Chapter 6

Summary, Conclusion and Future Scope

6.1 Summary and Conclusion

For the thesis work, dilute magnetic semiconducting alloys based on tin telluride, tellurium and tin selenide are chosen. The bulk powder samples of $Fe_{0.05}(SnTe)_{1-x}Sb_x$, $Fe_{0.05}(Te)_{1-x}Sb_x$; (x = 0, 0.01, 0.03 and 0.05) and $Fe_{0.05}(SnSe)_{1-x}Sb_x$; (x = 0, 0.03 and 0.05) are prepared by taking appropriate quantities of materials having high purity in quartz tube ampoules followed by sealing them in high vacuum. The ampoules containing the samples are repeatedly heated and ultimately quenched to obtain ingots that are finely crushes to obtain powder samples. An investigation of structural, optical, electrical and magnetic features of these samples are carried out. The present work was perceived thoughtfully to develop novel materials for potential use as a dilute magnetic semiconductor for which there is a requirement of room temperature ferromagnetism to be achieved. The results of the above studies are presented in the preceding three chapters. The present chapter summarizes the experimental results discussed in chapters 3, 4 and 5 and also suggests future work that can be carried out in continuation of the work in this thesis.

In chapter 3, the results of experimental work on dilute Fe doped $Te_{1-x}Sb_x$ (x = 0, 0.01, 0.03 and 0.05) bulk samples are presented. The room temperature X-ray diffraction pattern corresponds to a single phase of Te that has hexagonal structure (JCPDF No. 36 – 1452). The Te matrix has presence of Fe and Sb, which is validated by a minor shift in peak positions while maintaining the crystal structure. Doping induced lattice strain in the system is analyzed through Williamson-Hall and Size-Strain plots. From the FTIR spectra, band gap values that are determined show a decrease from that of pure Te. Slight variations in the band gap values are observed with Sb addition. Temperature dependent electrical resistivity measurements show a typical semiconducting nature as the temperature coefficient of resistivity of the curves are found to be negative. Additionally, reduced activation energy plot (W-T plot) is also used to decipher the semiconducting nature of the samples. Electrical transport property of the samples are assessed on the basis of SPH model in the high temperature region from 255 K – 300 K from the slope of which activation energy (E_a) values are deduced. On the other hand, in the temperature range of 150 K – 255 K and 2 K – 25 K of x = 0, 0.01 and 0.03 samples, VRH model is found to be the best fit that can explain transport mechanism at lower values of temperature. However, for x = 0.05 sample, VRH model is found to be suitable only in the range from 145 K – 195 K. There is a transition from negative trend to positive trend in the magnetoresistance plot of x = 0, 0.01 and 0.03 samples at 100 K which can be explained by quantum interference and wave shrinkage model. However, in the MR plot of x = 0.05 sample, only positive trend is observed suggesting an increased localization rise with increase in Sb concentration.

From the magnetization v/s temperature data obtained from the vibrating sample magnetometer (VSM), the ZFC and FC curve of x = 0 sample is seen to overlay on each other throughout the range of temperature suggesting paramagnetic features which is also the case in M-H curve. The curves of x = 0.01 and 0.03 samples, however, are paramagnetic only at higher values of temperatures and show ferromagnetic behaviour at lower temperatures. With increase in Sb concentration to x = 0.05, there are no paramagnetic features observed instead, the cusp around 115 K indicates presence of an antiferromagnetic property. Also, the inverse susceptibility plot of x = 0 sample is seen to perfectly follow Curie-Weiss law until it diverges at low temperature whereas in case of x = 0.01 and 0.03 samples, Curie-Weiss fitting is applicable only at high region of temperature. Ferromagnetic ordering in x = 0.03 sample is also reckoned from the inverse susceptibility curve. This weak ferromagnetic property results from substitution of Sb into the system that gives rise to hole impurities thereby creating an imbalance between the 'up' and 'down' spin states. The M-H plot of $x = 0.05$ sample represents antiferromagnetic property as the curve doesn't saturate and this is in accordance with the M-T plot.

