Transition of *p*- to *n*-Type Conductivity in Mechanically Activated Bismuth Telluride

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Bismuth telluride (Bi_2Te_3) exhibits a transition from *p*- to *n*-type conduction as a result of high-energy ball milling. The transition is monitored over mechanical activation through measurement of the thermoelectric properties in the temperature range of 1.9 K to 390 K. Data show a flip in polarity of the Seebeck coefficient from $225 \mu\text{V K}^{-1}$ for the bulk sample to $-120 \mu\text{V K}^{-1}$ (at 315 K) that correlates to fracturing the layered-like structure of stoichiometric Bi_2Te_3 into platelets and fine particles. The electronic transition is generated by fracturing the crystal 90° to the basal plane. This is the structural equivalent to inducing *n*-type, anti-site defects on grain boundaries. The observed phenomenon could be exploited to fabricate *p*- and *n*-type legs for thermoelectric devices from the same material. In this report, we demonstrate that the value of the Seebeck coefficient for bismuth telluride can be tuned using mechanical treatment. We also determine how mechanical activation of Bi_2Te_3 impacts physical properties of the system, including: particle size, crystal structure, band gap, electrical and thermal conductivity, carrier concentration and mobility, average hopping distance, and the concentration of localized charged centers.

Key words: Bismuth telluride, *p*- to *n*-type conduction, Seebeck coefficient, mechanical activation

INTRODUCTION

Bismuth telluride and its alloys are among the best thermoelectric materials near room temperature.¹ Since the early twentieth century, the physical properties of Bi_2Te_3 have intrigued researchers in its ability to generate electricity based upon a thermal gradient.² The reverse process is also possible and is referred to as Peltier cooling, where an electric power source is used to maintain a thermal gradient. Bulk stoichiometric Bi_2Te_3 is a *p*-type layered semiconductor with a narrow band gap of 0.15 eV with a trigonal unit cell.^{3,4} Bi_2Te_3 in its stoichiometric form is found to be an electron hole conductor that exhibits massive anisotropy, leading to layering of the material along the *c*-axis as shown in Fig. 1a.

Large anisotropy exists along the *c*-axis and is identified by considering the alternating Te(1)-Bi-Te(2)-Bi-Te(1) quintet atomic layers stacked along it as shown in Fig. 1b. Basis vectors of lengths 4.395 Å, 4.395 Å, and 30.44 Å have been measured for *a*, *b*, and *c* axes respectively.⁵ Van der Waals bonds between adjacent Te(1)-Te(1) quintets provides an easy cleavage plane to fracture the crystal, and correspond to the spatial separation between layers. The layered-like fracturing process is observable on the macro-scale when grinding bulk *p*-type chunks. The chunks break into thin platelets prior to their disintegration into micro- and nanoscale particles.

The traditional measure of thermoelectric performance is expressed by the thermoelectric figure of merit (*ZT*) that depends upon the Seebeck coefficient (α), temperature (*T*), thermal conductivity (κ), and the resistivity (ρ), yielding $ZT = \frac{\alpha^2 T}{\kappa \rho}$. The overall goal in thermoelectric materials design is to maximize *ZT* by expanding the absolute value of the α ,

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Fig. 1. (a) Schematic diagram of bismuth telluride depicting layers stacked along the *c*-axis. Bismuth is in green, and tellurium atoms are blue (mercury). (b) SEM image of bulk Bi_2Te_3 (Color figure online).

while minimizing κ and ρ . Although thermoelectric properties are greatly interrelated, α heavily impacts thermoelectric performance because it is squared when calculating ZT .

Most of the recent work on Bi_2Te_3 -based materials focuses on improving thermoelectric performance through nanoscale structuring leading to the development of synthesis methods for nanoparticles, nanoplatelets, nanowires, thin films, and nanocrystalline solids.^{6–8} These efforts highlight an overall trend in thermoelectric materials development, namely the search for low-dimensional materials, or so-called 1-, 2-, and 3-D quantum dot super lattices, where electrons are confined in regions of space less than 5 nm.^{9,10} A thermoelectric characterization of bismuth telluride of both *n*- and *p*-type is carried out, as a function of stoichiometric deviation.⁹ Highly pure *n*- and *p*-type samples were prepared from single crystalline ingots, using an annealing saturation technique at a temperature range of 560–585.5°C.

