

**STRUCTURAL, ELECTRICAL AND MAGNETIC
PROPERTIES OF $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ AMORPHOUS
ALLOYS**

**By
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Roll No. 1014142507 F
Session: October, 2014**



**DEPARTMENT OF PHYSICS
BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY
DHAKA-1000, BANGLADESH**

JANUARY, 2017

STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ AMORPHOUS ALLOYS

*A dissertation submitted to the Department of Physics of Bangladesh University of
Engineering & Technology in partial fulfillment of the requirements for the degree of
Masters of Science (M.Sc.) in physics*

**By
Md. Aminul Islam
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**DEPARTMENT OF PHYSICS
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DHAKA-1000, BANGLADESH**

JANUARY, 2017



CANDIDATE'S DECLARATION

I hereby declare that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

.....
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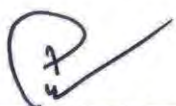
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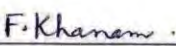


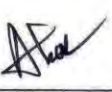
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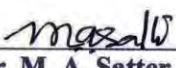
The thesis titled “STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ AMORPHOUS ALLOYS” submitted by **Md. Aminul Islam**, Roll No: 1014142507F Session: **October/2014**, has been accepted as satisfactory in partial fulfillment of the requirement for the degree of **Master of Science (M.Sc.) in Physics on 8 January , 2017.**

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LIST OF SYMBOLS AND ABBREVIATIONS

A - Stiffness Constant

O - Oxygen

Cu - Copper

Nb - Niobium

Ta - Tantalum

Si - Silicon

B - Boron

Co - Cobalt

Fe - Iron

C - Carbon

P - Phosphorus

$\rho/\rho(298\text{ K})$ - Normalized resistivity

$\Delta\rho/\rho(0)$ - Magnetoresistance

MR% - Magnetoresistance in percent

MI - Magnetoimpedance

GMR - Giant Magnetoresistance

GMI - Giant magnetoimpedance

R - Resistance

X - Reactance

QF - Quality factor

DF - Dissipation Factor

L - Inductance

Lex - Exchange interaction length

μ_0 - Permeability in free space.

μ_i - Initial permeability

μ' - Real part of complex permeability

μ'' - Imaginary part of complex permeability

$\tan\delta$ – Loss tangent

H_c - Coercivity

E_k - Anisotropy energy

M_s - Saturation magnetization

D - Grain diameter

T_c - Curie temperature

T_g - Glass transition temperature

KG - Kilo Gauss

MHz - Megahertz

GHz - Gigahertz

AHE - Anomalous Hall Effect

SWR - Spin wave resonance

FM - Ferromagnetic

AFM - Anti-ferromagnetic

FMR - Ferromagnetic resonance

WB - Bloch wall

DTA - Differential Thermal Analysis

TGA - Thermogravimetric Analysis

DTG - Differential Thermal Gravimetric

SEM- Scanning Electron Microscopy

EDX- Energy Dispersive X-ray

XRD- X-Ray Diffractometry

ABSTRACT

(Fe_{1-x}Mn_x)₇₅P₁₅C₁₀ amorphous alloys ribbons have been prepared by conventional melt-spinning technique (rapid cooling) with different wheel speeds in an argon atmosphere. The microstructural analysis were done by X-ray diffraction technique, Scanning electron microscopy (SEM). Both the XRD and SEM confirm the samples the amorphous (glassy) structure of the as made samples. The elemental analysis of the samples was carried out using energy dispersive X-ray spectroscopy (EDS) which reveals the presence of Fe, Mn, P and C elements in the sample. The glass transition temperature (T_g), the crystallization temperatures (T_x) and the mass loss and/or gain of all the samples were investigated by differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA). The electrical resistivity (ρ) of amorphous (Fe_{1-x}Mn_x)₇₅P₁₅C₁₀ alloy ribbons have been studied as a function of temperature between 77K to 600K. It has been observed that the resistivity increases slightly with increasing temperature upto room temperature then it is increasing rapidly for $x=0$ and 0.05. At larger x , $\rho(T)$ develops a minimum at room temperature which can have different slopes, $\frac{d\rho}{dT}$ which has been ascribed to a superposition of scattering from the structural topological disorder and the spin topological disorder. The magnetic field dependence of magneto-resistance $\Delta\rho(H)$ normalized to the resistivity of the sample in zero magnetic field ρ_0 have been studied. It is observed that an anomalous change of MR% around 0.3 tesla occurs. Both positive and negative magnetoresistance have been observed as a function of applied magnetic field. The magnetic hysteresis (M-H) loop of the as-made samples show high saturation magnetization (M_s). The value of saturation magnetization is found to decrease with increasing Mn. This is attributed to the magneto-elastic scattering. The coercivity increases gradually with increasing Mn content up to 30 at. % Mn content. The increase in coercivity seems to be related to the decrease in glass-forming ability with increasing Mn content. The variation of complex permeability (real and imaginary part respectively) as a function of frequency from 100Hz-120MHz show high effective permeability of 2.2×10^4 . The value of effective permeability is found to have decreased with increasing Mn contents. These anomalous magnetic properties lead to the suggestion that the antiferromagnetic

interactions introduced by Mn atoms cause deviations from a pure ferromagnetic structure at low Mn concentrations. However at higher Mn contents a competing ferro and antiferromagnetic interaction might result in a frustrating system resulting in magnetic relaxation.

Chapter One

Introduction

1.1. Introduction

1.2. Historical development of amorphous metallic alloys

1.3. Dependence of Grain Size on Coercivity

1.4. Aim of this Wok

References

Chapter One

Introduction

1.1 Introduction

Amorphous metallic alloys are metals and metal alloys with no long range atomic order. They have also been called glassy alloys or non-crystalline alloys. They are made by a variety of techniques all of which involve the rapid solidification of the alloying constituents from the gas or liquid phases. The solidification occurs so rapidly (1 micro-second) that the atoms are frozen in their liquid (disordered) configuration. However, there are clear structural indications from their various properties that nearest neighbour, or local, order does exist in most amorphous metallic alloys, but no long range atomic order.

There are unique magnetic, mechanical, electrical and corrosion behaviors which results from this amorphous structure. For example, they behave as very soft magnetic materials, in fact magnetic losses in high magnetization alloys have been measured which are lower than those measured in any other known crystalline alloys; they are exceptionally hard and have extremely high tensile strengths and in some alloys the coefficient of the thermal expansion can be made to be zero; they have electrical resistivities which are three to four times higher than those of conventional iron or iron-nickel alloys; and finally some of the amorphous alloys are exceptionally corrosion resistant.

There are two or possibly three technologically important classes of magnetic amorphous alloy; the transition metal-metalloid (TM-M) alloys, the rare earth-transition metal (RE-TM) alloys and possibly the transition metal-zirconium or hafnium alloys. The TM-M alloys typically contain about 80 atom per cent iron, cobalt or nickel with the remainder being boron, carbon, silicon, phosphorus or aluminum and are typically prepared by rapid quenching from the melt, although other techniques such as sputtering, electro deposition and chemical deposition have been used. The presence of the metalloids is necessary to lower the melting point making it possible to quench the alloy through its glass temperature rapidly enough to form the amorphous phase. Once made the same metalloids stabilize the amorphous phase but

their presence drastically alters the magnetic, mechanical and electrical properties of the alloy by donating electrons to the d-band. The presumed isotropic character of the TM-M amorphous alloys had been predicted to result in very low coercivities and hysteresis loss and high permeability; all the properties of technological significance for application as soft magnetic materials. These good properties have been achieved in some melt-quenched alloys and we can account for their behaviour by the same models as used for conventional crystalline soft magnetic materials. The same statements can be made for the recently reported TM-Zr-Hf alloys. These normally contain about 10 atom per cent zirconium or hafnium but the addition of even a few percent of boron greatly enlarges the amorphous forming region. Because they have properties which are very similar to the TM-M alloys it is expected that they will be used in similar devices.

The RE-TM alloys, however, are normally prepared by sputter deposition and have properties especially suited to bubble memory devices, for example, low saturation magnetization and high anisotropy perpendicular to the plane. These types of amorphous alloy will not be discussed in any detail in this monograph.

Amorphous alloys have been shown to have vastly superior magnetic properties for application in large transformers and to have a combination of mechanical and magnetic properties that makes them extremely likely candidates for application in recording heads, in some electronic size transformers and in various types of sensor. Thus, the application of amorphous alloys in various magnetic devices appears to be assured. Nickel-based amorphous alloys for brazing foil have also been in use for several years. This technique provides all-metallic brazing foils with no binders, resulting in greater strength and greater assembly precision in reduced time. Many other applications have been reported in the technical literature but none has appeared on the market yet.

Until recently the major efforts in solid state physics have been confined to understanding the properties of crystalline solids. Microscopic information has been obtained from studies of the properties of single crystals. Amorphous solids now represent a new state of matter. Some of their properties are entirely as predicted. Other properties have unexpected features and ambiguities. For example, although

amorphous solids consist largely of random aggregates of atoms their densities are only slightly different from the density of crystals of the same composition.

The broad theoretical question is: how does the amorphous atomic structure affect all of the characteristics, e.g. magnetic, mechanical, and chemical or corrosion, and electrical. Each of these will be discussed in some detail in the forthcoming sections of this review. Much of our understanding has come from comparing the properties of the amorphous alloy with the same or a similar crystalline alloy. However, this has only limited applicability because most of the interesting amorphous alloys have no simple or single crystalline counterpart. One of the singular advantages of studies on amorphous alloys is that we can vary the composition continuously, to prepare homogenous alloys which can be studied as a function of composition and temperature without complicating interference from structural phase transitions. Although these complications do not exist, more subtle changes do occur at temperatures well below crystallization. For example, phase separation, diffusion of various species and structural relaxations all occur even though the alloy remains amorphous. That is, the amorphous phase is not a stable ground state of the solid. All of these changes can have effects on the observed properties.

1.2 Historical development of amorphous metallic alloys

In the past 8000 years that humans have used metals their structure has consisted of crystalline aggregates. Historically, the first report in which a range of amorphous, i.e. non-crystalline, metallic alloys were claimed to have been made was by Kramer [1].

This was based on vapour deposition. Somewhat later Brenner et al.[2] claimed to have made amorphous metallic alloys by electrodepositing nickel-phosphorus alloys. They observed only one broad diffuse peak in the X-ray scattering pattern in the nonmagnetic high-phosphorus alloys. Such alloys have been in use for many years as hard, wear and corrosion resistant, coatings. It was not until 1960 that Duwez and his coworkers discovered a method of preparing amorphous alloys by direct quenching from the melt. The story of this discovery is a fascinating one and has been told by Duwez[3].

Giessen [4] alphabetically classified, by alloy, work published up to the end of 1968. Giessen and Willens[5] emphasized the underlying principles of the work reviewed and Anantharaman and Suryanarayana[6] classified the information obtained from the alloy systems studied. Giessen and Wagner [7] reviewed the structure and properties of amorphous metallic phases produced mainly by quenching from the melt.

Jones [8] provided an extensive compilation of developments in splat-cooling and metastable phases. It included an analysis of the methods available for quenching from the melt and an understanding of how they work, the structural features obtained in both metastable crystalline and amorphous phases, the response of the as-quenched structures to annealing, and finally the properties and applications of splat-cooled alloys. Jones and Suryanarayana [9] published a comprehensive annotated bibliography covering the period up to near the end of 1972. This has recently been extended to 1980[10]. The status of our knowledge of the structure of metallic alloy glasses, derived both experimentally and theoretically, is covered by Cargill [11]. Our understanding of the formation and stability of amorphous structures was reviewed by Takayama [12] and the structure and crystallization by Waseda et al[13]. A brief review of metallic glasses from fundamentals to practical prospects was presented by Cahn [14] as well as by Guntherodt [15] and by Gilman [16]. A complete review of the status of our understanding of the structure, transport and transformation kinetics, mechanical properties, magnetic properties, electrical properties and corrosion resistance has been published by Chen [17]. Also published in 1980 are some other rather less extensive general reviews by Chaudhari et al.[18], by Cahn[19], and by Luborsky[20] on magnetic properties. Furthermore, the first books are expected to appear soon [21, 22].

Extensive collections of papers on glassy metals can be found in the Proceedings of four Conferences on Rapidly Quenched Metals. The first was published in *Fizika (volume 1, supplement 2 (1970))*; the second was held at Massachusetts Institute of Technology, and the Proceedings, edited by N. J. Grant and B. C. Giersen, were published in two parts, by the MIT press (1976) and in *Materials Science and Engineering* (1976). The Proceedings of the third conference, held in Brighton, were edited by B. Cantor and published by The Metals Society, London (1978), and of the

fourth, held in Japan, and edited by T. Masumoto and K. Suzuki, were published by the Japan Institute of Metals, Sendai (1982).

Other extensive reports will be found in the Scientific Reports of the Research Institutes of Tôhoku University (**Series A, No. 1, (1976); Nos. 4 and 5 (1977); No. 2 (1979) and Nos. 1 and 2 (1980)**); the book 'Metallic Glasses', edited by J. J. Gilman and H. J. Leamy and published by the American Society for Metals (1978); the Annals of the New York

Academy of Sciences (1976); the Proceedings of the Fourth International Conference on Liquid and Amorphous Metals (**Supplement C8 to J. Phys (Fr.) (1980)**); Supplements to the Scientific Reports of Tôhoku University (1978 and 1980); the Proceedings of the Conference on Amorphous Metallic Materials, held in Smolenice, edited by P. Duhaj and P. Mraňko and published by VEDA, for the Slovak Academy of Science (1978); and the Proceedings of the Conference on Metallic Glasses : Science and Technology, held in Budapest and published by the Central Research Institute for Physics, Budapest (1980).

1.3 Dependence of Grain Size on Coercivity

The hysteresis loop of a ferromagnetic material is essentially determined by the microstructure of the material, to be precise, the grain size. **Figure 1.1** summarizes the present understanding of the coercivity, H_c , in the whole range of structural correlation lengths starting from atomic distances in amorphous alloys over grain sizes, D , in the nanometer regime up to macroscopic grain sizes – the permeability shows an analogous behavior being essentially inversely proportional to H_c . The $1/D$ -dependence of coercivity for large grain sizes [22] reflects the conventional rule that good soft magnetic properties require very large grains ($D > 100 \mu\text{m}$). Thus, the reduction of particle size to the regime of the domain wall width increases the coercivity H_c towards a maximum controlled by the anisotropies present. Accordingly, fine particle systems have been mostly discussed as hard magnetic materials [25]. Lowest coercivities, however, are again found for smallest structural correlation lengths like in amorphous alloys ("grain size" of the order of atomic distances) and in nanocrystalline alloys for grain sizes $D < 20 \text{ nm}$. Obviously, the new nanocrystalline material fills in the gap between amorphous metals and conventional poly-crystalline

alloys. The extraordinary D^6 -dependence of coercivity at small grain size moreover demonstrates how closely soft and hard magnetic behavior actually can be neighbored. Indeed, the soft magnetic alloys are only one manifestation of the novel and extraordinary magnetic properties which can be realized by establishing structural features on the nanometer scale. Thus, nanocrystalline microstructures are also of highly current interest in order to enhance the properties of rare earth hard magnets [26]. The decrease of coercivity in the new nanocrystalline materials has to be well distinguished.

From superparamagnetic phenomena i.e. the well-known decrease of coercivity in small, isolated or weakly coupled particles due to thermal excitation [23]. Although coercivity vanishes, the superparamagnetic regime is not very interesting for soft magnetic application since an appreciable change of magnetization requires large magnetic fields, i.e. the permeability is fairly low. In the present case we deal with small ferromagnetic crystallites well coupled by exchange interaction and with low coercivity and simultaneously high permeability [27, 28].

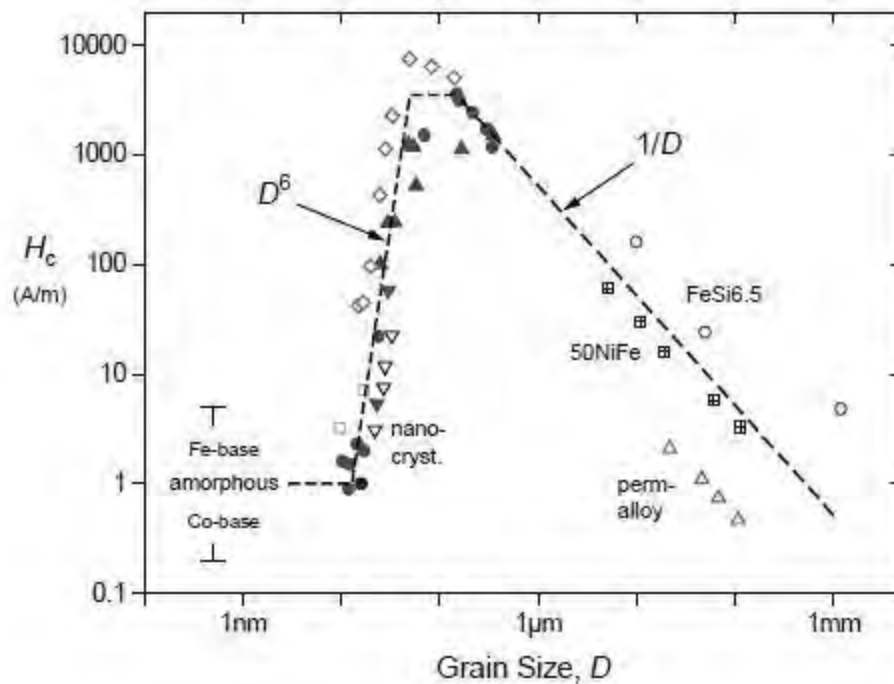


Figure 1.1 Coercivity, H_c , vs. grain size, D , for various soft magnetic metallic alloys (after [27, 28]): Fe-Nb₃Si_{13.5}B₉ (solid up triangles), Fe-Cu₁Nb₁₋₃Si₁₃B₉ (solid circles), Fe-Cu₁V₃₋₆Si_{12.5}B₈ (solid down triangles), Fe-Cu₁V_xSi_{19-x}B₈ (open down

triangles), Fe-Cu_{0.1}Zr_{~7}B₂₋₆ (open squares), Fe₆₀Co₃₀Zr₁₀ (open diamonds), NiFe-alloys (+ center squares and open up triangles) and FeSi6.5wt% (open circles).

The combination of small grain size and soft magnetic properties is surprising and fascinating from the classical point of view in magnetic engineering. Yet, this possibility was principally known from amorphous materials and the theoretical interpretation of their soft magnetic properties. Accordingly, magnetic softening should also occur as soon as the structural correlation length or grain size becomes smaller than the ferromagnetic exchange length which is in the order of the domain wall width. In this case the local anisotropies are randomly averaged out by exchange interaction so that there is no anisotropy net effect on the magnetization process. The degree to which the local anisotropies are finally averaged out can be addressed in terms of the so-called random anisotropy model. The model has been originally developed by Alben et al.[28] for amorphous metals and, later on, could be successfully applied to explain the behavior of the nanocrystalline materials [26, 27]. Accordingly, the average magneto-crystalline anisotropy, $\langle K \rangle$, scales with the structural correlation length, D , like

$$\langle K \rangle \sim K_1 (D/L_0)^6 \quad (1)$$

where $L_0 = (A/K_1)^{1/2}$ is the basic ferromagnetic correlation length determined by the local anisotropy constant K_1 and the exchange stiffness A .

The decrease of coercivity in the new nanocrystalline materials has to be well distinguished from superparamagnetic phenomena i.e., the well-known decrease of coercivity in small, isolated or weakly coupled particles due to thermal excitation. Although coercivity vanishes, the superparamagnetic regime is not very interesting for soft magnetic application since an appreciable change of magnetization requires large magnetic fields, i.e., the permeability is fairly low. In the present case we deal with small ferromagnetic crystallites well coupled by exchange interaction and with low coercivity and simultaneously high permeability.

The pioneering discovery of Yoshizawa and co-workers (1998) stimulated an intensive and still ongoing research for alternative alloy compositions. Thus, low magnetostrictive nanocrystalline Fe-(Cu)-Zr-B alloys or Fe-Hf-C thin films have been established which exhibit a still higher saturation magnetization up to 1.7 Tesla due to the higher Fe content in the alloy. Still, the outstanding soft magnetic properties of the original alloy system could not be reached up to now. Interestingly, as a kind of precursor, the first example for soft magnetic behavior in the nanocrystalline state was given by O'Handley et al. (1985) for a devitrified glassy cobalt base alloy. However, the soft magnetic properties were inferior to the amorphous state and, thus, not very attractive, which to the present seems to be typical for cobalt based nanocrystalline materials. Indeed, the most promising properties so far have been found in iron based alloys.

1.4 Aim of this Work

In recent years, amorphous alloys have received considerable experimental and theoretical attention owing to their anomalous magneto-transport and soft magnetic properties. These materials are interesting from both the fundamental and applied viewpoints. Because of various superior mechanical, magnetic and electrical properties, in comparison with those of the crystalline state, amorphous alloys form a class of technologically important materials. They have already been put into applications in the devices e.g., choke coils. High frequency transformers and the magnetic thin film heads [Yoshizawa *et al* [30].

The objective of this work is to study the temperature and field dependence of magnetic and electrical properties e.g., resistivity, magnetoresistance, frequency dependent complex permeability of the $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ magnetic alloy ribbons.

This research work is focused on studying the effect of Mn substitution in the quaternary magnetic alloy $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ system in the form of magnetic ribbons. Since Fe and Mn are two different magnetic species in this alloy, one being ferromagnetic while the other antiferromagnetic, a process of magnetic dilution is expected to change the thermo- magnetic and structural properties of this alloy. Also substitution of Fe by Mn is expected to increase the average magnetic moment of the alloy making it suitable as core material with a relatively lower loss of energy and

coercivity. The alloy would be useful in fabricating the miniaturized fast switching devices with a relatively lower loss factor.

In order to achieve the following main steps are included in the present work:

- Investigation of the crystallite size, structural phase surface morphology of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys.
- Investigation of compositional information of ribbon $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys.
- Investigation of the temperature dependence resistivity.
- Investigation of the magnetoresistance saturation magnetization, permeability.
- Investigation of thermal behavior by a computer controlled DTA/TGA system.

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Chapter Two

Preparation of Amorphous Ribbons

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 - 2.2 Formation of nanocrystalline state**
 - 2.3 Influence of alloying**
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Chapter Two

Preparation of Amorphous Ribbons

2.1 Introduction

Alloys produced by rapid quenching from the melt have been shown to exhibit metallurgical characteristics not obtainable by conventional casting methods. Such features include refined grain size, extended solid solutions metastable phases and metallic glasses [1, 2]

The quench rate achieved in the rapid solidification is primarily controlled by specimen thickness and the nature of interfacial contact between substrate and sample. Calculations by Ruhl have shown that average quench rate varies inversely with the square of specimen thickness for ideal cooling or as the inverse of thickness for Newtonian (interface-controlled) cooling. Aside from high quench rate, another important factor in the preparation of rapidly quenched samples is the ability to undercool the melt to such an extent that subsequent recalescence does not cause morphological destabilization of the product.

A high average sample quench rate can be achieved by promoting rapid heat removal from the bulk. Perhaps the simplest means by which this may be achieved is by maximizing the contact area between the melt and cooling medium by rapidly increasing the liquid alloy surface area. This may be effected either by altering the shape of the melt during processing (splat quenching, melt-spinning, etc.) or by physically segmenting the melt by various means (atomization, etc.). Of course, atom-by-atom preparation methods such as sputtering and vapor deposition have maximum sample surface-to-volume ratios on quenching [3]. An alternative means by which high quench rates can be achieved is by briefly subjecting the sample surface to a high power input, causing localized melting and rapid solidification of the melt using the bulk of the specimen as a substrate (self-substrate quenching). The morphology and characteristics of some rapidly quenched amorphous and crystalline alloys has been shown to depend significantly on the sample preparation method used. Comprehensive

reviews describing both the fabrication and physical properties of amorphous alloys have been written.

2.2 Formation of the nanocrystalline state

In accordance with a kinetic view of glass formation, it is likely that any metallic alloy containing more than, at most, a few atomic per cent of solute, and, possibly as little as a fraction of a percent, could be quenched to a glass, given a sufficiently high cooling rate T and, importantly, given that it is cooled to a temperature sufficiently low to avoid spontaneous crystallization. The situation of pure metals and very dilute alloys is less clear. Several studies have been made of thin films produced by condensation from the vapor phase at very low temperatures. This is a process that gives a much higher effective quench rate (of the order of 10^{13} K/s) than is normally attainable from the melt-, since deposition occurs atom by atom and the heat of condensation is rapidly removed through the thin film. Amorphous thin films of several transition metals, of generally unspecified purity, have been produced by vapor deposition and, for instance, crystallization temperatures T_x of up to 530 K have been reported for amorphous nickel films. In contrast, subsequent careful study of the influence of gaseous impurity on the condensed film structure indicated that amorphous films of nickel could not be produced at 4 K when the impurity content was 0.07 % (On the other hand, films of another close-packed metal, cobalt, and of chromium, iron and manganese, of similar nominal impurity content, condensed in the amorphous state at 4 K but it is possible that they were more susceptible to impurity stabilization than nickel).

In the case of quenching from the melt, a glassy phase was observed in very thin sections (about 100nm thick) at the edges of splat foils of nickel, quenched in air. This phase was found to crystallize at about 420 K and it is likely to have been stabilized by dissolved gaseous impurity, possibly up to 2 atom %. The cooling rate f corresponding to the 100 nm splat quenched thickness is estimated to be of the order of 10^9 — 10^{10} K/s.

