In this chapter, the detailed description of the methodology adopted for synthesizing the samples and various experimental techniques used for their characterization, are presented. Short descriptions of theoretical formalisms are also described. The experimental techniques utilized for the study of thermal, microstructural, morphological, optical, dielectric, and magnetic properties of nanostructured samples have been discussed.
2.1 Introduction

The fabrication and analysis of nanomaterials have become a very important area due to wide applications of nanotechnology in many fields. This chapter illustrates synthesis routes through simple acid modified sol-gel method and different techniques for the characterization of nanomaterials to analyze their various novel properties. The techniques like: thermogravimetric analysis (TGA), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX or EDS), high-resolution transmission electron microscopy (HRTEM), Fourier transforms infrared (FTIR) spectroscopy, Raman spectroscopy, UV-visible absorption and fluorescence emission spectroscopies, LCR meter, vibrating sample magnetometer (VSM), superconducting quantum interference device (SQUID) magnetometer etc., which are used for characterization of nanomaterials, are discussed in the following sections.

2.2 Synthesis of Nanomaterials

Nanoparticles can be produced with various shapes and morphologies like spheres, cylinders, spindles, tubes, flowers etc. Their synthesis with strict control over size, shape, composition and crystallinity is important due to their applications in numerous fields such as catalysis, medicine, gas sensing, electronics etc. The shape and size of nanomaterials depend on synthesis procedure, precursor materials, pressure, temperature, annealing time etc. All these parameters contribute to form different size and shape of nanomaterials [1]. Several procedures have been already developed and applied to prepare nanomaterials. They are typically grouped into two categories; “top-down” and “bottom-up”. Top-down approach includes breaking the bulk materials into nanoparticles via solid state routes, ball milling or other mechanical process. It involves breaking of course-grained solid into smaller and smaller pieces continuously to reach few nanometer sizes. The wet chemical synthesis routes like sol-gel, hydrothermal, reverse micelle, co-precipitation etc., lie in the class of bottom-up approach, which involves the condensation of atoms or molecules to reach few nanometer sizes. The schematic diagram of these two approaches is shown in Fig. 2.1. The bottom-up is far more popular and widely employed for the synthesis.
of nanomaterials owing to several advantages associated with it. There are many bottom-up methods for synthesizing metal oxide nanomaterials such as hydrothermal method [2], combustion synthesis [3], gas-phase methods [4], microwave synthesis [5], sol-gel processing [6, 7] etc. Sol-gel processing technique are discussed in detail in this chapter because the materials, reported in subsequent chapters, were fabricated using this method.

![Schematic of top-down and bottom-up approaches](image)

**Fig. 2.1 Schematic of top-down and bottom-up approaches.**
2.2.1 Sol-gel Method for Sample Preparation

Synthesize of materials through sol-gel [7] method is also known as wet chemical route. This technique has been practiced since 1930. Later, this procedure was reviewed in 90’s [6, 8]. Presently, it is a popular process to synthesize ceramic and glass materials in several forms like powders, thin films, fibers, inorganic membranes, and aerogels (Fig. 2.2). In general, the sol-gel method is based on transition of a system from liquid to gelatinous network phase. A sol is a dispersion of the solid particles (~ 0.1–1 μm) in a liquid where the Brownian motions of the suspended particles are involved. A gel is a state where both liquid and solid are dispersed in each other. It presents a solid network containing liquid components. The liquid phase method entails a wet chemistry. It is popular in the nanoparticles synthesis and has several advantages over solid-state reaction or co-precipitation technique. Easiness of the process is one of them. Sol-gel process is cost effective and low-temperature technique. It does not need any sophisticated equipment and special environment.

![Mechanism of sol-gel process](image)

**Fig. 2.2** Mechanism of sol-gel process [6].
Undoped and doped titania (TiO$_2$) nanoparticles (NPs) were synthesized by employing acid modified sol-gel method for the thesis work. Here, glacial acetic acid was used in the conventional sol-gel method for preventing titanium (IV) isopropoxide to be precipitated in water medium and make homogeneous solution of precursor and dopant starting materials. This process involves various steps like mixing, hydrolysis, densification, ageing, gelation, drying, grinding etc.

