Co-doped Sb$_2$Te$_3$ paramagnetic nanoplates

Lei Yang,$^{a}$ Zhi-Gang Chen,$^{a}$ Tianxiao Nie,$^{b}$ Guang Han,$^{a}$ Zhi Zhang,$^{a}$ Min Hong,$^{a}$ Kang L. Wang$^{b}$ and Jin Zou$^{a,ac}$

Co-doped Sb$_2$Te$_3$ nanoplates are fabricated using a facile and green solvothermal method. The as-synthesized nanoplates show uniform hexagonal morphology with a distribution of 1–2 μm in diameters and ~50 nm in thickness. The detailed structural and compositional characterization indicates that Co uniformly distributes in Sb$_2$Te$_3$ and leads to a lattice shrink of 1.22% along the a axis and 0.9% along the c axis. A Superconducting Quantum Interference Device magnetometer is used to determine the temperature-dependent magnetization in zero-field cooled and field-cooled processes. The paramagnetic state in our Co-doped Sb$_2$Te$_3$ nanoplates is found from 5 K to 300 K.

Introduction

Antimony telluride (Sb$_2$Te$_3$) has been extensively studied due to its multi-discipline application as topological insulators$^{1,2}$ and thermoelectric materials.$^{3,4}$ On the basis of theoretical calculations,$^{1,2}$ Sb$_2$Te$_3$ has robust and simple conducting surface states with a single gapless Dirac cone at the Fermi level. Additionally, several unique physical phenomena, namely, the quantum Hall effect,$^{1,2}$ the quantized anomalous Hall effect,$^{5}$ and the topological magnetoelectric effect,$^{6–8}$ have been theoretically predicted and experimentally demonstrated in Sb$_2$Te$_3$. In particular, introducing magnetic impurities, such as Fe,$^9$ Co$^{25,26}$ Mn$^{15,16}$ and V$^{17,18}$ to obtain dilute magnetic semiconductors, we found that Co ions are uniformly doped into Sb$_2$Te$_3$, resulting in a slight lattice shrink from the equilibrium Sb$_2$Te$_3$ crystal structure and introducing atomic moment in the Sb$_2$Te$_3$ lattice. The obtained Co-doped Sb$_2$Te$_3$ nanoplates reveal a paramagnetic behavior from 5 to 300 K.

According to the theoretical calculations and experimental results,$^{4,7,12,13}$ the electrical and magnetic properties of Sb$_2$Te$_3$ can be tuned by the substitution of transition metals, such as Fe,$^9$ Co$^{25,26}$ Mn$^{15,16}$ and V$^{17,18}$ to obtain dilute magnetic semiconductors from the diamagnetic un-doped Sb$_2$Te$_3$.$^{19,20}$ For example, Zhang et al.$^{13}$ suggested that cation-site substitution in the anion-rich environment is the most effective doping method. At a nominal dopant concentration of 4%, Cr-doped Sb$_2$Te$_3$ acts as an insulator, while the V-, Mn- and Fe-doped Sb$_2$Te$_3$ become metallic.$^{13}$ In another study, ferromagnetic ordering was observed in Mn-doped Sb$_2$Te$_3$ compounds at a Curie temperature ($T_C$) of 17 K.$^{21}$ Furthermore, the $T_C$ of Sb$_2$Te$_3$ can be tuned by adjusting the doping level in the dilute magnetic semiconductor p-type Sb$_{1-x}$Cr$_x$Te$_3$,$^8$ in which ferromagnetism was observed at $T_C$ ~ 5.8 K for $x = 0.0115$ and at $T_C$ ~ 2.0 K for $x = 0.0115$, respectively. However, most of these studies were performed in bulk materials; and the magnetic properties of doped Sb$_2$Te$_3$ nanostructures have rarely been investigated. Recently, nanostructured topological insulators have drawn much attention due to their novel physical properties,$^{22–24}$ which are exciting for the future development of new-generation spintronic devices. Due to the size effect, it is easier to manipulate the surface state of nanostructures when compared to their bulk counterparts,$^{22–25}$ which makes them preferred candidates for the practical applications in spintronic nano-devices.

In this study, we employed a facile and controllable solvothermal approach$^{25,26}$ to realize Co-doping into hexagonal shaped Sb$_2$Te$_3$ nanoplates. From our detailed structural and chemical characterizations, we found that Co ions are uniformly doped into Sb$_2$Te$_3$, resulting in a slight lattice shrink from the equilibrium Sb$_2$Te$_3$ crystal structure and introducing atomic moment in the Sb$_2$Te$_3$ lattice. The obtained Co-doped Sb$_2$Te$_3$ nanoplates reveal a paramagnetic behavior from 5 to 300 K.

