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Electrical resistivity and thermopower of intercalation compounds Bi_xTiS_2

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Abstract

The temperature dependence of DC electrical resistivity and thermopower of bismuth intercalated compounds Bi_xTiS_2 ($x = 0$–0.25) were investigated in the temperature range from 7 to 300 K. The resistivity and thermopower decreased as intercalated Bi content increased. However, the thermopower component originating from phonon-drag effect was found to have enhanced.

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Keywords: Intercalation compound; Electrical resistivity; Thermopower

1. Introduction

Thermoelectric materials have attracted much attention in recent years for possible applications to "environmentally friendly" electric-power generators and highly reliable, small-scale refrigerators used for electronic devices [1]. The efficiency of a thermoelectric material is determined by the dimensionless thermoelectric figure of merit, ZT ($ZT = S^2T/\rho\kappa$, here S, ρ, κ and T are the thermopower (or Seebeck coefficient), electrical resistivity, total thermal conductivity and absolute temperature, respectively), and currently the ZT values for best thermoelectric material, such as Bi_2Te_3 alloys, are usually not larger than unity, which are not enough for wider use in commercial applications. Thus, development of new materials with higher efficiency is one of the current main interests in research on thermoelectric materials.

TiS_2 has an anisotropic structure with a trigonal space group, $P\bar{3}m$. In the S–Ti–S sandwich layers (slabs), TiS_6 octahedrons are combined with each other tightly through strong covalent bonds, with each layer stacking together under weak van der Waals force. Due to this quasi-two-dimensional structure, TiS_2 was reported to have large thermopower of

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−251 μV/K at room temperature, and high power factor (S^2/ρ) of 37.1 μW/(K^2 cm) [2], a value that is comparable to that of Bi_2Te_3 alloy, indicating that TiS_2 is a potential candidate for thermoelectric applications. However, because of its large lattice thermal conductivity, its ZT value is too small for practical application [2]. Therefore, reduction of its conductivity is of great significance in raising its thermoelectric property.

As to reduction of thermal conductivity, Slack [3] proposed that a crystal structure containing weakly bound atoms or molecules that "rattle" within atomic cages can reduce lattice thermal conductivity, and latter experiments in skutterudite antimonides filled with heavy metals [4] proved that filling of the heavy metals is truly an effective way in reducing phonon thermal conductivity. Layered-structured TiS_2 is well known for its capability for intercalation of a wide range of both organic and inorganic materials into its van der Waals gap [5]. Specially, alkalis, such as Li and transition-metals, such as Fe, Co and Ni, have been successfully inserted into the gap of TiS_2, and their intercalation has strong influence on the transport properties of the corresponding intercalation compounds [6]. Nevertheless, to our knowledge, little work aimed at reducing the thermal conductivity and improving thermoelectric properties of TiS_2 by means of intercalation of heavy elements has been reported. As a heavy element, semi-metal bismuth is one of most important constituent elements used in thermoelectric materials. Bismuth intercalation into TiS_2 would have profound influence on the overall physical properties of its intercalated compounds, which one has hardly known in detail. Here, we report on the investigations of the effects of bismuth intercalation on the electrical resistivity and thermoelectric power as well as their temperature behavior of intercalation compounds Bi_xTiS_2 ($x = 0$–0.25). Correlative investigations on its thermal conductivity and other physical properties will appear in our further-coming paper.

2. Experimental methods

Polycrystals of bismuth intercalated compounds Bi_xTiS_2 were prepared by two-step procedure. Firstly, TiS_2 powder was prepared by direct reactions of titanium metal sponge (99.7%) to sulfur powder (99.5%) with reagent-grade iodine as transport agent. The reaction involving a mixture of Ti and S in an atomic Ti : S ratio of 1 : 2, which was transported by iodine vapor (5 mg cm^{-3}), was run typically for seven days at 710 °C in an evacuated quartz ampule at a vacuum of 10^{-2} Pa. Secondly, mixtures of TiS_2 and Bi of appropriate compositions were sealed in an evacuated quartz tube. Then they were heated slowly to 710 °C and isothermally kept for a week to form the intercalation compounds Bi_xTiS_2. The phase structure and the compositions of the obtained samples were checked by using X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS), respectively. Accurate measurements of lattice parameters were realized through calibration with silicon standard in XRD experiments. The stoichiometric ratio of Ti to S in pristine TiS_2 was determined to be 1.0450 : 2 by weight change upon oxidation of TiS_2 as heated to 700 °C in air. DC resistivity was measured by four-probe method in the temperature range from 25 to 298 K, and thermopower was measured in the temperature range from 7 to 300 K by the conventional constant ΔT method.

