Chapter II

Review of Literature
Introduction:

The term nanotechnology is employed to describe the creation and exploitation of materials with structural features in between those of atoms and bulk materials with at least one dimension is in the nanometer range (1nm = $10^{-9}$ m). The importance of nanotechnology was pointed out by Feynman as early as 1959, in his often cited lecture entitled “There is plenty of room at the bottom”. The main challenge is to beat Moore’s law, according to which the size of microelectronic devices shrinks by half every four years. This implies that by 2020, the size will be in the nm scale and we should be able to accommodate 1000 CDs in a wristwatch, there has been an explosive growth of Nano science and technology in the last few years, primarily because of the availability of new strategies for the synthesis of new tools for characterization.

The Nanomaterial’s are multicomponent crystalline ceramics in the range of the Nano scale (Less than 100 nm) with properties which differ from that material when are in bulk or in micron sized. This is due to the location of large number of atoms in the boundaries of the small crystalline, resulting in materials of High-K dielectric, Pyro electric, magnetic or Multiferroic properties and better mechanical, optical, electrochemical and catalytic properties. There is strong need to develop methods which are less cumbersome, more versatile and cost effective for their large scale production. This can only be achieved by having a thorough understanding of basics of magnetism, the electron spin, the atoms and their regular momentum (The Quantum) and the statistical mechanics.

The last two decades have seen a significant growth in the study of Nano particles such as ferrite Nano structured materials. They have attracted attention because of their surface effects [large surface to volume ratio] and quantum confinement effects [size dependent properties]. These factors affect their physical and chemical properties [Naseri et al. 2011]. Magnetic and spinal ferrite Nano crystals are regarded as one of the most important in-organic Nano materials because of their electronic, optical, electrical, magnetic and catalytic properties all of which are
different from their bulk counterparts [Naseri et al. 2011]. This chapter presents the
general methods being used for the synthesis of ferrite materials, their composites,
Multiferroics along with specific techniques being used for their evaluation and
analysis.

2.1 Ferrites:

History of ferrites could have begun many centuries ago as a material which
attracts iron, the major deposits of this ore were discovered in minor Asia’s district
Magnesia, thus named assigned to it was magnetite. It is thought that William Gilbert
was the individual who worked and reported properties of lodestone. Lodestone was
called magnes lapis, which was the origin of the word magnet [Chen et al. 1977].
Research on ferrite material was started in the late 19th century, and the term”ferrite”
was first used at the beginning of the 20th century, which is believed to be derived
from the latin word ferrum means iron [Zaspalis et al. 2004].

After Hans Christian Oersted (1800), many researchers of the like of Ampere,
Curie, Maxwell etc. worked and came up with wonderful properties of the material
and added their contributions in the development of Electromagnetic theory. A ferrite
produced by sintering and solution treatement was invented by Kato et al.in 1930, and
research data on ferrites were theoretically compiled by J.L. Snoek . The theory of
ferrimagnetism by L. Neel played a major role in the systemization of ferrite
technology.(he was awarded the Nobel prize for physics in 1970). Research work
carried out by scientist like Forestier, V. Kato, J.L. Snoek and L. Neel has been of
fundamental importance before 1950 [Moulson et al. 1990]. It is only after their work
progress could have been made towards the development of a theoretical description
of the magnetic materials. An attempt to provide insights of basic properties of ferrites
was made by J. Smit et al. [1959]. Generally the term ferrite is referred to all
magnetic oxides containing iron as a major component. They have a general chemical
formula MFe₂O₄ (M = any divalent cation (Zn, Cu, Ni, Co, Mg, Fe etc.)) [Chikazumi
and Charap 1964].

Ferrites continue to offer a rich display of a variety of physical phenomenon
attracting physicist, chemists and material scientist alike. The synthesis of Nano sized
magnetic oxide particles, such as spinel Nano ferrite of the type MFe₂O₄ (M is a
divalent metal cation), are intensively investigated in terms of their applications
magneto Ferro fluids, information storage system, high frequency devices and medical diagnostics [Phadate et al. 2013; Goldman 2006; Laokul et al. 2011; Prasad and Gajbhiye 1998; Hankare et al. 2010; Saafan et al. 2010; Salavati-Niasari et al. 2009]. These materials are also largely used in electric and electronic devices and in catalysis.

In order to improve properties, the investigation of alternative, nonconventional synthetic methods to obtain ferrites in the form of nanostructured powders is the current subject. Numerous methods of producing ferrites have been introduced and are still currently being developed. Important methods being sol-gel [Wang and Li 2001], hydrothermal [Upadhyay et al. 2003], glycothermal [Bae et al. 2003], citrate precursor [Dey et al. 2004; Verma et al. 1999; Panda et al. 2003] and combustion [Costa et al. 2003; Mangalaraja et al. 2003; R. V. Mangalaraja et al. 2004] which seek to produce better quality ferrites. In wet chemical methods the salt solutions of desired compositions are mixed thoroughly to ensure molecular level of mixing.

A base such as KOH or fuel cum chelating agent such as urea is added to the mixture. The final mixture is then heated in order to form the desired ferrite powder. The sintering temperature of the final product that ensures single phase formation tends to be much lower than for samples produced by solid state reaction. The incorporation of unwanted impurities and sample losses are much reduced in samples produced by wet chemical methods. In order to investigate the effect of different production techniques on the properties of ferrites, samples were produced by chemical combustion and hydrothermal methods studied in the current work.

Ferrites are considered as advance materials for their crucial role as pace setters and the role they find in pushing the development of civilization at a great pace. Based on the magnetic properties of high or low coercivity ferrites are classified as soft & hard ferrites.

**Soft ferrites:**

They have boosted up new electronic technology and are widely used in electromagnetic cores of transformers, switching circuits in computers and for motors and generators. Ferrites of Ni, Zn, Li, Mn, and Cu as individual or in mixed
compositions do have less value of coercivity causing low hysteresis loss at high frequency, and are the best material for new technologies.

**Hard ferrites:**

It is an integral property associated with material like Barium, Strontium ferrite having a characteristic feature of having high value of retentivity and coercivity. These retain magnetization even when magnetic field is taken off, and are considered as permanent magnets.

### 2.2 The Basic structure:

In general ferrites have spinel structure which gets deviated to small extent from it on substitution. It comprises of cubic close packed Case of oxygen ions with metallic ions occupying tetrahedral (A) and Octahedral (B) sites.

#### 2.2.1 Crystal Structure of Spinel:

Unit cell structure of spinel’s is derived from the structure of mineral spinel, MgAl₂O₄[Rath et al. 1999]. Ferrites are denoted by a formula AB₂O₄ where A stands for a divalent metal cation (Mg²⁺, Ni²⁺, Zn²⁺, Cu²⁺, Co²⁺ etc.) and B stands for trivalent cation(Fe³⁺, Cr³⁺, Al³⁺ etc.). There are a total of 56 atoms in a unit cell of ferrite which is made up of 8 formula units of Meo-Fe₂O₃.

![Figure 2.1 Crystal structure of Spinel](image)

**Figure 2.1 Crystal structure of Spinel**
Oxygen ions (32) are arranged in cubic close packing, which accommodate octahedral and tetrahedral sites for metal cations. The A site ions have four neighbouring oxygen ions forming a tetrahedron (tetrahedral site), on the other hand B sites ions are surrounded by six oxygen ions forming an octahedron (octahedral sites) [Rath et al. 1999]. This arrangement provides 64 A tetrahedral and 32 octahedral B sites available for cations. Among these 8 tetrahedral A and 16 octahedral sites B are occupied.

Array of oxygen ions create two interstitial sites, tetrahedral and octahedral. Metal cations do show a natural tendency of preference for A and B site, for example Zn has preference for A sites (Tetrahedral) while Ni has it for B Site (Octahedral).

![Figure 2.2 Tetrahedral and Octahedral sites in crystal structure of Spinel](image)

Figure 2.2 Tetrahedral and Octahedral sites in crystal structure of Spinel

Cation distribution in spinel’s is denoted by different bracket notations, Ions on tetrahedral sites whether divalent or trivalent are designated by Round brackets ( ) and those on octahedral one are by square brackets [ ]. Cations also have their site preference depending on their size and electron configuration. Those with smaller size prefer to occupy the small tetrahedral site while larger cations occupy octahedral sites. Zn$^{2+}$ show preference for A site because 4s, 4p, 5s, 5p electrons form covalent bond with six 2p electrons of oxygen ions prefer B site.

2.3 Types of spinels:

Preference of site by metal cations and displacements of others from that site in accordance with site preference energies lead to deformity /changes in structure of
spinel. In general array of oxygen ions form an FCC lattice and divalent (A) and trivalent (B) ions occupy interstitial sites.

**Normal Spinel:**

In this type of spinel structure 8 divalent metal ions occupy 8 tetrahedral sites and the 16 Fe$^{3+}$ ions occupy 16 octahedral sites [Aulock and Boxer 1965; Liu *et al.* 2005; Gibb 1976; Amer and Hemeda 1995] serves an excellent example of normal spinel structure. In ZnFe$_2$O$_4$ system Zn$^{2+}$ (non–magnetic ion) occupy B site, resulting into no interaction between these two. But Fe$^{3+}$ - Fe$^{3+}$ (B-B) interaction does occur, leading to anti-parallel alignment of trivalent ions and produce a zero net magnetization [Chikazumi and Charap 1978].

**Inverse spinel:**

In case of Inverse spinel’s the trivalent ions [M$^{3+}$] are equally divided/distributed between tetrahedral & octahedral sites (8 each out of 16) and all of the divalent cations [M$^{2+}$] occupy octahedral sites. Example of such a spinel is NiFe$_2$O$_4$ [Chinnasamy *et al.* 2001].In which Ni$^{2+}$ ions occupy 8 octahedral sites and among 16 Fe$^{3+}$ ions half go to occupy octahedral sites and remaining half occupy tetrahedral sites. As in ferrites magnetic moments of both sites A and B are antiparallel to each other and resultant magnetization is only due to divalent metal cation [Hemeda *et al.* 2001].

**Random / Mixed Spinel Structures:**

Mixed spinel structure, when cations M$^{2+}$ and Fe$^{3+}$ occupy both A and B-positions; In these type of spinel’s structures gets partially changed due to replacement of either A or B type of ions depending upon doping. It may be A$_{(1-x)}$B$_x$Fe$_2$O$_4$ or AB$_{(x)}$Fe$_{2(2-x)}$O$_4$. On the basis of ion and its preference site energy basic structure of unit cell gets partially mixed.

**2.4 Nanocomposites:**

One of the fascinating properties of ferrites is the possibility to prepare different compositions and thereby alter the magnetic properties. Recently, one of the challenges is to improve the magnetic properties of soft ferrites such as saturation magnetization, magnetic hysteresis, demagnetizing force and anisotropic energy.
People are trying to produce hard and soft ferrites by using simple methods. In view of this, many have focused on their study towards new systems, such as CoFe$_2$O$_4$/ZnFe$_2$O$_4$, earth-iron-boron and Fe/Z-type ferrite [Masala et al. 2006; Maeda et al. 2004; Liu et al. 2006].

The results suggest that coupling exchange exists between the nanoparticles and the interaction significantly influences magnetization and coercivity of the composite powders. [Masala et al. 2006] They reported that exchange interaction between hard and soft magnetic phases improve the microwave absorption and magnetic properties of Nanocomposites.

In the recent years, cumulative consideration has been paid in the area of Nano composite magnets [Asti et al. 2004; Erokhin et al. 2012] as it delivers an integrated system comprising of components whose properties are harmonizing to each other. One such dynamic field of research is the exchange spring magnets [Uzdin et al. 2012; Kneller and Hawig 1991; Shield et al. 2006; Zhou et al. 2005; Suess et al. 2005], where high saturation magnetization of the soft and the high magnetic anisotropy of the hard magnetic phases are exchange coupled in the Nano metric scale.

Nanocomposites include multiphase solid materials wherein one of the phases has a dimension of less than 100 nm. The mechanical, electrical, optical, electrochemical, and catalytic properties of these Nanocomposites will differ markedly from those of the component materials. Other kinds of Nano particulates may result in enhanced optical properties, dielectric properties or mechanical properties such as stiffness and strength [Roy et al. 2013].