Several published papers have proposed various approaches to increase the figure of merit ZT for Bi_2Te_3 , including compressing the Bi_2Te_3 nanowire powder through spark plasma sintering,^{11,12} doping,^{13,14} annealing the Bi_2Te_3 nanocrystals under argon protection,¹⁵ or mechanical activation through the ball milling process.^{16–18}

A significant improvement was achieved in ZT for un-doped Bi_2Te_3 . For example, Ref. 12 reported that an improved ZT for bulk un-doped Bi_2Te_3 after the mechanical activation is achieved with a peak value of $ZT \sim 1.1$. Many researchers have provided solid evidence to support a model in which point defects created during the milling process are responsible for this improvement.¹⁹ Nevertheless, the physical processes underlying this phenomenon are not clear. Moreover, Ref. 18 pointed out that the figure of merit is increased in *p*-type Bi_2Te_3 , but decreased in *n*-type material. They argued that the

Table I. Physical properties of milled powders and density of pellets

Milling time (min)	Avg. particle size (nm)
1	462
5	422
15	421
30	—
60	316
120	305

observed opposite change in ZT is due to the reduction in the hole concentration of *p*-type material and a rise in the electron concentration of *n*-type Bi_2Te_3 during the ball milling. Other studies have examined the effects of mechanical treatments on Bi_2Te_3 and report that the *p*- to *n*-type transition is due to the formation of donor-like defects that are of the anti-site variety.¹⁶ However, the total understanding of this very promising effect requires further detailed investigation to enable the optimization of a thermoelectric device based solely on bismuth telluride and its structural character.

In this report, we carefully examine changes in the Seebeck coefficient for *p*-type Bi_2Te_3 that are induced by high-energy ball milling. Measurements indicate that controlling the delivered milling dose energy provides a means to control the value of the Seebeck coefficient. Nanostructured Bi_2Te_3 samples also exhibit a significant decreased in thermal conductivity as the particle size decreases.

EXPERIMENTAL

Bi_2Te_3 chunks (Sigma Aldrich 99.999% purity) were subjected to high-energy ball milling in hexane

for different intervals of time: 1 min, 5 min, 15 min, 30 min, 60 min, and 120 min, using an MSK-SFM-3 high-speed vibrating ball mill with an oscillation frequency of 1200 cycles per min. The energy of the delivered milling dose is determined according to $E_D = \frac{E_B \eta t}{m_p}$, where E_D is the dose energy, E_B is the linear kinetic energy ($\frac{1}{2}m_B v^2$) of zirconium milling balls ($m_B = 20$ g and $v = 1.63$ m s⁻¹), η is the frequency of the mill, m_p is the mass of the powder, and t is the designated milling time.

After milling, the powdered samples were removed from the mill within a nitrogen-filled glove box, transferred to a stainless-steel die then hydraulically pressed at 2 tons cm⁻². Samples were sintered at 1000°C in an argon environment for 2 h and were subjected to electrical measurements. The resulting density of the samples was obtained through measurement of the mass and sample dimensions. Powders produced in milling were compacted to densities up to 93% of the 7.86 g cm⁻³ theoretical density.

Fig. 2. SEM images of (a) bulk sample and milled powders after (b) 1 min, (c) 15 min, and (d) 2 h. (e) Seebeck coefficient of various samples of Bi₂Te₃ versus temperature for different milling times.

Fig. 3. Seebeck coefficient plotted versus milling energy at different temperatures.

Particle sizes for powders were determined using dynamic light scattering using a Zetasizer Nano ZS90 particle size analyzer (Malvern). The distribution of particle sizes given in Table I represents one standard deviation of the Gaussian used to fit the data. Powders were placed in a liquid water solution and sonicated to minimize the amount of agglomeration. Distributions tend to be broad and indicate the presence of agglomerates as well as particles less than 500 nm. Notably, bulk bismuth telluride pieces broke into powders within the first minute of high-energy ball milling and showed a gradual decrease in particle size after the initial disintegration into powder.

