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INVESTIGATION OF MAGNETIC ION DOPING ON STRUCTURE AND MAGNETISM IN SOME DILUTE ALLOYS

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BY

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INVESTIGATION OF MAGNETIC ION DOPING ON STRUCTURE AND MAGNETISM IN SOME DILUTE ALLOYS

The advancement in the field of information technology has been possible mainly due to the progress made in the storage industry. Mass storage of information has been carried out with the help of magnetic recording. Till the recent past, everything about electronics and devices were about one of the important property of electron i.e. charge. Charge based devices did find success in the market, but the main drawback was that of sustainability. It was found that memory capability of charge based devices could not sustain for a long time i.e. all the information was lost as soon as the device as switched off. In order to overcome this drawback, researchers explored another important property of electron that is its spin. Spin is the root cause of magnetism and an intrinsic angular momentum that a particle cannot lose or gain. A spin can orient itself in one of the two directions i.e. spin-up or spin-down. Magnetic materials have the ability to remember their spin state for a very long time.

Efforts were made to combine spin and charge property of electron onto a single material that would simultaneously help in carrying out processing of information as well as storing them for a considerable time. In short, the material incorporates features of both semiconductor and magnetism. This gave rise to a new class of materials known as Dilute Magnetic Semiconductor (DMS). They consist of a semiconductor, where fraction of their original atoms are substituted by magnetic elements making them semi magnetic in nature. This leads to a merger of magnetic properties along with semiconducting properties. The host material is a semiconductor which is extremely influenced by doping, presence of defects and charge carriers and into it are added dilute quantity of magnetic ions. They are highly spin-polarised and contribute spin polarized charge carriers. An essential key to the formation of distinct magnetic moments is spin-spin exchange interaction. Different exchange interactions that could give rise to magnetism in DMS include interaction between s electrons present in the conduction band, p electrons in the valence band and d electrons obtained from the magnetic ions i.e. sp-d interaction as well as d-d interaction arising due to an exchange between d electrons from the magnetic ions [1, 2]. Over the past few decades, there are series of pioneering publications in the field of dilute magnetic semiconductors [3-7]. The main objective of developing and studying DMS materials is to achieve Curie temperature T_C greater than the room temperature as it is desirable in order to sustain ferromagnetism for a longer duration in practical device applications.

In the initial stages of research, rare-earth based compound semiconductors that served as magnetic semiconductors were looked into [8, 9]. The focus was then shifted and it later on involved transition metal doped II-VI semiconductor alloys like $Zn_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xTe$ which was found to have weak ferromagnetism and low Curie temperature [10, 11]. Later Mn doped III-V semiconductors like $In_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xAs$ were studied and the ferromagnetism were observed at higher Curie temperature [12-16]. Recent studies on DMS also involve oxide based semiconductors like ZnO, SnO_2 and others which when doped with magnetic elements significantly increased the Curie temperature [17-21]. Other systems include IV-VI group, elemental semiconductors, etc. The most commonly known elemental semiconductors are silicon and germanium that belong to group IV of the periodic table. In the past, germanium based alloy systems were explored in depth to identify its potential as a dilute magnetic semiconducting system [22-24]. Other examples of elemental semiconductors include tin (Sn) also a group IV element, selenium (Se) and tellurium (Te) belonging to group VI of the periodic table. The work concerning elemental semiconductors were mainly centered on analyzing their thermoelectric and optical properties [25-27]. Besides, tellurium has also been probed as a potential host semiconductor for DMS [28]. IV-VI group of semiconductors are categorized as having narrow band gap. Germanium telluride (GeTe), lead selenide (PbSe), tin selenide (SnSe), tin telluride (SnTe), lead sulphide (PbS), etc are some of the examples of this group. DMS based on IV-VI group semiconductors display carrier concentration induced ferromagnetic transition, light induced magnetization and high field magnetization [29-32].

Magnetic semiconducting materials can be used in a variety of electronic devices incorporating the spin property of charge carrier [33-35]. Semiconductor memory devices like Magneto-resistive random access memory (MRAM), computer hard disk, spin transistors, spin valves, etc. are some areas of its application where conventional ferromagnetic metals have failed to deliver desired spin polarized carriers.

