

Preparation and characterization

3.1 Synthesis method

3.1.1 Solid state reaction

The most common method of preparing metal oxides and other solid materials is by the ceramic method which involves grinding powders oxides, carbonates, oxalates or other compounds containing the relevant metals and heating the mixture at a desired temperature. Several oxides, sulphides, phosphides etc. have been prepared by this technique. The most common method of preparing metal oxides and other solid materials is by the ceramic method. In the ceramic method very pure and fine grains constituents in oxide forms are taken. Then they are thoroughly and uniformly mixed. This mixture is sintered for prolonged time at specific temperature so as to facilitate solid-state chemical reaction among the oxides and the formation of chemical compound. Pre-sintering of the samples can be done at about 900°C and final sintering of the ferrite sample can be done at above 1200°C depending on the constituents.

3.1.2 Hydrothermal synthesis

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed "hydrothermal method". The term "hydrothermal" is of geologic origin. Geochemists and mineralogists have studied hydrothermal phase equilibria since the beginning of the 20th 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.

Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal.

Possible advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can also be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality crystals while maintaining good control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows.

3.1.3 Micro emulsions synthesis

Micro emulsions are clear, thermodynamically stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. The aqueous phase may contain salt(s) or other ingredients, and the "oil" may actually be a complex mixture of different hydrocarbons and olefins. In contrast to ordinary emulsions, micro emulsions form upon simple mixing of the components and do not require the high shear conditions generally used in the formation of ordinary emulsions. The three basic types of micro emulsions are direct (oil dispersed in water, o/w), reversed (water dispersed in oil, w/o) and bicontinuous.

In ternary systems such as micro emulsions, where two immiscible phases (water and 'oil') are present with a surfactant, the surfactant molecules may form a monolayer at the interface between the oil and water, with the hydrophobic tails of the surfactant molecules dissolved in the oil phase and the hydrophilic head groups in the aqueous phase

Much of the work done on these systems have been motivated by their possible use to mobilize petroleum trapped in porous sandstone for enhanced oil recovery. A fundamental reason for the uses of these systems is that a micro emulsion phase sometimes has an ultra low interfacial tension with a separate oil or aqueous phase, which may release or mobilize them from solid phases even in conditions of slow flow or low pressure gradients. Microemulsions also have industrial applications, one of them being the synthesis of polymers. Microemulsion polymerization is a complex heterogeneous process where transport of monomers, free radicals and other species (such as chain transfer agent, co-surfactant and inhibitors) between the aqueous and organic phases, takes place. Compared with other heterogeneous polymerization processes (suspension or emulsion) microemulsion polymerization is a more complicated system. Polymerization rate is controlled by monomer partitioning between the phases, particle nucleation, and adsorption and desorption of radicals. Particle stability is affected by the amount and type of surfactant and pH of dispersing medium. It is also used in the process of creating nano particles. The kinetics of microemulsion polymerization has much in common with emulsion polymerization kinetics, the most characteristic feature of which is the compartmentalization, where the radicals growing inside the particles are separated from each other, thus suppressing termination to a high extent and, as a consequence, providing high rates of polymerization.

3.1.4 Citrate precursor synthesis

In the citrate precursor technique, the individual cations in the stoichiometric ratio are reacted with the poly functional organic acid, citric acid under controlled pH conditions to obtain a precursor at an atomic level bending of the constituent elements in the required stoichiometric ratio is achieved during the reaction in the solution state to form the citrate complex.

This precursor on proper thermal decomposition at right temperatures indicated by thermal analysis data loses all the organic moiety to give rise to the final ternary oxide. It is important to note that the diffusion controlled solid state

reaction between constituent compounds involved in ceramic method and co-precipitation method is not present in the precursor method. The final reaction is the decomposition process and it depend on the decomposition temperature of the precursor. The citrate precursors decompose at temperature less than 700°C and hence it has been possible to prepare barium hexaferrite and series of rare earth garnet at these relatively low temperatures [18].

Therefore in principle, if one can prepare precursor complexes using organic completing materials other than citrates, which decompose at lower temperatures than citrate, It may be possible to further reduce the preparation temperature. Lowering of preparation temperature will be extremely useful from the point of view of producing nano particles of the hexaferrite system.

3.1.5 Spray pyrolysis technique

The ferrite thin films can be prepared by spray pyrolysis technique using a citrate complex precursor. The preparation essentially consists of two stages, namely, the preparation of the citrate complex precursor and spray deposition of the "films using the precursor solution. At first aqueous solutions of stoichiometric amounts of nitrates of Ba and Fe were prepared. These solutions were reacted with 1:1 molar ratio of citric acid under controlled pH conditions. The reaction takes place in a slightly alkaline solution. Ammonia solution was added drop by drop to the reaction mixture with constant stirring until the desired pH is obtained. This solution was then refluxed for 6 h under controlled pH condition for completion of the reaction to form the citrate complex precursor. The preparation of the citrate complex is a crucial step in obtaining homogeneous single-phase films. Once the right complex was formed, ternary oxide phase could be obtained at relatively low temperatures by thermal decomposition of the complex at appropriate temperatures. Diluted precursor solution was sprayed onto the cleaned quartz plates previously heated to 350-400°C, using a sprayer and dry nitrogen as carrier gas. A highly adherent and homogeneous film of barium ferrite was formed by pyrolytic

decomposition of sprayed precursor. For crystallization the films were annealed in a tubular furnace at a temperature $\pm 70^{\circ}\text{C}$ for about 3 h in air.

3.1.6. Co-precipitation technique

In chemistry, coprecipitation (CPT) or co-precipitation is the carrying down by a precipitate of substances normally soluble under the conditions employed. Analogously, in medicine, coprecipitation is specifically the precipitation of an unbound "antigen along with an antigen-antibody complex". Coprecipitation 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, coprecipitation is a problem because undesired impurities often coprecipitate 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 redissolving the sample and precipitating it again.

