

Magnetic Properties and Raman Spectroscopy of Cr-Doped Bismuth Telluride Nanotubes

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Abstract

We have investigated the magnetic properties and Raman spectroscopy of doped bismuth telluride nanotubes. Chromium-doped bismuth telluride nanotubes are synthesized using a wet chemical reaction. The diameter of the nanotubes range from 20–70 nm. Various concentrations of chromium are incorporated in Bi₂Te₃ nanotubes. The Raman spectra of these nanotubes exhibit infrared active modes that are not active in bulk bismuth telluride. As the Cr concentration increases, the nanotubes exhibit ferromagnetic behavior. The ferromagnetic behavior exists even beyond room temperature. Large saturation magnetization is observed for $x = 0.076$ (Bi_{2-x}Cr_xTe₃), and for higher concentrations the samples become paramagnetic.

Keywords: nanotubes, ferromagnetism, Raman spectroscopy, topological insulators, semiconductors, paramagnetism

1. Introduction

In topological insulators, special edge states or surface states allow electrons to conduct at the surface of a material that otherwise behaves as an insulator (Bernevig, Hughes, & Zhang, 2006; Konig et al., 2007; Fu & Kane, 2007). Recently, it was found that Bi₂Te₃ and other thermoelectric compounds like Bi₂Se₃ are bulk topological insulators (Zhang et al., 2009; Xia et al., 2009). This has attracted much more interest from the scientific community with many novel applications in nanoelectronics and in spintronics. It has been reported that bismuth telluride quintuple films and bismuth telluride nanoplates synthesized using solvothermal process display infrared (IR) active modes in Raman spectra (Shahil, Hossain, Teweldebrhan & Balandin, 2010; Liang et al., 2011; He et al., 2012). These modes are not active in bulk Bi₂Te₃. The IR active modes arise as a result of the breakdown of inversion symmetry in the crystal structure (Cheng & Ren, 2011). In addition, ferromagnetism has been observed in Fe- and Mn-doped Bi₂Te₃ single crystals (Choi et al., 2004; Hor et al., 2010; Kulbachinskii et al., 2002), Fe-doped Bi₂Se₃ single crystals (Chen et al., 2010), V-, Cr- and Mn-doped Sb₂Te₃ single crystals (Dyck, Chen, Hajek, Lostak, & Uher, 2002; Dyck, Hajek, Lostak, & Uher, 2002; Dyck et al., 2005; Dyck et al., 2003). Ferromagnetism in Bi_{2-x}Mn_xTe₃ single crystals has been observed when x is 0.04 or greater. The Curie temperature was found below 20 K for $x = 0.04$ and 0.09 samples (Hor et al., 2010). On the other hand, in chromium doped Sb₂Te₃ thin films, a Curie temperature of 190 K was observed (Zhou, Chien & Uher, 2006). In heavily Cr-doped Bi₂Se₃ bulk crystals, antiferromagnetic behavior was reported (Choi et al., 2011). It is interesting to explore the effects of magnetic impurities on the surface states of bismuth telluride. Bismuth telluride nanotubes are excellent candidates for exploring the ferromagnetism on the surface states and to search for IR active modes in Raman spectra. A variety of techniques are available to grow such nanostructured bismuth telluride (Deng et al., 2006; Cao, Zhu, & Zhao, 2008; Xiao, Yoo, Lee, & Myung, 2007; Zhang, Yu, Yao, & Li, 2009). We have chosen a wet chemical synthesis and tailored the synthesis procedure to incorporate chromium to obtain ferromagnetic chromium doped bismuth telluride (Bi_{2-x}Cr_xTe₃) nanotubes. We have varied the chromium concentration, x from 0 to 0.2. It is interesting, as the chromium concentration is increased, ferromagnetic behavior emerges in these nanotubes, exhibiting large saturation magnetization around $x = 0.076$ and at x greater than 0.15, the ferromagnetic behavior completely disappears. We have observed the ferromagnetic behavior beyond room temperature that is not observed in bulk or in thin films. Also, the Raman

spectra of these nanotubes are investigated and they display infrared active modes that are not reported earlier in nanotubes.

