Crystal Growth and Characterization of Possible New Magnetic Topological Insulators FeBi$_2$Te$_4$

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Received: 18 March 2020 / Accepted: 29 April 2020 / Published online: 23 May 2020
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Abstract
Here, we report successful single crystal growth of new possible magnetic topological insulator (MTI) FeBi$_2$Te$_4$ by a self-flux method via a vacuum encapsulation process. The detailed Rietveld analysis of powder XRD data shows the as-grown MTI crystal to be mainly dominated by the FeBi$_2$Te$_4$ phase along with minority phases of Bi$_2$Te$_3$ and FeTe. Scanning electron microscope (SEM) image shows the morphology of as-grown MTI single crystal to be of layered type laminar structure. Raman spectroscopy of the crystal exhibited three distinct phonon modes at 65, 110, and 132 cm$^{-1}$ along with two split secondary modes at 90, and 144 cm$^{-1}$. The secondary split modes are the result of FeTe intercalation in the Bi$_2$Te$_3$ unit cell. Magnetoresistance (MR%) measurement has been performed at different temperatures, i.e., 200 K, 20 K, and 2 K in applied magnetic fields up to $\pm$ 12 Tesla, which showed very low MR in comparison with pure Bi$_2$Te$_3$ crystal. Temperature dependence of DC magnetization measurements shows the FeBi$_2$Te$_4$ crystal to be mainly of ferromagnetic (FM) or ferrimagnetic nature above 295 K, albeit a secondary weak magnetic transition is seen at 54–46 K as well. Detailed isothermal magnetization (MH) results showed that the FM saturation moment at 295 K is 0.00213 emu/g, which is nearly invariant until 400 K. In summary, we had grown an MTI FeBi$_2$Te$_4$ single crystal, which may be a possible entrant for the quantum anomalous Hall (QAH) effect at room temperature or above.

Keywords Magnetic topological insulator · Crystal growth · Structural details · Surface morphology · Magneto transport · Magnetism

1 Introduction
Topological insulators (TI) are among the newest wonder materials with various novel physical properties, including highly conducting surface/edge electronic states along with the insulating bulk [1, 2]. These highly mobile conducting states are spin-orbit coupled (SOC) as well as protected by time-reversal symmetry (TRS) [3, 4]. The most popular bulk TIs are Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$. As far as their structure is concerned, this exhibits a layered structure composed of quintuples, containing five atomic layers arranged in Te/Se-Bi/Sb-Te/Se-Bi/Sb-Te/Se fashion. These are further bonded by ionic-covalent bonds. Each quintuple layer is a reverse image of its adjacent quintuple layer and separated by weak van der Waals forces [2, 3]. The presence of van der Waals gap between the quintuple layers makes the compound easily cleavable and susceptible to various intercalations [2, 3, 5]. Suitable intercalation of some doping materials into these van der Waals gap results in various quantum phenomena including superconductivity [6–10] and quantum anomalous Hall (QAH) effect [11, 12].

The reports for the QAH effect are only scant, and that also for a particular magnetic topological insulator (MTI), i.e., MnBi$_2$Te$_4$ [11–14]. For observation of the QAH effect, one needs to insert a magnetically ordered layer between van der
Waals gap of bulk TI, viz., MnBi$_2$Te$_4$. Here, an antiferromagnetically (AFM) ordered ($T_N = 20$ K) MnTe layer is inserted between van der Waals gaps of bulk TI Bi$_2$Te$_3$ [11–14].

The quest is for elevated temperature and low magnetic field MTI that means the inserted magnetic layer must be near room temperature magnetically ordered. Besides MnBi$_2$Te$_4$, one such example could be FeBi$_2$Te$_4$. Here, FeBi$_2$Te$_4$ represents FeTe + Bi$_2$Te$_3$. The former is AFM ordered ($T_N = 80$ K) FeTe [15, 16] and later is bulk TI Bi$_2$Te$_3$. We managed successfully to grow single crystal of FeBi$_2$Te$_4$, and to the best of our knowledge, no report on crystal growth or characterization of FeBi$_2$Te$_4$ exists in literature. On the other hand, we failed to grow other possible TMI, viz., CoBi$_2$Te$_4$ and NiBi$_2$Te$_4$, which did not even look crystal alike as usual silvery shining. In the case of FeBi$_2$Te$_4$, we got a silvery shining (Fig. 1a) crystal with reasonably good X-ray diffraction (XRD) similar to that of MnBi$_2$Te$_4$ [11–14]. Interestingly, the compound seems to become ferromagnetic (FM) or ferrimagnetic above 250 K. These are preliminary results and more need to be done in terms of detailed characterization of the obtained crystal by a transmission electron microscope to assure its crystalline nature along with detailed Hall measurements. In this letter, we report the possible crystallization of new MTI, FeBi$_2$Te$_4$ along with its basic transport and magnetic properties. We believe this study will encourage the condensed matter physicist and solid-state chemist communities to follow up and establish a near room temperature (250 K) FeBi$_2$Te$_4$ quantum anomalous Hall (QAH) effect.

