Effect of Sb doping on the thermoelectric properties of Ti-based half-Heusler compounds, TiNiSn$_{1-x}$Sb$_x$

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Half-Heusler alloys (MgAgAs type) with the general formula MNiSn where M is a group IV transition metal (Hf, Zr, or Ti) are currently under investigation for potential thermoelectric materials. These materials exhibit a high negative thermopower ($-40$ to $-250 \mu$V/K) and low electrical resistivity values (0.1–8 mΩcm) both of which are necessary for a potential thermoelectric material. Results are presented in this letter regarding the effect of Sb doping on the Sn site (TiNiSn$_{1-x}$Sb$_x$). The Sb doping leads to a relatively large power factor of (0.2–1.0) W/m K at room temperature for small concentrations of Sb. These values are comparable to that of Bi$_2$Te$_3$ alloys, which are the current state-of-the-art thermoelectric materials. The power factor is much larger at $T\approx 650$ K where it is over 4 W/m K making these materials very attractive for potential power generation considerations. © 2000 American Institute of Physics.

Recently there has been renewed interest in thermoelectricity with the possibility of optimizing the electronic and thermal transport properties of both new and existing novel materials as possible thermoelectric (thermoelectric) materials for applications such as refrigeration and power generation. Thermoelectric materials and devices are important not only because of their reliability and durability, but also due to being an “environmentally friendly” technology. The efficiency of a thermoelectric is given by the dimensionless parameter $ZT$, the figure of merit, of the material and is given by ($a^2sT/\lambda$) where $a$ is the Seebeck coefficient or thermopower, $s$ is the electrical conductivity, and $\lambda$ is the thermal conductivity. The thermal conductivity is comprised of a sum of both lattice ($\lambda_L$) and electronic ($\lambda_E$) contributions.

The current state-of-the-art materials, Bi$_2$Te$_3$ and Si$_{1-x}$Ge$_x$, have a $ZT=1$ at their optimal temperature. It is desirable to have a higher figure of merit ($ZT\approx 2$) for any new thermoelectric material. Several new bulk materials are under investigation for potential thermoelectric applications such as skutterudites, complex chalcogenides, clathrates, and quasicrystals. Another new class of materials being investigated for thermoelectric applications are the half-Heusler alloys. These materials are intermetallic alloys with the general formula MNiSn where M is a group IV transition metal (M=Zr, Hf, Ti). Half-Heusler alloys have a MgAgAs type crystal structure, forming three interpenetrating face-centered-cubic (fcc) sublattices with one Ni sublattice vacant. Heusler alloys (e.g., Mn$_2$Sn, Fe$_2$P, and In$_2$As) differ from half-Heusler alloys in having the Ni sublattice fully occupied and are also metallic (or half-metallic) and exhibit interesting magnetic properties. Half-Heusler alloys, on the other hand, are small band gap semiconductors with a gap of 0.1–0.5 eV. These materials exhibit high thermopower ($S\approx -300 \mu$V/K) and low electrical resistivity values (0.1–8 mΩcm) which yield a relatively large power factor ($a^2sT$) at room temperature. One of the current challenges is to reduce the relatively high thermal conductivity ($\approx 10$ W/m K) that is evident in these materials or to greatly increase the power factor.

The ZrNiSn-based half-Heusler materials were investigated by Hohl et al., where they performed Nb and Ta substitutions on the group IV metal site and Sb or Bi on the Sn sites. They found that the (Hf$_{0.5}$Zr$_{0.5}$)$_{0.09}$Ta$_{0.01}$NiSn alloy displayed a power factor, $a^2sT$, of 0.66 W/m K at 300 K and 2.8 W/m K at 700 K which produced a $ZT=0.5$ at 700 K. Extensive investigations on the effect of temperature annealing were performed by Uher et al., on similar systems of ZrNiSn, HfNiSn, and pseudoternary (Zr,Hf)NiSn, where they found that both the electrical and the thermal properties were strongly dependent on annealing time and conditions. These are cubic materials and tend to order and intermix upon annealing of a week or more at 800 °C. The annealing is an important step in acquiring single-phase materials. This work focused primarily on In and Sb doping on the Sn site. The Sb doping had a pronounced effect on the transport driving the resistivity much more metallic, even with very small amounts of Sb. Extensive work related to the thermal conductivity in these materials was also presented, showing it is a strong function of the annealing. Another class of these materials based on LnPbSb where Ln=Ho, Er, Dy, were investigated by Mastronardi et al.. An important result of this work is that they were able to obtain p-doped materials with thermopower values between 60 and 250 $\mu$V/K. These materials appear to exhibit thermal conductivity values (3–5 W/m K) that are typically lower than many of the other half-Heusler alloys. Recently, we have focused our ef-
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The electrical transport data on this group of half-Heusler alloys efforts on the TiNiSn system and in this letter, we present electrical transport data on this group of half-Heusler alloys as a function of Sb doping, TiNiSn\textsubscript{1-x}Sb\textsubscript{x}. The Sb doping greatly enhances the power factor, as with the ZrNiSn, and yields one of the highest power factors known in any material.

Ingots with nominal alloy compositions were prepared by arc melting appropriate quantities of high purity elements together under an argon atmosphere. The overall purity of the starting materials was as follows: titanium (4N purity), zirconium (3N purity), antimony (5N purity), tin (5N purity), and nickel (5N purity) metal powders are mixed together and pressed into a pellet. This pellet was arc melted on a water-cooled copper hearth under argon atmosphere. The resulting button was remelted two or three times after turning upside down to ensure homogeneity. Then the button was wrapped in a Ta foil and sealed in an evacuated quartz tube for aning these materials much more metallic-like as apparent in the TiNiSn should be semiconducting at even the lowest temperatures and that this transition is probably due to trace amounts of impurities affecting the band structure and thus the electronic properties. These small amounts of Sb are obviously having a profound effect on the band overlap making these materials much more metallic-like as apparent in Fig. 1(a). However, upon addition of more Sb the thermopower starts to rapidly degrade as shown in Fig. 1(b), thus making them less attractive for potential thermoelectric applications. Extensive band structure studies would be very helpful in understanding the effects of the Sb substitution.