It is evident from the literature survey that dilute magnetic semiconductors are traditionally made by substituting fraction of magnetic impurities (M) into the cations of semiconductor compounds having general form $A_{1-x}M_xB$. However, past studies by our group explored DMS where substitution was incorporated through a non-magnetic element antimony (Sb). Sb acts as donor, releasing charge carriers into the system. The presence of these charges were found to induce magnetic properties that could sustain even at room temperature [24, 36]. Work of similar nature were not found in the literature despite having evidences of sustainability and enhancement of magnetism brought about by inclusion of charge carriers into the DMS system. This is possible due to an augmentation in exchange interaction between the magnetic ions resulting from these additional impurities. With a view to realize room temperature ferromagnetism and higher T_C value, the present work derived its motivation from the past work of our group. The study includes effect of charge carrier in elemental semiconductor tellurium and further the study is extended to compound semiconductors namely SnSe and SnTe. They belongs to group IV-VI semiconductor chosen as the host semiconductors. Transition metal Fe doped bulk alloys of these semiconductors having the form $(Te)_{1-x}Sb_x$, $(SnSe)_{1-x}Sb_x$ and $(SnTe)_{1-x}Sb_x$ are made wherein antimony, a group VI element is substituted which acts as the source of supplementary charge carriers in the system. The aforesaid semiconducting materials are selected largely because majority of the work on them focuses on improving their thermoelectric properties [37-39]. Tellurium being an elemental semiconductor has been found to be a good prospect as a photoconductor and for use in resistive switching devices [40, 41]. On the other hand, SnSe and SnTe that belong to group IV-VI semiconductor have found tremendous applications in optical and photovoltaic applications due to their narrow band gap [42-45]. Experimental studies that concerns with developing these materials as magnetic semiconductors are very few in number and this work is an attempt to fill the existing gap. In this respect, the above stated bulk alloy samples are prepared by doping the host semiconductor with dilute amount of transition element iron (Fe) followed by characterizing them for their structural, optical, electrical and magnetic properties which will be presented in the thesis. Additionally, charge carriers are introduced into the samples through the substitution of non-magnetic element antimony which will help to understand the kind of magnetic ordering that takes place in these systems. Throughout the process of sample preparation, the concentration of Fe is kept fixed at 0.05 so as to avoid formation of any Fe cluster or magnetic compounds.

The thesis will be divided into the following chapters that will cover the background information, motivation for the present work, experimental work carried out, methodology and techniques used, results obtained and conclusions drawn from them.

Chapter I Introduction:

The chapter provides a brief overview of elemental and compound semiconductors that belong to the groups II-VI, III-V and IV-VI with a specific focus on IV-VI group along with an introduction to dilute magnetic semiconductors. It also talks about the magnetic interactions that are responsible for instigating ferromagnetic behaviour in the materials. A description regarding the materials under consideration, their properties and motivation to carry out the work is discussed. Literature survey pertaining to past experimental and theoretical work done on these materials is also presented.

Chapter II Experimental Techniques utilized for characterizing the materials:

The chapter describes the technique that is utilized for the synthesis of the bulk samples. The technique involves vacuum sealing of desired materials in quartz tube followed by melting to achieve homogeneity. Also, details of experimental techniques that were adopted to characterize the samples are also explicitly explained. The methods that are deployed for the present work are mentioned as follows. They have been explained comprehensively.

1. Bulk sample preparation
2. X-ray Diffraction (XRD): To determine the structural phase of the samples.
3. Field Emission Scanning Electron Microscope (FESEM): To understand the surface properties of the bulk samples.
4. UV-Visible Spectroscopy: To find out band gap values of SnSe samples.
5. Fourier-Transform Infrared Spectroscopy (FTIR): To find out presence of functional groups and band gap values of SnTe and Tellurium samples.
6. Raman Spectroscopy: To understand the molecular structure and different bonds present in the sample.
7. Physical Property Measurement System (PPMS): To study the nature of samples from the DC electrical resistivity curves.
8. Superconducting Quantum Interface Device-Vibrating Sample Magnetometer (SQUID-VSM): To perform temperature dependent magnetization (M-T) studies and M-H studies to understand the magnetic properties of the samples. Magnetic

memory effect studies are also performed to see whether the sample is able to recollect the history of past measurements.

