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The effects of bismuth intercalation on structure and thermal conductivity of TiS_2

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Abstract

The structure and thermal conductivity of the bismuth (Bi) intercalated compounds Bi_xTiS_2 ($0 \leq x \leq 0.25$) were investigated by using X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and thermal conductivity measurements. The results indicated that besides lattice expansion and distortion, bismuth intercalation caused structural transition of Bi_xTiS_2 from stage-1 to stage-2 as $x \geq \sim 0.1$, which led to the appearance of D_4 and A_2 modes in Raman spectra. The enhancement of relative intensities of D_4 and A_2 peaks with increasing Bi content reflected increase of the concentration of stage-2 phase in the samples. The red shift of mode E_g as well as D_4 and A_2 would reflect weakening of intra-layer bonds, while the blue shift of A_{1g} after intercalation suggested the enhancement of chemical binding in the van der Waals gaps due to charge transfer. In addition, the weakening of A_{1g} intensity can be explained by the lattice distortion produced by bismuth intercalation. Remarkable reduction in (lattice) thermal conductivity of titanium disulfide (TiS_2) through Bi intercalation was realized, which could be attributed to the phonon scattering by ''rattling'' of the intercalated bismuth atoms in the van der Waals gaps of TiS_2.

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1. Introduction

Titanium disulfide (TiS_2) is an indirect-gap semiconductor and a member of the family of layered transition metal dichalcogenides. It has an anisotropic structure with a trigonal space group, $P\bar{3}m$ [1]. In the layers, TiS_6 octahedrons are combined with each other tightly through strong covalent bonds, where each layer stacks weakly by van der Waals force. Because of its layered-structure, TiS_2 is well known for its ability to form intercalation compounds with a wide variety of guest species [2–4]. The type and concentration of the intercalated species have a great effect on the physical properties of the host. Many studies have been pursued on these intercalated compounds [5–7].

Recently, TiS_2 has been reported to have large thermopower of $-251\ \mu V\ K^{-1}$ at room temperature, and high power factor of $37.1\ \mu W\ K^{-2}\ cm^{-1}$ [1], 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 energy

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conversion efficiency is too small for practical applications [1]. Therefore, reduction of its thermal conductivity is of great significance in raising its thermoelectric property.

According to the idea of ''phonon-glass and electron-crystal'' proposed by Slack [8,9], incorporation of heavy elements into the van der Waals gaps of TiS_2 would be a measure that is worthwhile to be tried in reducing its thermal conductivity. As a heavy element, semi-metal bismuth (Bi) is one of most important constituent elements used in thermoelectric materials. However, bismuth intercalation into TiS_2 would have profound influence on the structures and overall physical properties of its intercalated compounds, which one has hardly known in detail so far. For instance, interesting issues include: (1) how bismuth atoms intercalating into TiS_2 affects the microstructures of the host; (2) whether intercalated Bi gives rise to changes of vibration properties of the host lattice; (3) whether intercalated Bi reduces the thermal conductivity of TiS_2 and so on. Previous experiments seemed to indicate that the inclusion of atoms or molecules between the planes of layered compounds did not significantly influence the vibration properties of the atoms within the host layers [10]. Nevertheless, since bismuth element has large atomic weight with large atomic (ionic) radius, its intercalation into van der Waals gaps of TiS_2 would have strong influence on its micro- and/or electronic structures. In this report, the effects of bismuth intercalation on the structures of Bi_xTiS_2 ($0 \leq x \leq 0.25$) were investigated by using X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Its effect on thermal conductivity of Bi_xTiS_2 was investigated at the temperatures from 310 K down to 5 K.

2. Experimental details

Polycrystals of bismuth intercalated compounds Bi_xTiS_2 were prepared by two-step procedure. Firstly, 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 a week to form intercalation compounds Bi_xTiS_2.

Phase structures of the obtained samples were determined by using XRD (Cu Kα irradiation). Accurate measurements of lattice parameters were realized through calibration with silicon standard. Lattice strains were estimated from line broadening of the reflection peaks where instrumental broadening was calibrated using a silicon standard. The stoichiometric ratio of Ti to S in pristine TiS_2 was determined to be 1.045:2 by weight change upon oxidation of TiS_2 as heated to 700 °C in air. The Raman spectra were obtained by exciting the samples with 514.5 nm line of an argon-ion laser beam (LABRAM-HR, JY) focused on the sample surface with the aid of a cylindrical lens at room temperature. XPS experiments were carried out on a photoemission spectroscope (XPS, ESCALAB MKII, VG), in which data were collected in a constant analyzer energy (CAE) mode at 20 eV. Mg Kα ($h\nu = 1253.6$ eV) radiation was employed as excitation source with an anode voltage of 12 kV and an emission current of 20 mA. Thermal conductivity was measured by a physical property measurement system (PPMS, Quantum Design) in the temperature range from 5 K to 310 K.

3. Results and discussions

3.1. Microstructural information detected with XRD

Fig. 1 gives the XRD patterns for the synthesized pristine TiS_2 and intercalated Bi_xTiS_2 samples, as shown previously in ref. [11]. It can be seen from curve (a) that all the reflection peaks correspond to those of standard 1T-TiS_2. As compared to that of pristine TiS_2, no substantial change is observed in XRD patterns of bismuth intercalation compounds Bi_xTiS_2 when $x < 0.15$. As $x \geq 0.15$, however, two additional reflection peaks (P_1 and P_2) appear in the range $10^\circ \leq 2\theta \leq 70^\circ$, as marked by solid circles in the figure. Peaks P_1 and P_2 are found not to come from elementary Bi substance; instead they would originate from structural conversion from stage-1 to stage-2 [6]. The plane spacing corresponding to the first new peak (P_1, where $2\theta = 23.5^\circ$) and the second peak (P_2, where $2\theta = 39.5^\circ$) in Fig. 1 are 3.77 Å and 2.27 Å, respectively. By assuming that stage conversion from stage-1 to stage-2 occurred for part of material in the sample, the lattice parameter c of this converted material (stage-2 phase) doubles, and then the original peak (0 0 1) becomes (0 0 2′). Therefore, according to the Bragg formula, the two new peaks are (0 0 3′) and (0 0 5′) reflection, respectively. Because of the structural conversion, another new peak (0 0 1′) should appear at around 7.6°. As an example, Fig. 2 gives the XRD pattern in low angle range ($2\theta = 4^\circ$–20°) for intercalation compound $Bi_{0.20}TiS_2$.