



Original Article

Thermoelectric Performance of $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ Alloys under High Pressures

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Abstract: The pressure effect on the thermopower has been investigated for the $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ alloys. We have found an anisotropic pressure dependence on the thermopower for *p*- and *n*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ at room temperature. Along *a*-axis, for *p*-type, the thermopower value increased with increase of pressure at a rate of 13.9 %/Gpa, whereas, along *c*-axis, it keeps approximately constant. The absolute value of the thermopower decreased with pressure along both *a*- and *c*-axis for *n*-type. The power factor increased largely with increase of pressure for *p*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$, while it is approximately constant for *n*-type.

Keywords: Thermoelectric materials, high pressure, electrical resistivity, thermopower.

1. Introduction

The $(\text{Bi,Sb})_2\text{Te}_3$ doped alloys should be the most efficient thermoelectric materials so far developed for thermoelectric applications above room temperature. The studies on bismuth telluride (Bi_2Te_3) and antimony telluride (Sb_2Te_3) compounds have shown that these compounds are the semiconductors with a relatively small energy gap, namely about 0.16 eV at 300 K [1-2]. Katsuki et al., [3] have also calculated the band structure of Bi_2Te_3 compounds. The effect of pressure on the energy gap for Bi_2Te_3 has been investigated [4]. The decrease in energy gap with increase of pressure was observed. This decrease was associated with the anisotropic behavior of the material [4].

The $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ alloys are formed by the substitution of the Bi atoms with Sb atoms. Rossi et al., showed that the figure of merit was considerably improved in these alloys. The alloys exhibit *p*-type conduction when in their crystals exist the anti-site defects as Bi_{Te} and Sb_{Te} . These anti-site

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defects can be explained due to the non-stoichiometry toward Bi and Sb of Bi_2Te_3 and Sb_2Te_3 compounds [5]. The investigations were also performed for the structural and thermoelectric properties at low temperature for p -type and n -type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_3$ alloys with an initial composition of $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3+\delta}$ with δ being between 0.0 and 0.40 [6-8]. The p -type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_3$ alloys showed a high thermoelectric performance at low temperature: ZT reached 1.1 at 200 K for $\delta = 0.259$. For n -type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_3$ alloys, the largest value of thermopower was obtained at 200 K of $-400 \mu\text{V/K}$ but ZT reached only 0.2 at 200 K for $\delta = 0.30$.

In this work, we investigated the pressure effect on the thermoelectric properties of p - and n -type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ alloys.

2. Experiment

Single crystals of $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ alloys were prepared from Bi, Sb and Te with aa 6N purity. We have added an excess amount (δ) of Te ranging from 0 to 0.25 in the initial chemical formula of $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0+\delta}$ to control the carrier concentration in the ingots to prepare. These initial elements were sealed into a quartz ampoule at the pressure of $\sim 1.33 \times 10^{-3}$ Pa, melted at 610°C for 12 hours in an electric furnace and were cooled to room temperature. Then, $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ ingots were grown by using Bridgman method in a Gradient Freeze (GF) furnace. Before growing single crystals, we have kept the temperature at the bottom point of the ampoule at 610°C for 6 hours to ensure a complete melting of the ingot. Then, the temperature gradient of 40°C/cm was given at the ampoule position by controlling two independent heaters in the GF furnace [6].

Electrical resistance measurements under high pressures up to 1.2 GPa was generated by using a clamp type piston cylinder apparatus. The temperature range for the electrical measurements extends from 80 K to 300 K. The thermopower measurement under high pressures up to 0.5 GPa was performed by a steady-state longitudinal heat flow method.