9. AC susceptibility: To confirm the presence of magnetic glassy state.

Chapter III Study on hole impurity triggered magnetism in Fe doped $(Te)_{1-x}Sb_x$ bulk alloys:

The work in this chapter focuses on elemental semiconductor Tellurium which is doped with dilute amount of transition element Fe. Its functionality as a DMS system has been explored alongside the substitution of group V element Sb which acts as a hole dopant/acceptor impurity. The doping amount of Fe is limited to 0.05 in order to avoid formation of Fe clusters or other undesirable magnetic phases. The general sample composition is represented as $Fe_{0.05}(Te)_{1-x}Sb_x$ where x = 0, 0.01, 0.03 and 0.05. Hexagonal structure of Te is confirmed from the X-ray Diffraction spectra with presence of no additional peaks. Raman active modes are found to be splitting, seems to be due to the result of phase formation between Fe and Te which is assumed to be too weak to be detected using XRD. The electrical resistivity data and plot of temperature coefficient of resistance confirms the semiconducting nature of the samples. A crossover from negative to positive trend is observed in the magnetoresistance plot of the samples as temperature reaches 100 K. Since Tellurium is diamagnetic in nature, doping of Fe brings about paramagnetic feature in the sample. However, with the substitution of Sb, presence of weak ferromagnetic ordering is perceived from the magnetic studies which can be regarded as an interesting behaviour. Further interpretation of magnetic properties are also discussed in the chapter in addition to optical and transport properties.

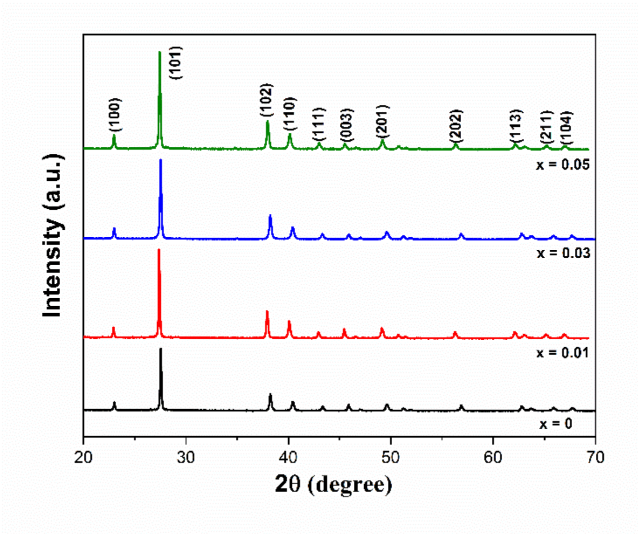

Fig. 1 XRD pattern of $Fe_{0.05}(Te)_{1-x}Sb_x$ sample where x = 0, 0.01, 0.03 and 0.05.