2.5 Multiferroics:

Recently, due to development of electronic technology, the trends of miniaturization and excellent electromagnetic properties are the utmost requirements of materials to be used for different purposes and these have been and are being fulfilled by the materials called Composites [Grössinger et al. 2008; Goldman 1990]. With the development of electronic technology composite materials have been widely used for electronic devices where higher densities, limited space and multifunction ability are required. Recently the ferroelectric - ferromagnetic composite materials
were intensively produced for their uses as the magnetic–electric sensor in radio-electronics, optoelectronics, microwave and transducer and the compact electrical filters for suppressing electromagnetic interference (EMI).

As for the magnetic–electric sensor, High ferroelectric content was necessary for the composite material with sufficient resistivity to generate electromagnetic effect.

**Figure 2.3(a) Different ferroic order in multiferroics**

In the recent research has been carried out on Multiferroic (MF) composite materials [Ma et al. 2011; Ramesh and Spaldin 2007] which have been under the focus of researchers due to their potential applications in electronics technology (as magnetic–electric sensors in radio-electronics, optoelectronics, microwave electronics and transducers). In MF materials, magnetic and electric orders coexist simultaneously and the coupling between spin and charge degrees of freedom gives rise to a wide range of magneto electric phenomenon [Eerenstein et al. 2006; Fitchorov et al. 2011; Verma and Negi 2010].

The control of polarization by applying magnetic fields or the magnetization by applying electric fields, which is known as the magneto electric (ME) effect, appears in the materials when the electric polarization and magnetic orders are coupled to each other [Fitchorov et al. 2011; Verma and Negi 2010].
The ME effect can also be given as direct ME effect which is characterized as magnetic-field-induced polarization and electric-field-induced magnetization, respectively [Chu et al. 2008]. The different types of single-phase Multiferroics such as BiFeO₃ [Chu et al. 2008], TbMn₂O₅ [Hur et al. 2004], BaTiO₃-CoFe₂O₄ [Agarwal et al. 2012], 0.62Pb(Mg₀.₃3/Nb₂/₃)O₃-0.38PbTiO₃, Ni₄₇.₄Mn₃₂.₁Ga₂₀.₅/PZT [Wang et al. 2010] etc. are investigated in reported work. Mostly these MF systems are extensively studied and they are the focus of current research because of the advancement in every field. To overcome the scarcity of single-phase Multiferroics, one approach is to enhance the specific characteristics by doping and the other is the development of new Multiferroic materials such as ferroelectric-ferromagnetic. However the composite of ferrite such as NiFe₂O₄, NiZnFe₂O₄ and CoFe₂O₄ etc. with Perovskites such as BaTiO₃, PbTiO₃ and CaTiO₃ is of technological importance. Because these ferrites based composites are results in Multiferroic properties of higher magnetization in spintronics devices. Also the electric behaviour of ferrites is highly usable in high frequency based devices.

Most of the work on Multiferroics has been directed towards to bring ferromagnetism and electricity together in one material. It is a very difficult problem, as to contrast these two order parameters turned out to be mutually exclusive. Most ferroelectrics materials are of the transition metal oxides. In the transition ions have empty d shells and there is collective shift of anions and cations inside crystal and induce the bulk electric polarization. It’s the contrary on Magnetism, as it requires transition metal ions with partially filled d shells, as the spins of electrons occupying completely filled shells add the zero magnetism and does not participate in magnetic ordering.

Furthermore, it has been observed that the simultaneous presence of magnetic dipoles and electric does not show strong coupling between the two, as microscopic mechanisms of Ferro-electricity and magnetism are quite different and they do not generally interfere with each other. For Ferro-electricity and magnetism to coexist in a single phase, therefore, the atoms that move off centre to form the electric dipole moment should be different from those that carry the magnetic moment. In the Perovskites Multiferroic is achieved by use of the stereo chemical activity of the lone pair on the large cation to provide Ferro-electricity, while keeping the small cation magnetic [Nechache and Rosei 2012].
2.5.1 The Concept of Multiferroics:

The term Multiferroic was first used by H. Schmidt in 1944. Multiferroic materials exhibit more than one ferroic order parameter coupling between different ferroic order parameters hold potential for electric field controlled magnetic memory, 4-state logic and magnetoelectric sensors. This has contributed to an increased research interest in Multiferroic materials in recent years [Fiebig 2005; Vaz 2012]. His original definition referred to Multiferroics as single phase materials which simultaneously possess two or more primary ferroic properties.

Today people extend the definition to include other long-range orders, such as antiferromagnetic. In this extended definition, we can say that this research field was born in the 60’s even the 50’s. From then people started to do related studies under the name magnetoelectric.

2.5.2 Types of Multiferroic:

2.5.2.1 Type-I Multiferroics:

This type of Multiferroics shows good ferroelectrics order and the critical temperature of the magnetic and ferroelectric transition can be well above room temperature. The coupling between magnetism and ferroelectricity in these materials are usually weak. The materials challenge for this group Multiferroics is to keep their all positive features, but enhance this coupling. The type-I Multiferroics further divided in following subclasses:

Lone pair Multiferroics:

In these types of Multiferroics the ferroelectricity exists mainly in Perovskites-based Multiferroics like BaTiO₃. The ferroelectric distortion occurs due to the displacement of cation (Ti) with respect to the oxygen octahedral cage. Hence in transition metal the empty d shell is required for the ferroelectricity. In order for the coexistence of magnetism and ferroelectricity (Multiferroic), one possible mechanism is lone-pair driven where the A-site drives the displacement and partially filled “d” shell on the B-site contributes to the magnetism. Examples include BiFeO₃, BiMnO₃. The active 6s² lone pairs, also called dangling bonds, have a high polarizability and are the source of the ferroelectricity in this mechanism due to which the the O 2p orbital come closer in energy to the Bi 6p (empty) orbital.
Charge ordering:

A possible origin for a Multiferroic state is charge ordering. Such an order can occur in a compound containing ions of mixed valence and with geometrical or magnetic frustration. These ions form a polar arrangement, causing improper ferroelectricity (i.e., no ionic displacement). If magnetic ions are present, a coexisting magnetic order can be established and may be coupled to ferroelectricity. One prominent example for a charge ordered Multiferroic is LuFe$_2$O$_4$, which shows improper ferroelectricity below 330 K. The arrangements of the electrons arise from the charge frustration on a triangular lattice with the mixed valence state of Fe$^{2+}$ and Fe$^{3+}$ ions. Ferromagnetic behaviour occurs below 240 K. In addition, charge ordered ferroelectricity is suggested in Fe$_3$O$_4$ and (Pr, Ca) MnO$_3$. The concept of electronic ferroelectricity is generally correlated with the concept of charge ordering. For example, certain divalent doped Perovskite R$_{1-x}$A$_x$MnO$_3$ that exhibit an intermediate state between site-cantered and bond-centred charge ordering should be ferroelectric.

Geometric Ferroelectricity:

Ferroelectricity is caused by the tilting of any block. This tilting occurs to get the closed packing, e.g., YMnO$_3$. In this crystal MnO$_5$ block is to prove closed packing. So the oxygen become equivalent to yttrium and this causes ferroelectricity in YMnO$_3$. The Geometric ferroelectricity is shown in Fig. 2.3(b).

Figure 2.3(b) Different types of Type-I Multiferroics.
2.5.2.2 Type-II Multiferroics:

In type- II of Multiferroics, there is very strong coupling between ferroelectric and magnetic order parameters. These are further divided in following types as below:

**Spiral Multiferroics:**

In these types of crystals ferroelectricity appears in conjunction with a spiralling magnetic phase, mostly of the cycloid type. Ferroelectricity is mainly due to spin-orbit coupling e.g., TbMnO$_3$.

**Collinear magnetic structure:**

![Image of different type of spinel structure relevant for type-II](image)

**Figure 2.3(c) Different type of spinel structure relevant for type-II**

The second type of magnetically driven ferroelectrics is those in which ferroelectricity appears in collinear magnetic structure. The magnetic coupling varies with atomic positions. e.g., CaCoMnO$_6$ Multiferroics.

2.6 Perovskite (PbTiO$_3$, BaTiO$_3$ etc.) based Multiferroics:

**Perovskites** are calcium titanium oxide minerals species composed of calcium titanium, with the chemical formula CaTiO$_3$. Perovskites are oxides having crystalline structure which is usually expressed as ABO$_3$. The structure contains two cation sites in the crystal lattice: the larger cation (A) resides on the corners of the unit cell and is usually an alkaline earth or rare earth element, and the smaller cation (B) is located in the centre of the lattice, could be 3d, 4d, and 5d transition metal elements. The oxygen ions (O) are on the centres of the faces, and the structure is formed via a network of corner-linked oxygen octahedra, with the larger cation (A) filling the dodecahedral holes and the smaller cation (B) filling the octahedral sites.

B site ions, on the centre of the lattice, could be 3d, 4d, and 5d transitional metal elements. A large number of metallic elements are stable in the Perovskite
structure, if the tolerance factor “t” is in the range of 0.75 – 1.0 [Freire and Katiyar 1988]

\[ t = \frac{(RA + RO)}{\sqrt{2} (RB + RO)} \]

Where, RA, RB and RO are the ionic radii of A and B site elements and oxygen, respectively. The structure of a Perovskite is usually depicted in pseudo cubic form, as shown in Figure-2.3(d) Examples include BaTiO$_3$ (A$^{2+}$B$^{4+}$O$_3$); NdAlO$_3$ (A$^{3+}$B$^{3+}$O$_3$), and complex Perovskites such as Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$. The A cations occupy the larger spaces in the 12-fold oxygen coordinated holes; the B cations occupy the much smaller octahedral holes (six fold co-ordination).

It can be observed that the coordination number of cation A is 12 and for cation B is 6. When the overall valence of the A-site and B-site cations (n+m) adds up to less than 6, the missing charge is made up by introducing vacancies at the oxygen lattice sites.

![Figure 2.3(d) Perovskite structure of BaTiO$_3$](image)

2.6.1 Multiferroic BaTiO$_3$:

Multiferroic BaTiO$_3$ belong to the family of ferroelectric oxide Perovskites (such as BaTiO$_3$ and PbTiO$_3$). The application of BaTiO$_3$ at Nano scale is very useful in ferroelectric non-volatile memory to increase the memory density a thousand-fold by writing and reading into single Nano-particles [Yun et al. 2002]. The Nano crystal structural and the physical properties of Multiferroic BaTiO$_3$ are strongly dependent
on the grain size. The crystal lattice of BaTiO$_3$ expands and the phase transition temperature decreases as the size of nanoparticles is decreased.

### 2.6.1.1 Multiferroic Composites:

A composite is a structural material that consists of two or more combined constituents that are combined at a macroscopic level and are not soluble in each other. The Multiferroic composite shows these characteristics, High specific strength and modulus, as well as high fatigue strength and fatigue damage tolerance, Anisotropic, Designable or tailor able materials for both microstructure and properties, Production of both material and structure or component in a single operation - manufacturing flexible, net-shape, complex geometry Corrosion resistance and durable Other unique functional properties - damping, low CTE (coefficient of thermal expansion). Ferroelectric- ferrite composites ceramics can provide both inductance and capacitance so these materials can be used to design and produce passive EMI filters integrating inductive and capacitive elements.

### 2.6.1.2 Need of Research (Why We Use Batio$_3$):

Barium titanate (BaTiO$_3$) has been of special interest for more than 60 years because of its attractive properties. Firstly, it is chemically and mechanically very stable, secondly, it exhibits ferroelectric properties at and above room temperature, and finally it can be easily prepared and used in the form of ceramic polycrystalline samples [Jona and Shirane 1993]. Due to its high dielectric constant and low loss characteristics, Barium titanate has been used in applications, such as capacitors and multilayer capacitors (MLCs).

As reported above solid state reaction or conventional ceramics method is usually followed to prepare BaTiO$_3$- ZnFe$_2$O$_4$ or BaTiO$_3$. Zinc ferrite (ZnFe$_2$O$_4$) is widely used as a soft ferrite in electronic devices. It is also used in catalysis. Zinc ferrite belongs to inverse spinel structure, in which the tetrahedral sites (A) are occupied by Fe$^{3+}$ ions and the octahedral sites (B) by Fe$^{2+}$ and Zn$^{2+}$ ions. BaTiO$_3$ is a typical ferroelectric material which has a large piezoelectricity. ZnFe$_2$O$_4$ is ferromagnetic with large magnetization. Multiferroics BaTiO$_3$-ZnFe$_2$O$_4$ composite could be regarded as model system illustrating magneto electric effect. Among
different composites $\text{BaTiO}_3\text{-ZnFe}_2\text{O}_4$ composite seems to be most promising for applications.