3. Results

Fig. 1 shows the XRD patterns for the synthesized pristine TiS_2 and intercalated Bi_xTiS_2 samples. It can bee seen from curve (a) that all the reflection peaks correspond to those of standard 1T-TiS_2, as marked in the figure. As compared to that of pristine TiS_2, no substantial changes were observed in XRD patterns of bismuth intercalation compounds Bi_xTiS_2 when $x < 0.15$. But, as $x \geqslant 0.15$ two additional reflection peaks appeared, as marked by solid circles in the figure. The two peaks did not come from elementary Bi substance; instead they originate from structural conversion from stage 1 to stage 2 [7], implying that after heavy intercalation ($x \geqslant 0.15$) some regular distributions of intercalated Bi occurred in the van der Waals gaps. Lattice parameter measurement (Fig. 2) indicated that lattice constant c expanded linearly from 5.7011 ± 0.0010 to 5.7330 ± 0.0010 Å as Bi content x increased from 0 to 0.25; correspondingly, lattice a changed slightly from 3.4083 ± 0.0008 to 3.4156 ± 0.0008 Å. These results indicated that bismuth atoms were successfully intercalated into the van der Waals gaps, forming intercalation compounds Bi_xTiS_2.

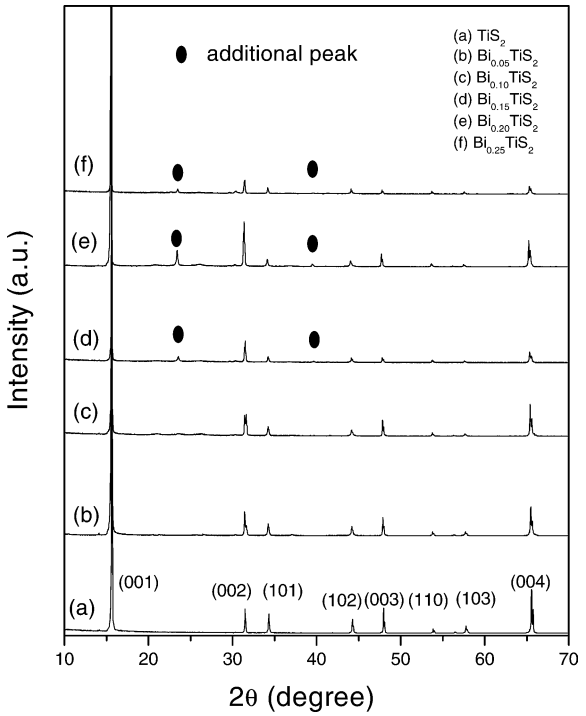

Fig. 1. XRD patterns (CuK$_\alpha$ irradiation) for TiS_2 (a) and bismuth intercalated compounds: (b) $Bi_{0.05}TiS_2$, (c) $Bi_{0.10}TiS_2$, (d) $Bi_{0.15}TiS_2$, (e) $Bi_{0.20}TiS_2$ and (f) $Bi_{0.25}TiS_2$.

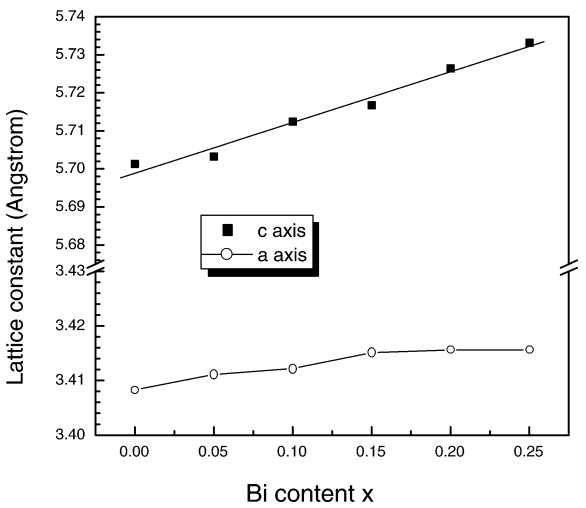

Fig. 2. Variations of lattice constant c and a with intercalated bismuth content.