Chromium and cobalt doped TiO$_2$ NPs with stoichiometric formula Ti$_{1-x}$Cr$_x$O$_2$ and Ti$_{1-x}$Co$_x$O$_2$ ($x = 0.00, 0.03, 0.05,$ and 0.07) were prepared by acid modified sol-gel route. All reagents, used in the synthesis work, were of analytical grade purchased from commercial sources and utilized without further purification. Titanium (IV) isopropoxide solution [C$_{12}$H$_{28}$O$_4$.Ti], chromium nitrate [Cr(NO$_3$)$_3$.9H$_2$O] and cobalt nitrate [Co(NO$_3$)$_2$.6H$_2$O] were purchased from Alfa Aesar used as titanium source and the dopant starting materials accordingly. Glacial acetic acid (99.9 %) was obtained from Thomas Baker and absolute ethanol (99.9 %, AR-grade) from Changshu Yangyuan Chemical, China.

Stoichiometric amount of chromium / cobalt nitrate was dissolved in 60 ml of deionized water at room temperature, followed by addition of 5 ml glacial acetic acid to obtain solution-1. Stoichiometric amount titanium (IV) isopropoxide was dissolved in 40 ml of absolute ethanol with constant stirring to form solution-2. The solution-2 was added drop-wise very slowly into the solution-1 within around 60 min under vigorous stirring. Subsequently, the obtained sol was stirred continuously for 2 hrs and was aged for 48 hrs at room temperature. Thereafter, as prepared gel was dried for 12 hrs at 80 °C. The obtained solid was grinded and calcined in open air at 450 °C for 6 hrs (heating rate 2.5 °C/min and cooling rate 1.5 °C/min) followed by grinding. The samples were ready for characterizations. The undoped or pure titania was prepared using the same method for comparative study. Synthesis procedures are also shown in flowchart given below (Fig. 2.3).
Fig. 2.3 Flow chart for acid modified sol-gel method used for synthesis of undoped, chromium and cobalt doped TiO$_2$ nanoparticles.
2.3 Characterization Techniques

2.3.1 Thermogravimetric Analysis (TGA)

In the thermogravimetric analysis (TGA) technique, the mass of a substance is monitored as a function of temperature. The schematic principle of the TGA measurement is displayed in Fig. 2.4 [9]. The sample is heated in controlled atmosphere at constant heating rate. The change of mass is measured during this process. The mass loss shows the degradation of the material. TGA can determine weight loss due to the removal of residual organics and added solvent during synthesis, which is useful in selecting the suitable annealing temperature. Measurement and analysis are performed by raising the temperature of a sample progressively from room temperature to 1200 °C in different gas atmospheres such as air, nitrogen or inert gases and plotting weight percentage as a function of temperature.

![Schematic principle of TGA measurement](image)

Fig. 2.4 Schematic principle of TGA measurement [9].

2.3.2 X-Ray Diffraction

In 1912 German physicist, Max Von Laue first demonstrated X-ray diffraction (XRD) which has become a well-established, versatile, non-destructive analytical technique to identify the crystalline phases of materials and to analyze its structural properties. These days, it is widely used as a routine technique for the characterization
of the materials [10] in the fields of chemistry, mineralogy, crystallography, material science, geology, petrology, natural sciences, biological science, industries, etc. All forms of samples (powders, crystals, thin films, etc.) can be characterized.

X-rays are electromagnetic radiation of shorter wavelength and are produced when electrically charged particles with sufficient kinetic energy are rapidly de-accelerated. One of the phenomena of interaction of X-rays with crystalline matter is diffraction, produced by the reticular planes of atoms in the crystal. A crystal to diffract an X-ray beam must incident at specific angles for maxima depending on the X-ray wavelength, the crystal orientation and the structure of the crystal. For certain angles of incidence, there will be constructive interference between the scattered radiations, but destructive interference will cancel the diffracted beams for all other angles as shown in Fig. 2.5. By measuring angles at which the constructive interference takes place, it is possible to study about the geometrical ordering of the atoms inside the crystalline materials [11-13]. Each compound has its own specific XRD peaks and hence can be differentiate from one another.