On the other hand, in the analysis of trace elements, as is often the case in radiochemistry, coprecipitation is often the only way of separating an element. Since the trace element is too dilute (sometimes less than parts per trillion) to precipitate by conventional means, it is typically coprecipitated 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 coprecipitating it with caesium salts such as caesium 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. 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 mainly used as a method of magnetic nano particle synthesis.

3.1.7 Sol-gel synthesis

In materials science, the sol-gel process is a method for producing solid materials from small molecules. The method is used for the fabrication of metal oxides, especially the oxides of silicon and titanium. The process involves conversion of monomers into a colloidal solution (sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers.

The sol-gel process may be described as: Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid. A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid, A gel consists of a three dimensional continuous network, which encloses a liquid phase, in a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. Generally, the sol particles may interact by van der Waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. The gelation process may be reversible if other interactions are involved.

In this chemical procedure, the 'sol' (or solution) gradually evolves towards the formation of a gel-like diphasic system containing both a liquid phase and 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 so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. 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 favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature.

The precursor sol can be either 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., to obtain monolithic ceramics, glasses, fibers, membranes, aerogels), 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 elements, can be introduced in the sol and end up uniformly dispersed in the 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. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio) sensors, medicine (e.g., controlled drug release), reactive material and separation (e.g., chromatography) technology.

The interest in sol-gel processing can be traced back in the mid-1800s with the observation that the hydrolysis of tetraethyl or thosilicate (TEOS) under acidic conditions led to the formation of SiO_2 in the form of fibers and monoliths. Sol-gel research grew to be so important that in the 1990s more than 35,000 papers were published worldwide on the process.

The sol-gel process is a wet-chemical technique used for the fabrication of both glassy and ceramic materials. In this process, the sol (or solution) evolves gradually towards the formation of a gel-like network containing both a liquid phase and a solid phase. Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a colloid. The basic structure or morphology of the solid phase can range anywhere from discrete colloidal particles to continuous chain-like polymer networks.

The term colloid is used primarily to describe a broad range of solid-liquid (and/or liquid-liquid) mixtures, all of which contain distinct solid (and/or liquid) particles which are dispersed to various degrees in a liquid medium. The term is specific to the size of the individual particles, which are larger than atomic dimensions but small enough to exhibit Brownian motion. If the particles are large enough, then their dynamic behavior in any given period of time in suspension would be governed by forces of gravity and sedimentation. But if they are small enough to be colloids, then their irregular motion in suspension can be attributed to the collective bombardment of a myriad of thermally agitated molecules in the liquid suspending medium, as described originally by Albert Einstein in his dissertation. Einstein concluded that this erratic behavior could adequately be described using the theory of Brownian motion, with sedimentation being a possible long term result. This critical size range (or particle diameter) typically ranges from tens of angstroms (10–10 m) to a few micrometres (10–6 m).

Under certain chemical conditions (typically in base-catalyzed sols), the particles may grow to sufficient size to become colloids, which are affected both by sedimentation and forces of gravity. Stabilized suspensions of such sub-micrometre spherical particles may eventually result in their self-assembly

yielding highly ordered microstructures reminiscent of the prototype colloidal crystal: precious opal. Under certain chemical conditions (typically in acid-catalyzed sols), the interparticle forces have sufficient strength to cause considerable aggregation and/or flocculation prior to their growth. The formation of a more open continuous network of low density polymers exhibits certain advantages with regard to physical properties in the formation of high performance glass and glass/ceramic components in 2 and 3 dimensions. In either case (discrete particles or continuous polymer network) the sol evolves then towards the formation of an inorganic network containing a liquid phase (gel). Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. In both cases (discrete particles or continuous polymer network), the drying process serves to remove the liquid phase from the gel, yielding a micro-porous amorphous glass or micro-crystalline ceramic. Subsequent thermal treatment (firing) may be performed in order to favor further polycondensation and enhance mechanical properties. With the viscosity of a sol adjusted into a proper range, both optical quality glass fiber and refractory ceramic fiber can be drawn which are used for fiber optic sensors and thermal insulation, respectively. In addition, uniform ceramic powders of a wide range of chemical composition can be formed by precipitation.

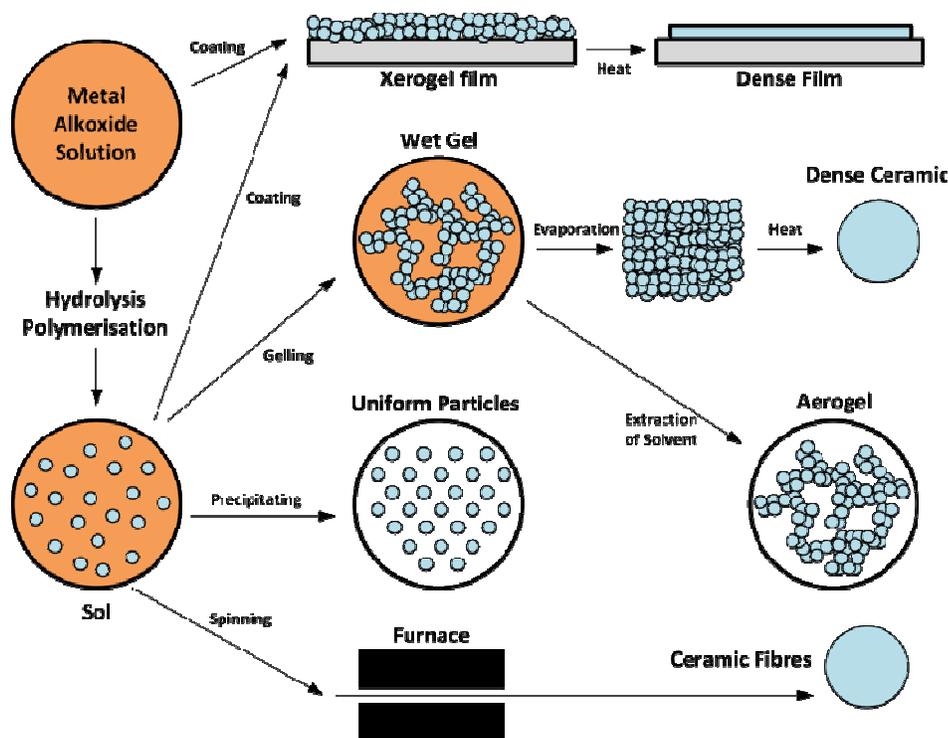


Fig. 3.1: Schematic representation of the different stages and routes of the sol-gel technology.

