SANDIA REPORT

SAND2009-5978

Unlimited Release

Printed September 2009

Extreme Solid State Refrigeration using Nanostructured Bi-Te alloys

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Prepared by
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Extreme Solid State Refrigeration using Nanostructured Bi-Te alloy

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Abstract

Materials are desperately needed for cryogenic solid state refrigeration. We have investigated nanostructured Bi-Te alloys for their potential use in Ettingshausen refrigeration to liquid nitrogen temperatures. These alloys form alternating layers of Bi_2 and Bi_2Te_3 blocks in equilibrium. The composition Bi_4Te_3 was identified as having the greatest potential for having a high Ettingshausen figure of merit. Both single crystal and polycrystalline forms of this material were synthesized. After evaluating the Ettingshausen figure of merit for a large, high quality polycrystal, we simulated the limits of practical refrigeration in this material from 200 to 77 K using a simple device model. The band structure was also computed and compared to experiments. We discuss the crystal growth, transport physics, and practical refrigeration potential of Bi-Te alloys

ACKNOWLEDGMENTS

We thank J. D. Sugar for discussions and M. Homer and M. Hekmaty for technical assistance.

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1. INTRODUCTION

Thermoelectric refrigerators that can spot cool a circuit from room temperature to cryogenic temperatures eliminate the need for expensive, bulky liquid cryogens and compressors. Materials are desperately needed for solid state refrigeration below ~ 200 K, the current practical cooling limit of the best Bi_2Te_3 based thermoelectrics. Compact spot cooling to $T < 100$ K could potentially double IR detector sensitivity and provide a viable route to realizing long-sought high- T_C superconducting electronics technology. Materials for practical thermoelectric cooling must have a figure of merit $zT = TS^2/\rho\kappa \sim 1$ in their operating temperature range. No traditional thermoelectric material has ever been found with a high enough zT below 200 K.

Ettingshausen devices, close relatives of thermoelectrics, are vastly superior for cryogenic cooling [1]. How does an Ettingshausen refrigerator work? Heat transfer occurs when a T gradient is created perpendicular to an applied electric current, both of which are perpendicular to an applied magnetic field (Fig. 1). Normally, charge carriers flow parallel to the electric field (y) in a material but are deflected (x) in a crossed magnetic field according to the Lorentz force $F = qv \times B$. If electrons coexist with holes in the material, they recombine at one side of the sample, releasing heat and enabling refrigeration. Good Ettingshausen refrigerators must have nearly equal numbers of high mobility electrons and holes and have a high figure of merit $z_E T = T(NB)^2/\rho\kappa$, where the Nernst coefficient, N , is the electric field response perpendicular to an applied T gradient in a magnetic field, T is temperature, B is magnetic field, ρ is electrical resistivity, and κ is thermal conductivity. This combination of transport properties leads to higher $z_E T$ in certain materials at cryogenic temperatures than that for the thermoelectric zT .

Figure 1 Principle of Operation for an Ettingshausen Refrigerator. Electric current (+y direction) drives a T gradient (+x direction) in the presence of a magnetic field (B , +z direction, into the paper)

Ettingshausen coolers are constructed out of a single material (separate p- and n-legs are not needed as in conventional thermoelectric devices) and suffer less thermal contact problems since heat is pumped perpendicularly to the applied current. Refrigeration performance can also be increased by changing the material's shape. In order to be practical, the magnetic field must be generated by a permanent magnet (~ 1 T). For this reason, most materials with high $z_E T$, such as intrinsic semiconductors, cannot be used for this kind of refrigeration. It

turns out that only semimetals have a high $z_E T$ at low magnetic fields due to their equal numbers of electron and holes each with high carrier mobility. Among the few existing semimetals, Bi is the best Ettingshausen material until about 128 K, where its thermal conductivity (κ) becomes too high, reducing $z_E T$ once again.