![Diagram](image)

**Fig. 2.5** The phase shift causes (a) constructive and (b) destructive interferences according to the 2θ deviation.

Bragg’s law depicts a relationship between the diffraction angles (Bragg’s angle), X-ray wavelength, and inter-planer spacing of the crystal planes. The quantitative account of Bragg’s law can be expressed by Bragg’s equation as

\[
2d_{hkl} \sin \theta = n \lambda
\]

where \(d_{hkl}\) is the spacing between the crystal planes with Miller indices \(hkl\); \(\theta\) is the...
angle between the radiation and the surface; \( n \) is an integer (order of diffraction), and \( \lambda \) is the wavelength of the X-ray. Diffraction occurs when the repeated distance between scattering centers are approximately of the same order of magnitude as the wavelength of the incident radiation. The constructive interference occurs when \( n \) is an integer.

An X-ray diffractometer consists of an X-ray source, a goniometer, a sample holder and an X-ray detector. The detector motion is coupled with the X-ray source in such a way that it always makes an angle 2\( \theta \) with the direction of the incident X-ray beam as shown in Fig. 2.6.

![Schematic diagram of X-ray diffraction.](image)

The Rigaku, Miniflex-II diffractometer was used for the phase detection of bulk and nanocrystalline powders at the Centre of Excellence in Materials Science (Nanomaterials), Department of Applied Physics, Aligarh Muslim University (AMU), Aligarh. The powder XRD studies of the samples were performed using Cu-K\(_{\alpha}\) radiation (\( \lambda = 1.5406 \) Å) at room temperature. The diffractometer was operated at a voltage of 30 kV, filament current of 15 mA, within the 2\( \theta \) range of 20\(^{\circ}\) to 80\(^{\circ}\). The lattice spacing \( d_{hkl} \) was calculated using Bragg’s law (equation 2.1), which is further utilized to compute lattice constants. The analysis of the XRD patterns was done using PowderX [11] and FULLPROF softwares.
2.3.2.1 Indexing and Determining Lattice Parameter

In powder X-ray diffraction, the observed pattern comes in the form of the intensity of the diffracted rays as a function of 2θ. The indexing of pattern has been completed using the PowderX software [11, 14]. With the knowledge of the crystal structure, different a, b and c values of lattice parameters are tried so that all the diffraction peaks may be assigned (h k l) values with an error less than 5% in 2θ values.

2.3.2.2 Determination of Particle Size

The diffraction method for determination of particle size is based on the effect of broadening of diffraction peak, which is associated with the sizes of the particles. For the diffraction maxima by a crystal, the incident X-ray beam must meet the reflection plane at one of the specified angles. The X-ray diffracted from the different planes should reach to the detector in phase to produce maximum. When the number of diffracting planes is considerably large, the diffraction maxima are sharp. Smaller crystallites have less number of cooperating planes and diffraction by these planes does not produce sharp diffraction maxima. Generally, crystallites size affects the width of the diffraction peaks and larger crystallites size leads to sharper peaks. Therefore, the particle or crystallite size can be calculated using the width of the peak [15, 16]. The crystallite size was determined using the Scherrer’s equation [11]:

\[ D = \frac{k\lambda}{B_{hkl} \cos \theta_{hkl}} \]  

(2.2)

where, \( D \) is the crystallite size; \( k \) is the shape factor (~0.9) for spherical crystal; \( \lambda \) is the X-ray wavelength; \( B_{hkl} = (B_M^2 - B_S^2)^{1/2} \); \( B_M \) and \( B_S \) are the measured peak width and standard width at half maximum intensity in radian, and \( \theta \) is Bragg's angle in degrees. This formula is satisfactory for small grains in the absence of significant microstrain. It describes the relative mean square deviation of the lattice spacing from its mean value. Based on the grain size dependence of the strain, it is reasonable to assume that there is a radial strain gradient. From X-ray diffraction, a homogeneous volume-averaged value is obtained.
2.3.2.3 Rietveld Refinement

The Rietveld analysis, a full-profile approach, was originally introduced for refinement of result of neutron diffraction. Dr. H. M. Rietveld [17, 18] gave computer based procedure to use the full information of powder data for quantitative phase-analysis. The least-squares refinements are made to get best fit between step-scan data of diffraction pattern and a simulated X-ray diffraction pattern [19]. By using Rietveld analysis, the phase abundances of the constituent phases can directly be determined from the refined scale-factors. The quantitative analysis can be performed without need of experiments on standard samples to calibrate it [20-22].