2.7 Review of literature:

The literature is full of methods used from time to time to produce Nano ferrite both in pure and doped form with variety of cations resulting in materials of versatile magnetic, electrical, mechanical and catalytic properties etc. The prominent research that was carried by different scientists and engineers regarding synthesis and improving the properties of Ferrites their composites and Multiferroics have been reviewed as under:-

2.7.1 Doped and Pure $\text{NiFe}_2\text{O}_4$ ($\text{Ni}_{(1-x)}\text{Zn}_{(x)}\text{Fe}_2\text{O}_4$):

Goodenough and Loeb 1955, in their investigations they found that the covalent bond in spinels has been shown to influence cation ordering, lattice distortions, and magnetic exchange interactions. Smit et al. 1959 in their book mentioned that $\text{Zn}^{2+}$ is used to improve electromagnetic properties as well as densification in the ferrite. It is substituted in spinel ferrite to improve magnetization. Murthy et al. 1969, measured lattice constant, Neél temperature, Debye temperature, magnetic moment and Yafet-Kittel angles of $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ ferrites using neutron diffraction in the range of $0 \leq x \leq 0.75$ prepared by the usual ceramic sintering process. It was noted that lattice parameter and Y-K angles increased whereas Neél temperature decreased with the rise in zinc concentration.

Srinivasan et al. 1988, measured lattice constant, theoretical density, saturation magnetization, Curie temperature, grain size and permeability of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites prepared by novel hydrazinium metal hydrazine carboxylate precursors. The lattice constant increased whereas the Curie temperature decreased with the rise in zinc concentration. Also it was observed that the theoretical density, grain size and permeability increased with the increase in sintering temperature. Rosales et al. 1998, quoted density, Curie temperature and permeability for $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ferrites prepared using the conventional ceramic powder methodology with $x$ ranging 0.3-0.4 sintered at different temperatures and time.
It was observed that density, Curie temperature and permeability all the parameters increased with the increase in sintering time. Tseng and Lin 1989, observed scanning electron micrographs, sintered density, average grain size, permeability and resistivity of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ferrites prepared by chemically co-precipitated. It was found that sintered density, average grain size and permeability increased whereas resistivity decreased with the rise in sintering temperature.

Rao and Rao 1997, reported the effect of sintering conditions on resistivity and dielectric properties of Ni$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$ ferrites. Resistivity decreased with the increase in sintering time as well as sintering temperature. Dielectric constant increased with the rise in sintering temperature. Dielectric constant as well as dielectric loss tangent both decreased with the increase in frequency.

Sickafus et al. 1999, examined the structure of spinel’s and studied in detail of the role of three structural parameters which determine the detailed atomic arrangements in spinel’s, The lattice parameter, a; the anion parameter, u; and the cation inversion parameter, i. Van der Zaag 1999, employed a neutron depolarization experiment on ferrites and reported that below a critical size, the grains of ferrites acted as mono domains those exhibit low power loss even at MHZ frequencies. They also indicated that resistance in domain wall motion contributed in hysteresis loss. Reddy et al. 1999, in their study investigated the dielectric behaviour of Ni-Zn ferrites with respect to temperature and frequency.

Bercoff and Bertorello 2000, presented localized canting effect in Zn-substituted Ni ferrites with a theoretical model of three sub lattices (A, B and B’) to describe their magnetic behaviour. Number of Bohr magnetons per formula unit and Curie temperature were also described as a function of Zn content. Verma et al. 2000 prepared and reported magnetic properties of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites with (x = 0.2, 0.35, 0.5, 0.6), by the citrate precursor method. The relative loss factor has been discussed with the variation in frequency. Also in his investigations it was seen that the coercivity decreased with the rise in average grain size.

Sun et al. 2002, stated density, lattice parameter, electrical resistivity, dielectric constant and loss tangent of Ni$_{0.5}$Zn$_{0.5}$Fe$_{2-x}$R$_x$O$_4$ ferrites (R = La or Gd, x = 0-0.04) prepared by solid state reaction method. Lattice parameter increased whereas
the density decreased with the increase in R concentration. They reported that dielectric constant and dielectric loss factor both decreased with the increase in frequency. Mangalaraja et al. 2002, prepared Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ ferrites by microwave-assisted flash combustion technique at sintering. They measured saturation magnetization, coercivity, remanent flux density, maximum flux density, dc electrical resistivity, activation energy, sintered density, porosity, grain size, ac resistivity, dielectric constant and dielectric loss factor for the sintered samples.

It was reported that sintered density, grain size, saturation magnetization, remanent flux density and maximum flux density increased whereas coercivity, activation energy and porosity decreased with the rise in sintering temperature. El-Sayed 2002, reported lattice constant, FTIRS, bulk density, X-ray density, apparent porosity and diameter shrinkage of Ni$_{1-y}$Zn$_y$Fe$_2$O$_4$ ferrites for 0.1 ≤ y ≤ 0.9 with the step increment of 0.2 prepared by usual ceramic technology and sintered at 1250 °C in static air atmosphere. Their investigation revealed that lattice constant and porosity increased whereas bulk density, X-ray density and diameter shrinkage decreased with the increase in zinc concentration.

Mangalaraja et al. 2003, studied Dielectric behaviour of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites prepared by flash combustion technique. It was observed that Dielectric constant and dielectric loss factor decreased with the rise in frequency for various concentrations of zinc sintered at different temperatures. Porosity decreased with the increase in Zn concentration for the final product sintered at different temperatures. Ott et al. 2003, suggested the design principles regarding the processing of ferrites by conventional mixed oxide method. According to them, a ternary diagram could be used to select right composition for a particular application.

They further explored that suitable additives could be used to control the microstructure. While appropriate sintering conditions helped to homogenize the microstructure and gave excellent magnetic properties. Rao and Rao 2003, noted grain size, sintered density, resistivity, saturation magnetization, initial permeability and magnetic loss factor of Ni$_{0.65-x}$Zn$_{0.35+x}$Fe$_{2-x}$Sc$_x$O$_4$ ferrites prepared by conventional ceramic. The initial permeability increased with the increase in x.
Mangalaraja et al. 2004, measured scanning electron micrographs, bulk density, porosity, dielectric constant and dielectric loss factor of Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ ferrites prepared by microwave-assisted flash combustion. It was observed from the findings that Dielectric constant and dielectric loss factor both decreased with the increase in frequency. Also bulk density increased whereas porosity decreased with the increase in sintering temperature. Ahmed et al. 2005, investigated the influence of zinc ion substitution on densification in Ni-Zn ferrite. They found rapid densification with increased Zn$^{2+}$ concentration. Sun et al. 2004, reported the initial permeability and relative loss factor increased while the cut off frequency decreased with increasing Zn content in (Ni$_{1-x}$Zn$_x$)$_{Fe_2}$O$_4$ ferrite.

Islam et al. 2004, prepared Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ by co-precipitation technique. They reported that resistivity and activation energy both increased up to $x = 0.25$ and then decreased with the rise in Zn concentration. Kikukawa et al. 2004, used glycerine nitrate process to synthesize Zn substituted M-Zn Ferrites, where M= Mg, Co, Mn, Ni, Cu, (Li, Fe). They suggested that glycerine to nitrate ratio (G/N) would be 0.5 to develop Mn-Zn ferrite system with good stoichiometry and Nano crystallinity. Pradeep et al. 2004, synthesis and structural studies on Ni$_{0.5+x}$Zn$_{0.5}$Fe$_2$O$_4$ ferrites prepared by conventional ceramic double sintering method were done by It was observed that lattice constant, Curie temperature and activation energy increased whereas magnetic moment decreased with the increase in Zn concentration.

Verma et al. 2005, reported the temperature dependence electrical properties of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites prepared by citrate precursor technique. Resistivity decreased and dielectric constant and dielectric loss angle both increased with the rise in temperature. Ghazanfar et al. 2005, studied room temperature resistivity and activation energy for Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ ferrites. They reported that resistivity and activation energy both increased with the increase in concentration of nickel. Resistivity decreased with the increase in temperature which shows the semiconductor like behaviour of the ferrites. Bera and Roy 2005, noted the bulk density, porosity, permeability, grain size, resistivity and relative loss factor for Ni$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ ferrites prepared by standard ceramic technique. It was stated that bulk density, grain size and permeability increased whereas porosity decreased with the rise in sintering time. Resistivity also decreased with the increase in grain size. Rao et al. 2005, measured
resistivity, dielectric constant and dielectric loss factor of Ni\(_{0.65}\)Zn\(_{0.35}\)Fe\(_2\)O\(_4\)+\(x\)V\(_2\)O\(_5\) ferrites prepared by conventional ceramic. The behaviour of the above mentioned parameters were discussed with the variation of concentration of vanadium pentoxide and the variation of frequency.

Hossain et al. 2007, prepared Ni\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\) ferrites using solid state reaction technique followed by sintering at various temperatures. They investigated the structural, electrical transport and magnetic properties. The variation in resistivity, saturation magnetization, bulk density and permeability were studied as a function of temperature. They reported that resistivity and saturation magnetization both decreased with the increase in temperature. Zhang et al. 2007, described the structural and magnetic properties of Ni\(_x\)Zn\(_{1-x}\)Fe\(_2\)O\(_4\) ferrites nanoparticles prepared by sol-gel auto-combustion method. Lattice parameter decreased with the increase in Ni contents. The change in saturation magnetization and coercivity has also been discussed with the variation in composition as well as the annealing temperature.

Gabal 2003, prepared Zinc substituted NiFe\(_2\)O\(_4\) via thermal decomposition of respective oxalates. They characterized samples by using X-ray diffraction, FT-IR and Mossbauer spectra and also studied dielectric properties. Zhao et al. 2009, synthesized nickel ferrite nanoparticles by the polyacrylamide gel method with acrylamide as the monomer and N.N’- Methylene acrylamide as lattice agent. They studied ferrite-polystyrene composites microwave absorbing properties. They found that complex permeability and complex permittivity of composites increases with increasing ferrite content. Mahalakshmi and Manja 2008, prepared Ni\(_x\)Fe\(_{3-x}\)O\(_4\) ferrites by chemical co-precipitation method and studied Dielectric constant, dielectric loss factor, ac electrical conductivity and saturation magnetization.

It was noted that dielectric constant decreased with the increase of nickel concentration as well as with the increase in frequency from 0 to 1 MHz. The dielectric loss factor increased with the rise in frequency. Saturation magnetization increased with the rise in nickel concentration. Gul et al. 2008, studied Crystallite size, lattice constant, volume of crystallite, measured density, X-ray density, resistivity, activation energy, correlation coefficient, drift mobility and transition temperature were for Ni\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\)ferrites prepared by chemical co-precipitation route. It was observed that lattice constant, volume of crystallite, measured density,
X-ray density and activation energy all increased whereas crystallite size and transition temperature decreased with the increase in Zinc concentration.

Nguyet et al. 201, prepared Nano sized nickel ferrites by the citrate precursor method. Curie temperature and lattice constant were found to be in agreement with those of bulk material. They explained variation of Ms in the temperature range 5 to 300k with respect to modified Bloch law. Jacob et al. 2011, studied changes in structure and magnetic properties of NiFe$_2$O$_4$ nanoparticles on role of methodology employed. They have reported that Co-precipitation results in smaller nanoparticles as compared to Sol-gel method. Maaz et al. 2010, prepared nanoparticles of NiFe$_2$O$_4$ by chemical Co-precipitation method. Their investigations showed increase in coercivity with decrease in temperature and also observed that saturation magnetization follows the modified Bloch’s law in the temperature range from 300 to 50 K. Raghavender et al. 2010, in their findings revealed that grain size decreases with increasing calcination temperature. Neel temperature was also found to be decreasing with decreasing grain size.

Sivakumar et al. 2012, prepared nanowires of NiFe$_2$O$_4$ by PEG assisted co-precipitation method. They also proposed mechanism for their preparation. These nanowires were found with room temperature ferromagnetic property with high coercivity. Nejati and Zabihi 2012, prepared NiFe$_2$O$_4$ nanoparticles by hydrothermal method using surfactant and surfactant free approach. They observed crystallinity of samples decreases by using surfactant. Nanoparticles prepared were superparamagnetic in nature at room temperature.

