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Co-doped Sb$_2$Te$_3$ Paramagnetic Nanoplates

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Co-doped Sb$_2$Te$_3$ nanoplates are fabricated by 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 characterizations indicate that Co uniformly distributes in Sb$_2$Te$_3$ and leads to a lattice shrink of 1.22% along the α 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. It is found the paramagnetic state in our Co-doped Sb$_2$Te$_3$ nanoplates 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, thermoelectric materials, and spintronic devices. On the basis of theoretical calculations, Sb$_2$Te$_3$ has robust and simple conducting surface states with a single gapless Dirac cone at the Γ point. Additionally, several unique physical phenomena, namely, quantum hall effect, quantized anomalous Hall effect, and topological magnetoelectric effect, have been theoretically predicted and experimentally demonstrated in Sb$_2$Te$_3$. Especially, introducing magnetic impurities, such as Fe, into Sb$_2$Te$_3$ can break the time reversal symmetry, inducing a gap at the Dirac point of the topological surface state, which is crucial for realizing exotic phenomena mentioned above. Therefore, the further understanding of the coexistence of both topological state and magnetic order in topological materials should be highly prompted.

According to the theoretical calculations and experimental results, the electrical and magnetic properties of Sb$_2$Te$_3$ can be tuned by the substitution of transition metals, such as Fe, Cr, Mn, and V, to obtain dilute magnetic semiconductors from the diamagnetic un-doped Sb$_2$Te$_3$. For example, Zhang et al. suggested that cation-site substitution in the anion-rich environment is the most effective doping method. Under the nominal dopant concentration of 4%, Cr-doped Sb$_2$Te$_3$ remains as insulators, while the V-, Mn-, and Fe-doped Sb$_2$Te$_3$ become metallic. In another study, ferromagnetic ordering was observed in Mn-doped Sb$_2$Te$_3$ compounds at a Curie temperature ($T_C$) of 17 K. 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$_2$O$_4$Cr$_{0.01}$Te$_3$, in which ferromagnetism was observed at $T_C$ ~ 5.8 K for x = 0.0215 and at $T_C$ ~ 2.0 K for x = 0.0115, respectively. However, most of these studies were performed in bulk materials; and 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, which makes them preferred candidates for the practical applications in spintronic nano-devices.

In this study, we employed a facile and controllable solvothermal approach 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$_x$Co$_{0.15}$Te$_3$. After stirring for 5 min, the prepared solution was mixed with 4 mL of NaOH solution (5 mol/L), 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 and maintained at this temperature for 24 h, then cooled naturally to the room temperature. The synthesized products were collected by a high-speed centrifugation, and the precipitates were washed with ethanol and finally dried at 60 °C for 12 h.
washed 6 times with distilled water and absolute ethanol, and finally dried at 50 °C for 12 h.

The structural feature of synthesized products were investigated by X-ray diffraction (XRD), recorded on an X-ray diffractometer equipped with graphite monochromated, in which the Cu Kα radiation (λ = 1.5418 Å) was employed. The morphological, structural, and chemical characteristics of 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 Sb₂Te₃ (blue pattern) and un-doped Sb₂Te₃ (black pattern) products compared with the diffraction peaks (red) of the rhombohedral structured Sb₂Te₃ 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 Sb₂Te₃ phase with the space group of R̅3m. There is no secondary phase or any observable impurities, indicating the high purity of our synthesized products. Nevertheless, our detailed comparison of obtained XRD pattern of Co-doped and un-doped Sb₂Te₃ diffraction peaks shows that the diffraction peaks of as-synthesized Co-doped Sb₂Te₃ products have right-shifted, indicating the existence of a lattice shrink in as-synthesized products. Fig. 1(b) shows the enlarged 0006* and 1120* diffraction peaks of Co-doped Sb₂Te₃ compared with diffraction peaks of un-doped Sb₂Te₃, from which the lattice parameters of as-synthesized Co-doped Sb₂Te₃ products can be determined as a = 4.20 Å and c = 30.20 Å - revealing a decrease of 1.22% along the a axis and a decrease of 0.9% along the c axis, respectively. This lattice shrinkage could be caused by the substitution of Sb ions by the relatively smaller Co ions. Fig. 1(c) shows a representative SEM image of the as-synthesized products, in which plate-shaped nanostructures can be observed with a lateral dimension of 1-2 µm. Fig. 1(d) is a zoom-in SEM image showing a typical hexagonal-shaped Co-doped Sb₂Te₃ nanoplate, and the inset shows a ~50nm thick nanoplate.

