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Yanzhong Pei, and Donald T. Morelli

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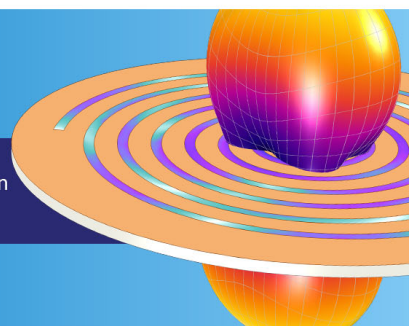
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Vacancy phonon scattering in thermoelectric In_2Te_3 – InSb solid solutions

Yanzhong Pei and Donald T. Morelli^{a)}

Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan 48824, USA

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Solid solution formation is a common and effective approach to reduce the lattice thermal conductivity for thermoelectric materials because of additional phonon scattering by point defects due to mass and strain fluctuations. This scattering is maximal for vacancies. In this paper we present an example of the strong effect of phonon-vacancy scattering for the InSb – In_2Te_3 system. The measured transport properties show a reduction by more than an order of magnitude of the lattice thermal conductivity. Further efforts are also made on optimization for thermoelectric applications through doping. Our results indicate that these solid solutions are a prospective new-type thermoelectric material. © 2009 American Institute of Physics. [DOI: 10.1063/1.3109788]

Mainly driven by worldwide energy concerns, researchers have, in recent years, refocused interest on thermoelectricity as a green energy conversion technology. Thermoelectric (TE) materials provide a valuable and unique opportunity, based on the Seebeck effect, for generating electricity from industrial waste heat. The use of TE power generation can increase the total heat-to-electricity conversion efficiency for these industrial processes. The critical factor for the TE application is the dimensionless figure of merit (ZT) of the TE materials themselves. Mathematically, $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the total thermal conductivity. It is evident from this relation that decreasing the thermal conductivity can be regarded as an efficient approach to enhance ZT . Since the total thermal conductivity has electron (κ_E) and phonon (κ_L) components, and the electrical thermal conductivity is related to the electrical conductivity by the Wiedemann–Franz law ($\kappa_E = L\sigma T$, where L is the Lorentz constant), an effective approach to decrease the thermal conductivity is to minimize κ_L .

During the past decades, much effort has been expended in developing approaches to reduce the lattice thermal conductivity: alloy scattering,¹ “rattle” scattering in phonon glass electron crystal,^{2,3} and, very recently, nanostructure scattering to reduce the phonon mean free path^{4,5} are some examples. The alloy scattering approach has already achieved significant increases in ZT for both the traditional TE SiGe (Ref. 6) and the recent half-Heusler TE compounds.^{7–9} It has also been clearly demonstrated that the atomic mass difference between the guest and host plays the key role on the reduction in the lattice thermal conductivity,^{10–12} and the scattering parameter (A) can be written as the following expression:¹⁰

$$A = \frac{\Omega_0}{4\pi v^2} x(1-x) \left(\frac{\Delta M}{M} \right)^2. \quad (1)$$

Here, Ω_0 , v , x , ΔM , and M stand for the volume of the unit cell, the lattice sound velocity, the fraction of the guest atom, the atomic mass difference between the guest and host, and

the average mass of the cell, respectively. According to this equation, one can find that the larger the mass difference, the larger will be the reduction in κ_L . The maximal phonon scattering by mass fluctuation should be expected in a defect crystal structure because the maximum atomic mass difference can be achieved on one or more lattice sites.

Here we focus on the zincblende-structure solid solutions and, in particular, the case of $(\text{In}_2\text{Te}_3)_x(\text{InSb})_{3-3x}$. The host InSb is an important semiconductor for use in long-wavelength optoelectronic devices and galvanomagnetic and magnetic sensors. It has also been demonstrated that InSb has excellent TE power factor ($\text{PF} = S^2\sigma$) due to its extremely high carrier mobility,^{13,14} further optimization for high-efficiency TE applications would require reductions in both electronic and lattice thermal conductivities. It is interesting to note that the compound In_2Te_3 also crystallizes in the zincblende structure, but with a vacancy on the indium sublattice site.¹⁵ Furthermore, Woolley^{16–18} found that the In_3Sb_3 – In_2Te_3 solid solutions also crystallize in the zincblende structure with a solubility of up to 15 mol %. It is reasonable to expect that the formation of solid solutions and the resulting occurrence of vacancies on the In site will induce large mass fluctuation (or vacancy scattering) and thus lead to an effective reduction in κ_L and an improved TE performance. Of course, the influence of the vacancy on the electrical transport properties of these compounds is also of critical importance.

