Crystal Growth and Basic Transport and Magnetic Properties of MnBi$_2$Te$_4$

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Abstract
We report successful growth of magnetic topological insulator (MTI) MnBi$_2$Te$_4$. The heating schedule basically deals with growth of the crystal from melt at 900°C and very slow cooling (1°C/hr) to around 600°C with 24 hours hold time, followed by cooling to room temperature. Our detailed, PXRD Reitveld analysis showed that the resultant crystal is dominated mainly by MnBi$_2$Te$_4$ and minor phases of Bi$_2$Te$_3$ and MnTe. The transport measurements showed a step like behavior at around 150 K followed by cusp like structure in resistivity at around 25 K (T$_f$) due reported anti-ferromagnetic ordering of Mn. Both the resistivity transitions are seen clearly in $\frac{d\rho}{dT}$ measurements at 150 K and 20 K, respectively. The 25 K transition of the compound is also seen in magnetic susceptibility. Low temperature (5 K) magneto-resistance (MR) in applied field of up to 6 Tesla exhibited –ve MR below 3 Tesla and + ve for higher fields. Also, seen are steps in MR below 1 Tesla. The studied MnBi$_2$Te$_4$ MTI crystal could be a possible candidate for quantum anomalous Hall (QAH) effect.

Keywords Magnetic topological insulator · Crystal growth · Structural details · Surface morphology magnetism · Electrical transport

1 Introduction

Topological insulators (TIs) are dominating the quantum condensed matter for over a decade by now [1–3]. In this direction, one of the most happening new advancements had been the magnetic topological insulators (MTIs). In case of MTIs, a magnetic layer or element is inserted among the running TI unit cells of bulk 3D topological insulators such as 3d metal doped Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ [4–6]. The insertion of magnetic layer along running 3D bulk topological insulators shifts the Dirac position and thus alters the quantum transport properties of the parent system [7–10]. One of the most fascinating properties of the MTIs is the appearance of quantum anomalous Hall (QAH) effect [7–9].

QAH happens due to the finite Hall voltage created due to magnetic polarization and spin-orbit coupling, while the external magnetic field is absent. QAH is found to be in integer multiple of $e^2/h$ which is called Landau level [9]. In principle, the inherent magnetism and topological electronic states are the necessary conditions for QAH. Though, ultra-thin films of TIs with enhanced surface area may exhibit QAH due to strong spin-orbit coupling (SOC), but is a rare possibility, and if at all, the same takes place at ultra-low temperatures [10]. Other possibility to realize QAH is to dope the 3D bulk topological material with transition metal elements, viz., Co, Cr, Eu, etc. [11, 12]. In this case as well because of randomly distributed 3d metal impurity to the realization of QAH is often difficult and if at all is at mK temperatures [10–13]. The best solution till date to observe QAH at higher temperatures is via the MTIs. A magnetic topological insulator having strong SOC exhibits quantized resistance and non-dissipative current at room temperature [14]. In case of MTIs, a 3d metal based magnetically ordered layer is inserted between the running 3D bulk topological insulator. An ideal example, being put forward by theoreticians [15–17] and very recently realized by experimentalists, is MnBi$_2$Te$_4$ [18–20].
MnBi$_2$Te$_4$ can be formulated as Bi$_2$Te$_3$ and MnTe; here, the former is the 3D bulk topological insulator and later the magnetically ordered layer being inserted in the periodic structure at van der Waals gaps [21]. MnBi$_2$Te$_4$ is the first 3D antiferromagnetic topological insulator [18–20, 22]. Interestingly, there are only scant reports on MnBi$_2$Te$_4$, in particular the single crystals [22].

Keeping in view, the importance of QAH, the MTIs’ and the first 3D antiferromagnetic topological insulator, i.e., MnBi$_2$Te$_4$, we report here the crystal growth and characterization of the same. Detailed, PXRD Rietveld analysis showed that the resultant crystal is dominated by MnBi$_6$Te$_7$, MnBi$_6$Te$_{10}$ phases along with some MnTe, and Bi$_2$Te$_3$ content. Resistivity measurements exhibited two transitions at 150 K and 25 K. The studied MnBi$_2$Te$_4$ MTI crystal could be a possible good candidate for quantum anomalous Hall effect (QAHE).