To understand the structural characteristics of as-synthesized Co-doped Sb₂Te₃ 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)-(c) show corresponding selected area electron diffraction (SAED) patterns and high resolution TEM (HRTEM) image, both showing the surface normal of the nanoplate is parallel to its c axis. By close correlating the six side edges shown Fig. 2(a) and the indexed diffraction spots in Fig. 2(b), the side edges of the nanoparticles can be determined to be {1010} facets. It is of interest to note that the transparent feature of this nanoplate shown in Fig. 2(a) and easy of taking 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 nanoparticles are well-crystallized with no observable lattice defects. To elucidate compositional characteristics of as-synthesized Co-doped Sb₂Te₃ nanoplates, EDS was used to determine their chemical compositions and distributions. Fig. 2(d) is the corresponding EDS spectrum for a typical Co-doped Sb₂Te₃ 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 Sb₂Te₃ nanoplates can be determined as Sb₂.9Co₀.1Te₃.

To clarify how Co is incorporated in the binary Sb₂Te₃, 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 Sb₂Te₃ nanoplate, in which Te-M₄,₅ and Co-L₂,₃ edges can be clearly observed in an energy loss region between 600 and 1000 eV. Especially, the existence of Co-L₂,₃ edges provides the direct evidence of the substitution of Sb ions by Co ions, the corresponding atomic

Figure 3 (a) A typical TEM image of Co-doped Sb₂Te₃ nanoplate; (b)-(d) EDS maps for Sb, Te and Co, respectively.

Figure 4 (a) EELS spectrum of a Co-doped Sb₂Te₃ nanoplate showing the Te-M₄,₅ and Co-L₂,₃ edges; (b) Atomic model illustrating the substitution of Sb ions by Co ions in the Co-doped Sb₂Te₃ nanoplate. The model can be schematically illustrated in Fig. 4(b).

Above detailed structural characterizations confirmed that Co has been successfully doped into Sb₂Te₃ by substituting Sb ions. On this basis, new magnetic properties may be introduced in our Co-doped Sb₂Te₃ nanoplates, which needs verifying. 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 showed in Fig. 5(a). As can be seen, the ZFC and FC curves are almost identical, no obvious turning point can be found within the measuring temperature range of 5-300 K, indicating that the Co-doped Sb₂Te₃ nanoplates show 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 showed in Fig. 5(b). The M-H curve reveals the typical paramagnetic behaviour of Co-doped Sb₂Te₃ nanoplates at both T= 5 K and 20 K, which is significantly different with diamagnetic un-doped Sb₂Te₃ and ferromagnetism Cr-, Fe- and Mn-doped Sb₂Te₃ and the doping of Co ions was considered originating the magnetic moments because the pure Sb₂Te₃ is diamagnetic. Curie constant (C) can be determined to further understand the contribution of Co ions to the paramagnetism.

Figure 5 (a) Temperature dependent magnetization moments in ZFC and FC processes under the field of 100 Oe; (b) M-H profiles at temperatures of 5 K and 20 K; (c) H/M plot of ZFC curve under the field of 100 Oe as a function of (1/T), the slope corresponding to the Curie constant.
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 Oe according to the Curie law $C = MT/H$, where $M$ is the resultant magnetization, $H$ is the magnetic field, and $T$ is 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 6.452×10$^{39}$ per unit gram due to the chemical composition has been estimated as Sb$_{1.8}$(Co$_{0.1}$)Te$_3$), $\mu$ is the effective moment of a magnetic atom, $\mu_0$ is vacuum permeability which is 1 in the centimetre–gram–second unit system and is dimensionless, and $k_B$ is Boltzmann constant (1.38×10$^{-23}$ J/K). In our study, $\mu = 1.42 \times 10^{24}$ J/T can be calculated by combining Curie law with the Langevin paramagnetic function. We can definite that each doped Co ion in our Sb$_{1.8}$(Co$_{0.1}$)Te$_3$ system distributes an effective moment of $0.15\mu_B$ 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 $\mu_B$ is the Bohr magneton$^{27}$ (9.274×10$^{-24}$ J/T). Therefore, $x$ can be determined as 0.15, which means every Co ion has an effective moment of 0.15$\mu_B$ in our Sb$_{1.8}$(Co$_{0.1}$)Te$_3$ nanoplates. The magnetic moments originated from doped Co ions and the paramagnetic behaviour are contributed from the spin polarization of electric band structure. These findings of paramagnetic Sb$_{1.8}$(Co$_{0.1}$)Te$_3$ nanoplates provide a significant progress in developing nanoelectronic and spintronic devices.

Conclusions

In this study, the compositional uniform and hexagonal-shaped Sb$_{1.8}$(Co$_{0.1}$)Te$_3$ nanoparticles were synthesized by a facile solvothermal method. Based on our detailed morphological, structural, chemical characteristics, we found that Co ions have substituted Sb ions in the crystal lattice, leading to (1) reduced lattice parameters, and (2) paramagnetic state from 5K to the room temperature. This study paves a way to develop magnetic Sb$_2$Te$_3$ topological insulators for design and development of future electronic and spintronic devices.

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Notes and references

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