Intrinsically Minimal Thermal Conductivity in Cubic I-V-VI$_2$ Semiconductors

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We report measurements of the thermal conductivity of high-quality crystals of the cubic I-V-VI$_2$ semiconductors AgSbTe$_2$ and AgBiSe$_2$. The thermal conductivity is temperature independent from 80 to 300 K at a value of approximately 0.70 W/mK. Heat conduction is dominated by the lattice term, which we show is limited by umklapp and normal phonon-phonon scattering processes to a value that corresponds to the minimum possible, where the phonon mean free path equals the interatomic distance. Minimum thermal conductivity in cubic I-V-VI$_2$ semiconductors is due to an extreme anharmonicity of the lattice vibrational spectrum that gives rise to a high Grüneisen parameter and strong phonon-phonon interactions. Members of this family of compounds are therefore most promising for thermoelectric applications, particularly as p-type materials.

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AgSbTe$_2$ is known as the bulk p-type thermoelectric material with the highest figure of merit ZT [1] of all simple semiconductors: ZT reaches 1.3 at 720 K, [2,3] a temperature range relevant to applications in electrical power generation that use fossil fuel combustion as a heat source. Like PbTe, it crystallizes in the rocksalt structure, with a similar lattice constant ($a = 0.6462$ for PbTe and $a/2 = 0.6076$ nm for AgSbTe$_2$). AgSbTe$_2$ is the paradigm for the class of I-V-VI$_2$ "semiconductors," where the group V element can be P, As, Sb, or Bi, the group VI element S, Se, or Te, and the group I element Cu, Ag, or Au [4], or alternatively an alkali metal [5]. Many I-V-VI$_2$ semiconductors are known to crystallize in the rocksalt structure [6], as do the classic IV-VI semiconductors.

One of the principal features of semiconductor thermoelectrics is a low lattice thermal conductivity. Anharmonicity of the chemical bond drives the phonon-phonon umklapp and normal processes that intrinsically limit the high-temperature lattice thermal conductivity [7]. Octahedral coordination in the rocksalt semiconductors such as PbTe has a high degree of anharmonicity, which lowers their lattice thermal conductivity κ_L by about a factor of 4 compared to tetrahedrally bonded semiconductors with similar or better electronic properties such as GaAs, InAs, and InSb [8]; this in turn leads to much larger ZT values, even though the III-V's have a higher mobility and thus often a higher power factor. The I-V-VI$_2$ semiconductors have twice the unit cell of the IV-VI's, and a correspondingly lower κ_L. In this Letter, we show, in particular, that the cubic I-V-VI$_2$ compounds AgSbTe$_2$ and AgBiSe$_2$ possess an anharmonicity even higher than that of PbTe, resulting in a phonon-phonon-limited lattice thermal conductivity κ_L that is smaller by an additional factor of 4. Because of this strong intrinsic phonon scattering, these compounds are a unique example of a crystalline material whose lattice thermal conductivity exhibits the minimum possible value due to intrinsic phonon processes alone. Such "minimum thermal conductivity" behavior has been observed before, of course, in crystalline materials such as KBr-KCN mixed crystals, but the glass-like thermal conductivity observed in that case is due to a resonant-type scattering from defect states.

Surprisingly little is known about the pure ternary I-V-VI$_2$ semiconductors, the first of which were identified [9] as chalcopyrites related to zinc-blende structures. By 1957, rocksalt AgSbSe$_2$ and AgSbTe$_2$ were synthesized [10], and have been identified as narrow-gap semiconductors or perhaps semimetals [11]. It was noted early on that the room temperature thermal conductivity of AgSbTe$_2$ is extremely small, on the order of $\kappa \sim 0.63$ W/mK [12], and similarly low values were measured on other I-V-VI$_2$ compounds [13]. Alloys of AgSbTe$_2$ and AgBiTe$_2$ with PbTe, SnTe [14], and GeTe [15] are well-known thermoelectric materials. The recently reported AgPb$_m$SbTe$_{2+m}$ bulk alloys [16] have $ZT = 2.1$ at 800 K, and, from a metallurgical perspective, can be viewed [14,15] as solid solutions of AgSbTe$_2$ with PbTe, although this picture is oversimplified [17]. Both AgPb$_m$SbTe$_{2+m}$ and (AgSbTe$_2$)$_{1-x}$(GeTe)$_x$ alloys are reported to contain nanoscale inclusions [16,18]. It is often assumed that carefully designed nanostructures limit the lattice thermal conductivity by scattering the long-wavelength phonons. The present report describes a lattice thermal conductivity which is intrinsically limited to the minimum possible value, solely by phonon-phonon interactions, and this creates a path to thermoelectrically relevant materials without the need for nanostructure; such materials are therefore inherently easier to prepare and control, and circumvent the possibility that the nanostructures may grow or dissolve during prolonged high-temperature operation. One also recognizes that, unlike most materials used in thermoelectric power generation, $AgSbTe_2$, $AgBiSe_2$, and their alloys are lead-free and thus environmentally friendly.