2. Materials and Methods

Bi_2Te_3 nanotubes are synthesized using a wet chemical synthesis, which is already reported in the literature (Zhang et al., 2009). We have modified the synthesis procedure so that chromium can be incorporated into Bi_2Te_3 nanotubes. In the synthesis of Bi_2Te_3 nanotubes, initially tellurium nanowires were synthesized using TeO_2 at 433 K and then bismuth precursor, $\text{Bi}(\text{NO}_3)_3$ was added to obtain Bi_2Te_3 nanotubes. The bismuth ions diffuse into tellurium nanowires to form Bi_2Te_3 nanotubes. The mechanism of the growth was discussed in Zhang et al. (2003). We have investigated different techniques to dope chromium into the Bi_2Te_3 nanotubes. The successful doping method is described here. In the modified synthesis, after the growth of tellurium nanowires at 433 K, the temperature was lowered to 363 K and the chromium precursor, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, was injected. The reaction was maintained at this temperature for one hour for diffusing chromium ions into the tellurium wires. Then the solution was heated to 433 K, and the bismuth precursor was added. After one hour of reaction, the solution was cooled down to room temperature. The final solution was diluted with isopropyl alcohol and centrifuged. The resulting black powder was washed with deionized water and ethanol. It was observed that this procedure yields ferromagnetic chromium-doped nanotubes with different concentrations of chromium. The nanotubes have been characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM). Raman spectra were obtained using an in-house built Raman system with a 514.5 nm Ar^+ laser (LEXEL Laser 3000). The magnetic behavior has been determined by vibrating sample magnetometer (VSM-Quantum Design).

3. Result and Discussion

Figure 1(a) shows the SEM image of chromium doped Bi_2Te_3 nanotubes. The nanotubes are 20–70 nm in diameter with the length varying from 10–15 μm . The synthesis yields pure nanotubes and there is no evidence of nanoparticles or any bulk clusters. The TEM analyses (Figure 1(b)) show that they are nanotubes with a saw tooth surface morphology. The average wall thickness of the nanotubes is around 10 nm. The XRD patterns of the chromium doped Bi_2Te_3 nanotubes are displayed in Figure 2(a). These patterns can be indexed with the hexagonal phase of Bi_2Te_3 structure (International Center for Diffraction Data # 00-015-0863). There are no peaks corresponding to chromium-based phases like Cr_2O_3 , CrTe , Cr_3Te_4 and Cr_2Te_3 . Very weak XRD peaks (marked with black circles) of TeO_3 are observed in long time air exposed samples. It was observed that as the chromium doping increases, the XRD peaks are shifted to higher two-theta values indicating that the chromium ions are incorporated into the Bi_2Te_3 lattice. We have carried out the Energy Dispersive X-ray Spectroscopy (EDS) for $x = 0.076$ and 0.1 samples and obtained the chromium concentration in the nanotubes near the initial doping levels within a 4% error. Chromium ions are smaller than the bismuth ions so the lattice volume is expected to shrink.

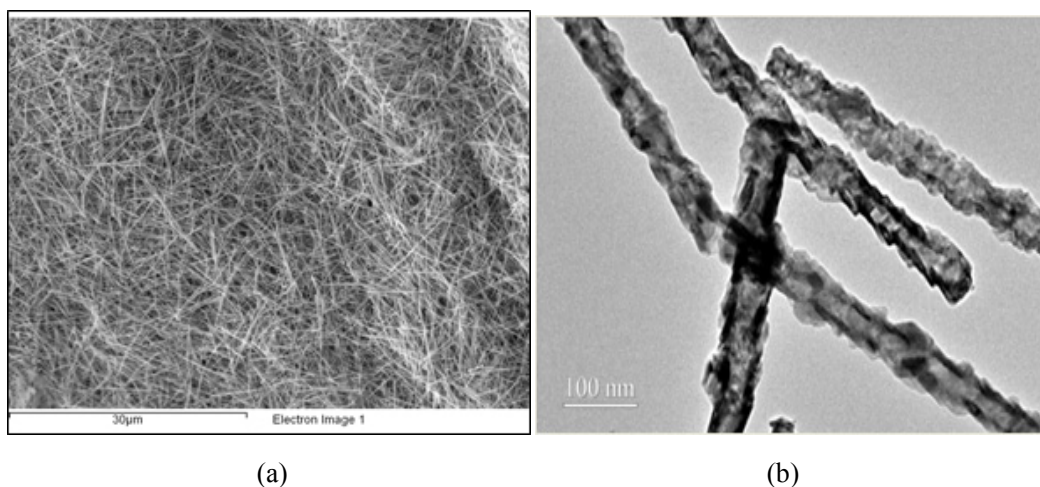


Figure 1. (a) SEM image of as-grown chromium doped bismuth telluride ($x = 0.076$) nanotubes; (b) TEM image of the nanotubes are shown

