High-Pressure Preparation and Thermoelectric Properties of $Bi_{0.85}Sb_{0.15}$

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Nanocrystalline $Bi_{0.85}Sb_{0.15}$ powders were prepared by a novel mechanical alloying method. The bulk samples were formed by applying a pressure of 6 GPa at different pressing temperatures and times. Electrical conductivity, Seebeck coefficients, and thermal conductivity were measured in the temperature range 80–300 K. The Seebeck coefficient reaches a maximum value of -173 μV/K at 150 K. The largest figure of merit, 3.46×10^{-3} K^{-1}, achieved in this experiment is 50% higher than that of its single-crystal counterpart at 200 K.

Key words: Thermoelectric materials, nanotechnology, low temperatures, high-pressure synthesis

INTRODUCTION

Thermoelectric refrigeration is a kind of solid-state cooling. The development of low-temperature (T < 200 K) thermoelectric refrigeration is very important for applications in the electronics industry. If thermoelectric refrigeration can provide efficient local cooling at temperatures below 200 K, it would greatly affect the electronics industry, because performance of many semiconductors and other electrical devices is dramatically enhanced below room temperature. Some applications of thermoelectric refrigeration are in the cooling of CCDs, infrared detectors, laser diodes, and CMOS computer processors.[1–4] Cooling of laser diodes and infrared detectors to temperatures of 100 < T < 200 K would greatly improve the performance and sensitivity.[1,2] Moreover, if the cooling temperature can reach ~90 K, prospects of using thermoelectric refrigeration for superconducting electronics become feasible. Thus, the potential payoff for the development of low-temperature thermoelectric refrigeration is of great interest. However, the performance of this material is still far from satisfactory for wider applications because the energy-conversion efficiency is still low.[4] The essence of defining a good thermoelectric material lies in determining the material's figure of merit, $Z = S^2\sigma/\lambda$, where S is the Seebeck coefficient, σ is the electrical conductivity, and λ is the thermal conductivity.[3] Typically p-$Bi_xSb_{2-x}Te_3$ and n-$Bi_2(Se_yTe_{3-y})$ are state-of-the-art materials for the 200–400 K temperature range.[4] The product of the figure of merit and temperature, ZT, at 300 K achieved so far is 1.14 for the p-type alloy $(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$.[5] At low temperature, ZT of p-type $CsBi_4Te_6$ is 0.8 at 225 K,[6] and single crystals of n-type $Bi_{1-x}Sb_x$ alloys exhibit the optimum thermoelectric performance at 80 K.[7–9] Bi and Sb are semimetals, which both exhibit a similar rhombohedral crystal structure (the so-called A7 structure) of space group $R\bar{3}m$. $Bi_{1-x}Sb_x$ alloys form a solid solution over the entire composition range. It becomes an n-type semiconductor between $0.07 < x < 0.22$.[10,11] A ZT value of 0.52 at 80 K and higher values under a magnetic field at ~100 K[6] have been reported for crystals of $Bi_{1-x}Sb_x$ alloys. However, high-quality homogenous single crystals of $Bi_{1-x}Sb_x$ alloys are still difficult to produce. The brittleness of the single crystals is another problem for practical applications. Some works have been engaged in the crystalline size effects on the transport properties of bismuth antimony alloys.[12] It is predicted that the Seebeck coefficient could be significantly increased by the introduction of multiple potential barriers[13] and be improved due to electronic topological transition under high pressure.[14] There has been a report of an estimated ZT > 2 at 300 K in BiSb-Te alloy under a hydrostatic pressure of 2 GPa.[15] The main objective of the current study is to examine the effect of mechanical alloying and high-pressure processing on the thermoelectric properties of the BiTe alloy at low temperatures.

EXPERIMENTAL DETAILS

The $Bi_{0.85}Sb_{0.15}$ powders were prepared in a planetary ball milling in jars of 250 cm³. Jars and balls were made of carnelian. The ratio of the ball to powder weight was 20:1. The rotation speed was fixed at 400 rotations per minute in all the experiments. The base bismuth and antimony of high purity (99.999%) were introduced in the vessels that were evacuated below 2×10^{-5} torr. The vessels were sealed under an argon atmosphere in order to prevent a possible oxidation and then milled for 50 h. The as-milled powders were pressed into pellets under 250 MPa and wrapped with silver foil at room temperature. They were pressed under 6 GPa at different temperatures (300 K, 373 K, 473 K, 523 K, 573 K) for 30 min. with a cubic-anvil high-pressure apparatus. In order to investigate transport properties of $Bi_{0.85}Sb_{0.15}$ with different crystalline sizes, the bulk samples were formed by pressing at 6 GPa for 10 min., 20 min., and 30 min. at 573 K, respectively.