Several polycrystalline ingots of cubic $AgSbTe_2$ and $AgBiSe_2$ were prepared using conventional solid-state chemistry techniques similar to those used for PbTe [19,20]. The $AbSbTe_2$ ingots have crystallites exceeding several mm on a side; the crystallites tend to grow preferentially along the $\langle 111 \rangle$ axis, and display de Haas–van Alphen quantum oscillations illustrating their homogeneity, very high crystalline quality, and single-crystal nature. The ingots of rocksalt $AgBiSe_2$ had to be quenched, as the stable crystallographic phase of that material below 287 °C is hexagonal [21], and the crystallites are consequently of much finer size. X-ray diffraction spectra of powder ground from one ingot each of $AgSbTe_2$ and $AgBiSe_2$ are shown in Fig. 1. The data reveal clean rocksalt structures with the correct lattice constants ($a_0 = 0.608$ nm for $AgSbTe_2$ and $a_0 = 0.583$ nm for $AgBiSe_2$); there is no evidence of any second phase. The Seebeck coefficient was uniform along the ingots, with several samples cut from the same ingot giving a repeatability of 2 to 3%. We also prepared an ingot of a I-III-VI_2 compound, $AgInTe_2$ (a chalcopyrite, $a_0 = 0.6406$ nm, $c_0 = 1.256$ nm) in order to contrast the thermal conductivity of compounds of this structure type with that of the I-V-VI_2 compounds.

The thermal transport data were measured using a conventional static heater-and-sink method. The samples were cut as parallelepipeds from the ingots using a diamond saw, and deliberately kept small in order to minimize the effects of potential inhomogeneities. The thermal conductivity data were taken on several samples with a large cross section (3×3 mm^2) cut from neighboring regions of the ingot, in order to maintain the samples' thermal conductance near 4 mW/K. While radiative heat exchange was minimized by the use of radiation shields to below 0.4 mW/K, it was not compensated for in the data presented. The inaccuracy in sample dimensions, and particularly in the distance between the longitudinal probes, is the main source of experimental inaccuracy; we estimate it to be approximately 5%.

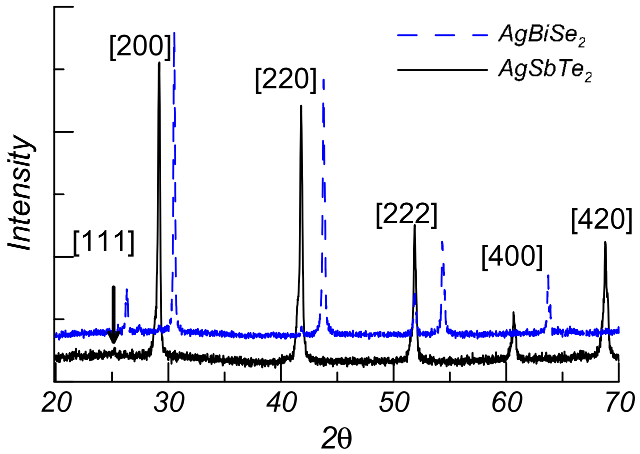

FIG. 1 (color online). X-ray diffraction spectra of ingots of $AgSbTe_2$ (solid line) and $AgBiSe_2$ (dashed line). The data are uniform over the ingots, and have been repeated on 3 different ingots.

The thermal conductivity measured on the three compounds $AgSbTe_2$, $AgBiSe_2$, and $AgInTe_2$ are displayed in Fig. 2, and compared to that of a single crystal of PbTe also synthesized and measured in our laboratories. We wish to point out here that for all of these samples, the carrier concentration is low enough that the lattice thermal conductivity is the overwhelmingly dominant heat conduction channel, with a maximum electronic thermal conductivity contribution of 5% for the $AgSbTe_2$ sample. Samples with higher carrier concentration exhibit significant electronic and ambipolar contributions to the thermal conductivity; this behavior is discussed elsewhere [20]. Here these electronic effects are negligible and we focus on the lattice thermal conductivity. For the two cubic structure I-V-VI_2 compounds the thermal conductivity is in the range 0.6–0.7 $W\,m^{-1}\,K^{-1}$ at room temperature, consistent with the literature value of 0.63 W/mK [12,13], and is practically independent of temperature over the entire range

