Experimental Details

2.1 Introduction

This chapter is motivated to describe different experimental methodologies we have used in our research works. A brief description will be given for the process of different sample preparation techniques and proper characterization procedures. Bulk and nanocrystalline materials of TMOs have been prepared using different synthesis techniques. I shall introduce various instruments used for experimental data recording and analysis. Detailed structural, magnetic and transport properties are investigated
for physical characterization of the samples.

2.2 Preparation of samples:

The synthesized samples can be categorized as polycrystalline and nanocrystalline TMOs. We have used mainly the solid state reaction technique to prepare the bulk polycrystalline samples. Nanoparticles are prepared using sol-gel technique and ball milling process. Single crystal we have worked was prepared in other lab by floating zone technique. The starting materials used for preparation of samples are purchased from Sigma-Aldrich and Alpha-Aesar of very high purity above 99.9% (sometimes above 99.99%). Bulk samples needed high temperature annealing in presence of different gas flow. Now we have to describe the thee different techniques for sample preparation i) Sol-gel Technique, ii)Solid State Reaction Technique and iii) Ball Milling.

2.2.1 Sol-Gel Technique:

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 constitute continuous polymer networks. Stoichiometric amounts of the starting chemicals may be taken in the form of oxides or nitrates or acetates so that they should be soluble in water either directly or through reaction with diluted nitric acid. Note that for all these process, very high purity water either double distilled
or preferably deionized water obtained from Millipore deionization system) is used. The aqueous solutions are then mixed and stirred thoroughly in a magnetic stirrer at elevated temperature of $\sim 80^\circ$C for 2 h to ensure homogenization. Note that boiling off of the solution should be avoided. Calculated amount of pure citric acid is then added for binding of the ions in the solution to the citrate ions (assuming that 2 ions bind per citrate ion). This is followed by stirring for 6 h at $\sim 80^\circ$C. Elevated $T$ favours binding of the citrate ions while sufficient time confirms completion of the process and homogeneity to finally produce the so called gel. The gel is then dried at moderate temperature $\sim 70^\circ$C to produce an off-white highly porous solid cake. The ions in this solid are homogeneously distributed and bound to the citrate network. For preparation of oxide powder, this solid is next heated at $\sim 550 - 80^\circ$C for 6 h. This heating decomposes and removes nearly all the organic and nitrate portion as gas, leaving behind a blackish powder. Spherical nano-particles of oxides can be prepared in this manner with comparatively low heating $T$ to obtain particles of diameter $\sim 5 - 50$ nm. However, for bulk polycrystalline samples, the powder is further heated and annealed in the form of compressed pellets at high-$T$ $\sim 900^\circ$C and above (depending on samples and article size required) for cycles of long periods $\sim 12$ h or $24$ h with repeated intermediate grindings. The sol-gel process has the advantage of high homogeneity and low annealing $T$. Besides, preparation of nano-particles, which requires low annealing $T$, can be done using this process. The disadvantage is the complexity and time consuming features of using solutions and acids and the initial process of gelation. Sometimes, there is even a chance of contamination from im-
purities, if present, in the acids or the water used for preparing solution. In sol-gel technique, samples are formed from the homogeneous solutions through gelation. A pre-annealing of the $\text{R}_2\text{O}_3$ oxides at 1000$^\circ$C was performed in order to eliminate possible traces of water and carbon dioxide. Then the starting materials are dissolved in dilute nitric acid solution and all the solutions are mixed and stirred at a temperature $\leq 100^\circ$C to obtain a homogeneous nitrate solution. After 2h a proper amount of citric acid was added to the solution of the mixed metal nitrates. The resulting solution was stirred at a temperature $\leq 100^\circ$C for 6h to ensure the formation of the metal citrates. After the completion of citration the solution was gently and slowly evaporated at the same temperature for long enough time to obtain dried citrate precursor powder. The precursor powder was then grounded and heated at 550$^\circ$C to obtain well-crystallized compounds by decomposition of mainly the citrates. Then they were fired at different annealing temperatures from 600 to 1400$^\circ$C to obtain different compounds with various grain sizes.