The XRD simulation is using crystal structural parameters of component phases, scale factor for constituent phases, the peak profiles and the background, parameters for aberrations, effects of size-related strain, preferred orientation, particle size etc. It is not a tool for ab initio structure calculation but it slightly modifies a preconceived model based on previous knowledge. The starting parameters must be close to the final result. An appropriate data collection method ideally involves the step size, FWHM/5, where FWHM is full width half maximum. The best least square fit of thousands of observed \( y_i \)'s is performed simultaneously [22]. The least-squares refinement (LSR) leads to a minimal residual quantity \( S_y \)

\[
S_y = \sum_i W_i (y_{oi} - y_{ci})^2
\]  

(2.3)

where, \( W_i = 1/y_{ci} \); \( y_{oi} \) is observed intensity at the \( i^{th} \) step; \( y_{ci} \) is calculated intensity at \( i^{th} \) step and the sum is over all data points. Bragg reflections contribute to the intensity \( (y_{oi}) \) observed at any arbitrarily chosen point ‘\( i \)’ in the pattern. The values of \( y_{ci} \) are determined from the \( |F_k|^2 \), calculated from the structural model by taking the contributions of neighboring Bragg reflections and the background. The calculated profile of powder X-ray pattern is governed by the equation [22]

\[
y_{ci} = S \sum_k L_k |F_k|^2 \Phi(2\theta_i - 2\theta_k) P_k A + y_{bi}
\]  

(2.4)

where \( S \) is the scale factor; \( k \) represents to the Miller indices \((hkl)\) for the Bragg reflection; \( L_k \) contains the Lorentz polarization and multiplicity factors; \( \Phi \) is the reflection profile function; \( P_k \) is the preferred orientation function; \( A \) is an absorption factor; \( F_k \) is the structure factor for the \( k^{th} \) Bragg reflection and \( y_{bi} \) is the background intensity at \( i^{th} \) step.
Least square minimization procedures lead to a set of normal equations involving derivatives of all calculated intensities, $y_{ci}$, with respect to each adjustable parameter and are soluble by inversion of normal matrix with elements $M_{jk}$ given by the following equation

$$M_{jk} = \sum_i 2w \left[ (y_{oi} - y_{ci}) \frac{\partial^2 y_{ci}}{\partial x_j \partial x_k} - \left( \frac{\partial y_{ci}}{\partial x_j} \right) \left( \frac{\partial y_{ci}}{\partial x_k} \right) \right]$$  

(2.5)

where the values of adjustable parameters $x_j$ and $x_k$ are same set and are given by equation

$$x_k = \sum_j M_{jk}^{-1} \frac{\partial S_y}{\partial x_j}$$  

(2.6)

where symbols have their usual meaning. The calculated shifts are applied to the initial parameters to produce improved fitting and the whole procedure is repeated. It is important to judge, whether to keep a parameter turned on for refinement or to turn it off to prevent the refinement from ‘blowing up’. Simultaneous refinement of highly correlated parameters causes this problem and must be avoided. For example, occupancies and displacements parameters should not be simultaneously refined. Similarly, the overall scale factor should not be refined at the same time as the occupancy factors of all the atoms [22]. One among these parameters must be fixed. The fit must be evaluated by visual comparison of calculated and experimental pattern. However, some numerical constraints are necessary to judge the refinement is proceeding satisfactorily and when it should be stopped. Several R-values can be used to evaluate the fit: structure factor ($R_F$), Bragg factor ($R_B$), pattern factor ($R_p$) and the weighted profile factor ($R_{wp}$). The FULLPROF 2000 software program is used and the refinement strategy is as follows [22].

- Scale factor - stable.
- Specimen displacement - stable.
- Lattice parameters - stable
- Flat background - stable.
- Atomic coordinates x, y, z - stable.
- More background - stable.
- $W$, in the Caglioti function for peak widths - poorly stable.
- Occupancies and isotropic (thermal) displacement parameters - generally not stable.
- U, V in the Caglioti function and other profile parameters - generally not stable.
- Anisotropic (thermal) displacement parameters - generally not stable and zero point stable.