In the processing of fine ceramics, the irregular particle sizes and shapes in a typical powder often lead to non-uniform packing morphologies that result in packing density variations in the powder compact. Uncontrolled flocculation of powders due to attractive Vander Walls forces can also give rise to microstructural in homogeneities.

Differential stresses that develop as a result of non-uniform drying shrinkage are directly related to the rate at which the solvent can be removed, and thus highly dependent upon the distribution of porosity. Such stresses have been associated with a plastic-to-brittle transition in consolidated bodies, and can yield to crack propagation in the unfired body if not relieved.

In addition, any fluctuations in packing density in the compact as it is prepared for the kiln are often amplified during the sintering process, yielding inhomogeneous densification. Some pores and other structural defects associated with density variations have been shown to play a detrimental role in the sintering process by growing and thus limiting end-point densities. Differential stresses arising from inhomogeneous densification have also been

shown to result in the propagation of internal cracks, thus becoming the strength-controlling flaws.

It would therefore appear desirable to process a material in such a way that it is physically uniform with regard to the distribution of components and porosity, rather than using particle size distributions which will maximize the green density. The containment of a uniformly dispersed assembly of strongly interacting particles in suspension requires total control over particle-particle interactions. Monodisperse colloids provide this potential.

Monodisperse powders of colloidal silica, for example, may therefore be stabilized sufficiently to ensure a high degree of order in the colloidal crystal or polycrystalline colloidal solid which results from aggregation. The degree of order appears to be limited by the time and space allowed for longer-range correlations to be established. Such defective polycrystalline structures would appear to be the basic elements of nano scale materials science, and, therefore, provide the first step in developing a more rigorous understanding of the mechanisms involved in micro structural evolution in inorganic systems such as sintered ceramic nano materials.

3.2 Characterization techniques

3.2.1 X-ray diffraction

A) Crystallography:

X-ray crystallography is a tool used for determining the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information.

Since many materials can form crystals such as salts, metals, minerals, semiconductors, as well as various inorganic, organic and biological molecules.

X-ray crystallography has been fundamental in the development of many scientific fields. In its first decades of use, this method determined the size of atoms, the lengths and types of chemical bonds, and the atomic-scale differences among various materials, especially minerals and alloys. The method also revealed the structure and function of many biological molecules, including vitamins, drugs, proteins and nucleic acids such as DNA. X-ray crystallography is still the chief method for characterizing the atomic structure of new materials and in discerning materials that appear similar by other experiments. X-ray crystal structures can also account for unusual electronic or elastic properties of a material, shed light on chemical interactions and processes, or serve as the basis for designing pharmaceuticals against diseases.

In an X-ray diffraction measurement, a crystal is mounted on a goniometer and gradually rotated while being bombarded with X-rays, producing a diffraction pattern of regularly spaced spots known as reflections. The two-dimensional images taken at different rotations are converted into a three-dimensional model of the density of electrons within the crystal using the mathematical method of Fourier transforms, combined with chemical data known for the sample. Poor resolution (fuzziness) or even errors may result if the crystals are too small, or not uniform enough in their internal makeup.

X-ray crystallography is related to several other methods for determining atomic structures. Similar diffraction patterns can be produced by scattering electrons or neutrons, which are likewise interpreted as a Fourier transform. If single crystals of sufficient size cannot be obtained, various other X-ray methods can be applied to obtain less detailed information; such methods include fiber diffraction, powder diffraction and small-angle X-ray scattering (SAXS). If the material under investigation is only available in the form of nano crystalline powders or suffers from poor crystallinity, the methods of electron crystallography can be applied for determining the atomic structure.

For all above mentioned X-ray diffraction methods, the scattering is elastic; the scattered X-rays have the same wavelength as the incoming X-ray. By contrast, inelastic X-ray scattering methods are useful in studying excitations of the sample, rather than the distribution of its atoms

B) Principle of technique

X-rays are electromagnetic radiation with wavelengths in the range 0.5-2.5 Å. Since this is of the same order of magnitude as the interatomic distances in solids, X-rays are frequently used to study the internal (crystalline) structure of materials. An X-ray beam impinging on a crystal will be scattered in all directions by the atoms of the crystal. In some directions, an increased intensity is observed due to the constructive interference of the scattered waves.

The conditions for constructive interference are easily derived from the simple geometrical picture for the scattering of an X-ray beam by planes of atoms in a crystal, shown in Fig. 3.2. Imagine the X-ray beam of wavelength λ , incident on the crystal at an angle θ with respect to equidistant hkl lattice-planes, with interplanar distance d_{hkl} . Constructive interference will be observed for X-rays that are reflected from the lattice planes at the specular angle, if the path length difference between X-rays scattered from different hkl -planes is an integer times the wavelength. This condition is summarized in the Bragg law:

$$n\lambda = 2d_{hkl} \sin(\theta) \quad (3.1)$$

where

d is the spacing between diffracting planes, θ is the incident angle, n is any integer, and λ is the wavelength of the beam