Chapter 4 analyses the properties of a compound semiconductor SnSe that belongs to group IV-VI by preparing bulk samples having general form Fe doped $SnSe_{1-x}Sb_x$ ($x = 0$, 0.03 and 0.05). Diffraction pattern obtained from XRD measurement confirms the orthorhombic crystal structure of the samples consisting of purely SnSe phase with JCPDF No. 48-1224. The position of the peaks corresponding to pure SnSe is slightly shifted as a consequence of presence of Fe and Sb in the SnSe matrix. Crystallite size values calculated from Williamson-Hall analysis and Size-Strain plot are found to be consistent with each other suggesting more accuracy than the values obtained from Scherrer equation. The presence of lattice strain in the system due to doping has helped in this realization. Both direct and indirect band gap values of SnSe bulk samples are determined from the UV-Vis spectra. Doping with Fe decreases the value of band gap from the reported value for pure SnSe. However, only an infinitesimal change in the values are observed on substitution of Sb into the system. The Raman active peaks corresponding to SnSe initially undergo a blue shift when doped with Fe followed by a red shift with substitution of Sb. With an increase in the concentration of Sb to $x = 0.05$, two additional peaks that corresponds to Sb-Sb and Sb-Se bond are seen to emerge in the spectra. DC electrical resistivity plot of samples with the presence of non-magnetic donor impurity Sb i.e. $x = 0.03$ and 0.05 are found to be purely metallic in nature. The transport mechanism of these samples has been explained on the basis of a qualitative model that considers different interactions and scattering processes like electron-electron scattering, two-magnon scattering, electron-electron interaction, electron-phonon interaction and Kondo-like scattering.

The ZFC – FC magnetization curves of x = 0 sample is seen to be crafting out a similar pattern without any overlap and a maximum value is observed. Decrease in magnetization beyond the maximum value suggests superparamagnetic behaviour among the particles. A huge bifurcation is observed between the curves of x = 0.03 sample where the ZFC curve is seen to decrease with decreasing temperature and the sample has been found to consist of weak ferromagnetic moments. x = 0.05 sample shows a hump in both ZFC and FC curve which can have its origins from magnetic domain pinning effect. A pronounced fall in the ZFC curve is observed below this hump that could be related to spin-glass state in the system. From the M-H curve of x = 0 sample, large hysteresis loop is observed whereas in x = 0.03 sample, there is suppression of the loop. This could result from the inhibition of hole concentration in the system brought about by the substitution of non-magnetic element Sb. Further increase in the Sb concentration to 0.05 increases the coercivity value of the hysteresis loop that can be stemming from the magnetic domain pinning effect as also confirmed from the ZFC-FC curve. The plot of magnetic memory effect measurement demonstrates x = 0 sample to have a good memory retaining capability as compared to x = 0.05 sample.

Chapter 5 discusses the preparation and experimental results of dilute Fe doped $SnTe_{1-x}Sb_x$ (x = 0, 0.01, 0.03 and 0.05) bulk samples. The X-ray diffraction pattern shows rock salt cubic phase structure of the samples at room temperature. The peaks reflect the phase of SnTe corresponding to JCPDF No. 08-0487. There is a slight change in the peak position values from that of pure SnTe suggesting inclusion of Fe and Sb into the system. The value of band gap deduced from FTIR spectra is found to increase from that of pure SnTe when doped with Fe. This is followed by a drastic decrease on substitution of Sb. However, at Sb concentration of x = 0.05 in the sample once again results in an increase in the band gap value. Electrical resistivity plots show a metal to insulator transition for x = 0 sample. However, the resistivity plot of x = 0.01 sample shows a metallic behaviour as evident from the increasing value of resistivity with temperature beyond a temperature known as Kondo-temperature (T_K). In x = 0.03 and 0.05 samples, there is a gradual decrease in resistivity with temperature suggesting semiconducting nature. The transport mechanism of the samples are explained on the basis of 3D – variable range hopping (VRH) mechanism at low range of temperatures between 3 K – 85 K and 5 K – 40 K for x = 0.03 and 0.05 samples respectively. For x = 0 sample, the range in which VRH model holds is too small to be held valid. Conduction in the high temperature region from 260 K – 300 K can be explained on the basis of small polaron hopping (SPH) as well as nearest neighbour hopping (NNH) models. Qualitative model is used to explain the conduction mechanism in x = 0.01 sample. Magnetoresistance plot of all the samples show a positive trend with its maximum value decreasing with increasing temperature. This positive nature of the curve indicates an increase in resistivity as presence of magnetic field brings about localization of charge carriers. A contraction of the wave functions of these localized carriers takes place reducing their probability of hopping between their neighbouring sites.