3. Results and Discussion

3.1. Pressure Effect on the Electrical Resistivity

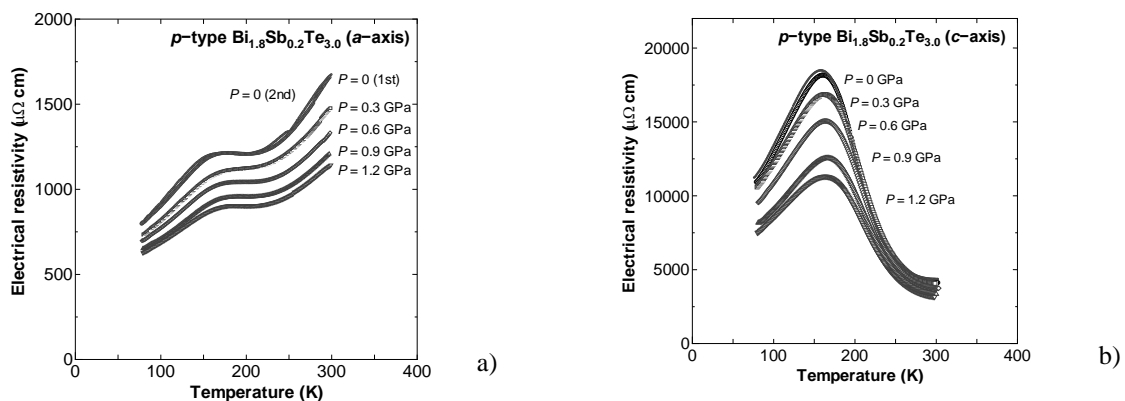


Figure 1. Temperature dependence of electrical resistivity for p -type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ along a -axis and c -axis at various pressures.

The temperature dependence of the electrical resistivity, $\rho(T)$, for *p*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ along *a*- and *c*-axis at various pressures is shown in Fig. 1. The resistivity decreases with increase of pressure in all the measured temperature ranging from 80 K to 300 K for *p*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ alloys. ρ increases with increase of temperature and takes a maximum at around 180 K along *c*-axis. This behavior may be explained by the mixed conduction [9]. ρ values are of 1.6 and 4.1 $\text{m}\Omega\cdot\text{cm}$ at zero pressure and room temperature for *p*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ along *a*- and *c*-axis, respectively. These results are in good agreement with the one reported in [6].

For *n*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$, the resistivity decreased with pressure in the temperature range from 80 K to 300 K (see Fig. 2). A peak appears in the $\rho(T)$ curves at around 210 K and 185 K along the *a*- and *c*-axis, respectively and shifted appreciably to higher temperature. The values obtained at room temperature are listed in Table 1. The magnitude of the resistivity along the *c*-axis is larger by a factor of 2.5 than that along the *a*-axis for both *p*- and *n*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$. This proves the anisotropic property of the electrical resistance of the samples.

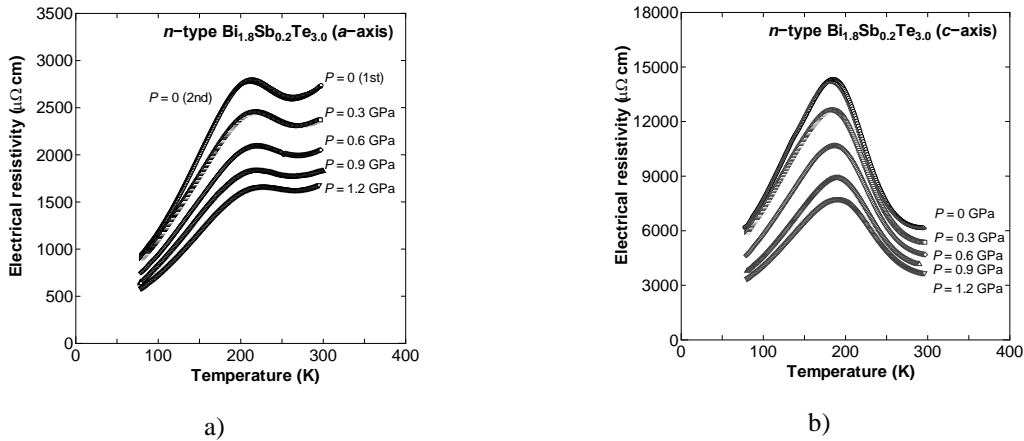


Figure 2. Temperature dependence of electrical resistivity for *n*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ along *a*-axis and *c*-axis at various pressures.