RESULTS AND DISCUSSION

The x-ray diffraction shows that there is no secondary phase. Table I lists the crystalline sizes calculated from the x-ray (012) diffraction peak using Scherrer's formula. Lattice constants are also listed in Table I. The temperature dependence of electrical conductivity is shown in Fig. 1a in the temperature range 80–300 K. As shown in this figure, the electrical conductivity of the alloys increases monotonically with increasing temperature for alloys pressed at 300 K and 373 K. For the alloys pressed at higher temperatures, the electrical conductivity tends to increase slowly (80–150 K) and then rapidly (150–300 K) with increasing temperature. Figure 1b shows the electrical conductivities of alloys prepared for difference pressing time at 573 K as a function of temperature. The electrical conductivity of the alloys was always lower than that of single crystals.[7] This has been known to be associated with phonon boundary scattering. The same phenomenon was found in reference[12] in which the conductivity values of BiSb polycrystalline alloys are of the same order of magnitude.
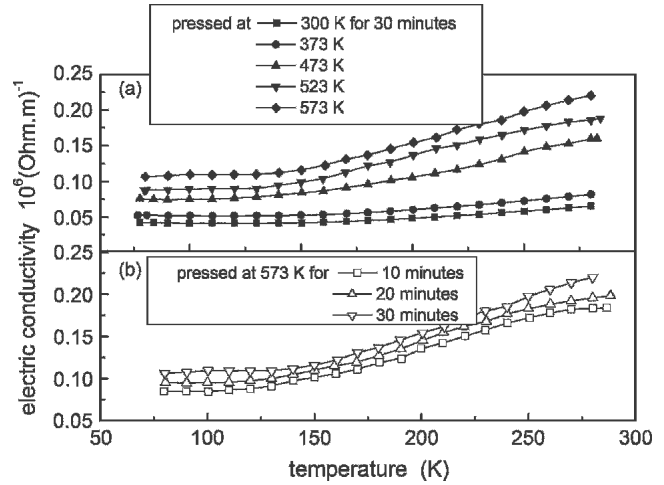

Fig. 1. Relationship between electrical conductivity and temperature (range 80–300 K) for alloys prepared at different (high) pressing temperatures (a) and times (b).
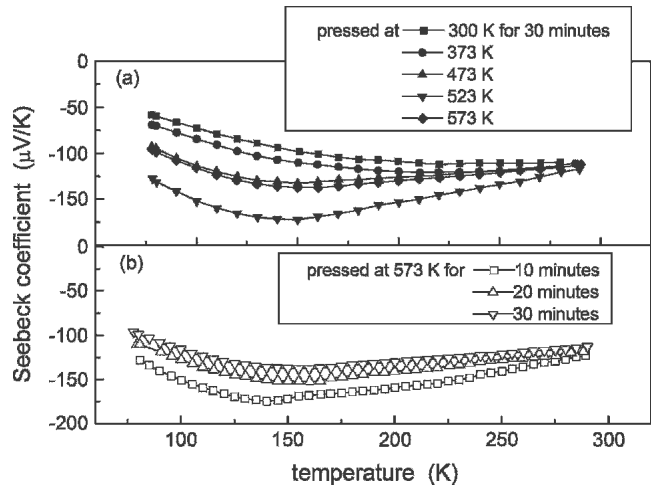

Fig. 2. Seebeck coefficient as a function of temperature (range 80–300 K) for alloys pressed at different (high) temperatures (a) and times (b).

The Seebeck coefficient of $Bi_{0.85}Sb_{0.15}$ alloys is shown as a function of temperature in Fig. 2a and b, respectively. The Seebeck coefficient is negative, indicating that the alloys are all n-type semiconductors. The absolute Seebeck coefficient increases with increasing pressing temperature (see Fig. 2a), and it reaches its maximum value (173 µV/K) with alloy pressed at 523 K for 30 min. The absolute value of the Seebeck coefficient of the sample is about 60% higher than that of single crystals above 150 K.[7] For the alloys pressed at 300 and 373 K, the absolute Seebeck coefficient also increases with increasing temperature. It can be seen that the alloys pressed at higher temperature exhibit the maximum coefficient at a critical temperature T_c, which is ~150 K. The absolute Seebeck coefficient increases with increasing temperature when temperature is lower than T_c. When the temperature is higher than T_c, the absolute Seebeck coefficient decreases with increasing temperature. The same behaviors are
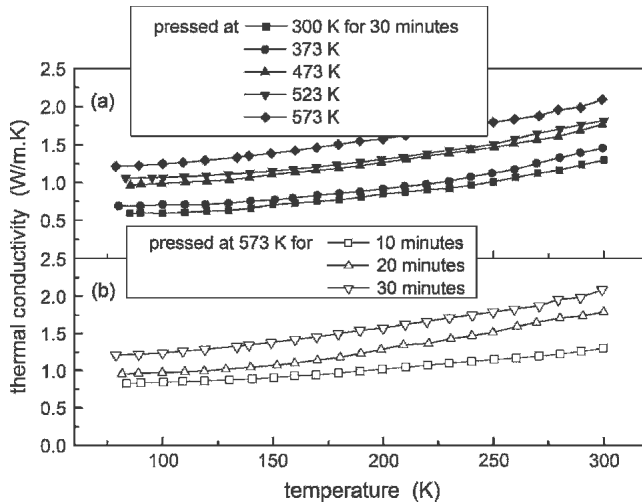
Table I. Crystalline Sizes and Lattice Constants of Materials Pressed at 6 GPa

Pressing Temp. (K)/Time (mins)	2θ (degrees)	Crystallite Size (nm)	a Axis (nm)	c Axis (nm)
300/30	27.36	34.8	0.4522	1.1762
373/30	27.34	43.5	0.4527	1.1812
473/30	27.36	38.5	0.4524	1.1765
523/30	27.28	43.5	0.4526	1.1818
573/10	27.34	38.5	0.4517	1.1787
573/20	27.30	43.5	0.4524	1.1804
573/30	27.24	49.6	0.4533	1.1836

Fig. 3. Thermal conductivity as a function of temperature (range 80–300 K) for alloys pressed at different (high) temperatures (a) and times (b).