The Seebeck coefficient, resistivity, and thermal conductivity of sintered pellets were measured between 1.9 K and 390 K using the thermal transport option for a physical properties measurement system (PPMS, EverCool-II, Quantum Design, USA). X-ray diffraction (XRD) measurements were performed with a BRUKER 2D Phaser with Cu-K α radiation ($\lambda = 1.5406$ Å) to provide the phase and structural data for milled samples. The particle morphology, composition, and size distribution analysis were performed using a JEOL 7800F field emission scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Figure 2a, b, c, and d shows SEM images of bulk sample and milled powders after 1 min, 15 min, and 2 h. The SEM images clearly demonstrated increasing the milling time up to 15 min decreases the particle sizes to the submicron level. The electronic transition from *p*- to *n*-type conduction in Bi₂Te₃ upon high-energy ball milling is illustrated in Fig. 2e where the Seebeck coefficient is plotted as a function of temperature for different milling

times. After 1 min of high-energy ball milling, the bulk material was crushed into a powder and α dropped significantly from a maximum value of $225 \mu\text{V K}^{-1}$ at 300 K for the un-milled sample to $90 \mu\text{V K}^{-1}$ at 300 K for the milled sample. This observation suggests that mechanical treatment breaks down the bulk *p*-type structure that decreases the Seebeck coefficient.

A shift in the majority charge carriers from holes to electrons is seen after 5 min of milling, indicated by negative values measured for the Seebeck coefficient. A prominent plateau in α for the 5-min-milled sample, appears between 175 K and 300 K. To the best of our knowledge, this feature has not been reported in studies that examine the effects of mechanical milling on the thermoelectric properties of bismuth telluride.

The largest negative values for the Seebeck coefficient as a function of temperature are found after 15 min of milling to be $-123 \mu\text{V K}^{-1}$ at 300 K. As the material is milled for longer time intervals, the magnitude of α gradually decreases. This trend is shown in Fig. 3, where the Seebeck coefficient is plotted as a function of milling dose energy at four different temperatures. All the graphs show a similar pattern with the Seebeck coefficient reaching a minimum between 5 min and 15 min of milling with doses of 330 J g^{-1} and 1000 J g^{-1} , respectively.

Takashiri et al.²⁰ reported similar Seebeck coefficient changes for mechanically milled and spark plasma-sintered Bi₂Te₃ measured at 300 K. Their samples were milled for longer durations (3 h, 6 h, and 9 h) and exhibited slightly smaller magnitude Seebeck coefficients: $-107 \mu\text{V K}^{-1}$, $-112 \mu\text{V K}^{-1}$, $-76 \mu\text{V K}^{-1}$ at 300 K for their 3-h, 6-h, and 9-h-milled samples, respectively, compared to our data.²⁰ The group's bulk *p*-type sample also exhibited a reduced Seebeck coefficient of $+166 \mu\text{V K}^{-1}$

Table II. Band gap and other parameters for Bi₂Te₃ samples

Milling time (min)	Type of conductivity	Band gap (E_g , eV)	Carrier concentration (cm^{-3})	Average hopping distance (a, nm)	Concentration of localized centers (N_0 , cm^{-3})	Mobility (μ , cm^2/Vs)
0 (bulk material)	<i>p</i> -type	0.145	3.0×10^{19}	6.7	2.08×10^{17}	189
1	<i>p</i> -type	0.054	1.2×10^{20}	29	2.46×10^{15}	10.3
5	<i>n</i> -type	—	8.5×10^{19}	192	9.00×10^{12}	2.32
15	<i>n</i> -type	0.086	4.9×10^{19}	210	6.87×10^{12}	3.65
30	<i>n</i> -type	0.092	5.7×10^{19}	136	2.57×10^{13}	4.96
60	<i>n</i> -type	—	8.7×10^{19}	202	7.74×10^{12}	2.16
120	<i>n</i> -type	0.091	7.6×10^{19}	202	7.74×10^{12}	2.47

when compared to our data and others reported in literature (measured at 300 K) presumably due to the lower purity of their starting materials. Other studies have examined the effects of mechanical treatments on Bi₂Te₃ and report that the *p*- to *n*-type transition is due to the formation of donor-like defects that are of the anti-site variety.^{4,7}