In Fig. 2, the power factor ($\alpha^2\sigma T$) is shown as a function of temperature from 10 to 300 K for TiNiSn\textsubscript{1-x}Sb\textsubscript{x} for small concentrations of Sb as given by the legend shown above. The inset shows the high temperature power factor ($\alpha^2\sigma T$) for $x = 0.05$ (squares) showing a power factor of 4.5 W/mK at 650 K, the highest temperature measured.

![FIG. 1. (a) Electrical resistivity and (b) thermopower as a function of temperature from 10 to 300 K for the system TiNiSn\textsubscript{1-x}Sb\textsubscript{x} for small concentrations of Sb, as given in the legend. The inset in (a) shows the electrical resistivity as a function of temperature for TiNiSn.](image1)

![FIG. 2. Power factor ($\alpha^2\sigma T$) as a function of temperature from 10 to 300 K for the system TiNiSn\textsubscript{1-x}Sb\textsubscript{x} for small concentrations of Sb as given by the legend shown above. The inset shows the high temperature power factor ($\alpha^2\sigma T$) for $x = 0.05$ (squares) showing a power factor of 4.5 W/mK at 650 K, the highest temperature measured.](image2)
small concentrations of Sb. The power factor maximizes for the Sb concentration in the range \( x = 0.01 \)–0.05. The Sb doping (~0.05) exhibits a relatively large power factor \((\alpha^2 \sigma T)\) of ~1.0 W/mK at room temperature, comparable to that of Bi$_2$Te$_3$ alloys.

As apparent in Fig. 2, the power factor near room temperature is observed to be rapidly increasing as a function of temperature as the temperature is being increased. This makes the need for high temperature measurements of the thermopower and electrical resistivity extremely compelling. The inset of Fig. 2 shows the high temperature power factor \((\alpha^2 \sigma T)\) at \( T \approx 650 \) K of 4.5 W/mK and 3.2 W/mK, respectively. The high temperature electrical resistivity and thermopower data for two of the samples with the highest power factor was melded with data from previous measurements on these same samples to show the power factor from 10 to 600 K. These data give an overlap in temperature between 80 and 300 K to compare the two measurement systems and very good agreement is observed. The data for the TiNiSn$_{0.95}$Sb$_{0.05}$ sample was more noisy than the other sample but for no apparent reason. This sample was measured multiple times. However, it is apparent that the trends with temperature and magnitude are essentially unaffected.

The power factor for TiNiSn$_{0.95}$Sb$_{0.05}$ of 4.5 W/mK at \( T \approx 650 \) K is one of the highest power factors reported on any material. Many of the half-Heusler alloys exhibit similarly high power factor values, which is what makes them so compelling for thermoelectrics. Hohl et al. reported a power factor of 2.8 W/mK at 700 K in an (Hf$_{0.5}$Zr$_{0.3}$)$_{0.93}$Ta$_{0.07}$NiSn alloy which gave a ZT ~0.5 at 700 K. However, the thermal conductivity must be determined in order to fully evaluate these materials for potential thermoelectric applications. The thermal conductivity for the two samples shown in the inset of Fig. 2 is approximately 10–12 W/mK at \( T \approx 300 \) K and these results are being presented elsewhere where a full investigation of the thermal conductivity in many of these materials will be discussed. The thermal conductivity in this system consists mainly of lattice contribution with a small electronic contribution, in contrast to the more favorable situation where \( \lambda_e \sim \lambda_l \) in order to obtain a “good thermoelectric.” We have extrapolated the lattice thermal conductivity to higher temperatures and added to this the calculated electronic part from the measured electrical conductivity via the Wiedemann–Franz relationship. Then an estimate of the figure of merit can be accomplished. These materials exhibit a ZT ~0.5 at the highest temperatures that we have measured and the data are comparable to that found by the Bell group.

An extensive investigation of the effect of Sb doping in the half-Heusler system TiNiSn$_{1-x}$Sb$_x$ is presented via electrical resistivity and thermopower measurements as a function of temperature. These materials exhibit both a high negative thermopower (~40 to ~250 µV/K) and low electrical resistivity values (0.1–8 mΩ cm) which are necessary for a potential thermoelectric material. A very high power factor has been observed in these materials for \( x = 0.05 \) (TiNiSn$_{0.95}$Sb$_{0.05}$) at \( T \approx 650 \) K where it is over 4 W/mK making them attractive for possible power generation considerations. Small amounts of Sb dramatically affect the band structure and thus the electrical transport properties of these materials. However, one of the challenges which remains is to reduce the relatively high thermal conductivity (~10 W/mK) observed in these materials. Efforts to utilize mass fluctuation scattering or control of the grain size, thus decreasing the lattice thermal conductivity due to increased phonon scattering are being employed. However, the high power factors must be maintained and investigations are in progress to further optimize or increase the power factor.

Hall measurements are also in progress to determine the carrier concentration and its effect on the power factor in this class of TiNiSn$_{1-x}$Sb$_x$ materials. Obviously much more work is ahead in order to fully evaluate the potential of these materials for thermoelectric applications. Extensive band structure calculations would certainly provide more guidance in the advancement and understanding in these materials.

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