Phadatare et al. 2013, prepared nanoparticles of NiFe$_2$O$_4$ by chemical combustion method using PVA, glycine and urea as fuels. Their results showed ferromagnetic behaviour of nanoparticles and also nanoparticles prepared by using Urea as fuel were found to be greater in crystallite size. Nikolic et al. 2013, used carboxylic acids of citric, malonic and tartaric along with Polyethylene glycol and potassium chloride as capping agent. They characterized nanoparticles via FTIR, FESEM, XRD and Mossbauer spectroscopy. Their investigations revealed that nanocrystallities prepared are of similar size and only distortions of tetrahedral and octahedral sites are present. Dumitrescu et al. 2013, synthesized NiFe$_2$O$_4$ by sol-gel auto-combustion method using different chelating agents. They came up with the
finding that usage of different chelating/fuel agents led to differences among the interionic distances along with difference in catalytic behaviour.

2.7.2 Hard and Soft composites:

Vogel and Evans 1979, studied detailed Mossbauer of 1:1 SrO:Fe$_2$O$_3$ system. According to them SrFe$_2$O$_4$ single phase material does not result from the high temperature solid state reaction between SrCO$_3$ and Fe$_2$O$_3$ in air.

Berthet et al. 1992, achieved the compound SrFe$_2$O$_4$. This phase is metastable; its preparation from a glass is related with the four-fold coordination of iron atoms in both the amorphous and the crystalline phases. Furthermore, the low symmetry of the unit cell of SrFe$_2$O$_4$ deduced from its XRD pattern, explains the high dispersion of the Sr-O and Fe-O distances indicated by the EXAFS data. The distortion of the framework of SrFe$_2$O$_4$ is likely to be too high for a stable compound.

Rakshit et al. 2007, used citrate-nitrate gel combustion method to prepare SrFe$_{12}$O$_{19}$(s), SrFe$_2$O$_4$(s), Sr$_2$Fe$_2$O$_5$(s) and Sr$_3$Fe$_2$O$_6$(s).XRD and measurement of emf as a function of temperature from 970 to 1151 K was carried out. Ashiq et al. 2009, prepared strontium hexaferrite nanoparticles with nominal composition SrZr$_x$Cd$_{1-x}$Fe$_{12-2x}$O$_{19}$ (for x=0.0-0.6) with step increment of 0.2 by the chemical co-precipitation technique. XRD, hysteresis loop measurements and LCR meter were employed to evaluate structure, magnetic and dielectric properties. The smaller crystallite size and increase in saturation magnetization while decrease in coercivity reveals that the synthesized materials are suitable for their applications in the recording media.

Zhao et al. 2010, synthesized the sample using the in situ sol-gel method. TEM and XRD investigations revealed coated surface of the CNTs with SrFe$_{12}$O$_{19}$.Also Coercive force of the sample with absorbent cotton as a template was improved as compared to without template. Jean et al. 2010, prepared SrFe$_{12}$O$_{19}$ by using hydrothermal method at 180$^\circ$C in alkaline medium. They obtained hexaferrite particles as plate like. Their findings include remanent specific magnetization and the saturation specific magnetizations are close to those of ceramic hexaferrite. Javed Iqbal et al. 2010, prepared calcium substituted strontium hexaferrite by co-
precipitation method. A single magnetoplumbite phase was confirmed by XRD. They observed that dielectric constant and dielectric loss factor decrease with frequency and also it was found that drift mobility increase with decrease in resistivity and vice versa.

Verma and Kotnala 2011b, prepared lithium strontium ferrite thin films by using sol-gel combined metallo organic decomposition method. The films were characterized by XRD and AFM measurements. They observed spring exchange magnetic hysteresis in both field and temperature dependent magnetization measurements.

2.7.3 On Multiferroics:

Mahajan et al. 2002, prepared CoFe$_2$O$_4$-BaTiO$_3$ composites using conventional ceramic double sintering process with various compositions. Presence of two phases in the composites was confirmed using X-ray diffraction. The dc resistivity and thermo-emf as a function of temperature in the temperature range 300 K to 600 K were measured. Variation of dielectric constant ($\varepsilon_0$) with frequency in the range 100 Hz to 1 MHZ and also with temperature at a fixed frequency of 1 KHz was studied. The ac conductivity was derived from dielectric constant ($\varepsilon_0$) and loss tangent ($\tan \delta$). The nature of conduction was discussed on the basis of small polar on hopping model. The static value of magneto-electric conversion factor had been studied as a function of magnetic field.

Mitoseriu et al. 2007, studied the characterization and magnetic properties related to the microstructures in the 0.5BaTiO$_3$–0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ magneto-electric composites prepared by two methods. Investigation revealed microstructural changes lead to changes of the magnetic properties which result by the ferrite concentration and by the degree of connectivity of the two phases.

Lin and Shi 2010, Synthesize Multiferroics ceramic with BaTiO$_3$, The (Ba$_{0.8}$K$_{0.2}$)(Ti$_{0.3}$Fe$_{0.7}$)O$_3$ ceramic was prepared by solid-state reaction, and post-annealed in oxygen ambient. By comparison with Ba(Ti$_{0.3}$Fe$_{0.7}$)O$_3$ made under identical conditions, the effect of non-isovalent A-site substitution of K+ on microstructure and magnetism of as-prepared and annealed Ba(Ti$_{0.3}$Fe$_{0.7}$)O$_3$ samples was investigated using X-ray diffraction. During the O$_2$ annealing process, the
presence of Fe$^{4+}$, an unusual valence for iron, besides Fe$^{3+}$ is observed, both distributed over octahedral Ti site. By A-site substitution of K$^+$ with a lower valence than Ba$^{2+}$, the charge compensation mechanism is further enhanced, and thus more Fe$^{3+}$ ions are oxidized to Fe$^{4+}$ in annealed (Ba$_{0.8}$K$_{0.2}$)(Ti$_{0.3}$Fe$_{0.7}$)O$_3$. Consequently, the ferromagnetic Fe$^{4+}$–O$^{2−}$–Fe$^{4+}$ super-exchange interactions are strengthened, which leads not only to a Paramagnetism–ferromagnetism transition but also to a higher saturation magnetization compared with annealed Ba(Ti$_{0.3}$Fe$_{0.7}$)O$_3$.

Brosseau et al. 2010, used various complementary experimental techniques to investigate a series of BaTiO$_3$/Ni Nanocomposites (NCs) produced by compaction of Nano powders. Their findings include that the microwave properties of NCs can be greatly modified by the compaction pressure used during production of the NCs and also the appropriate compaction pressure can improve the value of ME coupling coefficient. Curecheriu et al. 2010, investigated the diphasic ceramic composites with core–shell nanostructures formed by Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ core and BaTiO$_3$ shell. Their properties were compared with those of composites prepared by co-precipitation. The core–shell structure was confirmed by microstructural powder analysis. Homogeneous microstructures with a good phase mixing and percolated dielectric phase by the magnetic one were obtained from co-precipitated powders. Less homogeneous microstructures resulted in ceramics produced from the powder prepared by core shell method, with isolated small ferrite grains besides large ferrite aggregates embedded into the BaTiO$_3$ matrix.

Both the ferroelectric and magnetic phases preserve their basic properties in bulk composite form. By using the core–shell method, improved dielectric properties and limited hopping contributions can be realized. This is because the choice of the preparation method including the choice of compositions and the resulting microstructures (pore density, phase assemblage and reciprocal connectivity of the two phases), but there are some factors resulting from the combination of materials to form Nano composite to initiate extrinsic contributions (defects, interfaces and interconnectivity).

Bueno-Baques et al. 2010 studied the Multiferroic core–shell type nickel ferrite-barium titanate nanostructures synthesized by a novel wet chemical procedure. The structural and magnetic data suggest the insulation of the nickel ferrite core inside
a BaTiO$_3$ shell. The increase in the mass ratio of the phases leads to an increase in the degree of tetragonality of the BaTiO$_3$ shell as the crystallite size decreases. Furthermore, the reduction in the thickness of the shells results in a higher interaction between the magnetic cores.

Wang et al. 2011, study about magnetostrictive and piezoelectric laminate composites of Fe–Ga and BaTiO$_3$ and observe that at lower frequencies, the ME voltage coefficient of the laminate was 12.5 mV/Oe. Near the natural resonant frequency (~95 kHz) of the laminate, the ME voltage coefficient was found to be dramatically increased to 28.5 mV/Oe. In addition, the induced ME voltages were near linear functions of AC magnetic field. Rani et al. 2011, synthesized composites by conventional solid state method. Coexistence of both phases (ferroelectric and ferrite) was confirmed by X-ray diffraction technique. Their investigation revealed that with the increase in La content a decline in ferroelectric Curie temperature (Tc) and increase in room temperature dielectric constant.

Baji et al. 2011, works on Multiferroic composites and observe Ferroelectric nanostructures have broad applications in Nano scale electronic devices, sensors and actuators. In this study, a two-step electro spinning process was used to fabricate barium titanate (BaTiO$_3$)/ polyvinylidene fluoride (PVDF) composite fibres. X-ray diffraction (XRD) study revealed that crystalline phases corresponding to both PVDF and BaTiO$_3$ were found. Polarization–electric field hysteresis loops obtained using piezoresponse force microscopy (PFM) confirmed the polar domain switching behaviour of the fibres. Distinct strain-electric field hysteresis loops were also recorded.

Ahmed et al. 2013, prepared the magnetoelectric biferroic Nanocomposites with composition 0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/0.5BaTiO$_3$ by ceramic technique in order to study the electrical hysteresis behaviour. They characterize their Nano composite by XRD, SEM and FTIR. The variation of dielectric constant (e0), dielectric loss factor (e00) and the ac conductivity (rac) of 0.5Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/0.5 BaTiO$_3$ was investigated as a function of both frequency and temperature. Thermal hysteresis (first-order transition) was obtained during heating (300–830 K) and cooling runs (830–300 K). Another goal of this research work was to know about the advanced structure to choose which one was able to be applied in magnetic probes and thermistors.
Also, Nayek et al. 2013, performs on Multiferroics and report the magnetoelectric properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$–BaTiO$_3$ core–shell nanostructure synthesized by sol–gel method. X-ray diffraction analysis suggests that the BaTiO$_3$ undergoes large strain in the core–shell structure which can be attributed to lattice induced strain. The core–shell Nano powder shows enhanced magnetic property probably due to strain. Interestingly the magnetic measurement on the core–shell structure revealed an anomaly at the ferroelectric transition temperature indicating the existence of good phase connectivity which results in strong magnetoelectric coupling in the structure.

It is observed that the direct magneto electric voltage coefficient measurement on the La$_{0.7}$Sr$_{0.3}$MnO$_3$–BaTiO$_3$ core–shell structures based Nanocomposites exhibits the value as 54.4 mV/cm Oe, due to strain mediated magnetoelectric coupling. We believe that the ferromagnetic rare earth manganite’s as one of the constituent phases in the magnetoelectric Nano composite could provide better opportunity in device applications such as actuators and transducers by the way of enhancing its magneto electric effect.

Mohamed and El-Sayed 2013, prepared xBaTiO$_3$+(1-x)Ni$_{0.5}$Zn$_{0.5}$Fe$_{1.5}$Cr$_{0.5}$O$_4$ (x = 0.35, 0.5, 0.65) Nanocomposites were synthesized by the sol–gel method. The two corresponding intended Nanocomposites phases were confirmed by X-ray diffraction, no other foreign phases were present. The microstrain of the Nano composite was found to depend on the ratio amount of BaTiO$_3$ (BTO) in the Nanocomposites. The tetragonality ratio c/a of BTO approximates its values to be (a = c) at concentration of 65% BTO. Magnetic properties showed superparamagnetic behaviour at room temperature. The temperature dependent of dielectric constant measurements showed that the Curie temperature (Tc) of the ferroelectric phase transition varies with different composites ratio. The dielectric properties of the composite increased with increase of ferrite content.

