Chapter 2

Experimental Techniques
EXPERIMENTAL TECHNIQUES

2.1 Introduction

Various techniques have been successfully employed for the preparation and characterisation of nanocrystalline materials. In the present investigation, we have used simpler techniques for the synthesis and characterisation of samples. This chapter deals with the methods of preparation of the nanoparticles for the present study and the experimental techniques used for their characterization.

2.2 Chemical Precipitation Method

Chemical methods are found to be simpler for synthesizing nanometre-sized particles compared to other methods like gas evaporation, laser ablation, etc. Precipitation from aqueous solution is the most commonly used method for preparing nanocrystalline materials. A number of articles dealing with the preparation of nanoparticles have been appeared in the past two decades. Nanoparticles for the present study were prepared by controlled precipitation technique starting from the appropriate chemicals without the use of stabilizers. The exact preparation procedures employed in the present work are detailed in chapter 3 of this thesis.

2.3 Experimental Characterisation

2.3.1 X-ray Diffraction Studies

X-ray Diffraction (XRD) is an analytical technique with a very broad range of applications. Typical applications are in Physics, Materials Science, Geology, mineralogy, ceramics, etc. X-ray diffraction can be explained in simple terms by ‘reflection’ of an X-ray beam from a stack of parallel equidistant atomic planes. A small portion of the beam can be considered to be reflected at each atomic plane. If those
reflected beams emerge from the crystal in such a way that they do not cancel each other by interference, a diffracted beam can be observed. The condition where 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 integral number 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. If the material under investigation is crystalline, then well-defined peaks will be observed while non-crystalline or amorphous systems show a hallow instead of well defined peaks.

X-ray diffraction techniques are widely accepted for the characterization of small particles. Width and shape of the measured diffraction lines are characteristic of the crystallite size as well as the microstrain. Very small crystallites can be considered to be domains which are diffracting incoherently with respect to one another, resulting in a Lorentzian line broadening. Line profile analysis of XRD data is well suited for the determination of the crystallite size distribution.

**Scherrer's Equation**

If the line broadening is caused only by small crystallite size, the crystallite size can be estimated from the Scherrer's equation

$$L = \frac{k\lambda}{\beta \cos \theta}$$

where $\theta$ is the Bragg angle, $\lambda$ is the wavelength of the X-rays, $L$ is the mean dimension of the crystallite size composing the powder sample, $\beta$ is the full width at half maximum of the pure diffraction profile on the $2\theta$ scale in radians. $k$ is a constant approximately equal to unity. In the determination of particle size by this method, it must be realized that instrumental effects might also increase the width of reflection and correction for instrumental broadening must be applied. This method can be used for the determination of size of small crystals.

Profile fitting analysis is used to obtain very accurate line position, intensities and shape from both resolved and unresolved X-ray diffraction spectra using a least square
refinement technique. Such exactness is vital to many diffraction problems, such as qualitative phase analysis, lattice disorder, crystal size determination and stress measurements.

X-ray diffraction studies for the present investigation were performed using a AXS Bruker D5005 diffractometer (Germany) with a vertical goniometer. X-ray generator was operated at 40kV and 30mA. CuK\(_\alpha\) (\(\lambda = 1.5418\) A) radiation was used with Ni filter. High temperature X-ray diffraction studies were carried out using a high temperature camera HTK 16 (Anton Paar, Austria). The sample powder was mixed with alcohol and a droplet of zapon lacquer and the mixture was applied to the heating filament. Temperature was controlled using a Eurotherm controller (± 1K).

2.3.2 Thermal Studies

Thermal analysis is defined as a technique in which a physical property is recorded as a function of temperature.\(^{23}\) Thermogravimetric Analysis (TGA) is the technique of monitoring the change in mass of a sample under programmed heating. TGA measures the temperature and heat flow associated with transitions in materials. In differential thermal analysis (DTA) the differential temperature between sample and a reference material, both of which are heated under identical conditions, is measured. These measurements provide qualitative and quantitative information about changes that involve endothermic (heat absorbed) and exothermic (heat evolved) processes.

In polycrystalline materials, the grain size is sufficiently large to reduce the grain boundary energies and hence no influence on macroscopic properties. If the grain size is reduced to nanometer range, the influence due to grain boundaries cannot be neglected.\(^{24}\) Due to high amount of energies stored in grain boundaries, nanocrystalline materials are not in thermal equilibrium but in a metastable state.\(^{24}\) Thus it would be of great scientific interest to study the phase transitions of a superionic material when the size of the particles is reduced to nanometer range in view of the increased energies of the grain boundaries of nanoparticles. TGA/DTA measurements were carried out in the present investigation to study the phase transition temperature accurately.
In the present study, thermal analyses were carried out in a simultaneous TGA/DTA instrument, STA 15H+ (Rheometric Scientific).

2.3.3 FTIR analysis

In order to understand the contribution of quantum size effect to the infrared transmittance, Fourier Transform Infrared transmission studies have been carried out for the materials under investigation.

Fourier Transform Infrared Spectroscopy uses Michelson interferometer to produce an interferogram. The interferogram is related to IR spectrum by the mathematical operation, the Fourier transformation. The fundamental part of the instrument is the so-called Michelson interferometer. It consists of a beam splitter and two mirrors, one fixed and the other movable. The infrared radiation, emitted by a broad band source, is split into two beams of equal intensity. Either one beam or both are passed through the sample, but one beam is made to traverse a longer path than the other. Depending on the movable mirror's relative displacement, the beams are recombined either constructively or destructively. The recombination of the two beams produces an interference pattern. By changing the path difference the interference pattern changes to produce a detailed signal varying with optical path difference. This pattern is known as the interferogram. The interferogram is converted to a plot of absorption versus wave number by the Fourier transformation of the interferogram, using a computer built into the machine. There are several advantageous to FTIR over the traditional dispersive method, the most important being the much higher signal to noise ratio.