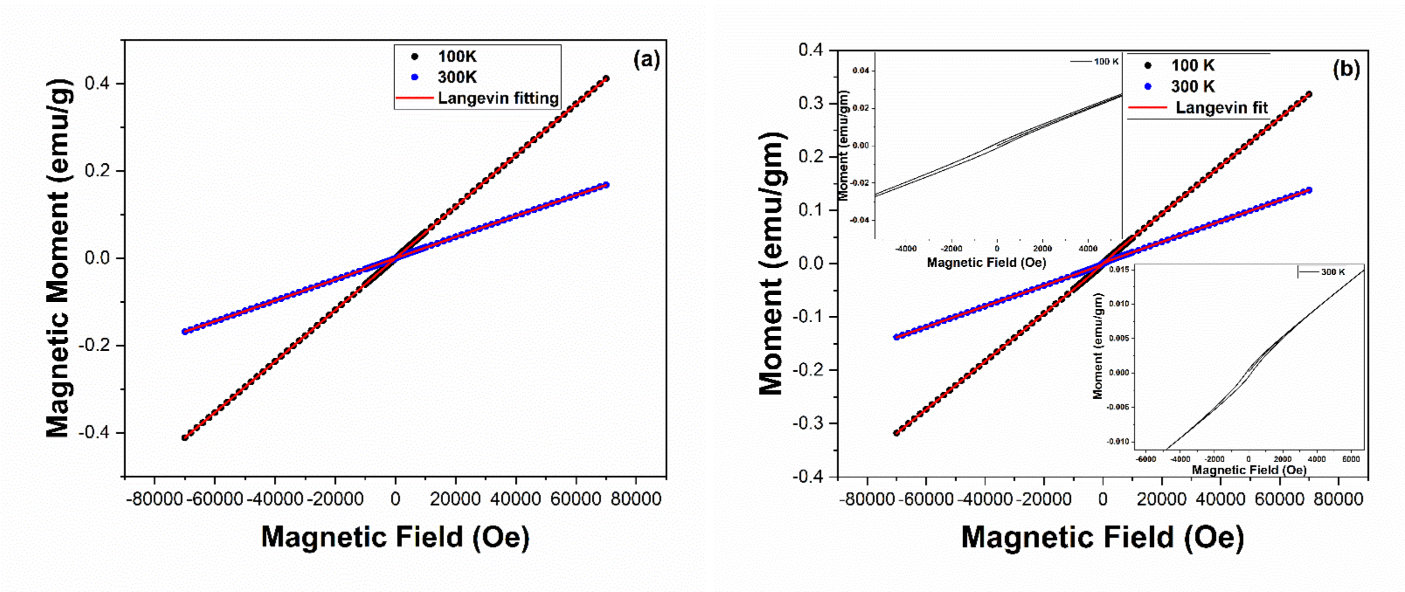

Fig. 2 M-H plots of $Fe_{0.05}(Te)_{1-x}Sb_x$ samples for (a) x = 0 showing paramagnetism and (b) x = 0.01 showing an emergence of a tiny hysteresis loop.

Chapter IV Effect of substitution of non-magnetic impurity Sb on ferromagnetism in dilute Fe doped SnSe:

This chapter focusses the work on group IV-VI semiconductor SnSe, doped with Fe followed by a co-doping of Sb having a general form $Fe_{0.05}(SnSe)_{1-x}Sb_x$ where x = 0, 0.03 and 0.05. The samples are prepared by sealing the quartz tube under vacuum and then melting the contents in an oxy-butane flame. An elaborate explanation and illustration of different studies carried out to get an understanding of the underlying properties has been elucidated in the chapter. Studies include structural, surface morphology, optical, R-T measurements in the presence of applied magnetic field, M-T and M-H measurements, magnetic memory effect, etc. Variation in the concentration of Sb results in changes in the direct and indirect band gap values from that of pristine SnSe. Resistivity measurements show a transition from metallic to semiconducting nature in x = 0 sample but a purely metallic nature for the other two samples. The metallic nature can also be confirmed from the temperature co-efficient of resistance plot. Magnetic memory effect measurement is also performed on the samples to check whether they can remember their past spin orientation and the findings of the same will also be discussed in the chapter.

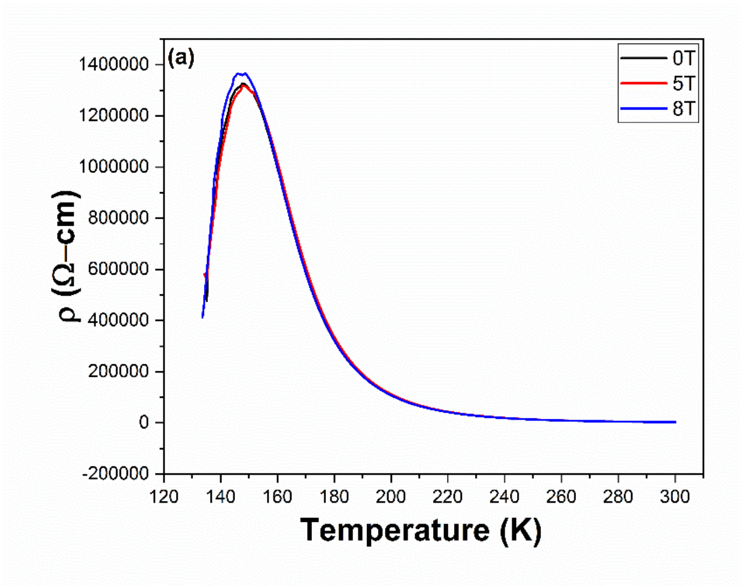

Fig. 3 Resistivity plot of (a) x = 0 sample showing metal to insulator transition.