In this letter, we describe our results on the synthesis and characterization of a series of In_3Sb_3 – In_2Te_3 solid solutions with and without doping. Transport properties between 80 and 300 K are presented. The influence of vacancy scattering on the lattice thermal conductivity is investigated. In agreement with the work of Aliev and Dzhangir,^{19,20} we find that these solutions, due to their high carrier concentrations, have very large electrical conductivity and thus a large electronic contribution to the thermal conductivity. Therefore we have also studied doping on the In site in $\text{In}_{2.85}\text{Sb}_{2.55}\text{Te}_{0.45}$ in an attempt to lower both the lattice thermal conductivity and the electrical conductivity. Finally, the potential of these materials, and the general approach of the use of vacancy compounds in high-efficiency TE applications, is discussed.

Solid solutions with a composition of $(\text{In}_2\text{Te}_3)_x(\text{InSb})_{3-3x}$ were synthesized by the vacuum melting

^{a)} Author to whom correspondence should be addressed. Electronic mail: dmorelli@egr.msu.edu.

method. Stoichiometric quantities of the constituent pure elements were loaded into a quartz ampoule that was subsequently sealed under vacuum. The ampoule was hung vertically in a tube furnace and heated to 1123 K at a rate of 5 K/min. After soaking at this temperature for approximately 5 h, the ampoule was slowly cooled (~ 0.3 K/min) to 750 K and held at that temperature for annealing for approximately 72 h before cooling to room temperature at a rate of 0.3–0.5 K/min. Slow cooling was used to avoid ampoule explosion during the process. Samples with a composition of $(\text{In}_{2.85})_{1-\delta}\text{Sb}_{2.55}\text{Te}_{0.45}$ were also synthesized in an attempt to reduce the electrical conductivity. The resulting ingots were sectioned into rectangular parallelepiped samples with approximate dimensions of $3.5 \times 3.5 \times 8.5$ mm³ for thermal and electrical transport measurements.

The phase compositions for the samples were determined by powder x-ray diffraction (XRD) analysis using Cu $K\alpha$ radiation. Both the electrical and the thermal transport properties were measured from 80 to 300 K using liquid nitrogen as the refrigerant. The samples were measured under vacuum using a steady state technique in a continuous flow or a bath-type cryostat. Copper-Constantan thermocouples were soldered directly to the sample along its length and were used to measure temperature along the sample. One end of the sample was soldered directly to the cryostat cold tip and the other to an 800 Ω metal film resistor which served as a heater. Electrical conductivity was measured by passing current through the sample and recording the voltage developed between the copper leads of the thermocouples. These copper leads were also used to measure the Seebeck voltage when energizing the heater. The Seebeck coefficient was calculated from the Seebeck voltage and the temperature difference induced by the heater. The heater power, sample dimensions, and temperature difference were used to determine the thermal conductivity.

As initially determined by Woolley,^{16–18} the solubility of In_2Te_3 in InSb can reach 15 mol %. It is also known that the addition of In_2Te_3 to InSb increases the electron concentration from $\sim 10^{16}$ to $\sim 10^{19}$ cm⁻³, and the carrier mobility remains roughly constant when the mole concentration of In_2Te_3 is higher than 5%.¹⁷ Based on Eq. (1), a larger concentration of In_2Te_3 (x) will produce a more effective scattering of phonons by the mass fluctuation effect. For this reason we have synthesized and investigated the transport properties for the solid solutions with high In_2Te_3 concentrations, which have not been investigated yet. Furthermore, as discussed above, in order to reduce the electrical conductivity and thus to lower the electronic contribution to the total thermal conductivity, we also have studied the effect of In deficiency. Figure 1 shows the XRD patterns for the solid solution with highest In_2Te_3 concentration both with and without In deficiencies. It is evident that we obtain a pure phase with the zincblende structure for x of up to 15%, consistent well with Woolley's¹⁸ observation. The XRD patterns also tell us that we can obtain single zincblende phase for In deficiency δ less than or equal to 1%. For the sample with 2% In deficiency, a small amount of secondary phase is detected, which is an alloy with a rocksalt structure according to the literature.^{18,21} It should be also addressed that all of the samples are fully crystallized since sharp XRD peaks are found here.

