CHAPTER 1
INTRODUCTION

1.1 CERAMICS

Ceramics are basically inorganic and non-metallic solids prepared from powdered materials and fabricated into products through the application of heat and display such characteristic properties as high hardness, low electrical conductivity and brittleness. In the early stages, porous articles made from fired mud were used. Later, the industrial development made the revolution in making clay products such as bricks, tiles, heat resistance materials and electrical insulators. But, these products are produced from naturally occurring minerals which are coarse and inconsistent in chemical purity and multiphase and are known as traditional ceramics. After World War II, there was a great demand for new ceramic materials such as oxides, carbides and nitrides to fulfill sophisticated applications for day-to-day life. These categories of ceramic materials are termed as advanced ceramics. Such ceramic materials are homogeneous, consistent in chemical purity and have controlled microstructure [1]. Thus, based on their properties and applications, ceramics are broadly divided into two main categories traditional ceramics and advanced ceramics.

1.1.1 Traditional ceramics
Traditional ceramic products are made from naturally occurring raw materials, such as clay minerals, feldspar and quartz. Products such as; sanity tableware, bricks, tiles, industrial abrasives, refractory linings and Portland cement are examples for traditional ceramics.

1.1.2 Advanced ceramics

Modern advanced ceramics may be defined as primarily inorganic and non metallic materials formed as a powder, which are compacted into various shape and consolidated or densified through firing at high temperatures. Thus production of ceramics requires not only the production of high quality powders, but also the production of the starting powder that has to be compacted to the required shape and then heated to a high temperature to achieve the final consolidated product having the required shape. Ceramic materials such as oxides, carbides and nitrides are some of the advanced ceramics. "Advanced Ceramics" which came on to the scene in the 20th century as the materials systems became more refined and special compounds and processes were developed for structural and electronic applications. These advanced ceramics are distinguished by their high chemical purity, careful processing and high values of the useful properties [2]. According to their properties and function, the “Advanced Ceramics” can be classified into several categories such as structural, electronic, optical, bio and magnetic ceramics.

1.1.2.1 Structural Ceramics

The structural ceramics are those materials used for load bearing applications at ambient as well as at elevated temperatures [3]. The important properties of structured ceramic materials are high hardness, high toughness, high creep resistance and high corrosion resistance to various environmental conditions. The materials such as alumina (Al₂O₃), zirconia (ZrO₂), silicon nitride (Si₃N₄), silicon carbide (SiC), titanium carbide (TiC) and boron carbide (B₄C) are some structural ceramic materials and are employed in many applications.

1.1.2.2 Electronic, Optical and Bio-Ceramics
The advanced ceramic materials used for electrical and electronic applications are termed as electro ceramics [4]. The dielectric materials such as BaTiO₃, SrTiO₃ and ionic conductors like β-Al₂O₃ are some of the electro ceramic materials. Conductivity, dielectric constant and dissipation factor, etc., are the essential properties of electronic ceramics. Also, it is possible to alter the property of some structural ceramic materials for electronic applications with addition of impurities called dopants. As an example, let us take the case of zirconia. Typically, because of its high hardness and fracture toughness, it is primarily an insulator and used for various structural applications. But, the same material can be converted into ionic conductor by doping a desirable amount of Y₂O₃ for electronic application such as solid electrolyte in sensors and fuel cell.

The optical ceramics like MgO and Y₂O₃ are used for making laser materials and optical windows. The ceramics, which find applications in biological field are termed as Bio-Ceramics. Alumina (Al₂O₃) and Hydroxy apatite (Ca₁₀(PO₄)₆(OH)₂) are found to be good in making artificial teeth, bones and joints [1].

1.1.2.3 Magnetic Ceramics

The ceramics which possess magnetism are termed as magnetic ceramics. Magnetic ceramics are oxide materials that exhibit a certain type of permanent magnetization called ferrimagnetism. Commercially prepared magnetic ceramics are used in a variety of permanent magnet, transformer, telecommunications, and information recording applications.

Magnetic ceramics are made of ferrites, which are crystalline minerals composed of iron oxide in combination with some other metal [5]. The magnetic behavior exhibited by the ferrites is called ferrimagnetism. It is quite different from the ferromagnetism that is exhibited by metallic materials such as Iron. In ferromagnetism, there is only one kind of lattice site and unpaired electron “spins” (the motions of electrons that cause a magnetic field) line up in one direction within
a given domain. In ferrimagnetism on the other hand, there is more than one kind of lattice site and electron spins align so as to oppose one another, some being “spin-up” and some being “spin-down” within a domain. Incomplete cancellation of opposing spins leads to a net polarization, which though somewhat weaker than for ferromagnetic materials can be quite strong. Ferrite materials such as NiFe₂O₄, Y₃Fe₅O₁₂ (Soft ferrites) and BaFe₁₂O₁₉, SrFe₁₂O₁₉ (hard ferrites) are the magnetic ceramics. Three basic classes of ferrites are made into magnetic ceramic products. Based upon their crystal structure, they are the spinel, the hexagonal ferrites and the garnets.

1.1.2.3.1 Spinel

Mineral composed of magnesium aluminum oxide (MgAl₂O₄) or any member of a group of rock forming minerals, all of which are metal oxides with the general composition AB₂O₄ in which ‘A’ may be Lithium, magnesium, iron, zinc, manganese, or nickel, B may be aluminum, chromium, or iron and O is oxygen [6].

1.1.2.3.2 Hexagonal Ferrites

Hexagonal Ferrites have the formula M(Fe₂O₁₉), where M is usually barium (Ba), strontium (Sr), or lead (Pb). The crystal structure is complex, but it can be described as hexagonal with a unique ‘c’ axis or vertical axis [7]. This is the easy axis of magnetization in the basic structure. Because the direction of magnetization cannot be changed easily to another axis, hexagonal ferrites are referred to as ‘hard’.