2.3.3 Field Emission Scanning Electron Microscopy (FESEM)

FESEM is widely used technique to get topographical features, surface morphology, crystal structure, crystal orientation, presence and location of defects as well as dimension, shape and density of the particles [23]. In FESEM, electrons are liberated from a source and are accelerated in a high electrical field gradient within the high vacuum column \((10^{-4} \text{–} 10^{-10} \text{torr})\). The accelerated beam of electrons (mono-energetic) having energies in the range of few hundred of eV to tens of keV, so-called primary electrons, is focused with the help of electromagnetic lens to produce a narrow scan beam that bombards the object. Secondary electrons are emitted from each spot on the object. These are detected to produces an electronic signal. The surface of the sample is scanned over an area. The obtained signal conveys information about the morphology of the sample. Some of these electrons get scattered elastically from the coulomb field of the nucleus whereas some electrons inelastically scattered from the electrons of the host atoms giving secondary or auger electrons. These auger electrons bare characteristic of the element from which they are emitted [23]. The secondary electrons, detected by a detector every position of the incident electron beam, are used to form an image. The collected signal is amplified and is made to form synchronous image on a cathode ray tube. A camera is used to capture the image or it may be digitized and processed on a computer. A schematic diagram of typical scanning electron microscope is given in Fig. 2.7.
In this technique, the sample should be conductive. Surface of non-conductive samples are made conductive usually by coating a thin layer of gold. The beam current and the final spot size determine the depth and resolution of field of the image respectively, which are adjusted with one or more condenser lenses and the probe forming objective lenses. The electrons interact with the sample from few nanometers to several microns of the surface of the sample depending on the beam parameters and the sample type. Primarily, electrons are emitted from the sample as either backscattered or as secondary electrons, and are detected by scintillation photomultiplier detector. Secondary electrons have the energy of 3–5 eV and are generally used for the visualization of surface morphology and roughness, as they can spot the exact position of the beam on the sample surface and give morphological information with high resolution [23]. FESEM has following advantages

- FESEM produces clearer and less distorted images with spatial resolution down to 1.5 nm, which is 3 to 6 times better than conventional scanning electron microscopy (SEM).
- Smaller-area contamination spots can be examined at electron accelerating voltages compatible with energy dispersive X-ray spectroscopy (section: 2.3.4).
Reduced penetration of low kinetic energy electrons probes closer to the material surface.

High quality and low voltage images are obtained with negligible electrical charging of samples.

Small variations of trace element can be detected.

Oil-free vacuum.

In the present work, morphological and microstructural features of Ti$_{1-x}$Cr$_x$O$_2$ and Ti$_{1-x}$Co$_x$O$_2$ ($x = 0.00, 0.03, 0.05$ and $0.07$) NPs samples were investigated with a FESEM (Bruker - NANO NOVA 450) at Jamia Millia Islamia University, New Delhi, India.

2.3.4 Energy Dispersive X-Ray Spectroscopy (EDX or EDS)

EDS or EDX is an analytical technique used for the compositional analysis. It is based on the analysis X-rays emitted by the sample when it is struck with charged particles. Every element has a unique atomic structure, allowing X-rays that are characteristic of the atomic structure [24]. There are four main components of the EDS set up: (1) beam source; (2) X-ray detector; (3) pulse processor; and (4) analyzer. EDS systems are usually equipped with a SEM or FESEM, sometimes with TEM or electron microprobes. However, a number of free standing EDS systems are also available. Since 1960, SEMs have been equipped with elemental analysis capabilities. A detector is used to change X-ray radiation into voltage signals, which is sent to a pulse processor. It measures the signals and surpasses them onto an analyzer for showing compositional data analysis [23]. The most common detector is silicon drift detectors (SDD) attached with Peltier cooling systems or cooled using liquid nitrogen. The EDS detector arranges the X-ray signal according to the energy and produce elemental images. Therefore, SEM or FESEM can detect the spatial distribution of a particular element. EDS is one of the alternatives of X-ray fluorescence (XRF).