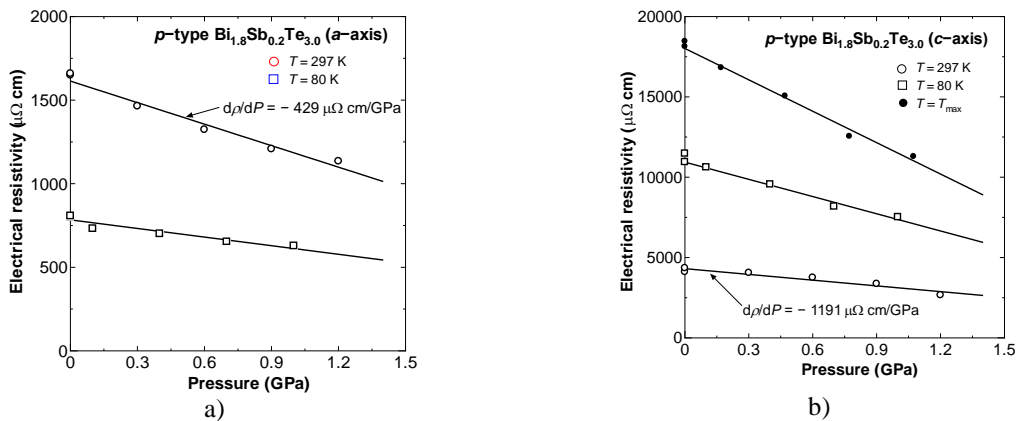


Figure 3. Electrical resistivity of *p*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ along the *a*-axis and *c*-axis as a function of pressure at 297 K and 80 K.

The resistivity of *p*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ along *a*-axis is plotted in Fig. 3, respectively as a function of pressure at 297 K and 80 K. At 297 K, ρ decreased linearly with increasing pressure. The reduction

rate of ρ is $-429 \mu\Omega\cdot\text{cm}/\text{GPa}$ ($-26 \%/ \text{GPa}$) along a -axis and $-1191 \mu\Omega\cdot\text{cm}/\text{GPa}$ ($-29 \%/ \text{GPa}$) along c -axis, respectively. The decrease in the electrical resistivity at 80 K is smaller than that at 297 K along a -axis, while it is larger than that at 297 K along c -axis.

Table 1. The thermoelectric parameters of the $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ alloys at room temperature

$\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ alloys		ρ ($\text{m}\Omega\cdot\text{cm}$)		S ($\mu\text{V}/\text{K}$)		$P.F.$ ($\mu\text{W}\cdot\text{cm}^{-1}\text{K}^{-2}$)	
		$P = 0$	$P = 1 \text{ GPa}$	$P = 0$	$P = 1 \text{ GPa}$	$P = 0$	$P = 1 \text{ GPa}$
p -type	a -axis	1.64	1.21	216	240.5	28.09	42.93
	c -axis	4.11	2.92	130	130.4	3.85	5.36
n -type	a -axis	2.72	1.77	-89.2	-74.0	2.97	2.99
	c -axis	6.13	3.93	-61.4	-39.1	0.62	0.38

The similar behavior has also been observed for n -type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ (Fig. 4). The resistivity value at 297 K decreases at a rate of $-891 \mu\Omega\cdot\text{cm}/\text{GPa}$ ($-35 \%/ \text{GPa}$) and $-2126 \mu\Omega\cdot\text{cm}/\text{GPa}$ ($-35 \%/ \text{GPa}$) along a - and c -axis, respectively.