Additionally, a strong similarity exists between our Seebeck coefficient measurements of Bi₂Te₃ and the data published by Fleurial et al.⁹ They demonstrated the dependence of α with respect to deviations in stoichiometry of Bi₂Te₃ single crystals. Their crystals were grown via the Bridgman method and represent a standard by which highly crystalline samples were grown. Seebeck coefficients obtained from their work show a rapid transition from *p*- to *n*-type conduction with excess tellurium concentration, as is expected.

It was demonstrated²¹ that a maximum value of the Seebeck coefficient α_{max} can be used to estimate the thermal band gap (E_g) through the following expression:

$$\alpha_{\text{max}} = \frac{1}{2} \frac{E_g}{qT_m} \quad (1)$$

Here, T_m is the temperature associated with a maximum value of α_{max} . Additionally, for degenerate narrow-band semiconductors, the Seebeck coefficient is described by the following expression:

$$\alpha = \frac{1}{3} \frac{\pi^2 k^2 T}{qE_F} \quad (2)$$

where E_F is the Fermi energy, and k is Boltzmann's constant. It follows from (2) that the Seebeck coefficient should be linear in T and a position of the Fermi level E_F can be derived from the slope of a linear part of a graph $\alpha(T)$. On the other hand, for degenerate semiconductors, the concentration of holes and electrons do not depend on temperature and can be described by the following formulas:

$$p = \frac{8\pi}{3} \left(\frac{2m_p^*}{h^2} \right)^{\frac{3}{2}} (E_v - E_F)^{\frac{3}{2}}, \quad n = \frac{8\pi}{3} \left(\frac{2m_n^*}{h^2} \right)^{\frac{3}{2}} (E_F - E_c)^{\frac{3}{2}} \quad (3)$$

where m_p and m_n are the effective mass of holes and electrons, respectively, h is the Planck constant, and $E_v - E_F$ and $E_F - E_c$ are the Fermi level position in *p*-type and *n*-type semiconductors, respectively. As shown in Fig. 2e, temperature dependence of the Seebeck coefficient was linear in T at low temperatures for all studied samples according to (2) and peaked at temperature T_m . Using the expressions (1–3) and taking into account that for *p*-type Bi₂Te₃, $m_p = 1.07m_0$ (m_0 —the electron mass),²² we estimated the band gap and concentration of holes and electrons in the studied samples shown in Table II. The energy band gaps have been determined using Eq. 1 with the use of experimental dependence of the Seebeck coefficient.

The band gap value obtained for the bulk Bi₂Te₃ is in a good agreement with generally accepted results.²³ At the present time, there is no complete understanding on how pressure influences the band structure of Bi₂Te₃. One of the possible explanations for the reduction in the band gap indicated in Table II can be attributed to the effect of mechanical impact on the band structure. It is considered that the observed decrease in energy gap with pressure is associated with the anisotropic behavior of the material,²³ i.e., with relative change in bond angle and length during a milling process.

At high temperatures, thermally activated smaller carriers decrease the magnitude of the Seebeck coefficient as observed in our experiments. In order to obtain more information about the charge transport mechanism, we investigated temperature dependence of electrical conductivity $\sigma(T)$ for Bi₂Te₃ samples, which is shown in Fig. 4. The exhibited conductivity is attributed to the metal–insulator transition.

In doped semiconductors, this transition takes place in an impurity band, due to the highly disordered potential energy of the random positions of the donors (or acceptors). A transition can be induced by a change in the density of donors, in the compensation, uniaxial stress, or magnetic field. The temperature dependence of conductivity shown in Fig. 4 is attributed to the case when there is a range of charge states at the bottom of the conduc-

Fig. 4. Temperature dependence of electrical conductivity $\sigma(T)$ of the studied Bi_2Te_3 samples.