Fig. 4. Variation of figure-of-merit with testing temperature for alloys pressed at different temperatures (a) and times (b).

found for alloys pressed for 10 min. and 20 min. at 573 K, as shown in Fig. 2b.

The total thermal conductivity λ is mainly the sum of the lattice contribution λ_L and of the electronic contribution λ_e associated with free carriers. At low temperature, the thermal conductivity λ is due entirely to the lattice contribution λ_L.[16,17] Size effect has a great effect on thermal conductivity at low temperature.[18] The λ_e increases with increasing temperature. At room temperature, heat transport is due mainly to free carriers. The thermal conductivity λ as a function of temperature is shown in Fig. 3a. The thermal conductivity of alloys increases with increasing temperature. These curves clearly show the dependence of the thermal conductivity on the pressing temperature. In fact, the increase in thermal conductivity with increasing pressing temperature is associated with the increase of crystallite size as listed in Table I. Note that the thermal conductivities of the samples prepared in this experiment are always lower than those of the single crystals.[7] The thermal conductivities of samples prepared under different pressing time are shown in Fig. 3b. The thermal conductivity increases with increasing pressing time shown in this figure is a clear indication of enlarged crystalline sizes.

The figure-of-merit as a function of temperature is shown in Fig. 4a and b. For comparison, the values of single crystals are also plotted in Fig. 4a. An interesting behavior observed is that, below 150 K, the figure-of-merit values calculated for $Bi_{0.85}Sb_{0.15}$ alloys pressed at different pressing temperature are significantly lower than those of single crystals. However, the situation is reversed at 200 K, that the figure-of-merit for the alloy pressed at 523 K for 30 min. exceeds the value of the single crystal. The figure-of-merit of alloys pressed at 573 K for different pressing time is shown in Fig. 4b. The figure-of-merit of alloys pressed at 573 K for 10 min. is comparable with that of crystal at 150 K.
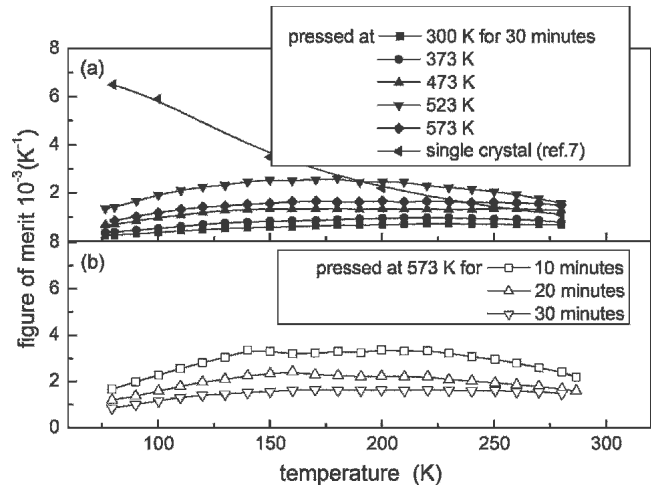
The value of the figure-of-merit of the sample is 50% higher than that of the single crystal at 200 K. The maximum Z value of the samples is 3.46×10^{-3}/K, and ZT is 0.69 at 200 K. ZT is ~0.48 for optimized crystalline BiSb[8] and is ~0.5 at 200 K for n-type commercial $Bi_2Te_{3-x}Se_x$.[19] Because the $Bi_{0.85}Sb_{0.15}$ samples reach optimum performance at 200 K, we exploited for application instead of $Bi_2Te_{3-x}Se_x$ and crystalline BiSb in the temperature range 150–200 K. A complete TE cooling device needs both a p-type and an n-type version of a material to operate. The n-type $Bi_{0.85}Sb_{0.15}$ and p-type $CsBi_4Te_6$ with ZT $\approx$ 0.8 at 225 K is a good choice.

SUMMARY

$Bi_{0.85}Sb_{0.15}$ alloys were prepared by a high-pressure method. The nanocrystalline sizes have been varied by applying high pressure at different temperature and time. The absolute Seebeck coefficient of the bulk samples reaches a maximum value of 173 μV/K at 150 K. The largest figure-of-merit, 3.46×10^{-3} K^{-1}, is 50% higher than that of its single-crystal counterpart at 200 K. The transport conductivity of the samples is found to be strongly affected by the nanocrystalline size, which is varied by adjusting synthesis parameters. We reported herein on the n-type $Bi_{0.85}Sb_{0.15}$ with ZT $\approx$ 0.69 at 200 K.

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