Sukhov et al. 2013, proposed their findings from the study of FMR spectrum. According to their magnetoelectric coupling coefficient estimates and Calculations based on the elongated MF chains they suggested MF contact should be consisting of thin FM layer (electrode) and a Thick FE layer.
Banerjee et al. 2014, prepared composite samples by chemical method and studied their magnetic, dielectric and magneto-dielectric properties. They obtained high value of magneto dielectric (MD) parameter of 2% at a magnetic field of 0.7 Tesla.

2.8 Synthesis routes:

In order to achieve materials of the desired physical and chemical properties, the preparation of the Nano structured materials through different route has become an essential part of the research and development. It is well known that the method of preparation plays a vital role in determining the chemical, structural and magnetic properties of ferrites and their composites. Synthesis of nanostructures is an important step for manufacturing as the performance of the material depends upon that as it greatly affects their properties as well as their applications. At the same time these techniques should be simple, economic and eco-friendly.

2.8.1 Micelle routes:

Surfactants when present in solution instinctively form spherical aggregates called micelles or micro emulsions. Aerosol OT or AOT (sodium dioctylsulphosuccinate) was the first and most characterised surfactant system used in the synthesis of magnetic nanoparticles. [Mittal and Lindman 1984; Zulauf and Eicke 1979; Pileni 1997] other systems, such as cetyltrimethylammonium bromide (CTAB), sodiumdodecylsulphate (SDS), [Stecker and Benedek 1984] and polyethoxylates [Dimitrova et al. 1996] have been used, and more are being established to improve morphology and chemical parameters. Many of the reactions carried out in micelles are very similar to those executed in bulk aqueous system, but with the added morphological controls afforded by the surfactant system [Wilcoxon and Provencio 1999]. The process for the formation of metals can be expanded to form metal alloys. Instead of using a single metal salt, mixed metal salts are used and reduced simultaneously [Tanori et al. 1995]. It is essential that the reduction is carried out simultaneously or mixed phase products will be formed. The precipitation of precursors that are subsequently fired to produce an oxide end product is an important synthetic process.
Particles synthesised by quenching the reaction after short reaction times developed polyhedral morphology and 13 nm average particle size. [Agnoli et al. 2001]. Reverse micelles are water in oil droplets stabilized by surfactant [Pileni 1989]. The water to surfactant concentration ratio, $w = [H_2O]/[S]$ linearly controls the size of the droplet. Reverse micelles are subjected to Brownian motion and during these collisions the droplets combine to form a dimer and this is accompanied by an exchange of their water contents. The dimer dissociates to restore the reverse micelles. These two properties (control of the droplet size and the exchange process) make possible the use of reverse micelles as a Nano-reactor. Two micellar solutions are prepared. Each contains one of the reactants. By mixing these solutions, a chemical reaction takes place and nanomaterial’s are produced [Pileni 1993; Pileni 1997]. The droplet size, which is controlled by $w$, stipulates the size of the particle. This procedure has been used to obtain a large variety of materials such as semiconductors, metals [Pileni 1989] and oxides. When the two reactants are present as salts, amorphous nanomaterials are formed. Vice versa, when one of the reactants is a functionalized surfactant (the reactant is the counter ion of the surfactant) Nano crystals are produced [Pileni 1989; Vaucher et al. 2002].

Although there are many examples of inverse micelles used as micro reactors, there are only a few examples of the use of direct micelles. Sodium dodecyl sulphate is the principle surfactant used in these reactions due to the morphology of the aggregate. The particles display a large size distribution and a plate like morphology with an average particle size of 100 nm. The micelle technique is preferred over the reverse micelle method due to size, homogeneity and small particle formation of the former in comparison to the later.

2.8.2 Hydrothermal synthesis of Nanomaterials:

The term "hydrothermal" is of geologic origin. Geochemists and mineralogists have studied hydrothermal phase equilibrium since the beginning of the twentieth century. George W. Morey at the Carnegie Institution and later, Percy W. Bridgman at Harvard University did much of the work to lay the foundations necessary to containment of reactive media in the temperature and pressure range where most of the hydrothermal work is conducted. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which reactants are
supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber so that the hotter ends dissolve the reactant and the cooler end causes seeds to take additional growth. Also the materials which have a high vapour pressure near their melting points can also be grown by the hydrothermal method.

Hydrothermal processing is a non-conventional method to obtain Nano crystalline inorganic materials. Both physical and chemical parameters can be varied systematically during the hydrothermal processing in such a way that a direct precursor-product correlation can be established. A direct precursor-product correlation exists allowing synthesis of almost any material without the presence of further structure directing agents [Ghobarkar et al. 1999; Whittingham et al. 1995]. The synthetic method uses the solubility of almost all inorganic substances in water at elevated temperatures and pressures, and subsequent crystallization of the dissolved material from the fluid. Water plays an essential role in the precursor material transformation at elevated temperatures.

**Principles and operation modes**

The precursor material used depends on the material to be synthesized and it has to be, to a certain extent, soluble in water under ambient conditions. Therefore, inorganic salt precursors with moderate to high solubility under ambient conditions are used. Hydrothermal processing is rather complex because a great number of interacting parameters play essential roles [Byrappa and Yoshimura 2001; Demazeau 1999]. Pressure, temperature and time of exposure to hydrothermal conditions are important parameters in order to obtain the desired Nanocystalline materials. The influences of these parameters are a problem which needs further research in this area. Temperature plays an important role in kinetics of product formation, as well as on the thermodynamic stability of the product phase. Pressure is essential for the solubility. To avoid the influence of the pressure generating temperature, the external pressure mode is actually preferred.

Time is also an important parameter because the synthesis of kinetically stable phases are favoured in short term processes while the thermodynamically stable phases are generally formed in long term experiments under corresponding temperature-pressure regime. This is because of the increased solubility and
recrystallization of the already formed phases. However, some reaction related conditions such as convection within the reaction vessel and the precursor materials state of aggregation should not be neglected in the effort to control the process parameters. Hydrothermal synthesis of Nano crystalline materials has to be controlled by the process parameters temperature, pressure and time, as well as the physical and the chemical parameters of the materials system under investigation.

Under extreme synthesis conditions, all the initial materials formed underwent dissolution and re-crystallization; that is why the hydrothermally obtained materials are formed under conditions close to equilibrium. To keep the product particle size in the nanometer range, all precursor reaction processes have to occur very rapidly, so that the whole process should be finished within several hours in order to avoid significant growth of the product particles. Various Nano crystalline materials have been obtained in this way. Hydrothermal synthesis is commonly used to grow synthetic quartz, gems and other single crystals with commercial value. Some of the crystals which have been efficiently grown are emeralds, rubies, quartz and others.

The method has proved to be extremely efficient both in the search for new compounds with specific physical properties and in the systematic physiochemical investigation of intricate multicomponent systems at elevated temperatures and pressure. In a sealed vessel (bomb, autoclave, etc.), solvents can be brought to temperatures well above their boiling points by the increase in autogenously pressures resulting from heating. Performing a chemical reaction under such conditions is referred to as solvothermal processing or, in the case of water as solvent, hydrothermal processing [Yu et al. 2009].

2.8.3 Sol-gel processing:

Sol–gel processing can be used to prepare a variety of materials, including glasses, powders, films, fibres, and monoliths. The sol-gel method offers specific advantages in preparation of multicomponent oxide ceramics. The sol-gel process is a wet-chemical technique that uses either a chemical solution (sol short for solution) or colloidal particles (Sol for Nano scale particle) to produce an integrated network (gel). Metal alkoxides and metal chlorides are typical precursors. They undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of nanoparticles dispersed in a solvent. The sol evolves then towards the formation of an inorganic
continuous network containing a liquid phase (gel). Formation of a metal oxide involves connecting the metal centres with Oxo $(M-O-M)$ or hydroxo $(M-OH-M)$ bridges, thereby generating metal-Oxo or metal-hydroxo polymers in solution. After a drying process, the liquid phase is removed from the gel. Then, a thermal treatment (calcination) may be performed in order to favour further polycondensation and enhance mechanical properties [Yu et al. 2009]. Generalized reaction scheme showing hydrolysis and condensation to polymeric species is:

\[
M(OR)_x + H_2O \rightarrow M(OR)_{x-1}(OH) + ROH
\]

\[
2M(OR)_{x-1}(OH) \rightarrow M_2O(OR)_{2x-2} + H_2O
\]

\[
M(OR)_x + M(OR)_{x-1}(OH) \rightarrow M_2O(OR)_{2x-2} + ROH
\]

Factors that need to be considered in a sol–gel process are solvent type, temperature, precursors, catalysts, pH, additives and mechanical agitation. These factors can influence the kinetics, growth, hydrolysis and condensation reactions [Brinker and Scherer 1990]. The solvent influences the kinetics and conformation of the precursors, and the pH affects the hydrolysis and condensation reactions. The pH also affects the isoelectric point and the stability of the sol. These in turn affect the aggregation and particle size. By varying the factors that influence the reaction rates of hydrolysis and condensation, the structure and properties of the gel can be tailored. Because these reactions are carried out at room temperature, further heat treatments need to be carried out to achieve the final crystalline state. Due to the metastability of the as synthesised particles, annealing and sintering can be performed at low temperatures. Sol–gel routes have been used to prepare pure, stoichiometric, and dense and monodispersed particles of TiO$_2$ and SiO$_2$, but this control has not been extended to the ferrites. Generally, the particles produced are agglomerated. The narrow particle size distribution could not be achieved if the sol–gel processing was performed without complexation of metal ions.

Size distribution of semiconductor, metal and metal oxide nanoparticles can be manipulated by either dopant introduction or heat treatment. Better size and stability control of quantum confined semiconductor nanoparticles can be achieved through the use of reverse micelles, polymer matrix architecture based on block copolymers or
polymer blends, porous glasses, and ex-situ particle-capping techniques [Majetich and Carter 1993; Olshavsky and Allcock 1997]

2.8.4 Co-precipitation:

In chemistry, co-precipitation is the carrying down by a precipitate of substances normally soluble under the conditions employed [Patnaik and Dean 2004]. Analogously, in medicine, Co-precipitation is specifically the precipitation of an unbound "antigen along with an antigen-antibody complex". Co-precipitation is an important issue in chemical analysis, where it is often undesirable, but in some cases it can be exploited. In gravimetric analysis, which consists on precipitating the analyte and measuring its mass to determine its concentration or purity, Co-precipitation is a problem because undesired impurities often co-precipitate with the analyte, resulting in excess mass. This problem can often be mitigated by "digestion" (waiting for the precipitate to equilibrate and form larger, purer particles) or by re-dissolving the sample and precipitating it again [Harvey 2000].

On the other hand, in the analysis of trace elements, as is often the case in radiochemistry, Co-precipitation is often the only way of separating an element. Since the trace element is too dilute (sometimes less than a part per trillion) to precipitate by conventional means, it is typically co-precipitated with a carrier, a substance that has a similar crystalline structure that can incorporate the desired element. An example is the separation of Francium from other radioactive elements by co-precipitating it with cesium salts such as Cesium perchlorate. Otto Hahn is credited for promoting the use of Co-precipitation in radiochemistry. There are three main mechanisms of Co-precipitation: inclusion, occlusion, and adsorption [Harvey 2000]. An inclusion occurs when the impurity occupies a lattice site in the crystal structure of the carrier, resulting in a crystallographic defect; this can happen when the ionic radius and charge of the impurity are similar to those of the carrier. An adsorbate is an impurity that is weakly bound (adsorbed) to the surface of the precipitate. An occlusion occurs when an adsorbed impurity gets physically trapped inside the crystal as it grows.

Besides its applications in chemical analysis and in radiochemistry, Co-precipitation is also "potentially important to many environmental issues closely related to water resources, including acid mine drainage, radionuclide migration in
fouled waste repositories, metal contaminant transport at industrial and defense sites, metal concentrations in aquatic systems, and wastewater treatment technology". Co-precipitation is also used as a method of magnetic nanoparticle synthesis [Lu et al. 2007]. Co-precipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening, and/or agglomeration processes. Co-precipitation reactions exhibit the following characteristics:

(i) The products are generally insoluble species formed under conditions of high super saturation. (ii) Nucleation is a key step, and a large number of small particles will be formed. (iii) Secondary processes, such as Ostwald ripening and aggregation, dramatically affect the size, morphology, and properties of the products. (iv) The super saturation conditions necessary to induce precipitation are usually the result of a chemical reaction.