1.1.2.3.3 Garnets

Garnet ferrites have the structure of the silicate mineral garnet and the chemical formula M₃(Fe₂O₁₂), where M is yttrium or a rare-earth ion [8]. In addition to tetrahedral and octahedral sites such as those seen in spinels, garnets have dodecahedral (12-coordinated) sites. The net ferrimagnetism is thus a complex result of antiparallel spin alignment among the three types of sites. Garnets are also magnetically hard.
1.1.2.3.4 Magnetic Ceramics Applications

They are used for the making magnetic recording heads and temperature sensors. Hard magnetic ferrites are used as permanent magnets in refrigerator seal gaskets. They also are used in microphones, high frequency microwave absorbers and speaker gaskets. The largest market for permanent magnets [9] is in small motors for cordless appliances and in automobile applications.

1.2 MAGNETISM

Movement of an electrical charge (which is the basis of electric currents) generates a magnetic field in a material. Magnetism is a characteristic property of all materials that contain electrically charged particles and for most purposes can be considered to be entirely of electronic origin. In an atom, the magnetic field is due to the coupled spin and orbital magnetic moments associated with the motion of electrons. The spin magnetic moment is due to the precession of the electrons about their own axes whereas the orbital magnetic moment is due to the motion of electrons around the nucleus. The resultant combination of the spin and orbital magnetic moments of the constituent atoms of a material gives rise to the observed magnetic properties.

Magnetization is the magnetic moment per unit volume within the material and depends on density of magnetic dipole moments within material. Significant contribution to magnetization in materials arises from unpaired electron spins and the orbital motion of electrons within the material contributes to a lesser extent.

1.2.1 Physical Basis of Magnetism

The physical basis of the magnetic properties of engineering materials is the current loops produced by the motion of electrons. As shown in Figure 1.2 and Figure 1.3, the two relevant types of electron motion are

(1) Spin of an electron about its own axis of rotation
(2) Orbital motion of electrons around the atomic nucleus

The interaction of the electron induced magnetic moments with an externally applied magnetic field varies continually from material to material and macroscopic magnetic properties depend on the atomic and micro structural characteristics of a material.

Figure 1.2 Spin of an electron about its own axis of rotation
1.2.2 CLASSES OF MAGNETIC MATERIALS

The magnetic materials can be classified into the following five major groups

1.2.2.1 Diamagnetism

1.2.2.2 Paramagnetism

1.2.2.3 Ferromagnetism

1.2.2.4 Ferrimagnetism

1.2.2.5 Antiferromagnetism
1.2.2.1 Diamagnetism

Diamagnetism is the effect caused by the magnetic moment due to the orbiting electrons, which produces a slight opposition to the imposed magnetic field [10]. Diamagnetism is a fundamental property of all matter, although it is usually very weak. It is due to the non-co-operative behavior of orbital electrons when exposed to an applied magnetic field. Diamagnetic substances are composed of atoms which have no net magnetic moments (i.e., all the orbital shells are filled and there are no unpaired electron). However, when exposed to a field, a negative magnetization is produced and thus the susceptibility is negative.

1.2.2.2 Paramagnetism

Some of the atoms or ions in this class of material have a net magnetic moment due to the unpaired electrons in partially filled orbitals. One of the most important atoms with unpaired electrons is iron. However, the individual magnetic moments do not interact magnetically and like diamagnetism, the magnetization is zero when the field is removed. In the presence of a field, there is a partial alignment of the atomic magnetic moment in the direction of the field resulting in a net positive magnetization and positive susceptibility [11]. In addition, the efficiency of the field in aligning the moments is opposed by the randomizing effects of temperature. This results in a temperature dependent susceptibility known as the Curie Law.

1.2.2.3 Ferromagnetism

Alignment of the magnetic moment of atoms in the same direction so that the net magnetization remains even after the magnetic field is removed. The atomic moment in these materials exhibit very strong interactions. These interactions are produced by electronic exchange forces and result in a parallel or antiparallel alignment of atomic moment. Exchange forces are very large equivalent to a field of the order of 1000 Tesla or approximately a 100 million times the strength of the earth's field. The exchange force is a quantum mechanical phenomenon due to the relative orientation of the spins of two electrons. Ferromagnetic materials exhibit
parallel alignment of moments resulting in large net magnetization even in the absence of a magnetic field [12]. The elements Fe, Ni, and Co and many of their alloys are typical ferromagnetic materials.

1.2.2.4 Ferrimagnetism

Magnetic behavior obtained when ions in a material have their magnetic moments aligned in an antiparallel arrangement such that the moments [11] do not completely cancel out and a net magnetization remains. In ionic compounds such as oxides, more complex forms of magnetic ordering can occur as a result of the crystal structure. One type of magnetic ordering is called ferrimagnetism. The magnetic structure is composed of two magnetic sublattices (called A and B) separated by oxygen. The exchange interactions are mediated by the oxygen anions. When this happens the interactions are called indirect or superexchange interactions. The strongest superexchange interactions result in an antiparallel alignment of spins between the A and B sub lattice. In ferrimagnets, the magnetic moments of the A and B sub lattices are not equal and result in a net magnetic moment. Ferrimagnetism is similar to ferromagnetism. It exhibits all the hallmarks of ferromagnetic behavior namely spontaneous magnetization, Curie temperatures, hysteresis, and remanence. However ferro and ferrimagnets have different magnetic ordering. Magnetite is a well known ferrimagnetic material. Indeed, magnetite was considered as a ferromagnet until Neel, in the 1940's provided the theoretical framework for understanding ferrimagnetism.

1.2.2.5 Antiferromagnetism

Arrangement of magnetic moments such that the magnetic moments of atoms or ions cancel out causing zero net magnetization. If the A and B sub lattice moments are exactly equal but opposite, the net moment is zero [11]. This type of magnetic ordering is called antiferromagnetism. The antiferromagnetism is the behavior of susceptibility above a critical temperature called the Neel temperature \( T_N \). Above
$T_N$, the susceptibility obeys the Curie-Weiss law for paramagnets but with a negative intercept indicating negative exchange interactions.