Harmonic oscillators-like states can occur in solids where ions are in random translational motion. The local potential of the moving ion will fluctuate on a very small time scale because of its interaction with the neighbours and hence the ions can be assumed to be behaving like a highly damped harmonic oscillator. Both the lattice vibration of the bound nuclei or the local motion of the moving ion are characterised by a characteristic frequency which can be seen in the far-IR region.
It has been shown that the optical absorption and scattering in the fundamental lattice absorption region is size dependent.\textsuperscript{27} As the crystal size decreases the surface band increases in intensity relative to the bulk band and shift to higher frequencies. In order to study the modifications in the IR spectra when the crystal size is reduced, far-IR transmission spectra of the nanoparticles were recorded.

The FTIR spectra of the nanoparticles and nanocomposites were carried out using a BOMEM DA-8 FTIR spectrometer with polyethylene as the dielectric medium surrounding the particles.

2.3.4 Impedance Measurements

Impedance spectroscopy is a widely recognised tool for investigating the electrical behaviour at or near grain boundaries.\textsuperscript{28} It can reveal the degree of structural uniformity, variation in electrical conduction paths, stability, degradation, time-dependant processes etc. in homogeneous composite based devices and components. It elucidates inter-granular electrical barriers, origin of resistance or capacitance, their dispersion with small signal frequency and the role of defects within the regime of the electric field.

The most common and standard method is to apply a monochromatic signal \( V(t) = V_m \sin(\omega t) \), involving the signal frequency \( f = \omega/2\pi \) to the sample to be tested and to measure the resulting steady state current \( I(t) = I_m \sin(\omega t + \theta) \). Here \( \theta \) is the phase difference between the voltage and the current. The complex impedance given by

\[
Z'(\omega) = Z' - iZ'' = \frac{V(t)}{I(t)}.
\]

The real and imaginary parts of the complex impedance are given by

\[
Z' = |Z| \cos \theta \quad \text{and} \quad Z'' = |Z| \sin \theta, \text{ respectively.}
\]

The real and imaginary parts are plotted in 'Nyquist' format\textsuperscript{28} which will give a semicircle or a set of semicircles corresponding to each process, in the complex impedance plane. This represents the total ac response, which incorporates all the
mechanisms in the material in a systematic manner under a given set of experimental conditions. The appearance of three clear semicircular arcs indicates the presence of grain, grain boundary and electrode processes of the system since these three have three response times. The grain response will be at the high frequency side and electrode responses at low frequency side. The behaviour of the sample can be explained by an equivalent circuit consisting of resistors and capacitors. Since a parallel RC circuit has one time constant, it can be modeled to represent one polarization process. The semicircles are often inclined with the origin below the real impedance axis. Such impedance plots are commonly interpreted on the basis of the so-called distribution of relaxation times.

The structures of nanophase materials are dominated by their very small grain sizes, and grain boundaries containing a large fraction of the total number of atoms. To study the effect of the small grain sizes and the grain boundaries, impedance spectroscopy can be employed. In the present study, the impedance plots of the consolidated nanoparticles were analyzed at different temperature. Impedance measurements were carried out with a HP 4192A LF impedance analyser in the frequency range 5 Hz to 13MHz.

2.3.5 Electrical Conductivity Measurements

Dielectric constant, dielectric loss and ac conductivity measurements were carried out using a HP 4192A LF impedance analyser. The instrument can directly measure eleven impedance parameters (|Z|, |Y|, G, Θ, R, X, B, L, C, D and Q).

The measuring range of the instrument for capacitance (C) is 0.0001pF to 100.00mF with a maximum resolution of 0.01pF, and for dielectric loss (D) from 0.1 to 1999.9 with a maximum resolution of 0.01. All measurements had a basic accuracy of 0.1%. The built-in frequency synthesizer can be set from 5Hz to 13MHz. An internal dc bias source provides voltage range from -35V to +35V in 10 mV steps. The frequency can be varied in steps of 0.01Hz, 0.1Hz and 1Hz in the ranges 10 to 100kHz, 100kHz to 1MHz and 1 to 13 MHz respectively. The zero offset adjustment function measures the
residual impedance and stray admittance inherent to the test fixture used, and offsets the
effects of this parasitic parameters to zero with respect to the measured values.

The ac conductivity\textsuperscript{30} has been calculated from the measurements of capacitance
and dielectric loss (\(\tan \delta\)). The dielectric constant (\(\varepsilon'\)) is calculated from the measured
capacitance (\(C\)) using the relation
\[
\varepsilon' = 11.3 CL/A
\]
where \(C\) is in pF, \(L\) the thickness in cm and \(A\) the area of cross section of electrode on the
sample in cm\(^2\)

Then the ac conductivity (\(\sigma_{ac}\)) is given by the relation
\[
\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon' \tan \delta
\]
where \(f\) is the frequency and \(\tan \delta\) is the dielectric loss tangent. The measurements were
carried out at different temperatures over frequency range from 5\(\text{Hz}\) to 13\(\text{MHz}\).

### 2.4 References

5. M Abdul Khadar and K C George, Solid State Commun. 84, 603 (1992)


29. W P Halperin, Rev. Mod. Phys. 23, 533 (1972)