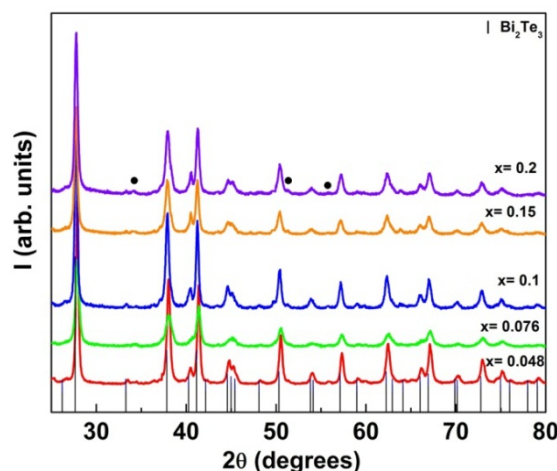


Figure 2. X-ray diffraction patterns of chromium doped bismuth telluride ($\text{Bi}_{2-x}\text{Cr}_x\text{Te}_3$) nanotubes ($x = 0.048, 0.076, 0.1, 0.15$ and 0.2). Small black circles correspond to TeO_3 peaks

As shown in Table 1, the a -axis lattice constant decreases initially and then shows an increasing trend, but remains lower than the lattice constant of the undoped nanotubes. Similar behavior is observed with the c -axis lattice parameter. The chromium ions can occupy either bismuth sites or interstitial regions. It is evident from the lattice parameter change that as the chromium concentration increases, more chromium ions are occupying the interstitial regions in the van der Waals gaps. This is probably the reason for the increasing trend observed in the c lattice parameter after $x = 0.076$. Raman spectroscopy studies were carried out on different chromium doped nanotubes.

Table 1. Variation of lattice constants of $\text{Bi}_{2-x}\text{Cr}_x\text{Te}_3$ with Cr-doping

$\text{Bi}_{2-x}\text{Cr}_x\text{Te}_3$ (x)	$a(\text{\AA})$	$c(\text{\AA})$
0	4.3852	30.483
0.048	4.3578	30.0448
0.076	4.3578	30.1154
0.1	4.372	30.3823
0.12	4.3721	30.4508
0.15	4.3721	30.4353

Figure 3(a) shows the Raman spectrum from a set of a few nanotubes ($x = 0.1$) with an average diameter around 60 nm. The two optical phonon peaks are identified, they are E_{1g}^1 (102.5 cm^{-1}) and A_{1g}^2 (139.27 cm^{-1}) respectively. These peaks are close to the reported Raman peaks for Bi_2Te_3 bulk sample (Kullmann et al., 1984). In addition to these two peaks, there is an intense peak at 118.07 cm^{-1} . This peak is the A_{1u}^2 mode (IR active) of the longitudinal optical phonons. Theoretically, in crystals with inversion symmetry, the A_{1u} mode is IR active and possesses odd parity while the Raman active modes E_g and A_{1g} have even parity under inversion (Yu & Cardona, 2005). In the bulk samples, when the crystal retains its symmetry, the odd parity phonons do not appear in the Raman spectra (Russo et al., 2008; Gonclaves et al., 2010). The A_{1u} mode appears in the Bi_2Te_3 nanotubes because of the crystal symmetry breaking due to the one-dimensional nature of the nanotubes. In thinner nanotubes with an average diameter around 30 nm, one more additional peak is observed around 96 cm^{-1} as shown in Figure 3(b). This peak corresponds to A_{1u}^1 IR active mode. The A_{1u}^2 mode in thinner nanotubes is displayed at 116.1 cm^{-1} . Similar Raman spectra were obtained for other chromium doped Bi_2Te_3 nanotubes. Our results are in agreement with the recent Raman study on a few-quintuple bismuth telluride films and the synthesized nanoplates (Shahil et al., 2010; Liang et al., 2011; He et al., 2012).