In the present work, elemental analysis of undoped, Cr and Co doped titania were probed using EDS equipped with the FESEM system at Jamia Millia Islamia University, New Delhi, India.
2.3.5 Transmission Electron Microscopy (TEM)

In 1925, Busch discovered an inhomogeneous, rotationally symmetric magnetic field, which acts as a lens for an electron beam. Ernst Ruska and Max Knoll used electron beam for producing enlarged images in 1932 and the first commercial TEM was made available in 1939 [25]. It has been mass-produced since the beginning of the 1950s. The basic principle of working of TEM is same as the light microscope but it uses electrons instead of light. The wavelength of energetic electrons is much smaller than that of light. Therefore, the resolution attainable in TEM is many orders of magnitude higher than that of a light microscope. In SEM or FESEM the electron beam generates from the surface of specimen or sample. However, TEM is a system where an electron beam interacts and passes through an ultra thin specimen and image of internal structure of crystal is formed as bright-dark image. The TEMs can resolve the finest details of the sample.

There is a great variety of TEM depending on its specific characteristics.

- Conventional transmission electron microscope (CTEM) detects only the transmitted electrons.
- High resolution transmission electron microscope (HRTEM) can detect electrons diffracted at a wide range of angles.

Simplified schematics of a TEM are shown in Fig. 2.8. The basic parts in a TEM are the electron gun, vertical column and fluorescent screen [25]. The electron gun, which generates the accelerated electron beam, is attached to the top of the microscope. In the electron gun, thermal emission, indirect heating or field emission can produce the electrons [26]. Thermal emission is the most usual method in conventional TEM; whereas indirect heating and field emission are used in high-resolution transmission electron microscope (HRTEM) because they give a greater intensity. Materials with either a high melting point (tungsten) or those with a low work function (LaB₆ and WZr) are used for the source of electrons. For field emission, monocrystal of tungsten are used as shown in the inset of Fig. 2.8. Beam is accelerated by means of a voltage applied between the filament and an anode as shown in Fig. 2.8. In the vertical column, the electron beam interacts with the sample.
and the first images are formed. An excellent vacuum system is needed to ultra high vacuum in order to prevent crashing between the electrons of the beam and air gases.

**Fig. 2.8** Schematic diagram of basic component of a transmission electron microscope.

The principle of working of TEM is simple. The beam of electrons emitted from the electron gun is focused to get fine energetic beam by the use of the
condenser lens, which is restricted by the condenser aperture to eliminate high angle electrons. Groups of electromagnetic lenses are used to focus the beam and resolve the image [25]. This magnetic lens produces intense magnetic field that acts as a thin convex lens for electron beam. When the electron beam strikes the specimen and it is transmitted. Its transmission depends upon the thickness and electron transparency of the sample. The transmitted electrons are focused by the objective lens into an image on phosphor screen or charge coupled device (CCD). The sample must be very thin because transmitted electrons through the sample are detected and image of internal structure of crystal is formed.

The complimentary imaging, diffraction and spatial resolution microanalysis techniques in TEM provides the information about the crystal structure, size and shape of nanomaterials. The TEM can also produce diffraction image of the sample that allows better characterization of the sample. Of course, for this purpose microscope needs ultra high vacuum in order to prevent crashing between the beam of electrons and the atoms of the air gases. The selected area electron diffraction (SAED) produces complete circular bright ring pattern similar to XRD that can be used to analyze the purity of phase of the samples [27].

The resolution of microscope depends on the wavelength of the radiation employed. Smaller is the wavelength of the radiation greater is the resolution. An important advantage of the TEM is its excellent horizontal resolution. In TEM, the incident radiation is a beam of electrons that has a wavelength

\[
\lambda \text{(nm)} = \sqrt{\frac{1.5}{V}}
\]  

(2.7)

where V is the voltage (in volts) applied to accelerate the electrons. The interaction between the incident beam of electrons and the sample is not only superficial but in a certain volume of the sample. This volume is greater at greater acceleration potentials but is smaller at greater average atomic number of the sample.