Pure germanium was found to vitrify at a similar $\tilde{A}$, both by splat quenching in argon and by dispersion of melt as 30 nm particles in argon. However, although germanium is metallically bonded in the liquid state, it assumes tetrahedral, covalent bonding on

vitricification and the structural rearrangement required for crystallization stabilizes the glass to high temperatures, even in the absence of impurity atoms. Similarly, pure silicon has also recently been vitrified in very thin sections by use of a pulsed laser surface melting technique.

Notwithstanding the various reports of amorphous films of nominally pure metals, the balance of evidence suggests that a minimum concentration of impurity atoms is required to promote the vitrification of a metal but which may depend on the chemical nature of the impurity. For pure metals having close- or densely-packed crystal structures, crystallization of a glassy phase would require little structural adjustment and no thermal activation, which, in effect, means that the presence of a free surface, where atomic packing is relatively loose, would lead to spontaneous crystallization.

2.3 Influence of alloying

The effect of adding solute atoms to a pure metal, and especially if they are of different size and chemical character from the host atoms, is to require that significant diffusive rearrangement occur during crystallization of the glass phase, i.e. to stabilize the glass. As the solute concentration increases, T_g generally increases and T_x , when measured dynamically under conditions of relatively rapid heating (more than about 1 K/s), approximates more closely to T_g . On the other hand, on alloying, the temperature at which freezing begins under equilibrium conditions, i.e. the liquidus temperature T_u often decreases. In such cases, the interval between T_x and T_g generally decreases with increasing solute concentration, so that the probability of being able to cool through the interval without inducing crystallization is enhanced, i.e. the glass forming ability GFA is increased. (The GFA is, as indicated earlier, measured by the magnitude of f_c and thus of x_c . In practice, however, the observed x_c is always smaller than the theoretical limit because of resistance to heat flow at the interface between the melt and the heat sink.) Accordingly, the alloy systems for which glass formation occurs most readily, i.e. having the highest GFA, are those that manifest either one or more deep eutectics, or a steep and substantial decrease in T_x with increasing percentage of solute, to a 'plateau' over which T_x is low in comparison with the melting point T_m of the host metal. Thus, there is a tendency for the GFA to vary inversely with the ratio T/T_x , which is referred to as the reduced glass temperature T_{rg} . The lower is T_x and

the higher is T_g , then the higher tends to be the GFA. The highest known values of T_g for metallic alloys are in the range 0.66—0.69, e.g. 0.69 for Ca₆₅Al₃₅21.

The meaning of 'readily glass forming' is somewhat arbitrary; by convention, it has been taken to indicate completely glass forming either when splat-quenched as foils about 10—20 μm thick or, more recently, with the advent of melt spinning processes, when continuously cast as ribbon or strip 10—20 μm thick. Thus, the glass forming range (GFR) for an alloy system is conventionally defined as that within which x_c is more than about 10—20 μm . In reality of course, the GFR will depend on the value of x_c chosen, the smaller is x_c the wider being the GFR. Values of x_c of 10—20 μm correspond to f_c of the order of 10⁶—10⁷ K/s, for most of the melt quenching processes commonly employed, and to T_{JTX} generally about 0.45. In practice, also, there is the additional requirement that T_g be higher than room temperature, unless the alloy is quenched below ambient.

For condensation processes such as vapour deposition and cathodic sputtering, the ranges of alloy systems and compositions over which amorphous phases are formed are wider than for liquid quenching at 10⁶ K/s, because of the higher effective quench rate, though care may be required to control the rate of deposition and the substrate temperature, to avoid crystallization. Amorphous film formation by electrolytic or electrodeless deposition has been reported for both metal-metalloid alloys (e.g. Ni-P, Co-P) and metal-metal alloys (e.g. Cr-W, Cr-Mo). Interestingly, for the former, it is at compositions close to eutectics that amorphous films form most easily.

2.4 Influence of process variables

The techniques available for producing metallic glasses in various forms, ranging from powder, through fibre and wire to strip, and the major process variables, have been reviewed [4]. The principal developments since then have been the evolution of the planar flow casting process for wide amorphous alloy strip production¹⁰⁴ and of an improved method for casting amorphous alloy wire¹⁰⁵. The aim in all the techniques is to bring the melt into clean contact with (a) cool and highly conducting heat sink(s) at a high relative velocity, in order to promote efficient and uniform melt spreading or subdivision and intimate thermal contact. The higher is f_c for an alloy, then the smaller must be the section thickness x , i.e. the length of the heat path.

The cooling rate achieved is also clearly a function of the heat transfer coefficient h (i.e. the efficiency with which heat is conducted) across the interface(s), with the heat sink. Where no interfacial resistance to heat flow exists ('ideal cooling conditions'), the cooling rate is then determined by the conductivity and thickness of the liquid medium (for a highly conducting sink). In practice, ideal cooling conditions are not achieved, except in the case of 'laser glazing' where a self-substrate exists. For chill block melt spinning, h has been estimated experimentally to be approximately $10^5 \text{ W m}^{-2} \text{ K}^{-1}$, with a variation from system to system of about half an order of magnitude 10^6 - 10^7 , and it is presumed to be similar for planar flow casting. The computed variation of f with x for a RGF alloy $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$, for ideal cooling, for the range of A appropriate to melt spinning and to 'gun' splat quenching, where h is higher at about $3 \times 10^6 \text{ K/s}$ 10^8 , is given in **Figure 2.1**. The estimated maximum glass thickness x_c derived from **Figure 2.1** is then plotted against T_{Tg} in **Figure 2.2**.

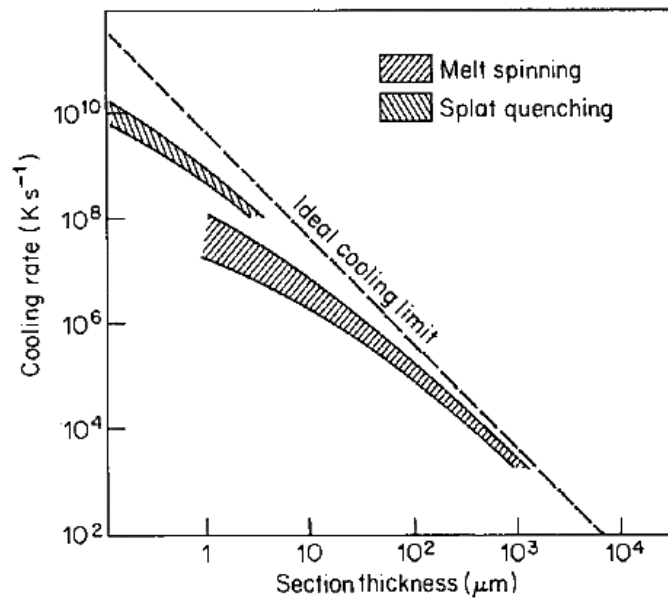


Figure 2.1 Cooling rate f as a function of section thickness x computed for the glass forming alloy $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$, based on experimentally derived values of heat transfer coefficient (cross hatched areas) and ideal cooling, i.e. no interface resistance (dashed line), for splat quenching and for chill block melt spinning. Unidirectional cooling of a rectangular plate section to one heat sink is assumed in all cases.

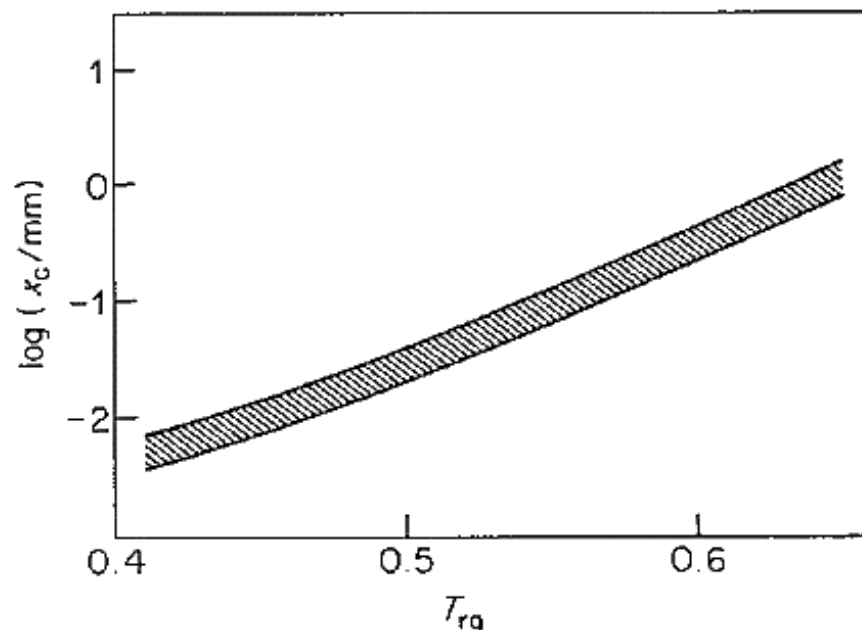


Figure 2.2 Estimated range of maximum section thickness of glass phase as a function of T_{rg} , derived from data in Figure 2.1 for chill block melt spinning.

Also of importance in a casting technique is the duration of contact t_c with the heat sink. Clearly, t_c should be sufficiently large that the temperature of the material being quenched has decreased to close to, or below, T_g before contact is lost. On loss of contact T can decrease catastrophically, depending on the relative velocity of the ambient gas and the section thickness. If t_c is too short either the material will not vitrify or it will devitrify during the low f phase, after removal from the heat sink. The magnitude of t_c can also determine the state of quench of the glass, since a glass that leaves a substrate at higher temperature will tend to undergo more relaxation during the low T phase, down to ambient temperature.

2.5 Conditions to be prepared amorphous materials

In terms of viscosity and diffusion co-efficient we can find the conditions for formation glass.

Metals atomic bonding is metallic and viscosity is lower than the diffusion co-efficient and mobility is high.

In the case of amorphous material viscosity is very high and the mobility and the diffusion co-efficient are low. Atomic bonds tend to be covalent as in the case of silicate (SiO_2)

2.6 Preparation technique of amorphous ribbon

There are various techniques in use to produce a metallic alloy in an amorphous state where the atomic arrangements have no long-range periodicity. The different experimental techniques developed to produce amorphous metallic glass can be classified into two groups.

The atomic deposition methods and
The fast cooling of the melt

2.6.1 The atomic deposition methods

Deposition can be described in terms of whether the added atom is prevented from diffusing more than an atomic distance before it is fixed in position due to cooling and increased viscosity. The atomic deposition methods include condensation of a vapor on a cooled substrate by

Vacuum deposition
Sputter deposition
Electron deposition
Chemical deposition

2.6.2 The fast cooling of the melt

For producing of an amorphous state by any of the liquid quenching devices, the alloy must be cooled through the temperature range from the melting temperature (T_m) to the glass transition temperature (T_g) very fast allowing no time for crystallization. The factors controlling T_g and crystallization are both structural and kinetic. The structural factors are concerned with atomic arrangement, bonding and atomic size effects. The kinetic factors as discussed by Turnbull [5] are the nucleation, crystal growth rate and diffusion rate compared to the cooling rate. The interest in this method stems from the

wide variety of alloys that can be made as well as from the potential low of cost of preparation. In the pioneering work of Duwez et. al. a number of devices has been reported for obtaining the necessary high quenching rates and for producing continuous filaments. The methods using the principle of fast cooling of melt techniques are:

- The gun technique
- Single roller rapid quenching technique
- Double roller rapid quenching technique
- Centrifuge and rotary split quenching technique
- Torsion catapult technique
- Plasma-jet spray technique
- Filamentary casting technique
- Melt extraction technique
- Free jet spinning technique and
- The melt spinning technique

Although the different methods used in preparing amorphous metallic ribbons are mentioned here, only the melt spinning technique which was used to prepare the specimens for the present work will be discussed.

2.6.2.1 The Melt Spinning Technique

The metallic glasses (which were discovered at Caltech in the late 1950s) required very rapid cooling - around one million degrees Celsius per second - to avoid crystallization. One way to do it is by single-roller melt spinning, as shown here:

SINGLE-ROLLER MELT SPINNING

In the melt spinning process, small quantity of the alloy composition is melted in a crucible (usually quartz tube). The molten metal is ejected under pressurization through an orifice and the exiting molten metal is allowed to solidify on a chilled substrate (such as a fast rotating copper wheel). Upon impingement/in contact with the moving substrate, rapid heat extraction occurs and solidification of the metal occurs.

Various parameters such as the alloy composition, melt temperature, exit pressure, nozzle dimension, vacuum conditions, rpm of the rotating wheel influence the size, shape, thickness, and quality of the ribbons. Usually, the outer surface of the wheel is polished to remove surface roughness as the wheel side of the ribbon imitates that of the wheel. Also, the faster the rpm of the wheel, the thinner is the ribbon. The presence of vacuum/inert conditions during melt spinning is also very essential, as ribbons when produced in air atmosphere result in porosity (air side) thus resulting in ribbons of low quality. In most cases, the difference in heat extraction between the wheel side and air side result in inhomogeneous surface characteristics/composition, affecting their surface/mechanical properties. It should be noted that although various composition of melt spun amorphous alloy ribbons/metallic glasses have been produced successfully, the high solidification rates involved (10^5 – 10^6 K s⁻¹) pose a constraint in the dimension (thickness) of the specimens (10–60 μ m in the form of ribbons, wires, pulverized and consolidated powders), and hence on the applicative prospects of these materials. The schematic of the method is shown in **Figure 2.3**.

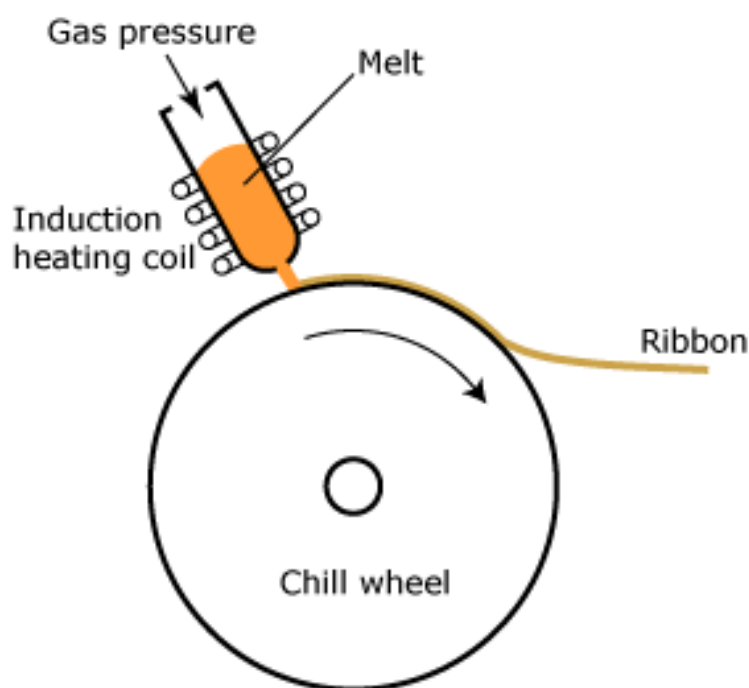


Figure 2.3: Block Diagram for Single Roller Melt Spinning Technique

2.7 Experimental details for the preparation of amorphous ribbon

The metallic glass ribbons are usually prepared in a furnace with an argon atmosphere (0.2 to 0.3 atmps.). The buttons prepared are of about 50 grams each. Care is taken to ensure thorough mixing and homogeneity of the alloy composition, by turning over and re-melting each button few times. The mother alloys, formed in the form of buttons in a furnace by sudden cooling, are then cut into small pieces and is inserted in the quartz tube.

The quartz tube is connected from the top by rubber 'O' rings and metal rings to the argon cylinder through a valve and a pressure gauge. After proper cleaning of the roller surface and adjusting its speed to the desired value, as measured by stroboscope, the induction furnace is powered using high frequency generator. When the melting temperature is reached as observed through a protective spectacle, the injection pressure is applied by opening the pressure valve. To avoid the turbulence of the wind, arising from the high-speed roller in distributing the melt puddle, cotton pad and metallic shield are usually used just beneath the roller. To avoid oxidation of the ribbon during its formation, an inert atmosphere is created around the roller by a slow stream of helium gas. The speed of the roller, the volumetric flow rate while, the orifice diameter, the substance orifice distance, the injection angle etc. are adjusted by trial and error to get the best result in respect of the quality and the geometry of the ribbons. Important factors to control the thickness of ribbons are as follows.

Rotating speed

- (a) Angular velocity. ω 2000rev/min.
- (b) Surface velocity, $v \sim 25\text{m/s}$
- (i) Gap between the nozzle and rotating copper drum is ~ 100 to $150\ \mu\text{m}$
- (ii) Oscillations of the rotating copper drum both static and dynamic have maximum displacement of $\sim 1.5\ \mu\text{m}$
- (iii) Pressure = 0.2 to 0.3 argon atmosphere.
- (iv) Temperature of the metal $T_m \approx 1500^\circ\text{C}$. The temperature should not exceed 1800°C otherwise quartz tube would melt.
- (v) Stability is ensured for the drop to fall on the surface of the spinning drum.

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Chapter Three

Theoretical Perspective

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3.1.1.1 Scanning electron Microscopy

3.1.1.2 Energy dispersive analysis of X- rays (EDAX)

3.1.2 X-ray Diffraction (XRD)

3.1.2.1 Introduction

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3.2.1 Differential thermal analysis (DTA)

3.2.1.1 Introduction

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3.2.1.3 Application of DTA

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3.2.2.2 Description

3.2.2.3 Principle of operation from TGA

3.2.2.4 Application of TGA

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3.3.1 Electrical Resistivity

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Chapter Three

Theoretical Perspective

In this Chapter we describe basic theories which are needed for calculations and the explanation of experimental results. We describe here the theories for Structural properties, Thermal properties, Electrical Resistivity, Magnetoresistance, Magnetization, and AC Permeability.

3.1 Structural Properties

There are several methods for surface morphology and structural characterization of Amorphous ribbons such as Scanning Electron Microscopy (SEM), Energy Dispersive Analysis of X-rays (EDAX) and X-ray Diffraction (XRD)

3.1.1 Surface morphology and Compositional analysis

In this thesis scanning electron microscopy (SEM) method is used to study the surface morphology and EADX is used to study compositional analysis of prepared amorphous ribbons.

3.1.1.1 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, in wet conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures. The most common SEM mode is detection of secondary electrons emitted by atoms excited by the electron beam. The number of secondary electrons that can be detected depends, among other things, on the angle at which beam meets surface of specimen, i.e. on specimen topography. By scanning the sample and

collecting the secondary electrons that are emitted using a special detector, an image displaying the topography of the surface is created.

The types of signals produced by an SEM include secondary electrons (SE), reflected or backscattered electrons (BSE), photons of characteristic X-rays and light (cathode luminescence) (CL), absorbed current (specimen current) and transmitted electrons. Secondary electron detectors are standard equipment in all SEMs, but it is rare that a single machine would have detectors for all other possible signals. The signals result from interactions of the electron beam with atoms at various depths within the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the secondary electrons are emitted from very close to the specimen surface. Consequently, SEM can produce very higher resolution images of a sample surface, revealing details less than 1 nm in size. Backscattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. They emerge from deeper locations within the specimen and consequently the resolution of BSE images is generally poorer than SE images. However, BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays, because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen. BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immune labels of 5 or 10 nm diameter, which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown above. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful handlens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapor pressure of all metals, thereby allowing it to be electrically heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB₆) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded or field emission guns (FEG), which may be of the cold cathode type using tungsten single crystal emitters or the thermally assisted Schottky type, that use emitters of zirconium oxide. The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to approximately 5 μm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a computer monitor (or, for vintage models, on a cathode ray tube).

Each pixel of computer video memory is synchronized with the position of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. In older microscopes images may be captured by photography from a higher resolution

cathode ray tube, but in modern machines they are digitised and saved as digital images. Schematic diagram of an SEM is shown in **Figure 3.1**

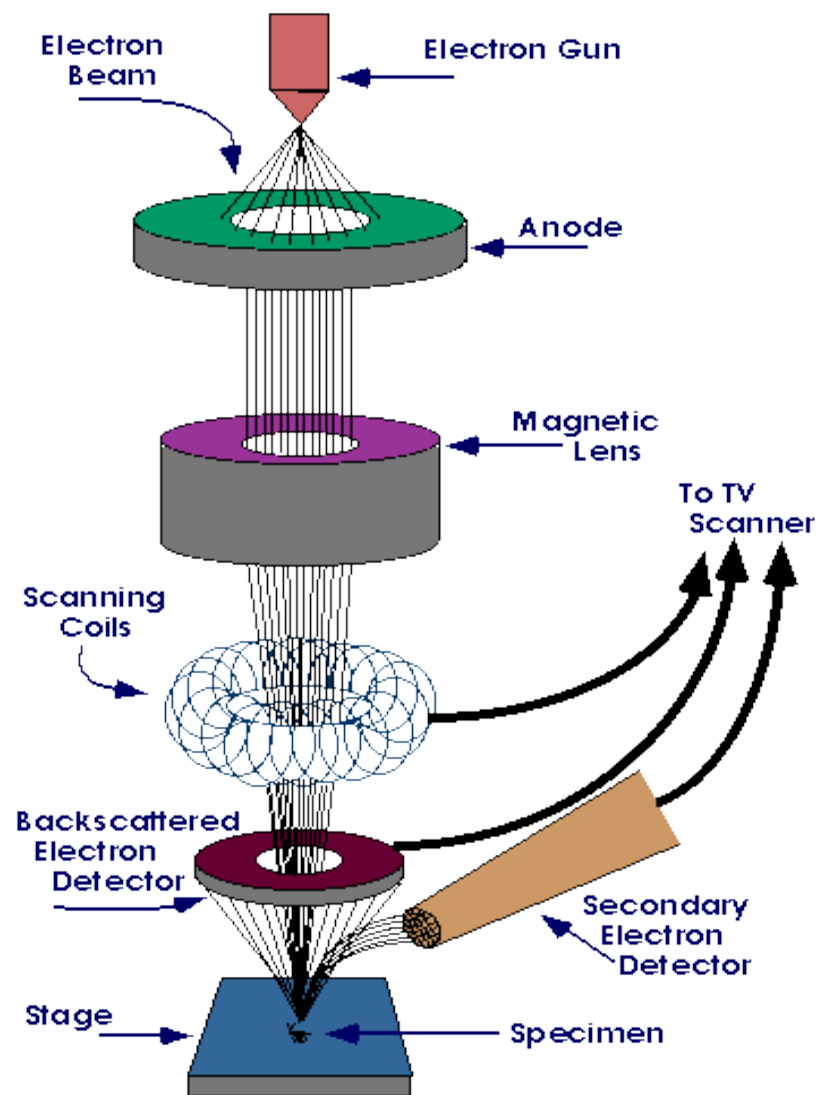


Fig 3.1 Schematic diagram of an SEM.

3.1.1.2 Energy Dispersive Analysis of X-rays (EDAX)

In x-ray energy-dispersive spectroscopy (XEDS), the dispersive device is a semiconductor diode, fabricated from a single crystal of silicon (or germanium) and somewhat similar to the BSE detector in an SEM. If an X-ray photon enters and penetrates to the transition region (between p- and n doped material), its energy can release a considerable number of outer-shell (valence) electrons from the confinement of a particular atomic nucleus. This process is equivalent to exciting electrons from the valence to the conduction band (i.e., the creation of electron-hole pairs) and results in electrical conduction by both electrons and holes for a brief period of time. With a reverse-bias voltage applied to the diode, this conduction causes electrical charge to flow through the junction (and around an external circuit), the charge being proportional to the number N of electron-hole pairs generated.

Assuming that all of the photon energy (hf) goes into creating electron-hole (e-h) pairs, each pair requiring an average energy ΔE , energy conservation implies:

$$N = hf / \Delta E$$

For silicon, $\Delta E \approx 4 \text{ eV}$ (just over *twice* the energy gap between valence and conduction bands), therefore a Cu-K α photon creates about $(8000\text{eV}) / (4\text{eV}) = 2000$ e-h pairs.

To ensure that essentially *all* of the incoming x-rays are absorbed and generate current pulses in an external circuit, the p-n transition region is made much *wider* than in most semiconductor diodes. In the case of silicon, this can be done by diffusing in the element lithium ($Z = 3$), which annihilates the effect of other electrically-active (dopant) impurities and creates a high-resistivity (intrinsic) region several mm in width; see **Figure 3.2** If the semiconductor diode were operated at room temperature, *thermal* generation of electron-hole pairs would contribute too much electronic noise to the x-ray spectrum. Therefore the diode is cooled to about 140 K, via a metal rod that has good thermal contact with an insulated (Dewar) vessel containing liquid nitrogen at 77 K. To prevent water vapor and hydrocarbon molecules (present at low concentration in an SEM or TEM vacuum) from condensing onto the cooled diode, a thin protective window precedes the diode; see **Figure3.2** Originally this window was

a thin ($\approx 8 \mu\text{m}$) layer of beryllium, which because of its low atomic number ($Z = 4$) transmits most X-rays without absorption. More recently, ultra-thin windows (also of low- Z materials, such as diamond or boron nitride) are used to minimize the absorption of low-energy ($< 1 \text{ keV}$) photons and allow the XEDS system to analyze elements of low atomic number ($Z < 12$) via their K-emission peaks. The analysis represents the individual weight (%) of the element that is present in the amorphous ribbons.

