Certificate Declaration by the Candidate	ii iii		
		Copyright Transfer Certificate	iv
Acknowledgements	v		
Contents List of Figures List of Tables	ix xii xviii		
		Preface	xix
		Chapter 1: Introduction: A bibliographic review	23-51
1.1 Introduction	23		
1.2 Topology	25		
1.3. Berry Phase and Chern number	27		
1.4 Time Reversal Symmetry (TRS)	27		
1.5 Background of Topological Insulator	28		
1.5.1 Hall Effect	28		
1.5.2 Effect of the magnetic field in 3D system	30		
1.5.3 Effect of the magnetic field in 2D system	32		
1.5.4 Quantum Hall Effects (QHE)	32		
1.5.5 Quantum Spin Hall Effect (QSHE)	34		
1.5.6 Spin-orbit coupling	37		
1.5.7 Quantum Anomalous Hall Effect (QAHE)	38		
1.5.8 Shubnikov-de Haas (SdH) Oscillations	40		
1.5.9 Weak Localization (WL) and Weak Antilocalization (WAL)			
Effects	41		
1.6 Historical Developments of 2D and 3D Topological Insulators	42		
1.6.1 The first 2D topological insulator HgTe	42		
1.6.2 3D Topological Insulators	44		
1.6.3 The First 3D Topological Insulator Bi <sub>1-x</sub> Sb <sub>x</sub>	44		
1.6.4 New materials Bi <sub>2</sub> Se <sub>3</sub> , Bi <sub>2</sub> Te <sub>3</sub> and Sb <sub>2</sub> Te <sub>3</sub>	46		
1.6.5 Crystal structure and Symmetry Properties	47		
Chapter 2: Sample Synthesis and Characterization Tools	53-66		
2.1 Introduction	54		
2.2 Sample synthesis of TIs	54		
2.3 Experimental characterization tools	55		
2.3.1 X-Ray diffraction (XRD)	55		
2.3.2 Laue diffraction pattern	57		

2.3.3 Transport properties measurements	58
2.3.3.1 Electric resistivity ( $\rho_{xx}$ )	58
2.3.3.2 Hall resistivity ( $\rho_{xy}$ )	59
2.3.3.3 Thermoelectric measurement	60
2.3.4 Magnetic property measurement System (MPMS)	61
2.3.5 Photoemission Spectroscopy	63
2.3.5.1 Angle-resolved photoemission spectroscopy (ARPI	ES) 65
Chapter 3: Evidence of surface and bulk magnetic ordering in Fe and Mn doned Big(SaS): topological insulator	67 83
will doped Di2(SeS)3 topological insulator	07-03
3.1 Introduction	69
3.2 Experimental details	70
3.3 Results and discussions	72
3.3.1 Experimental Study	72
3.3.2 Theoretical Study	81
3.4 Conclusion	82
Chapter 4: Anomalous Hall effect in Cu doped Bi <sub>2</sub> Te <sub>3</sub> Topological	
Insulator	84-107
4.1 Introduction	86
4.2 Experimental details	87
4.3 Results and Discussion	88
4.4 Conclusion	107
Chapter 5: Correlation between change-over from Weak Anti	
Localization (WAL) to Weak Localization (WL) and	
coexistence of positive and negative magneto-resistance in	100 105
S-doped Bi1.5Sb0.5Te1.3Se1.7	108-125
5.2 Experimental	110
5.2 Experimental 5.3 Results and Discussion	111
5.4 Conclusion	112
5.4 Conclusion	124
Chapter 6: The study of Raman and transport properties in Fe doped	
Bi <sub>2</sub> (SeS) <sub>3</sub>	126-144
6.1 Introduction	128
6.2 Experimental details	129
6.3 Results and Discussion	129
6.3.1 Raman study	140
6.4 Conclusion	143

Chapter 7: Summary and future perspectives	145-149
<ul><li>8.1 Summary</li><li>8.2 Future perspectives</li></ul>	147 148
References	150-164
List of Publications	165
Schools / Meetings / Workshops / Conference Attended	166

Figure 1.1: Band diagram for metal, semiconductor and insulator Z	23
<b>Figure 1.2:</b> Schematic representation of topology showing smooth deformation from cup to doughnut.	25
Figure 1.3: The sphere and the doughnut are topologically non-equivalent and have different genus numbers. 2	26
Figure 1.4: schematic diagram of motion of two electrons having opposite spins wipreservation of TRS in TSS.2	th 28
Figure 1.5: Schematic diagram of Hall effect.3	60
Figure 1.6: Energy band diagram for electrons vs. wave vector for different Landa levels in 3D system.   3	au 1
<b>Figure 1.7:</b> Quantization of energy levels into discrete Landau levels under the applied magnetic field (left) and the variation in longitudinal ( $\rho_{xx}$ ) and transverse resistivity ( $\rho_{xx}$ ) with applied magnetic field showing QHE.	ed <sub>xy</sub> ) 33
Figure 1.8: Skipping orbits at the edge state and cyclotron orbits in bulk in 2D electro   gas in the presence of the magnetic field. 3	on 34