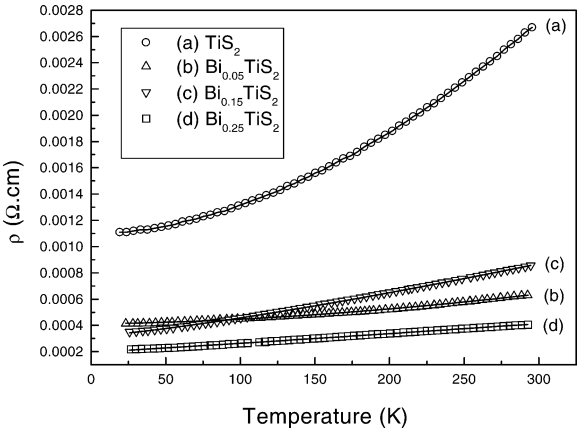

Fig. 3. Variation of electrical resistivity with temperature for TiS_2 (a) and intercalation compounds Bi_xTiS_2 with different bismuth content ($x = 0.05, 0.15, 0.25$) (b)–(d). The symbols are experimental data (for clarity, not all data points are shown here, instead one symbol represents sixteen datum points in this figure), and the solid lines are the best fit of the data to formula (1).

Fig. 3 shows variations of the electrical resistivity ρ for TiS_2 phase (curve (a)) and its intercalation compounds Bi_xTiS_2 with different bismuth content ($x = 0.05, 0.15, 0.25$) (see curves (b)–(d)). It can be seen that as compared to TiS_2, the resistivity ρ of all the intercalation compounds Bi_xTiS_2 decreased. In the temperature range from 298 K to 25 K, its resistivity ρ dropped from $2.6 \times 10^{-3}\ \Omega\,\mathrm{cm}$ down to $1.1 \times 10^{-3}\ \Omega\,\mathrm{cm}$, while the resistivity of intercalation compounds $Bi_{0.25}TiS_2$ changed from $0.3 \times 10^{-3}\ \Omega\,\mathrm{cm}$ to $0.2 \times 10^{-3}\ \Omega\,\mathrm{cm}$ in the same temperature range, which is about one order smaller than that of TiS_2. Furthermore, the temperature behavior of the resistivity for intercalation compounds Bi_xTiS_2 is different from that for TiS_2, and changes with increasing Bi content. Specially, for the intercalation compounds Bi_xTiS_2 with $x = 0.25$ its resistivity changes almost linearly with temperature. The temperature dependence of resistivity of TiS_2 intercalation compounds was usually described well by the power law [8]:

$$\rho(T) = \rho_0 + aT^{\gamma}. \tag{1}$$

By best fit of the resistivity data obtained here to formula (1), one obtains the parameter ρ_0, a, and γ, which are listed in Table 1. It can be seen from Table 1 that ρ_0 decreased from $1.1 \times 10^{-3}\ \Omega\,\mathrm{cm}$ to $0.2 \times 10^{-3}\ \Omega\,\mathrm{cm}$ with increasing the bismuth content. Meanwhile, γ also drops from 1.83 to 1.05. This result

Table 1
List of parameters ρ_0, a, γ, Debye temperature θ_D, Fermi energy E_F and carrier concentration n for TiS_2 and intercalation compounds Bi_xTiS_2

x	ρ_0 (10^{-3} Ω cm)	A	γ	θ_D (K)	E_F (eV)	n (10^{21} cm^{-3})
0	1.1	4.84×10^{-8}	1.83	215	0.51	1.6 (3.3)[a]
0.05	0.4	1.20×10^{-8}	1.73	340	1.41	7.6
0.15	0.3	4.27×10^{-7}	1.26	350	1.92	12
0.25	0.2	5.36×10^{-7}	1.05	370	2.91	22 (22)[b]

[a] Value in parenthesis for $Ti_{1.05}S_2$ [15]; [b] Value in parenthesis for $LiTiS_2$ [15].