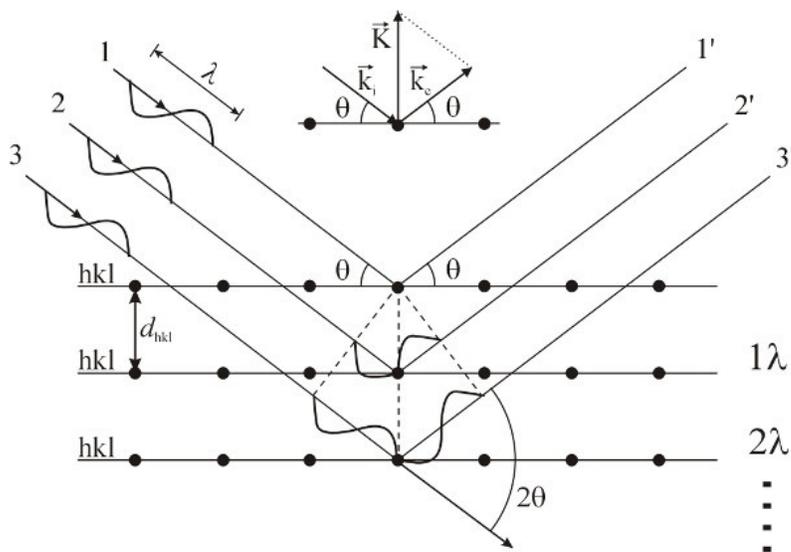


Fig. 3.2. Scheme of X-ray diffraction pattern

From Fig. 3.2, it is clear that diffraction from a set of planes will only occur if the normal to these planes is bisecting the angle between the incident and the scattered beam. Alternatively, one defines a scattering vector $\mathbf{K} = \mathbf{k}_e - \mathbf{k}_i$ as the difference between the wave vector \mathbf{k}_e of the scattered wave, and the wave vector \mathbf{k}_i of the incident X-ray, as shown in the inset of Fig. 3.2. Diffraction (i.e. constructive interference of the scattered X-rays) will occur if the Bragg condition (eq. 3.1) is fulfilled *and* of the scattering vector \mathbf{K} is parallel to the normal of the hkl-planes. By scanning crystalline samples in search of interference peaks, one can obtain information about the lattice parameters, strain, texture, etc.

C) Principle of analysis:

A whole gamma of X-ray diffraction measurements can be performed with an X-ray setup. Each of these measurements reveals a different property of the specimen under investigation.

i) θ -2 θ measurement

A θ -2 θ scan allows to determine the interplanar distance d . This can be achieved in several geometries, corresponding to the orientation of the set(s) of planes. A *symmetric θ -2 θ scan* is used to determine the interplanar distance of the planes parallel to the sample surface [see Fig. 3.3(a)]. In this type of scan, the angle θ of the incoming beam with respect to the sample surface is varied, while simultaneously keeping the detector at an angle of 2θ with respect to the incoming beam. The angle θ at which a diffraction peak is observed, can then be inserted into (eq. 3.1) to give the interplanar distance.

In order to determine the interplanar distance of a set of planes that are tilted by an angle with respect to the sample surface, an *asymmetric θ -2 θ scan* can be performed [see Fig. Eq. 3.3(b)]. As in the case of a symmetric scan, the detector is placed at an angle of 2θ with respect to the incoming beam. The incoming beam, however, makes an angle of Ψ with respect to the sample surface. Note that θ - Ψ is a fixed offset when scanning through θ values.

An alternative to the asymmetric scan method is the *skew-symmetric measuring geometry* [Fig. 3.3(c)]. As in the case of the symmetric scan, the incoming beam forms an angle Ψ with respect to the sample surface, while the

detector is put at 2θ . The difference is that the sample is tilted over a fixed angle $\chi = \Psi$ around the axis that is parallel to the sample surface and the plane of the incoming and outgoing beam.

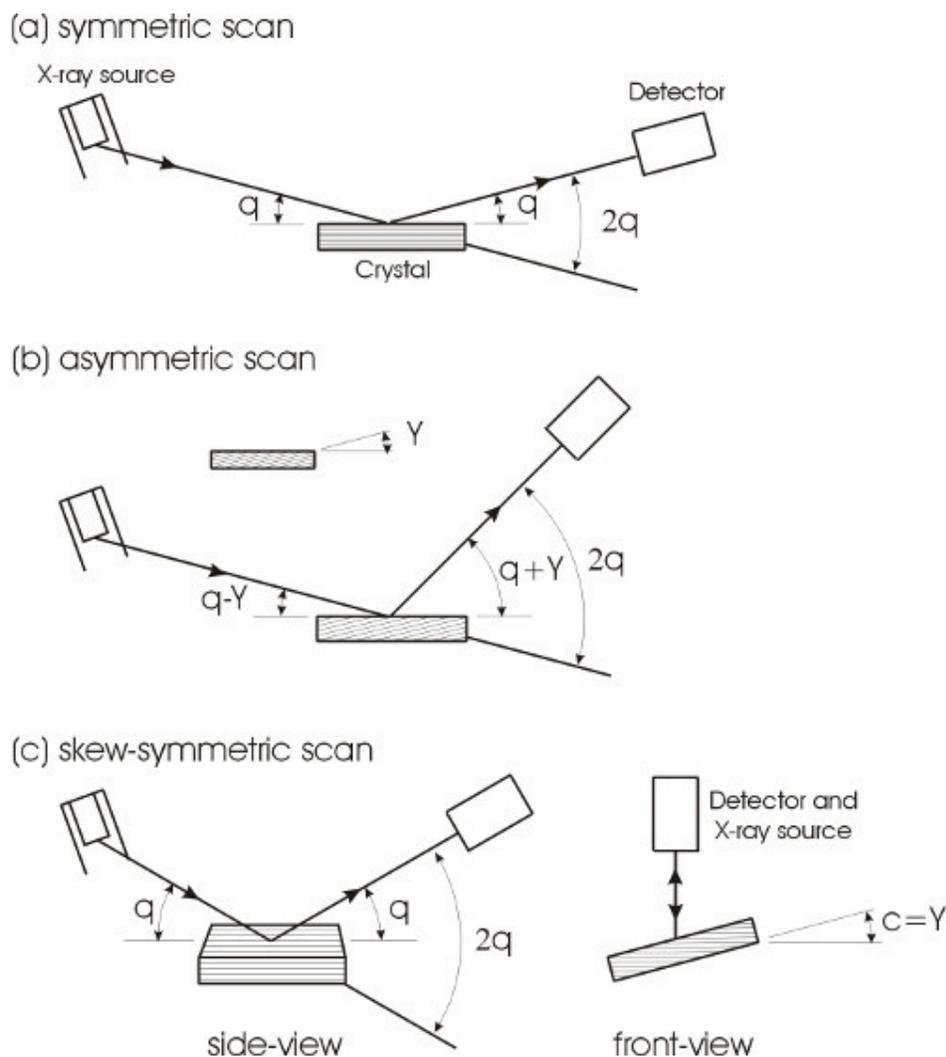


Fig. 3.3: Steps of asymmetric θ - 2θ scan

The determination of the interplanar distance with a θ - 2θ measurement does not only allow to identify the phases present in the specimen. In thin film studies in particular, this type of scan is used to determine stress and strain epitaxial or implatend layers. Stress and/or strain result in the deviation of the interplanar distances within a crystal from the situation for a completely relaxed thin film. This stress can be induced by the presence of implanted impurities,