**Figure 1.9:** Two copies of the quantum Hall effect (QHE) with the opposite magnetic field (left) and (right) the amalgamation of these two QHE states makes a quantum spin Hall effect (QSHE) without applied magnetic field 35

**Figure 1.10:** (Left) QHE with both right moving and left moving edge states. These states are robust against backscattering. (Right) QSHE with upper state right moving spin up and left moving spin down. Backscattering is suppressed from nonmagnetic impurities. 35

**Figure 1.11:** schematic diagram of two opposite scattering paths around an impurity for the QSH state. The total path difference between them is  $2\pi$ , leading to suppression of the backscattering for Fermions. 36

**Figure 1.12:** schematic diagram of insulating state with a bandgap between the conduction and valence band (b) bulk is insulating but skipping orbits at the edges allows the conduction of electron giving rise to the conduction edge i.e. no band gap (c) in QSHE, both type of left and right moving path having opposite spins are allowed which is protected by time-reversal symmetry. 37

**Figure 1.13:** The variation of Hall resistivity  $\rho_{xy}$  with the applied magnetic field B. (a) ordinary Hall effect (b) anomalous Hall effect (AHE) (c) measured hysteresis loop from quantum anomalous Hall effect (QAHE). 39

**Figure 1.14:** (a) The two time-reversed scattering loops without spin-momentum locking exhibiting weak localization in magnetoconductivity ( $\Delta G$  (B)). (b) The two time-

reversed scattering loops with spin-momentum locking exhibited weak antilocalization in  $\Delta G$  (B). 42

**Figure 1.15:** (a) bulk energy bands for HgTe and CdTe at  $_{\Gamma}$  point (b) CdTe/HgTe/CdTe quantum well in normal regime d < dc and in inverted regime d > dc.

43

**Figure 1.16:** The surface band dispersion second-derivative image of  $Bi_{0.9}Sb_{0.1}$ . There are five crossing between  $\Gamma$  and M which confirms topological non-trivial surface state. 46

**Figure 1.17:** Calculated band structure of Sb<sub>2</sub>Se<sub>3</sub>, Sb<sub>2</sub>Te<sub>3</sub>, Bi<sub>2</sub>Se<sub>3</sub> and Bi<sub>2</sub>Te<sub>3</sub> by *ab initio* density functional theory. Red represents occupied bulk and surface states, and blue signifies bulk band gap. 47

**Figure 1.18:** (a) Crystal structure of Bi<sub>2</sub>Se<sub>3</sub>, the red box shows single quintuple layer (b) shows that three different A, B, and C sites are assigned to a triangular lattice in one quintuple layer (c) Se and Bi atoms are arranged in a sequence in quintuple layer. 49

**Figure 1.19:** Schematic picture of the band inversion of Bi and Se p orbitals in  $Bi_2Se_3$  at the r point. Stage I represents the effect of chemical bonding, Stage II represents the crystal field splitting, Stage III represents the effect of SOC. 50

**Figure 2.1:** (a) Flow chart of synthesis process (b) Photograph of cleaved crystal sample. 55

Figure 2.2: (a) Photographic demonstration of Bragg's law (b) Actual photograph ofRigaku Mini Flex II DESKTOP X-ray diffractometer set up.56

**Figure 2.3:** Schematic diagram of (a) Transmission Laue diffraction geometry (b) Back-reflection Laue diffraction geometry. 57

Figure 2.4: Schematic of four-probe measurement geometry.58

Figure 2.5: Schematic diagram for Hall Effect measurement.60

**Figure 2.6:** Schematic diagram of sample holder for thermoelectric measurement. Temperature difference at the both ends of the sample creates a temperature gradient.61

Figure 2.7: (a) Schematic diagram of SQUID-VSM detection system (b) Photograph of<br/>actual QD-MPMS measurement system.63

Figure 2.8: Illustrational of photoemission process.64

**Figure 2.9:** (a) Schematic of ARPES measurement setup (b) Shows ARPES spectra of pure Bi<sub>2</sub>Se<sub>3</sub> TI. 66

Figure 3.1: XRD pattern for all the prepared single crystal samples cleaved along (00l)plane.71

**Figure 3.2:** The variation of Hall resistivity as a function of applied magnetic field a) x=0.06, (b) x=0.18 for Bi<sub>2-x</sub>Fe<sub>x</sub>Se<sub>2.79</sub>S<sub>0.21</sub>, (c) 0.18 for Bi<sub>2-x</sub>Mn<sub>x</sub>Se<sub>2.79</sub>S<sub>0.21</sub> at different temperatures. 73

Figure 3.3: ARPES spectra for (a) x=0.06, (b) x=0.12, (c) x=0.18, and (d) 0.24 of  $Bi_{2-x}Fe_xSe_{2.79}S_{0.21}$ .