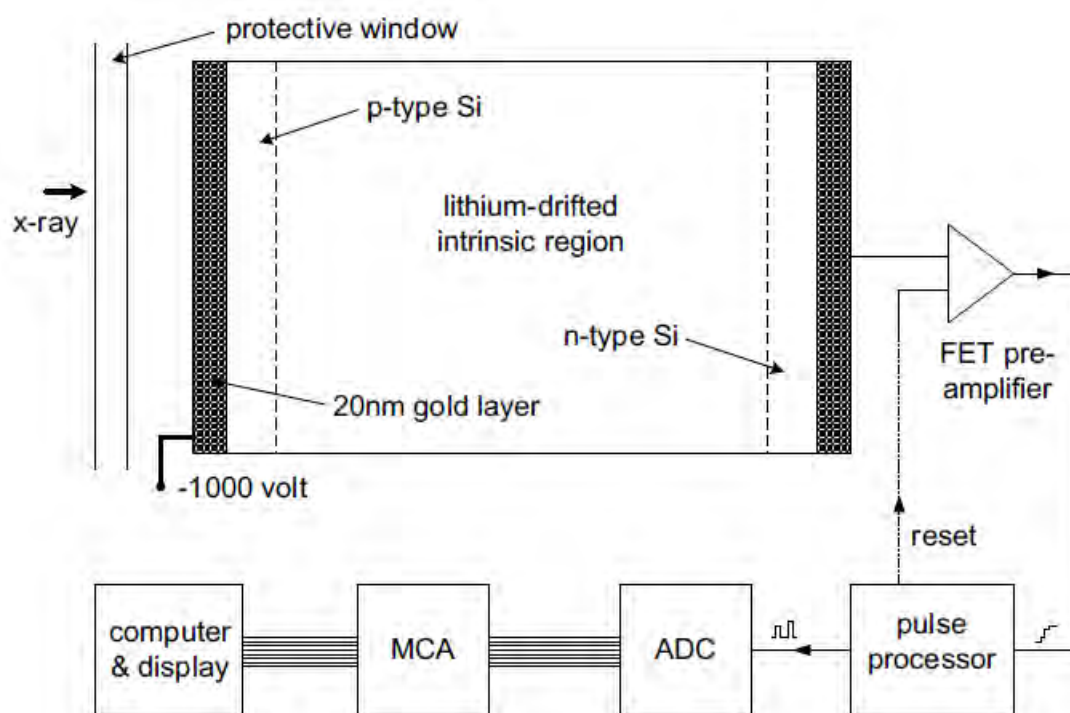


Figure 3.2 Schematic diagram of a XEDS detector and its signal-processing circuitry.

3.1.2 X-ray Diffraction (XRD)

3.1.2.1 Introduction

X-ray diffraction (*XRD analysis or XRPD analysis*) is a unique method in determination of crystallinity of a compound. XRD is primarily used for identification of crystalline material and different polymorphic forms. Distinguishing between amorphous and crystalline material. Quantification of the percent crystallinity of a sample.

3.1.2.2 Basic theory of (X-ray) diffraction

Any radiation striking a material is both scattered and absorbed. Scattering is most easily approached by thinking of a plane wave. This is formally defined as one whose phase is constant over any plane normal to its direction of travel, its wave front is a plane. It is more easily thought of as a point source of waves at an infinite distance; a perfectly collimated wave. When such a wave strikes a three-dimensional atomic lattice, each scattering point (electron or nuclear particle) acts as a source of spherical waves, whose wave fronts lie on spheres centred on the scattering points. The addition of the amplitudes of all these waves in given directions results in almost zero intensity in most directions but strong beams in some directions if the wave-lengths of the wave are comparable with the spacing of the scattering centres. This is the phenomenon of diffraction.

The simplest and most useful description of crystal diffraction is still that obtained by Bragg [1]. Strong diffraction occurs when all the wavelets add up in phase. By considering an entire crystal plane as the scattering entity, rather than each individual electron, it is easy to see from Fig 3.3 that strong diffraction results when

$$n\lambda = 2d \sin \theta$$

where n is an integer representing the order of diffraction, λ is the wavelength, d the interplanar spacing of the reflecting (diffracting) plane and θ is the angle of incidence and of diffraction of the radiation relative to the reflecting plane. The requirement for the angle of incidence to equal that of diffraction is not seen directly from Fig 3.3, but arises from the incorporation of scattering from many planes normal to the surface. A small number of planes give a very broad peak, and large numbers of planes a narrow

peak, converging to a value characteristic of a thick crystal. Thus, diffraction for a given plane and wavelength does not take place over the zero angular range defined by the Bragg law, but over a small finite range. This range, called the rocking curve width,

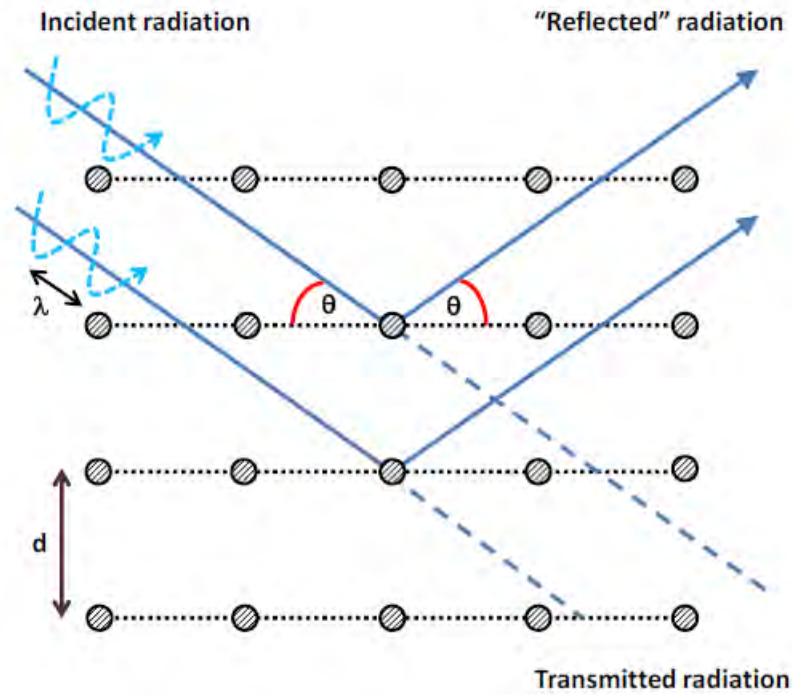


Figure 3.3 Diffraction of a plane wave off successive crystal planes.

Strong diffraction results when the angles of incidence and diffraction, are equal and the path difference between the two beams is equal to n , an integral number of wavelengths. Hence the Bragg law, $n\lambda = 2d \sin \theta$ varies tremendously and it governs the strain sensitivity of the technique.

Any radiation is also absorbed to a greater or lesser extent by a material. This is well described by the usual absorption equation:

$$I/I_0 = \exp\{-\mu t\}$$

where I is the transmitted and I_0 the incident intensity, μ is the linear absorption coefficient and t the specimen thickness in the direction of the X-ray beam.

The intensities of diffracted beams, or reflections as they are commonly called, depend upon the strength of the scattering that the material inflicts upon the radiation. Electrons are scattered strongly, neutrons weakly and X-rays moderately. The basic scattering unit of a crystal is its unit cell, and we may calculate the scattering at any angle by multiplying the scattering strength of an electron or nucleus, the scattering strength of an atom, the scattering strength of a unit cell, the scattering strength of the total number of unit cells all with regard to the direction of scattering and the relative phase of the scattered waves.

3.2 Thermal Properties

3.2.1 Differential Thermal Analysis (DTA)

3.2.1.1 Introduction

Differential thermal analysis (or DTA) is a thermo analytic technique. Similar to differential scanning calorimetry. In DTA, the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between samples and reference [2]. This differential temperature is then plotted against time, or against temperature (DTA curve, or thermogram). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak is the enthalpy change and is not affected by the heat capacity of the sample.

3.2.1.2 Description of DTA

A technique in which the difference in temperature between the sample and a reference sample (ΔT_{SR}) is monitored against time while the samples are exposed to a temperature programme [3].

The instrument is a differential thermal analyser shown on **Figure 3.4** and the record is the differential thermal or DTA curve shown on **Figure 3.4**. The temperature difference (ΔT) should be plotted on the ordinate with endothermic reactions downwards and t or T increasing from left to right.

The first recommendations [4] clarified the terminology to be used, such as the sample, reference material, block and differential thermocouple. It is stated that "in DTA it must be remembered that, although the ordinate is conventionally labelled ΔT the output from the thermocouple will in most instances vary with temperature and the measurement recorded is normally the e.m.f. output, E , i.e. the conversion factor, b in the equation

$$\Delta T = bE$$

is not constant since $b = f(T)$, and that a similar situation occurs with other sensor systems".

There should be clear distinction between different instrumental conditions and experimental regimes. The International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommendations [5] specify that the nature, history and size of the sample, the geometry of the system, and sample holder, the temperature program used, the gaseous atmosphere and flow rate, and the type, sensitivity and placement of the sensors, as well as the design of the sample holder should ideally be given. It has already been pointed out that the methods of data collection and processing also need to be described carefully.

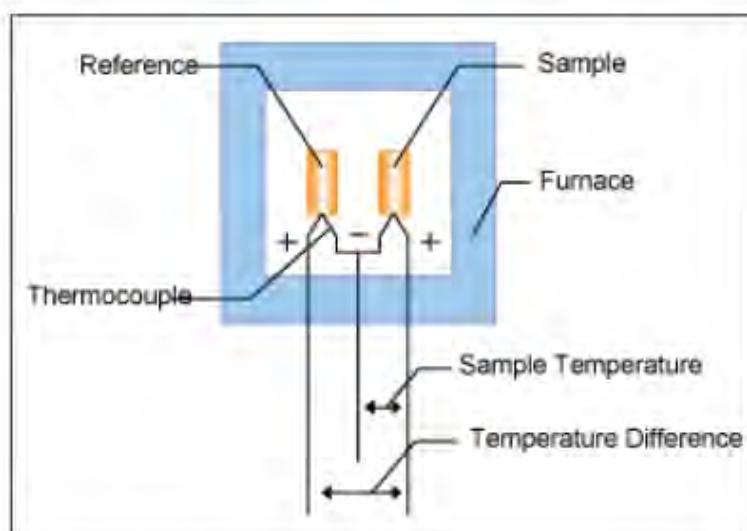


Figure 3.4 Block diagram of DTA.

The sample and the reference are placed symmetrically in the furnace. The furnace is controlled under a temperature program and the temperature of the sample and the reference are changed. During this process, a differential thermocouple is set up to detect the temperature difference between the sample and the reference. Also, the sample temperature is detected from the thermocouple on the sample side.

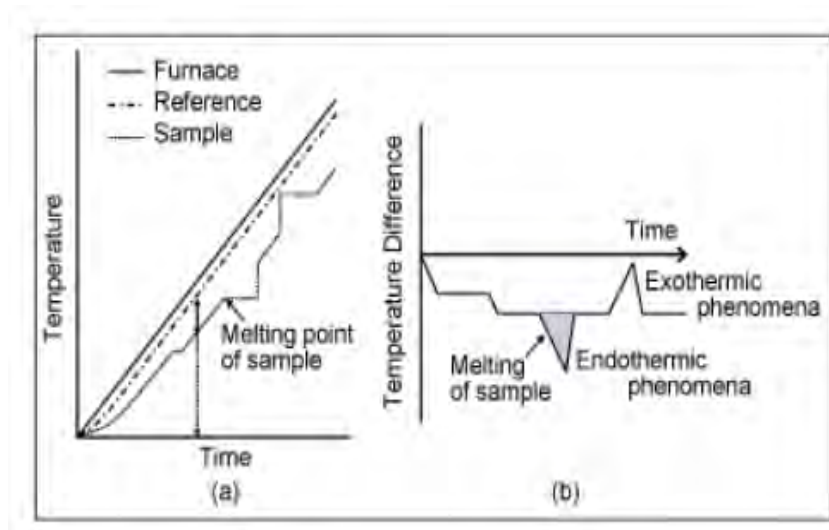


Figure 3.5 Measurement principle of DTA

Graph (a) shows the temperature change of the furnace, the reference and the sample against time.

Graph (b) shows the change in temperature difference (ΔT) against time detected with the differential thermocouple.

Matters that do not change in the measurement temperature range (usually α alumina) are used as reference.

When the furnace heating begins, the reference and the sample begin heating with a slight delay depending on their respective heat capacity, and eventually heat up in according to the furnace temperature.

ΔT changes until a static state is reached after the heating begins, and after achieving stability, reaches a set amount compliant with the difference in heat capacity between the sample and the reference. The signal at the static state is known as the baseline.

When the temperature rises and melting occurs in the sample, for example, the temperature rise stops as shown in graph (a) and the ΔT increases. When the melting ends, the temperature curve rapidly reverts to the baseline.

At this point, the ΔT signal reaches the peak, as shown in graph (b).

From this, we can detect the sample vs transition temperature and the reaction temperature from the ΔT signal (DTA signal).

In graph (b), the temperature difference due to the sample vs endothermic change is shown as a negative direction and the temperature difference due to the sample vs exothermic change is shown as a positive direction.

3.2.1.3 Application

A DTA curve can be used only as a finger print for identification purposes but usually the applications of this method are the determination of phase diagrams, heat change measurements and decomposition in various atmospheres.

DTA is widely used in the pharmaceutical and food industries.

DTA may be used in cement chemistry, mineralogical research and in environmental studies.

DTA curves may also be used to date bone remains or to study archaeological materials.

Using DTA one can obtain liquidus & solidus lines of phase diagrams.

3.2.2 Thermogravimetric analysis (TGA)

3.2.2.1 Introduction

Thermogravimetric analysis (TGA) is a thermal analysis technique which measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. TGA measurements are used primarily to determine the composition of materials and to predict their thermal stability up to elevated temperatures.

However, with proper experimental procedures, additional information about the kinetics of decomposition and in-use lifetime predictions can be obtained.

Traditionally, isothermal and constant heating rate thermogravimetric analysis have been used to obtain kinetic information with the constant heating rate method developed by Flynn and Wall [7] being preferred because it requires less experimental time. However, the Flynn and Wall method is limited to well-resolved single step

decompositions and first order kinetics. High resolution TGA [8], a new approach developed and patented by TA Instruments, provides an alternative not only for improving the separation (resolution) of overlapping decomposition peaks, but also provides a means for determining the kinetic parameters for more complex decompositions. High-resolution TGA is based on varying (slowing) the heating rate during decomposition regions and consists of a collection of heating algorithms which employ both historical algorithms namely, constant reaction rate [9] and stepwise isothermal [10], as well as a novel method, dynamic heating rate [8]. This paper explores the theory behind extracting kinetic parameters from each approach as well as illustrate where each approach provides maximum benefit.

3.2.2.2 Description

Thermogravimetric analysis (TGA) relies on a high degree of precision in three measurements: mass change, temperature, and temperature change. Therefore, the basic instrumental requirements for TGA are a precision balance with a pan loaded with the sample, and a programmable furnace. The furnace can be programmed either for a constant heating rate, or for heating to acquire a constant mass loss with time.

Though a constant heating rate is more common, a constant mass loss rate can illuminate specific reaction kinetics. For example, the kinetic parameters of the carbonization of polyvinyl butyral were found using a constant mass loss rate of 0.2wt % min [11-13]. Regardless of the furnace programming, the sample is placed in a small, electrically heated furnace equipped with a thermocouple to monitor accurate measurements of the temperature by comparing its voltage output with that of the voltage-versus-temperature table stored in the computer's memory. A reference sample may be placed on another balance in a separate chamber. The atmosphere in the sample chamber may be purged with an inert gas to prevent oxidation or other undesired reactions. A different process using a quartz crystal microbalance has been devised for measuring smaller samples on the order of a microgram (versus milligram with conventional TGA).

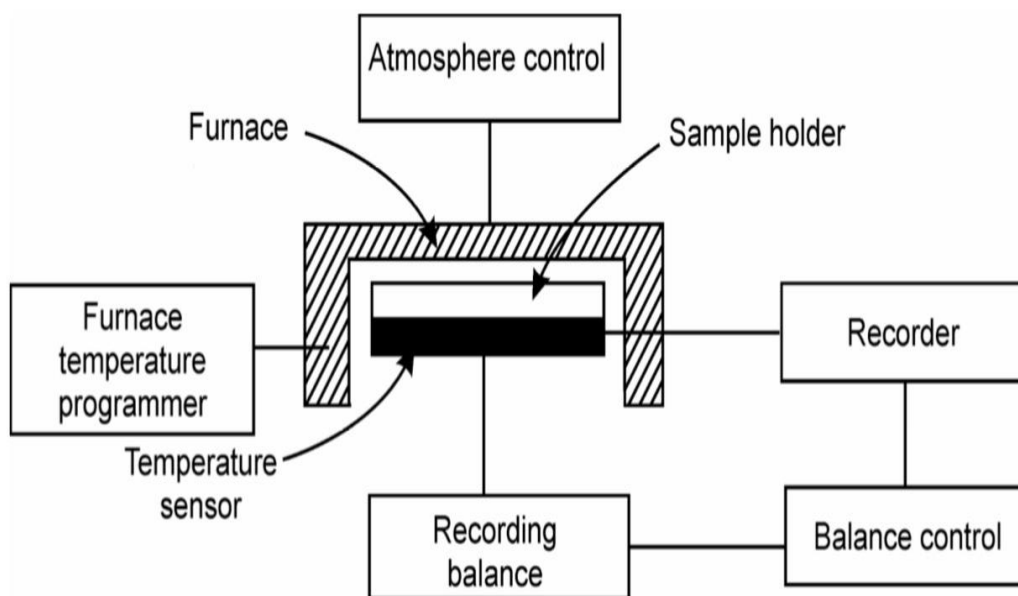


Figure 3.6 Block Diagram of TGA

3.2.2.3 Principle of Operation from Thermogravimetric Analysis (TGA)

A TGA analysis is performed by gradually raising the temperature of a sample in a furnace as its weight is measured on an analytical balance that remains outside of the furnace. In TGA, mass loss is observed if a thermal event involves loss of a volatile component. Chemical reactions, such as combustion, involve mass losses, whereas physical changes, such as melting, do not. The weight of the sample is plotted against temperature or time to illustrate thermal transitions in the material – such as loss of solvent and plasticizers in polymers, water of hydration in inorganic materials, and, finally, decomposition of the material.

3.2.2.4 Application from Thermogravimetric Analysis (TGA)

Principle uses of TGA include measurement of a material's thermal stability and its composition. Typical applications include:

- Filler content of polymer resins
- Residual solvent content
- Carbon black content
- Decomposition temperature
- Moisture content of organic and inorganic materials
- Plasticizer content of polymers
- Oxidative stability
- Performance of stabilizers
- Low molecular weight monomers in polymers

3.3 Transport Properties

3.3.1 Electrical resistivity

The law of electrical conduction in metals is obtained from Ohm's law which is given by

$$I = \frac{V}{R} \quad 3.1$$

Where, I is the current, V is the potential difference, and R is the resistance. From laws of resistance, we have

$$R = \rho \frac{L}{A} \quad 3.2$$

Where ρ is the resistivity that is the characteristic property of a metal, L is the length and A is the cross-sectional area of the material under test (MUT). Again by the definition of electric field, we know that the electric field, E is

$$E = \frac{V}{L} \quad 3.3$$

Now putting the values from equation- 3.2 and 3.3 into equation- 3.1, we get

$$I = \frac{EA}{\rho} \quad 3.4$$

In general the current density is defined, as the current per unit cross-sectional area of the specimen, hence, the current density using equation-3.4, will be as:

$$J = \frac{I}{A} = \frac{E}{\rho} = \sigma E \quad 3.5$$

Equation-3.5 is another form of Ohm's law, where σ is the electrical conductivity, which is again the inverse of resistivity ρ . Since the dimension of resistivity is ohm-m, so the conductivity σ has dimension $(ohm - m)^{-1}$.

Now we want to express σ in terms of the microscopic properties pertaining to the conduction electrons. These conduction electrons are responsible for the current flow under the influence of electric field because the ions are attached to and vibrate about their lattice sites. They have no net translation motion, and hence do not contribute to the current. For the purpose, let us now treat the motion of the conduction electron in an electric field. In this regard we consider one typical electron: The field exerts a force $-eE$ on the electron. There is also a frictional force due to collision of the form $-m^* \frac{v}{\tau}$, v is the velocity of the electron and τ is a constant called the collision time.

Using Newton's law of motion, we have

$$m^* \frac{dv}{dt} = -eE - m^* \frac{v}{\tau} \quad 3.6$$

Where m^* is the effective mass of electron. We see that the effect of the collision as usual in friction or viscous forces tends to reduce the velocity to zero. If we consider the steady-state condition for our purpose, then after putting $dv/dt \sim 0$, the appropriate solution of equation- 3.6 will be as:

$$v = \frac{e\tau}{m^*} E \quad 3.7$$

This is the steady-state velocity of the electron, which is also known as terminal velocity that arises from the friction. It is opposite to the electric field, E because the charge of electron is negative. When a field is applied to a metallic wire/or material under test, there will be two different velocities associated with the electron. The velocity appearing in equation-3.7 is called the drift velocity. This is superimposed on a much higher velocity or speed, known as the random velocity that arises from the random motion of electron like gas even in the absence of electric field. This is due to the fact that the electrons move about and occasionally scatter and change direction. This random motion contributes zero current and also exists in the presence of electric field, but in that case, there is an additional net velocity opposite to the field, as given by equation- 3.7 v_d and v , denote these two velocities for distinction. Now the current

density can be calculated from equation-3.7. Since there is a charge $(-Ne)$ per unit volume, and since each electron has a drift velocity given by equation-3.7, it follows that the amount of charge crossing per unit area per unit time is

$$J = -(Ne) \left(-\frac{e\tau}{m^*} E \right) = \frac{Ne^2\tau}{m^*} E \quad 3.8$$

This current is parallel to the electric field. E . Now comparing equation-3.5 and equation-3.8, we get the expression for the conductivity as:

$$\sigma = \frac{Ne^2\tau}{m^*} \quad 3.9$$

From equation-3.9, it is seen that σ increases as N increases. This is reasonable because N , the concentration, increases; there are more current carriers. The conductivity σ is inversely proportional to m^* which is also expected, since the larger m is, the more sluggish the particle, and harder it is for move. The proportionality to τ follows because τ is actually the time between two consecutive collisions, i.e. the mean free life time. Therefore the larger τ is, the more time the electron has to be accelerated by the field between collisions, and hence the large the drift velocity (equation-3.7), and also the larger

σ is. The time τ is also called the relaxation time. To see the reason for this naming, let us apply an electric field to the material long enough for a drift velocity $v_d(0)$ to be established. Now let the field is suddenly removed at some instant. The drift velocity after this instant is governed by the following relation with $E=0$ as:

$$m^* \frac{dv}{dt} = -eE - m^* \frac{v}{\tau} = -m^* \frac{v}{\tau} \quad 3.10$$

The solution appropriate to the initial condition is now,

$$v_d(t) = v_d(0) e^{-\frac{t}{\tau}} \quad 3.11$$

Since t is the time between two successive collisions, it may be expressed as:

$$\tau = \frac{l}{v_r} \quad 3.12$$

Where l is the distance between two successive collisions and v_r is the random velocity. In terms of these σ becomes:

$$\sigma = \frac{ne^2l}{m^*v_r} \quad 3.13$$

Let us now discuss the origin of collision time. It seems natural to assume that the frictional force is caused by the collision of electrons with ions. According to this particular model of collision, an electron, as it moves in the lattice, collides with ions, which has the effect of slowing down the electrons momentum. This model turns out to be untenable because it leads to many points of disagreement with experiment. To cite only one: the mean free path l can be calculated from equation- 3.12. If we substitute the values $\tau \cong 10^{-14} \text{ s}$, $v_r = 10^6 \text{ ms}^{-1}$ we find that $l = 10^2 \text{ \AA}$. This means that, between two collisions, the electron travels a distance of more than 20 times the inter-atomic distance, which one, would expect. But in closed-packed structures, in which atoms are densely packed, it is difficult to see how the electrons could travel so far between collisions. This paradox can only be explained by the use of quantum concept. According to quantum mechanics, an electron has a wave character. The De-Broglie relation gives this wavelength in the lattice:

$$\lambda = \frac{h}{m^*v_r} \quad 3.14$$

It is well known from the theory of wave propagation in discrete structures that, when a wave passes through a periodic lattice, it continues propagating indefinitely "without scattering. The effect of atoms in the lattice is to absorb energy from the wave and radiate it back, so that the net result is that the wave continues without modification in either direction or intensity. The velocity of propagation, however, is modified. This is what happens in the case of an electron wave in a regular lattice, except that in this case we are dealing with a matter wave

3.3.2 Magnetoresistance

The magnetoresistance refers to the change in electrical resistance of a specimen in response to the magnetic field applied to the specimen externally. The resistance change occurs with the magnetic field when the field is sufficient enough to change the orientation of the electrons of the atoms. In that case the path of the electron becomes curved and do not go exactly in the direction of the superimposed electric field. The change of orientation of the atomic electrons occurs such that the conduction electron find more mean free path with less number of collision with the atomic ions and the atomic electrons, then the resistance decreases otherwise it increases or remain constant. When the resistance of a material changes with the application of the magnetic field then the material is said to have the magnetoresistance. The magnetoresistance usually expressed in percentage and is calculated by the following way

$$MR\% = \frac{R(H) - R(O)}{R(O)} \times 100\% \quad 3.15$$

Where, R(H) is the resistance in presence of magnetic field and R(O) is the resistance in absence of magnetic field.