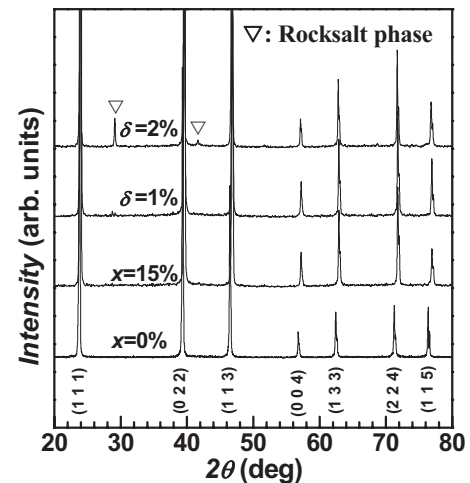


FIG. 1. XRD patterns for $(\text{In}_2\text{Te}_3)_x(\text{InSb})_{3-3x}$ (bottom 2) and $(\text{In}_{2.85})_{1-\delta}\text{Sb}_{2.55}\text{Te}_{0.45}$ (top 2).

Of highest interest here for the solid solutions is the significant reduction in the thermal conductivity. The huge thermal conductivity of pure InSb at both low and high temperatures frustrates its application as a high-efficiency TE material, although the TE PF is very large due to extremely high electron mobility.^{13,14} Figure 2 plots the lattice thermal conductivity for $(\text{In}_2\text{Te}_3)_x(\text{InSb})_{3-3x}$ solid solutions at 80 and 300 K. Here, the lattice thermal conductivity is obtained by subtracting the electrical component, estimated by Weidemann–Franz law, from the measured total thermal conductivity. We see that the lattice thermal conductivity has been reduced by more than an order of magnitude. The reduction is stronger at low temperatures because the relative contribution of umklapp scattering of phonons is decreased compared to that at high temperature. According to the Callaway–Klemens model^{10–12} and based on the simple case of Te substitution for Sb, the reduction in lattice thermal conductivity should be quite limited for $(\text{In}_2\text{Te}_3)_x(\text{InSb})_{3-3x}$ solid solutions due to the negligible mass and atomic size difference between Te and Sb. Our results are not consistent with this picture, and we speculate that this is due to the introduction of the vacancy on the indium sublattice site when the solid solution is formed. This ability of the vacancy to strongly reduce lattice thermal conductivity can be best appreciated by comparing these compounds to other solid solutions. For instance, the alloying approach has been ap-

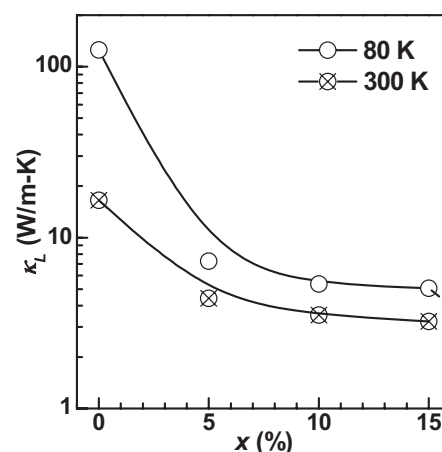


FIG. 2. Lattice thermal conductivity vs In_2Te_3 fraction for $(\text{In}_2\text{Te}_3)_x(\text{InSb})_{3-3x}$ at 80 and 300 K.