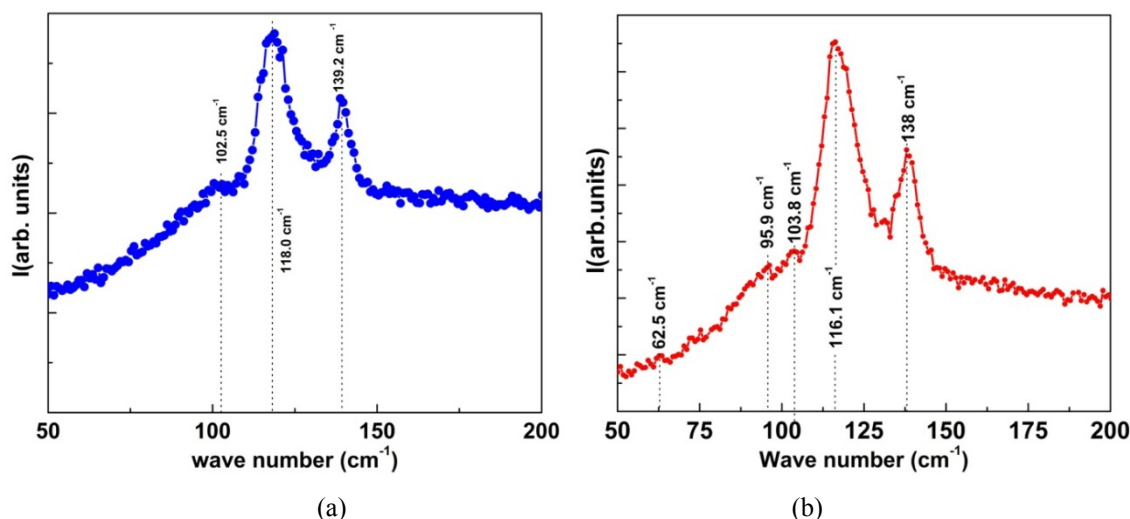


Figure 3. Raman spectrum of a few nanotubes of average size range (a) 60 nm and (b) 30 nm

The magnetic measurements are carried out using the nanostructures inside a polypropylene sample holder. The nanotubes with different chromium concentrations display interesting magnetic behavior. The background signal is corrected from all the reported magnetic data. Nanotubes with $x = 0.048$ show diamagnetic behavior, as we increase the chromium concentration hysteresis loops are observed at room temperature as displayed in Figure 4. For $x = 0.076$, the coercivity is 70 Oe at 300 K and it increases to 120 Oe at 10 K. For $x = 0.1$, the coercivity is 50 Oe at 300 K and the saturation magnetization decreases by a factor of 60. A further increase in chromium weakens the ferromagnetic behavior and at $x = 0.2$, purely paramagnetic behavior is observed. Ferromagnetic behavior weakens after $x = 0.076$, which may be due to fact that more and more chromium ions occupy the interstitial regions that reduces the ferromagnetic exchange interaction and as the chromium concentration further increases, their exchange interaction completely weakens. Purely paramagnetic behavior is observed after $x = 0.15$. If phases such as Cr_2Te_3 , CrTe and Cr_3Te_4 were present in the nanotubes, they are ferromagnetic and their Curie temperature range from 180–340 K (Sato, Aman, Hirai, & Fujisawa, 1990; Oda et al., 2001). Chromium metal clusters do not exhibit ferromagnetic behavior, they are antiferromagnetic. The Curie temperature of the chromium doped nanotubes appears higher than 400 K as displayed in the inset in Figure 4. Our results show that in Bi_2Te_3 nanotubes with chromium incorporation, ferromagnetic behavior can be observed at room temperature and beyond. Additionally no Cr-based secondary phases are observed in XRD, Raman or high-resolution TEM analyses. The chromium doped bismuth telluride nanotubes show a systematic change in the magnetic behavior with the increase in chromium content. The magnetic behavior observed depends strongly on the chromium content. The low-doped nanotubes exhibit diamagnetism similar to the undoped sample; as the chromium content increases, ferromagnetic behavior emerges and when there is large increase in chromium, they display paramagnetic behavior. Also, the magnetic behavior displayed supports the lattice parameter change observed from x-ray diffraction. It is interesting to explore whether the large magnetic effect observed in these nanotubes is the result of the surface magnetic impurity effect, coupled with the fact that we observed novel features in the Raman spectra of these nanotubes. Nanotubes with fairly small wall thickness may enhance the surface magnetic interaction leading to enhanced ferromagnetic behavior. This is especially significant because in Mn or Fe-doped Bi_2Te_3 single crystals, ferromagnetic behavior was observed only below 20 K.

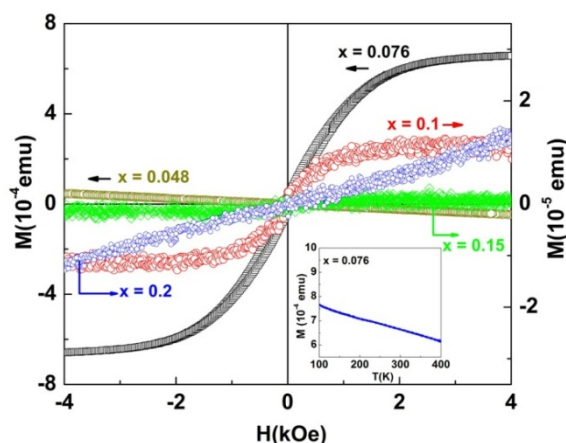


Figure 4. The hysteresis loops of chromium doped nanowires for various x values. The inset shows the magnetization as a function of temperature for $x = 0.076$ sample. A magnetic field of 5000 Oe is applied for the measurement

In summary, we have synthesized ferromagnetic Cr-doped Bi_2Te_3 nanotubes via wet chemical synthesis. Large magnetization saturation is observed for $x = 0.076$. Also, these nanotubes exhibit infrared active modes in the Raman spectra due to its one-dimensional nature.

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