In the magnetization v/s temperature measurement, there is a huge bifurcation between the ZFC and FC curve of x = 0 sample below 300 K suggesting thermal irreversibility. A drop in the magnetization value observed in the ZFC curve below 50 K could be the result of weak spin-glass state in the system. The M-T plot of x = 0.01 sample speculates a superparamagnetic behaviour beyond 200 K and an antiferromagnetic/spin glass state at lower values of temperature. In the ZFC curve of x = 0.03 sample, two cusps are observed around 132 K and 50 K that correspond to antiferromagnetic phases in the system. Presence of ferromagnetic clusters are also indicated from the decreasing value of magnetization in ZFC curve. A similar antiferromagnetic transition is observed in the ZFC curve of x = 0.05 sample at around 135 K. Below this temperature, a bifurcation between the two curves suggests a change in the spin ordering of the system. The magnetic moment v/s applied field plot shows presence of ferromagnetism as evident from the hysteresis loop in x = 0, 0.03 and 0.05 samples with the curve attaining saturation as observed in x = 0 and 0.05 samples. In addition, x = 0.03 sample shows magnetic glassy behaviour which is also confirmed from the AC susceptibility measurement by indicating presence of cluster-glass state in the system. On the other hand, x = 0.01 sample does not show any ferromagnetic feature, but rather an antiferromagnetic feature at 50 K and a superparamagnetic behaviour at 300 K which confirms the findings of M-T plot.

The results from the present work as discussed above demonstrate achievement of room temperature ferromagnetism through appropriate doping. Te that is diamagnetic in nature, is found to become paramagnetic when substituted with Fe. With introduction of Sb, presence of small hysteresis curve is observed that suggests an emergence of weak ferromagnetic ordering in the system. SnSe system is also able to achieve room temperature ferromagnetism when doped for x = 0 and x = 0.05 samples as observed from the broad hysteresis curve in the M-H plot. In case of SnTe, except x = 0.01 sample, the other samples are able to achieve the desired goal of ferromagnetism at room temperature. These results can give more insight to the realization of developing novel DMS materials.

6.2 Future scope of the present work

The following ideas are recommended for the future work that can be carried out as an extension of the present work on Fe doped $Te_{1-x}Sb_x$ (x = 0, 0.01, 0.03 and 0.05), Fe doped $(SnSe)_{1-x}Sb_x$ (x = 0, 0.03 and 0.05) and Fe doped

$(SnTe)_{1-x}Sb_x$ (x = 0, 0.01, 0.03 and 0.05) systems. These ideas could significantly contribute to the study and research on these systems as well as in this field.

1. To look into the effect of other 3-d transition elements and even rare earth elements on the above semiconducting systems. As rare earth elements have their f-orbitals partially filled, they can lead to unconventional properties that could make the materials an ideal DMS system.
2. Studies can also be performed by varying the concentration of magnetic dopants into the system to probe the apt amount of magnetic ion dopant that can elevate Curie temperature value above room temperature.
3. To prepare thin films of the above samples in order to understand their properties that would differ from that of bulk composition, with the aim of examining their application as a device.
4. Magnetic memory effect measurement of thin films with respect to time and temperature to check their memory retaining capability.