Fig. 5. Band diagram of the Bi_2Te_3 sample with positively charged grain boundaries. The dashed line represents the potential barriers for holes due to grain boundary scattering.

tion band (top of the valence band) for which an electron (hole) can move solely through a thermally activated hopping process and this result is consistent with Ref. 24. Hopping conduction takes place when the concentration of electrons is low and the Fermi energy E_F is situated below E_c , corresponding to the rising or horizontal part of electronic conductivity versus temperature shown in Fig. 4, but with higher charge concentration and $E_F > E_c$, the standard band conduction mechanism is observed. A decreasing electronic mean-free path is indicated by the declining part of $\sigma(T)$ dependence in Fig. 4. At high temperatures, when $E_c - E_F < kT$, the main conduction process is band conduction, but at low temperatures, when $E_c - E_F > kT$, the hopping or tunneling dominates. If E_F lies below E_c , then at low T , conduction is by variable-range hopping and at high T by thermal activation of carriers to the mobility edge, when the conductivity is of the form²⁵

$$\sigma = \sigma_{\min} \exp \left[-\frac{E_c - E_F}{kT} \right] \quad (4)$$

Fig. 6. Seebeck coefficient versus temperature for the 30-min-milled sample before (squares) and after sintering (triangles).

Here, $\sigma_{\min}$ is the lowest non-activated conductivity at the low-temperature limit (minimum metallic conductivity). In the case of compensated semiconductors, $\sigma_{\min}$ can be denoted as²⁵:

$$\sigma_{\min} \approx 0.025 \frac{q^2}{\hbar a} \quad (5)$$

where q is an elemental charge, $\hbar$ is the reduced Planck constant, and a is a hopping distance. It can be clearly seen from Fig. 4 that at low temperatures, all samples lead to non-activated hopping conductivity (minimum metallic conductivity) according to (5) that can be used to obtain the intercept of the linear part of $\ln(\sigma) - T$. Moreover, according to Ref. 26, the concentration of localized charged centers can be estimated as:

$$N_{0\approx} \left(\frac{0.4}{a} \right)^3 \quad (6)$$

The charge mobility was calculated using measured minimal conductivity $\sigma_{\min}$ and carrier concentration p (or n) according to: $\mu = \sigma_{\min}/nq$. Hopping distance, mobility, and the concentration of the localized charged centers N were estimated using (5) and (6) for the studied samples and are presented in Table II. At higher temperatures ($T > 150$ K), the sample after 1 min of milling manifests thermally activated conductivity, which can be attributed to the barrier-scattering mechanism affecting charge transport in the studied samples.

In the metallic phase, when the metal-insulator transition is approached, a sharp decrease in $\sigma(T)$ dependence occurs²⁶ as observed in our case (see Fig. 4). One possible explanation of the transition from *p*-type to *n*-type conductivity can be found taking into account grain boundary effects on the

Fig. 7. X-ray intensity plotted versus angle 2θ , for 1-min, 5-min, and 1-h mill times.

charge transport mechanism. As it has been stressed, electron energy filtering is another effective method of the power factor enhancement.²⁷ The enhancement is based on the fact that the power factor depends strongly on the Seebeck coefficient through the following expression:

$$PF = \alpha^2 \sigma \quad (7)$$

On the other hand, the Seebeck coefficient α , to the first order, is proportional to the mean excess energy $\langle E - E_F \rangle$ of electrons (the higher mean excess energy the higher α), where E_F is the Fermi level. As a result, the presence of a high potential barrier in the conduction band of an *n*-type semiconductor or valence band of a *p*-type material, higher-energy carriers can be selectively transmitted through the grain boundaries by filtering out the lower-energy carriers through the scattering process as shown in Fig. 5.

