12-15}$ The lower limit of the lattice thermal conductivity in FeSb$_2$ has been calculated$^{16}$ to be as low as 0.3 Wm$^{-1}$ K$^{-1}$ at 50 K through the model proposed by Cahill et al.$^{17}$ It will be shown in this report that the thermal conductivity of nanostructured FeSb$_2$ is drastically decreased leading to an improvement in $ZT$.

The nanostructured FeSb$_2$ were synthesized by first ingot formation through melting and solidification, and then followed by ball milling and hot pressing with different processing parameters. Scanning electron microscopy (SEM, JEOL 6340F) was used to investigate the grain size distributions of the above processed samples. Transmission electron microscopy (TEM, JEOL 2010F) was used to investigate the grain size distribution and the microstructure. The thermal conductivity and $ZT$ of the single crystal counterpart for the strongly correlated system FeSb$_2$ through a nanostructure approach was presented, leading to a significant increase of thermoelectric figure-of-merit ($ZT$). For the samples processed with the optimal parameters, the thermal conductivity reached 0.34 Wm$^{-1}$ K$^{-1}$ at 50 K, leading to a $ZT$ peak of about 0.013, compared to 0.005 for single crystal FeSb$_2$, an increase of about 160%. This work suggests that nanostructure method is effective and can be possibly extended to other strongly correlated low temperature thermoelectric materials, paving the way for future cryogenic temperature cooling applications.
An enlarged area from Fig. 2(a) was shown in Fig. 2(b). It is clearly shown that the grains are well-crystallized with dimensions of $20 \times 15 \text{ nm}$ and a lattice spacing of 0.276 nm, which can be indexed to the (101) planes of orthorhombic $Pnmm$ FeSb$_2$. The nano-sized grains and the boundaries between these nano-sized crystals would contribute to the dramatic thermal conductivity reductions in the samples.

Figure 3(a) shows the temperature dependence of thermal conductivity for all samples and also the single crystals grown from vapor transport (VT) and self-flux (SF) methods. A substantial decrease of thermal conductivity was found for all samples throughout the temperature range, decreasing as grain size decreases. The thermal conductivity of sample S15hr-600C is 17 Wm$^{-1}$K$^{-1}$ at 40 K, compared with 0.34 Wm$^{-1}$K$^{-1}$ for S15hr-200C at the same temperature due to a decrease in the lattice portion of the thermal conductivity. The peak positions of $\kappa$, which reveal the competition between the phonon-phonon (Umklapp) scattering or impurity scattering and the grain boundary scattering, shift to higher temperatures and nearly disappear on samples S15hr-200C and S15hr-room temperature. This demonstrates that grain boundary scattering is the dominant scattering mechanism in samples with smaller grain sizes. Moreover, fittings for all the curves below 100 K show a shift from $T^{2.04}$ to $T^{1.31}$ with the decreasing of grain sizes, as is also seen in nanocrystalline silicon, which indicates that other parameters besides $C_V$ such as porosity, phonon frequency ($\omega$), and the effective mean free path ($A_{eff}$) also play important roles in thermal conductivity reduction. When compared with single crystal FeSb$_2$, there is a reduction by more than three orders of magnitude in the thermal conductivity from 500 Wm$^{-1}$K$^{-1}$ down to around 0.1 Wm$^{-1}$K$^{-1}$ at 20 K in the nanostructured sample S15hr-200C. Such a large thermal conductivity suppression by nanostructuring at low temperature is much larger than any other nanostructured thermoelectric materials at high temperatures. Nanostructured $p$-type Bi$_2$Sb$_2$Te bulk alloy achieved 83% thermal conductivity reduction compared with its ingot counterpart at 250°C, half-Heuslers achieved 33% in high temperature ranges, and a 100% reduction for $p$-type silicon germanium alloy.

