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Transition-metal pentatellurides as potential low-temperature thermoelectric refrigeration materials

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The importance of the future development of materials for use in low-temperature thermoelectric refrigeration devices is discussed. Specifically, results are presented on an interesting class of materials called pentatellurides, $HfTe_5$ and $ZrTe_5$, which have shown promising low-temperature thermoelectric properties ($100\,K < T < 250\,K$). Substitutional doping occurs both on the metal site as $Hf_{1-x}Zr_xTe_5$ solid solutions, and on the Te site with Se. Proper doping leads to a decrease in resistivity and an enhancement of thermopower which results in a doubling of the power factor (electronic properties) which is then very competitive with the power factor of existing thermoelectric materials in these temperature regimes. [S0163-1829(99)06743-0]

INTRODUCTION

A recent article emphasized that the development of low-temperature ($T < 200\,K$) thermoelectric devices is the most important need of new thermoelectric refrigeration materials.[1] Materials that provide efficient local cooling at temperatures below 200 K would greatly affect the electronics industry, since the performance of many semiconducting and other electronic devices is dramatically enhanced below room temperature. Since thermoelectric cooling of electronics requires only small scale spot cooling, the demands on the materials and devices are not as great as for larger scale cooling applications, such as packaged refrigeration. As the field of cryoelectronics and ‘‘cold computing’’ grows, the need for lower temperature (100–200 K) thermoelectric materials has become more evident. The advantages of ‘‘cold computing’’ are discussed in a recent article by Sloan,[2] where he states that ‘‘speed gains of 30–200 % are achievable in some CMOS computer processors’’ and that ‘‘cooling is the fundamental limit to electronic system performance.’’ Also, a severe limitation to cellular phone technology, using superconducting narrowband spectrum dividers to increase frequency band utilization, is a reliable cooling technology. Cooling of laser diodes and infrared detectors to temperatures of $100\,K < T < 200\,K$ would greatly improve performance and sensitivity and thus would be extremely important to many technologies.[3] Huebener and Tsuei recently discussed the prospects of using existing Bi_2Te_3 Peltier coolers for superconducting electronics.[4] However, they concluded that new materials will have to be developed to achieve solid-state cooling to temperatures on the order of 90 K for the development of superconducting electronics to become feasible. Thus, the potential payoff for the development of low-temperature thermoelectric refrigeration devices is great, and the requirement for compounds with properties optimized over wide temperature ranges, has led to a much expanded interest in new thermoelectric materials.[5–7]

Approximately 30 years ago alloys based on the Bi-Te compounds $\{(Bi_{1-x}Sb_x)_2(Te_{1-x}Se_x)_3\}$, and $Si_{1-x}Ge_x$ compounds, were developed as thermoelectric materials for solid-state thermoelectric refrigeration and power generation applications, respectively.[8–10] These materials have been extensively studied and fully optimized for their use in thermoelectric devices and are the current state-of-the-art materials. Thus, entirely new classes of compounds will have to be investigated if substantial improvement is to be realized. The need for improvement is particularly acute in the lower temperature regime, because most conventional thermoelectric materials show optimal performance well above room temperature ($T > 700\,K$). While there are a considerable number of applications in the high-temperature regime, there is even greater potential device applications for refrigeration at lower temperatures, between 80 and 400 K. The dearth of potential applications in this area makes the need for the investigation of entirely new systems for this regime even more acute.