1.3 FERRITE

Ferrite is a ceramic material formed by reacting metal oxides [13] into a magnetic material. Ferrite is categorized as electro ceramics with ferromagnetic properties. Ferrite exhibits Ferromagnetism due to the superexchange interaction between electrons of metal and oxygen ions. The opposite spins in ferrite results in the lowering of magnetization compared to Ferromagnetic metals where the spins are parallel. Due to the intrinsic atomic level interaction between oxygen and metal ions, ferrite has higher resistivity compared to ferromagnetic metals. This enables the ferrites to find applications at higher frequencies and makes it technologically very useful.

In a bulk ferrite, there are domains called Weiss domains in which all these molecular moments are aligned in one direction. Domain walls separate different domains aligned in random directions and in the presence of an external magnetic field these moments can be forced to align in one direction. Some energy has to be spent for this process and the magnetization always lags behind the magnetizing field and results in a magnetization loop [14]. This is called as B-H Loop (Hysteresis)

1.3.1 Hexagonal ferrites

Hexagonal ferrites are another class of magnetic ferrites that have a complex hexagonal structure similar to that of the mineral magnetoplumbite. These ferrites have the formula $M\overline{6}Fe_2O_3$ or $MFe_{12}O_{19}$ where $M$ is Ba, Sr, or Pb. Per formula unit the $12Fe^{3+}$ ions are arranged on several different sites as follows: $2Fe^{3+}$ ions are in tetrahedral sites with spin up; $2Fe^{3+}$ ions are in octahedral sites with spin up; 7$Fe^{3+}$ ions are in octahedral sites with spin down; 1$Fe^{3+}$ ion is in fivefold
coordination with spin down [15]. Hexagonal Ferrites are used to make permanent magnets.

1.3.2 Hysteresis Loop

Magnetic hysteresis refers to the irreversibility of the magnetization and demagnetization process. If an alternating magnetic field is applied to the material, its magnetization will trace out a loop called a hysteresis loop [16]. If one’s asked to mention the experimental fact giving the most distinctive fingerprint of ferromagnetism then, depending on our scientific background one would probably propose either the existence of the Curie point or the observation of hysteresis loops. Removing the field does not necessarily return domain structure to original state; hence results in magnetic hysteresis. Three quantities of particular importance in this respect are the Saturation magnetization (M_s), remanent magnetization (M_r) and the coercivity (H_c).

1.3.2.1 Saturation Magnetization (M_s), Remanent Magnetization (M_r), and Coercivity (H_c)

Saturation magnetization occurs when all of the dipoles have been aligned by the field producing the maximum net magnetization. When the field is reduced to zero after magnetizing, remaining magnetic induction is the remanent induction (B_r) and remaining magnetization is remanent magnetization (M_r). Coercivity (H_c) is the magnetic field needed to reduce magnetization to zero from saturation [17].

1.3.2.2 Curie Temperature

All ferromagnets become paramagnetic when heated to high temperature. Transition temperature from Ferromagnetic to paramagnetic behavior is Curie temperature [18]. At curie temperature permeability drops suddenly and both coercivity and remanence become zero. Materials can be classified according to the values taken by hysteresis parameters. In particular, it is common to sub divide materials into soft and hard magnetic materials.
1.3.2.2.1 Soft Magnetic Materials

The term soft material is used to refer to materials that are easy to magnetize destined to applications where a low coercivity and high permeability [19] are prime requirement. The coercivity is of the order of 50-100 Am$^{-1}$ in non oriented Si-Fe alloys and low carbon steels used in electric motors and other components and decreases down to 10 Am$^{-1}$ in grain oriented Si-Fe alloys employed in transformer cores. This is also the typical coercivity value in Mn-Zn and Ni-Zn ferrites. Extremely soft materials can be obtained from nickel based alloys with approximately 80% Ni and 20% Fe generically known as perm alloys. The advent of the rapid solidification technology, it has become possible to produce amorphous alloys composed of about 80% transition metals (chiefly Fe and/or Co) and 20% metalloids (B, Si, C) and nanocrystalline alloys with grains of dimensions in the nanometer range immersed in an amorphous matrix, which rival perm alloys in softness.

There have also been dramatic improvements in the properties of soft magnetic materials. Decreases in coercivity have decreased the energy losses of soft materials in ac applications. Many transformers today use amorphous Fe rich alloys cooled so rapidly from the melt that they are unable to crystallize. An area of extensive current research is materials for recording heads. Improved materials have contributed to the remarkable increases in the density of information storage (bits per square inch).

1.3.2.2.2 Hard Magnetic Materials

Ferromagnetic or ferrimagnetic materials are classified as hard magnetic materials that have coercivity value higher than 10$^4$ Am$^{-1}$. The high coercivity of the hard magnetic materials arises from the large magnetocrystalline anisotropy of the materials [19]. The coercivity is of the order of 50-100 kAm$^{-1}$ in alnico alloys containing various proportions of Fe, Ni, Co, Al and Cu. In hexagonal ferrites,
which are iron oxides of the type BaFe$_{12}$O$_{19}$ or SrFe$_{12}$O$_{19}$. $H_c$ can be around 300 kAm$^{-1}$, but it can exceed 1000 kAm$^{-1}$ in rare earth magnets of the Sm-Co or Nd-Fe-B type. More coercivity, a parameter important in estimating the strength of a hard magnet is the maximum energy product which gives a measure of the energy made available by the magnet for external work [20]. Hard magnetic materials are used in applications requiring a steady magnetic field. An increase in coercivity has greatly increased the use of permanent magnets in modern technology.

### 1.3.2.2.3 Hard Ferrite (Ceramic) Magnets

Ceramic magnets are composed of iron oxide, barium and strontium oxides. These magnets have higher magnetic flux density, higher coercivity and higher resistance to demagnetization and oxidation compared to other non rare earth permanent magnets. The biggest advantage of such magnets is the low cost, which makes the hard ferrite magnets very popular in many permanent magnet applications. Due to their ceramic nature, ferrite magnets are very hard and brittle. Special machining techniques must be utilized for these magnets. Ceramic or hard ferrite magnets come in discs, cylinders, rings, blocks and arcs which are charcoal grey in colour [21].