the match of an epitaxial thin film with a substrate of slightly different lattice parameter, etc. Not only the peak position in a θ - 2θ measurement contains valuable information on the specimen under investigation, the width or full width at half maximum of the diffraction peak contains information on the as well. In case of a perfect crystal, the width of the interference peak (as a function of θ) is inversely proportional to the thickness of the crystalline layer. The full width at half maximum (FWHM) of the peak is given by the Scherer formula:

$$\text{FWHM} = 0.9 \lambda / t \cos(\theta_B) \quad (3.2)$$

where the FWHM is expressed in radians, λ is the wavelength of the X-rays, t is the thickness of the layer and θ_B the Bragg angle of the reflection. A non-perfect crystal can be divided into different crystalline domains (crystallites) that all have a slightly different orientation. This will be the case when long-range stacking faults and other extended defects are present in the sample. The thickness t in the Scherer formula will, in that case, be related to the crystallite particle size.

ii) **Reflectivity measurements**

A special type of symmetric θ - 2θ scan is the reflectivity measurement. In a normal θ - 2θ measurement the distance between crystallographic planes, which is of the order of 0.5-5Å, is measured. In a reflectivity measurement one measures thickness of a thin film which is of the order of tens of nanometer. The principle of the measurement is the same as for the θ - 2θ scan described above, apart that the measurement is now performed at much lower reflection angles, due to the larger thickness involved. Scattering of the X-rays now does not occur at the atomic planes, but at the interface between the layers in the film due to the difference in electron density between adjacent layers. This type of measurement does not only allow determining the distance between adjacent layers, it also enables the determination of the roughness of the films.

iii) **Rocking curve measurement**

Another type of scan that is closely related to a θ - 2θ scan is a rocking curve (RC) scan. From a rocking curve measurement it is possible to determine

the mean spread in orientation of the different crystalline domains of a non perfect crystal. If the crystalline particles are very small, it is also possible to determine their size by measuring a RC scan. In order to obtain a rocking curve scan, one first performs a θ - 2θ scan. Note that this can be carried out in symmetric, asymmetric or skew-symmetric geometry. In the next step, the angle θ , and the detector position 2θ , is fixed at the Bragg angle of the corresponding reflection. A rocking curve scan is then acquired by varying the orientation of the sample by an angle $\Delta\omega$ around its equilibrium position, while keeping the detector position fixed. The situation for a skew-symmetric geometry is schematically depicted in Fig. 3.4. For $\Delta\omega = 0$ the sample and detector are at the exact positions for constructive interference, so a peak will be observed. The width of this peak W will be determined by several factors. The first and most interesting contribution comes from the spread in crystalline orientation between the different domains. The corresponding rocking curve peak will have a full width at half-maximum (FWHM) W , where W_{tt} is the mean spread in orientation for the set of planes belonging to the chosen Bragg reflection. The second factor is based on the lateral size of the crystalline domains. This is similar to the Scherrer broadening described above for θ - 2θ scans, but depends here on the lateral size of the crystallites instead of their thickness. It can be calculated that this leads to a broadening with FWHM W_{inc} :

$$W_{inc} = \lambda / 2b \sin(\theta_B) \quad (3.3)$$

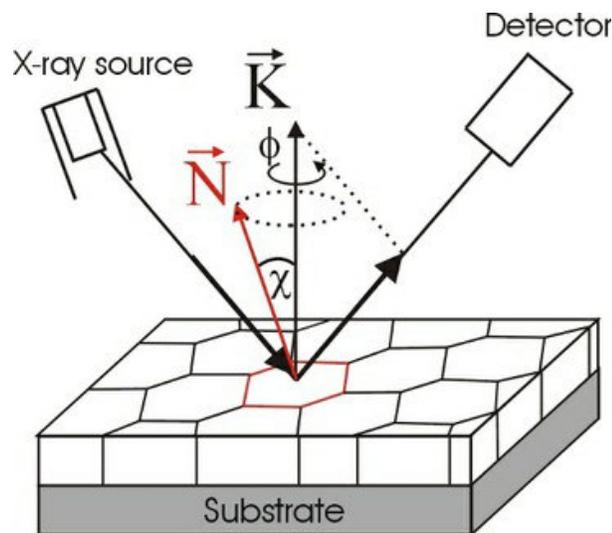
where b is the mean width of a crystalline particle. For example, for $\theta_B = 30^\circ$, $b = 500 \text{ \AA}$ and $\lambda = 1.54 \text{ \AA}$, the rocking curve will have a width $W_{inc} = 0.2^\circ$. A last contribution comes from the detector resolution W_d . Our D8 Discover from Bruker, has an angular resolution of $< 0.005^\circ$ when the monochromator is mounted. Since the other two contributions are usually far larger than the detector resolution, this factor can often be neglected. The total width of the rocking curve peak then depends on a combination of these three factors, and is given by the convolution.

iv) *Pole figure measurements*

In a θ - 2θ scan only the planes that are parallel to the surface will be detected. The number of peaks in an experimental θ - 2θ XRD spectrum and

their relative intensity give an indication of the texture, i.e. the statistical distribution of grain orientations, of the film. However, the complete texture of a thin film is accessible only with pole figure measurements.