Thermoelectric materials transfer heat via the Peltier effect when subjected to an electric current which in turn produces a temperature gradient. Heat is absorbed on the cold side and rejected at the heat sink, thus providing a refrigeration capability. An imposed ΔT will act conversely and result in a voltage or current, i.e., small scale power generation. The essence of a good thermoelectric is given by the determination of the material's dimensionless figure of merit, $ZT=(\alpha^2\sigma/\lambda)T$, where α is the Seebeck coefficient, σ the electrical conductivity, and λ the total thermal conductivity ($\lambda=\lambda_L+\lambda_E$; the lattice and electronic contributions, respectively). The power factor of a material, α^2T/ρ (or $\alpha^2\sigma T$), is typically optimized as a function of carrier concentration, through doping, to give the largest ZT. Semiconductors have long been the material of choice for thermoelectric applications since initially identified for their potential in the mid 1950s by the Russian scientist, A. F. Ioffe, (which led to a huge research effort in that country during the 1950s and 1960s).[11] High mobility carriers which have the highest electrical conductivity for a given carrier concentration are most desirable, and typically the most promising materials have carrier concentrations of approximately 10^{19} carriers/cm^3. The best thermoelectric materials have a value of $ZT\approx 1$. This $ZT\approx 1$ has been an experimental upper limit for more than 30 years, yet no theoretical or thermodynamic reason exists for why it cannot be larger. The value of ZT can be raised by decreasing the lattice thermal conductivity, λ_L, or by increasing the Seebeck coefficient, α, or the electrical conductivity, σ. However, σ is tied to the electronic thermal conductivity, λ_E through the Wiedemann-Franz law ($\lambda_E=L_0\sigma T$, where L_0= Lorentz number), and the ratio (λ_E/σ) is essentially constant at a given temperature.

In 1995 Slack published a paper describing the anticipated chemical characteristics of materials which might lead to an effective thermoelectric material.[12] The successful candidate requires several specific characteristics. The compound should be a narrow band-gap semiconductor with highly mobile carriers, while the thermal conductivity must be minimized. In semiconductors, the Seebeck coefficient and electrical conductivity (both in the numerator of ZT) are strong functions of the doping level and chemical composition, which must therefore be optimized for good thermoelectric performance. Doping can also have a very profound effect on the thermal conductivity of complex materials. Understanding these various effects in complex materials is important because the factors are often related. Hence optimization usually requires tradeoffs, and there are often many possible degrees of freedom. Slack has previously stated that the most promising thermoelectric materials should behave as a phonon-glass/electron crystal (PGEC). The paradigm of the PGEC material is that it should behave thermally as a glass (large phonon scattering and thus low lattice thermal conductivity) and as an electronic crystal (low scattering for the electrons, thus high electrical conductivity).

One of the important issues relative to the development of low-temperature thermoelectric materials is identifying mechanisms which might give high thermopower (α) at low temperatures. Possibilities include phonon drag, heavy fermion materials, Kondo systems, materials which exhibit phase transitions, as well as quasi-one-dimensional materials. Low-dimensional systems are known to be susceptible to Van Hove singularities (or cusps) in their density of states, electronic phase transitions, and exotic transport phenomena which can add structure in $g(E)$ near E_F. In most materials, at temperatures far from a phase transition, the electrical conductivity and thermopower are related to the electron density of states near the Fermi-energy $D(E_F)$. The conductivity is proportional to $D(E_F)$ while α is proportional to $(1/D)dD(E)/dE$ at $E=E_F$. Hence, as n (or D) is increased, σ typically increases while α decreases. Doping can produce very substantial effects in these types of materials and can drastically change their electronic transport. Quantum well systems take advantage of a low-dimensional character through physical confinement in thin film structures to enhance the electronic properties of a given material.[13] In this paper we present results on a family of low-dimensional semiconductors called pentatellurides ($HfTe_5$ and $ZrTe_5$) which we believe exhibit such behavior, and show promise as potential low-temperature thermoelectric materials.