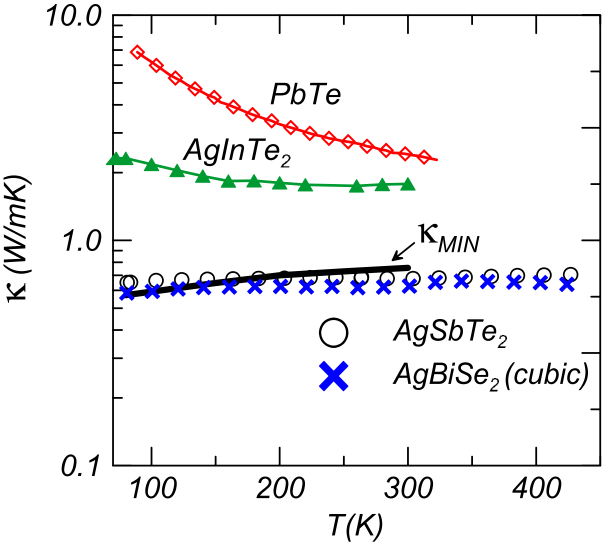

FIG. 2 (color online). Experimental temperature dependence of the thermal conductivity of two I-V-VI_2 cubic semiconductors $AgSbTe_2$, $AgBiSe_2$, of single-crystal PbTe, and of the chalcopyrite compound $AgInTe_2$. The electronic contributions to the thermal conductivity are negligible in all samples; thus, the data shown represent the lattice thermal conductivity. Also shown is a calculation of the minimum thermal conductivity for $AgSbTe_2$.

studied. The thermal conductivities of $AgInTe_2$ and PbTe, on the other hand, are close to 1.8 and 2.4 $W\,m^{-1}\,K^{-1}$ at room temperature, respectively, and show a temperature-dependence characteristic of umklapp-process scattering.

The reproducibility of the low lattice thermal conductivity of the different I-V-VI_2 compounds suggests that it is not limited by defect structures but by an intrinsic and inherently very reproducible mechanism, such as a phonon-phonon process. The intrinsic thermal conductivity of a solid in a temperature range in which heat is conducted only by acoustic phonons, and in which there are only interactions among the phonons themselves by anharmonic umklapp processes, is given by [22]

$$\kappa_L = A\frac{\bar{M}\theta^3\delta}{\gamma^2 n^{2/3}T}. \tag{1}$$

Here n is the number of atoms in the primitive unit cell, δ^3 is the volume per atom, θ is the Debye temperature, $\bar{M}$ is the average mass of the atoms in the crystal, and A is a collection of physical constants ($A \approx 3.1 \times 10^{-6}$ if κ is in W/mK, $\bar{M}$ in amu, and δ in Angstroms). The high-temperature limit of the acoustic phonon mode Grüneisen parameter is γ, which is a direct measure of the anharmonicity of the bonds, and defined as [23]

$$\gamma = \frac{3\beta B V_m}{C_V} \tag{2}$$

where β is the volume thermal expansion coefficient, B is the isothermal bulk modulus, C_V the isochoric specific heat per mole, and V_m is the molar volume. For $AgSbTe_2$, we have $n = 4$, and find B [24] and β in the literature. In order to determine θ for Eq. (1) and C_V for Eq. (2) we have measured the heat capacity of our samples; see Fig. 3. From these data we determine both the Debye temperature (125 K) and high-temperature limit of the specific heat (0.205 $J\,g^{-1}\,K^{-1}$) for $AgSbTe_2$; similar values are found for the $AgBiSe_2$ compound and are in good agreement with literature values [25] for $AgSbSe_2$. From all of these data we calculate that $\gamma \approx 2.05$ for $AgSbTe_2$, an extremely high value for any solid. In contrast, for PbTe, both Landolt and Börnstein [26] and Slack [27] give $\gamma \approx 1.45$, a factor of 1.4 less. The resulting calculated value for the umklapp-limited thermal conductivity for PbTe (using a value of $\theta = 120$ K [28]) is 2.8 $W\,m^{-1}\,K^{-1}$, in good agreement with the single-crystal experimental value of 2.4 $W\,m^{-1}\,K^{-1}$ shown in Fig. 2; for $AgSbTe_2$, on the other hand, we find $\kappa_L \sim 0.68$ W/mK, in excellent agreement with the measured value.

Figure 2 illustrates that the lattice thermal conductivity of $AgSbTe_2$ reaches the minimum value possible, where the phonon mean free path reaches the interatomic distance. The value of this so-called "minimum thermal conductivity" is readily estimated from the formula $\kappa_L = \frac{1}{3}C_V \nu \ell$, where the phonon mean free path $\ell = 0.303$ nm, the interatomic distance. The sound velocity $\nu = 4800$ m/s was measured by Wolfe *et al.* [29]. Using, as above, the measured specific heat of $AgSbTe_2$ in the temperature range of 77 to 300 K, the minimum thermal conductivity can be calculated and is shown in Fig. 3 as a full line: it corresponds almost exactly to the measured value.

