

Enhanced thermoelectric properties of bismuth intercalated compounds Bi_xTiS_2

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Abstract

The thermoelectric properties of Bi intercalated compounds Bi_xTiS_2 have been investigated at the temperatures from 5 to 310 K. The results indicate that Bi intercalation into TiS_2 leads to substantial decrease of its electrical resistivity (one order low for $x=0.05$ and two orders low for $x=0.15, 0.25$ at 300 K) and lattice thermal conductivity (22, 115 and 158% low at 300 K for $x=0.05, 0.15$ and 0.25 , respectively). Specially, the figure of merit, ZT , of lightly intercalated compound $\text{Bi}_{0.05}\text{TiS}_2$ has been improved at all temperatures investigated, and specifically reaches 0.03 at 300 K, which is about twice as large as that of TiS_2 . © 2005 Elsevier Ltd. All rights reserved.

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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 figure of merit, ZT ($ZT = S^2 T / \rho \kappa$, here S , ρ , κ and T are the thermopower, electrical resistivity, thermal conductivity and temperature, respectively). Hence, a good thermoelectric material should have high S , low ρ and κ .

TiS_2 has an anisotropic structure with a trigonal space group $P\bar{3}m$. In the S–Ti–S sandwich layers, 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 and power factor

(S^2/ρ) at room temperature [2], 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 properties.

As to reduction of thermal conductivity, Slack [3] proposed that a crystal structure containing weakly bound atoms or molecules that 'rattle' within atomic cages could 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 thermal conductivity of skutterudite antimonides. This measure may also apply to other materials systems, such as TiS_2 with quasi-two-dimensional structure. Nevertheless, to our knowledge no attempt aiming at reducing thermal conductivity of this layered compound by filling guest species has been realized, or even no such kind of work has ever been reported. Layered-structured TiS_2 is well known for its capability for intercalation of a wide range of elements into its van der Waals gap [5]. Intercalation of heavy element into TiS_2 may reduce its

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thermal conductivity by atomic ‘rattling’ and raise its thermoelectric properties. As a heavy element, semi-metal bismuth is one of most important constituent elements used in thermoelectric materials. Bismuth intercalation into TiS_2 would not only cause reduction of thermal conductivity, but also could have profound influences on the overall physical properties of its intercalated compounds, which one hardly known in detail. In the present work, thermoelectric properties of Bi intercalated compounds Bi_xTiS_2 are investigated, and the results indicate that proper Bi intercalation into TiS_2 can improve its thermoelectric properties effectively.

2. Experimental methods

Polycrystals of neodymium intercalated compounds Bi_xTiS_2 were prepared by two-step procedure. First, TiS_2 powder was prepared by direct reactions (in an evacuated quartz ampoule) of titanium metal powder (99.7%) to sulfur powder (99.5%) at 610 °C for 7 days. Secondly, mixtures of TiS_2 and Bi of appropriate compositions were sealed in an evacuated quartz tube, and heat-treated at 600 °C for 1 week to form intercalation compounds Bi_xTiS_2 . The phase structures and the compositions of the obtained samples were checked by using X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS), respectively. Thermoelectric properties were measured by PPMS (quantum design) in the temperature range from 5 to 310 K.

3. Results and discussions

Fig. 1 shows variation of electrical resistivity for Bi_xTiS_2 ($x=0, 0.05, 0.15$ and 0.25). It can be seen that as compared to TiS_2 , the resistivity of the intercalation compounds

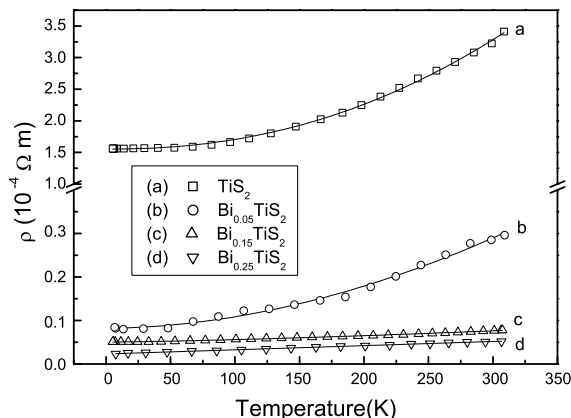


Fig. 1. Dependence of the electrical resistivity ρ on temperature for TiS_2 (a), and for Bi intercalation compounds Bi_xTiS_2 (b) $x=0.05$, (c) $x=0.15$ and (d) $x=0.25$). The solid lines are the best fit of formula (1) to the experimental data.