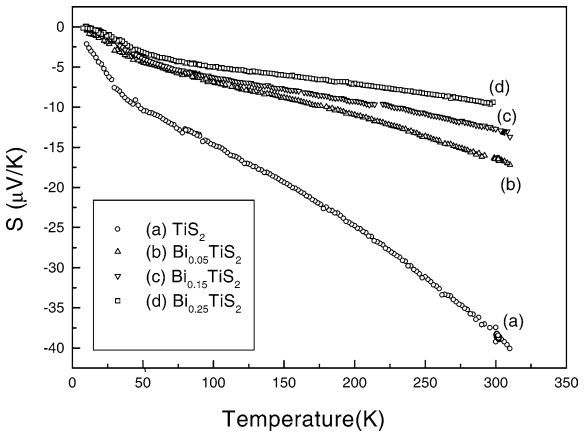

Fig. 4. Dependence of the thermopower S on temperature for TiS_2 (a), and for intercalation compounds Bi_xTiS_2 ((b) $x = 0.05$, (c) $x = 0.15$, and (d) $x = 0.25$).

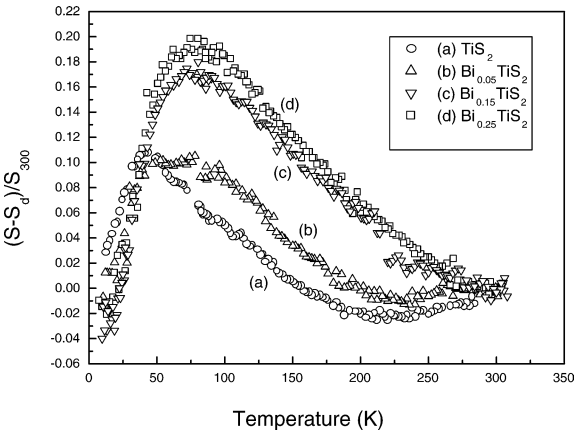

Fig. 5. Plot of $(S - S_d)/S_{300}$ versus temperature for TiS_2 (a), and for intercalation compounds Bi_xTiS_2 ((b) $x = 0.05$, (c) $x = 0.15$, and (d) $x = 0.25$).

indicates that bismuth intercalation into the host TiS_2 has great influence on its electrical transport behavior.

The thermopower of both TiS_2 and its intercalation compounds Bi_xTiS_2 is given as a function of temperature in Fig. 4. It can be seen that the thermopower of either TiS_2 or intercalation compounds Bi_xTiS_2 is negative over the whole temperature; at the temperatures above 100 K, the thermopower for both TiS_2 and intercalation compounds Bi_xTiS_2 has approximately linear relationship with temperature, and at the temperatures around 50 K there is small valley in the plot of S vs. T for each of them. However, as compare to TiS_2, all the intercalation compounds Bi_xTiS_2 have smaller absolute thermopower that decreased with increasing bismuth content. Moreover, with decreasing temperature thermopower S of intercalation compounds Bi_xTiS_2 decreased more gently as bismuth content x increased, indicating the temperature behavior of the thermopower of TiS_2 varied for different amounts of bismuth intercalation.

The small valley spotted in the plot of S vs. T would result from phonon-drag effect [9]. In order to show this effect clearly for different intercalation compounds Bi_xTiS_2 as well as TiS_2, Fig. 5 shows $(S - S_d)/S_{300}$ (here, S_{300} is the room temperature thermopower of respective compound, and S_d is the diffusion thermopower derived from extrapolation based on the slope of high-temperature ($T > 200$ K) portion of the S–T plots) as a function of temperature. It can be seen that with increasing Bi content, the height of phonon-drag peak increased, and peak position, T_p, shifted from about 42 K to 75 K (Fig. 6), implying phonon-drag effect enhanced after Bi intercalation.

