CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 Introduction

Different techniques are used by scientists and researchers for the production and characterization of nanophase materials.\textsuperscript{1-3} In the present study, simple techniques were used for the synthesis and characterization of the samples. The methods of preparation of the nanoparticles for the present study and the experimental techniques used for their characterization are given in this chapter.

2.2 Chemical Method

Chemical methods are found to be simple for the synthesis of nanoparticles and have the advantage of improved compositional homogeneity since the reactant constituents are mixed at a molecular level.\textsuperscript{4,5} Precipitation from aqueous solution is the most commonly used method for preparing nanoparticles. There are a number of reports dealing with the preparation of nanoparticles.\textsuperscript{2,6-10} The samples used in the present study were prepared by (1) controlled precipitation technique\textsuperscript{11,12} (without the use of stabilizers) (2) the thermolysis of polymer matrix based precursor solution starting from the appropriate chemicals.\textsuperscript{10} The detailed procedure used for the preparation of nanoparticles in the present work is given in chapter 3 of this thesis.

2.3 Experimental Characterization

2.3.1 Transmission Electron Microscopy (TEM) Studies

TEM observation offers a unique technique for imaging submicrostructure of materials. TEM imaging of samples is the most convenient and direct method
to see and analyze the structure of nanoparticles. This technique primarily consists of (i) regular TEM (plane view) and (ii) high resolution TEM (HRTEM). In the case of plane view TEM, the observation can be utilized to provide (1) Morphology and size distribution of grains (2) observation of porosity (3) Distribution of ceramic phases, including carbides, oxides, etc. (4) Phase identification by means of selected area electron diffraction (SAED) (5) Distribution of elements by means of energy dispersive spectrometry (EDS). HRTEM distinguishes itself from the conventional TEM in its ability to produce high resolution microstructure images on the atomic scale. Surface defects which are common in nanoparticles can be imaged directly using HRTEM.

Images in TEM are usually characterized by a contrast called diffraction contrast which is produced due to a local distortion in the orientation of the crystal, so that the diffracted intensity of the incident electron beam is perturbed, leading to contrast observed in bright-field image. The nanocrystals oriented with their low-index zone-axis parallel or nearly parallel to the incident beam direction usually exhibit dark contrast in the bright field image, that is formed by selecting the central transmitted beam. Thus it would be of great interest in the case of nanoparticles to characterize it by TEM imaging to identify whether it belongs to nanometer size range. TEM imaging and the corresponding SAED patterns were taken for the samples in the present study to find the size, structure, morphology and the phase identification of the nanoparticles.

In the present study TEM imaging of the samples was carried out using Philips CM-200-Analytical Transmission Election Microscope working at 120 kV. The powder samples were supported on conventional carbon coated film on copper grid for TEM imaging.
2.3.2 Scanning Electron Microscope (SEM) Imaging

SEM is another powerful technique used to study the morphology (surface structures) of nanoparticles. In SEM, high-energy electrons impinging on a solid sample experience elastic scattering by atomic nuclei and inelastic scattering by sample electrons. Inelastic scattering results in the transferring of energy from the high-energy electrons to the sample electrons. Thus, sample electrons can be excited to high-energy states. Some of the excited electrons travelling to the sample surface can be emitted out of the sample as secondary or Auger electrons. By collecting these low energy electrons, high-resolution surface images can be obtained to give morphological information about the sample.

In the present study, SEM imaging of the samples was carried out using Philips Electron Scanning Electron Microscope XL 30.