All metals show some MR, but up to only a few percent. Nonmagnetic metals such as Au, exhibits small MR, but the magnitude is somewhat greater (up to 15%) in ferromagnetic metals such as Fe and Co. The semimetal Bi also shows ~18% MR in a transverse field of 0.6T which rises to a 40fold change at 24T Cu is more typical in the same very powerful field (24T) gives rise to change of only ~2% at room temperature. This is the classical positive magnetoresistance that varies as, B^2 (B=applied magnetic field) in half metallic ferromagnets such as CrO_2 , Fe_2O_4 at low temperature. It is absent in the free electron gas but appears when the Fermi surface is non spherical. This MR originates from the impact of the Lorentz force on the moving charge carriers similar to the Hall Effect. Its value is ~10% at 10T. A classification of magnetoresistance phenomenon is based on the distinction familiar in magnetism between intrinsic composition and purity and extrinsic properties on the sample.

The phenomenology of the magnetoresistance effect is similar to that of magnetostriction. This effect can be classified into two categories: one is the part, which depends on the intensity of spontaneous magnetization that corresponds to the volume magnetostriction.

The second is that change caused by the rotation of spontaneous magnetization, which corresponds to the usual magnetostriction. Mott interpreted this phenomenon in terms of the scattering probability of the conduction electrons into 3d holes. If the substance is in a ferromagnetic state, half of the 3d shell is filled up, so that the scattering of 4s electrons into the plus state of 3d shell is forbidden. This scattering is however, permitted in a nonmagnetic state in which both the plus spin state and the minus spin state of the upper 3d levels are vacant, Mott explained the temperature variation of resistivity fairly well by this model. Kasuya interpreted this phenomenon from a standpoint quite different from Mott theory. He considered that d electrons are localized at the lattice points and interact with the conduction electrons through the exchange interaction. At 0 K the potential for the conduction electron is periodic, because the spin of 3d electrons of all the lattice points is in the same direction. At finite temperature, spins of 3d electrons are thermally agitated and the thermal motion may break the periodicity of the potential. The 4s electrons are scattered by an irregularity of the periodic potential which results in additional resistivity. Kasuya postulated that the temperature dependence of the resistivity of ferromagnetic metal is composed of a monotonically increasing part due to lattice vibration and an anomalous part due to magnetic scattering, the magnitude of the latter being explained by this theory. The effect of high temperature has been treated in two different approaches. The first approach is given by Harris *et al.* considers a constant exchange interaction between magnetic atoms and a random distribution of the local anisotropy field is considered which changes with temperature. The other approach is to consider a distribution of exchange integral is assumed in order to take into account the fluctuation in the amorphous alloys as taken by Handrich. Both the approaches are unrealistic and in fact no rigorous theory of the high temperature behavior for amorphous material has been developed. We have determined the experimental power law from the temperature variation of magnetization in the high temperature range.

3.4 Magnetic Properties

3.4.1 Magnetization

3.4.1.1 Introduction

In classical electromagnetism, magnetization (magnetisation in British English) or magnetic polarization is the vector field that expresses the density of permanent or induced magnetic dipole moments in a magnetic material. The origin of the magnetic moments responsible for magnetization can be either microscopic electric currents resulting from the motion of electrons in atoms, or the spin of the electrons or the nuclei. Net magnetization results from the response of a material to an external magnetic field, together with any unbalanced magnetic dipole moments that may be inherent in the material itself; for example, in ferromagnets. Magnetization is not always uniform within a body, but rather varies between different points. Magnetization also describes how a material responds to an applied magnetic field as well as the way the material changes the magnetic field, and can be used to calculate the forces that result from those interactions.

The magnetization (M) is defined as the magnetic moment per unit volume or mass of the specimen [16]

i.e.

$$M = \frac{m}{Volume} \text{ Or } M = \frac{m}{mass}$$

In the present thesis magnetization has been determined by using a Vibrating Sample Magnetometer (VSM) at room temperature with covering a wide range of magnetic field.

3.4.1.2 Saturation magnetization

If a material has n elementary atomic magnetic dipoles per unit volume each of magnetic moment m then the magnetic moment per unit volume of the material when all these moments are aligned parallel is termed the saturation magnetization. This is equal to the product of n and m . A distinction can be made between technical saturation M_s and complete saturation M_0 . In order to fully understand this distinction a discussion of domain processes must first be presented. At this stage we shall merely note that technical saturation magnetization is achieved when a material is converted to a single magnetic domain, but at higher fields the magnetization increases very slowly beyond technical saturation. This slow increase of magnetization at high fields is due to an increase in the spontaneous magnetization within a single domain known as forced magnetization.

3.4.1.3 Magnetic Hysteresis

Hysteresis is at the heart of the behavior of magnetic materials. All applications, from electric motors to transformers and permanent magnets, from various types of electronic devices to magnetic recording, rely heavily on particular aspects of hysteresis.

Hysteresis loop may take many different shapes and it is important to list a few parameters that give some prime characteristics of loop properties.

A hysteresis loop can be represented in terms of $B(H)$ or $M(H)$. The relation between magnetization and induction is $B = \mu_0(H + M)$. In a soft material the fields involved in the hysteresis loop are much smaller than the corresponding magnetization values, so that to a very good approximation $B \cong \mu_0 M$ and $B(H)$ or $M(H)$ makes a tiny difference that can be safely neglected. Conversely in hard materials H and M have comparable orders of magnitude and the $B(H)$ loop is significantly differently from the $M(H)$. For example there are two possible definitions for the coercive field, depending on whether one considers the point where the induction or the magnetization is reduced to zero. The $M(H)$ loop better reflects the intrinsic properties of the magnet but the $B(H)$ loop gives a more useful description of the system behavior

under working condition. For instance, the maximum energy product previously mentioned is directly related to the $B(H)$ loop.

Two quantities of particular importance in this respect are the remanant magnetization or remanance, M_r and coercive field H_c

Remanance This represents the magnetization obtained after applying a large field to the specimen and then removing it. It is the natural quantity expressing the fact that a ferromagnet can be spontaneously magnetized, even in the absence of external actions. The order of magnitude of M_r is that of the spontaneous magnetization M_s , but various geometrical or structural features may contribute to decreasing M_r well below M_s .

Coercive field. This is the field needed to bring the magnetization from the remnant value to zero. The coercive field measures the order of magnitude of the fields that must be applied to a material in order to reverse its magnetization. Unlike remanance, the coercive field spans an astonishingly wide interval, from less than 1 Am^{-1} to more than 10^6 Am^{-1} .

3.4.2 AC Permeability

The primary requirement is the highest possible permeability, together with low losses in the frequency range of interest. The initial permeability μ_i is defined as the derivative of induction B with respect to the initial field H in the demagnetization state.

$$\mu_i = \frac{dB}{dH}, \quad H \rightarrow 0, \quad B \rightarrow 0 \quad 3.15$$

At microwave frequencies and also in low an isotropic amorphous materials. dB and dH may be in different directions, the permeability then has a tensor character. In the case of amorphous material containing a large number of randomly oriented magnetic atoms the permeability will be scalar. As we have

$$B = \mu_0(H + M) \quad 3.16$$

And susceptibility

$$\chi = \frac{dM}{dH} = \frac{d}{dH} \frac{1}{\mu_0} (B - H) = \frac{1}{\mu_0} (\mu - 1) \quad 3.17$$

The magnetic energy density

$$E = \frac{1}{\mu_0} \int \vec{H} \cdot d\vec{B} \quad 3.18$$

For time harmonic fields $\mathbf{H} = H \sin \omega t$, the dissipation can be described by a phase difference δ between H and B. In the case of permeability, defined as the proportional constant between the magnetic field intensity B and applied magnetic field intensity H

$$B = \mu H \quad 3.19$$

This naive definition needs further sophistication. If a magnetic material is subjected to an ac magnetic field as we get,

$$H = H_0 e^{i\omega t} \quad 3.20$$

Then it is observed that the magnetic flux density experiences a delay. This is caused due to the presence of various losses and is thus expressed as

$$B = B_0 e^{i(\omega t - \delta)} \quad 3.21$$

Where δ the phase is angle and marks the delay of B with respect to H. The permeability is then given by

$$\begin{aligned} \mu &= \frac{B}{H} \\ &= \frac{B_0 e^{i(\omega t - \delta)}}{H_0 e^{i\omega t}} \\ &= \frac{B_0 e^{-i\delta}}{H_0} \\ &= \frac{B_0}{H_0} \cos \delta - i \frac{B_0}{H_0} \sin \delta \\ &= \mu' - i\mu'' \end{aligned} \quad 3.22$$

$$\text{Where,} \quad \mu' = \frac{B_0}{H_0} \cos \delta \quad 3.23$$

$$\text{and } \mu'' = \frac{B_0}{H_0} \sin \delta \quad 3.24$$

The real part μ' of complex permeability μ as expressed as equation 3.22 represents the component of B which is in phase with H, so it corresponds to the normal permeability. If there no losses we should have $\mu = \mu'$. The imaginary part μ'' corresponds to that part of B which is delayed by phase angle from H. The presence of such a component requires a supply of energy to maintain the alternating magnetization regardless of the origin of delay. It is useful to introduce the loss factor or loss tangent ($\tan \delta$). The ratio of μ'' to μ' as is evident from equation gives.

$$\frac{\mu''}{\mu'} = \frac{\frac{B_0}{H_0} \sin \delta}{\frac{B_0}{H_0} \cos \delta} = \tan \delta \quad 3.25$$

The Q-factor or quality factor defined as the reciprocal of this loss factor, i.e.

$$Q = \frac{1}{\tan \delta}$$

The behavior of μ' and μ'' versus frequency is called the permeability spectrum.

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Chapter Four

Experimental techniques

4.1 Examining Properties

4.2 XRD

4.3 SEM

4.4 DTA and TGA

4.5 Resistivity Measurement Technique

4.6 Magnetoresistance Measurement Technique

4.7 Magnetization Measurement Technique

4.7.1 Vibrating Sample Magnetometer (VSM)

4.7.2 Calibration of the V.S.M.

4.8 Permeability Measurement

Chapter Four

Experimental techniques

4.1 Examining properties

The structural property of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ ribbon shaped samples have been investigated through X-ray diffraction (XRD) technique. The transport properties have been investigated through measurements of electrical resistivity, temperature dependence resistivity, and magnetoresistance of the material. The magnetic properties, AC permeability and thermal property was carried out by DTA and TGA measurements.

4.2 XRD

The X-ray diffraction was done in a commercial X-ray Diffractometer (EMPYREAN, Company: PANanalytical) at the Glass and Ceramic Engineering Department of the Bangladesh University of Engineering and Technology (BUET).

4.3 SEM

The surface morphology was examined in a commercial SEM (JEOL JSM 7600F) at the Glass and Ceramic Engineering Department of the Bangladesh University of Engineering and Technology (BUET).

4.4 DTA and TGA

The crystallization temperature was investigated in a commercial DTA and TGA (TG/DTA 6300) from BCSIR, Dhaka-1000

4.5 Resistivity Measurement:

There are various types of electrical methods for resistivity/conductivity measurements. The technique, that has been used here to measure temperature dependent resistivity of the Metallic glass ribbon by conventional 4-probe technique using following equation,

$$\rho = R \frac{A}{L}$$

Where A and L are the cross-sectional area and the length or thickness of the specimen between the electrodes respectively. And $R = \frac{V}{I}$ is the resistance of the investigated samples, V is the potential difference between two electrodes shown on **Figure 4.1** and I is the constant current. **Figure 4.2** shows schematic diagram of home build temperature controlling sample chamber on vacuum system. **Figure 4.3** shows the device arrangement for resistivity measurement.

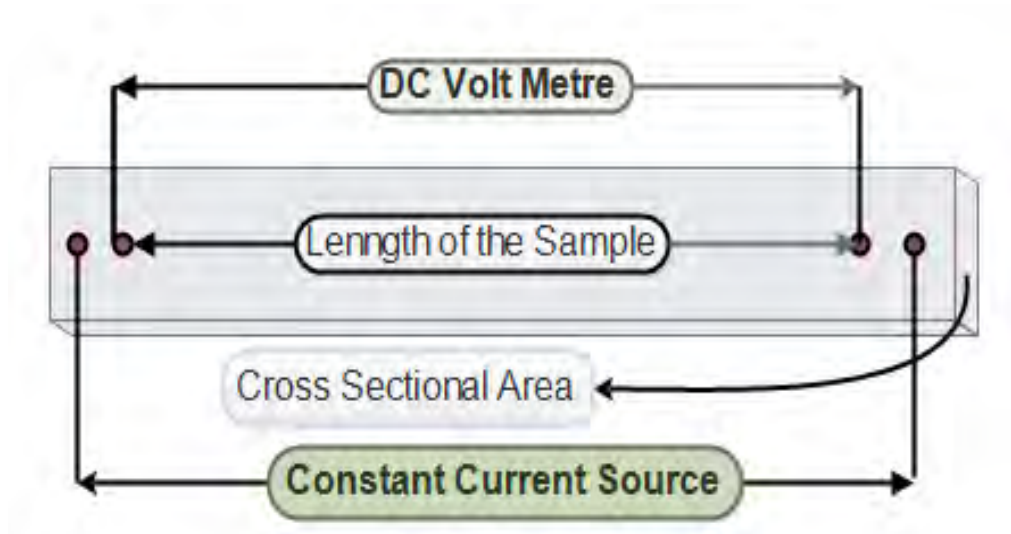


Figure 4.1 Sample connection for resistivity measurement

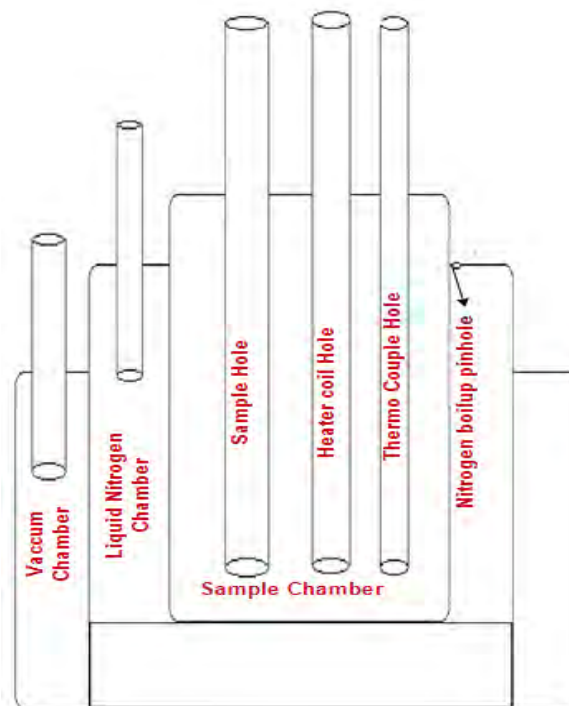


Figure 4.2 Schematic diagram of home build temperature controlling sample chamber

4.6 Magnetoresistance measurement Technique

Magnetoresistance measurement is done by the calculation method from the resistivity, measured by the magnetic field dependent voltage measurement with constant current at room temperature on various circuit combination shown on **Figure 4.4**.

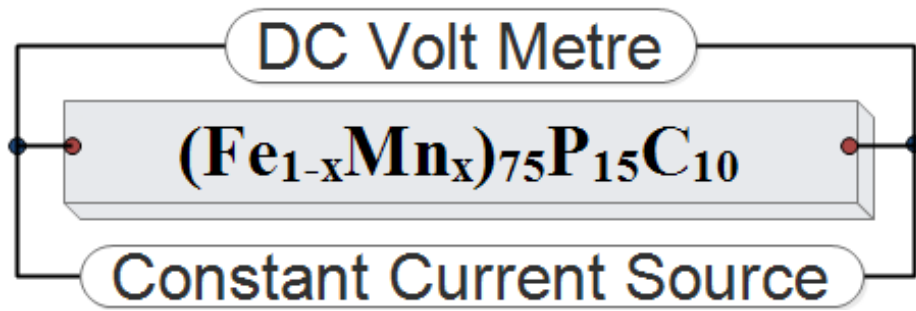


Figure 4.3(i) Sample connection on single sample

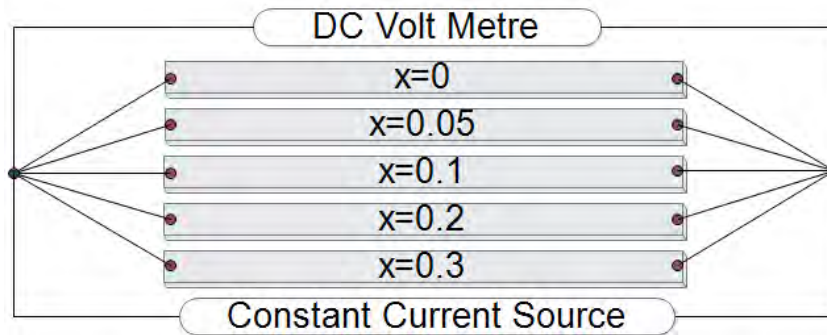


Figure 4.3(ii) Sample connection on all sample with parallel connection

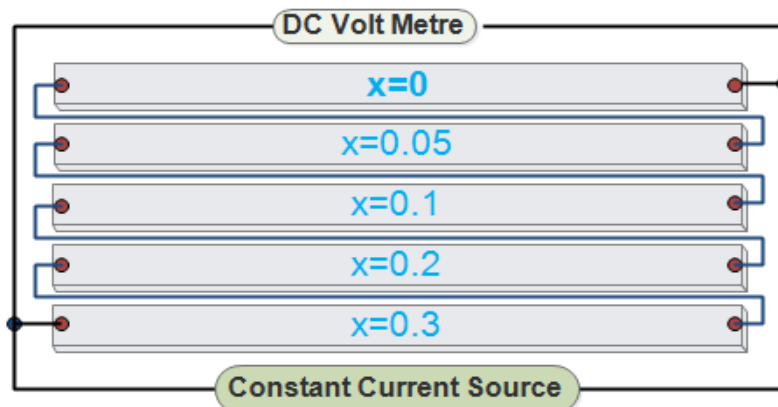


Figure 4.3(iii) Sample connection on all sample with series connection



Figure 4.4 Magnetoresistance measurement setup.

4.7 Magnetization measurement Technique

Magnetization is the magnetic moment per unit volume. There are various ways of measuring the magnetization of a material. In the present work, magnetization was measured by using a home built Vibrating Sample magnetometer (VSM) at room temperature covering a wide range of magnetic field.

4.7.1 Vibrating Sample Magnetometer (VSM)

A vibrating sample magnetometer (VSM) operates on Faraday's Law of Induction, which states that a changing magnetic field will produce an induced emf in coil placed nearby electric field. A VSM is used to measure the magnetic properties of a magnetic material.

A VSM operates by first placing the sample to be studied in a constant magnetic field. When a magnetic field is applied on the sample, the sample is magnetized. When the magnetized sample is vibrated perpendicular to the field a time varying magnetic flux is created which induces an emf in the pick-up coil. The magnetic dipole moment of the vibrating sample will create an induced.

The induced emf is amplified by a lock-in amplifier. The strength of the constant magnetic field is set.

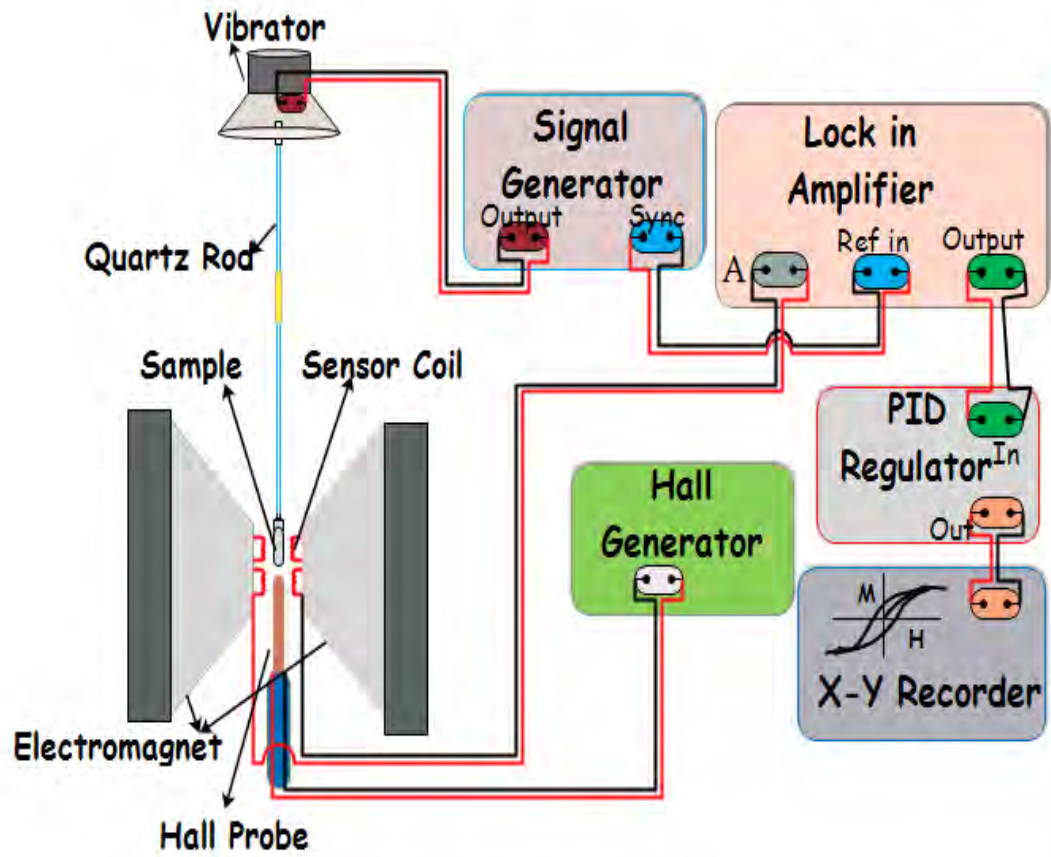


Figure 4.5 schematic diagram of various part of VSM



Figure 4.6 Vibrating Sample Magnetometer with PID Regulator
(Materials Science Laboratory, Dept. of Physics, BUET)

Ribbon form of sample is mounted by folding as sandwich system on the basis of same direction. Then sample is attached with sample rod of the VSM.

4.7.2 Calibration of the V.S.M.

There are usually two methods of calibration of a V.S.M.

- by using a standard sample (Fe) and
- by using a pair of pick-up coils of small size the magnetization was measured.

We have calibrated the V.S.M. using a 76.4 mg spherical Fe sample of 99.9% purity. The saturation magnetic moment of the sample has been calculated using the M-H data.

Calibration Data using a PAR Lock-in-Amplifier

Sensitivity=1 mV

Reference phase = 89.9°

Time constant=300 ms

Bandwidth=12dB

Reference frequency, $f=37$ Hz

Pole gap=32 mm

Mass of the pure Iron sample, $m_r = 76.4$ mg

Saturation magnetization of the pure iron, $M_{rs}=171$ emu/g

The magnetization of the ribbons sample were calculated by using the following eqⁿ

$$M = \frac{KV}{m} \text{ emu/g} \quad 4.2$$

Where, M =Magnetization of the experimental sample

m = Mass of the experimental sample

V = Voltage corresponding to the magnetization

$$K = \text{Calibration constant of the VSM} \left(K = \frac{m_r M_{rs}}{K'} \right)$$

K is calibrated from available data .

The typical calibration curve of magnetic field vs ratio transformer reading is shown in Figure 4.5

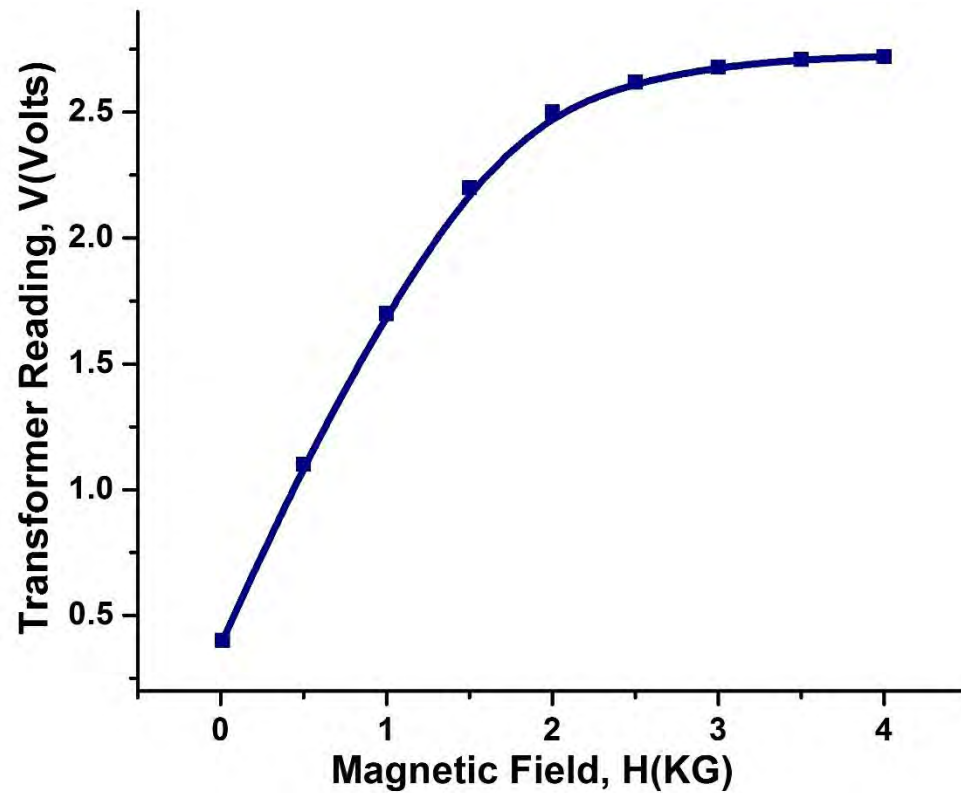


Figure 4.7 Calibration curve for vibrating sample magnetometer

4.8 Permeability measurement

The frequency dependent complex permeability on toroid shape samples were measured at room temperature using an **Waynekerr 6500B** Impedance Analyzer which is shown on **Figure 4.9**.