The increase in the electrical conductivity (σ) with increase of pressure at room temperature both for p - and n -type is consistent with the electronic band structure calculations for Sb_2Te_3 alloys by Thonhauser et al., [10-11]. All the material dependent properties can be combined in to the transport distribution, which is defined by the relation as follow:

$$\Xi(\varepsilon) = \sum_k \tau_k v_k v_k \delta(\varepsilon - \varepsilon_k) \quad (1)$$

where τ_k denotes the relaxation time, v_k is the group velocity, ε_k is the band structure and $\delta(\varepsilon - \varepsilon_k)$ denotes the delta function. Transport properties such as the electrical conductivity, the power factor and the thermal conductivity can be derived from the transport distribution by performing material independent operations [12],

$$\sigma = \frac{1}{\rho} = e^2 \int \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \Xi(\varepsilon) d\varepsilon \quad (2)$$

where e and f_0 denote the electronic charge and the Fermi function.

In Eq. (2), σ is the integral over the transport distribution multiplied by the derivative of the Fermi function. In general, $\Xi(\varepsilon)$ increases under pressure, so σ increases. Note that both negative and positive energies, contribute toward increase of conductivity because the derivative of the Fermi function is asymmetric function. Thus, the electrical conductivity increased strongly with increase of pressure.

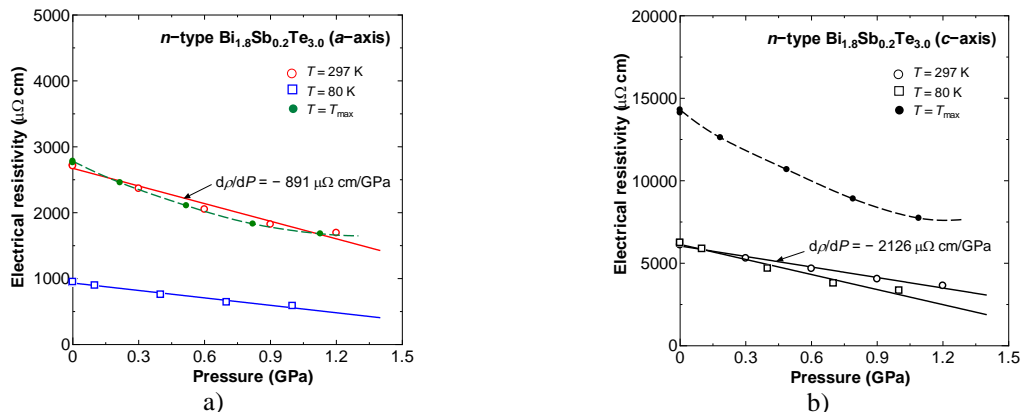


Figure 4. Electrical resistivity of n -type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ along a -axis and c -axis as a function of pressure at 297 K and 80 K.

3.1.2. Pressure Effect on Thermopower

Fig. 5a shows the pressure dependence of the thermopower for *p*-type Bi_{1.8}Sb_{0.2}Te_{3.0} along *a*- and *c*-axis at 297 K. At zero pressure, the thermopower value (*S*) along *a*-axis is + 216 μV·K⁻¹. Along *c*-axis, *S* value at zero pressure is + 130 μV·K⁻¹.

The magnitude of the thermopower along *a*-axis increases with increase of pressure at a rate of + 29.4 μV·K⁻¹/GPa (+14%/GPa). While the measured thermopower along *c*-axis keeps approximately constant with increasing pressure (Fig. 5). Thus, one can conclude that the pressure dependence of the thermopower is highly anisotropic depending on the crystallographic orientation for *p*-type Bi_{1.8}Sb_{0.2}Te_{3.0}. The increase in the thermopower with pressure may be associated with the change in the electronic band structure which has a major impact on transport properties [13-14].

Fig. 5b shows the pressure dependence of the thermopower for *n*-type Bi_{1.8}Sb_{0.2}Te_{3.0} along *a* and *c*-axis at 297 K. At zero pressure, the thermopower values are -89.2 and -61.4 μV·K⁻¹ along *a*- and *c*-axis, respectively. The absolute value of the thermopower for *n*-type Bi_{1.8}Sb_{0.2}Te_{3.0} was found to be decreased with increase of pressure. Along *a*-axis the decrease rate of the thermopower is -15.2 μV·K⁻¹/GPa (-17.0 %/GPa). A larger decrease in the absolute value of thermopower was found along *c*-axis at a rate of -20.8 μV·K⁻¹/GPa (-35.5 %/GPa).