Typical Co-precipitation synthetic methods: (i) metals formed from aqueous solutions, by reduction from non-aqueous solutions, electrochemical reduction, and decomposition of metallorganic precursors; (ii) oxides formed from aqueous and nonaqueous solutions; (iii) metal chalconides formed by reactions of molecular precursors; (iv) microwave/sonication-assisted Co-precipitation.

2.8.5 Combustion method:

In recent years, there has been great interest in the combustion method because of advantages compared to other methods: reagents are very simple compounds, special equipment is not required, dopants can be easily introduced into the final product, and agglomeration of powders remains limited. Important parameters that control combustion synthesis such as the particle size and shape of the reactants, ignition techniques, stoichiometric ratio, processing of reactant particles and the adiabatic temperature which is a measure of the exothermicity of the reaction are needed to be thoroughly explored.

The process makes use of highly exothermic redox chemical reactions between metals and non-metals, the exchange reaction between reactive compounds or reactions involves redox compounds/mixtures. The combustion method has been successfully used in the preparation of a large number of technologically useful oxide (refractory oxides, magnetic, dielectric, semiconducting, insulators, catalysts, sensors,
phosphors etc.) and monoxide (carbides, borides, silicides, nitrides etc.) materials. The energy produced by the exothermic decomposition of a redox mixture of metal nitrates with an organic compound is utilised. In the combustion mixture nitrates and the organic compounds behave similarly to conventional oxidants and fuels. The reaction is carried out by dissolving metal nitrates and fuel in a minimum amount of solvent and followed by heating the mixture. The resulting viscous liquid foams, ignites, and undergoes a self-sustained combustion, producing ashes containing the oxides as product. During the combustion, exothermic redox reactions associated with nitrate decomposition and fuel oxidation take place.

Gases such as NO$_x$, H$_2$O, and CO$_2$ evolve, favouring the formation of fine particle ashes after only a few minutes. The properties of the final product (particle size, surface area, and porosity) depend on the way combustion is conducted. The departure of gases favours the desegregation of the products (increasing the porosity) and heat dissipation (inhibiting the sintering of the products). The exothermicity of the combustion is controlled by the nature of the fuel and the ratio of the oxidizer/fuel. Fuels are organic compounds, frequently hydrazine derivatives that undergo highly exothermic combustion. When fuels are heated in the presence of nitrates, the mixture of gases generated is always hypergolic: it reacts readily with evolvement of heat. The stoichiometric composition of the metal nitrate: fuel mixtures are given by the equivalence ratio which reflects the relative ratio of intramolecular fuel/oxidizer, considering the total reducing and oxidizing power of both fuel and oxidizer compounds [Jain et al. 1981]. Other factors influencing combustion are the evaporation time, the total mass of the redox mixture, the dish capacity, and the amount of solvent used to dissolve the reagents. The synthesis of solids possessing desired structures, composition and properties continues to be a challenge to chemists, material scientists and engineers [Ekambaram and Patil 1997]. Attempts have recently been made to eliminate the diffusion control problems of solid synthesis by using various innovative synthetic strategies.

2.9 Fundamental of material characterization techniques:

To investigate different properties of ferrites and their composites some definite techniques have been used. Each technique provides different information
such as chemical, physical properties, structure and morphology etc. The different techniques used in this research work are given below:

1) Fourier Transform Infrared Spectroscopy (FTIR)
2) X-Rays Diffraction (XRD)
3) Transmission Electron Microscope (TEM)
4) Vibrating Sample Magnetometer (VSM)
5) LCR meter
6) Perkin Elmer UV spectrometer λ 35*

Lattice constant, X-Ray density, porosity and size were calculated using X-rays diffraction data. Morphology and size of samples was confirmed by the use of Transmission Electron Microscope. Magnetic measurements such as saturation magnetization, remanence magnetization, coercivity and $\mu_B$ were calculated with the help of Vibrating Sample Magnetometer. LCR meter was used to get information about Dielectric constant and Dielectric loss factor. Perkin Elmer UV spectrometer was utilized for optical properties of prepared samples.

2.9.1 FTIR: Infrared Spectroscopy:

Infrared spectroscopy has been used to identify the compounds from their characteristic absorption frequencies of the infrared radiation in range of 4000 cm$^{-1}$ to 400 cm$^{-1}$. This has been especially useful for identifying the functional groups of the organic compounds within the solution and solid state. Basically the infrared spectrum of the compounds is the absorption bands of the specific functional groups along with superposition of their interactions with the surrounding groups in the molecules. In a typical absorption spectrum presence of absorption or the lack of absorption in specific frequency regions can be correlated with specific stretching and bending motions and in some cases, with the relationship of these groups to the remainder of the molecule. Thus, by interpretation of the spectrum, it is possible to state that certain functional groups are present in the material and that the certain others are absent by comparison with a library of pure spectra.
The solution chemistry of powdered material have been probed by Fourier transformed infrared (FTIR) spectroscopy using a Perkin Elmer Spectrum over the wave number range 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) was used to investigate the phase evolutions in the nanoparticles and Nano composites. The powders for FTIR investigation were subjected to heat treatment at 500 °C for 5h and were then pressed into a pellet, which was then placed on a sample holder in the FT-IR chamber before measurement. The importance of infrared spectrometry as a tool of identification of organic group is readily apparent from literature wholly or in part to discussions of applications of infrared spectrometry. In this thesis work this tool has been used for all prepared samples to check their purity along with their identification as it can display the various chemical bonding in a material [Ryoo et al. 2003; Pontes et al. 2005].

2.9.2 X-Ray Diffraction:

The crystallographic parameters such as phase, distortion ratio, particles size, indices etc. from structure of nanostructures have been investigated by X-ray
diffraction (XRD) using X-Pert PRO Panaltical system by using a monochromatic beam of Cu [K-Alpha1 (Å)] radiation of 1.54060 Å.

Figure 2.5(a) Shows X-Pert PRO Panaltical system.

Figure 2.5(b) Shows the incident X-ray beam interacting with the atoms arranged in a periodic manner

The specimen Length was 10.00 (mm) and at the time of measurement temperature was 25°C of the system (Figure 2.5(a)). The shape of the nanostructures must be taken into account to calculate their size, lattice parameter and density.

X-rays are electromagnetic radiation used are in the range of 100 ev – 100 keV. For diffraction applications, only short range wavelengths in the range of a few angstroms to 0.1 angstrom (1 keV -120 keV) are used. Because the wavelength of x-
rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X-rays can penetrate deep into the materials and provide information about the bulk structure.

Lattice planes and Bragg’s law: X-rays primarily interact with electrons in atoms. When X-rays photons collide with electrons some photons from the incident beam get deflected away from the direction from the original line of travelling, similar to billiard balls bouncing off one another. If the wavelength of these scattered X-rays did not change (meaning that X-rays photons did not lose any energy), the process is called elastic scattering (Thompson Scattering) that only momentum has been transferred in the scattering process. These are the X-rays those are measured in diffraction experiments, as the scattered X-rays provide information about the electron distribution in the materials.

If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows deducing the distribution of atoms in a material. The peaks in X-ray diffraction pattern are directly related to the atomic distances. The incident X-ray beam interacting with the atoms arranged in a periodic manner as shown in Figure 2.5(b) in two dimensions in the following illustration. The atoms represented as green spheres in the graph, can be viewed as forming different sets of planes in the crystal (coloured lines in graph on left).

For a given set of lattice plane with an inter-plane distance of d, the condition for a diffraction (peak) to occur can be simply written as

$$2d \sin \theta = n \lambda$$ (Ref)

This is known as the Bragg’s law, after W.L. Bragg, who first proposed it. In the equation $\lambda$ is the wavelength of the X-ray, $\theta$ the scattering angle and $n$ is an integer representing the order of the diffraction peak. The Bragg’s Law is one of most important laws used for interpreting X-ray diffraction data.

Powder XRD (X-ray Diffraction) is perhaps the most widely used x-ray diffraction technique for characterizing materials. As the name suggests, the
sample is usually in a powdery form, consisting of fine grains of single crystalline material to be studied. The technique is used also widely for studying particles in liquid suspensions or polycrystalline solids (bulk or thin film materials).

The term ‘powder’ really means that the crystalline domains are randomly oriented in the sample. Therefore when the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various d spacing’s in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. For example, the diffraction lines of graphite would be different from diamond even though they both are made of carbon atoms. This phase identification is important because the material properties are highly dependent on structure (just think of graphite and diamond).

Powder diffraction data can be collected using either transmission or reflection geometry, as shown below. Because the particles in the powder sample are randomly oriented, these two methods will yield the same data. In the MRL X-ray facility, powder diffraction data are measured using the Philips XPERT MPD diffractometer, which measures data in reflection mode and is used mostly with solid samples, or the custom built 4-circle diffractometer, which operates in transmission mode and is more suitable for liquid phase samples.

**Particle size or Grain size:**

In 1918, P. Scherer showed that when parallel monochromatic radiation falls on a random oriented mass of crystals, the diffracted beam is broadened when the particle size is small. By an approximation method he obtained an expression for the half – value breadth of the diffracted beam in the form

\[ B = \frac{K\lambda}{(L \cos \frac{x}{2})} \]  \hspace{1cm} (2.1)

Where \( \lambda \) is the wavelength of the incident X- rays, \( L \) is the linear dimension of the particle, \( x/2 \) the Bragg angle and \( K \) a numerical constant for which he obtained the value

\[ (2 \ln 2/\pi^{1/2} = 0.93 \]  \hspace{1cm} (2.2)
Since the various workers [N Seljakow, M V Laue, C C Murdock etc.] using different approximations for the breadth B have obtained different values for the constant K. As a result, those interested in using the relation 2.3 for the determination of particle size have rightly been doubt as to its correct value. In 1957, Debye-Scherer [Cullity 1957] gave the exact formula for calculating the average value of particles or grain size of the crystallites

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \] (2.3)

Where \( \lambda \) is the X-ray wavelength, \( \theta \) is the angle of diffraction and \( \beta \) is calculated from full width half maxima of the X-ray peak. As a whole X-rays diffraction do find their applications in many fields some of them are: Characterizing thin films, crystalline materials, Unit cell dimensions, Sample purity, Ease of sample preparation, Rapidity of measurement, Ability to analyse mixed phases. The analysed material is finely grounded, homogenized and average bulk composition is determined.

2.9.3 Microstructural Characterization:

Transmission Electron Microscopy (TEM) has been widely used in this study to obtain an accurate analysis of the nanostructured behaviour of various nanostructures. An electron microscope is a type of microscope that uses electrons to illuminate a specimen and create an enlarged image. Electron microscopes have much greater resolving power than light microscopes and can obtain much higher magnifications. Some electron microscopes can magnify specimen up to 2 million times. The electron microscope uses electrostatic and electromagnetic lenses in forming the image by controlling the electron beam to focus it at a specific plane relative to the specimen. The detailed discussions about TEM are given below:

**Transmission Electron Microscopy (TEM):**

The Hitachi H-7500 transmission Electron Microscope (Figure 2.6) is an instrument suitable for high magnification examination of microstructures in research. In this microscopy technique a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through it. The image as is formed from the electrons transmitted through the specimen, magnified and focused.
by an objective lens and appears on an imaging screen, a fluorescent screen in most TEM’s, plus a monitor or on a layer of photographic film, or to be detected by a sensor such as CCD camera.

The first TEM was built by Max. Knoll and Ernst Ruska in 1931 (Germany) with this group developing the first TEM with resolving power greater than that of light in 1933 and the first commercial TEM in 1939. It is one of the most effective tools for structural characterization of the material. TEM analysis can provide various information regarding morphological, phase and crystallographic information of materials. Its basic instrumentation includes an electron gun (electron source), condenser lenses and mini condenser lenses (the illumination system) and objective lens, intermediate lenses and projector lenses (the imaging system). TEM can be used to examine particles that are too small for investigation with optical microscopes. TEM provides a powerful method for determining particle shapes as well as their size and degree of agglomeration. TEM is an imaging technique commonly used for studies of microstructures at various micrometre, nanometer and atomic scales. For better dispersion of the material, the powdered samples were made into suspension using deionized water before being transferred into the copper grid.

Figure 2.6 Shows Transmission electron microscope, Hitachi H-7500
As a whole this technique is widely used to have a clear insight view of nanotechnology, life sciences, medical, biological and material research, forensic analysis, gemmology, metallurgy, industry and education.