We have recently discovered that a series of nanostructured Bi-Te compounds are very promising for Ettingshausen cooling [2]. Transport properties and first principle calculations show that they are semimetals (zero or negative energy gap) with similar numbers of electrons and holes (ambipolarity). In addition, their thermal conductivity is sharply reduced compared to both Bi and Bi_2Te_3 . For example, these alloys have a κ over 100 times lower than that of Bi at 77 K. The superlattice structure of the alloys is likely responsible for both the low thermal conductivity (phonon group velocity reduction and interface scattering [3]) and semimetallic properties (change in band structure). The combination of ambipolarity and low thermal conductivity makes these materials promising candidates for Ettingshausen refrigeration.

We synthesized and measured bulk superlattice Bi-Te alloys that show the most promise for Ettingshausen cooling. All of the materials possess a reduced κ (Fig. 2), but their relative amounts of electrons and holes and Ettingshausen figure of merit must be analyzed. Bi_2Te and Bi_4Te_3 show the most promise from Seebeck coefficient and Hall effect measurements (Fig. 2). When multiple (n and p type) carriers are present in a material, S commonly changes sign as a function of T as the relative concentration and mobility of each carrier changes. Bi_4Te_3 shows this change in sign at ~ 150 K. If n and p concentrations are similar and carrier mobility is high, a high $z_E T$ is expected to occur [4]. In the following report, we measured $z_E T$ of Bi_4Te_3 and evaluated the potential of this material for Ettingshausen cooling. We will make frequent comparisons to elemental Bismuth, the standard material for this type of refrigerator.

Figure 2 Transport Properties of Bi-Te alloys. Top panel: Nanostructured BiTe, Bi₂Te, and Bi₄Te₇ all have reduced κ at low T compared to both Bi₂Te₃ and elemental Bi. Bottom panel: Bi₄Te₃ shows signatures of coexisting n and p-type carriers due to the change of sign in S at ~ 150 K.

2. SYNTHESIS OF BI-TE SINGLE AND POLY-CRYSTALS

The Bi-Te nanostructured alloys occur on the Bi-rich side of the binary phase diagram (Fig. 3) [5]. We synthesized both polycrystals and single crystals. While polycrystals can be made in sizes large enough for devices, single crystals typically have larger carrier mobility due to the lack of grain boundaries and have the potential for larger zET .

2.1. Polycrystalline synthesis of Bi_4Te_3

According to Fig. 3, Bi_4Te_3 melts incongruently. This is to say that at $T > 420$ C, this compound decomposes into a mixture of Bi/Te liquid and solid. The conventional method of slow cooling a stoichiometric melt will then result in a significantly inhomogeneous ingot. Solid state synthesis can achieve homogeneity and good crystallinity, but is plagued by oxidation at grain boundaries (from precursor powders) and high porosity [2]. Instead, high purity (99.99%) Bi and Te elements combined in the Bi_4Te_3 stoichiometry were melted (within a sealed, evacuated quartz tube) at 650 C for 5 days. The melted charge was then quenched by inserting the 650 C tube into a bottle of liquid nitrogen (boiling point of 77 K). This fast quenching was supposed to arrest phase formation in the inhomogeneous liquid/solid region above the (incongruent) melting point of Bi_4Te_3 . The quenching process then yields an ingot with a minimal amount of inhomogeneity but poor crystallinity.

Figure 3 Bi-Te binary phase diagram reported in [5] and used as the basis for sample synthesis in this study.

The quenched Bi_4Te_3 melt was then subsequently annealed at 400 C for 10 days in order to achieve good crystallinity. Given long enough annealing times, the equilibrium Bi_4Te_3 phase should be preferred over other phases that might have persisted during the quenching process. We obtained polycrystalline, single phase Bi_4Te_3 with good crystallinity, as judged from the powder X-ray diffraction pattern (Fig. 4). Samples were large enough to perform all transport measurements. This procedure for producing polycrystals was reproducible.

Figure 4 Powder X-ray diffraction pattern for polycrystalline Bi_4Te_3 prepared by quenching followed by post-annealing. Good crystallinity was achieved without significant impurity phases. The red lines are peak positions.