In the present study, TEM micrographs, SAED pattern and HRTEM images of pure as well as Cr and Co doped titania nanoparticles were captured with a JEOL, JEM-2100 at the University Sophisticated Instrument Facility (USIF), Aligarh Muslim University, Aligarh, India.
2.3.6 Fourier Transformation Infrared (FTIR) Spectroscopy

Optical spectroscopy has been widely used for the characterization of nanomaterials. Infrared (IR) spectroscopy is a most popular characterization tool to measure IR frequencies absorbed by a sample when it is kept in the path of an IR radiation source [28]. Transitions between the vibrational levels result in infrared spectroscopy of molecules. Each molecule has its own unique signatures. The information regarding structure, symmetry, bond strength, inter and intra molecular interactions etc., are obtained from IR spectra. Therefore, IR spectroscopy is employed to identify the type of bonds between atoms of a molecule and consequently identifies functional groups. Solid, liquid and gaseous all samples can be characterized by this technique.

An IR spectrometer contains a source, a monochromator and a detector. The ideal IR source gives a continuous and high radiant energy output over wide IR region. The two most commonly used sources are the Nernst Glower and the Globar [29]. The deuterated triglycine sulfate (DTGS), L-alanine doped deuterated triglycine sulfate (DLaTGS), mercury cadmium telluride (MCT) etc., are commonly used detectors in IR spectroscopy. DTGS detectors have significantly lower sensitivity than MCT detectors, which have to be cooled typically using liquid nitrogen. The basic description of the sources, monochromators, filters and detectors are given in the book of Colthup et al. [29] and the references therein.

IR spectroscopy is widely used for measurement of vibrational frequencies, molecular structure, chemical analysis and molecular interactions. It is also used to identify the ligands attached to nanoparticles. Generally, all organic compounds absorb IR radiation, but inorganic materials are less commonly characterized as heavy atoms show vibrational transitions in the far IR region which requires different beam splitter and detector. Some vibrations show extremely broad peaks due to presence of some interactions that hampers the identification of the particular functional groups. Moreover, the peak intensities of some ionic inorganic compounds may be too weak to be detected [30, 31].

The entire infrared spectrum of polyatomic molecule can be divided into functional group region and the fingerprint region. The functional group region is generally considered from 4000 cm\(^{-1}\) to 1500 cm\(^{-1}\). The fingerprint region exits.
within the wavenumber range 1500 cm\(^{-1}\) to 400 cm\(^{-1}\) [32]. The fingerprint region involves usually bending vibrations that are characteristic of the entire molecule or large fragments of the molecule and are used for identification. The functional group region includes generally stretching vibrations, which are more localized and characteristic of the typical functional groups found in organic molecules [33]. These bands are not very useful to confirm identity. They provide some very useful information about components of the sample.

**Fig. 2.9 A schematic diagram of FTIR spectrometer.**

At the present time, Fourier transformation infrared (FTIR) spectrometer has replaced conventional IR spectrophotometers. A schematic diagram of FTIR spectrometer is shown in Fig. 2.9. In FTIR, the dispersive device, prism or grating monochromator, is replaced by Michelson interferometer. The beam splitter splits the radiation into two beams that are reflected back from mirrors to beam splitter. The recombined beams at beam splitter produce interference. If beam passes through sample, absorptions cause gaps in frequency distribution. One mirror of the interferometer is moved toward and away from splitter at constant speed. The detector sees a time domain signal (called interferogram) which is converted into frequency domain spectrum by Fourier transform using software and computer. It is more faster
and sensitive system than the older dispersive instruments. FTIR measurement has high resolution, high signal to noise ratio and better accuracy.

The Perkin Elmer FTIR spectrometer (Spectrum 2) were used in the thesis work to characterize $\text{Ti}_{1-x}\text{Cr}_x\text{O}_2$ and $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ ($x = 0.00, 0.03, 0.05$ and $0.07$) NPs. In case of powder, sample is compressed into a thin KBr pallet. FTIR spectra of the samples were recorded in the range of 4000 to 400 cm$^{-1}$ at the Department of Applied Physics, AMU, Aligarh.

2.3.7 Raman Spectroscopy

Raman spectroscopy is a sensitive, fast and nondestructive technique. It is one of the most effective tools for detecting the phase, crystallinity, incorporation of dopants and the resulted defects as well as lattice disorder of the sample. This technique is based on inelastic scattering of monochromatic light usually from a laser source. When intense monochromatic radiation is incident on samples, the scattered radiation contains the same frequency as that of the source (Rayleigh radiation), higher frequencies (anti-Stokes radiations) and lower frequencies (Stokes raditions) [34, 35]. This process is called Raman effect. Since, Raman lines appears at different frequencies from the incident one, the shifts from Rayleigh line are also called Raman shifts (cm$^{-1}$). They are independent of the excitation wavelength. The shifts provide the information about the vibrational and rotational structure of molecules.