In this kind of measurement, a certain set of hkl -planes is selected. This fixes d_{hkl} in (eq. 3.1), which is achieved by fixing the detector (2θ) and incident beam (θ) angle. Hence, the scattering vector \mathbf{K} is fixed in space, as can be seen from Fig. 3.4. Diffraction will only occur if the normal to the selected hkl -planes \mathbf{N} is parallel to the diffraction vector. Therefore, the sample has to be tilted and rotated in space. The situation is shown for the middle grain in Fig. 3.4



(a)

Fig. 3.4

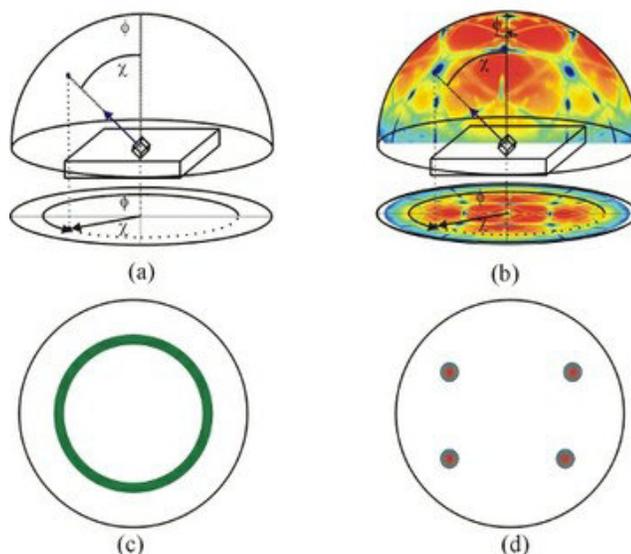


Fig. 3.5

$$W^2 = W_{tt}^2 + W_{inc}^2 + W_d^2$$

On the same figure, the tilt χ and the rotation angle Φ are defined. Pole figures can be interpreted by considering the intersections of the normal to the selected hkl-planes with an imaginary hemisphere, situated above the sample surface (see Fig. 3.5). The projection of this hemisphere on a planar surface results in a pole figure, for which the intensity in each point is proportional to the number of grains in the film that have their normal to the selected hkl-planes pointing to the point with coordinates (χ, Φ) on the hemisphere. For a random orientation of the grains in the thin film, the pole figure will be featureless. No preferred orientation for the normal to the hkl-planes is observed. *Fiber texture* can be identified by the occurrence of circles centered around the origin of the pole figure (Fig. 3.5 (c)). For an epitaxial thin film, only one grain orientation will be present in the film and the pole figure is characterized by a small, discrete number of spots (Fig. 3.5 (d)). In the case of axiotaxy, the pole figure shows a pattern of symmetrical lines (Fig. 3.5 (b)).

v) Contributions to chemistry and material science

X-ray crystallography has led to a better understanding of chemical bonds and non-covalent interactions. The initial studies revealed the typical radii of atoms, and confirmed many theoretical models of chemical bonding,

such as the tetrahedral bonding of carbon in the diamond structure, the octahedral bonding of metals observed in ammonium hexachloroplatinate (IV), and the resonance observed in the planar carbonate group and in aromatic molecules. Kathleen Lonsdale's 1928 structure of hexamethyl benzene established the hexagonal symmetry of benzene and showed a clear difference in bond length between the aliphatic C–C bonds and aromatic C–C bonds; this finding led to the idea of resonance between chemical bonds, which had profound consequences for the development of chemistry. Her conclusions were anticipated by William Henry Bragg, who published models of naphthalene and anthracene in 1921 based on other molecules, an early form of molecular replacement.

Also in the 1920s, Victor Moritz Goldschmidt and later Linus Pauling developed rules for eliminating chemically unlikely structures and for determining the relative sizes of atoms. These rules led to the structure of brookite (1928) and an understanding of the relative stability of the rutile, brookite and anatase forms of titanium dioxide.

The distance between two bonded atoms is a sensitive measure of the bond strength and its bond order; thus, X-ray crystallographic studies have led to the discovery of even more exotic types of bonding in inorganic chemistry, such as metal-metal double bonds, metal-metal quadruple bonds, and three-center, two-electron bonds. X-ray crystallography or, strictly speaking, an inelastic Compton scattering experiment has also provided evidence for the partly covalent character of hydrogen bonds. In the field of organometallic chemistry, the X-ray structure of ferrocene initiated scientific studies of sandwich compounds, while that of Zeise's salt stimulated research into "back bonding" and metal-pi complexes. Finally, X-ray crystallography had a pioneering role in the development of super a molecular chemistry, particularly in clarifying the structures of the crown ethers and the principles of host-guest chemistry.

In material sciences, many complicated inorganic and organ metallic systems have been analyzed using single-crystal methods, such as fullerenes, metalloporphyrins, and other complicated compounds. Single-crystal

diffraction is also used in the pharmaceutical industry, due to recent problems with polymorphs. The major factors affecting the quality of single-crystal structures are the crystal's size and regularity; recrystallization is a commonly used technique to improve these factors in small-molecule crystals. The Cambridge Structural Database contains over 500,000 structures; over 99% of these structures were determined by X-ray diffraction.

3.2.2 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is a well-known technique for imaging solid materials at atomic resolution. Structural information can be acquired both by (high resolution) imaging as well as by electron diffraction. Additional detectors allow for elemental and chemical analysis down to this sub-nanometer scale.

Basic principles

The design of a transmission electron microscope (TEM) is analogous to that of an optical microscope. In a TEM high-energy (>100 kV) electrons are used instead of photons and electromagnetic lenses instead of glass lenses. The electron beam passes an electron-transparent sample and a magnified image is formed using a set of lenses. This image is projected onto a fluorescent screen or a CCD camera. Whereas the use of visible light limits the lateral resolution in an optical microscope to a few tenths of a micrometer, the much smaller wavelength of electrons allows for a resolution of 0.2 nm in a TEM.