2.2. Flux Growth of Bi-Te Single Crystals

While an obstacle to polycrystalline synthesis, the large liquid/solid phase coexistence region of the phase diagram facilitates single crystal synthesis using the flux growth technique [6]. In flux growth, the stoichiometry is chosen such that at some temperature, the charge will consist, at equilibrium, of a liquid and a solid. The liquid is then separated from the solid, which is typically in the form of separated single crystals. The stoichiometry is usually chosen such that there exists a much greater volume fraction of liquid compared to solid in the charge.

The process we used is shown in Fig. 5. The charge was contained in an alumina crucible to improve temperature stability and nucleation sites for crystal growth. A section of

quartz wool (10 micron fibers) was placed above the charge. The whole charge was melted (typically at 700 C), then slow cooled (~ 2.5 C/hour) into the liquid-solid coexistence region. The stoichiometry for a representative sample was 26 at.% Te and 74 at. % Bi, which was approximately 5 parts Bi for 1 part of Bi_4Te_3 . Both manual methods and centrifugation worked for separating the crystals from the flux.

Figure 5 Flux growth synthesis of single crystals. a) The charge is loaded into an alumina crucible placed inside a sealed, evacuated quartz tube with a section of quartz wool in between. b) At high T , the charge will melt and form an equilibrium solid/liquid mixture. c) The entire apparatus is inverted, either manually or using a centrifuge, in order to separate flux and solid

Single crystals grown this way grew in plates with habits expected from the hexagonal symmetry [2, 7]. Crystals were typically 2-5 mm long and 0.5-1 mm thick. When viewed with polarized optical microscopy (Fig. 6), no crystallographic domains were visible. We identified the Bi_4Te_3 phase using an X-ray diffractometer, orienting the crystal in-plane, and checking the position of the hexagonal (0001) peak (Fig. 7), which varies systematically with Bi content for Bi_xTe_y compounds [7]. Small amounts of Bi, the flux, and $\text{Bi}_{10}\text{Te}_9$, an impurity phase, were discovered.

Figure 6 Representative polarized optical micrograph of a Bi_4Te_3 . No crystallographic domains were detected in any part of the sample.

Figure 7 X-ray diffraction pattern of oriented Bi_4Te_3 crystal synthesized using flux growth. The large (0001) peak in the main panel is at the 2θ value corresponding to Bi_4Te_3 .

3. ETTINGSHAUSEN FIGURE OF MERIT OF Bi_4Te_3 POLYCRYSTAL: EXPERIMENT AND THEORY

3.1. Transport Measurements

In order to evaluate $z_E T$, the quantities N , ρ , and κ had to be measured. In addition, Hall effect, magnetoresistance, and S measurements were necessary to characterize the extent of ambipolar (simultaneous n- and p-type) conduction.

S , N , and κ measurements were conducted using the setup shown in Fig. 7. A T gradient (typically 1-3 K/cm) was maintained across the sample using a chip resistor ($\sim 200 \Omega$), and measured using a Constantan-Chromel differential thermocouple. S (squares) and N (circles) voltage measurements were measured using phosphor bronze wires. All wires had 1 mil diameters to prevent parasitic heat conduction. A radiation shield (gold plated copper) surrounded the sample to mitigate radiative losses. Good electrical contacts ($< 1 \Omega$) were achieved by electroplating a Ni film at the contact area and attaching wires using silver epoxy (cured at 120 C for 15 minutes). This setup was tested using a calibrated nickel sample. By measuring the thermal conductivity of a piece of glass as a function of magnetic field, B , we found that the thermocouple was insensitive to B within a few % under the conditions presented. Magnetoresistance (ρ vs. B) and Hall effect measurements were conducted on the same sample used for S , N , and κ measurements using the same leads and electrical contacts. The N contacts served as Hall probe contacts.

Special attention must be paid to the sign convention for the Nernst effect measurements. In a Nernst experiment, B is applied perpendicular to ΔT . As can be inferred from Fig. 1, both n and p-type carriers are deflected towards the same end of the sample, so N does not depend on the sign of the (majority or minority) charge carriers as in e.g. the Hall effect. Therefore, there is an ambiguity in the sign of the N . In order to fix the polarity of the Nernst voltage, we used the sign convention due to Gerlach [8, 9].