The constituent elements Mn, Bi, and Te of better than 3 N purity are weighed (1 g) in stoichiometric ratio and grind in a glove box filled with argon. Proper care is taken to avoid the exposure of the material from air. After grinding, the powder is converted into pallet, which is further sealed into a vacuum tube under the pressure of 10$^{-15}$ mbar. No sealed tube is held in the electronically controlled furnace at high temperature. The temperature goes up to 900°C with heating rate of 120°C/h and the temperature of furnace remains hold at 900°C for 12 h. Now the temperature starts to decrease at the rate of 1°C/h and goes down to 600°C. This temperature remains hold for 12 h followed by normal cooling to room temperature. The schematic of details of the heat treatment is given in inset (a) of Fig. 1.

The powder X-ray diffraction pattern (PXRD) of the gently crushed part of crystal is taken on Rigaku X-ray diffractometer in the range 10° to 80° of 2θ at scan rate of 2°/min. Scanning Electron Microscope (SEM) make Bruker is used to visualize the morphology of the studied crystal. Raman spectrum of the crystal piece is taken on LabRam HR800-JY equipped with a laser source of 514 nm. The spectrum is taken in wave number range of 50 cm$^{-1}$ to 400 cm$^{-1}$. Resistivity versus temperature measurements are done on a physical property measurement system (PPMS) in temperature range of 300 K down to 10 K on a close cycle refrigerator.

Figure 1 shows the powder XRD (X-ray diffraction) pattern of the part of crushed MnBi$_2$Te$_4$ crystal. The full proof Rietveld analysis is carried out on the observed pattern. The PXRD pattern is similar to that as observed recently for MnBi$_2$Te$_4$ self-flux grown crystals [23]. The sample is found to be crystallized within space group R-3 m and lattice parameters a = 4.3825(4)Å and c = 42.6849(1)Å. There are some unreacted lines not fitting with the main pattern and these belong to Bi$_2$Te$_3$ shown in inset (a) of Fig. 1. The Wyckoff and coordinate positions obtained from Rietveld analysis are given in Table 1. The situation is very similar to that as reported in ref. [23]. The goodness of fitting parameters is χ$^2$ = 3.05, which is reasonably good. The VISTA based software drawn unit cells for major MnBi$_2$Te$_4$ is given in inset (b) of Fig.1. The c-parameter for is around 40 Å. The general formula for these homologous series of compounds can be simplified as follows: MnTe + nBi$_2$Te$_3$, with n = 1, 2, 3, as MnBi$_2$Te$_4$, MnBi$_4$Te$_7$, and MnBi$_6$Te$_{10}$. So, principally, it depends upon the fact that after how many unit cells of Bi$_2$Te$_3$, MnTe magnetic layer is inserted [23]. In present case, the PXRD of our crushed crystal showed mainly the MnBi$_2$Te$_4$ phase along with minor content of Bi$_2$Te$_3$ and MnTe. To elaborate further, the expanded part of the fitted and observed PXRD is shown in inset (a) of Fig. 1. In earlier attempt, we tried to fit the PXRD data in MnTe + nBi$_2$Te$_3$, with n = 1, 2, 3, as MnBi$_2$Te$_4$, MnBi$_4$Te$_7$, and MnBi$_6$Te$_{10}$ phases as well, and the main phase was found to be distorted MnBi$_2$Te$_4$, i.e., MnBi$_6$Te$_{10}$ (56%) with space group R-3 m, followed by MnBi$_2$Te$_4$ along with MnBi$_4$Te$_7$ [24].

Figure 2 depicts the scanning electron microscope (SEM) picture of the surface of the as grown crystal. The slab-like layered growth can be visualized and the unidirectional-

| Wyckoff | x  | y  | z     |
|---------|----|----|-------|
| Bi1     | 6c | 0  | 0.4304(1) |
| Te1     | 6c | 0  | 0.1429(5) |
| Te2     | 6c | 0  | 0.2873(6) |
| Mn1     | 3a | 0  | 0     |

Table 1 Crystal structure data and details of data refinement for the investigated phases of as grown MnBi$_2$Te$_4$ crystal
layered structure is clearly visible. We also did the EDAX to
know the composition of the crystal at various points on the
micrograph. The resultant composition was although near
stoichiometric for Bi and Te but less in Mn content. The
Raman spectrum of the as grown MnBi₂Te₄ taken at Laser
wavelength of 514 nm is given in Fig. 3. A broad peak with
two to four main shoulders is seen in the range of 50 to 200
\( \text{cm}^{-1} \). We deconvoluted the main peak being at 120 \( \text{cm}^{-1} \)
consisting of 102 \( \text{cm}^{-1} \) and 140 \( \text{cm}^{-1} \) shoulders. The main
peak at 120 nm is having maximum intensity, and two others
at lower and higher wave numbers show much lesser intensity.