4. Discussions

It has been established that an electron–phonon scattering is responsible for the temperature-dependent transport properties of layered TiS_2 crystal. According to the detailed analysis by Klipstein et al. [10], longi-

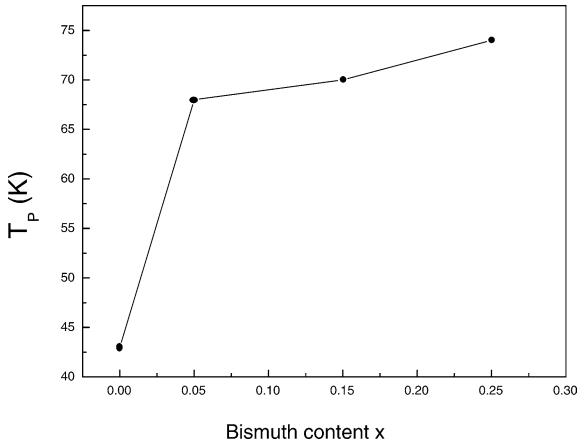

Fig. 6. Variation of the peak (caused by phonon-drag effect) position with bismuth content.

tudinal acoustic phonons provide the dominant contribution to the electron scattering below room temperature. The power γ for titanium self-intercalated compounds $Ti_{1+y}S_2$ was found to vary from 2.3 in good-stoichiometry samples to 1.6 in poor-stoichiometry samples at the temperatures above 20–110 K [11]. In comparison with literature values [11], the smaller magnitude of γ (1.83) implies that there was a small number of self-intercalated titanium atoms in the van der Waals gap, which is consistent with determination of stoichiometric ratio of Ti to S (1.045 : 2), with surplus titanium $y = 0.045$ (as reported in [11], y is usually more than 0.004 and less than 0.05 by using conventional synthesis methods). Upon bismuth intercalation a large decrease of the electrical resistivity was observed (Fig. 3). Meanwhile, with increasing x, its temperature dependence transited gradually from non-linearity to nearly linearity (typical pure metallic behavior) that is manifested by the magnitude of power γ reaching unity in heavy intercalation compound ($x = 0.25$). Present result has some similarities to that reported for Li_xTiS_2 [12], where charge-transfer mechanism was used to account for the observed phenomenon. It is reasonable to assume here that the valence electrons of the metallic bismuth atoms would transfer to Ti3d band of the host after intercalation, leading to enhancement of the pure metallic behavior of Bi_xTiS_2. This viewpoint is consistent with the decreased resistivity for the intercalated compounds (Fig. 3), and also the thermopower measurement results (see following discussions). Therefore, it seems reasonable that gradual transition to pure metallic behavior for intercalation compounds Bi_xTiS_2 could be ascribed to the charge-transfer of bismuth atoms to host TiS_2.

As mentioned above, the resistivity of the intercalation compounds Bi_xTiS_2 displayed metallic behavior in a certain degree. As a first approximation, we use the free electron gas model in which thermopower is described by Mott formula [13]

$$S = \frac{\pi^2 K^2 T}{3e}\left(\frac{d\ln\sigma(E)}{dE}\right) = \frac{\pi^2 K^2 T}{3eE_F}\left(\frac{d\ln\sigma(E)}{d\ln E}\right)\Big|_{E=E_F}, \quad (2)$$

where E_F is the Fermi level, E the electron energy, K the Boltzmann constant, e the electron charge, and $\sigma(E) = An(E)v^2\tau$ is the conductivity (here A is constant at the Fermi level, $n(E)$ the electron concentration, v the Fermi velocity of electrons, and τ relaxation time). Roughly speaking formula (2) is expected to be true at high temperatures when electron scattering by high frequency phonons predominates. For free electrons, there are relationships: $n(E) \propto E^{1/2}$, $v^2 \propto E$, and according to Wilson [14] $\tau(E) \propto E^{3/2}$. Hence, formula (2) becomes:

$$S = \frac{\pi^2 K^2 T}{eE_F}. \quad (3)$$

According to formula (3), thermopower S has linear relationship to temperature T with a slope inversely proportional to Fermi level. It is noted that the temperature dependence of thermopower for the Bi_xTiS_2 at the $T > 150$ K basically obeys linear relationship to temperature (Fig. 4). Moreover, by best fit of formula (3) to the data in high-temperature regime ($T = 200$–300 K), one can evaluate E_F that is included in Table 1. As shown in Table 1, Fermi level increased with increasing Bi content, which can give an explanation to the drop of thermopower as Bi content increased. For free electron gas, carrier concentration $n = (2m^*E_F)^{3/2}/3\pi^2\hbar^3$ (here m^* effective electron mass, $\hbar$ Planck's constant), which, by using free electron mass ($m^* = 9.11 \times 10^{31}$ kg), gives an evaluation of the carrier concentrations from the magnitudes of E_F, as listed in Table 1. The evaluated magnitude $n = 1.6 \times 10^{21}$ cm^{-3} for pristine TiS_2 here agrees with the reported value (3.3×10^{21} cm^{-3}) (determined