A bar shaped sample $4.3 \times 1.6 \times 0.6 \text{ mm}^3$ was used for all measurements. As of the present writing, only the polycrystalline sample was large enough for all samples. Only ρ measurements were conducted on single crystal samples. For clarity, we will focus only on the full set of measurements taken on the polycrystalline sample. We will briefly comment on the need for single crystal measurements later. For Nernst and Hall experiments, measurements were taken at positive and negative B ($\pm 9 \text{ T}$) in order to subtract out spurious longitudinal components due to contact misalignments [9]. T was varied from 2-300 K. We used a Quantum Design *Physical Property Measurement System* as a T and B platform.

Figure 8 Setup for N , S , and κ measurements. Circles refer to N measurements. Squares refer to S measurements. The Nernst sign convention due to Gerlach [8] has been used.

3.2. Results of Transport Measurements for Polycrystalline Bi_4Te_3

3.2.1 Figure of Merit: Nernst Effect, Electrical Resistivity, and Thermal Conductivity

The first quantity of interest for refrigeration is the Nernst effect. The Nernst signal, $e_N = \underline{E}_y/|\nabla_x T|$, is the electric field response to a given ΔT in a perpendicular applied magnetic field. Representative Nernst measurements for a Bi_4Te_3 polycrystal are shown in Fig. 9. The largest order of magnitude for the Nernst effect is $\sim 1\text{-}2 \mu\text{V/K}$ per 1 T magnetic field in this material. The largest magnitude of the Nernst effect in elemental Bi is $\sim 1 \text{ mV/K}$ per 1 T magnetic field, one thousand times larger than Bi_4Te_3 [10]. A low value of the Nernst effect in semiconductors and semimetals is often due to low carrier mobility [4]. Bismuth has a carrier mobility of $\sim 10^5 \text{ cm}^2/\text{V sec}$ for both p- and n-type carriers [11].

The value of $z_E T$ for this polycrystalline sample was much smaller than found in Bismuth for the entire T range measured. In Fig. 10, we compare κ , ρ , and $N=e_N/\mu_0 H$ for a practical magnetic field of 1 T from 10-300 K, then compute the T dependence of $z_E T$. The maximum (dimensionless) figure of merit reaches $\sim 0.8 \times 10^{-4}$. It is instructive to compare numbers with elemental Bismuth, where $z_E T \sim 0.5$ at $\sim 100 \text{ K}$. For Bi_4Te_3 at $T \sim 100 \text{ K}$, $\kappa \sim 2 \text{ W/Km}$, $\rho \sim 1 \text{ m}\Omega \text{ cm}$, and $N \sim 1 \mu\text{V/K T}$. Although ρ and κ are ~ 10 times smaller [10] than Bi at this H and T , N is ~ 1000 times smaller, which explains the factor of $\sim 10^4$ difference between the figures of merit. Evidently, the small Nernst response is the cause of the poor $z_E T$ compared to Bismuth.

Figure 9 Nernst signal, e_N , versus magnetic field. This graph shows that the largest order of magnitude of the Nernst signal is about $\sim 2 \mu\text{V/K}$ per 1 T magnetic field. This value is typical for materials with low carrier mobilities. The inset shows the directions of the temperature gradient and electric field established within the sample. The magnetic field points along the +z-direction.

Figure 10 Determination of the Ettingshausen figure of merit for a Bi_4Te_3 polycrystal. In the middle plot, the blue and red points are the N and ρ measurements, respectively. In the κ plot, the second line is a different Bi_4Te_3 sample. κ is more than 100 times smaller than that of

Bismuth below 100 K. However, the largest figure of merit is more than 1000 times smaller than found in Bismuth. The small figure of merit can be traced to a 1000 times smaller N and 100 times larger ρ . The solid lines are guide to the eye.

3.2.2 Hall effect, Magnetoresistance and Carrier Mobilities

The ambipolar Nernst response is determined by the proportion of n- and p-type carriers, and their respective mobilities. N is proportional to carrier mobility at low H [4]. Hall effect and magnetoresistance experiments allow simple estimates of carrier mobility.