2 Experimental

The constituent elements Fe, Bi, and Te (at least 3N purity) were weighed (1 g) in stoichiometric ratio and ground in a glove box filled with Argon. After grinding, the powder was converted into pallets, sealed in a tube under the pressure of $10^{-5}$ mb, and inserted in a controlled furnace at high temperature. First, the temperature was raised to 950 °C with a heating rate of 120 °C/h, which is held for 12 h. Then, the temperature was decreased slowly at the rate of 1 °C/h down to 600 °C. This temperature was kept for 12 h followed by normal cooling to room temperature. Schematic details of the heat treatment are given in Fig. 1a and the photograph of the as-grown crystal (MTI) is shown in Fig. 1b.

Powder X-ray diffraction pattern (PXRD) of the gently crushed part of crushed crystal was taken on Rigaku X-ray diffractometer in the range of 10° to 80° of 2θ at a scan rate of 2°/min. Bruker make scanning electron microscope (SEM) was 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 was taken in wave number range of 50 to 400 cm$^{-1}$.
QD MPMS magnetometer. The DC measurements under external field ($H$) of 1 kOe, at the temperature of 5–300 K, and in 250–485 K intervals were done on two separate pieces cut from the same crystal.

### 3 Results and Discussion

Figure 1 c shows the typical SEM picture of the as-grown FeBi$_2$Te$_4$ crystal. The layered structure is clearly visible, which is known and reported earlier for other bulk topological insulator single crystals [1–4, 17]. Figure 2 depicts the PXRD of the gently crushed FeBi$_2$Te$_4$ crystal. Three options including their Rietveld analysis are depicted. (a) The lower panel shows the PXRD of FeBi$_2$Te$_4$ crystal with solely FeBi$_2$Te$_4$ phase; (b) the middle panel, the co-existing phases of FeTe and FeBi$_2$Te$_4$; and (c) the upper panel, with FeTe and Bi$_2$Te$_3$ only (without FeBi$_2$Te$_4$). These three fitting panels are required, because the single-phase FeBi$_2$Te$_4$ option (lower panel) could not account for a low angle peak at around $\theta = 18^\circ$ and for some other small intensity peaks. The goodness of fitting parameters ($\chi^2 = 11\%$) with the sole FeBi$_2$Te$_4$ phase is poor. This interpretation is quite similar to that of MnBi$_2$Te$_4$ [11–14]. However, for option b when both FeBi$_2$Te$_4$ and FeTe are considered, the fitting parameter $\chi^2$ is reduced to around 7.15%. The lattice parameters thus calculated for the majority (75%) phase Bi$_2$Te$_3$ are $a = 4.3851(4)\AA^\circ$ and $c = 30.4952(4)\AA^\circ$ and for the minority FeTe (25%) $a = 3.826(1)\AA^\circ$ as in option b. Details of various phases are given in Table 1.

Figure 3 shows the Raman spectrum of as-grown FeBi$_2$Te$_4$ crystal. Three distinct peaks are seen at 65, 110, and 132 cm$^{-1}$ (assigned as 1, 3, and 4). Furthermore, two secondary split modes are seen at 90 and 144 cm$^{-1}$ (assigned as 2 and 5). The general appearance of the Raman spectrum in Fig. 3 is similar to that as reported earlier for MnBi$_2$Te$_4$ [11, 14]. The main phonon modes at 65, 110, and 132 cm$^{-1}$ are known to be due to three different Raman vibrational modes, namely $A_1g_1$, $A_1g_2$, and $Eg_2$ for Bi$_2$Te$_3$, and are comparable to the earlier reported result [17, 18]. In the case of MnBi$_2$Te$_4$, various split modes are seen in ref. 12 and are attributed to the van der Waals gap–inserted MnTe bonds with parent Bi$_2$Te$_3$ in MnBi$_2$Te$_4$ unit cell. Furthermore, it is suggested that not only the MnBi$_2$Te$_4$ but various other possible crystallographic arrangements depending upon super structures are possible, viz.., MnTe + nBi2Te3, with $n = 1, 2, 3$, as MnBi$_2$Te$_4$, MnBi$_3$Te$_7$, and MnBi$_6$Te$_{10}$ phases [12]. A more consolidated and detailed overview of the Raman data analysis for similar van der Waals gap–inserted Ti, i.e., PbB$_2$Te$_4$ (PbTe+Bi$_2$Te$_3$), is reported recently, highlighting the splitting of parent phonon modes due to intercalation [19]. Keeping in view the reported Raman spectroscopy results on MnBi$_2$Te$_4$ [12, 14], PbB$_2$Te$_4$ [19], and the observation of split secondary modes for FeBi$_2$Te$_4$ crystal, one may safely conclude that to a large extent FeTe is inserted in van der Waals gaps of parent Bi$_2$Te$_3$ layers in the studied FeBi$_2$Te$_4$ crystal.