Low coercivity steel magnets requires long bar magnets or horseshoe shapes to minimize demagnetization from reverse fields produced by the north and south poles at the ends of the magnet. Before the advent of alnico magnets in the 1930’s, telephone receivers were long and separate from the speakers because they included a long horseshoe shaped steel magnet. Difference between hysteresis curves for soft and hard magnetic materials as shown in Figure 1.4. Typically $H_c < 40$ Am$^{-1}$ in good soft magnets and $H_c > 40$ kAm$^{-1}$ in good hard magnets.
1.3.2.2.4 Applications of Magnetic Materials

Ferromagnetic materials are often used to enhance the magnetic flux density \((B)\) produced when an electric current is passed through the material. Applications include data storage, strong permanent magnets, cores for electromagnets, electric motors, transformers, generators and other electrical equipment.

1.4 PREPARATION METHODS

Ceramic products are normally made from powders. These powders are consolidated and densified by sintering. Solid state mixing is a commercial method to prepare large quantity of powders by mixing and firing at high temperatures. The powders prepared by solid state mixing are usually inhomogeneous in nature. A major issue in the preparation of powdered precursors especially for magnetic ceramic applications is the chemical homogeneity after many grinding and firing steps. A number of chemical approaches have been developed in order to improve
mixing even down to the atomic level. Often these techniques involve the decomposition of salts like nitrates, sulphates and chlorides into the desired chemical form. The various chemical techniques such as Co-precipitation, combustion, spray drying, pechini method and sol-gel process are used in practice for achieving homogeneous, fine grained, high pure ceramic powders.

1.4.1 Co-Precipitation

Co-precipitation occurs when solutions of two or more metal salts are mixed to form insoluble solid precipitate due to chemical reaction and it is separated from the solid mixture by filtration [22].

1.4.2 Combustion

Self propagating low temperature combustion synthesis [23] or simply combustion synthesis is both energy and time efficient. A solution mixture of metal precursor and an organic fuel (e.g., urea, glycine) is first dehydrated then ignited and finally brought to combustion. The exothermicity of reaction provides the energy requirement for the synthesis and in some cases temperatures are instantaneously attained. Added bonuses to the reduction in external energy input are the following features:

(a) Reaction times are very short for synthesis (typically only a few seconds)

(b) The high reaction rate results in a finely dispersed morphology and large surface area for the synthesized product

(c) The equipment needed is simple and cost effective

From a chemical perspective another attractive feature of combustion synthesis lies in its intrinsic ability to tune the solid state chemical composition of the product by simply varying the precursor (metal salt + fuel) mixture chemistry.
1.4.3 Spray Drying

Spray drying is the most widely used industrial process for producing large quantity of powder by drying. Using this process homogeneous powder of salts that can be calcined to oxide later can be prepared [24]. It is well suited for continuous production of dry solids in powder, granulate or agglomerate particle form from liquid feedstocks. Feedstocks can include solutions, emulsions and pumpable suspensions. The technology is ideal when the end product must comply with precise quality standards. This regards particle size distribution, residual moisture content, bulk density and particle morphology.

1.4.4 Pechini Method

A process related to the sol-gel route is the Pechini or liquid mix process (named after its American inventor, Maggio Pechini). In this method, aqueous solutions of suitable salts are mixed with an alpha-hydrocarboxylic acid such as citric acid. Chelation or the formation of complex ring shaped compounds around the metal cations takes place in the solution. A polyhydroxy alcohol is then slowly added and the liquid is heated to 150°C-250°C to allow the chelates to polymerize or to form large cross linked networks. As excess water is removed by heating a solid polymer resin results. Eventually, at still higher temperature of 500°C to 900°C the resin is decomposed and ultimately a mixed oxide is obtained. The powder prepared via this route is very fine [25].

1.4.5 Sol-Gel Process

The sol-gel process is a wet chemical technique widely used recently in the fields of Materials Science and Ceramic Engineering. Such methods are used for the fabrication of materials (typically a metal oxide) starting from a chemical solution which acts as the precursor for an integrated network (or gel) of either discrete particles or network of polymers. Typical precursors are metal alkoxides and metal chlorides which undergo various forms of hydrolysis and polycondensation
reactions. The formation of a metal oxide involves connecting the metal centres with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution [26]. Thus the sol evolves towards the formation of a gel like mono or di-phasic system containing both a liquid phase and a solid phase whose morphologies range from discrete particles to continuous polymer networks.

In the case of the colloid the volume fraction of particles (or particle density) may be very low that a significant amount of fluid may need to be removed initially for the gel like properties to be recognized. Centrifugation can also be used to accelerate the process of phase separation.

Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing. Afterwards a thermal treatment or firing process is often necessary in order to favour further polycondensation and to enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages of using this methodology is that densification is often achieved at a much lower temperature.

The precursor sol can either be deposited on a substrate to form a film (e.g., by dip-coating or spin-coating), cast into a suitable container with the desired shape (e.g., monolithic ceramics, glasses, fibers, membranes, aero gels), or used to synthesize powders (e.g., microspheres, nanospheres). The Sol-Gel approach is a cheap and low temperature technique that allows for the fine control of the product’s chemical composition. Even small quantities of dopants such as organic dyes and rare earth metals can be introduced in the sol to end up in an uniformly dispersed final product. It can be used in ceramics processing and manufacturing as an investment
casting material or as a means of producing very thin films of metal oxides for various purposes.

1.4.5.1 Advantages of Sol-Gel method

The crystallization temperature is reduced much as compared to any conventional preparation method.

- The additives can be mixed with the matrix uniformly and the homogeneous composite power is possible at the end.
- It can easily shape materials into complex geometries in the gel state.
- It can produce high purity products.