Bi_xTiS_2 decreases in the whole temperature range investigated. 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. The temperature dependence of resistivity of TiS_2 intercalation compounds is usually described well by the power law [6]:

$$\rho(T) = \rho_0 + aT^\gamma \quad (1)$$

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 1.6×10^{-4} to 2.0×10^{-6} Ω m with increasing Bi content from 0 to 0.25. Meanwhile, γ also drops from 2.20 to 1.04. Present results have some similarities to that reported for Li_xTiS_2 [7], 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 transfer to Ti 3d band of the host after intercalation, leading to increase of electron concentration and enhancement of pure metallic behavior for Bi_xTiS_2 . This speculation is consistent with the decreased thermopower for the intercalated compounds (see the text below).

The thermopower of Bi_xTiS_2 is given as a function of temperature in Fig. 2. It can be seen that the thermopower of Bi_xTiS_2 is negative over the whole temperature, indicating that the major charge carriers in Bi_xTiS_2 are electrons. At the temperature above 100 K the thermopower for Bi_xTiS_2 has approximately linear relationship to temperature with its slope decreasing with increasing Bi content; while there is small valley at the temperature around 50 K for each of them in the plot of S vs. T , which is ascribed to the phonon-drag effect [8]. However, as compared to TiS_2 , the intercalation compounds Bi_xTiS_2 have smaller absolute thermopower that decreased with increasing Bi content. The room temperature thermopower obtained here for $x=0, 0.05, 0.15$ and 0.25 is $-240, -89, -33$ and -25 $\mu\text{V}/\text{K}$, respectively. The diffusive part of thermopower (T -linear thermopower) can be described by formula [8]:

$$S = \frac{\pi^2 k^2 T}{eE_F} \quad (2)$$

where k , E_F , e is the Boltzmann constant, Fermi level, and electron charge, respectively. This formula indicates that the slope of the plot S vs. T is inversely proportional to Fermi

Table 1
List of parameters ρ_0 , a , γ for TiS_2 and intercalation compounds Bi_xTiS_2

x	ρ_0 (10^{-4} Ω m)	a (10^{-10})	γ
0	1.6	6.00	2.20
0.05	0.08	4.52	1.88
0.15	0.05	9.00	1.40
0.25	0.02	73.6	1.04

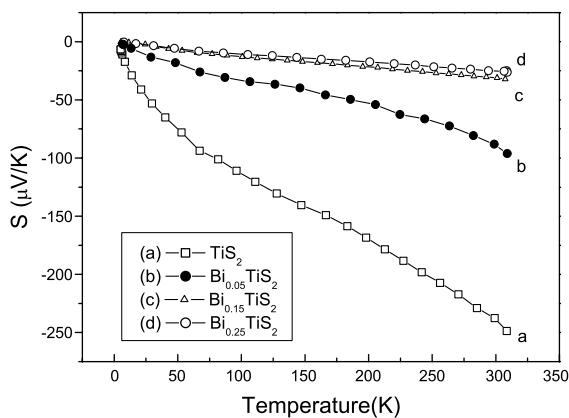


Fig. 2. Variation of thermopower S with temperature for Bi_xTiS_2 ((a) $x=0$, (b) $x=0.05$, (c) $x=0.15$ and (d) $x=0.25$).

level. Hence, the decrease of thermopower or reduction of the slope of the plot S vs. T (Fig. 2) with increasing Bi content would reflect rise of E_F , which is consistent with increase of electron concentration originating from charge transfer, as mentioned above.

Temperature dependence of thermal conductivity κ of Bi_xTiS_2 is presented in Fig. 3. It can be seen that intercalation of Bi into the host TiS_2 causes large decrease of its total thermal conductivity in the whole temperature range. The value of the thermal conductivity at 300 K is $3.07 \text{ W m}^{-1} \text{ K}^{-1}$ for $x=0$, $2.67 \text{ W m}^{-1} \text{ K}^{-1}$ for $x=0.05$, $2.58 \text{ W m}^{-1} \text{ K}^{-1}$ for $x=0.15$ and $2.37 \text{ W m}^{-1} \text{ K}^{-1}$ for $x=0.25$, respectively. Thermal conductivity can be expressed by the sum of lattice component (κ_L) and electronic component (κ_e) as $\kappa = \kappa_L + \kappa_e$. The κ_e values can be estimated from Wiedemann–Franz’s law as $\kappa_e = LT/\rho$, where L is the Lorentz number ($2.44 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ for free electrons). Consequently, κ_L can be obtained from κ and κ_e , as shown in Fig. 4. One can see that as Bi content increases, the lattice thermal conductivity decreases signifi-

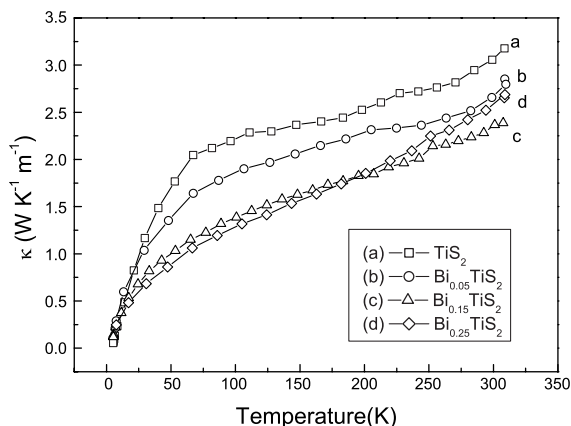


Fig. 3. Plot of thermal conductivity κ vs. temperature for Bi_xTiS_2 ((a) $x=0$, (b) $x=0.05$, (c) $x=0.15$ and (d) $x=0.25$).