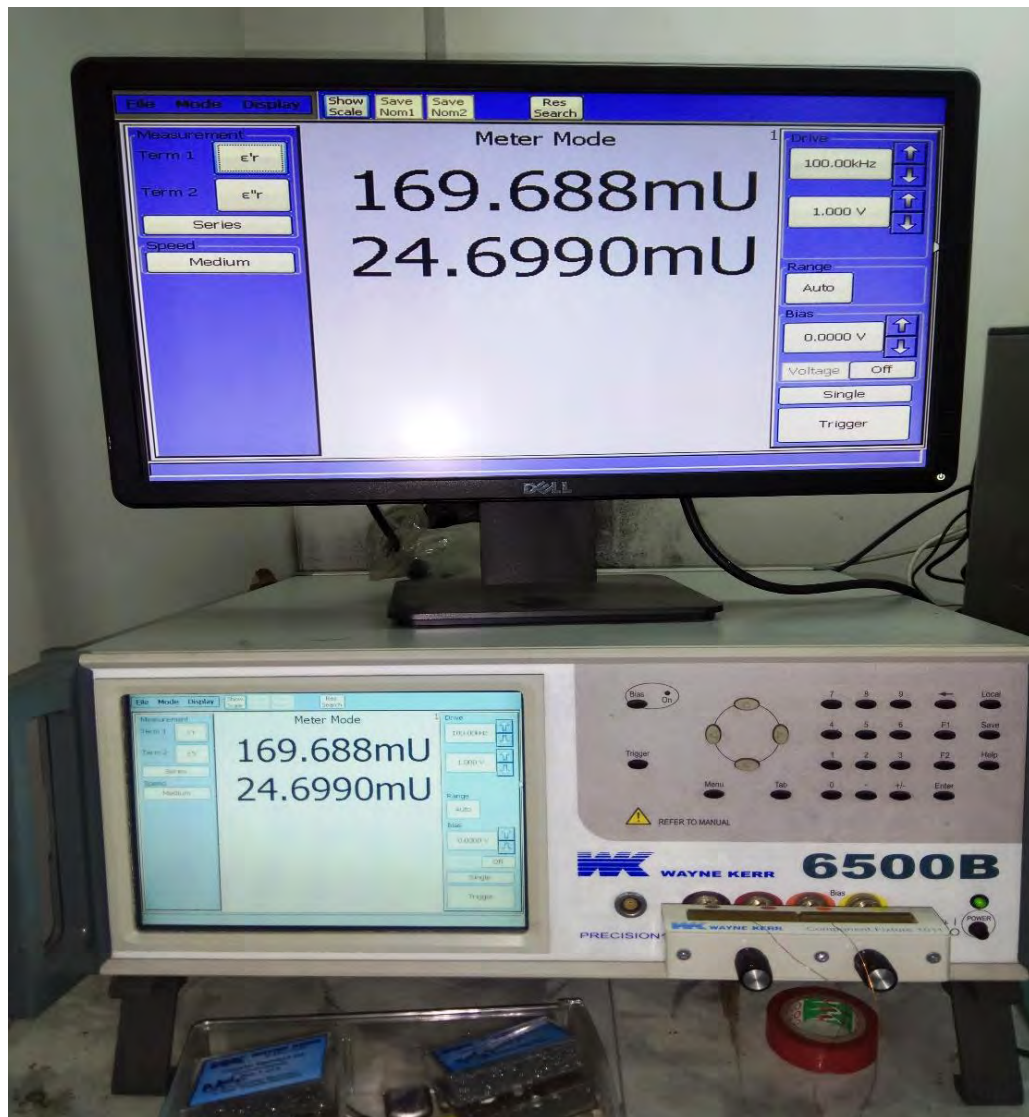


Figure 4.8 Waynekerr 6500B Impedance Analyzer

At first the Impedance Analyzer was calibrated using standard calibration kits.

Then a section of ribbon was wound in the form of a toroid shape sample.

The length of the ribbon shaped sample were used as the magnetic path length of the toroidal sample and Cross sectional area of the sample were used as the product of thickness and width of the ribbon shape sample.

Chapter Five

Result and Discussion

5.1 Structural Properties

5.1.1 XRD

5.1.2 Surface morphology and composition analysis

5.1.2.1 SEM

5.2 Thermal Properties

5.3 Transport Properties

5.3.1 Temperature Dependent Resistivity

5.3.2 Magnetoresistance

5.4 Magnetic Properties

5.4.1 Magnetization

5.4.2 Permeability

Reference

Chapter Five

Result and Discussion

Characterization of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$

We have investigated in our thesis work the dc and ac magnetic properties and also the structural properties, and their thermal effect of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys in the form of ribbons.

5.1 Structural Properties

5.1.1 XRD

The structural properties were investigated using X-ray diffraction (XRD) with Cu-K α radiation (Cu-K α , $\lambda = 154050 \text{ \AA}$) on as-cast samples of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ ($x=0, 0.05, 0.1, 0.2\&0.3$) ribbons. **Figure 5.1** illustrates the X-ray diffraction patterns for all the as-cast ribbons within scanning angular range from 10° to 80° . These ribbons show pure amorphous phase, as there are no sharp Bragg peaks and all diffraction curved lines show the typical broad halo pattern. The broad halo patterns indicate that these ribbons consist of a fully amorphous phase. The x-ray diffraction patterns have not shown any remarkable changes in the structure with the addition of Mn except for the sample with $x=0.3$. There are traces of some additional peaks which might have resulted from manganites. Also there is a noticeable tendency of forming a mixed phase structure as the diffraction pattern show the portion of a broader peak at higher angles.

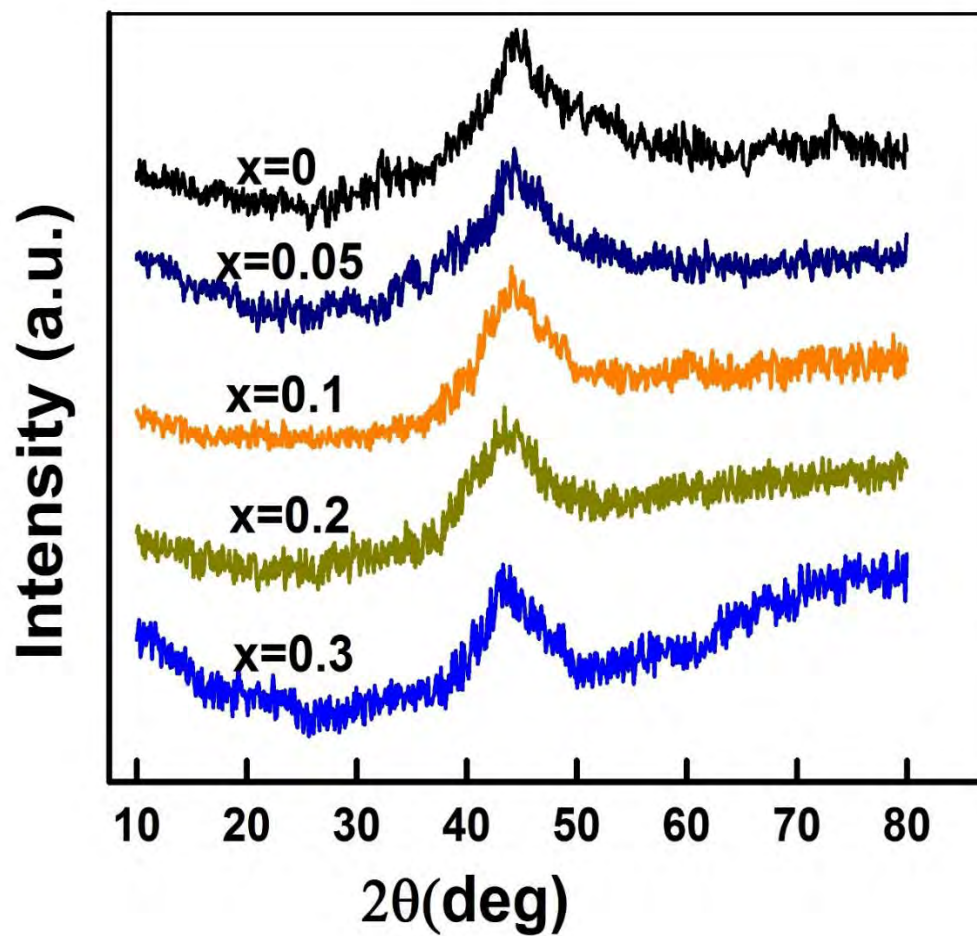


Figure 5.1: XRD patterns of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ ($x=0, 0.05, 0.1, 0.2$ & 0.3) ribbons.

5.1.2 Surface Morphology and Composition Analysis

5.1.2.1 SEM

SEM images were taken to examine the surface morphology of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ for all the samples. **Figure 5.2.** shows the SEM images of all the as made samples. These images with magnifications of 10000 and 100000 times of the original structure of the amorphous ribbon. In the figure within the 100 nm range we see that SEM micrograph shows not any crystalline or any other grain boundary shape formation. The structure of this fracture surface thus confirms that the sample is amorphous in nature. The SEM images show region of clusters assumed to be formed due to the addition of Mn. It is known that the binary Cu and iron system show complete immiscibility because of the higher enthalpy of mixing. In our case both Fe and Mn as 3-d transition metal elements have higher electrical conductivity, although they are magnetically fall in different classes with Fe being ferromagnetic and manganese antiferromagnetic. We presume that the Fe and Mn with addition of C and P would improve the ductility of the ribbons and improve the overall magnetic properties. The images also show that there might be regions in the sample which still maintains the crystallinity. It is important to note that the samples freezing time is in the microscopic time scale and Fe, Mn, P, and C all have different melting temperatures. Therefore freezing in a microscopic time scale might affect formation of total glassy structures.

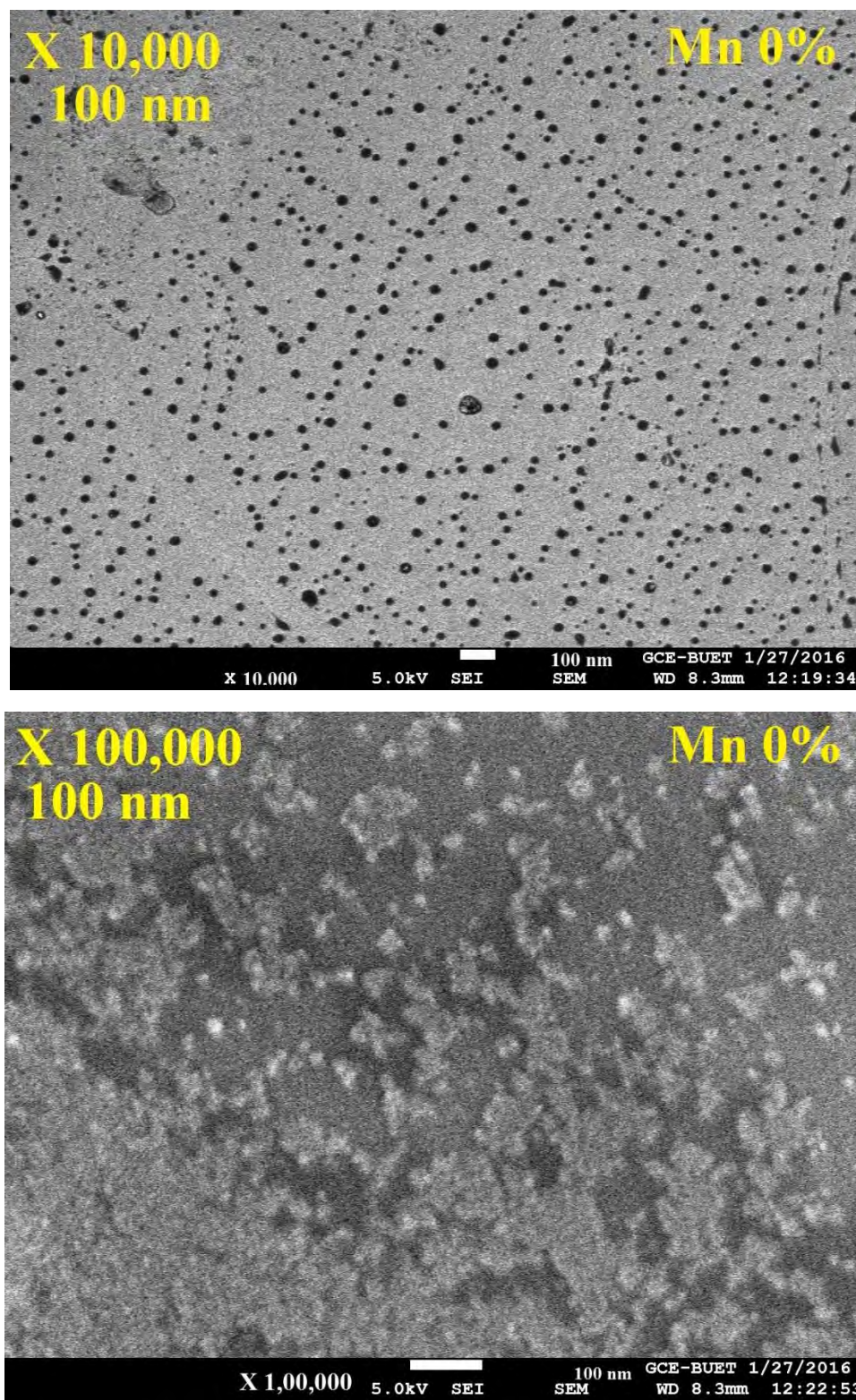


Figure 5.2.1(a): Scanning electron micrographs (SEM) of $\text{Fe}_{75}\text{P}_{15}\text{C}_{10}$ alloy

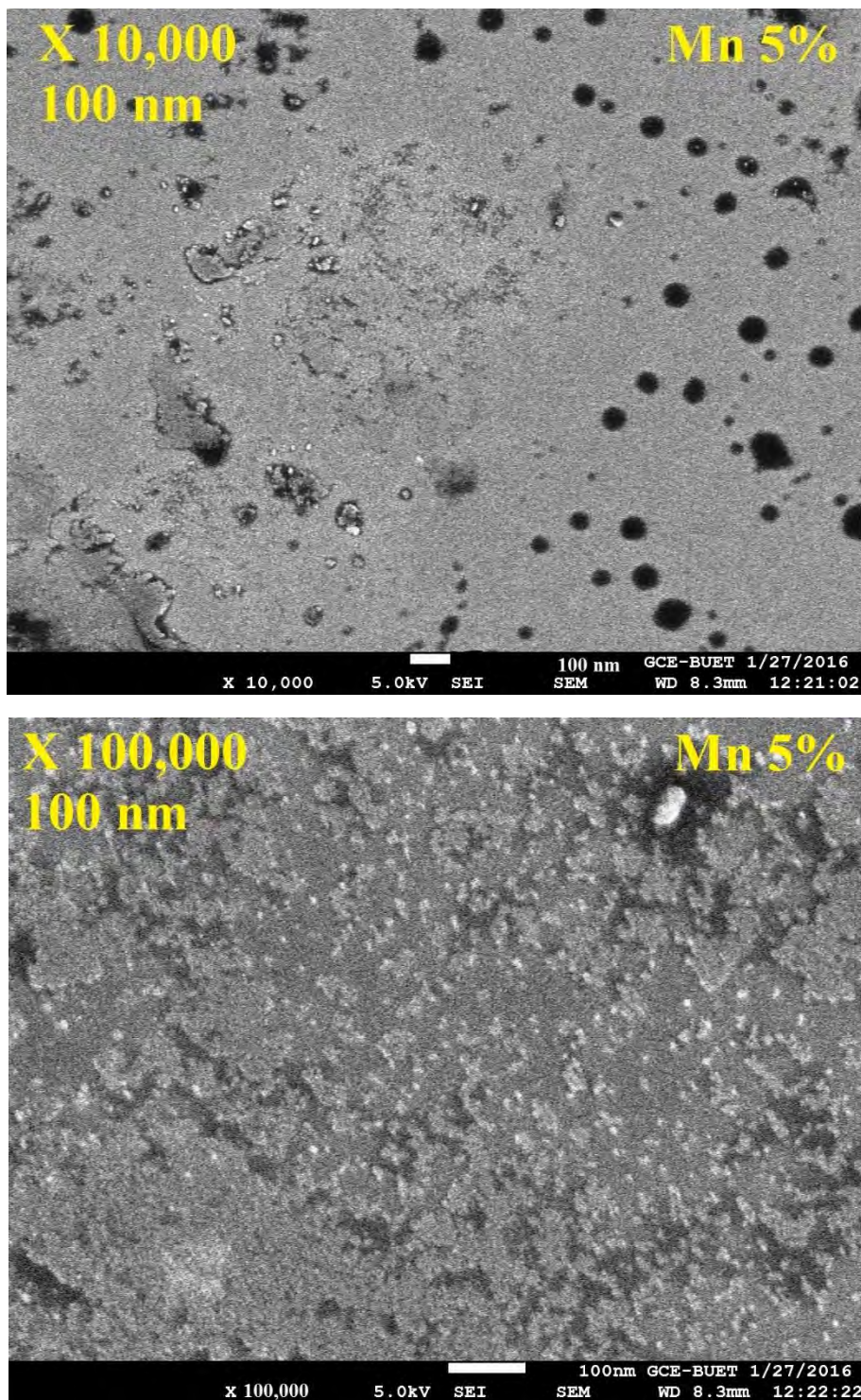


Figure 5.2.1(b): Scanning electron micrographs (SEM) of $(\text{Fe}_{0.95}\text{Mn}_{0.05})_{75}\text{P}_{15}\text{C}_{10}$ alloy

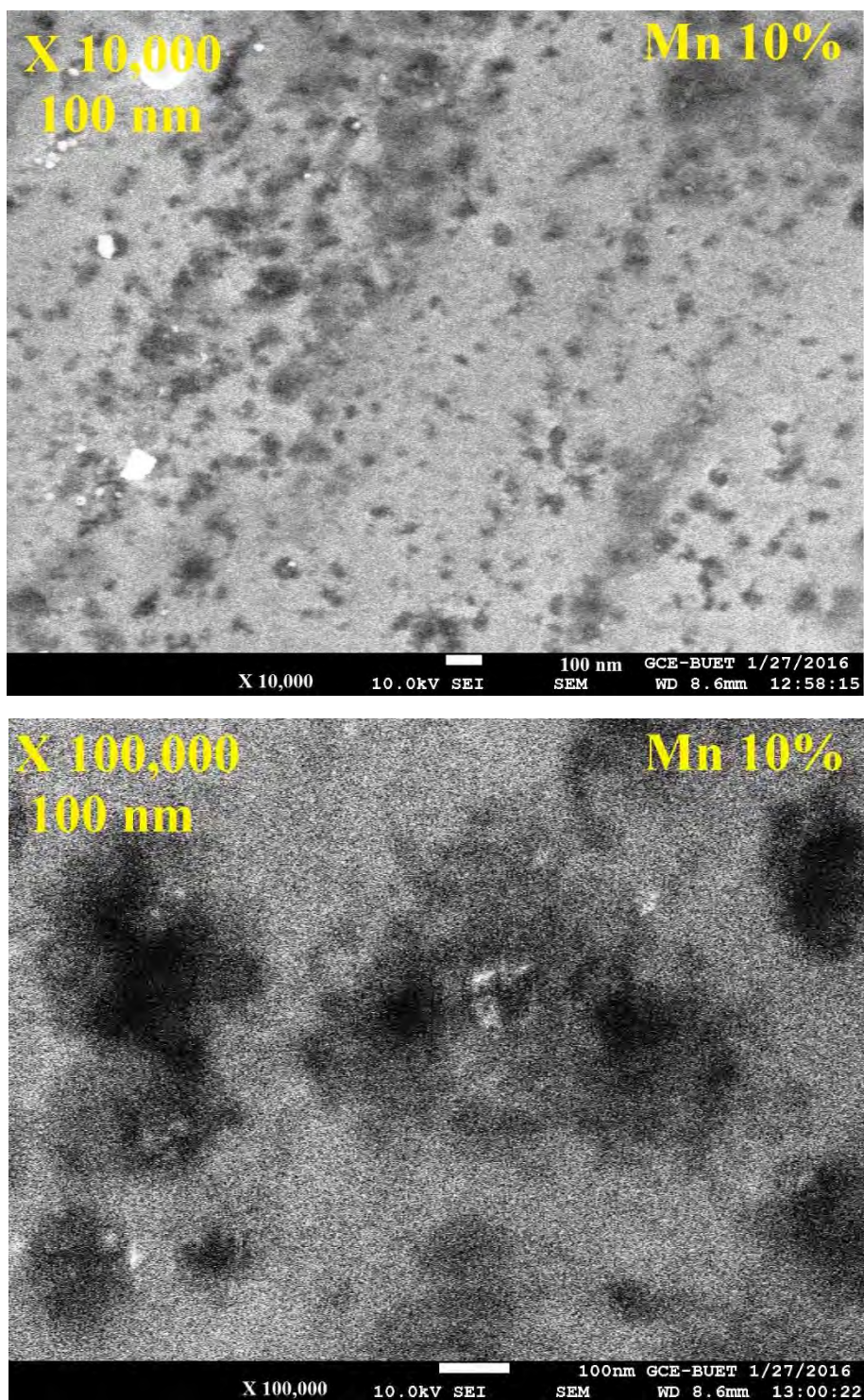


Figure 5.2.1(c): Scanning electron micrographs (SEM) of $(\text{Fe}_{0.9}\text{Mn}_{0.1})_{75}\text{P}_{15}\text{C}_{10}$ alloy

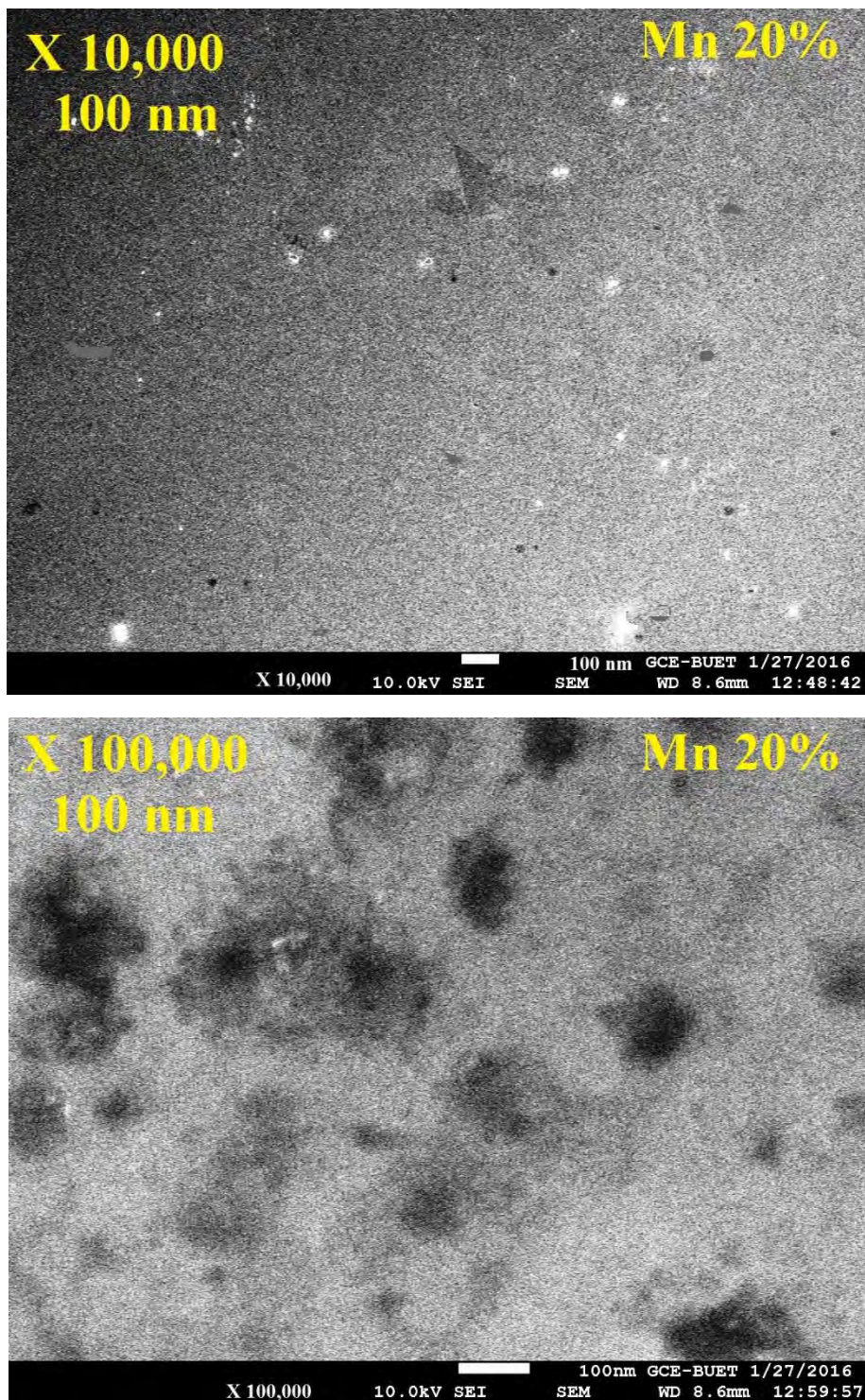


Figure 5.2.1(d): Scanning electron micrographs (SEM) of $(\text{Fe}_{0.8}\text{Mn}_{0.2})_{75}\text{P}_{15}\text{C}_{10}$ alloy