Chapter V An interplay between ferromagnetic and magnetic glassy state in Fe doped $(SnTe)_{1-x}Sb_x$ bulk alloys:

This chapter discusses work on dilute Fe doped SnTe bulk alloys having general form $Fe_{0.05}(SnTe)_{1-x}Sb_x$ where x = 0, 0.01, 0.03 and 0.05. The alloys are prepared by varying the concentration of Sb to see the effect of donor impurities on the properties of samples. The samples were characterized for their structural, optical, electrical resistivity, magneto-resistance and magnetic properties. The XRD pattern of all samples show Rock salt crystal structure. The band gap values calculated from the FTIR spectrum also showed unusual variations with a decreasing as well as increasing trend. The increase in band gap values can be explained on the basis of Burstein-Moss effect. The electrical resistivity data show a transition from metallic to insulating nature in x = 0 sample. However, with the substitution of Sb, the resistivity values are found to decrease with temperature thereby showing semiconducting nature. Magnetoresistance plot of all the samples at different temperature values is seen to show a positive trend with the maximum value undergoing a decrease with temperature. In addition, detailed analysis of magnetic studies will also be done in this chapter. The samples are found to showcase ferromagnetic behaviour at room temperature.

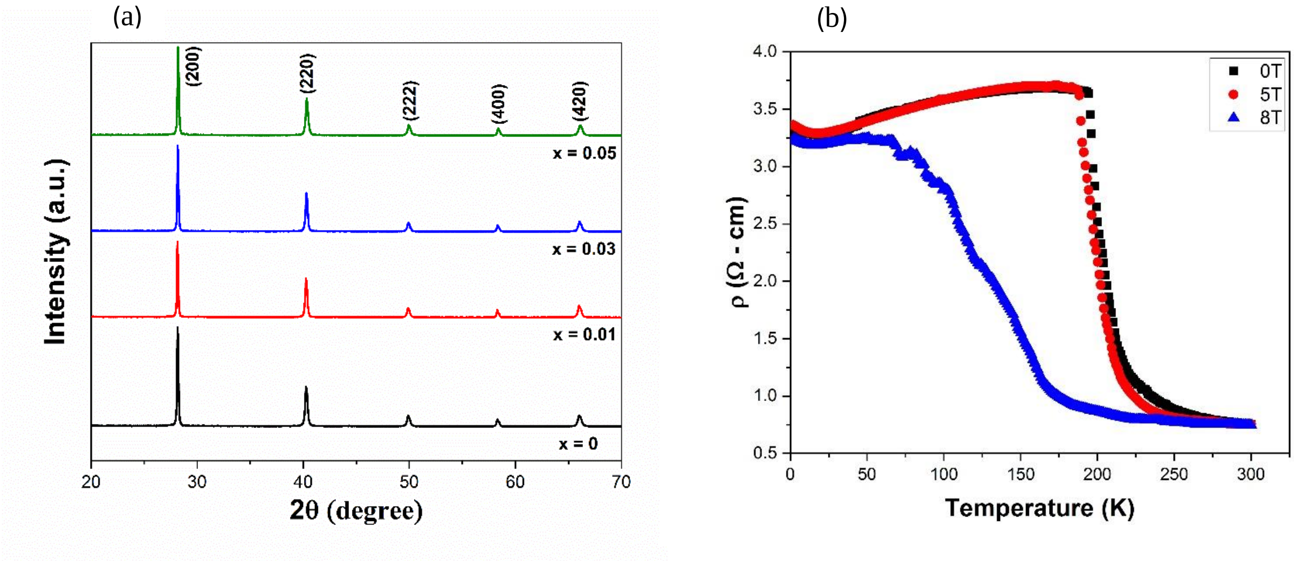

Fig. 3 (a) XRD pattern of $Fe_{0.05}(SnTe)_{1-x}Sb_x$ samples where x = 0, 0.01, 0.03 and 0.05 and (b) Electrical resistivity plot of x = 0 sample showing metallic to insulator transition.

Chapter VI Summary:

In this chapter, an overall summary and conclusion derived from the work carried out on Fe doped $(Te)_{1-x}Sb_x$ bulk alloys, $(SnSe)_{1-x}Sb_x$ bulk alloys and $(SnTe)_{1-x}Sb_x$ bulk alloys will be presented. The future prospects of extending the above work in terms of device making that could be utilized for different applications will also be discussed.

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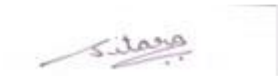

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