The general overall look of the Raman spectrum shown in Fig.
3 is similar to that as reported in ref. [23] for MnBi₂Te₄.

The resistivity (\( \rho \)) versus temperature (T) plot for studied
MnBi₂Te₄ crystal is given in Fig. 4 in temperature range of
300 K down to 10 K, which is metallic in nature with a step-
like change in slope at around 150 K (\( T_P \)), followed by a small
kink (inset Fig. 4) at around 25 K (\( T_N \)). The 25 K transition is

![Fig. 3 Raman of MnBi₂Te₄ single crystals](image)

![Fig. 4 Resistivity versus temperature plot of MnBi₂Te₄ crystal, inset shows the zoom part of same, marking the possible 25 K magnetic ordering of Mn](image)
very feeble and hence for more clarity is shown as the derivative of resistivity (dρ/dT) plot against temperature (T) in Fig. 5. The inset of Fig. 5, clearly marks the 25 K (T\text{N}) transition of MnBi\textsubscript{2}Te\textsubscript{4} is reported earlier [15–18, 22] and is due to the antiferromagnetic ordering of Mn spins [18, 22] in MnTe layers of running Bi\textsubscript{2}Te\textsubscript{3} 3D topological insulator. To elaborate more on the transport behavior, here not only the 150 K transition of metallic resistivity is seen but the Mn magnetic ordering related 25 K transition is also seen clearly. Though magnetic transition in the range of 20 to 30 K is known to be due to Mn ordering [15–18, 22–26], the origin of 150 K transition is not clear as of now.

The magnetic moment (M) versus temperature plot in temperature range of 50 to 10 K in both field cooled (FC) and zero field cooled (ZFC) situations at 0.1 Tesla for studied MnBi\textsubscript{2}Te\textsubscript{4} is depicted in Fig. 6. An anomaly is seen in M(T) plot at below 30 K, and the same seen visibly in 1/M versus T plot in inset of Fig. 6. The anomaly in magnetic susceptibility occurs nearly at the same temperature as being seen in transport measurements in Figs. 4 and 5.

Figure 7 shows the magneto-resistance measurements done to 5 K in applied magnetic field of up to 6 Tesla. The magneto-resistance decreases with increase in field of up to say 1 Tesla (H\textsubscript{1}) and for higher fields starts increasing and becomes positive above 3 Tesla (H\textsubscript{2}). Clearly, the magnetic ordering of Mn in MnTe layer of MnBi\textsubscript{2}Te\textsubscript{4} has an effect on the magneto transport of the same. The expanded region (below H\textsubscript{1}) of resistivity against magnetic field for the studied crystal is shown in inset of Fig. 7. It is clear that initially, the resistivity versus field plot is linear but starts showing step above say 0.5 Tesla, which are reminiscent of quantum transport. Detailed experiments for observation of quantum anomalous Hall (QAH) effect are underway in the magnetic field regime of much less than H\textsubscript{1} in different protocols.

In summary, the short communications report the growth and basic physical properties of the magnetic topological insulator MnBi\textsubscript{2}Te\textsubscript{4}. Interestingly, the growth of topological insulators and so much so the newest one, i.e., magnetic topological insulator, viz., the presently studied MnBi\textsubscript{2}Te\textsubscript{4} is not straight forward. Long heat treatments with slow-cooling rates of up to 1 °C/h are required. Most of the literature on MnBi\textsubscript{2}Te\textsubscript{4} single crystal growth and its characterization is to or exceed most authors (cond-mat arXiv [15, 18, 19, 24–31]). Keeping in view that MnBi\textsubscript{2}Te\textsubscript{4} is an important new...
bulk 3D magnetic topological insulator hence its quality crystals are warranted, the present communication adds detailed growth parameters and basic electrical and magnetic characterization of the same to the scientific literature. We also synthesized the MnBi\textsubscript{2}Te\textsubscript{4} crystal from higher temperature melt (1000 °C) as well and found that though the crystallized phase is same as in present case, the magneto transport is slightly different albeit with similar features [32]. We conclude that present growth parameters are the optimum ones for obtaining the MnBi\textsubscript{2}Te\textsubscript{4} magnetic topological insulator.

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