Figure 4 shows the isothermal magnetoresistance (RH) of FeBi$_2$Te$_4$ up to $H = 12$ Tesla at 200, 20, and 2 K. At 200 K, the studied FeBi$_2$Te$_4$ crystal shows positive non saturating magnetoresistance (MR%) of up to 40% under 12 Tesla. Here, MR% is calculated as $MR\% = [(RH - R_0)/(R_0)] \times 100$. Albeit quite small but an interesting feature is seen in low fields of below say 0.5 Tesla, where MR is negative in both directions, which turns non saturating positive above this field. This feature is very similar to that as observed below the AFM ordering temperature (25 K) of Mn spins in MnBi$_2$Te$_4$ [11–14]. It is known that MnBi$_2$Te$_4$ exhibits a quantum anomalous Hall (QAH) effect below 25 K [11–13]. Here, at 200 K, a similar phenomenon, i.e., signature of quantum anomalous Hall (QAH) effect albeit small, is seen. Surprisingly at 20 and 2 K, the positive MR magnitude increases to around 5% and 2% only at 12 Tesla, and the low field negative MR feature is missing. It is expected that deep below the magnetic ordering of van der Waals gap–inserted magnetic FeTe, the MTI would demonstrate better QAH effect. This does not look to be the case. Maybe because QAH is more expressed close to the magnetic transition to a FM state as observed hereafter. Yet, a lot more needs to be done in...
terms of phase purity and long-range magnetic ordering of the new MTI, FeBi$_2$Te$_4$.

Figures 5 a and b show the ZFC and FC plots of FeBi$_2$Te$_4$ measured at 106 Oe and 1 kOe (0.1 Tesla) respectively. All plots show a moderate increase at low temperatures, indicating the presence of a tiny amount of a paramagnetic extra phase. In addition, three anomalies are observed: (i) A pronounced peak in the ZFC branches at 54 and 46 K respectively, (ii) a tiny rise at 118 K, and (iii) both ZFC and FC plots increase sharply around 250 K ($T_{\text{mag}}$) and tend to emerge at 295 K. On a second piece of the same crystal, an extended ZFC (at $H$ = 1 kOe) measurement up to 385 K was performed as depicted in Fig. 5b (inset).

(i) Due to the relatively large magnitude of ZFC peak at 54 K Fig. 5a, the FC branch crosses the ZFC at a certain temperature range ZFC > FC. This is a unique phenomenon seldom observed [20, 21]. On the other hand, at 1 kOe, the peak magnitude at 48 K is lower and the normal FC > ZFC behavior up to room temperature (RT) exists. Note also the bumps in both FC branched around these temperatures. The reproducibility of the peak in the second ZFC plot (at 1 kOe) excludes the peculiar observations of ZFC > FC observed, e.g., in amorphous carbon in the past, in which this phenomenon was observed in the first ZFC run only, irreproducible and washed up in the second ZFC run [20, 21]. The origin of the peaks around $T \sim 50$ K is debatable. The peaks may originate from adsorbed traces of solidified oxygen [22]. Actually, traces of solidified oxygen are visible, but they are negligible in single crystals in which the bulk properties are dominated [20]. It is important to note that the presence of oxygen always appears as sharp peaks at the same temperature in both ZFC and FC branches [20, 21]. Alternatively, these peaks may arise from the presence of the AFM FeTe ($T_N = 60$ K) extra phase as suggested above (option b). The lower temperatures obtained are probably caused by the possibility that the FeTe extra-phase is not stoichiometric or alternatively that this phase is doped by a tiny amount of Bi. Anyhow, this AFM transition is extremely sensitive to the external field and shifts by 8 degrees (54 to 46 K), when $H$ increases from $H = 106$ to 1 kOe.