Figure 3.4: ARPES spectra for (a), (b) for x=0.12, (c), (d) for x=0.18 of  $Bi_{2-x}Mn_xSe_{2.79}S_{0.21}$ .

**Figure 3.5:** Magnetization (M) as a function of applied magnetic field (H) of  $Bi_{2-x}Fe_xSe_{2.79}S_{0.21}$  with (a) x=0.06, (b) x=0.12, (c) x=0.18, (d) 0.24 and of  $Bi_{2-x}Mn_xSe_{2.79}S_{0.21}$  for (e) x=0.12, (f) x=0.18 at different temperatures. 78

**Figure 3.6:** (a) magnetization vs. temperature (M-T (ZFC)) curve of  $Bi_{2-x}Fe_xSe_{2.79}S_{0.21}$ . The Variation of Magnetic Susceptibility as a function of temperature (b)  $Bi_{1.88}Mn_{0.12}Se_{2.79}S_{0.21}$  (c)  $Bi_{1.82}Mn_{0.18}Se_{2.79}S_{0.21}$  (d) MFM image of  $Bi_{2-x}Fe_xSe_{2.79}S_{0.21}$ , for x=0.06 and (e) for x=0.18 (f) Arrott plot of  $Bi_{2-x}Fe_xSe_{2.79}S_{0.21}$ , for x=0.06 and (g) x=0.18.

79

Figure 3.7: Density of States (DOS) from DFT Calculation for (a)  $Bi_{1.82}Fe_{0.18}Se_{2.79}S_{0.21}$ and (b)  $Bi_{1.82}Mn0_{.18}Se_{2.79}S_{0.21}$ .

Figure 4.1: X-ray diffraction pattern of  $Bi_2Cu_xTe_{3-x}$  topological insulators and Laue diffraction Pattern. 88

**Figure 4.2:** ARPES spectra for x = 0.03 (a) and 0.15 (b) of Bi<sub>2</sub>Cu<sub>x</sub>Te<sub>3-x.</sub> (c) and (d) Show the electron distribution curve. 90

**Figure 4.3:** Constant energy contours of  $Bi_2Cu_xTe_{3-x}$  at the Fermi energy for (a) x = 0.03 and (b) 0.15 from ARPES measurement. (c) and (d) Show the stacked plots of the constant energy contours at different binding energies. 92

**Figure 4.4:** Temperature variation of resistivity of  $Bi_2Cu_xTe_{3-x}$  for (a) x = 0.03 and (b) 0.09. 94

**Figure 4.5:** Magnetic field variation of magnetoresistance of  $Bi_2Cu_xTe_{3-x}$  for (a) x = 0.03 and (b) 0.09 at different temperatures. 96

**Figure 4.6:** (a) SdH oscillations (b) Landau level fan diagram (c) first Fourier transform curve (d) L–K fitting curve and average calculated cyclotron mass  $(m_{cyc})$  [in inset of (d)] of Bi<sub>2</sub>Cu<sub>x</sub>Te<sub>3-x</sub> for x =0.03. 97

**Figure 4.7:** (a) SdH oscillations (b) Landau level fan diagram (c) first Fourier transform curve (d) L–K fitting curve and cyclotron mass calculation [in inset of (d)] of  $Bi_2Cu_xTe_{3-x}$  for x = 0.09.

**Figure 4.8:** The variation of Hall resistivity as a function of applied magnetic fields of  $Bi_2Cu_xTe_{3-x}$  for (a) x = 0, (b) x = 0.03 (c) x = 0.09 and (d) x = 0.15 at different temperatures. 102

**Figure 4.9:** Calculated anomalous Hall effect (AHE) of Bi2CuxTe3 x for (a) x = 0.03 and (b) 0.09 at different temperatures. (c) and (d) Estimated AHE at diff. temperatures of Bi<sub>2</sub>Cu<sub>x</sub>Te<sub>3-x</sub> for x = 0.03, 0.09, 0.15 at 10 K and 100 K. 103

**Figure 4.10:** (a) Magnetization vs. temperature (M - T) and (b) magnetization (M) vs applied magnetic field (M - H) of Bi<sub>2</sub>Cu<sub>x</sub>Te<sub>3-x</sub> (with x = 0.03, 0.09 and 0.15). 105