Measurements of the Hall resistivity (ρ_{XY}) were conducted as a function of H at fixed T (Fig. 11). ρ_{XY} varies non-monotonically with H and changes sign with T , a common signature of ambipolar conduction. ρ exhibited a simple $\sim H^2$ behavior, and changed by about 25% at 9 T.

While a full carrier model can be used to fit the data, we performed a few simple estimates to understand the magnitude and ratio of carrier mobility. In Fig. 12, we plot R_h (at $H \rightarrow 0$) and ρ versus $1/T$. One can estimate, using the values A and B shown in Fig. 11, the ratio $c = \mu_p/\mu_n$ using the formula:

$$\frac{A}{B} = -\frac{(c-1)^2}{4c}.$$

We found $c \sim 0.105$. We also wanted to estimate absolute mobility in the present sample. Taking the low H limit and assuming the Hall factors are equal for n and p type carriers, the Hall coefficient is:

$$R_h = \frac{\mu_p^2 p - \mu_n^2 n}{e(\mu_n n + \mu_p p)}.$$

Here all quantities are taken as positive. This expression will be 0 when $\mu_p^2 p = \mu_n^2 n$, which for the present data occurs at ~ 150 K. Using the value $c \sim 0.1$, we find that in order to observe the low H data of Fig. 11, p must be greater than $100n$. At low T , ρ_{XY} becomes nearly linear, and so one carrier dominates the transport. Therefore, we estimated $\mu_p \sim R_h/\rho \sim 22 \text{ cm}^2/\text{V s}$ and $\mu_n \sim 212 \text{ cm}^2/\text{V s}$. In addition, $p \sim 1/eR_h \sim 10^{20} \text{ cm}^{-3}$, so $n < 10^{18} \text{ cm}^{-3}$. In Bismuth, $n \sim p \sim 10^{17} \text{ cm}^{-3}$ and $\mu \sim 10^5 \text{ cm}^2/\text{V s}$.

Figure 11 Isothermal Hall resistivity measurements for polycrystalline Bi_4Te_3 . The non-monotonic behavior of $\rho_{XY}(H)$ and change of sign with T reveal the presence of p- and n-type carriers.

Figure 12 $R_h = \rho_{XY}/B$ at $B \rightarrow 0$ (left scale) and ρ (right scale) as a function of $1/T$. Using the magnitudes of R_h shown at A and B, we inferred a carrier mobility ratio of ~ 0.105 . By estimating $\mu_p \sim R_h/\rho \sim 22 \text{ cm}^2/\text{V s}$ at 2 K, we found $\mu_n \sim 212 \text{ cm}^2/\text{V s}$ as the estimated mobility in the liquid Nitrogen regime.

3.2.3 Refrigeration performance of Bi_4Te_3 polycrystal

The performance of an Ettingshausen refrigerator depends on both zET and the material shape. The optimum shape is shown in Fig. 13 and described by the equation [4]:

$$\frac{z(x)}{z(0)} = \left(\frac{z(L_x)}{z(0)} \right)^{x/L_x}.$$

The hot and cold side occur at $z(0)$ and $z(L_x)$, respectively.

Figure 13 Optimum shape for an Ettingshausen refrigerator.

We explored the potential for Bi_4Te_3 by varying the ratio $z(L_x)/z(0)$ and computing the maximum cold-side T given a fixed hot-side T , related by the following equation:

$$\frac{z(L_x)}{z(0)} = \left(\frac{T_L}{T_0} \right)^{1/\alpha}.$$

The exponent $\alpha = (1 + \delta)/(1 - \delta)$, where $\delta = (1 - z_E(T_0)T_{\text{average}})^{1/2}$. By choosing a reasonable value of $z(L_x)/z(0)$ of 100, a T_L of 200 K (the low T limit of present thermoelectric coolers) and the maximum value of $z_E T$ for Bi_4Te_3 , we found a $T_L - T_0 \sim 0.020$ K. Adjusting $z(L_x)/z(0)$ to 1000 gives $T_L - T_0 \sim 0.035$ K. Changing the shape of this material will not result in a practical Ettingshausen refrigerator.