2.3.3 X-ray Diffraction (XRD) Studies

X-ray diffraction (XRD), based on wide-angle elastic scattering of X-rays, has been the most important technique for determining the structure of materials characterized by long-range order. Typical applications are in Physics, Materials science, Geology, Mineralogy, Ceramics, etc. The wavelength of X-ray is of the order of the distance between neighbouring atoms in a crystal and exhibits interference and diffraction effects. X-rays are reflected from successive planes of various hkl groups in a crystal. The reflected beams interfere positively to give a strong diffracted beam is represented by Bragg’s law and is given by \(2d \sin \theta = n\lambda\) where \(n\) is the integer describing the order of reflection, \(\lambda\) is the wavelength of X-rays, \(d\) is the interplanar spacing and \(\theta\) is the Bragg angle at which a maximum in diffracted intensity occurs. The diffraction analysis of the powder samples can be carried out by powder diffraction method. If the material under study is crystalline, well-defined peaks can be observed while amorphous systems show a halo instead of well-defined peaks.
The XRD patterns of nanometer sized particles are quite striking because of the size-dependent and structure-specific features observed. Therefore XRD techniques are widely used for the particle size determination and structure determination of nanoparticles. Width of the diffraction lines and their shape are characteristic of the crystallite size and the microstrain. Lorenzian line broadening results from nanocrystallites which are considered as domains diffracting, incoherently with respect to one another.

Particle Size Determination

If the line broadening is only due to small crystallite size, the size of the crystallites can be estimated from the Scherrer’s formula,

\[ L = \frac{k\lambda}{\beta\cos\theta} \]

where \( \theta \) is the Bragg angle, \( \lambda \) is the wavelength of the X-rays, \( L \) is the mean dimension of the crystallite size of the powder sample, \( \beta \) is the full width at half maximum of the diffraction peaks on the 2\( \theta \) scale in radians, \( k \) is a constant approximately equal to 0.9 (The instrumental effects may increase the width of reflection peaks and so a correction for instrumental broadening is usually applied in this method).

The XRD studies of the samples for the present work were carried out using Philips (1710PW) powder X-ray diffractometer using Cu K\( \alpha \) radiation over a wide range of Bragg angles fitted with nickel filter. The diffraction peaks so obtained are compared with X-ray powder data file published by the joint committee on powder diffraction standards (JCPDS).

2.3.4 Thermal Analysis

The thermal analysis of a material is a technique in which the physical and chemical transitions is recorded as a function of temperature. In thermogravimetric analysis (TGA), the mass of the sample is recorded
continuously as a function of temperature on heating in an inert atmosphere, at a controlled rate.\textsuperscript{16,17} TGA curves are specific for a given compound or system due to the unique sequence of physiochemical reactions that occur at definite temperatures and at rates controlled by the molecular structure. Changes in the mass of the sample take place as a result of the rupture and formation of various chemical bonds at higher temperatures, which leads to the evolution of volatile products or formation of reaction products. Hence the TGA curve gives information about the thermodynamics and kinetics of various chemical reactions and reaction products.

In differential thermal analysis (DTA), the difference in temperature of the sample and a thermally inert reference material are measured as a function of temperature. When the sample is heated, it absorbs or emits energy depending on the transitions taking place. The corresponding change in sample temperature and that of the reference material ($\Delta T$) against the programmed temperature ($T$) is recorded and this provides qualitative and quantitative information about changes that involve endothermic (heat absorbed) and exothermic (heat evolved) processes. The DTA studies alongwith TGA provide detailed information regarding the dehydration, decomposition and phase transition of a material during heating. The thermal data helps to assess the stability of the material under thermodynamic conditions.\textsuperscript{10,16-19}

In the case of nanoparticles, the grain boundary energy is larger compared to coarser grained materials and the influence of grain boundaries cannot be neglected.\textsuperscript{20} Due to large amount of energy stored in grain boundaries, nanophase materials are not in thermal equilibrium but in a metastable state.\textsuperscript{20} Hence it would be interesting to study the transitions taking place in a nanomaterial when the temperature of the sample is increased. TG/DTA measurements were carried out in the present study to know the thermodynamical property and stability of the samples.
In the present study, thermal analysis of the samples was carried out in a TG/DTA instrument, 92-18 (Setaram) in Argon atmosphere at a heating rate of 10⁹C/minute.