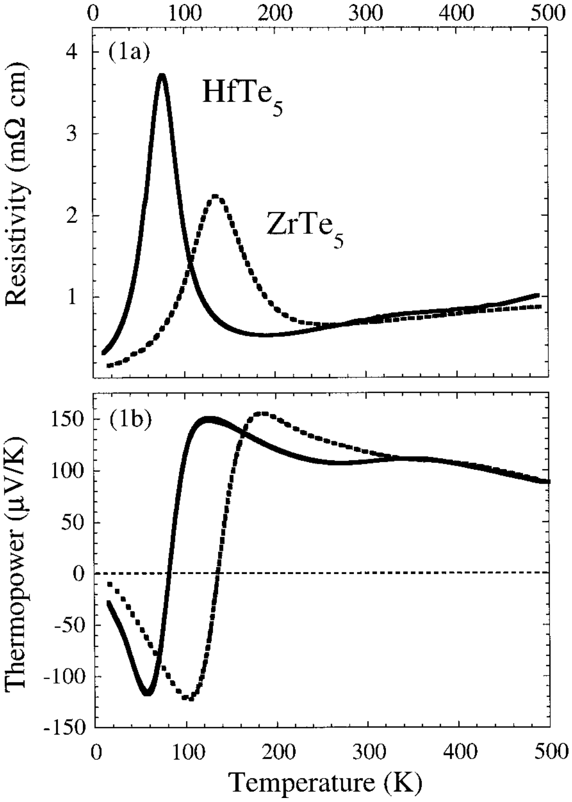

FIG. 1. (a) Resistivity ρ as a function on temperature for $HfTe_5$ and $ZrTe_5$. (b) The absolute thermopower as a function on temperature for for $HfTe_5$ and $ZrTe_5$.

TRANSITION-METAL PENTATELLURIDES

The electrical resistivity, ($\rho=1/\sigma$), and thermopower for single crystals of the pentatelluride materials as a function of temperature ($10\,\mathrm{K}<T<500\,\mathrm{K}$) are shown in Figs. 1(a) and 1(b) for $HfTe_5$ and $ZrTe_5$, respectively. Both parent materials exhibit a unique resistive transition peak, $T_P\approx 80$ K for $HfTe_5$ and $T_P\approx 145$ K for $ZrTe_5$. In addition, each displays a large positive (p-type) thermopower ($\alpha\geqslant +125\,\mu$V/K) around room temperature, which undergoes a change to a large negative (n-type) thermopower ($\alpha\leqslant -125\,\mu$V/K) near the resistivity peak temperature. The magnitude of this resistive anomaly is typically 3–7 times the room temperature value of $\rho\approx 0.7\,\mathrm{m}\Omega$ cm which is comparable to the best known thermoelectric materials. These materials exhibit thermopower that is relatively large over a broad range at low temperatures for both *n* type ($T<T_p$) and *p* type ($T>T_p$). The large values of thermopower ($|\alpha|\approx 100\,\mu\mathrm{V/K}$) at temperatures below 250 K make these materials very interesting for potential low-temperature applications.

Several aspects of the electrical transport properties of these materials, specifically in relation to the broad resistive peak, were studied in the early 1980s, albeit not in relation to the materials' properties for applications in thermoelectrics. Early data suggested a possible charge density wave (CDW) peak but no evidence of a CDW transition or spin-density wave behavior was found. DiSalvo, Fleming and Waszczak.[14] performed Zr and Ta substitution for Hf in the $HfTe_5$ material and found that doping and substitutions substantially change the resistivity peak temperature, while also affecting the magnitude of the resistivity of these materials. This indicated that the transition is most likely electronic in origin. The thermopower was not reported in that study. An investigation by Jones *et al.*[15] found that the magnitude of the thermopower was highly sample dependent, probably due to small amounts of trace impurities or differences in growth conditions.

In this study, single crystals of pentatellurides, $HfTe_5$ and $ZrTe_5$, were grown in conditions similar to previously reported methods.[16] A stoichiometric ratio of the materials was sealed in fused silica tubing with iodine ($\approx$5 mg/mL) and placed in a tube furnace. The starting materials were at the center of the furnace with the other end of the reaction vessel near the open end of the furnace to provide a temperature gradient. Crystals of these materials were obtained in excess of 1.5 mm long and 100 μm in diameter with the preferred direction of growth along the *a* axis, with the x-ray crystal structure determined by face indexing. The structure is orthorhombic, of space group *Cmcm* and unit cell dimensions $a=3.974$ Å, $b=14.492$ Å, and $c=13.730$ Å. These materials are complex, infinite chain systems with 24 atoms in an orthorhombic unit cell. As shown in Fig. 2, the structure of the pentatellurides is comprised of MTe_3 ($M=$ Hf or Zr) chains which are subsequently bridged into large two-dimensional (2D) sheets by tellurium atoms. The sheets are then weakly bound to one another through a van der Waals gap, leading to the highly anisotropic nature of the bulk crystals. Figure 2 clearly shows both the MTe_3 chains and the van der Waals gap between the individual layers.