1.5 PROCESSING OF CERAMIC MATERIALS

1.5.1 Calcination

Calcination is a thermal treatment process applied to ores and other solid materials in order to bring about a thermal decomposition, phase transition or removal of a volatile fraction. The calcination process normally takes place at temperatures much below the melting point of the product materials. Calcination condition is an important factor controlling shrinkage during sintering [1]. The calcination can be carried out by placing the mixed powders in the crucible.

Examples of calcination processes include the following:

- Decomposition of hydrated minerals as in calcination of bauxite to remove crystalline water as water vapor
- Decomposition of carbonate minerals as in the calcination of limestone to drive off carbon dioxide
- Decomposition of volatile matter contained in raw petroleum coke
Heat treatment to effect phase transformations, as in conversion of anatase to rutile or devitrification of glass materials.

1.5.2 FORMING OR SHAPING

There are various methods for shaping the ceramic products like pressing the powder, slip casting, tape casting and injection moulding, extrusion and hot isostatic pressing etc., Before shaping, organic binders like PVA (Polyvinyl alcohol) and Polyethylene Glycol (PEG) are added to give a sufficient green strength so that it is easy to handle the green body before sintering. One of the most important requirements for the binders is that it should be possible to eliminate them from the compact without any disruptive effect. Some of the frequently used consolidation techniques are pressing, tape casting and injection moulding etc.,[1]

1.5.3 SINTERING

Sintering is the process whereby a heat treatment is used to convert a powder compact into a dense polycrystalline solid. When the material of the separate particles diffuse to the neighboring powder particles. There has been a different type of sintering used according to the type of application. The type of sintering may be either solid state sintering or liquid phase sintering and the sintering technique may either be pressure less sintering or pressure assisted sintering.

The fabrication of ceramics commonly includes a heat treatment step in which the powder compact already formed into a required shape is converted into a dense solid. This step is referred to as sintering (or firing). In general a Ceramist, wishing to produce a material with particular properties must identify the required microstructure and then design processing conditions that will produce this required microstructure. The objective of sintering studies is commonly to understand how the processing variables such as temperature, particle size, applied pressure, particle packing, composition and sintering atmosphere influence the microstructure of the product. In the present chapter, we outline the basic principles of sintering and how
they are applied practically to the production of ceramics with controlled microstructures.

1.5.3.1 Stages of sintering

The initial stage of sintering would begin as soon as some degree of atomic mobility is achieved on heating and during this stage sharp concave necks form between the individual particles. Typically, the amount of densification is small and it can be considerably lower if coarsening mechanisms are very active. In the intermediate stage the high curvatures of the initial stage have been moderated and the microstructure consists of a three dimensional interpenetrating network of solid particles and formation of continuous channel like pores. This stage is considered till the porosity reaches approximately 5 to 10% and therefore covers most of the densification. As sintering proceeds the channel like pores break down into isolated, closed voids, which mark the start of the final stage. Grain growth can be more extensive in the final stage and difficulties are commonly encountered in the removal of the last few percent of porosity [27].

1.5.3.2 Mechanism of Sintering

Sintering of crystalline materials can occur by several mechanisms such as vapour transport, surface diffusion, lattice (volume) diffusion, grain boundary diffusion and dislocation motion etc. Distinction is commonly made between densifying and non densifying mechanisms. Vapour transport, surface diffusion and lattice diffusion from the particle surfaces to the neck lead to neck growth and coarsening of the particles without densification. Grain boundary diffusion and lattice diffusion from the grain boundary to the neck are the most important densifying mechanisms in polycrystalline ceramics. Diffusion from the grain boundaries to the pores permits neck growth as well as shrinkage. Plastic flow by dislocation motion can cause neck growth and densification through deformation of the particles in response to the sintering stress. Plastic flow is more common in the sintering of metal powders. For
glass powders, which cannot have grain boundaries, densification and neck growth occurs by viscous flow involving deformation of the particles.

### 1.5.3.3 Effects of Grain Boundaries

When sintering occurs in polycrystalline materials due to the elimination of internal surface area associated with the pores goes into creates new grain boundary area. The grains also have a tendency to grow by migration of the boundaries to reduce the energy associated with the grain boundaries, thereby leading to an increase in the diffusion distance. The presence of the grain boundaries also dictates the equilibrium shape of the pores at the intersection with the boundaries. At equilibrium condition the chemical potential of the atoms in the pore surface must be the same everywhere, which is equivalent to saying that the curvature of the pore surface is the same everywhere. This means that the pore surface must consist of circular arcs in two-dimensional models and of spherical caps in a very limited number of three dimensional geometries for isotropic solids. There must also be a balance of forces at the junction between the grain boundary and the pore surface.

### 1.5.3.4 Grain Growth and Coarsening

Grain growth is the term used to describe the increase in the average grain size of a polycrystalline material. The grain boundary is a region with a complex structure of glassy phase between two crystalline grains or domains. It has a higher energy than the bulk crystal and hence a reduction in the grain boundary area will reduce the free energy of the system. The grain boundary moves by diffusion of atoms (ions) from one side of the boundary to the other so that atoms previously aligned with one grain become aligned with the other causing it to grow at the expense of its neighbour. Growth occurs in such a way that the convex grains lose atoms while the concave grains gain atoms with the result that the boundary moves towards its center of curvature [27].
Grain growth in ceramics is generally divided into two types: (i) Normal grain growth and (ii) Abnormal grain growth, which is sometimes referred to as exaggerated grain growth or discontinuous grain growth. In normal grain growth, the average grain size increases with time but the grain size distribution remains the same (invariant in time). Abnormal grain growth is the process whereby a few large grains grow rapidly at the expense of the smaller grains giving a bimodal grain size distribution. Anisotropic grain growth is a type of abnormal grain growth in which the abnormal grains grow in an elongated manner commonly with faceted straight sides. In porous ceramics, abnormal grain growth is accompanied by the breakaway of the boundaries from the pores and must be avoided if high densities are to be achieved.