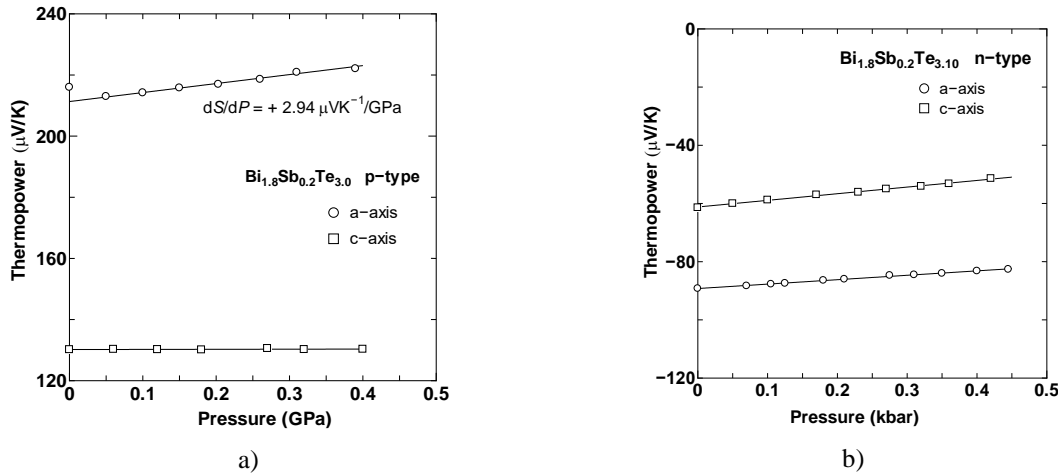


Figure 5. Dependence of thermopower on pressure for *p*- and *n*-type Bi_{1.8}Sb_{0.2}Te_{3.0} along the *a*- and *c*-axis at 297 K.

According to theoretical calculation, the thermopower value can be expressed including the transport contribution, as follows:

$$S = ek_B \sigma^{-1} \int \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \Xi(\varepsilon) \frac{\varepsilon - \mu}{k_B T} d\varepsilon \tag{3}$$

where *k_B* is the Boltzmann’s constant, *μ* is the chemical potential and *T* is the temperature.

Similarly to the electrical conductivity, the thermopower is also given by an integral over the transport distribution multiplied with the derivative of the Fermi function. The term (*ε* - *μ*) is added and it is an asymmetric function. The calculation shows that the thermopower decreased with uniaxial stress both for *p*- and *n*-types.

The results obtained in the increase of the thermopower under hydrostatic highpressure at room temperature for *p*-type along *a*-axis are not consistent with the theoretical calculation. However, the

decrease in the absolute value of thermopower with pressure for *n*-type is consistent with the theoretical calculation.

4. Conclusion

The following conclusion can be drawn from the investigation on the pressure effect of the electrical resistivity and thermopower in the *p*- and *n*-types $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ alloys: i) A strong anisotropy was confirmed in the electrical resistivity and thermopower for both *p*- and *n*-types $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$; ii) The electrical resistivity decreased linearly with pressure at 297 K for *p*- and *n*-types. The *n*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ exhibits a larger decrease in the electrical resistivity with increase of pressure along *a*- and *c*-axis.; and iii) The pressure dependence of thermopower exhibits anisotropic dependence on the crystallographic orientation for both *p*- and *n*-types $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ at 297 K. The thermopower value at 297 K increased with increase of pressure along *a*-axis and is approximately constant along *c*-axis for *p*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$. At 297 K, the absolute value of the thermopower decreased with increase of pressure for *n*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$ along *a*- and *c*-axis. The thermoelectric performance can be improved by increasing pressure for *p*-type, while it is pressure independent for *n*-type $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_{3.0}$.

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