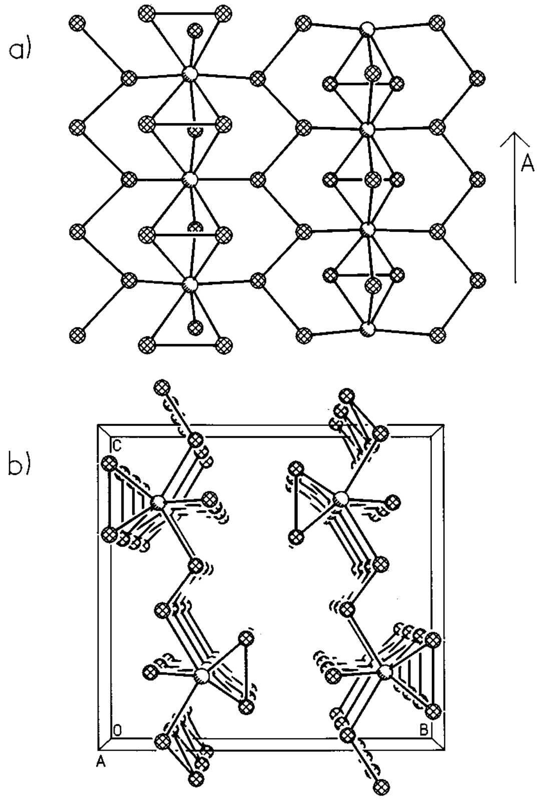

FIG. 2. (a) A unit cell of MTe_5 ($M=$ Hf, Zr), along the *a* axis which shows the van der Waals gap that separates the individual layers. The open spheres are the metal (*M*) atoms and the cross-hatched spheres are the Te atoms. (b) A projection of a layer in MTe_5 as viewed down the *b* axis, showing the chains of MTe_3 pyramids. The open spheres are the metal (*M*) atoms and the cross-hatched spheres are the Te atoms.

The samples grow as ribbons with the growth axis as the *a* axis and the thin part of the ribbon being the *b* axis. These materials do, in fact, exhibit anisotropic transport properties with the high conductivity axis being the growth axis (*a* axis). Electrical contact was made using Au wires bonded to the crystal with Au paint. The residual iodine vapor on the samples prevents using Ag paint, which forms a AgI layer on the sample, preventing good electrical contact. Typical sample dimensions are 1–5 mm, 0.01–0.03 mm, and 0.05–0.3 mm in the *a*, b, and *c* directions, respectively. Much care was taken in the measurement of these materials and excellent agreement was achieved in measuring the resistivity and thermopower of a 0.003-in.-diam constantan wire for comparison. The details of the sample measurement techniques are described elsewhere.[17] The small size of these materials makes the measurement of thermal conductivity very difficult. Accurate ($\approx$10%) determinations of the thermal conductivity have not yet been performed on these materials.

Resistivity and thermopower measurements have previously been reported on single crystals of $Hf_{1-x}Zr_xTe_5$ where x varies from $0\leqslant x\leqslant 1$.[18] As Hf is replaced by Zr, the resistivity peak temperature is shifted to higher temperature. For $Hf_{1-x}Zr_xTe_5$, the thermopower undergoes a systematic shift in temperature as the Zr concentration is increased, similar to the resistivity. However, the effect of metal doping on the magnitude of the thermopower is relatively small and the large values of thermopower and the magnitude of the resistive peak remain essentially unchanged. We have also observed that small substitutions (<5%) of Ti for either Hf or Zr (also isoelectronic) shifts the peak temperature to lower temperature, but also results in a lowering of the magnitude of the thermopower values.[19] An even more dramatic effect is observed with the addition of small amounts of Sb into the system and these results are reported elsewhere.[20] The addition of Sb completely washes out the resistive anomaly and corresponding thermopower behavior. The doped pentatellurides, $HfTe_{4.75}Sb_{0.25}$ and $ZrTe_{4.75}Sb_{0.25}$, both exhibit thermopower and resistivity values which decrease with decreasing temperature in a metalliclike behavior from $T=300$ K to $T\approx 10$ K. The thermopower behaves in a similar ''metallic'' or Mott-diffusion manner, decreasing from large values of $\alpha\approx 120\,\mu\mathrm{V/K}$ at $T=300$ K and decreasing as the tempera-

