Thermoelectric properties of Tl_2SnTe_5 and Tl_2GeTe_5

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We report on the thermoelectric properties of two ternary tellurides with known crystal structures. Both compounds have a very low lattice thermal conductivity. Tl_2SnTe_5 appears to have a *p*-type figure of merit about the same as that of Bi_2Te_3, the best thermoelectric material among binary compounds. We have synthesized mainly polycrystalline samples, but a few small crystals have been grown and used for electrical measurements. Prospects for further improvement of these materials are discussed. © *1999 American Institute of Physics.* [S0003-6951(99)02925-3]

The thermoelectric effect is used for a wide variety of small-scale cooling applications. In the important temperature range of 250–350 K, the best materials known are solid solutions found in the Bi_2Te_3–Sb_2Te_3–Bi_2Se_3 system. We are engaged in an exploration of ternary tellurides and antimonides aimed at discovering a material with advanced thermoelectric performance in this temperature range. In this letter, we report on the properties of two tellurides selected for study as novel thermoelectric materials. One of these compounds seems to have a thermoelectric figure of merit comparable to that of *p*-type Bi_2Te_3.

With a few exceptions, binary compounds that are plausible thermoelectric candidates have been considered. Many ternary compounds have been investigated also,[1] but most of these have been adaptations of binary compounds, with or without a preservation of the overall stoichiometry. For instance, Cu_2GeSe_3 and $CuIn_2Se_4$ are derived from the binary zincblende structure.[2] By contrast, our approach is to investigate the thermoelectric properties of ternary tellurides and antimonides that adopt advantageous and largely unexplored crystal structures. These ternary systems are an opportune field in which to search for crystalline semiconductors that approach the ideal ''phonon glass.''[3]

The Tl–Sn–Te[4] and Tl–Ge–Te[5] systems both contain several ternary compounds, including a 2-1-5 composition in both systems. Some crystal structure data for Tl_2SnTe_5 (TST) and Tl_2GeTe_5 (TGT) are given in Table I. Both compounds are tetragonal and contain columns of Tl ions along the crystallographic *c* axis. The large interatomic distances for the eight-fold coordinated Tl ions (Table I) are one of the main reasons these compounds were selected as thermoelectric candidates. Transverse to the *c* axis these columns alternate with chains of composition $(Sn/Ge)Te_5$. In TST (Fig. 1), the chains can be described as $SnTe_4$ tetrahedra linked by Te atoms that are in square-planar coordination. The $GeTe_5$ chains in TGT are better described as the alternation of Te_4 square rings and edge-sharing pairs of $GeTe_4$ tetrahedra (corresponding to a composition of Ge_2Te_6 for each pair of tetrahedra). TST and TGT can be viewed as polytypes of one another, with different stacking sequences of $(Ge/Sn)Te_4$ tetrahedra and $TeTe_4$ square planar units linked into chains by edge sharing.[6]

For polycrystalline sample synthesis, the starting materials were sealed in silica tubes that were coated with pyrolytic carbon, evacuated and backfilled with argon (approximately one-third atmosphere). Single phase samples of TST and TGT were made by mixing the elements at 750 °C, quenching the melt and annealing for a few days at temperatures just below the melting points. We find that both compounds melt incongruently, and the melting points are approximately 285–290 °C for TST and 265–270 °C for TGT. For TGT, our results contradict the report of congruent melting at approximately 322 °C,[7] a temperature at which we have observed a second melting event.

X-ray diffraction patterns of our polycrystalline samples agree well with the powder pattern calculated from the reported crystal structures. Neutron scattering experiments were performed at the High Flux Isotope Reactor of Oak Ridge National Laboratory using a powder neutron diffractometer equipped with a closed-cycle liquid helium refrigerator. Neutron diffraction was used to refine the structure and calculate atomic displacement parameters (ADP). ADP values measure the mean-square displacement amplitude of an atom about its equilibrium position in a crystal. A large ADP value means that the atom is weakly bound in the structure. ADP information can be used to identify new crystalline solids with abnormally low values of the lattice thermal conductivity (κ_L).[8] In both structures, there are large ADPs for the Tl ions and some of the Te atoms. This is an expected result for eight-fold coordinated Tl atoms with nearest neighbors (Te atoms in this case) that are distant relative to the sum of the corresponding covalent or ionic radii. As seen in Table I, our neutron diffraction data show the same ADP trends as the x-ray diffraction data in the literature. For TGT, the ADP values are from a structure refinement[7] that has been questioned,[9] but the atomic coordinates changed little in the revised cell.

Polycrystalline samples ($\sim 6\times 6\times 13\,mm^3$) for transport measurements were taken from quenched and annealed specimens or from hot pressed specimens. Adequate conditions for hot pressing TGT and TST to approximately 97% of x-ray density are 23.5 kpsi for one hour at 250–270 °C. A graphite die was used and lined with graphite foil to ease

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TABLE I. Crystal data for Tl_2SnTe_5 and Tl_2GeTe_5. In each case, the second isotropic thermal parameter value is from our neutron diffraction data.