The term ‘coarsening’ is frequently used to describe the process in porous ceramics whereby the increase in the average grain size is accompanied by an increase in the average pore size. Coarsening as we have observed, reduces the driving force for sintering and increases the diffusion distance for matter transport and thereby reducing the rate of sintering. The suppression of coarsening mechanisms therefore forms a key requirement for the achievement of high density. Another requirement is that the microstructure be stabilized such that the pores and the grain boundaries remain attached. This second requirement depends primarily on the ability to reduce the intrinsic (pore-free) mobility of the grain boundaries, an understanding of grain growth in dense ceramics. Therefore forms a key step towards controlling grain growth during the sintering of powder compacts. Coarsening of precipitates or particles in a solid, liquid or gaseous medium is commonly referred to as Ostwald Ripening. It is especially important in liquid phase sintering, where matter transport driven by chemical potential differences causes the smaller grains to become smaller and the larger particles to grow, resulting in an increase in the average grain size. Many features of coarsening in solid state sintering are also shared by the Ostwald Ripening Process.
1.5.3.5 Solid State Sintering

In the solid state sintering, the neck growth between contacting particles is an obvious aspect of sintering [26]. No liquid is present and atomic diffusion in the solid state produces joining of the particles and reduction of the porosity. The volume conservation and surface energy minimization dictates a final geometry of the sphere. As the neck grows, the compact becomes stronger. In reality, there are many sintering contacts on each particle, each contact enlarges and merges eventually to form isolated pores.

1.5.3.6 Liquid Phase Sintering

A small amount of liquid, typically less than a few volume percent of the original solid mixture is present when heated at the sintering temperature. The liquid volume is insufficient to fill the pore space and so additional processes are required to achieve full densification. Liquid phase sintering is an important method for the industrial fabrication of many ceramics. While the liquid phase can allow enhanced densification at lower temperatures, a difficulty particularly in the case of ceramics for structural applications is that the maximum service temperature of the material may be controlled by the softening temperature of the solidified liquid phase. The liquid phase sintering mechanism comprises of three stages such as particle rearrangement, solution precipitation, Oswald Ripening.

During the first stage, the liquid is formed between the particles and the particles rapidly rearrange themselves under the action of surface tension forces to produce more stable packing. The solid particles take the smooth edges in this stage and aid the rearrangement process faster. As far as the traditional ceramic is concerned, the full densification is achieved during this initial stage itself. In the second stage, it is assumed that the solid particles slightly dissolve in the liquid present and hence this stage is termed as solution precipitation. The micro structural coarsening by the solute precipitation mechanism dominates in the final stage and
the excess liquid present in the packed region flows into the isolated pores and leads the densification [26].

1.5.3.7 Vitrification

For a mixture where a relatively large volume of liquid is formed on heating the liquid volume is sufficient to fill the volume of the remaining pores. Thus a dense product can be achieved by the formation of the liquid, flow of the liquid into the pores and either crystallization or vitrification (glass formation) of the liquid on cooling. Vitrification is particularly important for the production of ceramics from naturally available raw materials such as clays.

1.5.3.8 Viscous Sintering

A consolidated mass of glass particles is heated near to, or above its softening temperature. Densification occurs by viscous flow of the glass under the influence of surface tension [28].

1.5.3.9 Microwave Sintering

New developments and innovative ideas in the area of materials processing have often led to the discovery of new materials with interesting and useful properties and/or new technologies which are faster, better, cheaper and greener. A striking example of such innovations is recent developments in the area of microwave processing of ceramics. Although many potential advantages of utilizing microwaves to process ceramics have long been recognized, it is only now that this field has finally been shown to be at the take off stage. Although microwave heating was conceived over 50 years ago its use in ceramic processing is relatively new.

Microwave heating is fundamentally different from conventional heating. Microwaves are electromagnetic radiation with wavelengths ranging from 1 mm to 1 m in free space with a frequency between 300 GHz to 300 MHz, respectively. Now a day microwave at the 2.45 GHz frequency is used almost universally for
industrial and scientific applications. In the microwave process, the heat is generated internally within the material instead of originating from external sources and hence there is an inverse heating profile, heating is very rapid as the material is heated by energy conversion rather than by energy transfer, which occurs in conventional techniques. Microwave heating is a function of the material being processed and there is almost 100% conversion of electromagnetic energy into heat, largely within the sample itself, unlike the conventional heating where there are significant thermal energy losses. Microwave heating has many advantages over conventional heating methods [29,30]; some of these advantages include, time and energy saving, very rapid heating rates (>400°C/min), considerably reduced processing time and temperature, fine microstructures and hence improved mechanical properties, it is environmentally friendly and so on. Other than radar, communication purposes and home cooking, microwaves are widely used in industrial applications such as meat tempering, potato chips processing, bacon cooking, drying of pharmaceuticals products and vulcanization of rubber. In the case of ceramic processing microwave energy has been used since the late 1910s with a big push in the eighties: however, this did not result in the formation of useful products in the field of ceramics. Ceramic processes where microwaves have been applied include: process control, drying of ceramic sanitary wares, calcination, and decomposition of gaseous species by microwave plasma and sintering of oxide ceramics by microwave plasma. However, except for the drying of ceramic wares there is hardly any other area where microwave technology has not been commercially exploited [31].

1.6 CHARACTERIZATION TECHNIQUES

Material characterization is important to know the properties of a material and its behavior at different conditions like temperatures, pressures and other variables. These data are useful to know its applications in industry.
1.6.1 Thermal analysis

Thermal analysis comprises a group of techniques in which a physical property of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature programme [1]. In differential thermal analysis, the temperature difference that develops between a sample and an inert reference material is measured when both are subjected to identical heat treatments. The related technique of differential scanning calorimetry relies on differences in energy required to maintain the sample and reference at an identical temperature. Figure 1.5 shows thermal analysis of solids.