2.3.5 FTIR Analysis

Fourier transform infrared (FTIR) studies have been carried out for the samples under present investigation to understand the effect of particle size on IR transmission spectrum compared to its bulk counterparts. FTIR spectroscopy is currently a relevant technique for surface analysis of particles because it allows the investigation of the chemical composition and the nature of the chemical bonds on the outermost layer. In the case of nanoparticles, due to imperfection in the structural arrangement of atoms on the surface layer, the bond length or interatomic distance may change producing a change in atomic vibration and hence a change in infrared absorption frequency. It has been shown that as particle size decreases increase in frequency for the band (blue shift) is observed in nanoparticles compared to the bulk. In order to study the modification in the IR spectra with small size effect, mid IR [4000-400 cm⁻¹] and far IR [400-10cm⁻¹] studies have been carried out for the samples. When the molecule is excited with IR radiation, the frequency of the incident radiation coincides with the vibrational frequency of some part of the molecule. Hence, resonance occurs and energy is absorbed. This absorbed energy transforms the vibrational energy of the molecules due to change in dipole moment. When the molecule returns to the ground state from its excited state, the absorbed energy is released resulting in distinct IR peaks in the spectrum.

FTIR spectroscopy uses Michelson interferometer to produce an interferogram. IR spectrum and the interferogram are related by a mathematical operation called Fourier transformation. Michelson interferometer consists of a beam splitter and two mirrors, one fixed and the other movable. The IR radiation emitted by a source is split into two beams of equal intensity, one
having a fixed length and the other a variable length. Either one beam or both are passed through the sample and depending on the movable mirror’s relative displacement, the beams are recombined either constructively or destructively. The combination of the two beams produces an interference pattern known as interferogram. This is converted to a plot of transmission versus wave number by the Fourier transformation, with the help of a built-in computer in the machine.

The mid IR and far-IR spectrum of the samples were recorded on a Bruker model IFS 66V FT-IR spectrometer.

2.3.6 Impedance Measurement

Impedance spectroscopy (IS) is an appropriate experimental technique to obtain information about the electrical characteristics of polycrystalline materials and nanophase materials.\textsuperscript{23,24} It can probe the electrical response as a function of frequency, of components, the grains and grain boundaries. This technique is capable of revealing the structural uniformity, variation in electrical conduction paths, stability, etc.\textsuperscript{23} IS can be used to study the intergranular electrical barriers, origin of resistance or capacitance and their dispersion with small signal frequencies and the role of defects within the regime of the electric field.

In this method, a monochromatic signal $V(t) = V_m \sin(\omega t)$ where $\omega = 2\pi f$, $f$ being the signal frequency is applied to the sample and the resulting steady current is $I(t) = I_m \sin(\omega t + \theta)$ where $\theta$ is the phase difference between voltage and current. The total complex impedance $Z$ is given by

$$Z = Z' - jZ'' \quad \text{where}$$

$Z' = |Z| \cos\theta$ is the real part of the complex impedance and

$Z'' = |Z| \sin\theta$ is the imaginary part of the complex impedance
The real part $Z'$ is plotted along the X-axis and the corresponding imaginary part $Z''$ along Y-axis at different frequencies, which will give a semicircle or a set of semicircles corresponding to each relaxation processes in the complex impedance plane. The total AC response is represented by this diagram, which incorporates all mechanisms in the material under a given set of experimental conditions. The presence of three semi circular arcs represents three different relaxation processes and three response times in the grain, grain boundary and sample-electrode interface of the system.

The contribution of each of the components, grain, grain boundary and sample electrode interface can be represented by a suitable combination of resistance and capacitance in parallel. The sample can thus be represented by an equivalent circuit containing three, parallel R-C element connected in series. The appearance of three overlapping semi-circular arcs indicate the presence of three polarization processes in the system with different response times, the grain response being at the high frequency side and electrode response at the low frequency side. One parallel R-C circuit has one time constant and hence can be conveniently used a model to represent one polarization process.

The overall impedance behaviour of the samples, constituted of the contributions from grains, grain boundaries and sample electrode interface can be studied using impedance spectroscopy.

In the present study, impedance measurements were carried out with a HP 4192A LF impedance analyzer in the frequency range 5Hz to 13 MHz at room temperature.