	Tl_2SnTe_5[a]	
Tetragonal		
$a=8.306$ Å, $c=15.161$ Å	Interatomic distances	Isotropic thermal parameters
Space group $I4/mcm$ 32 atoms/cell x-ray density=7.40 g/cm^3	Tl(1): 8 Te at 3.49 Å Tl(2): 8 Te at 3.66 Å	Tl(1): 1.34, 2.02 Å^2 Tl(2): 3.71, 3.87 Å^2
	Tl_2GeTe_5[b,c]	
Tetragonal		
$a=8.243$ Å, $c=14.918$ Å	Tl–Te distances (Å)	Isotropic thermal parameters
Space group P4/mbm 32 atoms/cell x-ray density=7.34 g/cm^3	Tl(1): 4 at 3.53, 4 at 3.79 Tl(2): 4 at 3.38, 4 at 3.54	Tl(1): 3.81, 3.28 Å^2 Tl(2): 1.95, 1.66 Å^2

[a]Reference 6.
[b]Reference 7.
[c]Reference 9.

ejection of the sample. An average grain size in the polycrystalline samples was 25 μm, with a wide distribution. Small single crystals ($\sim 2.5\times 2.5\times <1$ mm^3) were grown (flux composition$\cong TlTe_2$) and used for electrical measurements in the *ab* plane. All samples appear to be stable in air, water and common solvents.

The transport properties of four samples are shown in Figs. 2–4. The data shown here were collected by using a small heater to create the temperature gradient, with thermocouples (1 to 3 mil wires) epoxied onto a lateral face of the sample. Current was injected via a conductive epoxy with which the 6×6 mm^2 sample faces were coated. All three properties are measured in the same direction. The transport properties of similar samples have been tested in two additional systems. One of these also uses a heater to create the temperature gradient. In this apparatus, the heat flow through the sample was calibrated by a comparative technique[10] using Pyrex 7740 standards and published thermal conductivity (κ) data taken by the 3ω method.[11] The third measurement system employs the Harman method, in which the Peltier effect is used to create the required temperature gradient. In this apparatus, the probe wires are connected to copper caps that are soldered to samples that have been nickel plated. All three systems give results consistent with one another.

The Seebeck coefficient (S) data (Fig. 2) indicate that TST and TGT are small band gap semiconductors and that these undoped samples are p type. From the maxima of the Seebeck coefficients as a function of temperature, we estimate the band gaps as approximately 0.25 and 0.17 eV for TST and TGT, respectively.[12] Hall measurements on a TST sample with a Seebeck coefficient of 210 μV/K at room temperature yielded a carrier concentration and mobility of $p=2.8\times 10^{19}$ cm^{-3} and $\mu=55$ cm^2/V s. Similarly, for a TGT sample with $S=270\,\mu$V/K at 300 K, we found $p=2.0\times 10^{19}$ cm^{-3} and $\mu=26$ cm^2/V s. While solid solutions are

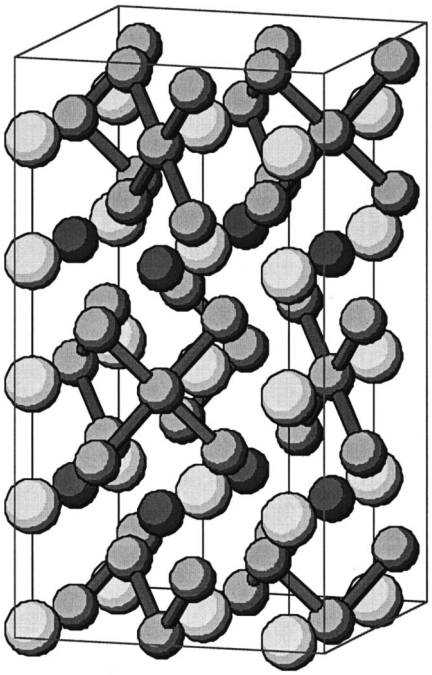

FIG. 1. Crystal structure of Tl_2SnTe_5. The larger spheres represent Tl, and the darker small spheres represent Sn. There are no Tl–Tl bonds, but the Tl atoms have been connected by thin lines to show their arrangement along the (vertical) c axis. $TeTe_4$ square planar units have been emphasized. For clarity, the Sn–Te (tetrahedral Sn) and Tl–Te bonds are not shown. There are two eightfold sites for Tl: cubic and square antiprism.

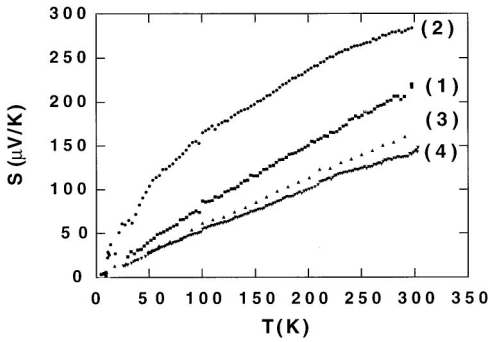

FIG. 2. Seebeck coefficient data for three polycrystalline samples and one single crystal sample: (1) TST, (2) TGT, (3) hot pressed TST, (4) TST single crystal. Samples 1 and 2 were melted, quenched, and annealed. Electrical properties were measured in the *ab* plane of the platelet-shaped single crystal.