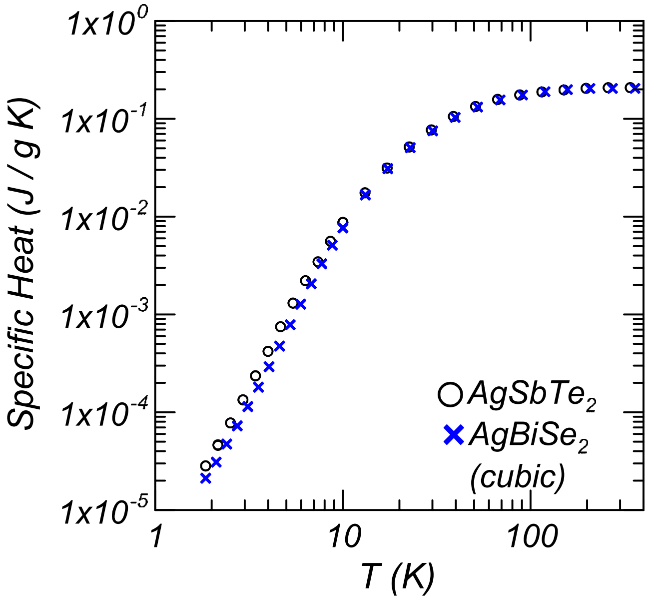

FIG. 3 (color online). Experimental heat capacity of $AgSbTe_2$ and $AgBiSe_2$. From the low temperature T^3 dependence we determine Debye temperatures of 125 and 135 K, respectively.

The temperature dependence of the lattice thermal conductivity given in Eq. (1) follows a $1/T$ law, which is observed in Fig. 2 for PbTe and $AgInTe_2$ but not for $AgSbTe_2$ or $AgBiSe_2$. This "law" is valid only in the regime where the phonon mean free path exceeds the interatomic distance. In the I-V-VI_2 compounds studied here, the lattice thermal conductivity already has reached its lowest limit by 77 K, because the phonon mean free path is limited to the interatomic distance and cannot decrease further. The temperature independence of κ_L simply reflects that of the mean free path, of the sound velocity, and of C_V at $T > \theta$.

We conclude that, due to the extremely high anharmonicity in the I-V-VI_2 semiconductors, the phonon thermal conductivity is limited to its minimum possible value, where the mean free path equals the interatomic distance, by intrinsic phonon-phonon processes alone.

The difference in the thermal conductivity between the I-III-VI_2 and the I-V-VI_2 semiconductors is a direct consequence of the difference in the nature of the chemical bonding. In the I-III-VI_2 semiconductors all electrons of the outer shell take part in the formation of hybridized sp^3 bonds. In the rocksalt I-V-VI_2 semiconductors the external s electrons and part of the p electrons are non-bonding and are expected to form a shell of relatively large radius. This is the fundamental reason for the high anharmonicity of the bonds in these materials and the ultimate cause of their low lattice thermal conductivity. During thermal vibrations atoms approach one another, and this leads to overlapping of the wave functions of electrons which have not interacted. This variable wave function overlap during the vibrating motion leads to a repulsive force, or an anharmonicity in the force. The same phenomenon is expected to occur when an external electric field is applied, and thus we predict that these semiconductors will have a high dielectric constant. As this in turn implies reduced ionized impurity scattering, it should be possible to maintain a high mobility even in highly doped material, assuming that this can be achieved metallurgically.

In conclusion, we have shown that the lattice thermal conductivity of $AgSbTe_2$ and $AgBiSe_2$, two cubic I-V-VI_2 semiconductors, is limited to its minimum possible value by intrinsic phonon-phonon scattering processes. This intense intrinsic phonon scattering arises due to strong anharmonicity of the bonding arrangement in these compounds. This low intrinsic thermal conductivity makes these materials very promising candidates for high efficiency thermoelectric semiconductors.

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[1] The thermoelectric figure of merit is a measure of the efficiency of thermoelectric devices, and is defined as $Z = S^2\sigma/\kappa$, where S is the thermoelectric power or Seebeck coefficient, σ the electrical conductivity, and κ the thermal conductivity. It is customary to express the figure of merit as the unitless product of Z with the average operating temperature T. As most thermoelectric materials are semiconductors in which κ is dominated by lattice conduction, it is also customary to group the electronic contributions into the "power factor" $P = S^2\sigma$.

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