### 2.2.2 Solid State Reaction Technique:

This process does not involve preparation of any solution and is hence called a dry media reaction and is a rather direct method. Stoichiometric amounts of the starting chemicals in the form of oxides or carbonates are thoroughly mixed and ground in a mortar-pestle. The grinding and mixing generally requires a sufficiently long time $\sim 2 - 3$ h to ensure homogeneity. The first step, called calcination, is to heat the mixture in powder form at $\sim 1000^\circ$C for 12h to decompose any carbonates to oxides. Then
the mixture is again ground thoroughly and heated to final temperature in powder form for 12 - 24 h. Finally the powder is compressed to pellets and annealed at the final temperature for cycles of 12 - 24 h with thorough intermediate grinding until a single phase is reached. The reaction occurs through direct contact of the chemicals at high-T and through diffusion assisted by very high thermal energy at high-T. It is thus very important to achieve minimum particle sizes of the starting chemicals and uniform mixture of the same through prolonged grinding and mixing. The advantage of this process is the low processing time and lower chance of contamination from impurities. However the disadvantage is tedious grinding, chances of inhomogeneity and high annealing temperature requiring the infrastructure of high-T furnaces. Although sol-gel technique is more than sufficient for our sample preparation, sometime to see the bulk properties of the compounds we have used solid-state method. This method often requires high temperatures and controlled atmosphere, for which we use different types of high temperature furnace. The basic principle of a solid state reaction is to mix the correct quantities of starting materials whose atoms will diffuse at a sufficiently high temperature. The chemical phase that minimizes the free energy will nucleate and grow. It is extremely important not only to mix the starting materials but to grind them thoroughly in order to obtain a better diffusion and increase, if possible, the rate of the reaction. After repeating the process of grinding and heating several times until the result is a single phase material the powder samples are pressed into a pellet and annealed at final temperature. Sometimes controlled atmosphere is necessary to achieve a desired stoichiometry. We have used alumina tube furnace to
achieve a controlled atmosphere like oxygen or inert gas atmosphere.

\section*{2.2.3 Ball Milling}

Ball milling method is a top to bottom approach to produce nano particles starting from bulk materials. Ball mill is a hollow cylindrical device used for grinding materials like ores, alloys, ceramic materials etc. This device rotates horizontally partially filled with the material to be ground along with the grinding balls, and the internal cascading effect reduces the particle size of the material. The grinding balls are made using various materials depending on the requirements. Smaller the size of the ball smaller is the final particle size. Nanoparticles of NiO and Cr$_2$O$_3$ was prepared using a \textit{Fritsch pulverisette-7 premium line} ball milling machine. A ball machine with the bowl or sample holder is displayed in Fig. 2.1.

\section*{2.3 Structural and chemical characterization:}

Initially the as prepared compounds were subjected to X-ray diffraction (XRD) measurements prior to other experiments being carried out to conrm about the phase composition and purity of each sample. And then scanning electron microscopy (SEM) or tunneling electron microscopy (TEM) or both were used to determine the particle size, morphology, elemental or compositional analysis (through energy dispersive spectroscopy or EDS) and crystallographic nature of the studied compound.
2.3.1 X-ray diffraction and the Rietveld refinement method:

Diffraction techniques are the most powerful tools available for the characterization and determination of crystalline materials. Powder X-ray diffractometer was used for structural characterization. Two instruments (Seifert XRD 3000P and Bruker AXS D8 Advance) were used, using CuK radiation having a wavelength of 1.54184 Å. The operating voltage was 40 kV and the current was 20 mA. The X-ray diffraction patterns were obtained at room temperature and sometimes at low temperature up to 100 K. While scanning the sample and the detector rotate in a coupled fashion to ensure the X-ray scattering angle is twice the angle between the incident X-ray and the scattered plane in the samples. The sample plane remains fixed. Using these detectors one can vary $\theta$ within the range from 1° to 100°.
If a X-ray beam incidents on a polycrystalline sample, it scatters in all possible directions. Although, the scattered waves mostly cancel each other, they interfere constructively in some directions as predicted by Bragg’s law:

$$2d \sin \theta = n\lambda$$  \hspace{1cm} (2.1)

here $d$ is the interplanar spacing, $\theta$ is the incident angle, $n$ is the order of diffraction, and $\lambda$ is the wavelength of incident X-ray. To ensure the phase purity of the samples, XRD was performed for all the samples at room $T$ in SEIFERT XRD 3000P and BRUKER D-8 ADVANCE diffractometers having Ni filtered Cu K$_\alpha$ source ($\lambda = 1.5418$ Å). The Rietveld method is a technique utilized to refine the crystal structures from X-ray and neutron diffraction data. Due to the random orientation of crystallites
in a polycrystalline sample, a large amount of overlap of independent Bragg peaks occur and information is lost, particularly in low symmetry materials. In this method the individual reflections are not analyzed. Instead, a curve fitting procedure is used over the entire pattern. The difference between the observed and calculated profiles is minimized by least squares refinement and it is therefore very important to have a good structural starting model including space group, lattice parameters and atomic co-ordinates. The parameters that can be refined by Rietveld method, in addition to those already mentioned include the cell parameters, the atomic coordinates, the temperature factors, site occupancies and intensity corrections. In the refinement process the parameters will be adjusted until the best fit between the calculated and observed pattern is obtained. Having a starting model close to the correct one will prevent the system from diverging or reaching a false minimum. It should be noted that, as well as having low residual R factors from the refinement, the refined model has to make sense both chemically and physically. All structural refinements of powder X-ray diffraction data in this thesis were performed with the Fullprof and Maud (Material Analysis Using Diffraction) program suite.