![Thermal analysis diagram](image)

**Figure 1.5 Thermal analysis for the characterization of solids**

1.6.1.1 Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis (TGA) is the most widely used thermal method. It is based on the measurement of mass loss of material as a function of temperature. In thermo gravimetry, a continuous graph of mass change against temperature is obtained when a substance is heated at a uniform rate or kept at constant temperature. A plot of mass change versus temperature (T) is referred to as the thermo gravimetric curve (TG Curve). TGA is commonly employed in research and
testing to determine the characteristics of polymers, ceramics to determine
degradation temperatures, absorbed moisture content of materials, the level of
inorganic and organic components in materials, decomposition points of explosives
and solvent residues. It is also often used in phase transition, melting,
crystallization, glass transition and decomposition [32].
Analysis is carried out by raising the temperature of the sample gradually and
plotting weight (percentage) against temperature. The temperature in many testing
methods routinely reaches 1000°C or greater. After the data are obtained, curve
smoothing and other operations may be done to find the exact points of inflection.

1.6.1.1.1 Working Principle

Thermal gravimetric analysis (TGA) is a simple analytical technique that measures
the weight loss (or weight gain) of a material as a function of temperature. As
materials are heated they can loose weight from a simple process such as drying or
from chemical reactions that liberate gases. Some materials can gain weight by
reacting with the atmosphere in the testing environment.

1.6.1.1.2 Instrumentation

The instrument used in thermo gravimetry (TG) is called a thermo balance. It
consists of several basic components in order to provide the flexibility necessary for
the production of useful analytical data in the form of TGA Curve as shown in
Figure 1.6. Basic components of a typical thermo balance are listed below:

i) Balance

ii) Furnace (Heating device)

iii) Unit for temperature measurement and control Programmer and Recorder
The basic requirement of an automatic recording balance includes accuracy, sensitivity, reproducibility and capacity. Recording balances are of two types, null point and deflection type. The null type balance which is more widely used, incorporates a sensing element which detects a deviation of the balance beam from its null position; A sensor detects the deviation and triggers the restoring force to bring the balance beam back to the null position. Temperature may be controlled or varied using a program controller with two thermocouple arrangement; the signal from one actuates the control system whilst the second thermocouple is used to record the temperature.

![Diagram of a Thermo Balance]

**Figure 1.6 Block diagram of a thermo balance**

Graphic recorders are preferred to meter type recorders. X-Y recorders are commonly used as they plot weight directly against temperature. The present instrument facilitate microprocessor controlled operation and digital data acquisition and processing using personal computer with different types of recorder and plotter for better presentation of data.

The furnace and control system must be designed to produce linear heating at over the whole working temperature range of the furnace and provision must be made to
maintain any fixed temperature. A wide temperature range generally 150°C to 2000°C of furnaces is used in different instruments manufacturers depending on the models. Temperature measurements are commonly done using thermocouples; Chromal-alumel thermocouples are often used for temperature up to 1100°C.

1.6.1.3.3 Applications

- Compositional analysis of materials
- Decomposition temperatures
- Rate of degradation
- Oxidative stability
- Thermal stabilities
- Effects of reactive atmospheres on materials
- Purity and thermal stability.
- Solid state reactions.
- Decomposition of organic and inorganic compounds.
- Determining composition of the mixture.
- Evaluation of gravimetric precipitates.
- Oxidative and reductive stability.
- Desolvation, sublimation, vaporizations, desorption, chemisorptions.

1.6.1.2 Differential thermal analysis (DTA)

Differential thermal analysis is carried out by heating the sample together with a reference standard under identical thermal conditions in the same oven and measuring the temperature difference between the sample and reference substance during the period of heating. This differential temperature is then plotted against time or against temperature. Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference. The key features of
a differential thermal analysis kit are as shown in Figure 1.7. Basic components of
DTA are listed below

1. Sample holder comprising thermocouples, sample containers and a ceramic or
metallic block.

2. Furnace.

3. Temperature programmer.

4. Recording system.

![Diagram of DTA cell]

Figure 1.7 Schematic illustration of a DTA cell

A temperature programmer is essential in order to obtain constant heating rates. The
recording system must have a low inertia to faithfully reproduce variations in the
experimental set up. The sample holder assembly consists of a thermocouple each for the sample and reference, surrounded by a block to ensure an even heat distribution. The sample is contained in a small crucible designed with an indentation on the base to ensure a snug fit over the thermocouple bead.

The rate of heat evolution may be high enough to saturate the response capability of the measuring system; it is better to dilute the test sample with inert material. For the measurement of phase transformation temperatures, it is advisable to ensure that the peak temperature does not vary with sample size.

The shape of a DTA peak does depend on sample weight and the heating rate used. Lowering the heating rate is roughly equivalent to reducing the sample weight; both lead to sharper peaks with improved resolution, although this is only useful if the signal to noise ratio is not compromised. The influence of heating rate on the peak shape and disposition can be used to advantage in the study of decomposition reactions, but for kinetic analysis it is important to minimize thermal gradients by reducing specimen size or heating rate.

1.6.1.2.1 Working principle

DTA involves heating a test sample and an inert reference under identical conditions, while recording any temperature difference between the sample and reference. Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference. This thermogram provides data on the chemical and physical transformations that have occurred, such as melting, sublimation, glass transitions, crystal transitions and crystallization [32]. Chemical identification of a material (qualitative interpretation) comparing and for thermal stability of materials. Such informations can be used to select material for certain endues application, predict product performance and improve product quality.
1.6.2 Powder X-Ray diffraction

X-ray diffraction (XRD) is a versatile, non destructive technique that reveals detailed information about the chemical composition, lattice parameters and crystallographic structure of natural and manufactured materials [19,33]. A crystal lattice is a regular three dimensional distribution (cubic, rhombic, etc.) of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by a distance d, which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations each with its own specific d-spacing. When a monochromatic X-ray beam with wavelength λ is projected onto a crystalline material at an angle θ, diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number n of wavelengths.