with Hall coefficient measurement) for less stoichiometric $Ti_{1.05}S_2$ [15]. Moreover, as compared to the carrier concentration (2.2×10^{22} cm^{-3}) measured for $LiTiS_2$ [15], the evaluated $n = 2.2 \times 10^{22}$ cm^{-3} for $Bi_{0.25}TiS_2$ would indicate that the derived high Fermi energy (2.91 eV) in free electron gas model is reasonable, considering the fact that bismuth atoms have more valence electrons than lithium atoms. Present result is also in agreement with our resistivity measurements (Fig. 3) as discussed above, supporting the assumption that the valence electrons of the metallic bismuth atoms transfer to the host TiS_2. It is worthwhile to note here that the room temperature thermopower ($S \approx -40$ μV/K) obtained here for TiS_2 is much smaller than the reported value (~ -250 μV/K) [2]. The reason for this difference may be related to relatively greater amount of surplus titanium ($y = 0.045$) in our TiS_2 specimens than that in their samples ($y = 0.0048$) [2]. Obviously, as a self-intercalant the surplus titanium in the van der Waals gap should donate its valence electrons to TiS_2 host, giving rise to ascent of Fermi level, just as bismuth intercalation. According to formula (3), thermopower is inversely proportional to Fermi level at fixed temperatures, and the more surplus titanium, the higher of the Fermi level due to more charge transfer to the host, which explains why smaller absolute magnitude of thermpower was obtained for the pristine TiS_2. In fact, the room temperature value $S \approx -40$ μV/K here for TiS_2 is similar to that (-56 μV/K) for less stoichiometric TiS_2 [16].

According to MacDonald [13], phonon-drag component (S_g) increases as T^3 at very low temperatures ($T \ll \theta_D$ (Debye temperature of the lattice)) and decays as T^{-1} at high temperatures ($T \gg \theta_D$), and there is a semiempirical expression [9]:

$$S_g = C_g \frac{(T/\theta_D)^3}{\alpha^4 + (T/\theta_D)^4}, \tag{4}$$

where C_g is a parameter and α a constant ($= 0.15$) which is to be determined such that S_g attains a maximum ($T \approx \theta_D/5$), as is often observed [17]. Following formula (4) one can therefore estimate Debye temperature θ_D of TiS_2 and the intercalation compounds Bi_xTiS_2 by using the data given in Fig. 4 (as shown in Table 1). It can be seen from Table 1 that with increase of Bi content Debye temperature increases monotonously from 215 K for TiS_2 to 370 K for $Bi_{0.25}TiS_2$.

Present results indicate that bismuth intercalation into TiS_2 gives rise to substantial enhancement of phonon-drag effect. This enhancement would result from the low-frequency vibrations (or "rattling") of the Bi atoms in the van der Waals gap, which provides additional phonon scattering to the charge carriers (electrons) in the slabs of the TiS_2 host. The fact that Debye temperature increased after bismuth intercalation would be related to changes of binding strength in the van der Waals gaps. After charge-transfer from inserted bismuth atoms to either side of the S–Ti–S slabs, Bi ions with positive charge would interact with adjacent S ions (with negative charge), enhancing the chemical bonds in-between the van der Waals gaps. It is conceivable that as such binding strength enhanced in the gaps, the elastic modulus of the intercalation compounds, as a whole, should become greater, which would lead to rise of Debye temperature.

5. Conclusions

DC electrical resistivity and thermopower of host TiS_2 and the intercalation compounds Bi_xTiS_2 were investigated. The results indicated that with increasing Bi content the temperature behavior of the resistivity of intercalation compounds changed from power law ($\gamma = 1.83$) of TiS_2 to linearity of $Bi_{0.25}TiS_2$, which was accompanied by substantial drop of its resistivity. The temperature dependence of thermopower of Bi_xTiS_2 changed with intercalated Bi content. Although the absolute value of the thermopower decreased after Bi intercalation, the component originating from phonon-drag effect enhanced. Based on a free electron gas model, Fermi level and Debye temperature of intercalation compounds Bi_xTiS_2 were evaluated, both of which were found to increase with intercalated Bi content.

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