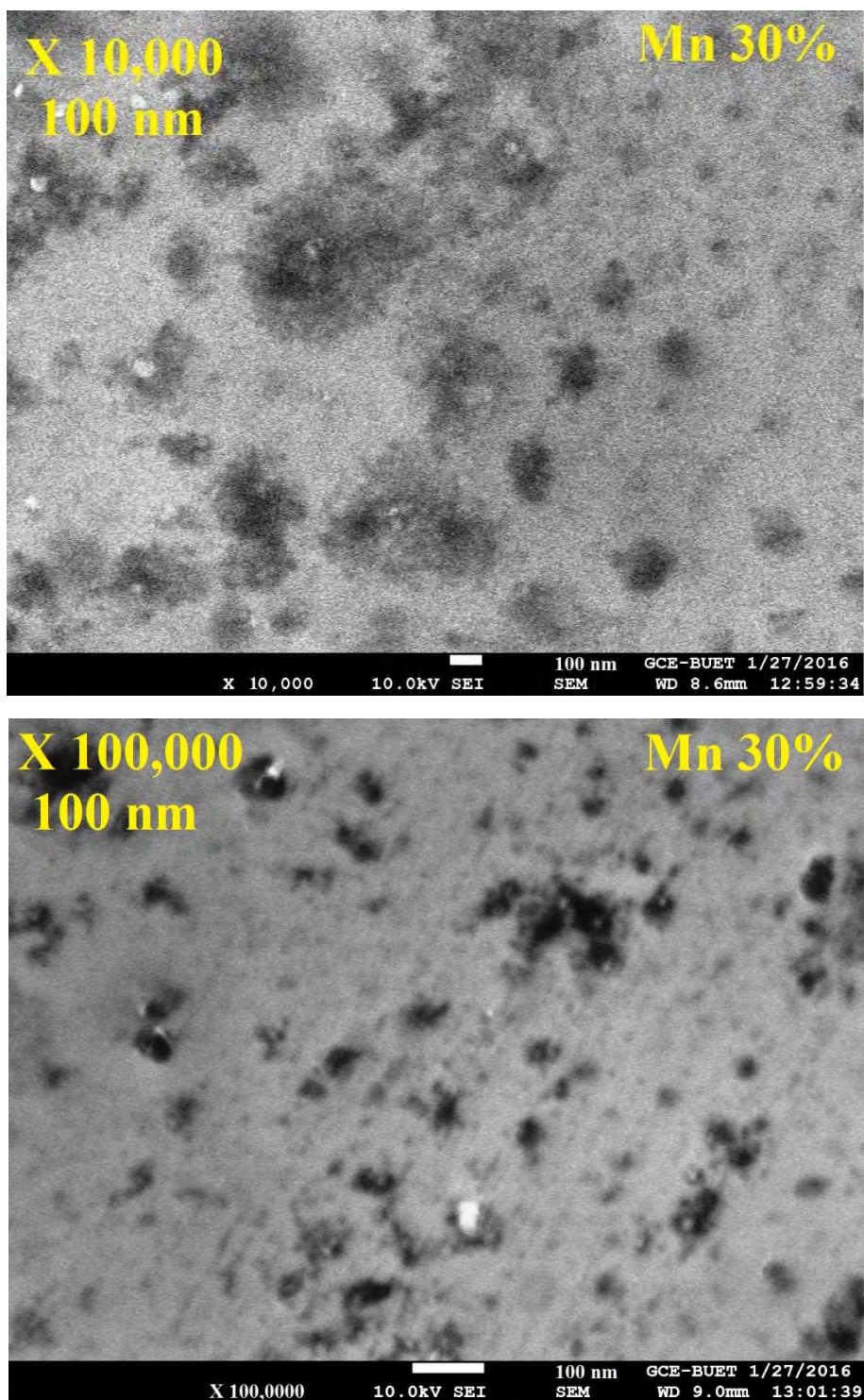


Figure 5.2.1(e): Scanning electron micrographs (SEM) of $(\text{Fe}_{0.7}\text{Mn}_{0.3})_{75}\text{P}_{15}\text{C}_{10}$ alloy

5.1.2.2. EDS

The elemental analysis of samples was carried out using energy dispersive X-ray spectroscopy (EDS). The typical EDS pattern of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ sample has been shown in **Figure. 5.3** (EDS spectra for other compositions is not shown). The EDS spectrum was taken from the area shown in the SEM micrograph in **Figure. 5.3**. The EDS pattern reveals the presence of Fe, Mn, P & C elements in the sample. No extra peaks have been traced which indicates that there is no contamination in the sample. The atomic percentage of Mn obtained from the EDS spectra for the $x = 0, 0.05, 0.1, 0.2$ and 0.3 samples, respectively. Thus the atomic % obtained from EDS spectra agrees well with the nominal values and hence confirms the purity of the samples.

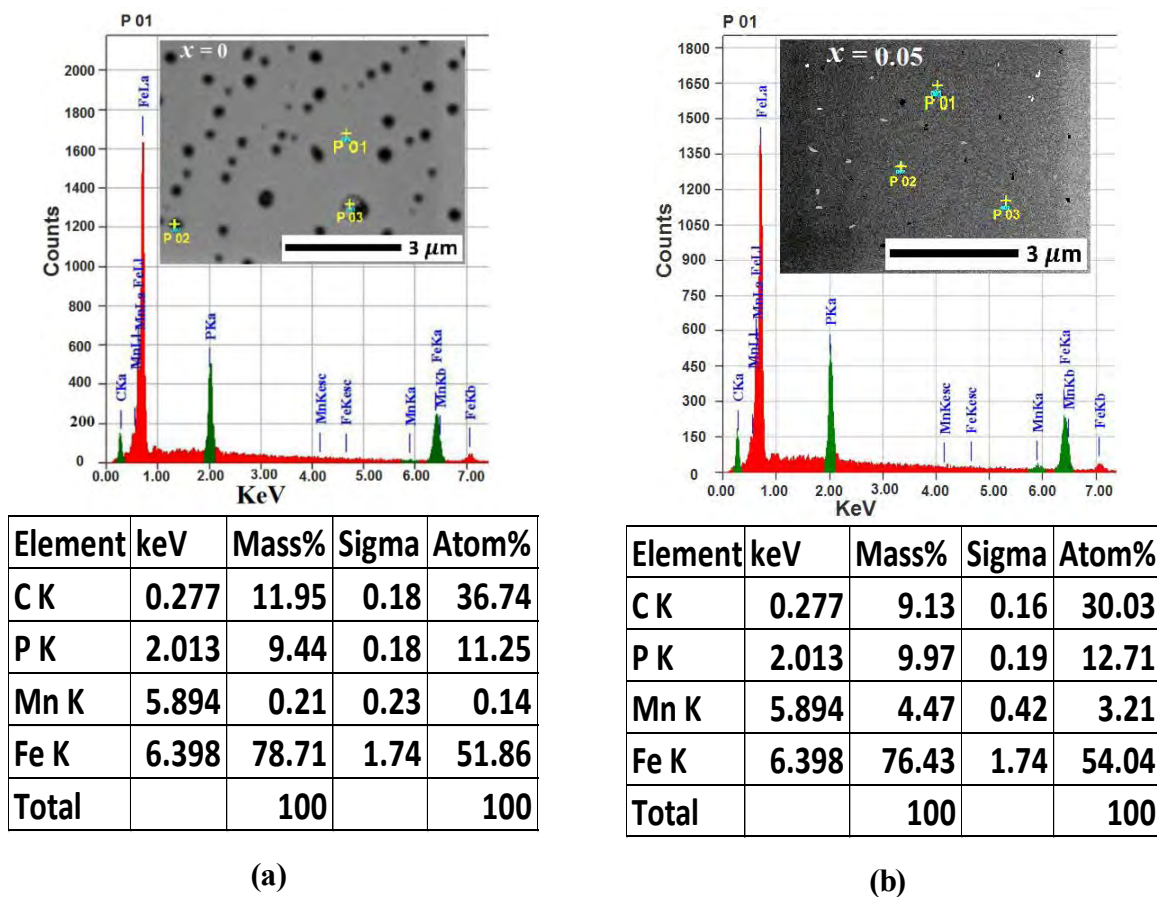
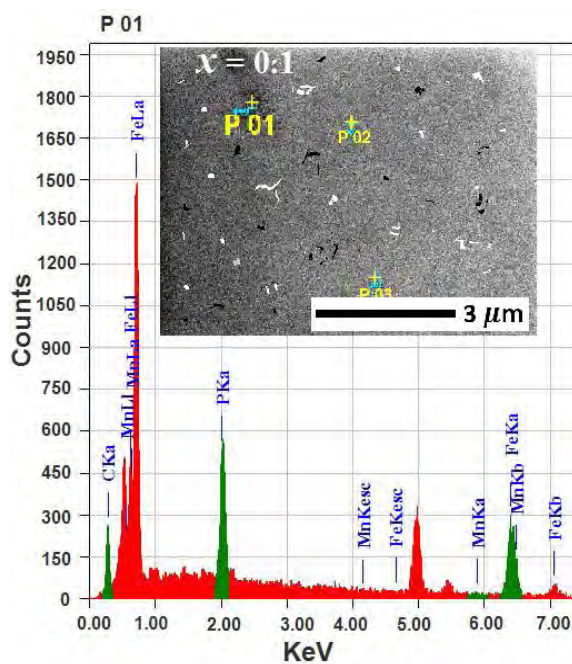
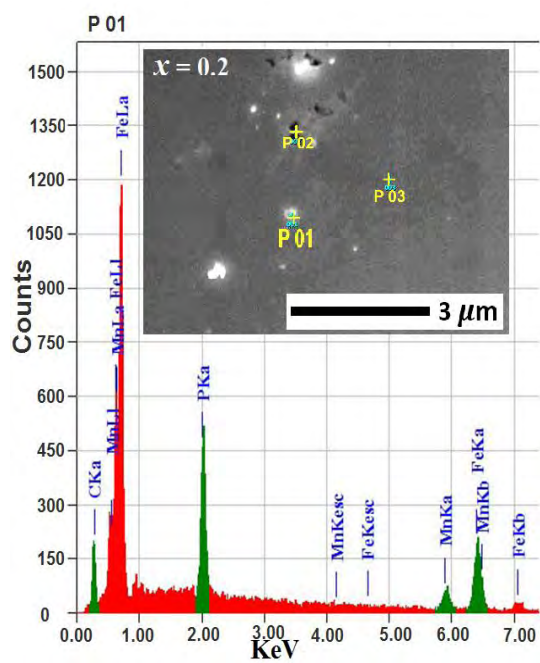


Figure 5.3.1: EDS spectra of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ sample for and inset shows the FE-SEM image (a) $x = 0$ (b) $x = 0.05$.



Element	keV	Mass%	Sigma	Atom%
C K	0.277	9.96	0.2	32.14
P K	2.013	9.25	0.21	12.05
Mn K	5.894	10.24	0.33	6.83
Fe K	6.398	70.54	1.96	48.98
Total		100		100

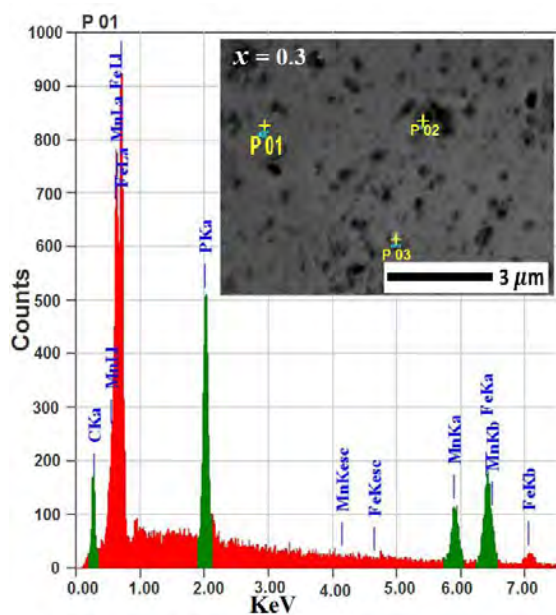
(c)



Element	keV	Mass%	Sigma	Atom%
C K	0.277	11.33	0.04	35.23
P K	2.013	9.95	0.19	11.99
Mn K	5.894	14.01	0.68	9.52
Fe K	6.398	64.72	1.63	43.27
Total		100		100

(d)

Figure 5.3.2: EDS spectra of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ sample for and inset shows the FE-SEM image (c) $x = 0.1$ (d) $x = 0.2$.



Element	keV	Mass%	Sigma	Atom%
C K	0.277	9.1	0.16	29.86
P K	2.013	10.06	0.19	12.8
Mn K	5.894	25.77	0.89	18.49
Fe K	6.398	55.07	1.51	38.86
Total		100		100

(e)

Figure 5.3.3: EDS spectra of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ sample for and inset shows the FESEM image (e) $x = 0.3$.

5.2 Thermal Properties

DTA and TG

The thermal properties of the samples have been investigated by Differential Thermal Analysis (DTA) and also by Thermo Gravimetric (TG) analysis. Some thermal traces such as DTA and TG of the $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ ($x=0, 0.05, 0.1, 0.2$ & 0.3) samples are shown in **Figures 5.4(a-e)**. From DTA trace of **Figures 5.4(a-e)** it can be seen that the peak crystallization temperature (T_x) rises with increasing manganese content (**Figure 5.5**). **Figures 5.4(a-e)** show the sharpness of DTA peak developed with increasing Mn content. With the increasing temperature the micro voids which formed during the growth process of the ribbon during melt spinning are gradually eliminated [1]. At higher temperature both Fe and Mn ions are oxidized by the environment and hence the mass could be slightly enhanced (**5.4(a-e)** TG). It is assumed that the grain size might have increased since the Mn ionic radius of Mn ($0.89 \text{ \AA}$) is larger than the ionic radius of Fe ($0.74 \text{ \AA}$) [2].

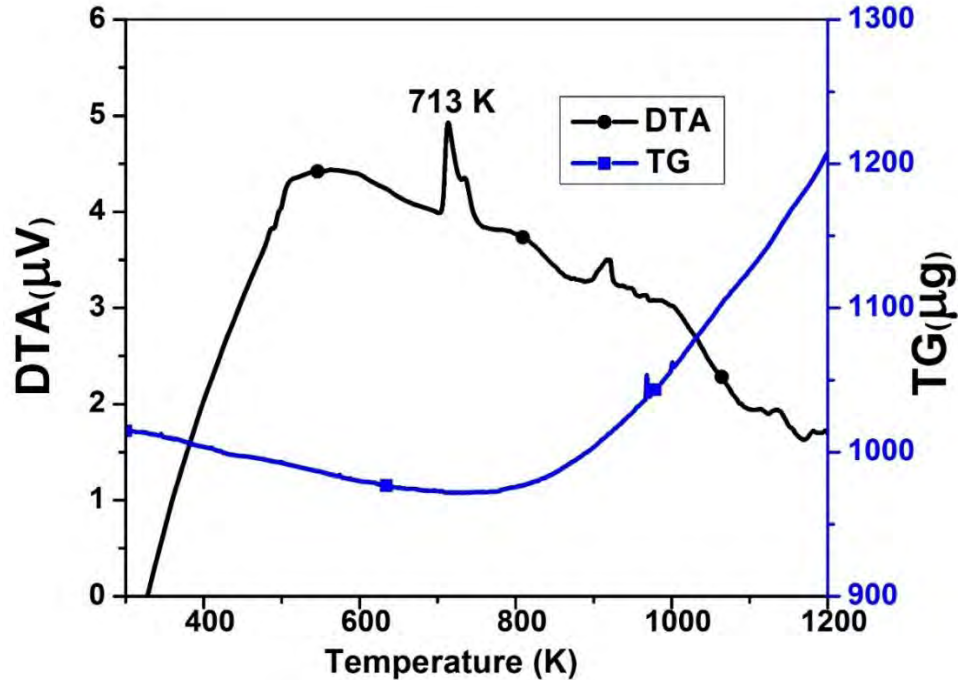


Figure 5.4 (a) DTA and TG Curve of $\text{Fe}_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

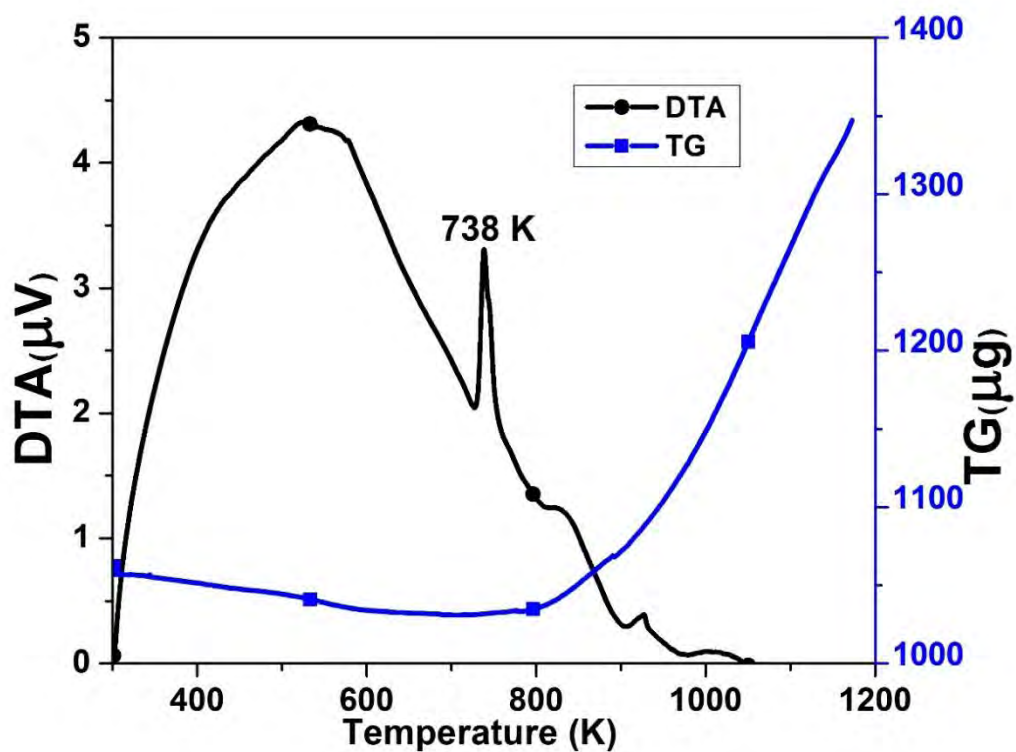


Figure 5.4 (b) DTA and TG Curve of $(\text{Fe}_{0.95}\text{Mn}_{0.05})_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

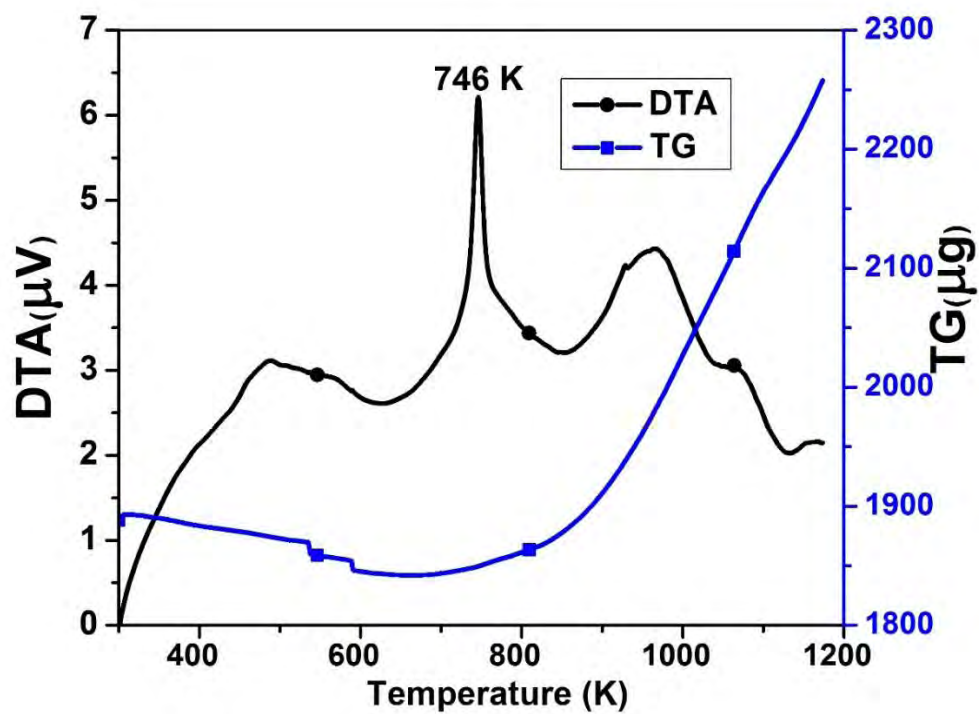


Figure 5.4 (c) DTA and TG Curve of $(\text{Fe}_{0.9}\text{Mn}_{0.1})_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

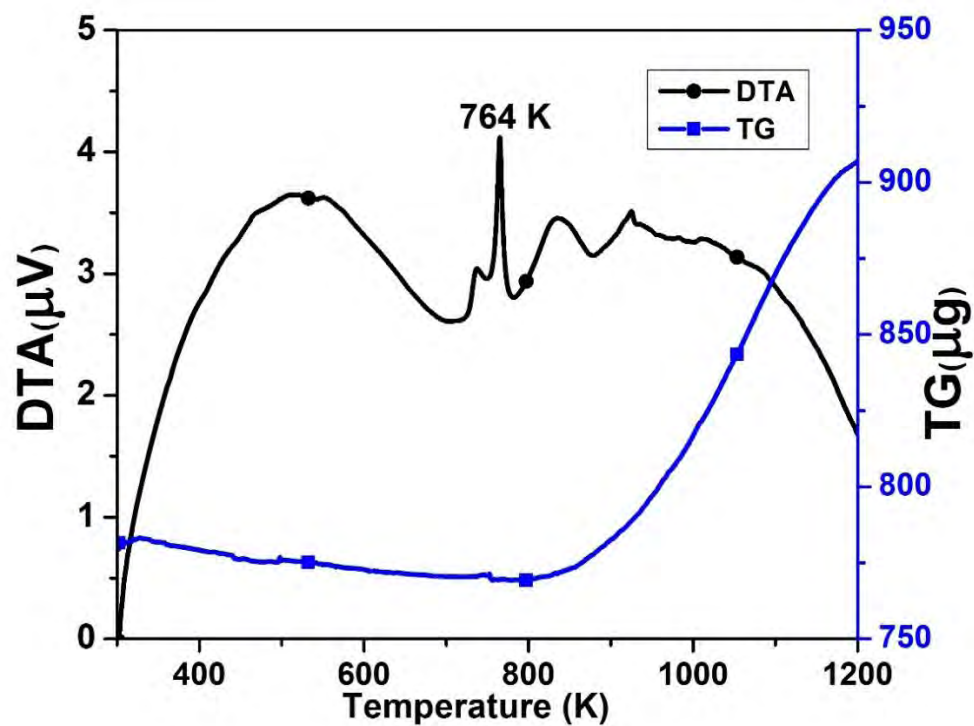


Figure 5.4 (d) DTA and TG Curve of $(\text{Fe}_{0.8}\text{Mn}_{0.2})_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