Experimental

The Co-doped Sb$_2$Te$_3$ nanoplates were solvothermally synthesized, in which analytical grade Sb$_2$O$_3$, Te, CoCl$_2$, ethylene glycol, polyvinylpyrrolidone (PVP) and NaOH solution were used as the precursors. In a typical synthesis, 0.2 g of PVP was first dissolved in ethylene glycol (36 mL) to form a clear solution,
followed by adding Sb$_2$O$_3$, CoCl$_2$, and Te powders with defined ratios to achieve Sb$_{1.9}$Co$_{0.1}$Te$_3$. After stirring for 5 min, the prepared solution was mixed with 4 mL of NaOH solution (5 mol L$^{-1}$), the resulting suspension was stirred vigorously for 30 min at 65 °C, and subsequently sealed in a 120 mL autoclave. The autoclave was then heated to 230 °C in an oven, maintained at this temperature for 24 h, and then cooled naturally to room temperature. The synthesized products were collected by a high-speed centrifugation, washed 6 times with distilled water and absolute ethanol, and finally dried at 50 °C for 12 h.

The structural feature of the synthesized products was investigated by X-ray diffraction (XRD), recorded on an X-ray diffractometer equipped with graphite monochromatized, in which the Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å) was employed. The morphological, structural, and chemical characteristics of the as-synthesized products were investigated using scanning electron microscopy (SEM, JEOL 7800F, operated at 5 kV) and transmission electron microscopy (TEM, Philips FEI Tecnai F20, operated at 200 kV, equipped with an electron Energy-dispersive X-ray spectroscopy (EDS) and an electron energy loss spectroscopy (EELS) system for chemical analysis). A Superconducting Quantum Interference Device (SQUID) magnetometer was used to obtain the temperature dependent magnetization in zero-field cooled (ZFC) and field cooled (FC) processes.

Results and discussion

Fig. 1(a) shows the XRD pattern of as-synthesized Co-doped Sb$_2$Te$_3$ (blue pattern) and un-doped Sb$_2$Te$_3$ (black pattern) products compared with the diffraction peaks (red) of the rhombohedral structured Sb$_2$Te$_3$ found in the standard identification card (JCPDS 15-0874, lattice parameters $a = b = 4.262$ Å and $c = 30.48$ Å), in which all diffraction peaks can be exclusively indexed as the Sb$_2$Te$_3$ phase with the space group of $R\bar{3}m$. There is no secondary phase or any observable impurities, indicating the high purity of our synthesized products. Nevertheless, our detailed comparison of the obtained XRD pattern of Co-doped and un-doped Sb$_2$Te$_3$ diffraction peaks shows that the diffraction peaks of the as-synthesized Co-doped Sb$_2$Te$_3$ products have right-shifted, indicating the existence of a lattice shrink in the as-synthesized products. Fig. 1(b) shows the enlarged 0006* and 1120* peaks of Co-doped Sb$_2$Te$_3$ (blue) compared with un-doped Sb$_2$Te$_3$ peaks (black); (c) SEM image showing the high-yield of the synthesis; (d) high magnification SEM image showing a typical hexagonal-shaped nanoplate, and the inset showing the thickness of a typical nanoplate.

To understand the structural characteristics of as-synthesized Co-doped Sb$_2$Te$_3$ nanoparticles, detailed TEM investigations were employed. Fig. 2(a) is a TEM image showing a typical hexagonal-shaped nanoplate, its lateral dimension fits well with the lateral...
dimension determined by SEM. Fig. 2(b) and (c) show the corresponding selected area electron diffraction (SAED) patterns and the high resolution TEM (HRTEM) image, both showing the surface normal of the nanoplate parallel to its c axis. By closely correlating the six side edges shown Fig. 2(a) and the indexed diffraction spots in Fig. 2(b), the side edges of the nanoplates can be determined to be \( \{10\overline{1}0\} \) facets. It is of interest to note that the transparent feature of this nanoplate shown in Fig. 2(a) and ease of taking the HRTEM image shown in Fig. 2(c) suggest that this nanoplate is very thin (~30 nm). In addition, the facts of the sharp diffraction spots shown in Fig. 2(b) and the nature of perfect crystalline found in Fig. 2(c) indicate that our synthesized nanoplates are well-crystallized with no observable lattice defects. To elucidate compositional characteristics of as-synthesized Co-doped Sb\(_2\)Te\(_3\) nanoplates, EDS was used to determine their chemical compositions and distributions. Fig. 2(d) shows the corresponding EDS spectrum of a typical Co-doped Sb\(_2\)Te\(_3\) nanoplate, from which, Co, Te and Sb peaks can be clearly observed while Cu peaks are due to the Cu TEM grid. According to our quantitative EDS analysis, the composition of our Co-doped Sb\(_2\)Te\(_3\) nanoplates can be determined as Sb\(_{1.9}\)Co\(_{0.1}\)Te\(_3\).

To clarify how Co is incorporated in the binary Sb\(_2\)Te\(_3\), EDS mappings were performed. Fig. 3(a) is a TEM image of a nanoplate, and Fig. 3(b)–(d) are EDS maps for Sb, Te and Co, respectively. The relative uniform contrast of the Co map [refer Fig. 3(d), in which the dotted contrast is caused by the rough probe size] suggested that Co has uniformly distributed in the nanoplate.