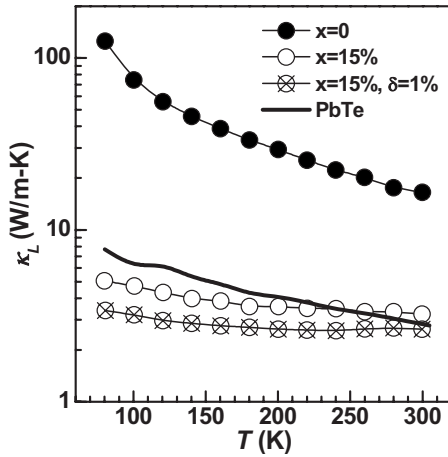


FIG. 3. Temperature dependent lattice thermal conductivity for InSb, $(\text{In}_2\text{Te}_3)_{0.15}(\text{InSb})_{2.55}$, $(\text{In}_{2.85})_{1-\delta}\text{Sb}_{2.55}\text{Te}_{0.45}$, and a typical PbTe sample for comparison.

plied successfully to reduce the lattice thermal conductivity for half-Heusler compounds,⁷⁻⁹ and the most effective κ_L -reduction reported so far can be found in the fully substituted $(\text{Zr}_{0.5}\text{Hf}_{0.5})_{0.5}\text{Ti}_{0.5}\text{NiSn}_{0.994}\text{Sb}_{0.006}$.⁹ The κ_L -reduction for the sample with $x=15\%$ in the present work is comparable with that report, although the concentration of the scattering center (vacancies on In site) is only $x/3=5\%$. This strongly suggests that the vacancy scattering process is highly effective for the reduction in the lattice thermal conductivity. Furthermore, doping on indium site results in a further κ_L -reduction as well as optimization of the electrical transport properties; we will discuss this in detail in the following paragraphs.

To discuss the potential application of these solid solutions as thermoelectrics, we plot in Fig. 3 the temperature dependent lattice thermal conductivity for several typical compounds. Introducing deficiency on the In site results in an even higher vacancy concentration and κ_L can be further lowered as shown in the figure. We note that the reduction is more than an order of magnitude over a wide temperature range for $\delta=1\%$ when compared with the vacancy-free InSb sample. It should be also noted that the ordering state of the vacancies may play an important role in κ_L -reduction;²² a more detailed study of the nature of vacancies induced by In deficiency and the formation of solid solution and their effects on κ_L in these compounds will be the next step in our study. For comparison, one typical state-of-the-art TE material, PbTe, is also plotted in Fig. 3. We can find that the κ_L for some of the solid solutions are comparable to or even lower than that of PbTe.

As has been pointed out in previous paragraphs, to further optimize the electrical properties for these solid solutions, we have tried creating a deficiency on the indium site to reduce the electron concentration and thus to lower the electrical conductivity. The room temperature transport data are shown in detail in Fig. 4. Here we find that the lattice thermal conductivity is further lowered from 3.2 W/m K for $\delta=0$ to 2.4 W/m K for $\delta=2\%$ due to the introduction of additional vacancies. Simultaneously, the electrical conductivity is also reduced while the TE PF remains unchanged and is comparable with that of PbTe samples synthesized and characterized in our laboratory.

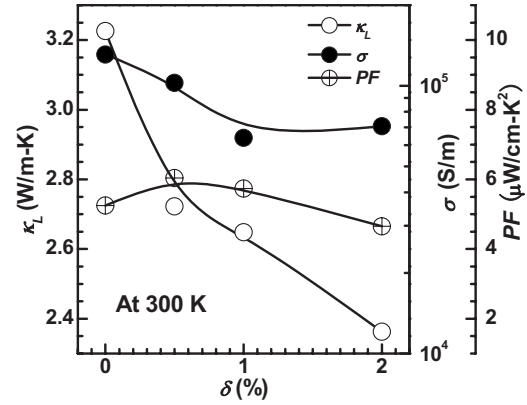


FIG. 4. Room temperature transport properties vs d for solid $(\text{In}_{2.85})_{1-\delta}\text{Sb}_{2.55}\text{Te}_{0.45}$ solutions.