Imaging

Image contrast is obtained by interaction of the electron beam with the sample. Several contrast effects play a role. In the resulting TEM image denser areas and areas containing heavier elements appear darker due to scattering of the electrons in the sample. In addition, scattering from crystal planes introduces diffraction contrast. This contrast depends on the orientation of a crystalline area in the sample with respect to the electron beam. As a result, in a TEM image of a sample consisting of randomly oriented crystals each crystal will have its own grey-level. In this way one can distinguish between different

materials, as well as image individual crystals and crystal defects. Because of the high resolution of the TEM, atomic arrangements in crystalline structures can be imaged in large detail.

Electron Diffraction

By adjusting the magnetic lenses such that the back focal plane of the lens rather than the imaging plane is placed on the imaging apparatus a diffraction pattern can be generated. For thin crystalline samples, this produces an image that consists of a pattern of dots in the case of a single crystal, or a series of rings in the case of a polycrystalline or amorphous solid material. For the single crystal case the diffraction pattern is dependent upon the orientation of the specimen and the structure of the sample illuminated by the electron beam. This image provides the investigator with information about the space group symmetries in the crystal and the crystal's orientation to the beam path. This is typically done without utilising any information but the position at which the diffraction spots appear and the observed image symmetries.

Diffraction patterns can have a large dynamic range, and for crystalline samples, may have intensities greater than those recordable by CCD. As such, TEMs may still be equipped with film cartridges for the purpose of obtaining these images, as the film is a single use detector.

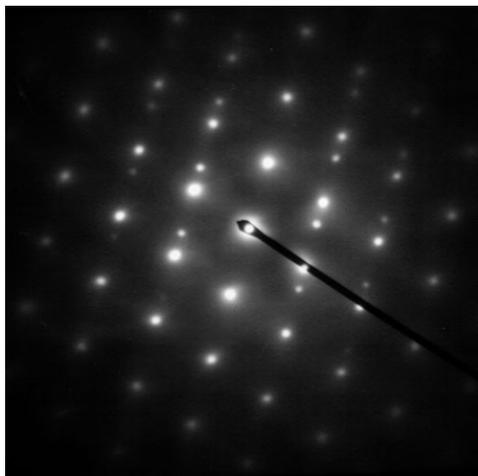


Fig. 3.6 (a): Crystalline diffraction pattern from a twinned grain of FCC Austenitic steel

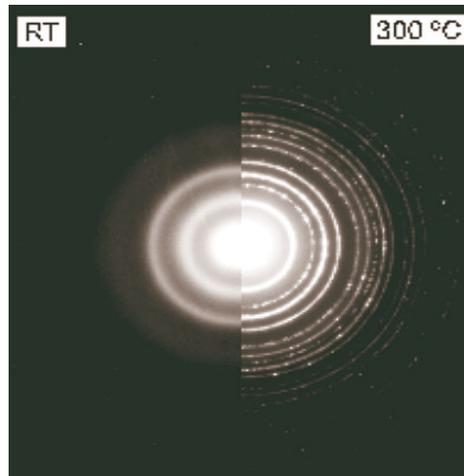


Fig. 3.6 (b): Electron diffraction patterns of an as-deposited (room temperature) and an annealed (300 °C) Al-Ge film. The left part shows a set of a few, broad rings, characteristic of an amorphous film. The right part shows a large number of sharp rings. The diameters of these rings are characteristic for the crystal structure present. In this case a mixture of crystalline Al and crystalline Ge.

In case of a crystalline material, electron diffraction will only occur at specific angles, which are characteristic for the crystal structure present. As a result, a diffraction pattern of the irradiated area is created that can be projected onto the CCD camera. In this way, electron diffraction can provide crystallographic information from thin films, bulk materials as well as from nanometer sized particles (figure 3.6).

Chemical analysis

As a result of the interaction of the electron beam with the specimen, some energy is transferred from the electrons to the sample. The excitation and de-excitation of atoms and molecules in the sample allow (local) chemical analysis. This analysis can either be performed using the broad beam used for normal imaging, or by focusing the beam size down to 0.2 nm. The combination of Scanning TEM (STEM), a mode in which this narrow beam scans a selected area of the specimen, with chemical analysis techniques such

as Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive X-Ray analysis (EDX) allows for mapping of the lateral distribution of elements with high spatial resolution.

3.2.3 Scanning electron microscope (SEM)

A scanning electron microscope is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

The types of signals produced by the SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathode), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown to the right. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal goldimmuno-labels of 5 or 10 nm diameter which would

otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

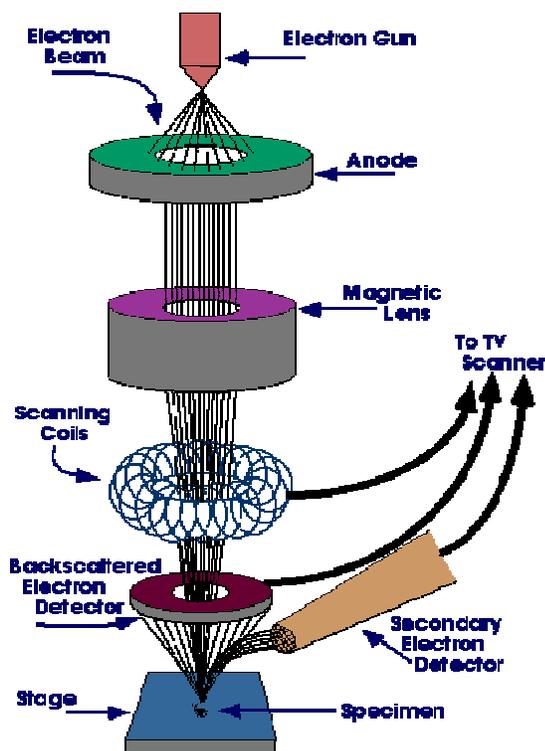


Fig. 3.7: Schematic diagram of scanning electron microscope.

The electron beam comes from a filament, made of various types of materials. The most common is the Tungsten hairpin gun. This filament is a loop of tungsten which functions as the cathode. A voltage is applied to the loop, causing it to heat up. The anode, which is positive with respect to the filament, forms powerful attractive forces for electrons. This causes electrons to accelerate toward the anode. Some accelerate right by the anode and on down the column, to the sample. Other examples of filaments are Lanthanum hexaboride filaments and field emission guns.