2.3.2 Transmission Electron Microscope (TEM)

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen. The electrons interact with the specimen as it passes through and an image is formed from the transmitted electrons. The de Broglie wavelength of electrons is much smaller than visible
light; hence an electron beam is used. The image is magnified and focused onto an imaging device, such as a CCD camera. Some of my samples are characterized using TEM to study the particle size morphology and the microscopic single phase nature of the specimen. For this, a tiny amount of the sample powder is dispersed in alcohol using an ultrasonic sonicator. A drop of the dispersed liquid is then put on a carbon coated copper grid used for loading sample in TEM. Microscopic study of phase purity and crystalline nature such as grain boundary morphology, lattice-fringe pattern, interplanar spacing, etc. are studied in a high resolution TEM (HRTEM). The interplanar spacings match well with that obtained from XRD analysis, often corresponding to the most intense peak. Besides, no impurity phases are detected, even at the grain-boundaries.

2.3.3 Field Emission Scanning Electron Microscope (FESEM)

A scanning electron microscope (SEM) 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. A source emits electrons by a field emission technique under high vacuum and is hence called a field emission–SEM. The electrons are then accelerated under a high field gradient and focused by an electromagnetic lens system. The electron bombardment on the surface of the sample produces both scattered secondary electrons (inelastic scattering) and back scattered electrons (BSE — reflected from the sample by elastic scattering). Normally, the secondary electrons are used for imaging of the sample surface topography in a detector (SEI — Secondary Electron Imaging mode). BSE
are often used in analytical SEM along with the spectra made from the characteristic X-rays. 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. FESEM is also equipped with energy dispersive X-ray spectrometer used for analysis of elemental composition in a sample. The high energy electron beam, incident on the sample, produces characteristic X-rays due to electronic transitions in the inner shell of the elements. Since each element poses a unique atomic structure allowing X-rays that are characteristic of an element’s atomic structure to be identified uniquely from one another, this technique can be effectively used to identify the composition of a sample by analyzing the relative intensities of the peaks. Elements higher atomic weight than Beryllium (Be) can be generally detected. Particle sizes and surface morphologies of some of the samples were checked using JEOL JSM 6700F FESEM. A little powder specimen was spread over a sticky carbon tape attached to a sample holder stub. The sample was then coated thinly with platinum in a vacuum deposition chamber (for poorly conducting samples) for producing a conductive path of the incident electrons (otherwise, space-charge accumulation over the sample may spoil the image). Analysis using EDS confirmed the elemental composition of the samples to be within the error limits of nominal compositions.
2.4 Magnetic and transport measurements and analysis:

After the structural and elemental analysis, the high quality bulk polycrystalline single phase samples are subjected to further study. To investigate different physical properties of all single phase compounds and alloys, a number of experiments were performed. All the techniques are given in details in the next few subsections.

2.4.1 Magnetization

Magnetic measurements were performed either in a commercial Quantum Design superconducting quantum interference device (SQUID) magnetometer (magnetic property measurement system (MPMS) 6, Ever-cool model) or a commercial cryogen free high magnetic field system from Cryogenic Ltd., UK in a temperature range between 2 K and 300 K. In case of dc magnetic measurements, the variation of magnetization (M) was measured as a function of both T and H. To perform these measurements different protocols were used as described below.

1. **Zero-field-cooling (ZFC):** In this protocol, sample was cooled from room temperature to lowest temperature of measurement in zero magnetic field. Data were recorded in the heating cycle after switching on a constant magnetic field for this measurement.
2. **Field-cooling (FC):** Here data were recorded in the cooling cycle when the sample was cooled to the lowest temperature from room temperature in presence of a finite magnetic field.

3. **Field-cooled heating (FCH):** After the obtaining the FC condition, FCH protocol was followed by recording the data in warming cycle in presence of the same magnetic field.

Complex ac susceptibility ($\chi'_{ac}$) was measured in SQUID magnetometer. T dependence of the real ($\chi'$) and imaginary part ($\chi''_{ac}$) of ac susceptibility was recorded at different frequencies within the allowed frequency range of the instrument.

### 2.4.2 Transport measurement

Electrical transport is one of the significant measurements to characterize a sample. The magneto transport behaviour of the sample supplies useful information on spin dependent scattering which provides valuable informations about the intrinsic magnetic properties of the compound.