| Table 1 | Rietveld refined structural parameters including lattice constants, space group, co-ordinates, and phase proportions for various phases of FeBi$_2$Te$_4$ |
|----------------|----------------|----------------|----------------|
| Bi$_2$Te$_3$ + FeTe | FeBi$_2$Te$_4$ + FeTe | FeBi$_2$Te$_4$ |
| Cell ($a = b$) | 4.3851(4) | 4.3922(1) | 4.3926(4) |
| c | 30.4952(4) | 3.826(1) | 3.826(1) |
| Angle ($\alpha = \beta$) | 90 | 90 | 90 |
| $\gamma$ | 120 | 90 | 120 |
| Space group | R - 3 m | P 4/n m m | R - 3 m |
| Percentage | 49.77 | 50 | 70 |

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**Fig. 3** Raman spectrum of as-grown FeBi$_2$Te$_4$ crystal

**Fig. 4** Isothermal magnetoresistance (RH) at 2, 20, and 200 K in the applied field of up to 12 Tesla of as-grown FeBi$_2$Te$_4$ crystal
The deviation at 118 K is certainly caused by the presence of a tiny amount of magnetite (Fe₃O₄), the so-called Verwey transition. The rise in the ZFC branch at 118 K and 106 Oe is 7.3 × 10⁻⁸ emu/gOe. For the sake of comparison, we measured pure bulk Fe₃O₄ under similar conditions, for which the rise at 118 K accounts to 7.8 × 10⁻² emu/gOe. That means that the amount of Fe₃O₄ in the sample is around 1 ppm.

Under all measured fields, a sharp increase of the magnetization exists around 250 K. Figure 5 b (inset) shows that the magnetization (measured on a second piece) is almost constant in 300–385 K intervals. Thus, we tend to believe that in the major part of FeBi₂Te₄, a magnetic phase transition from AFM (for T < 250 K) to ferromagnetic or ferrimagnetic occurs above 250 K, and that its magnetic transition temperature is well above 400 K. This observation is consistent with the bifurcation of ZFC(T) and FC(T) branches around RT and also supported by the isothermal magnetization M(H) exhibited in Figs. 6 and 7.

It is readily observed that the M(H) curves first increase up to 1–1.5 kOe, tend to saturate, and then linearly decrease up to 50 kOe. The experimental M(H) plot clearly reveals an admixture of magnetic and diamagnetic components and can be fitted as $M(H) = M_{\text{Sat}} + (-\chi H)$, where the saturation moment $M_{\text{Sat}}$ is the intrinsic magnetic phase contribution and $-\chi H$ is the linear diamagnetic contribution stem, e.g., from the sample holder. Figure 7 demonstrates this procedure for $T$ = 295 K. The $M_{\text{Sat}}$ values obtained are 0.0035, 0.0011, 0.00098, and 0.00213 emu/g for $T$ = 5100, 200, and 295 K respectively. Note that $M_{\text{Sat}}$ for 100 and 200 K are almost the same and are half than that for 295 K. Due to these relatively low $M_{\text{Sat}}$ values obtained, the diamagnetic signals are easily pronounced. That indicates that below 250 K the major phase of FeBi₂Te₄ is AFM ordered. All M(H) plots were also measured under negative external fields from which the various coercive fields ($H_C$) shown in Fig. 6 (inset) can be deduced.

![Figure 5](image1.png)

**Fig. 5** a Magnetic moment versus temperature (MT) at 106 Oe in both ZFC and FC modes from 300 K down to 5 K. Note the sharp peak at 54 K and that around the peak ZFC > FC. b Magnetic moment versus temperature (MT) at 1000 Oe in both ZFC and FC modes from 300 K down to 5 K. The inset shows the same moment at high temperatures up to 385 K in ZFC mode for the as-grown FeBi₂Te₄

![Figure 6](image2.png)

**Fig. 6** Isothermal magnetization (MH) plots at 5, 100, 200, and 295 K for up to 50 K Oe field for as-grown FeBi₂Te₄. The inset shows the temperature dependence of coercive field values

![Figure 7](image3.png)

**Fig. 7** Isothermal magnetization (MH) plot at 5 K along with –ve susceptibility of the parent Bi₂Te₃ and thus the resultant for as-grown FeBi₂Te₄
Similar to the $M_{\text{Sat}}$ behavior, $H_C = 390(10)\text{Oe}$ at 5 K decreases to 170(10)\text{Oe} at both 100 and 200 K and increases (by a factor of 7) to 1150(10)\text{Oe} at 295 K. That confirms our statement that around 250 K (Fig. 5) a magnetic phase transition from AFM to FM (or ferrimagnetic) occurs.

In conclusion, we have grown an MTI FeBi$_2$Te$_4$ single crystal, having a ferromagnetic ordering well above 400 K, which may be a possible new entrant for quantum anomalous Hall effect at elevated temperatures.

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