It is known that anti-site defects are the principle defects for Bi_2Te_3 -related compounds, and the carrier concentration is dominated by these anti-site defects inducing *p*-type conductivity according to the following reaction.²²

Here, the bullet and prime superscripts mean positive and negatively charged vacancies, respectively, e denotes an electron, h denotes a hole, V_{Bi}''' denotes a Bi vacancy, $V_{\text{Te}}^{\bullet\bullet}$ denotes a Te vacancy, Bi_{Bi} denotes a Bi atom on a regular site of the crystal lattice, and Bi_{Te}' denotes a Bi atom on a Te site. On the other hand, both mechanical and thermal energy induced by ball milling can create various defects such as positively charged vacancies $V_{\text{Te}}^{\bullet\bullet}$ according to the following equation.²⁸

Any positively charged defects on the grain boundaries (interfacial charged defects) act as a potential

Fig. 8. The lattice parameters of Bi_2Te_3 obtained from XRD patterns as a function of the milling time.

Fig. 9. Thermal conductivity plotted as a function of temperature for Bi_2Te_3 bulk and sintered pressed pellet samples.

barrier that filters selectively lower-energy minority carriers (holes in *n*-type Bi_2Te_3). However, donor-like defects generated at the grain boundaries according to (9) can inject electrons to the grain's bulk, contributing to electronic conductivity. When the defect concentration induced by the milling process reaches the critical value, bipolar conductivity of nanostructured Bi_2Te_3 becomes *n*-type. The analogous *p*- to *n*-type transition was revealed in our recent work for LiNbO_3 films and was also related to defect concentration in the studied films.²⁹

The right-hand side of Eq. 9 can be visualized according to the fracture shown in Fig. 1 that is 90° to the basal plane. The phenomenon is observed while breaking the material in a mortar and pestle. Rapid disintegration of the bulk structure occurs along weak Van der Waals bonds between adjacent layers, resulting in the formation of thin macroscopic platelets. With greater mechanical agitation, the material fully decomposes into a powder that,

with a high concentration of defects, demonstrates *n*-type conduction.

A prominent plateau in α , for the 5-min-milled sample, appearing between 175 K and 300 K (Fig. 2e) can be described in the framework of the hopping-carrier transport mechanism. As it was demonstrated³⁰ in the systems having high density of carriers and interactions stronger than the thermal energy (when binding energy $E_{\text{bind}} \gg kT$), the Seebeck coefficient becomes temperature-independent and can be expressed through the Heikes formula.³¹

$$\alpha = \left(\frac{k}{q}\right) \left[\ln\left(\frac{c}{1-c}\right) + \beta \right] \quad (10)$$

where k is the Boltzmann constant, q is the elementary charge, and c is the ratio of particles-to-sites ($c = 2n/N_0$). β is a constant, which in the case for the hopping regime, lies between 0.1 and 0.2.³¹ Apparently, after 5 min of milling, electrons with a high degree of interaction exceeding the thermal energy are responsible for the behavior of the Seebeck coefficient in the temperature range of 200–300 K. The sample prior to sintering exhibits an agglomerated microstructure. After sintering, plate-like grain growth emerges, reminiscent of the layered-like structure of the bulk material. Sintering impacted the Seebeck coefficient of the 30-min-milled sample, measured to be $-115 \mu\text{V K}^{-1}$ before and $-104 \mu\text{V K}^{-1}$ at 300 K after sintering, as shown in Fig. 6.

Most noticeably, a point of inflection in the Seebeck coefficient versus temperature emerges at 25 K, similar to the plateau in the Seebeck coefficient observed for the 5-min-milled sample. This indicates that the *p*-type character of the material can be restored through sintering, a result that has been reported in the literature.³² XRD data on bismuth telluride samples are presented in Fig. 7. Primary reflection planes labeled in the

figure conform to JCPDS: 08-0021 standards for Bi_2Te_3 . Sharp peaks indicative of long-range crystalline order are seen in the 1-min-milled sample. Milled samples show gradual broadening of x-ray peaks that indicate progressively smaller crystallite sizes developing with extended milling time. The lattice parameters obtained from XRD patterns are shown in Fig. 8 as a function of the milling time. The lattice parameters of *c*-axis of the unit cell increase with milling time and reach the peak 30.7 Å for the 10-min samples, and then decrease up to 28.7 Å, while the values of the *a*-axis are decreased from 4.41 Å to 4.39 Å.