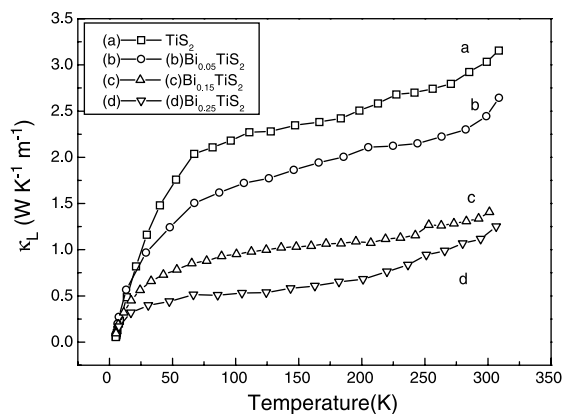


Fig. 4. Plot of lattice thermal conductivity κ_L vs. temperature for Bi_xTiS_2 ((a) $x=0$, (b) $x=0.05$, (c) $x=0.15$ and (d) $x=0.25$).

cantly. Specifically, κ_L of Bi_xTiS_2 at 300 K is 22% ($2.49 \text{ W K}^{-1} \text{ m}^{-1}$), 115% ($1.42 \text{ W K}^{-1} \text{ m}^{-1}$) and 158% ($1.18 \text{ W K}^{-1} \text{ m}^{-1}$) smaller than that of TiS_2 for $x=0.05$, 0.15 and 0.25, respectively. This reduction in lattice thermal conductivity would originate from phonon scattering by low-frequency vibrations, or ‘rattling’, of the intercalated bismuth atoms in the van der Waals gaps.

Fig. 5 shows the temperature dependence of figure of merit ZT for Bi_xTiS_2 . The ZT values for all samples tend to increase with increasing temperature. However, the ZT for the heavy intercalated compound Bi_xTiS_2 ($x=0.15, 0.25$) is slightly smaller than that of pure TiS_2 because of large decrease in their thermopower, although their resistivity and thermal conductivity decrease considerably. But, the ZT of lightly intercalated compound $\text{Bi}_{0.05}\text{TiS}_2$ has been improved substantially in the whole temperature range investigated. Specially, ZT value of $\text{Bi}_{0.05}\text{TiS}_2$ is about twice as large as that of TiS_2 at 300 K. Evidently, this improvement of the thermoelectric properties for $\text{Bi}_{0.05}\text{TiS}_2$ could be ascribed to both decreased resistivity resulting from increase of carrier

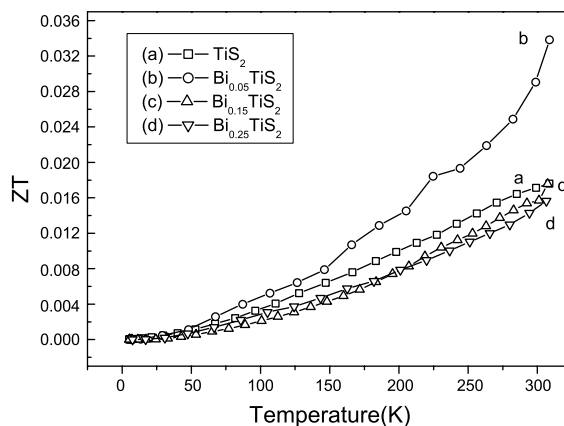


Fig. 5. Variation of ZT with temperature for Bi_xTiS_2 ((a) $x=0$, (b) $x=0.05$, (c) $x=0.15$ and (d) $x=0.25$).

concentration due to charge-transfer and decreased lattice thermal conductivity presumably caused by ‘rattling’ of Bi atoms in van der Waals gaps of TiS_2 .

4. Conclusions

The thermoelectric properties of Bi intercalated compounds Bi_xTiS_2 have been studied in the temperature range from 5 to 310 K. The results indicate that Bi intercalation into TiS_2 leads to substantial decrease of both electrical resistivity and lattice thermal conductivity as compared to those of pristine TiS_2 . Specially, the figure of merit, ZT, of lightly intercalated compound $\text{Bi}_{0.05}\text{TiS}_2$ has been improved in the whole temperature range investigated, and specifically is about twice as large as that of TiS_2 at 300 K. Present result suggests that intercalation of heavy metals into TiS_2 layered compound is a promising way in improving its thermoelectric properties.

Acknowledgements

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