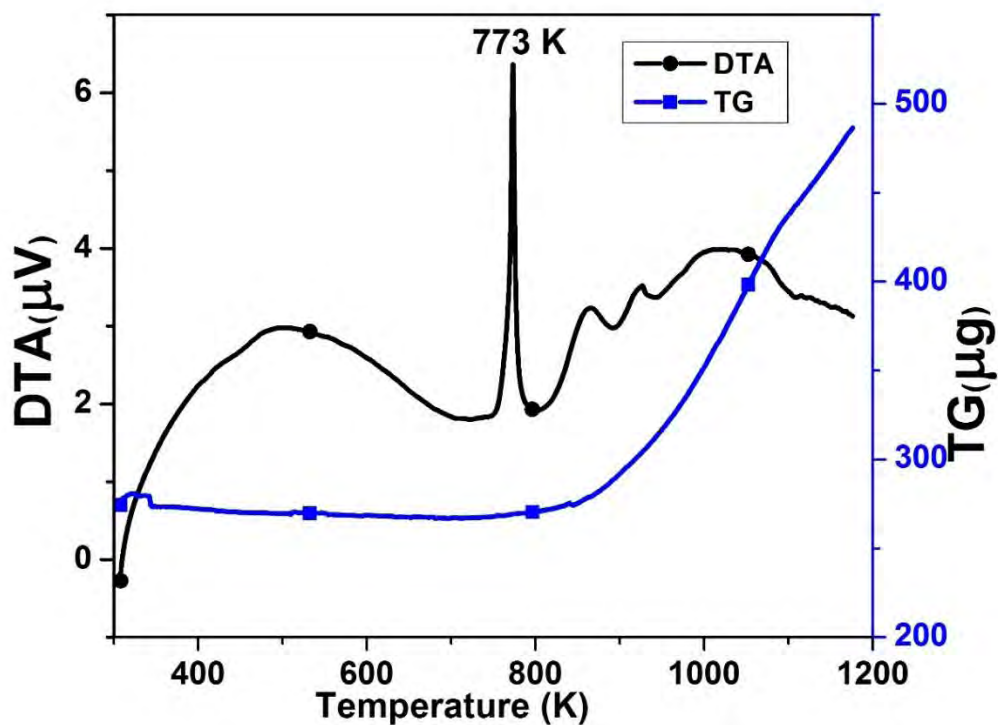


Figure 5.4 (e) DTA and TG Curve of $(\text{Fe}_{0.7}\text{Mn}_{0.3})_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

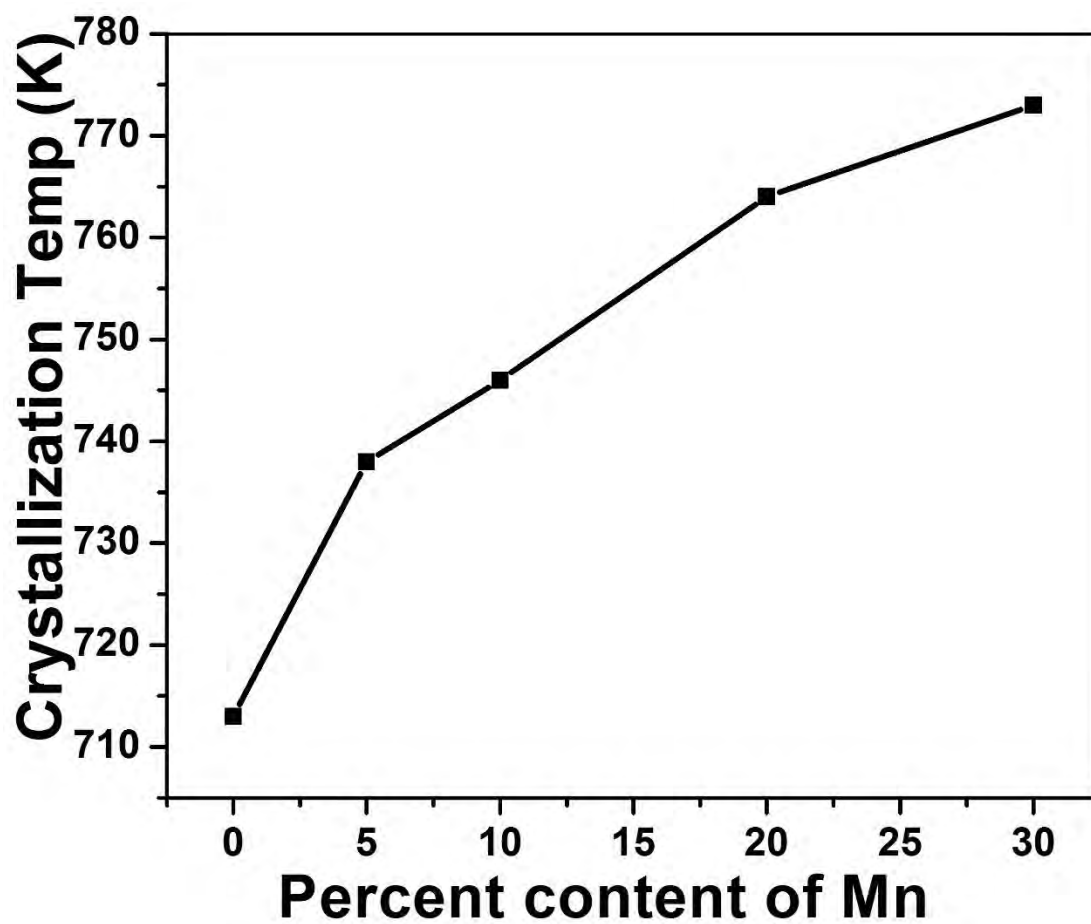


Figure 5.5 Crystallization Temperature (T_x) versus Mn concentration of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

5.3 Transport properties

The transport properties of $\text{Fe}_{1-x}\text{Mn}_x\text{P}_{15}\text{C}_{10}$ metallic amorphous alloys have been investigated through measurements of dc electrical resistivity, magnetoresistance as a function of Mn content

5.3.1 Temperature Dependent Resistivity

Figure 5.6 shows the temperature dependence of the resistivity of amorphous alloys is quite different from that of the crystalline state. **Figure 5.7** shows the resistivity versus percent concentration of Mn graph. It is observed that all the samples go through a resistivity transition around 300K which is around the room temperature and thus considered to be a promising behavior for technological applications since many devices are used around the room temperature. Also it is interesting to note that with increasing temperature the absolute values of resistivity increase slightly upto the room temperature then show a sharp increase in values for $x=0$ and 0.05. The very slight increase of $\rho(T)$ for small x , **Figure 5.6**, is expected both from the Ziman theory of structural topological scattering and the Mooij correlation [3, 4]

At larger x , $\rho(T)$ develops a minimum at room temperature (**Figure 5.7**), which has been ascribed to a superposition of scattering from the structural topological disorder and the spin topological disorder (magnetic Ziman theory [5, 6] which can have different slopes,

$$\frac{d\rho}{dT}.$$

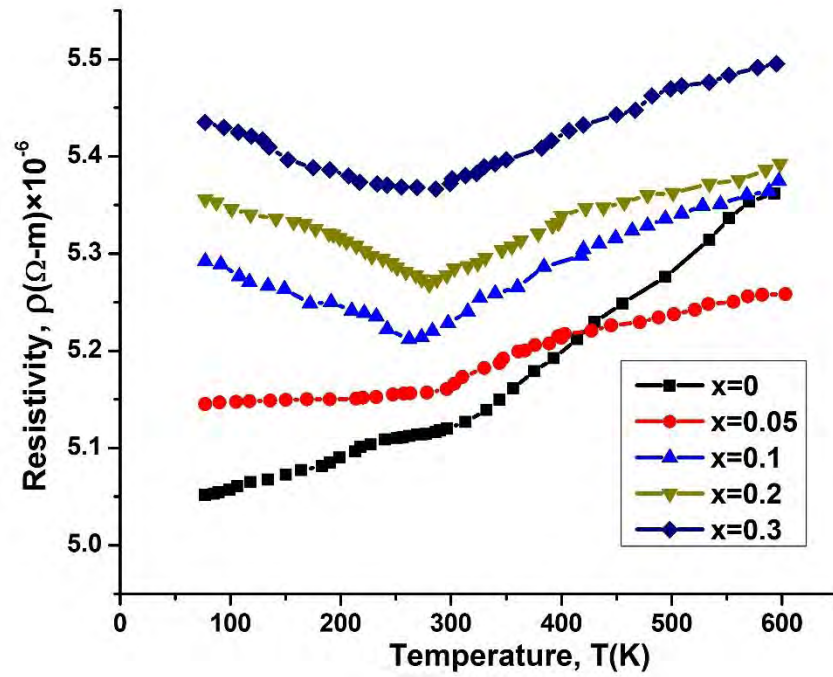


Figure 5.6: Electrical resistivity (ρ) versus temperature (T) of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

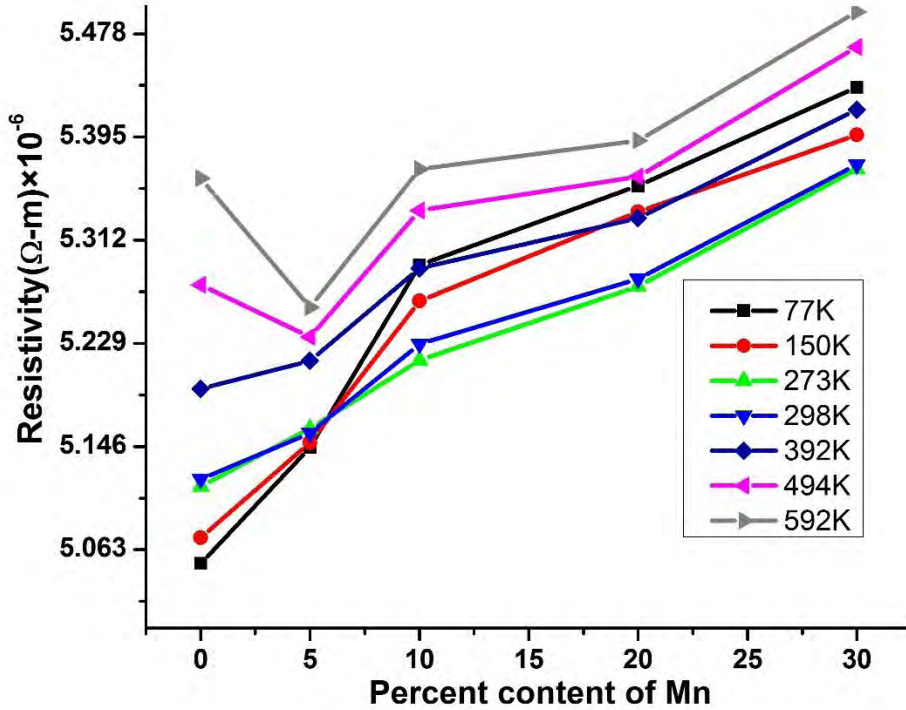


Figure 5.7: Electrical resistivity (ρ) versus Mn concentration of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

Figure 5.8 shows the normalized resistivity $\rho(T)/\rho_{(298\text{ K})}$ versus temperature.

It is worth noting that at the low temperature regime (below 273 K) the normalized resistivity curves show anomalous behavior. It is observed that the samples with higher Mn content ($x = 0.1, 0.2, 0.3$) show an increase in resistivity, while the samples with lower Mn content ($x = 0$, and 0.05) show lower resistivity values as the temperature goes down. This behavior is attributed to the interference of elastically backscattered electronic wave functions causing the resistivity increase at low temperature. Since the inelastic scattering increases at higher temperatures, the quantum interference is suppressed because of the fact that at low temperature the angle of scattering is increased while at higher temperature the angle of scattering is relatively smaller.

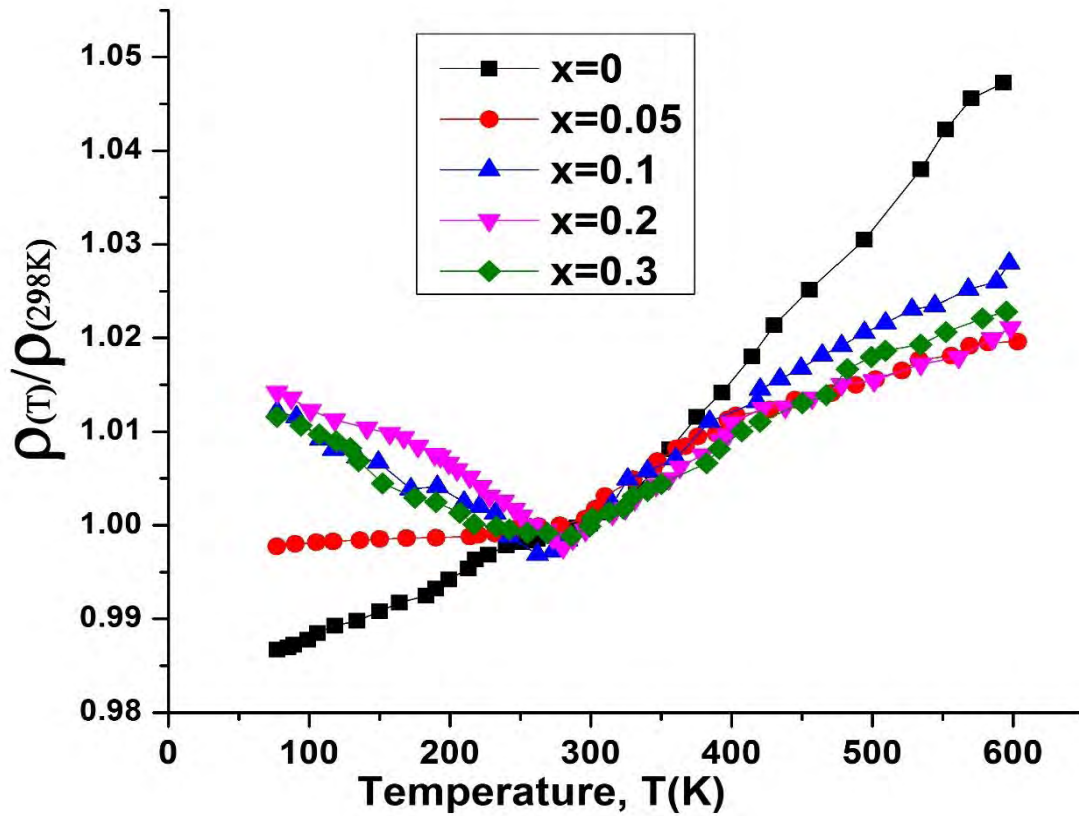


Figure 5.8: Reduced resistivity versus temperature (T) of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

The $\ln T$ dependence of the resistivity in the amorphous alloys shown in **Figure 5.9** is usually ascribed to the Kondo effect and the tunneling levels model [7] Grest and Nagel [8] have shown that the Kondo effect can cause a resistivity minimum even in concentrated ferromagnetic alloys if there is antiferromagnetic super-exchange interaction between next-nearest-neighbor magnetic atoms which are separated by a metalloid atom. The room temperature resistivity minimum observed in the present crystalline and amorphous alloys can be also attributed to the modified Kondo mechanism mentioned above.

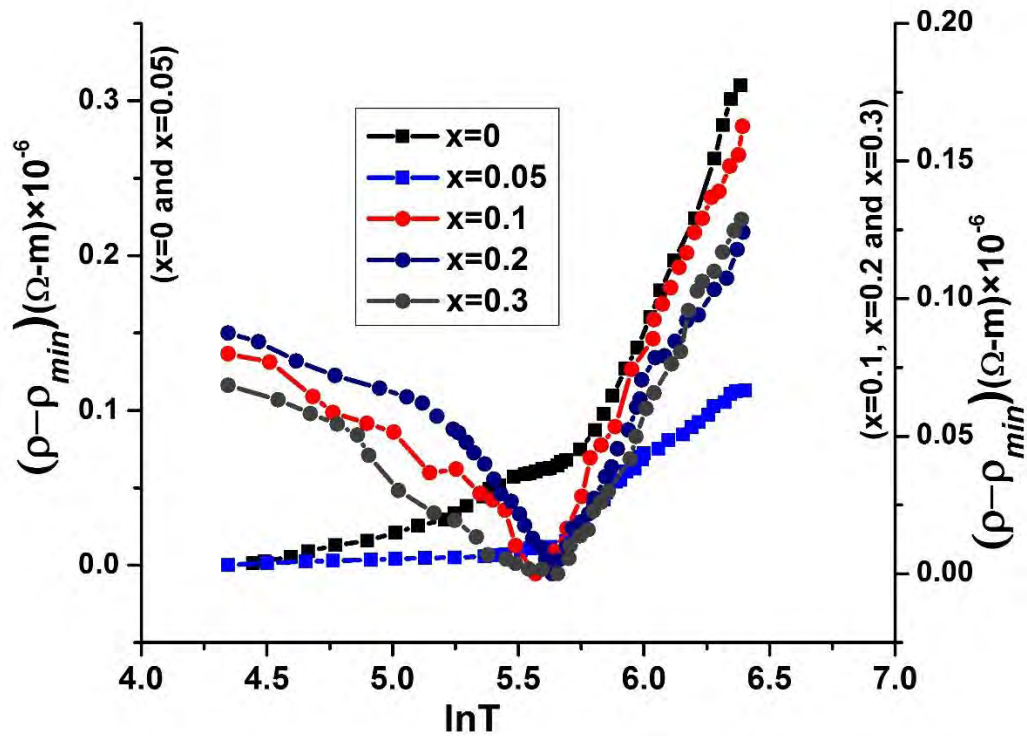


Figure 5.9: Resistivity versus $\ln T$ of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

5.3.2 Magnetoresistance

The magnetoresistance of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ ($x=0, 0.05, 0.1, 0.2$ & 0.3) sample was measured at room temperature by means of a four point probe method. The distance between voltage contacts were taken from the region with 99% homogeneity. The magnetic field was applied by a precision Varian Electromagnet which attains a magnetic field of 1.2 Tesla.

The magnetic field dependence of magnetoresistance $\Delta\rho(H)$ normalized to the resistivity of the sample in zero magnetic field ρ_0 for single sample connection is shown in **Figure 5.10**. MR% decrease with increasing magnetic field upto 0.3 tesla then it increase continuously. As the field is increased further all curves tend to saturate. The increase in MR% against field is called the force effect.

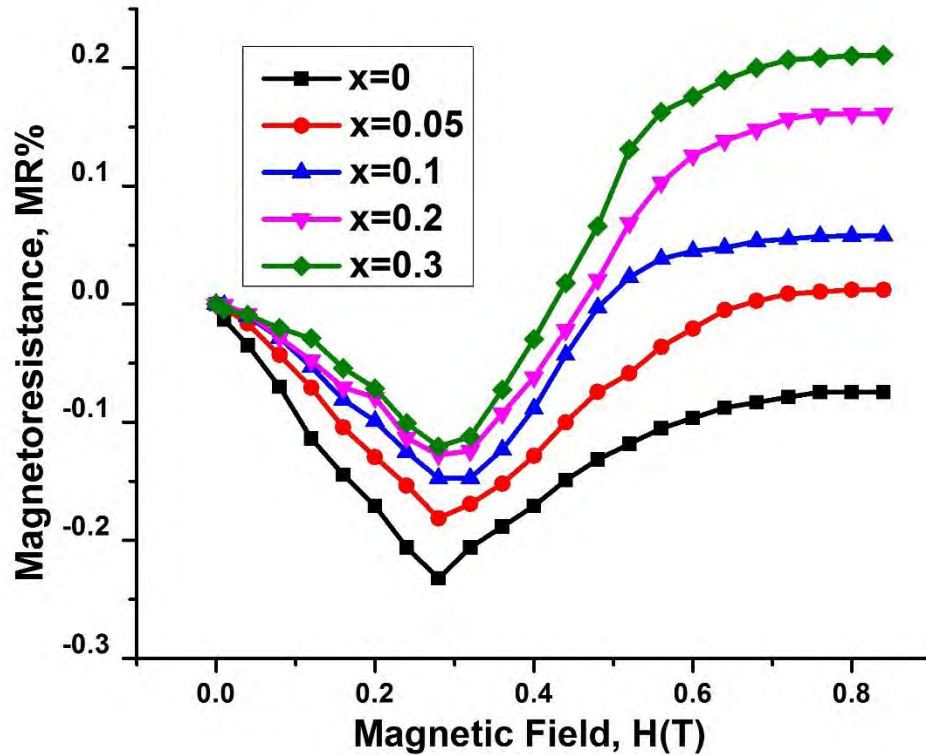


Figure 5.10: MR% vs H(T) For Single Connection of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

Figure 5.11 shows magnetic field dependence of magnetoresistance for parallel combination of $x = 0$, $x = 0.05$, $x = 0.1$, $x = 0.2$ & $x = 0.3$. MR% increases sharply with increasing magnetic field upto 0.3 tesla then it falls down sharply and then the absolute values of magnetoresistance increase continuously then it tend to saturate.

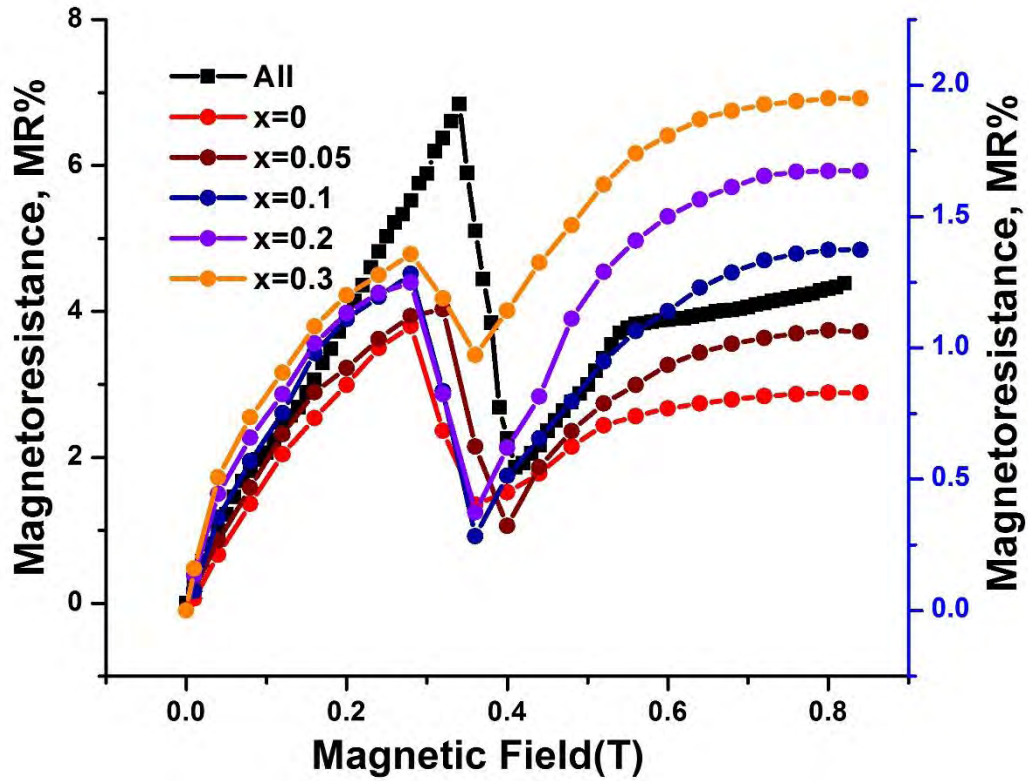


Figure 5.11 MR% vs H(T) For Parallel Combination of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys left vertical axis for All concentration and right vertical axis for separate concentration

Figure 5.12 shows magnetic field dependence of magnetoresistance for series combination of $x = 0$, $x = 0.05$, $x = 0.1$, $x = 0.2$ & $x = 0.3$. MR% decreases sharply with increasing magnetic field upto 0.3 tesla then the absolute values of magnetoresistance increase continuously then tend to saturate.

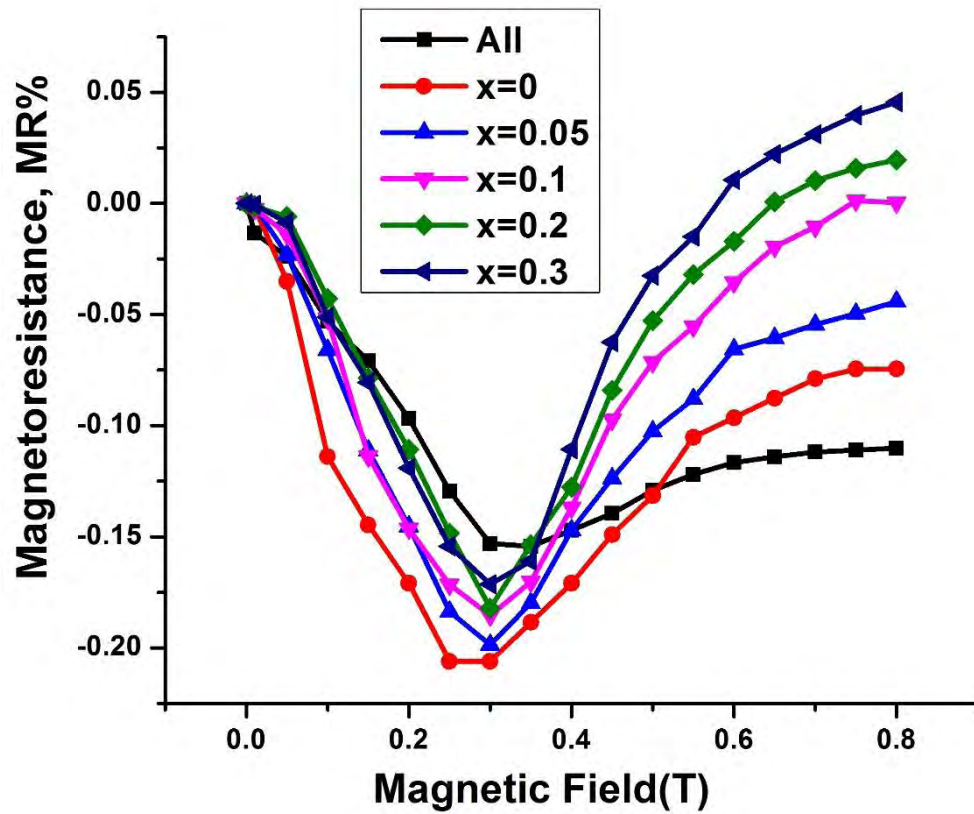


Figure 5.12 MR% vs H(T) For Series Combination of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

From above three figures it is observed that the anomalous of MR% around 0.3 tesla have been studied and understood in terms of a suppression of quantum localization corrections in the Drude equation for the magneto-conductance which is explained by the Kondo type magnetic scattering. [9]

The observed result on MR% for the $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys used for the investigation are summarized in fig 5.13 as a function of composition x . It is to be noted that values of MR% is increases for all type connection at large magnetic field. The main reason for the small MR% in the amorphous alloys is thought to be related to the large electrical resistivity of the amorphous alloys. The change in sign from positive to negative magnetoresistance is evaluated to be embedded in residual amorphous matrix. [10].