2.3.7 Dielectric Measurements

Alternating current response as a function of frequency gives valuable information about the dynamic response of the system under study and makes it possible to characterize many materials. The variation of dielectric constant
with temperature can give information about the ferroelectric/diffused phase or any other transition of the material and on the behaviour of localized electric charge carriers leading to greater understanding of the mechanism of dielectric polarization.

Dielectric measurements were carried out using HP 4192A LF impedance analyzer. With the instrument capacitance $C$ and dielectric loss ($\tan\delta$) were measured. Dielectric constant $\varepsilon$ is calculated using the relation

$$\varepsilon = \frac{Cd}{\varepsilon_0A}$$

where $C$ is the capacitance, $d$ the thickness of the consolidated sample, $\varepsilon_0$ the permittivity of free space and $A$ is the cross sectional area of electrode on the sample. The ac conductivity $\sigma_{ac}$ is calculated using the relation $\sigma_{ac} = 2\pi f\varepsilon\varepsilon_0\tan\delta$, where $f$ is the frequency and $\tan\delta$ is the loss tangent. The measurements were carried out at different temperature (300–500K) over a frequency range from 100Hz to 13MHz.

2.3.8 Magnetic Measurements

The study of magnetic properties of materials is a basic requirement for understanding electronic behaviour in condensed matter. Magnetic behaviour depends upon the strength of Coulomb and exchange interactions among electrons and to study about this, magnetic measurement at low temperatures and high magnetic field is required.

But the magnetic properties of nanoscale particles are of great interest since they are expected to differ substantially from their bulk counterparts. This is partly due to the dominant role of the surface magnetic ions with lower co-ordination and broken exchange bonds. The size reduction of a magnetic material leads to novel properties as compared to bulk material such as superparamagnetism and spin canting. In bulk magnetic materials,
magnetostatic and bulk magneto crystalline energies are the main sources of anisotropy, whereas in nanoparticles, strong interfacial effects are expected.

In the present study, room temperature magnetic moment and magnetic susceptibility measurements of the samples were carried out using EG&G 155 model vibrating sample magnetometer (VSM). The ESR measurements were carried out using a standard reflection type X-band (9.25 GHz) spectrometer equipped with a Varian microwave cavity and a variable temperature cryostat system (4-350K). Measurements of magnetization as a function of temperature were done on a commercial super conducting quantum interference device (SQUID) magnetometer.

ESR is a useful tool for studying the magnetic structure and its change under the influence of external parameters like magnetic field and temperature. Superparamagnetism is exhibited by nanoparticles of many magnetic substances, which can be studied using SQUID magnetometry. In this method, a single particle is studied at a time whereas in VSM an ensemble average measurement in an assembly of many particles is carried out. ESR measurements and magnetic susceptibility measurements support each other.

Valuable information about the spin dynamics of the system can be obtained from the excited state X-band ESR at low temperatures. ESR spectrum and hence the line broadening at different temperatures can give useful information about the electron dipole-dipole interaction, anisotropic hyperfine interaction, misorientation of the crystals or distribution of magnetizing fields. From Ψ-T graph, the Neel temperature and blocking temperature can be noted. Magnetic moment formation and exchange interaction in metals can be strongly influenced by surfaces and interfaces.

The direction of the magnetic moment in a small particle is determined by both the shape of the particle and by its crystal structure through the anisotropy effects. The magnetic anisotropy energy, which keeps a particle...
magnetized in a particular direction, is generally proportional to the particle volume. Therefore, the energy barrier that has to be overcome to reverse the particle magnetization $E = KV$, where $K$ is an effective anisotropy constant and $V$ is the volume of the particle. Shape anisotropy accounts for preferential orientation of the magnetic polarization (magnetization) along long axis for elongated particles so as to minimize total magnetic field energy. The magnetization also prefers alignment along specific crystallographic axes. This is the crystalline anisotropy effect, which dominates over the shape anisotropy in very small particles. Axes of preferential magnetization are called the easy axes of magnetization.

2.4 References