3.3. *ab initio* Band Structure Calculations of Bi_4Te_3

3.3.1. Methods

We performed *ab initio* calculations on the Bi_4Te_3 compound using the density functional theory (DFT) formalism with the local-density approximation (LDA) for the exchange correlation potential [12]. We employed a plane-wave basis set including plane waves up to a cutoff energy of 80 Ry. The electron-ion interaction was modeled by making use of first-principles norm-conserving pseudopotentials of Troullier-Martins [13]. The 4f and 5d states of Bi and the 4d states of Te were frozen into the core. Partial core corrections [14] as well as scalar relativistic corrections were also introduced. Spin-orbit interaction effects were not included in our calculations and we believe they are not important for the ionic optimization. We used a hexagonal unit cell and the Brillouin Zone (BZ) was sampled, during the structural relaxation, using a $9 \times 9 \times 1$ Monkhorst-Pack grid [15]. An $18 \times 18 \times 2$ Monkhorst-Pack grid was used to converge self-consistently the electron charge density. Band-structure calculations were performed for k -points along several high-symmetry directions of the hexagonal BZ.

Computational resources have been provided by the New Mexico Computing Applications Center, an SGI/Intel Altix ICE 8200 cluster with 1792 Intel 3.0 GHz Clovertown

nodes/14,336 cores, with a performance of 127 teraflops. The calculations were performed using the Quantum-Espresso package [16].

3.3.2. Results

The density of states (DOS) was computed in order to gain a coarse understanding of the band structure (Fig. 14). The finite DOS at the Fermi level is a strong indicator of the semimetallic nature of Bi_4Te_3 . A semimetal is sometimes defined as a material having some overlap between conduction and valence bands, which will lead to a finite DOS at the Fermi level.

Figure 14 Density of Electronic States for Bi_4Te_3 . The finite density of states suggests semimetallic behavior (band overlap).

The detailed band structure was computed as shown in Fig. 15. The main feature of interests are (1) there are several bands that overlap the Fermi level ($E=0$ in the plot). We can also infer something about the preponderance of electrons or holes and the Fermi surface from Fig. 15. The band structure calculations probably show that this stoichiometry has p-type majority carriers, in agreement with our Hall effect measurements. While more calculations would be needed to confirm this, one can see that most of the bands (e.g near the Γ and A points) that cross the Fermi level are inverted parabolas. These kinds of bands give rise to hole carriers. We can also see that no bands cross near the Γ point. The Fermi surface then probably has the topology of several disconnected ellipsoids. In this respect, the Fermi surface of Bi_4Te_3 is similar to that of Bismuth.

Figure 15 Band structure along selected high symmetry directions. Several bands overlap the Fermi energy. From these few calculations, p-type behavior is expected.

4. CONCLUSIONS

We investigated the potential of Bi-Te alloys for Ettingshausen refrigeration in the liquid Nitrogen range. The basis for this study was that these alloys were likely semimetals and exhibit much reduced thermal conductivity compared to Bi, the best existing Ettingshausen material. Bi_4Te_3 was identified a good candidate for this study and both large polycrystals and smaller single crystals were synthesized. The transport properties ρ and κ were superior to that of Bismuth. However, the Nernst response of a polycrystalline sample of Bi_4Te_3 was much too small for practical refrigeration, even considering the optimum shape for an Ettingshausen refrigerator.

We identified the root cause of the small Nernst response. Although Bi_4Te_3 possesses both p and n-type carriers, p and n are different by a factor of 100 and they possess very low carrier mobilities. One speculation is that the layered structure of these alloys results in both the reduced κ and reduced mobility. Our band structure calculations qualitatively predict p-type majority carriers, in agreement with experiment, and a disconnected, ellipsoidal Fermi surface similar to that found in Bismuth.

We identify some future directions for these materials. Further studies in large size single crystals would be needed to understand the low mobility values in this polycrystalline sample. Grain boundaries can sometimes substantially lower carrier mobility. An enhanced mobility/Nernst response is also dependent on crystallographic orientation, as is well known in Bismuth, which can only be measured with single crystals. In fact, many of these issues were encountered before Bismuth was identified as a good material for cooling. Band structure calculations could be used to provide a model for these transport quantities given some understanding of the scattering rate.

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