2.9.4 Magnetic properties/ Magnetism:

The Magnetic nanomaterial’s show remarkable new phenomenon such as super magnetism, high field irreversibility, high saturation field, extra anisotropy contribution or shifted loops after field cooling. The phenomenon associated with finite size and surface effects that dominate magnetic behaviour of individual nanoparticles. Frenkel and his team were first to predict that a particle of ferromagnetic material, below a critical particle size (15 nm), would consist of a single magnetic domain i.e. a particle that is a state of uniform magnetization at any field.

The magnetization behaviour of these particles above a certain temperature i.e. the blocking temperature, is identical to that of atomic paramagnets (Super Paramagnetism) except that an extremely large moment and thus, large susceptibilities are involved [Bean and Livingstone 1959]. The industrial applications of magnetic nanomaterial’s include magnetic ink of bank cheques, magnetic seals of motors, magnetic recording media and biomedical applications such as magnetic resonance contrast media and therapeutic agents in cancer treatment.

Categorization or Classification of materials has been done on the basis of their behaviour under the effect of external magnetic field of alignment of magnetic dipole moments. It is observed that magnetism arises due to the presence of permanent and induced magnetic moments at constituent atoms and their corresponding metal interaction [Kim et al. 2002; Bhargava et al. 2000; Parvatheeswara Rao et al. 2004]. There are five main classes of magnetic materials, Diamagnetic, Paramagnetic, Ferromagnetic, Ferrimagnetic and Antiferromagnetic [Pillai 2005].

In General magnetic materials are classified by their response to externally applied magnetic fields. These response differ greatly in strength, some of these oppose applied magnetic field (Diamagnetic materials), some produces magnetization in direction of applied field (Paramagnetic materials), and few produces magnetization greater than applied field (Ferromagnetic materials) etc.
Diamagnetism:

Electronic diamagnetism occurs in all substances; whenever magnetic field is applied to a material it interacts with electron of it in such manner that it induces a magnetic moment which opposes applied field. It can be considered as atomic version of Lenze’s law, wherein induced magnetic field tends to oppose the charge which created them. In case the net atomic magnetic moments are found to be zero or very small, substance is diamagnetic. It is seen that diamagnetism effect is observed in all those materials which have even number of electrons.

Diamagnetism is the residual magnetic behaviour when materials are neither paramagnetic nor ferromagnetic. Diamagnetic materials have a weak, negative susceptibility to magnetic fields. Diamagnetic materials are slightly repelled by a magnetic field and the material does not retain the magnetic properties when the external field is removed. In diamagnetic materials all the electron are paired so there is no permanent net magnetic moment per atom. Diamagnetic properties arise from the realignment of the electron paths under the influence of an external magnetic field. Most elements in the periodic table, including copper, silver, and gold, are diamagnetic.

Paramagnetism:

Generally it is observed that it is found in those materials in which atoms or molecules contain odd number of electrons. These materials exhibit proportional magnetization to the applied field (Figure. 2.7). Chemistry behind this behaviour is response of dipole moment on subjection to applied magnetic field. On the application of external magnetic field each dipole experiences torque which aligns the dipole in the direction of applied field resulting in finite dipole moment in the direction of external field [Kittel and McEuen 1986]. Paramagnetic materials are said to follow Curies law:

\[ M = C(B/T) \]

Where, M= Magnetization, B = Magnetic field, C = Curies Constant and T = Temperature in Kelvin.
It occurs in a system with non−interaction or weakly interacting magnetic moments. This is characterized by positive susceptibility (Temperature dependent). This temperature dependency was discovered by P Curie in 1895. Paramagnetic materials include magnesium, molybdenum, lithium, and tantalum.

**Ferromagnetism:**

Ferromagnetic materials have a large, positive susceptibility to an external magnetic field. These materials are said to be strongly magnetized in the direction of the field (Figure. 2.7). In absence of external magnetic field dipole moment is oriented randomly resulting zero net dipole moment and on application of external applied field favourably oriented domain grow in size and unfavourable one reduce in size resulting net dipole moment in the direction of the applied field.

Atoms in certain elements have permanent magnetic moments which impulsively align themselves parallel to each other below some critical temperature called Curie temperature, (Tc). All Ferro magnets have a maximum temperature where the ferromagnetic property disappears as a result of thermal agitation. Ferromagnetic materials (iron) possess large permanent magnetizations even in the absence of an applied magnetic field. The origin of ferromagnetism is the quantum mechanical exchange interaction between the constituent atoms and results in regions of the material possessing permanent magnetization [Smith 1986].

At temperatures above Tc, ferromagnetism is lost and the material becomes paramagnetic. The variation of magnetization with temperature in ferromagnetism materials was first explained by the Weiss Mean Field theory (1907). Iron, nickel, and cobalt are examples of ferromagnetic materials.

**Anti-ferromagnetism:**

In antiferromagnetic materials magnetic moments are arranged in two groups/sub lattices, which attribute equal opposite net magnetization (Figure. 2.7). This kind of antiparallel alignment is due to negative exchange interaction between magnetic moments. In this type of crystal system, the spins in one sublattice point one way and in the other point in the opposite direction.
These materials have small susceptibility. The net dipole moment/magnetization are zero in the absence of external magnetic field and when it is applied a small field is produced in direction of external field which increases with increase in temperature. The temperature at which magnetization is maximum is known as Neel Temperature. It is observed that on further increase in temperature magnetization decreases and antiferromagnetic material becomes paramagnetic in nature [Kittel and McEuen 1986].

**Ferrimagnetism:**

It is taken as a spinel case of Antiferromagnetic wherein magnetization of one sublattice is different from the other sublattice resulting in non-zero magnetization of the unit cell (Figure. 2.7). Ferrimagnetism is seen in ferrites, where spins are induced anti-ferromagnetically. Tc Curie temperature is also observed in these materials, they behave differently at low & below Tc.

![Spin alignment in Paramagnetism, Ferromagnetism, Anti-Ferrromagnetism and Ferrimagnetism](image)

**Figure 2.7 Showing Spin alignment in Paramagnetism, Ferromagnetism, Anti-Ferrromagnetism and Ferrimagnetism**

Paramagnetic behaviour is observed above Tc and below it they have spontaneous magnetization. The origin of ferrimagnetism is based on magnetic ordering, having all one type (A) atoms have spins aligned in one direction & all other type (B), have their spins aligned in the opposite direction. Magnetic moment of (A) atom is found to be greater than that of (B) atom, resulting magnetization in crystal. So even in the absence of applied field these materials possess magnetization [Smith 1986].
Domains:

In general it is believed that a magnetic material become magnetized in presence of magnet which is not only because their atoms carry a magnetic moment but also because the material is made up of small regions known as magnetic domains in case of ferromagnetic materials. In these materials numerous small regions are present which are called as domains. Domains are small (1-100’s microns), but much larger than atomic distances. In each domain, all of the atomic dipoles are coupled together in a preferential direction. The existence of domains is hinted by the observation that some magnetic properties, and in particular, coercively and remanence vary greatly with grain size. In absence of external applied magnetic field these domains align in different direction, results zero net magnetization. However pressure of external applied field aligns the magnetization of different domains in the field direction.

This alignment develops as the material develops its crystalline structure during solidification from the molten state. Magnetic domains can be detected using Magnetic Force Microscopy (MFM). During solidification, a trillion or more atom moments are aligned parallel so that the magnetic force within the domain is strong in one direction. When all of the domains are aligned, the material is said to be magnetically saturated. When a material is magnetically saturated, no additional amount of external magnetization force will cause an increase in its internal level of magnetization.

The magnetic behaviour can be subdivided on the basis of grain size into following ranges: Single Domain, Pseudo-single domain and multidomain. As the grain size decreases it reaches a critical size where the grain cannot accommodate a wall. Below this critical size, the grain contains a single domain. Single domain grains are magnetically hard and have high coercivities and remanence. To change magnetization of a multidomain grain is to translate domain wall which can be accomplished in relatively low fields. Multidomain grains are magnetically soft with low values of coercivities and remanence.
Figure 2.8 Shows state of a magnetized and unmagnified material.

Interactions in solids:

In solids interactions between magnetic moment play crucial role. These are of two types namely, Exchange interactions and dipole –dipole interactions. Exchange interactions are of two types direct and indirect. Direct exchange interactions, magnetic moments are very close and almost overlapping. In case of indirect exchange interactions, they are at a distance from each other and do occur through the help of an intermediate. Indirect exchange interactions in case of Ferrites do occur via oxygen between metal ions.

Hysteresis Loop:

The magnetization versus magnetizing field was studied on powder samples using vibrating sample magnetometer (VSM-735). A great deal of information can be learned about the magnetic properties of a material by studying its hysteresis loop. A hysteresis loop shows the relationship between the induced magnetic flux density (B) and the magnetizing force (H). It is often referred to as the B-H loop. An example of Hysteresis loop is shown in fig. 2.9. The loop is generated when measuring the magnetic flux of a ferromagnetic material, while the magnetizing force is changed. A ferromagnetic material that has never been previously magnetized or has been thoroughly demagnetized will follow the dashed line as H is increased.

As the line demonstrates, the greater the amount of current applied (H+), the stronger the magnetic field in the component (B+). At point “a” almost all of the magnetic domains are aligned and an additional increase in the magnetizing force will produce very little increase in magnetic flux. The material has reached the point of magnetic saturation and is denoted by Ms . When H is reduced to zero, the curve will
move from point “a” to point “b”. At this point, it can be seen that some magnetic flux remains in the material even though the magnetizing force is zero.

**Figure 2.9 Shows magnetic Hysteresis Curve**

This is referred to as point of retentivity on the graph and indicates the remanence or level of residual magnetism in the material. In general it is the left behind magnetization after removal of applied magnetic field. Mr is the symbol used to denote it. For calculation purpose it is taken as the intersections of the Hysteresis loop with the vertical magnetization axis. As the magnetizing force is reversed, the curve moves to point “c”, where the flux has been reduced to zero.

This is called the point of coercivity on the curve. Coercivity value describes a material; to be soft magnet or hard magnet. It is denoted by Hc and is measured in Oersted or ampere/meter. Coercivity is the strength of applied field required to reduce magnetization of a material after it attain magnetic saturation. As the magnetizing force is increased in the negative direction, the material will again become magnetically saturated but in the opposite direction (Point “d”). Reducing H to zero brings the curve to point “e”. It will have a level of residual magnetism equal to that achieved in the other direction. Increasing H back in the positive direction will return
B to zero. Notice that the curve did not return to the origin of graph because some force is required to remove the residual magnetism.

The curve will take a different path from point “f” back to the saturation point where it will complete the loop. From the hysteresis loop, a number of primary magnetic properties of a material can be determined. From the hysteresis loop, a number of primary magnetic properties of a material can be determined such as Retentivity, Residual magnetism or Residual Flux, Coercive Force, Permeability and reluctance.

**Temperature effect on magnetization:**

Temperature has key role in characterizing behaviour of magnetic materials. There are certain temperature limits to which materials are bound and behave accordingly. As below this temperature limit magnetic moments are aligned and above it thermal agitation disturbs this alignment. In case of ferromagnetic materials this temperature limit is said to be Curie point or Curie temperature (Tc) above this ferromagnetic material lose their characteristic property of ferromagnetism.

Similarly antiferromagnetic materials behave as paramagnetic above a certain temperature limit, generally known as Neel temperature (T_N).

**Magnetic anisotropy:**

This term is generally used for revealing dependence of magnetic properties on a preferred direction. It is of commercial importance as it affects the shape of magnetic hysteresis loops and has effect on coercivity and remanence which in turn are utilized in the designing/ fabrication of materials of technological importance. There are three types of anisotropy, magneto crystalline, and shape and stress anisotropy.

There are easy and hard directions which arouse due to interaction between spin magnetic moment with crystal lattice. Magneto crystalline Anisotropy is considered as energy which defects magnetic moment from easy to hard directions. Shape anisotropy is resultant outcome of the shape of grain. Magnitude of shape anisotropy depends upon saturation magnetization and stress anisotropy is a measured
as a function of applied field along the principle crystallographic axes where in a diamagnetized crystal experience strain on subjection to magnetization.