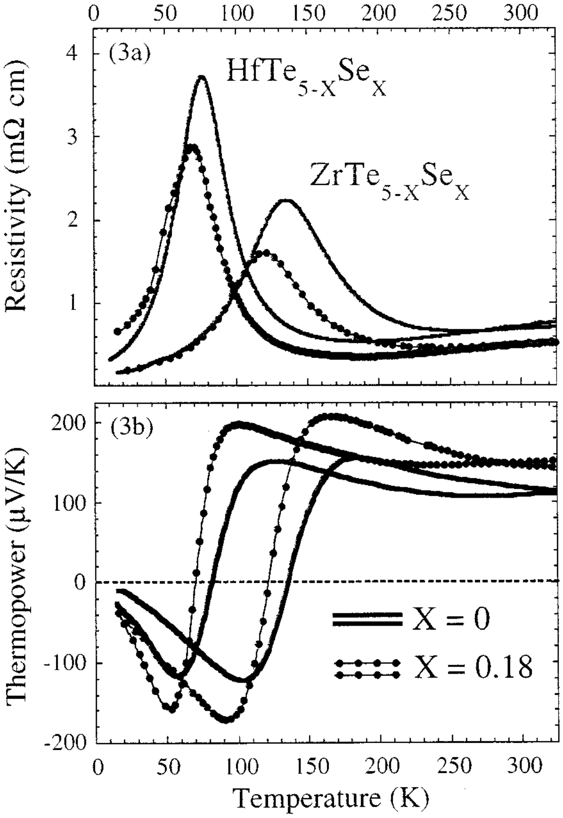

FIG. 3. (a) Resistivity ρ as a function on temperature for $HfTe_{5-x}Se_x$ and $ZrTe_{5-x}Se_x$ for $x=0$ and 3.6% up to $T=500$ K. (b) The absolute thermopower as a function on temperature for $HfTe_{5-x}Se_x$ and $ZrTe_{5-x}Se_x$ for $x=0$ and 3.6% up to $T=500$ K.

ture decreases. The samples have relatively low room temperature resistivity values of 0.48 and 0.36 mΩ cm for $HfTe_{4.75}Sb_{0.25}$ and $ZrTe_{4.75}Sb_{0.25}$ respectively. X-ray analysis confirm the parent pentatelluride structure is retained in these Sb-doped materials, eliminating the possibility of another structural phase being formed.

Regarding the use of these pentatelluride materials in possible low-temperature applications, certainly, the most important effect occurs with the substitution of small amounts of Se for Te in $MTe_{5-x}Se_x$. We have found that substitutions in $MTe_{5-x}Se_x$ where x corresponds to 3.6% Se for Te raises the power factor substantially over the parent materials. These concentrations were determined by Inductively coupled plasma chemical analysis. The resistivity and thermopower for the 3.6% substitution is shown in Figs. 3(a) and 3(b) and compared to the parent materials. The thermopower values increase by $\approx$20% while the resistivity values decrease by 25%. T_p and T_0 are reduced nearly 10–15 K from $HfTe_5$ to $HfTe_{4.82}Se_{0.18}$, and $ZrTe_5$ to $ZrTe_{4.82}Se_{0.18}$. Thermopower values exceeding 200 μV/K were measured for both $HfTe_{4.82}Se_{0.18}$ and $ZrTe_{4.82}Se_{0.18}$ at temperatures of $\approx$95 K and $\approx$185 K, respectively. These are very large thermopower values for the low temperatures shown and very linear in T below the negative maximum.[21] This increase in the thermopower, combined with the decrease in the resistivity, results in an enhancement of the power factor, α^2T/ρ, by a factor of 2. Power factors (PF) of Se doped pentatellurides