Figure 3(b) shows the temperature dependence of electrical resistivity for all the samples. The data was fit using Arrhenius’ law to find approximate energy gaps. Sample S15hrs-600C has two gaps of 28.2 meV and 4.2 meV. When the pressing temperature is lowered further, e.g., sample S15hrs-300C, only one gap appears with a value of 21 meV. The change in the band gaps corresponds to the increasing of crystal defects that are probably due to the decreased grain size and increased carrier concentration. It appears the smaller energy gap located in the temperature range of 7-20 K was suppressed; and the larger band gap was decreased as can be seen in the sample pressed at room temperature whose band gap is reduced to 18 meV. Measurements of the carrier concentration, inset of Fig. 3(c) increased as well, confirming the narrowing of the energy gaps.

The temperature dependent Seebeck coefficients ($S$) are shown in Fig. 3(c). It shows that $S$ decreases as grain size is decreased, which could mean that carriers are generated. This is not the case for S10min-400C, which has smaller grains than S15hr-600C. From the relationship of the electrical property and the quality of crystal, it is believed that S10min-400C has fewer defects than that of S15hr-600C due to the longer ball milling time of the latter. Defects typically increase carrier concentration, which decreases the $S$. An increase in the carrier concentration will also lead to a decrease in the resistivity, which is the case as seen in Fig. 3(b). Mobility and carrier concentration measurements are shown for two samples in the inset of Fig. 3(c). Carrier concentration at 25 K is higher for the S15hr-300C sample with a value of $9.75 \times 10^{19}$ cm$^{-3}$ and while its mobility is lower at 4.52 cm$^2$V$^{-1}$s$^{-1}$, when compared to S15hr-600C at 25 K, whose carrier concentration is decreased to $8.36 \times 10^{17}$ cm$^{-3}$ while its mobility is as high as 160 cm$^2$V$^{-1}$s$^{-1}$. These properties directly correlate to the increase seen in the $S$. There is a cross over between the two samples in the Seebeck coefficient found at 65 K. This cross over is also seen in the measurements for carrier concentration at 65 K while the mobility remains relatively constant.
FeSb$_2$ is broadened significantly over that of the single crystal counterpart, which is much more useful for applications between 10 and 150 K. For the same reason, peak values of the Seebeck coefficient have been intensively investigated recently by researchers like Sun et al.. It was found that an enhancement by a factor of 30 or larger could be applied to the calculated Seebeck coefficient based on the free-electron model. Due to this enhancement, it is quite likely that an increase in the Seebeck coefficient can be realized by tuning carrier concentration through doping or composition adjustment, providing the potential for much future work.

Figure 3(d) shows the temperature dependence of $ZT$ for the nanostructured samples as well as those for single crystals. The $ZT$ increases from 0.001 of sample S15hr-600C to 0.013 of S15hr-200C, which is an unambiguous indication of grain size effect. The optimal $ZT$ value reaching 0.013 at 50 K in S15hr-200C is much higher than $ZT = 0.005$ at 10 K for single crystal samples. Though the power factor is much larger than that of single crystal, the drastic reduction in thermal conductivity contributes to the increase in $ZT$. One feature worth pointing out is that the $ZT$ curve in nanostructured FeSb$_2$ is broadened significantly over that of the single crystal counterpart, which is much more useful for applications between 10 and 150 K.

In conclusion, substantial thermal conductivity suppression for the strongly correlated system FeSb$_2$ through a nanostructure approach was reported in this letter. Thermal conductivity was reduced by more than three orders of magnitude over its single crystal counterpart. As grain size decreases from tens of microns to around 20 nm, the corresponding thermal conductivity decreases by 50 times, reaching 0.34 Wm$^{-1}$K$^{-1}$ at 50 K. $ZT$ was found to be 0.013, compared to 0.005 for single crystal FeSb$_2$, an increase of 160%. Although this is still far from the state-of-the-art requirement of $ZT = 1$, nanoscale structure to reduce thermal conductivity in FeSb$_2$ is clearly the right way, and a combination with other methods of $ZT$ enhancement including doping or composition adjustment is expected to further increase the $ZT$.

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