**Resistivity:**

Temperature variation of resistivity $\rho$ was measured by the four probe method using a Keithley 2400 source meter and a Keithley 2182A nano voltmeter. A Lakeshore 325/331 temperature controller was used for temperature control. A laboratory designed sample holder was used for this measurement. It is consisted of an aluminium
rod with a brass brass plate attached to one end of it. A mica sheet is placed over the brass plate and sample is placed above it to avoid the direct contact of brass and sample. Sample is connected to the electrodes using copper wire and the electrodes are connected with source meter and nano voltmeter. Brass plate is covered with a metallic shield wounded with heater coil. The brass plate consists of Pt 100 temperature sensor also. Another end of the sample holder is fixed with a rubber cork. This entire arrangement is inserted into a glass made cryostat. The cryostat is pumped out for several minutes using a rotary vacuum pump and the complete set up is then partially immersed in a liquid nitrogen dewar. A small amount of He gas is inserted as exchange gas to improve the thermal conductivity and temperature stability of the system. The system measures in temperature range 77K to 400 K properly. Fig. 2.3 shows a labeled diagram of the sample holder used to measure resistivity. Another resistivity set up consists of a CCR cryostat, which measures from 6 K to room temperature. A high vacuum $10^{-6}$ mbar is maintained inside the CCR cryostat. Here, the cooling of the sample occurs through thermal contact to base of the sample holder (no exchange gas).

Magneto-transport measurements were done in standard PPMS system. The temperature range of the PPMS is 2K to 300 K. The highest magnetic field achieve by the system is 90 kOe.
2.5 Mössbauer Spectroscopy

Mössbauer spectroscopy is a technique, based on the emission and resonant absorption of $\gamma$-rays in a recoil-free way in solids, that is, without any energy loss to the lattice. The extremely well-defined energy of these $\gamma$-rays makes it possible to study static as well as dynamic hyperfine interactions. Detailed chemical, structural and magnetic information can be obtained about atoms on the surface or in the bulk of materials. In addition, in situ investigations, which are indispensable in case of particle structure or surface state changing with the surrounding conditions, can easily be achieved. Mössbauer spectroscopy is thus very well suited to studies of fine-particle systems.
The application of this technique is restricted to solids or frozen liquids containing a Mössbauer isotope. For practical reasons, $^{57}$Fe is almost the only isotope easily utilizable for studies of magnetic materials. Magnetic compounds not containing iron can often be studied by doping the sample either with $^{57}$Fe or the radioactive parent isotope, $^{57}$Co. Similar to bulk materials, through the recoilless fraction and static hyperfine interactions, Mössbauer spectroscopy can be sensitive to a wide range of phenomena relevant to fine-particle systems. The main differences with respect to bulk studies come from the specific properties of the atoms near the surface. Our Mössbauer spectroscopy measurement set up is shown in Fig. 2.4. $^{57}$Fe Mössbauer spectra were recorded in a transmission geometry using a 25 mCi $^{57}$Co source in a Rh matrix with a velocity drive unit of Fast Comtec GmbH in a constant acceleration mode which was coupled with a closed-cycle cryogenics (JANIS) fitted to a vibration-free isolation stand. All the hyperfine parameters obtained from the fits are estimated with respect to the values of metallic $\alpha$-Fe.

2.6 Neutron Scattering

The neutron scattering technique is a valuable tool for investigating many features of materials, molecules, and condensed matter. Due to the specific properties of neutron, the static and dynamic properties of a sample can be measured. For paramagnetic materials X-ray and neutron diffraction patterns are same. But for materials with magnetic ordering produce a different diffraction pattern for neutron diffraction.
Fig. 2.4: Mössbauer Set up in the Laboratory

tion contrary to the X-ray diffraction pattern. For antiferromagnetic ordering, there will be extra peaks in addition to structural peaks which corresponds to the magnetic ordering. In case of ferromagnetic samples, an enhancement will be noticed in the structural peaks associated with ferromagnetic ordering. Thus the combination of nuclear and magnetic peaks represent the neutron diffraction pattern of a material. Usually, a neutron beam contains neutrons with magnetic moments pointing in all directions. If we measured the number of neutrons with moments parallel and antiparallel to a given direction say an applied magnetic field we would find equal populations. However, various special techniques can generate a polarized neutron beam, that is, one where the majority of neutron moments are in the same direction. Neutron diffraction experiment was carried out on polycrystalline and nanocrystalline LSFO
using polarised diffractometer DNS at the FRMII (Garching, Germany). The neutron wave length was 4.74 Å. We placed samples in an Al foil that was wrapped in to a hollow cylindrical shape. We then put the wrapped samples in side an Al container in the He atmosphere. We recorded diffraction intensities at selective temperatures in the range 3 - 300 K. The diffracted intensity could be separated by the polarization analysis into following three contributions: (1) coherent nuclear scattering, (2) spin-incoherent nuclear scattering, and (3) magnetic scattering.[79] The refinement of the magnetic diffraction data is done using FULLPROF refinement program.