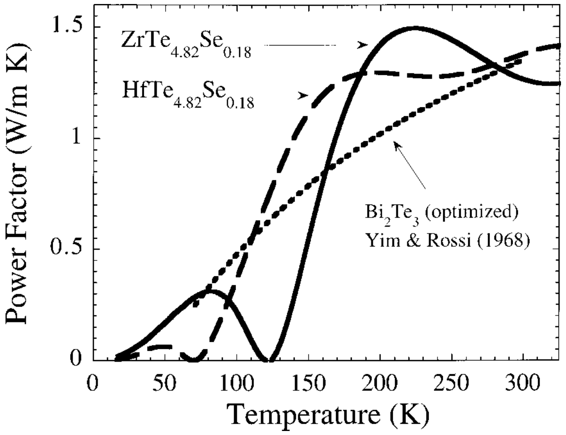

FIG. 4. Power factor, α^2T/ρ (or $\alpha^2\sigma T$), as a function of temperature for $HfTe_{4.82}Se_{0.18}$ and $ZrTe_{4.82}Se_{0.18}$. These are compared to the power factor for optimized Bi_2Te_3 materials which are also shown.

range from $PF=\alpha^2T/\rho \geqslant 1.25$ W/m K@150 K$\leqslant T \leqslant$320 K for $HfTe_{4.82}Se_{0.18}$ and $\alpha^2T/\rho \geqslant 1.50$ W/m K@225 K$\leqslant T \leqslant$320 K for $ZrTe_{4.82}Se_{0.18}$.

Similar substitution of Se in the Bi_2Te_3 compounds led to a series of related alloys and pseudoternary compounds, i.e., $\{(Bi_{1-x}Sb_x)_2(Te_{1-x}Se_x)_3\}$ with enhanced properties that have resulted in effectively optimized thermoelectric materials.[10,22] Similarly, initial results from Se substitutions on Te sites of both parent pentatelluride materials are quite promising as well. The importance of these results is illustrated in Fig. 4, where the power factor of the Se doped (3.6%) samples are compared to the power factor of optimally doped Bi_2Te_3, i.e., $\{(Bi_{1-x}Sb_x)_2(Te_{1-x}Se_x)_3\}$. The Bi_2Te_3 data were taken from the literature.[22] As clearly shown in Fig. 4, the power factor of the Se doped pentatellurides exceeds that of the optimally doped Bi_2Te_3 compound over the temperature range of measurement. At low temperatures, 150 K$<T<$250 K, the power factor of the pentatellurides significantly exceeds that of the state-of-the-art bismuth telluride compound. Thus far, the small size of these single crystal materials has made accurate ($\approx$10%) determinations of the thermal conductivity very difficult. We have performed thermal conductivity measurements on cold pressed pellets. This gave values of 1$\approx$1.5 W/m K or less over the temperature range 150 to 250 K. However, it is not valid to compare values from such thermal conductivity measurements on pressed pellets which average over the anisotropy of the crystals to single crystal electronic transport measurements. Nevertheless, these results on the electronic properties are very encouraging and we are currently pursuing methods of larger crystal growth and techniques of thermal conductivity measurement on larger crystals. We are very hopeful that we will have this much needed data in the very near future.

In summary, we have identified a promising class of materials, the transition-metal pentatellurides, for possible development as low-temperature thermoelectric materials. These materials, when properly doped, exhibit very high power factors in the temperature range 150 K$<T<$300 K, with values exceeding those of existing state-of-the-art thermoelectric materials over a comparable temperature range. It should be noted that these are early doping results which are not yet optimized, so it is anticipated that even high power factors may be achieved. The prospect of the development of new materials for low-temperature thermoelectric refrigeration applications would greatly impact many high tech industries, and could revolutionize low-temperature electronic component performance. Also, if cooling to temperatures of 100 K or less can be achieved with thermoelectric devices then the development of thermoelectrically refrigerated superconducting electronics could possibly be realized.

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