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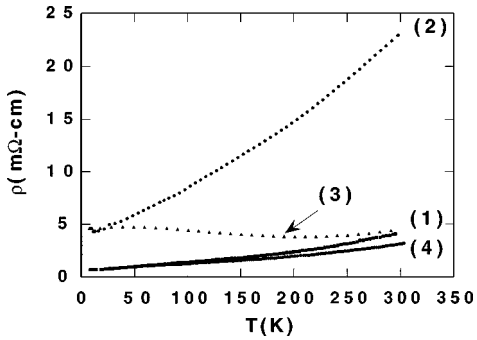

FIG. 3. Electrical resistivity data for three polycrystalline samples and one single crystal sample. The geometry (length-to-area ratio) uncertainty is ±15%. Refer to Fig. 2 for sample descriptions.

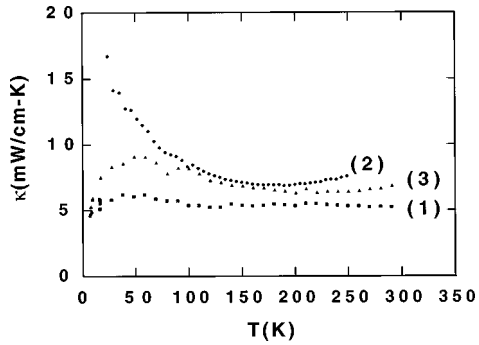

FIG. 4. Thermal conductivity data for three polycrystalline samples. The geometry (length-to-area ratio) uncertainty is ±15%. Refer to Fig. 2 for sample descriptions.

often studied in thermoelectric materials research to lower κ_L, we have mixed TST and TGT in order to change the Seebeck coefficient, which increases in going from TST to TGT. It appears that there is full solubility between TST and TGT. We believe that the TGT structure is found except when the Ge fraction is less than 10%, but the TST and TGT powder patterns are quite similar. A sample with 10% Se substitution for Te was multiphase. We have not been able yet to make *n*-type samples for either TST or TGT.

The behavior of the electrical resistivity (ρ) as a function of temperature (Fig. 3) has been less straightforward. The single crystals and a few quenched/annealed or hot pressed samples exhibit a resistivity that decreases approximately linearly with T between 150 and 300 K. However, the resistivity of many quenched/annealed or hot pressed samples reaches a minimum between 200 and 250 K and increases as the temperature is lowered further. We believe this behavior indicates a contribution from cracking and/or grain boundary resistance. Hot pressed samples have a higher resistivity, especially below 250 K, if they are powdered before pressing than if they are pressed from larger fragments. Also, the resistivity of some samples displays a hysteresis as the temperature is cycled, being lower during cooling than during warming.

κ is very low for both TST and TGT (Fig. 4). Apparently κ_L in these samples is not more than 5 mW/cm K. This is less than 1/3 of the value for pure Bi_2Te_3. κ is rather flat from 100 to 300 K, which is typical for crystalline compounds in which the thermal conductivity approaches the glass-like limit.[13] The measured increase in κ for TGT above 200 K probably is a radiation effect that is more or less significant depending on sample geometry. Because no corrections have been applied to the thermal conductivity data, we expect that the curves in Fig. 4 are slightly higher than reality, except for cases in which the thermocouple spacing is underestimated. At room temperature, the electronic contribution to κ is estimated to be about 20% for TST, but less than 10% for TGT due to the higher resistivity.

For sample 1 (Figs. 2–4), the dimensionless thermoelectric figure of merit, $ZT = S^2T/\rho\kappa$, reaches a value of 0.6 at 300 K and is estimated to peak at 0.85 at 400 K. For comparison, the maximum ZT for Bi_2Te_3 at 300 K also is 0.6.

In summary, the thermoelectric properties of two ternary tellurides have been studied. Both compounds have very low values of κ_L. In the case of Tl_2SnTe_5, the electronic properties obtained to date yield a dimensionless figure of merit equal to that of *p*-type Bi_2Te_3. Regarding further improvements of this compound, there is little expectation of lowering κ_L, and near optimum Seebeck coefficients have been achieved already. It may be possible to improve the electrical properties, if in fact grain boundaries are hindering current flow in the present samples. Also, it could be that *n*-type samples, if they can be fabricated, will possess a larger figure of merit. Solid solutions containing K_2SnTe_5 or Rb_2SnTe_5, which have structures equivalent to that of TST, might yield *n*-type samples. Regardless of whether any further improvement can be realized for TST, we are encouraged by the present results and by those of others taking a similar approach.[14]

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