X-ray Diffraction (XRD) is a material characterization technique that can be useful for analyzing the lattice structure of a material. X-rays Diffraction is related to interplanar spacing’s in the crystalline powder according to a mathematical relation called “Bragg’s Law” [34]:

\[ n\lambda = 2dsin\theta \]

Where,  

n is an order of diffraction

λ is the wavelength of the X-rays

d is the interplanar spacing generating the diffraction and

θ is the diffraction angle

λ and d are measured in the same units, usually angstroms.

Based on the principle of X-ray diffraction, a wealth of structural, physical and chemical information about the material investigated can be obtained. A host of
application techniques for various material classes is available, each revealing its own specific details of the sample studied.

1.6.2.1 Fundamental Principles of X-ray Powder Diffraction (XRD)

Max Von Laue, in 1912, discovered that crystalline substances act as three dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg’s Law (nλ = 2d sinθ). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

1.6.2.2 Working Procedure

X-Ray diffractometers consist of three basic elements: an X-ray tube, a sample holder and an X-ray detector. X-rays are generated in a Cathode Ray Tube by
heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being Kα and Kβ. Kα consists in part of Kα1 and Kα2. Kα1 has a slightly shorter wavelength and twice the intensity as Kα2. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering by foils or crystal monochrometers is required to produce monochromatic X-rays needed for diffraction. Kα1 and Kα2 are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single crystal diffraction with CuKα radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The angles and intensities of diffractions are recorded electronically using a detector, electronics and specialized software [26]

1.6.2.3 Application of X-Ray diffraction

The most widespread use of x-ray powder diffraction is identification of crystalline compounds by their diffraction pattern. Listed below are some of the applications like identification of single phase materials, minerals, chemical compounds, ceramics or other engineered materials.

- Identification of multiple phases in microcrystalline mixtures (i.e., rocks)
- Determination of the crystal structure of identified materials
- Identification and structural analysis of clay minerals
- Recognition of amorphous materials in partially crystalline mixtures
- Crystallographic structural analysis and unit cell calculations for crystalline materials
- Quantitative determination of amounts of different phases in multi phase mixtures by peak ratio calculations
- Quantitative determination of phases by whole pattern refinement
- Determination of crystallite size from analysis of peak broadening
- Determination of crystallite shape from study of peak symmetry
- Study of thermal expansion in crystal structures using in situ heating stage equipment

1.6.3 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron sample interactions reveal information about the sample including external morphology (texture), chemical composition, crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques. Because of the high magnification of SEM instruments [33] ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample.
1.6.3.1 Fundamental Principles of Scanning Electron Microscopy

Accelerated electrons in SEM carry significant amounts of kinetic energy and this energy is dissipated as a variety of signals produced by electron sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-Rays), visible light (cathodoluminescence-CL) and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing surface morphology [35,36] and topography of samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-Ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus the characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

1.6.3.2 Working Principles

From Figure 1.8, the "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons. The stream is condensed by the first condenser lens (usually controlled by the "coarse probe current knob"). This lens is used to both form the beam and limit the amount of current in the beam. It works in conjunction with the condenser aperture to eliminate the high angle electrons from the beam. The beam is then constricted by the condenser aperture (usually not user selectable), eliminating some high angle electrons. The second
condenser lens forms the electrons into a thin, tight, coherent beam and is usually controlled by the "fine probe current knob". A user selectable objective aperture further eliminates high angle electrons from the beam. A set of coils then "scan" or "sweep" the beam in a grid fashion (like a television), dwelling on points for a period of time determined by the scan speed (usually in the microsecond range). The final lens “the Objective” focuses the scanning beam onto the part of the specimen desired. When the beam strikes the sample (and dwells for a few microseconds) interactions occur inside the sample and are detected with various instruments. Before the beam moves to its next dwell point these instruments count the number of interactions and display a pixel on a CRT whose intensity is determined by this number (the more reactions the brighter the pixel. This process is repeated until the grid scan is finished and then repeated, the entire pattern can be scanned 30 times per second.
Figure 1.8 Schematic diagram of scanning electron microscope
1.6.4 VIBRATING SAMPLE MAGNETOMETER (VSM)

1.6.4.1 Working Principle

A vibrating sample magnetometer (VSM) operates on Faraday's Law of Induction, which tells us that a changing magnetic field will produce an electric field. This electric field can be measured and can tell us information about the changing magnetic field. A VSM is used to measure the magnetic behavior of magnetic materials.

A sample is placed in a uniform magnetic field and magnetized. The sample is then physically vibrated sinusoidally, typically through the use of a piezoelectric material. Commercial systems use linear attenuators of some form and historically the development of these systems was done using modified audio speakers, though this approach was dropped due to the interference through the inphase magnetic noise produced, as the magnetic flux through a nearby pickup coil varies sinusoidally. The induced voltage in the pickup coil is proportional to the sample's magnetic moment, but does not depend on the strength of the applied magnetic field. In a typical setup, the induced voltage is measured through the use of a lock-in amplifier using the piezoelectric signal as its reference signal. By measuring the field of an external electromagnet it is possible to obtain the hysteresis curve of a material [19].

If a magnetic material is placed in a uniform magnetic field, created between the poles of an electromagnet and a dipole moment will be induced. If the sample vibrates with sinusoidal motion, a sinusoidal electrical signal can be induced in a suitably placed pick-up coils. The signal has the same frequency of vibration and its amplitude will be proportional to the magnetic moment, amplitude, and relative position with respect to the pick-up coils system. The basic instrument includes the electromechanical system and the electronic system including a personal computer, while the customer should select the electromagnet or superconducting coil system with the appropriate bipolar power supply (Figure 1.9).
1.6.4.2 Applications

Using a vibrating sample magnetometer, one can measure the DC magnetic moment as a function of temperature, magnetic field, angle and time. So, it allows performing susceptibility and magnetization studies. Some of the most common measurements done are hysteresis loops [37,38], susceptibility as a function of temperature (thermo magnetic analysis), magnetization curves as a function of angle (anisotropy) and magnetization as a function of time.

Figure 1.9 Vibrating sample magnetometer