To summarize our present work, $\text{In}_3\text{Sb}_3\text{-In}_2\text{Te}_3$ solid solutions with and without In deficiencies have been synthesized and characterized. Due to strong phonon-vacancy scattering, significant reduction in the lattice thermal conductivity is obtained for the solid solutions. The resulting electrical and thermal transport properties of these solid solutions are comparable to typical TE semiconductors such as PbTe. The use of vacancy structures such as these thus represents a new route to high-efficiency TE materials. Further investigations of the electrical transport properties and the high temperature TE properties of these compounds will be carried out in the near future.

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- ¹A. F. Ioffe, *Physics of Semiconductors* (Academic, New York, 1960), p. 282.
- ²G. A. Slack, in *CRC Handbook of Thermoelectrics*, edited by D. M. Rowe (CRC, Boca Raton, FL, 1995), Chap. 34.
- ³G. S. Nolas, J. L. Cohn, G. A. Slack, and S. B. Schujman, *Appl. Phys. Lett.* **73**, 178 (1998).
- ⁴B. Poudel, Q. Hao, Y. Ma, Y. Lan, A. Minnich, B. Yu, X. Yan, D. Wang, A. Muto, D. Vashaee, X. Chen, J. Liu, M. S. Dresselhaus, G. Chen, and Z. Ren, *Science* **320**, 634 (2008).
- ⁵W. Kim, J. Zide, A. Gossard, D. Klenov, S. Stemmer, A. Shakouri, and A. Majumdar, *Phys. Rev. Lett.* **96**, 045901 (2006).
- ⁶C. B. Vining, in *CRC Handbook of Thermoelectrics*, edited by D. M. Rowe (CRC, Boca Raton, FL, 1995), Chap. 28.
- ⁷C. Uher, J. Yang, S. Hu, D. T. Morelli, and G. P. Meisner, *Phys. Rev. B* **59**, 8615 (1999).
- ⁸J. Yang, G. P. Meisner, and L. Chen, *Appl. Phys. Lett.* **85**, 1140 (2004).
- ⁹S. Sakurada and N. Shutoh, *Appl. Phys. Lett.* **86**, 082105 (2005).
- ¹⁰J. Callaway and H. C. von Baeyer, *Phys. Rev.* **120**, 1149 (1960).
- ¹¹P. G. Klemens, *Proc. Phys. Soc., London, Sect. A* **68**, 1113 (1955).
- ¹²B. Abeles, *Phys. Rev.* **131**, 1906 (1963).
- ¹³D. L. Rode, *Phys. Rev. B* **3**, 3287 (1971).
- ¹⁴S. Yamaguchi, T. Matsumoto, J. Yamazaki, N. Kaiwa, and A. Yamamoto, *Appl. Phys. Lett.* **87**, 201902 (2005).
- ¹⁵V. P. Zhuze, A. I. Zaslavskii, V. A. Petrushevich, V. M. Sergeeva, I. A. Smirnov, and A. I. Shelyhh, Proceedings of the 17th International Conference on Physics of Semiconductors, 1960 (unpublished), p. 871.
- ¹⁶J. C. Woolley and B. A. Smith, *Proc. Phys. Soc. London* **72**, 867 (1958).
- ¹⁷J. C. Woolley, C. M. Gillet, and J. A. Evans, *J. Phys. Chem. Solids* **16**, 138 (1960).
- ¹⁸J. C. Woolley, *J. Electrochem. Soc.* **113**, 465 (1966).
- ¹⁹M. I. Aliev and A. Y. Dzhangir, *Sov. Phys. Solid State* **6**, 1916 (1965).
- ²⁰M. I. Aliev and A. Y. Dzhangir, *Sov. Phys. Solid State* **5**, 2447 (1964).
- ²¹S. I. Radautsan and I. P. Molodtsov, *Izv. Moldavsk. filial AN SSSR* **3**, 37 (1960).
- ²²K. Kurosaki, H. Matsumoto, A. Charoenphakdee, S. Yamanaka, M. Ishimaru, and Y. Hirotsu, *Appl. Phys. Lett.* **93**, 012101 (2008).