To investigate the valence state of Co, EELS analysis was applied. Fig. 4(a) shows an EELS profile acquired from an as-prepared Co-doped Sb\(_2\)Te\(_3\) nanoplate, in which Te-M\(_{4.5}\) edges and Co-L\(_{2,3}\) edges can be clearly observed in an energy loss region between 600 and 1000 eV. In particular, the existence of Co-L\(_{2,3}\) edges provides the direct evidence of the substitution of Sb ions by Co ions\(^{25,26}\) and the corresponding atomic model is schematically illustrated in Fig. 4(b).

The above detailed structural characterization confirmed that Co has been successfully doped into Sb\(_2\)Te\(_3\) by substituting Sb ions. On this basis, new magnetic properties may be introduced in our Co-doped Sb\(_2\)Te\(_3\) nanoplates, which needs verification. A SQUID magnetometer was used to obtain the temperature dependent magnetization in zero-field cooled (ZFC) and field cooled (FC) processes. The sample was cooled in the absence of a magnetic field from 300 K down to 5 K and then the magnetization was measured from 5 to 300 K under a magnetic field of 100 Oe; the temperature-dependent ZFC and FC plots are shown in Fig. 5(a). As can be seen, the ZFC and FC curves are almost identical, and no obvious turning point can be found within the measuring temperature range of 5–300 K, indicating that the Co-doped Sb\(_2\)Te\(_3\) nanoplates show a similar magnetic state in this temperature range no matter whether the magnetic field was applied or not. The magnetic field dependent magnetization and hysteresis \((M-H)\) loops were obtained at 5 K and 20 K, respectively, and the results are shown in Fig. 5(b). The \(M-H\) curve reveals the typical paramagnetic behaviour of Co-doped Sb\(_2\)Te\(_3\) nanoplates at both \(T = 5\) K and 20 K, which is significantly different with diamagnetic un-doped Sb\(_2\)Te\(_3\)\(^{19,20}\) and ferromagnetism Cr, Fe and Mn-doped Sb\(_2\)Te\(_3\)\(^{8,9,15}\) and the doping of Co ions was considered originating the magnetic moments because the pure Sb\(_2\)Te\(_3\) is diamagnetic.

The Curie constant \((C)\) can be determined to further understand the contribution of Co ions to the paramagnetism.\(^{26}\) Fig. 5(c) is the re-plotted figure from Fig. 5(a), where the \(C\) value can be determined by obtaining the slope of the plot shown in Fig. 5(c) as \(C = 3.18 \times 10^{-6}\) emu K g\(^{-1}\) Oe according to the Curie law \(C = MT/\chi_H\),\(^{27}\) where \(M\) is the resultant magnetization, \(H\) is the magnetic field, and \(T\) is the absolute temperature. Moreover, the susceptibility \((\chi)\) of the paramagnetic materials in a small field can be expressed as \(\chi = N\mu_B^2 /3k_B T = M/H\) with the Langevin paramagnetic function, where \(N\) is the number of magnetic atoms per unit gram (in our Co-doped Sb\(_2\)Te\(_3\), the number of Co can be estimated as \(6.452 \times 10^{19}\) per unit gram due to...
the chemical composition which has been estimated as Sb₁.₉Co₀.₁Te₃, μ is the effective moment of a magnetic atom, μ₀ is the vacuum permeability which is 1 in the centimetre-gram-second unit system and is dimensionless, and k_B is the Boltzmann constant (1.38 × 10⁻²³ J K⁻¹). In our study, μ = 1.42 × 10⁻²⁴ J T⁻¹ can be calculated combining the Curie law with the Langevin paramagnetic function. We can define that each doped Co ion in our Sb₁.₉Co₀.₁Te₃ system distributes an effective moment of μ = xμ_B when we consider the doping of Co ions originating the magnetic moments, where x is the amount of Bohr magneton from each doped Co ion and μ_B is the Bohr magneton (9.274 × 10⁻²⁴ J T⁻¹). Therefore, x can be determined as 0.15, which means that every Co ion has an effective moment of 0.15μ_B in our Sb₁.₉Co₀.₁Te₃ nanoplates. The magnetic moments originated from doped Co ions and the paramagnetic behaviour are contributed from the spin polarization of the electric band structure. These findings of paramagnetic Sb₁.₉Co₀.₁Te₃ nanoplates provide significant progress in developing nano-electronic and spintronic devices.

Conclusions

In this study, the compositionally uniform and hexagonal-shaped Sb₁.₉Co₀.₁Te₃ nanoplates were synthesized using a facile solvothermal method. Based on our detailed morphological, structural, and chemical characteristics, we found that Co ions have substituted Sb ions in the crystal lattice, leading to the (1) reduced lattice parameters, and (2) paramagnetic state from 5 K to room temperature. This study paves a way to develop magnetic Sb₂Te₃ topological insulators for the design and development of future electronic and spintronic devices.

Acknowledgements

This work was financially supported by the Australian Research Council; ZGC thanks the QLD government for a smart state future fellowship (2011002414). LY thanks the China Scholarship Council for providing his PhD stipend. The Australian Microscopy & Microanalysis Research Facility is acknowledged for providing characterization facilities.

Notes and references