**Figure 4.11:** (a) and (c) The variation between  $\sigma_{xx}$  and  $\sigma_{AHE}$  and (b), (d) temperature variation of tangent of anomalous Hall angle [tan( $\theta_{AHE}$ )] for Bi<sub>2</sub>Cu<sub>x</sub>Te<sub>3-x</sub> respectively for x = 0.03 and 0.09. 106

**Figure 5.1:** (a) X-ray diffraction pattern of  $Bi_{1.5}Sb_{0.5}Te_{1.3}Se_{1.7-y}S_y$  Topological insulators (b) Laue pattern of BSTSS-5 and (c) BSTSS-10. 113

**Figure 5.2:** (a) and (b) Resistivity variation with temperature of BSTSS-5 and BSTSS-10.

**Figure 5.3:** (a) and (c) Arrhenius Fitting of BSTS-5 and BSTS-10 (b) and (d) VRH fitting BSTS-5 and BSTS-10. 115

**Figure 5.4:** The variation of Hall resistivity as a function of applied magnetic fields of  $Bi_{1.5}Sb_{0.5}Te_{1.3}Se_{1.7-y}S_y$  (a) BSTSS-5, (b) BSTSS-10 at different temperatures (mobility vs. Temperature curve in inset). 116

**Figure 5.5:** Magnetic Fig. field Variation of Magnetoresistance of  $Bi_{1.5}Sb_{0.5}Te_{1.3}Se_{1.7-y}S_y$  (a) BSTSS-5 and (b) BSTSS-10 at different temperatures; WAL fitting (c) and (d) for BSTSS-5 and (e) and (f) BSTSS-10 at different temperatures; Fitting for n-MR correction (g) BSTSS-5 and (h) BSTSS-10.

**Figure 5.6:** (a) and (b) ARPES spectra for BSTSS-5 and BSTSS-10 (c) and (d) Lorentzian Fit for BSTSS-5 and BSTSS-10 respectively. 124

**Figure 6.1:** Temperature Variation of resistivity of  $Bi_{2-x}Fe_xSe_{3-y}S_y$  for (a) x=0.06, (b) x=0.12, (c) x=0.18, and (d) 0.24.

**Figure 6.2:** Magnetic field Variation of Magnetoresistance of  $Bi_{2-x}Fe_xSe_{3-y}S_y$  for (a) x=0.06, (b) x=0.12, (c) x=0.18, and (d) 0.24 at different temperatures. 132

**Figure 6.3:** Magnetic field Variation of Magnetoresistance of  $Bi_{2-x}Mn_xSe_{3-y}S_y$  for (a) x=0.12, (b) x=0.18 at different temperatures. 133

**Figure 6.4:** Landau Level Fan diagram of  $Bi_{2-x}Fe_xSe_{3-y}S_y$  (a) x=0.06, (b) x=0.12, (c) x=0.18, and (d) 0.24.

**Figure 6.5:** Kohler scaling of  $Bi_{2-x}Fe_xSe_{3-y}S_y$ . (a) x=0.06, (b) x=0.12, (c) x=0.18, and (d) 0.24.

**Figure 6.6:** (a) Measured value of Seebeck coefficient for all the samples and calculated value of power factor with respect to temperature (b) x=0.06, (c) x=0.12, (d) x=0.18, and (e) 0.24.

**Figure 6.7:** Temperature dependent Raman Spectra for (a) x=0.06, (b) x=0.18. 141

**Figure 6.8**: Variation of Peak positions and FWHM with the Raman shift (a) x=0.06, (b) x=0.18.

**Table-3.1:** The obtained different parameters from ARPES and Hall effect measurements.75

**Table 4.1:** Lattice parameters of  $Bi_2Cu_xTe_{3-x}$  (with x = 0, 0.03, 0.09 and 0.15) obtained from the Reitveld refinement. 88

**Table 4.2:** Obtained parameters of  $Bi_2Cu_xTe_{3-x}$  (with x = 0.03 and 0.09) from SdH oscillations, first Fourier transform calculation and Hall effect measurements. 99

**Table 4.3:** Different parameters of  $Bi_2Cu_xTe_{3-x}$  (with x = 0, 0.03, 0.09 and 0.15) at 2 K. 100

**Table 5.1:** btained parameters from Hall effect measurements, SdH calculation and Ioffe -Regel parameter.117

Table 6.1. All the obtained parameters from Hall and LL calculations. 135

**Table 6.2.** The value of First order temperature coefficient of each Raman mode for $Bi_{1.94}Fe_{0.06}Se_{2.79}S_{0.21}$  and  $Bi_{1.82}Fe_{0.18}Se_{2.79}S_{0.21}$ 144