Figure 9 illustrates the thermal conductivity of milled samples as a function of temperature. The milling process further decreases thermal conductivity within the material, as progressively smaller particles are generated. In solids, three main scattering mechanisms can be observed: phonon–phonon scattering, boundary scattering, and point-defect scattering. Boundary scattering and point-defect scattering are responsible for the magnitude of the thermal conductivity at low temperatures with dependence $k \sim T^p$ ($1 < p < 3$ depending on the scattering conditions). The phonon–phonon scattering does not contribute to the thermal conductivity at low temperatures because only long-wavelength phonons with energies smaller than kT are excited. By contrast, at high temperatures, phonon–phonon scattering dominates, reducing the thermal conductivity as $k \sim \exp(\theta_D/T)$, where θ_D is the Debye temperature. It is generally accepted that thermal conductivity can be divided into two major components: electronic (related to the electrical resistivity) and lattice conductivity due to the heat transported by phonons, which is low for disordered or amorphous materials.

In case of disordered materials, interfaces scatter the phonons strongly, but the role of the phonon–phonon scattering becomes insignificant. Interfaces have very little effect when the mean-free paths are

Fig. 10. Thermoelectric element where *p*- and *n*-type legs are composed entirely of bismuth telluride.

lower than the distance between interfaces, but scatter phonons and long mean-free-path electrons effectively. Therefore, milling tends to increase the density of grain boundaries, enhancing the role of boundary scattering and point-defect scattering, while decreasing phonon-phonon scattering. As a result, for the samples obtained through milling, a decreasing in thermal conductivity obeying $k \sim \exp(\theta_D/T)$ is not observed. Weak temperature dependence (or even saturation for milling times greater than 30 min) is qualitatively understood by considering that the phonon mean-free path is as short as interatomic distances, and the thermal conductivity is consequently independent of temperature.

A decrease in particles size leads to increase in density of particle interfaces, which scatter phonons and reduce thermal conductivity. Several previous studies report this effect as a means to improve thermoelectric efficiency.^{9,10,16,33–35} On the other hand, optimization of the milling regime can improve thermoelectric efficiency through elimination of the minority carrier's effect which are holes after the p -type to n -type transition. Minority carriers are undesirable for two reasons. They have thermoelectric coefficients that are opposite in sign to those of the majority carriers, reducing the Seebeck coefficient. Additionally, they make a large contribution to thermal conductivity through the bipolar effect. One possible way to eliminate this effect is to increase the concentration of majority carriers. Another possibility, that would allow a higher Seebeck coefficient to be achieved through a narrow gap, is to increase scattering for minority carriers. From this point of view, the results reported in our work pose a promising perspective for improvement of the thermoelectric properties of Bi_2Te_3 .

A schematic of a thermoelectric element is shown in Fig. 10, the novelty being that both p -type and n -type legs are composed completely of bismuth telluride. The p -type leg demonstrates the characteristic layered-like defect-free Bi_2Te_3 structure, while the n -type leg exhibits a high defect density that promotes electron conduction in the material. Enhancement of the thermoelectric properties of samples generated in this study is achievable by increasing the electrical conductivity in n -type samples.

CONCLUSIONS

It was demonstrated that the thermoelectric properties of stoichiometric Bi_2Te_3 relate directly to its structural properties. Long-range ordering of its layered-like structure expresses p -type character, while defect-rich samples conduct electrons and expresses n -type conduction. Experiments show that the magnitude of the Seebeck coefficient is tunable through purely mechanical processes, between $225 \mu\text{VK}^{-1}$ and $-123 \mu\text{VK}^{-1}$ measured at

315 K. This enables the optimization of a thermoelectric device based solely on bismuth telluride and its structural character.

It is important to highlight the fundamental role that semiconductors, with tunable band gaps, have in computing and electronics industry. Increased attention has been focused on three-dimensional topological materials like Bi_2Te_3 that preserve electronic spin states, because of their application in spintronics and quantum computing. However, as demonstrated within this paper, the electronic character of this material is very tenuous, causing minor deviations in the chemical composition and/or structural ordering to result in significantly different electronic behavior. Ultimately, it seems that the dual nature of bismuth telluride can be exploited to produce industrially relevant materials that are unique to the current state of the art.

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