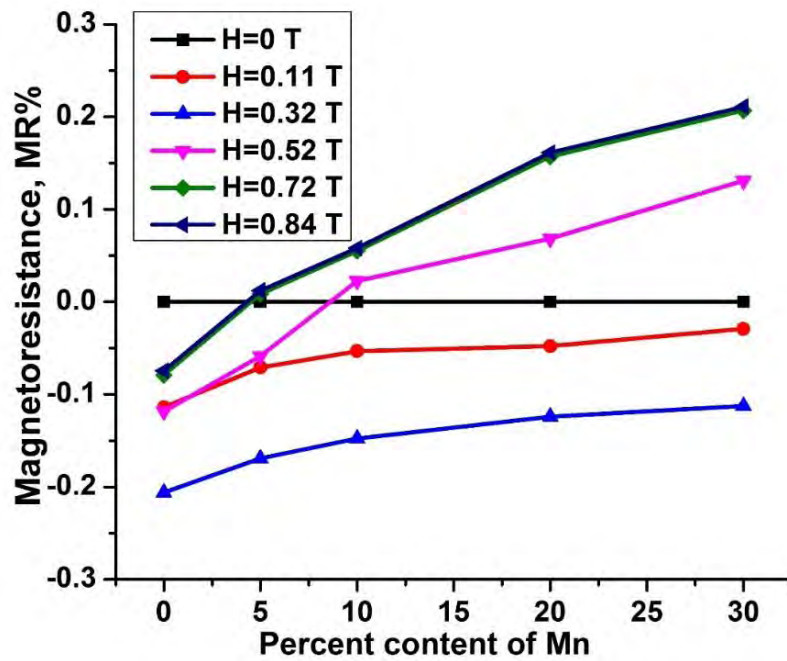


Figure 5.13 MR% vs Mn concentration of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

Negative MR% was observed in all investigated samples for low-conductivity ones. Assuming that conductance of the low-conductivity samples is described by the relevant theory of negative hopping magnetoresistance. The $\ln \frac{R(H)}{R_0}$ versus H for samples are shown in fig 5.14. The above facts rule out interference of forward paths of hopping carriers as the mechanism responsible for observed negative MR%.

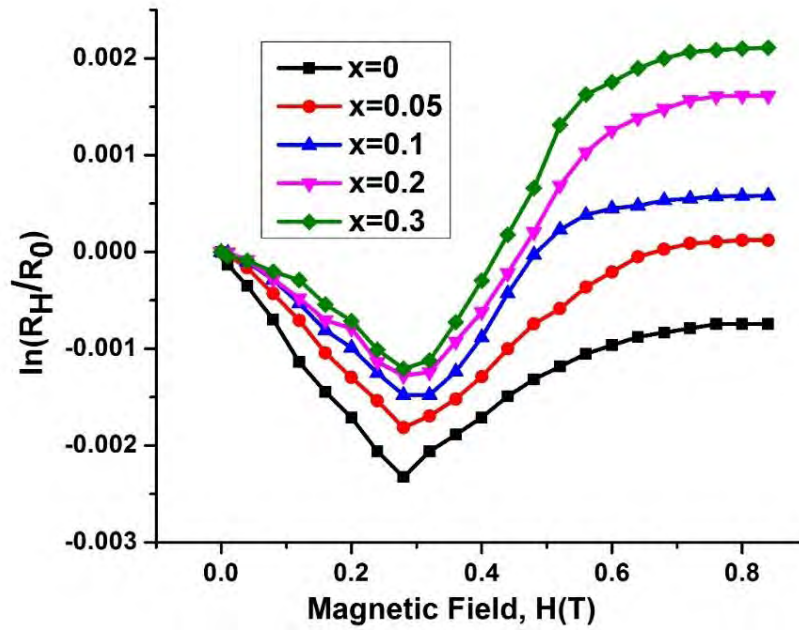


Figure 5.14 $\ln \frac{R(H)}{R_0}$ vs H(T) of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

5.4 Magnetic Properties

5.4.1 Magnetization

Magnetic properties of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous ribbon samples were measured using a home built VSM. The hysteresis M–H loop of the as-made samples for $x = 0, 0.05, 0.1, 0.2$ and 0.3 are presented in **Figure 5.15**. The $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous ribbons presented high saturation magnetization (M_s) of 156.95 emu/g for $x=0$. But the value of saturation magnetization is found to decrease with increasing Mn contents of $x=0.05, 0.1, 0.2$ and 0.3 which is responsible for magnetoelastic scattering.

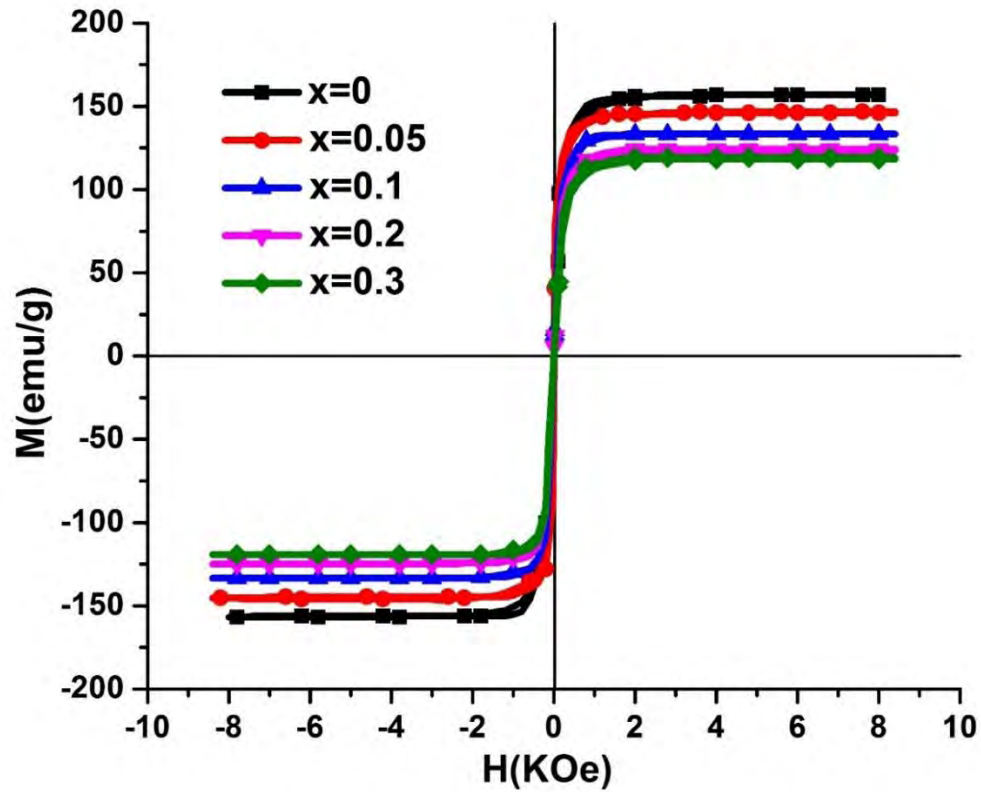


Figure 5.15 M-H loop for $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

The $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous ribbons presented soft magnetic properties with low coercivity(H_c) of 0.018 Oe for $x=0$ which is responsible for intrinsic fluctuations of the exchange and of the local anisotropy. [11]

As shown in **Figure 5.16** the coercivity increases gradually from 0.018 Oe (1.42 A/m) to 0.051 Oe (4.06 A/m) with increasing Mn content up to 30 at. % but saturation magnetization decreases with increasing Mn content. The increase in coercivity seems to be related to the decrease in glass-forming ability with increasing Mn content. That is, the decrease in the degree of structural disorder caused by the decrease in glass-forming ability causes the reduction in homogeneity of disordered atomic configurations, which realizes the increases in the high density of the quasi-dislocation dipole-type elastic stress sources and the high pinning force due to the elastic stress [12, 13].

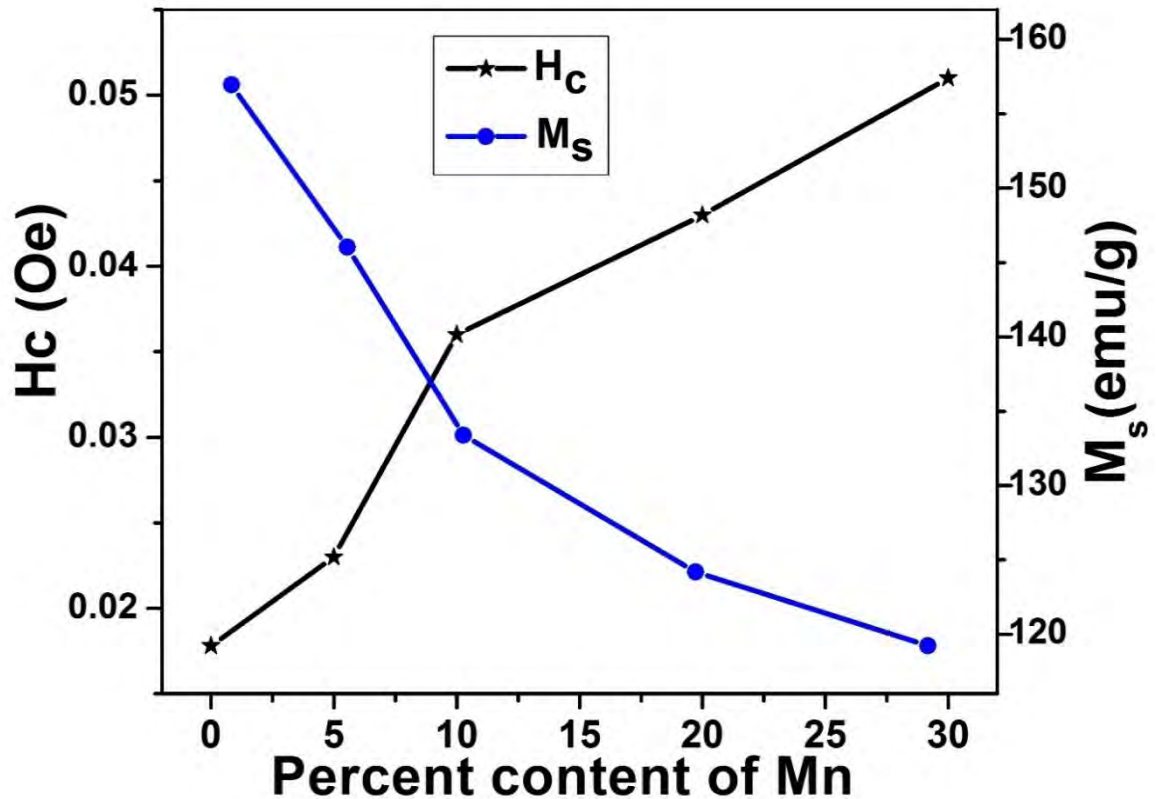


Figure 5.16: Coercivity (Left axis) and Saturation Magnetization (Right axis) versus Mn content of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

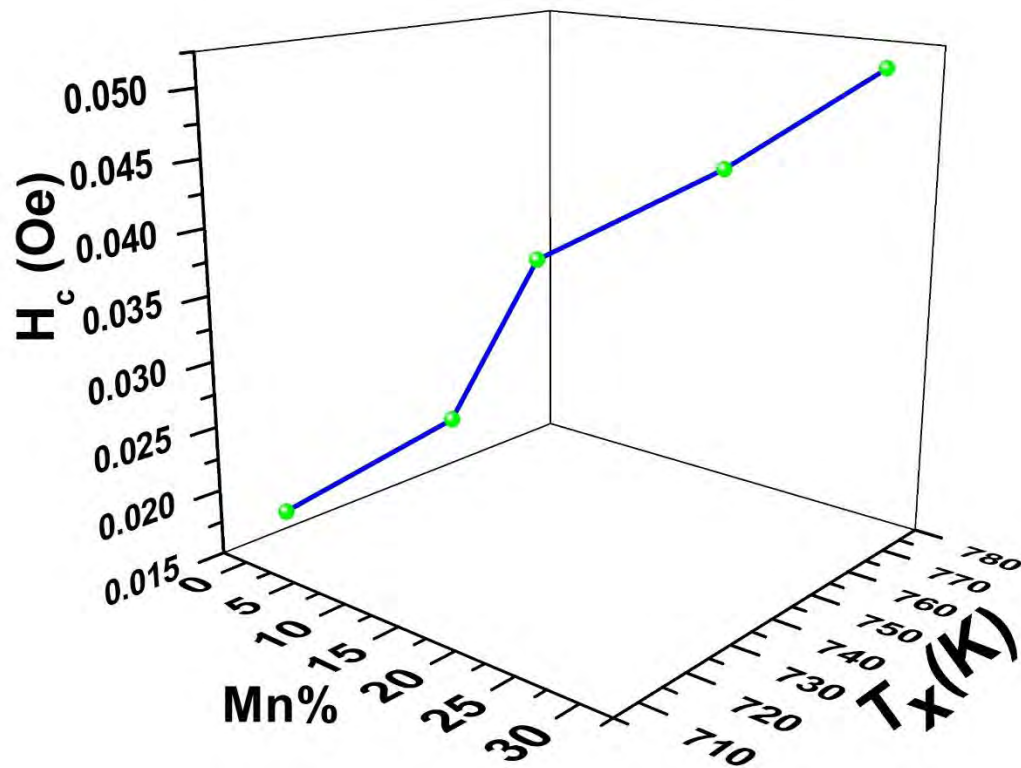


Figure 5.17 3D Graph for coercivity and crystallization temperature versus Mn%

Figure 5.17 shows the 3D Graph for coercivity and crystallization temperature versus Mn% which indicates that both the coercivity and crystallization temperature increases with increasing percent content of Mn which is described that the softness is decreasing with increasing crystallization temperature and antiferromagnetic material. This result explained by kinetics of the stress relaxation [14].

5.4.2 Permeability

Figure 5.18 and **Figure 5.19** shows the variation of complex permeability (real and imaginary part respectively) as a function of frequency from 100Hz-120MHz for the $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ with $x = 0, 0.05, 0.1, 0.2$ & 0.3 in the as cast amorphous ribbons. The $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous ribbons presented high effective permeability of 2.2×10^4 for $x=0$ up to 3 KHz which is shown in **Figure 5.18**. But the value of effective permeability is found to have decreased with low magnetic loss (shown on **Figure 5.20**) with increasing Mn contents of $x=.05, 0.1, 0.2$ and 0.3 . For all Mn content it is observed that the effective permeability fall down slightly upto 12 MHz then it fall down rapidly. The frequency at which μ' starts to fall off depends on the occurrence of various types of resonance; e.g., dimensional resonance due to the size of the core or magnetic resonance due to the rotation of the magnetization against the action of the anisotropy field or due to the resonant oscillation of domain walls [15]; Typical curves of μ'' as a function of frequency are shown in **Figure 5.20** which shows that μ'' fall down rapidly up to 3KHz then it shows very low magnetic loss which is exactly presented on **Figure 5.20**. This type of curve is compared with those of some conventional crystalline alloys [15-17] Supermalloy.

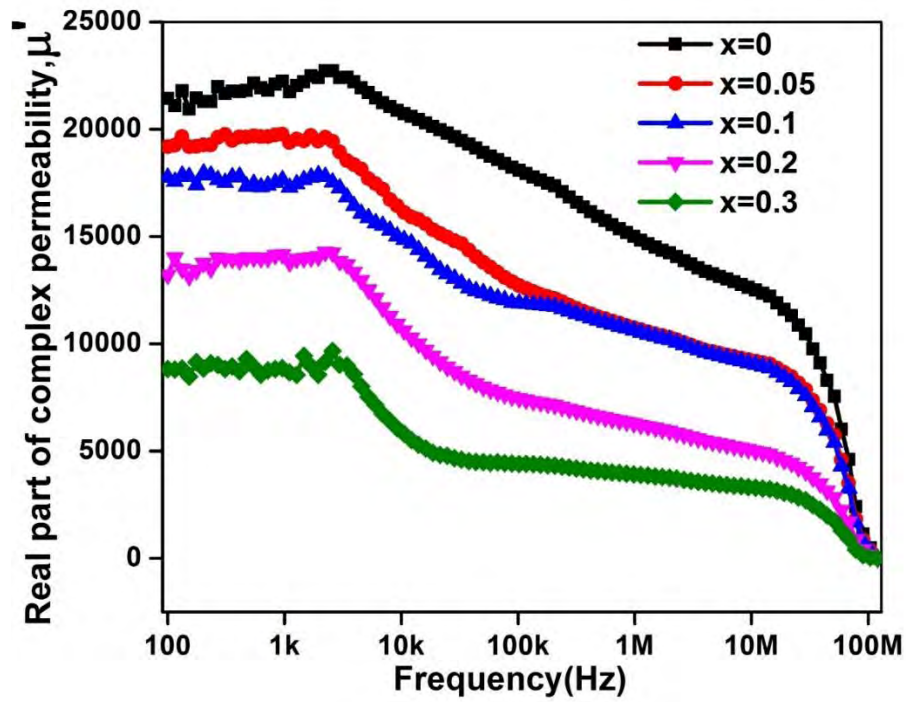


Figure 5.18: Frequency dependent complex permeability (Real part) of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

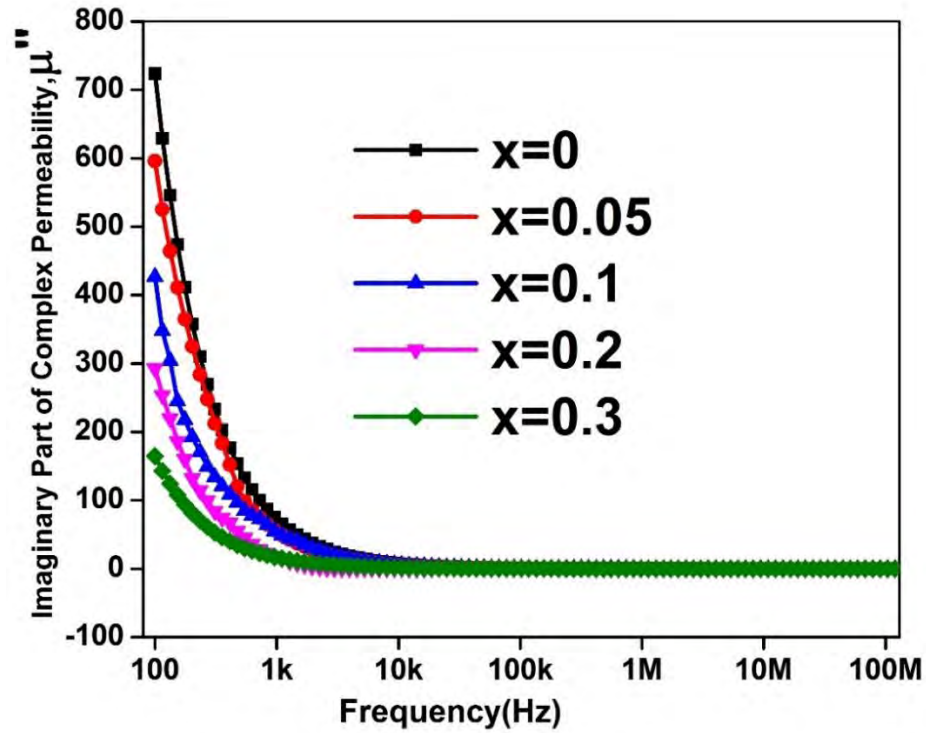


Figure 5.19: Frequency dependent complex permeability (Imaginary part) of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

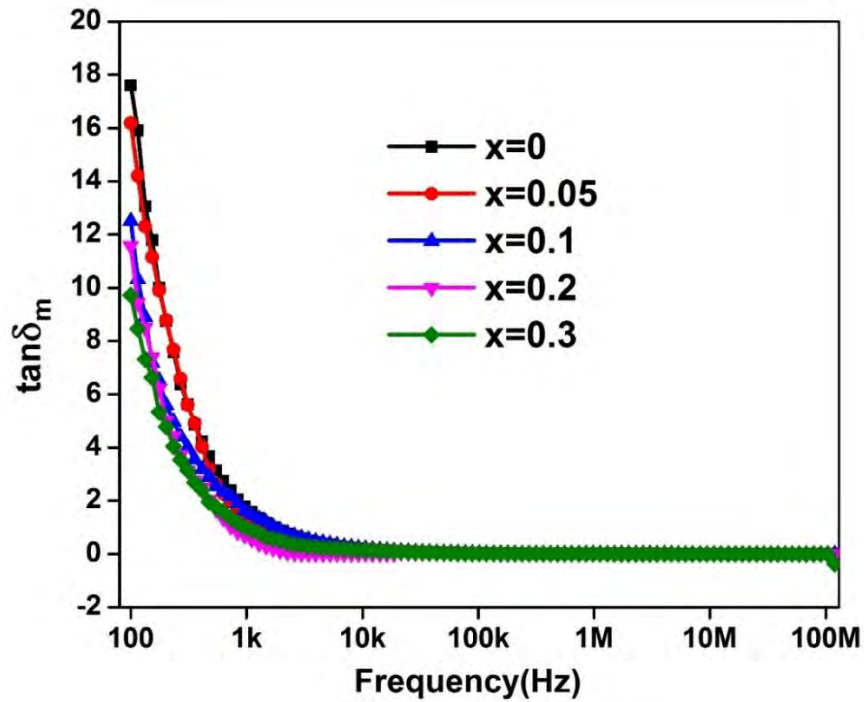


Figure 5.20: Frequency dependent Magnetic loss of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloys

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Chapter Six

Conclusions and Future Work

6.1 Conclusions

6.2 Suggestions for future Research

Chapter Six

Conclusions and Future Work

6.1 Conclusions

The structural, thermal electrical and magnetic properties of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ ($x=0, 0.05, 0.1, 0.2$ and 0.3) amorphous alloys have been studied by XRD, SEM, EDS DTA and measuring temperature dependent resistivity (from 77K to 600K) , magnetoresistance, magnetization complex permeability at room temperature. From all the study it is to be conclude that-

- The XRD patterns shows that samples are amorphous structure.
- The SEM micrograph shows not any crystalline or any other grain boundary shape formation which confirms that the all samples are amorphous in nature.
- The EDS pattern reveals the presence of Fe, Mn, P & C elements in the sample. No extra peaks have been traced which indicates that there is no contamination in the sample. The atomic % obtained from EDS spectra agrees well with the nominal values.
- The DTA trace shows seen that the peak crystallisation temperature (T_x) rises and the sharpness of DTA peak develops with increasing manganese content.
- The electrical resistivity (ρ) graph as a function of temperature (T) indicates both from the Ziman theory of structural topological scattering and the Mooij correlation for lower Mn concentration. But at larger Mn concentration, it is ascribed to a superposition of scattering from the structural topological disorder and the spin topological disorder. From the

normalized resistivity graph it is concluded that the interference of elastically backscattered electronic wave functions causes the resistivity increase at low temperature. Since the inelastic scattering increases at higher temperatures, the quantum interference is suppressed.

- There is an anomalous change of MR% is shown for all type of connection system around the magnetic field 0.3T on the MR% graph as a function of magnetic field strength which is reason for suppression of quantum localization corrections in the Drude equation for the magnetoconductance which is explained by the Kondo type magnetic scattering. The change in sign from positive to negative magnetoresistance is evaluated to be embedded in residual amorphous matrix which is described by the relevant theory of negative hopping magnetoresistance.
- The hysteresis M–H loop of the as-made samples presented high saturation magnetization but the coercivity is very low. The coercivity increases gradually but saturation magnetization decreases with increasing Mn content. The increase in coercivity seems to be related to the decrease in glass-forming ability with increasing Mn content.
- The complex permeability graph as a function of frequency shows high with low magnetic loss real permeability at low frequency but at which μ' starts to fall off at high frequency depends on the occurrence of various types of resonance; e.g., dimensional resonance due to the size of the core or magnetic resonance due to the rotation of the magnetization against the action of the anisotropy field or due to the resonant oscillation of domain walls.

- Both the study of M-H loop and permeability it is to be conclude that the $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloy ribbons are soft magnetic material at lower Mn concentration although the softness is decreasing with increasing of Mn concentration. And coercivity is increasing with increasing crystallization temperature.

6.2 Suggestions for future Research

The following experiments can be carried out for understanding the magneto-transport and the structural properties of $(\text{Fe}_{1-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$ amorphous alloy ribbons.

1. Grain size can be done by high resolution of SEM.
2. Structure of the samples may be examined by high resolution TEM.
3. Temperature dependent magnetic field dependent magnetic a,c, permeability and magnetization may be measured to determine the Curie Temperature (T_c),
4. Temperature dependent of MR% may be measured.
5. Magnetostriction and magnetic anisotropy constant may be measured.
6. Crystallization behavior may be studied of the annealed sample for various temperature by XRD may be measured.
7. Magneto-impedance may be measured.
8. Neutron scattering can be done to identify the magnetic structure.