2.9.5 Dielectric Properties:

Electrical measurements are basic means of evaluating electronic components and materials. Every material has a unique set of electrical characteristics that are dependent on its dielectric or insulation properties. Accurate measurements of these properties can provide valuable information to ensure an intended application or maintain a proper manufacturing process. The annealed powder was then pressed into pellets with pressure 5 bars for 10 minutes and sintered at 1000ºC for 5 h to measure dielectric and other properties.

Figure 2.10 Shows Agilent 4284A Precision LCR meter.

A dielectric material (dielectric for short) is an electrical insulator that can be polarized by an applied electric field. When a dielectric is placed in an electric field, electric charges do not flow through the material as they do in a conductor, but only slightly shift from their average equilibrium positions causing dielectric polarization. Because of dielectric polarization, positive charges are displaced toward the field and negative charges shift in the opposite direction.

This creates an internal electric field that reduces the overall field within the dielectric itself. If a dielectric is composed of weakly bonded molecules, those molecules not only become polarized, but also reorient so that their symmetry axis aligns to the field. The study of dielectric properties concerns storage and dissipation of electric and magnetic energy in materials. Dielectrics are important for explaining various phenomena in electronics, optics, and solid-state physics.
Dielectric Constant:

The dielectric properties of nanoparticles were measured using Agilent 4284A Precision LCR meter with frequency range 0.075-30 MHz. The dielectric constant measurement, also known as relative permittivity, is one of the most popular methods of evaluating insulators such as ceramics. It is used to determine the ability of an insulator to store electrical energy. The complex dielectric constant consists of a real part ($\varepsilon_r$), which represents the storage capability and an imaginary part (tanδ), which represents the loss. Dielectric constant measurements can be performed easier and faster than chemical or physical analysis techniques making them an excellent material analysis tool.

The dielectric constant is defined as the ratio of the capacitance of the material to the capacitance of the air, or $\varepsilon_r = \frac{C}{Co}$ Where C = Capacitance with a dielectric material and Co = Capacitance without material, or vacuum. The $\varepsilon_r$ value of dry air is 1.00053, which for most measurement applications is usually close enough to the value of vacuum, which is 1. Thus if material is to be used for insulating purposes only, it would be better to have a lower dielectric constant, or as close to air as possible. To the contrary, if a material is to be used in electrical applications for storage of electrical charge, the higher the dielectric constant the better. More charge is stored when a dielectric is present than if no dielectric (air) is present. The dielectric material increases storage capacity of the plate capacitor; hence the dielectric constant of any solid or liquid would be greater than 1. In experimentally, the measurement of dielectric constant from the parallel plate capacitor form is given by equation

$$C = \frac{\varepsilon_r \varepsilon_o A}{d}$$

Where $C$ is the capacitance of the dielectric material, $\varepsilon_o$ is the absolute permittivity of free space, $A$ is the area, and $d$ is the thickness of the capacitor and $\varepsilon_r$ is the relative permittivity or dielectric constant.

Dielectric Loss factor:

Dissipation factor (tan δ), is defined as the ratio of an insulating materials resistance to its capacitive reactance at a specified frequency. It measures the
inefficiency or loss of the material, is always greater than zero, but usually much smaller than the dielectric constant. The \( \tan \delta \) measurements are an excellent means of quality control, which can yield indication of contamination or deterioration. Excessive moisture would increase the dissipation factor value telling us something has changed as compared to previously established values. LCR meter and specimen cells are readily available that make it easy to perform impedance measurements on materials.

A measuring instrument with a wide programmable frequency range is important since the insulation properties can vary substantially with frequency. Accuracy of results can be enhanced by averaging several measurements and calculating results which can be simplified through computer programs. This leads to better process control, increased efficiency and superior products.

The dielectric loss tangent is defined by the angle between the capacitor's impedance vector and the negative reactive axis. It determines the looseness of the medium. Similar to dielectric constant, low loss tangents result in a "fast" substrate while large loss tangents result in a "slow" substrate. Beware that the exact values can vary greatly depending on the particular manufacturer's process, so you should seek out data from the manufacturer for critical applications. The dielectric constant can be calculated using:

\[
\varepsilon = \frac{C_s}{C_v}
\]

Where \( C_s \) is the capacitance with the specimen as the dielectric, and \( C_v \) is the capacitance with a vacuum as the dielectric.

The dissipation factor can be calculated using:

\[
D = \tan \delta = \cot \theta = \frac{1}{2 \pi f R_p C_p}
\]

Where \( \delta \) is the loss angle, \( \theta \) is the phase angle, \( f \) is the frequency, \( R_p \) is the equivalent parallel resistance, and \( C_p \) is the equivalent parallel capacitance.
2.10 Multiferroic properties/ferromagnetism and ferroelectricity:

Magnetism and ferroelectricity are indispensable to many forms of current technology, and the quest for multiferroic materials, where these two phenomena are closely coupled, is of great technological and fundamental importance. Ferroelectricity and magnetism tend to be reciprocally exclusive and interact weakly with each other when they coexist. The exciting new development is the discovery that even a weak magnetoelectric interaction can lead to spectacular cross-coupling effects when it induces electric polarization in a magnetically ordered state. Such magnetic ferroelectricity, showing an unprecedented sensitivity to applied magnetic fields, occurs in 'frustrated magnets' with competing interactions between spins and complex magnetic orders.

Multiferroic materials, which show simultaneous ferroelectric and magnetic ordering, exhibit unusual physical properties and in turn promise new device applications as a result of the coupling between their dual order parameters.

**Ferroelectricity (PE):**

Ferroelectric testing includes ferroelectric hysteresis loop. Ferroelectric test was conducted using ferroelectric test system (RT6000S Ferroelectric Test System Radiant Technologies). This system is capable of P-E loop measurement. For P-E loop measurement, a triangular signal is used. The maximum drive voltage is -20.00, +19.99 volt, and maximum points are 500. An exciting new area of scientific exploration examines the potential usefulness where magnetic field effects occur simultaneously with ferroelectric effects in materials and structures.

Where these two properties, ferromagnetism and ferroelectricity, are coupled in the same material, the material is called a multiferroic. In a normal polarization vs. voltage test, the DRIVE output of a Precision tester stimulates the capacitor sample with a voltage waveform while counting electrons coming out of the sample into the RETURN input. The Magnetoelectric Response Task in the Vision Library drives a magnetic coil with the tester DRIVE output while capturing any charge transfer into or out of the sample. It is the symmetrical parallel to the polarization hysteresis test with the exception that the sample is stimulated by a magnetic field waveform instead of an electric field waveform.
Polarization Measurement in Radiant Ferroelectric Testers From a theoretical point of view, the sample under test can be considered a Voltage-to-Charge converter with infinite impedance between its input and output nodes. In other words, the absolute value of the DRIVE voltage does not show up in the response of the sample.

**Magnetoelectric coupling:**

To measure the ME effect ($\alpha_E = \partial E/\partial H$) in ME nanostructures, it is common to record the dynamic change in voltage or charge induced by the application of a magnetic field parallel to the film plane. This is the same method as applied for bulk ME composites. Generally, there are two characteristic modes, active and passive, for measurement of the direct ME effect.

The active mode is similar to measurement of the magneto dielectric effect, and requires a test current to be passed through the sample to obtain the capacitive signal change induced by a magnetic field. Alternatively, a direct-current pulse test voltage can be applied to the samples to obtain the polarization signal change induced by a magnetic field, giving the polarization–electric field (P–E) hysteresis loop.

Thus when making ME measurements for composite samples in the active mode, by direct measurement of the P–E loop or dielectric constant change under an applied magnetic field, the contribution from the magneto resistive and interfacial capacitive effects (or Maxwell–Wagner interfacial polarization effect) must be considered. By comparison, a variety of approaches have been developed to probe the converse ME coupling effect, that is, electric-field control of magnetization.

A direct method is to use a vibrating sample magnetometer to measure the magnetization–magnetic field (M–H) behaviour. By applying an electric field to samples, the change in M–H can be measured. At high frequency, the magnetic tunability of ME composite nanostructures, for applications in tunable microwave devices, can be measured through electric field-induced changes in the ferromagnetic resonance (FMR) field.

**2.11 Optical properties:**

The optical spectra of transition-group metal ions have been the subject of intense investigations attempted in order to obtain a fundamental understanding of the
varied colours and luminescent properties exhibited by the internal transitions in different crystalline environments. Some much more intense absorptions are due to electron transfer: LMCT (ligand-metal charge transfer), IVCT (inter valence charge transfer) and MMCT (metal-metal charge transfer).

One of the most enthralling and advantageous characteristics of nanomaterial’s is their optical properties. Applications based on optical properties of Nanomaterial’s include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photo catalysis, photo electrochemistry and biomedicine. The optical properties of Nanomaterial’s depend on parameters such as size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures. Also shape can have intense impact on optical properties of metal nanostructures when anisotropy is added to the nanoparticle, such as growth of Nanorods, the optical properties of the nanoparticles change dramatically.

**UV-visible electronic absorption spectroscopy:**

**Operating principle: Beer’s law:**

For the prepared samples UV-Vis spectrum has been performed, measured and recorded on Perkin Elmer UV spectrometer λ 35* .The basic operating principle of electronic absorption spectroscopy is based on the measurement of light absorption due to electronic transitions in a sample. Since the wavelength of light required for electronic transitions is typically in the UV and visible region of the electromagnetic radiation spectrum, electronic absorption spectroscopy is often called UV visible or UV-Vis spectroscopy.

It is named electronic absorption spectroscopy because the absorption in the UV-visible regions involves mostly electronic transitions. Based on Beer’s law, the absorbance, A, is related to the incident light intensity, I0, and transmitted light intensity, I, concentration of a solution sample, c, path length of the sample, l, absorption coefficient, α, and molar absorptivity, ε, by the following equation:

\[ A = \log \frac{I_0}{I} = \varepsilon c = \alpha c \quad (2.1) \]
In an experiment, both I0 and I can be measured and thus A can be determined experimentally. If l and c are known, the absorption coefficient can be determined by Eq. (2.1). The absorption coefficient is wavelength dependent and a plot of α as a function of wavelength λ is the spectrum of interest.

The spectrum is often characteristic of a given sample and reflects the fundamental electronic properties of the sample. For solid samples, concentration, c, has no meaning and similar expression can be derived in terms of the thickness of the sample. The solid sample needs to be thin enough to avoid saturation of absorption.

**Instrument: UV-visible spectrometer:**

Electronic absorption or UV-visible spectroscopy is one of the simplest and yet most useful optical techniques for studying optical and electronic properties of nanomaterial’s. This technique is based on the measurement of light absorption by a sample, typically using commercially available spectrometers at reasonable cost. As illustrated in Fig. 2.1, the intensity of light from a light source, e.g. a lamp, is measured by a light detector, e.g. photodiode, photomultiplier tube (PMT) PMT or charge coupled device (CCD) detector, without (blank) and with a sample between the light source and detector.

If the sample absorbs light at some wavelength, the transmitted light will be reduced. The intensity of the transmitted light plotted as a function of light wavelength will give a spectrum of the sample absorption. Most spectrometers cover the wavelength range from about 200 nm to 800 nm. Extending the measurement beyond 800 nm is possible but usually requires different light source, optics, and detector. UV-visible spectrum is relatively easy to measure. However, there are still some common mistakes that beginners tend to make. First, the sample concentration cannot be too high. An optical density (OD) or absorbance (A), defined as −log10(T) with T being the transmittance I/I0, should usually be around 1 and not more than 3. Too high a concentration or OD leads to saturated absorption and distorted, unreal spectrum. Second, proper blank or background needs to be taken before the sample spectrum is measured. Ideally, one should use the same cuvette and solvent.

If there are other species in the sample that could have absorption in the region measured but is of no interest, they should be part of the “blank” or background
measurement if at all possible. Third, one needs to make sure that the sample is clear and has no floaters in a solution sample that are visible to the eye. Visible floaters will cause significant scattering and distort the measured spectrum. One common cause for floaters in nanomaterial solutions is agglomeration or aggregation of particles to form large structures with dimension on the scale of a few hundreds of nm or larger, thereby being visible to eye. If the sample contains only a small amount of aggregates, they can usually be filtered away or precipitated out by centrifugation before measurement is made.

Figure 2.11 Perkin Elmer UV spectrometer λ 35°