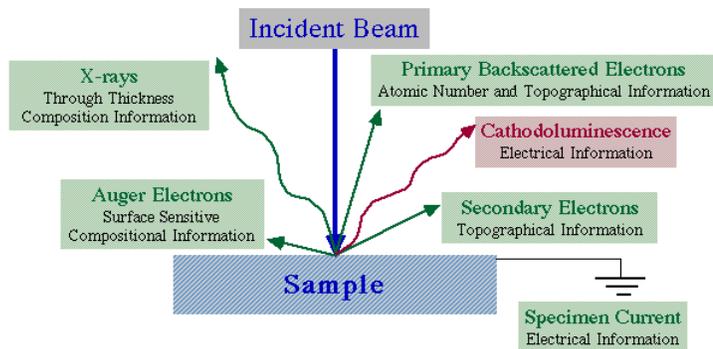


Fig 3.8:Electron specimen interaction.

The SEM uses electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by heating of a metallic filament. The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses which focus and direct the beam down towards the sample. Once it hits the sample, other electrons (backscattered or secondary) are ejected from the sample. Detectors collect the secondary or backscattered electrons, and convert them to a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image.

3.2.4 Infrared Spectroscopy (IR)

Infrared spectroscopy is the method of choice of qualitative analysis of organic material and it has wide application to inorganic substances as well. The infrared spectrum of a material has aptitude for the fingerprint, a unique property of that material and of its physical state. The spectrum is unique because it reflects the vibration between atoms within the molecule, and even slight changes in geometry or bond strength between atoms cause noticeable shift in the infrared absorption pattern.

When a molecule interacts with the radiation of the proper frequency, it absorbs energy and molecule is set into vibration. By measuring the transmitted energy as a function of radiation frequency, we can determine which frequency

has been absorbed by the sample. The resulting plots of energy versus frequency are the infrared spectrum of the sample.

The infrared spectra of all the samples of the present series were recorded at room temperature in the range $300 - 800\text{cm}^{-1}$ on a Perkin Elemer spectrometer (Model 783). To study the IR spectra of all the samples, about one gram of fine powder of each sample was mixed with KBr in the ratio 1:250 by weight to ensure uniform distribution in the KBr pellet. The mixed powder was then pressed in a cylindrical die to obtain clean disc of approximately 1 mm thickness. The IR spectra were used to locate the band position. The IR spectra were used to determine bond length R_A and R_B , in a cubic crystal for tetrahedral (A) and octahedral [B] site using formula given by Gorter [1]. Using the analysis of Waldron [2], the force constant K_0 and K_t were calculated.

3.2.5 Vibrating sample magnetometer (VSM)

A vibrating sample magnetometer or VSM is a scientific instrument that measures magnetic properties invented in 1955 by Simon Foner at Lincoln Laboratory MIT. The paper about his work was published shortly afterward in 1959 [3]. A sample is placed inside a uniform magnetic field to magnetize the sample. The sample is then physically vibrated sinusoidally, typically through the use of a piezoelectric material. Commercial systems use linear actuators 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 in-phase 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 in the field of an external electromagnet, it is possible to obtain the hysteresis curve of a material.

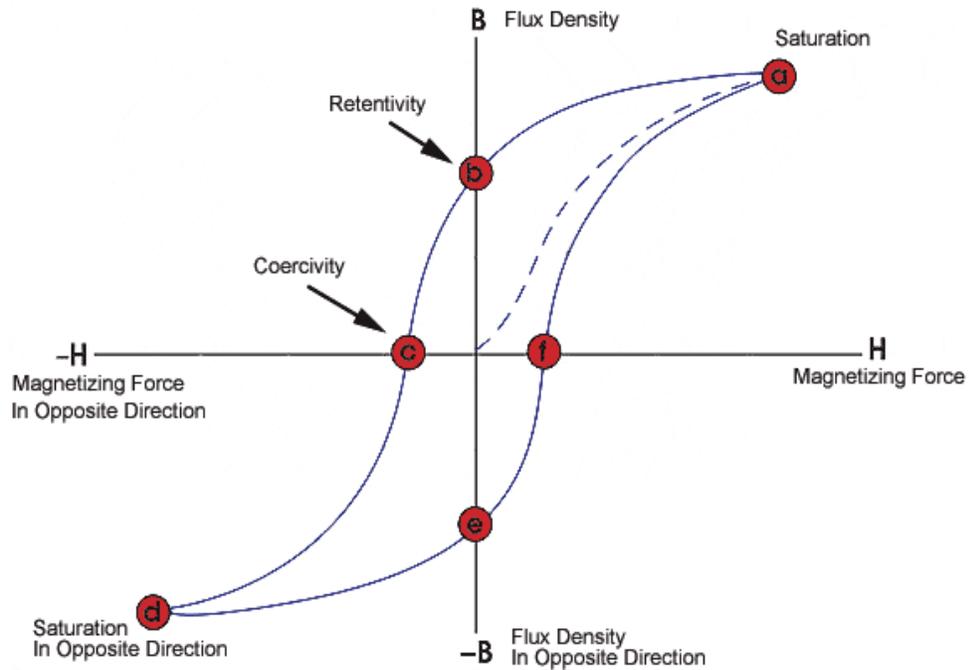


Fig. 3.9: A typical hysteresis curve of a spinel ferrite.

A typical hysteresis curve of a spinel ferrite is also shown in Fig. 3.9. 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 or M-H loop. From the hysteresis loop, a number of primary magnetic properties of a material can be determined such as magnetization (M_s), coercivity (H_C), remanence magnetization (M_r) etc.

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- [1] E.W. Gorter, Philips Res. Rep. 9 (1954) 295.
- [2] R.D. Waldron, Phys. Rev. 99 (1955) 1727.
- [3] S. Foner, "Versatile and Sensitive Vibrating-Sample Magnetometer".Rev. Sci. Instrum 30 (7) (1959) 548.