![A schematic diagram of micro Raman spectrometer.](image-url)
A Raman system consists of the components [29]: Intense monochromatic excitation source such as laser, sample illumination system, light collection optics, monochromator or interferometer and detector (CCD or PMT). A schematic diagram of micro Raman spectrometer is shown in Fig. 2.10. A conventional optical microscope is added in Raman setup. It has the advantages of easy handling of samples, requirement of low power laser and Raman mapping. It is used for the identification of material microstructural phase, microstructural disorder and their analysis. A Raman spectrometer (Renishaw, UK), which is sensitive for ultra-low signal detection with spectral resolution of 0.2 cm\(^{-1}\) attached with Ar ion laser of wavelength, 514.5 nm and power, 50 mW. It was used in this thesis work to analyze Ti\(_{1-x}\)Cr\(_x\)O\(_2\) and Ti\(_{1-x}\)Co\(_x\)O\(_2\) (x = 0.00, 0.03, 0.05 and 0.07) NPs at Inter University Accelerator Centre (IUAC), New Delhi, India.

### 2.3.8 UV–Visible Spectroscopy

Absorption and emission spectroscopy are powerful nondestructive techniques to investigate the optical properties of semiconductors as the optical properties of semiconductor are generally determined by its electronic structure. Ultraviolet-visible (UV-vis) absorption spectroscopy is widely used to characterize organic and inorganic molecules, polymers, transition metal ions, supermolecules, nanoparticles, bulk materials, etc. The sample for investigation is irradiated with the UV-vis radiation. The absorption of photons excites the molecule to excited electronic states. The absorbed light is analyzed using a spectrophotometer to give absorption spectrum [36, 37]. Size dependant properties can be observed in the spectrum. Due to broadening and shifting of peak, the spectrum of the nanomaterials is different from their bulk counterparts. The absorption spectrum of nanocrystals is broadened due to quantum confinement effects [38, 39]. The absorption peaks of semiconductor nanoparticles shift towards the smaller wavelengths as their crystal size reduces [39-42]. Electronic transitions and energy band gap of a material can be obtained using UV-visible spectroscopy technique. Energies associated with the UV-visible radiations are sufficient to excite molecular electrons to higher energy states [43, 44].

Fig. 2.11 shows a typical UV-vis absorption experimental arrangement for a liquid sample. A beam of light is splited into two beams. One of which passes through
the solution of sample and the other passes a reference containing solvent [45]. The two beams, after transmission through the sample and reference, are compared at detector. The difference between the signals is measured. Liquid samples are usually contained in a fused quartz cuvette, which is transparent to both UV and visible lights. This double beam technique has many advantages over single beam measurement such as compensation of intensity fluctuation of source as well as subtraction of solvent and cuvette absorption.

![Diagram of UV-visible spectrophotometer](image)

**Fig. 2.11** A schematic representation of UV-visible spectrophotometer used for the thesis work.

In the present study, an UV-vis spectroscopy system, Perkin Elmer - Lambda 35, was used for this work to analyze Ti$_{1-x}$Cr$_x$O$_2$ and Ti$_{1-x}$Co$_x$O$_2$ ($x = 0.00, 0.03, 0.05$ and $0.07$) NPs at the Department of Applied Physics, AMU, Aligarh.

### 2.3.9 Photoluminescence (PL) Spectroscopy

Photoluminescence (PL) spectroscopy is nondestructive technique to study optical characteristic of materials [46]. It is suitable for the characterization of both organic and inorganic materials and the samples can be in solid, liquid, or gas. In photoluminescence spectroscopy, incident light is absorbed by molecule and emitted radiations from molecules are analyzed [46]. The emitted photons correspond to the
energy differences between the states involved in transitions. The fluorescence from sample is characterized using four parameters of the spectrum: intensity, emission wavelength, bandwidth of the emission peak, and the emission stability [47]. The fluorescence of material also depends on ambient environments. As dimensions of the sample are reduced to the nanoscale, the properties of PL emission can change. A size dependent shift in the emission spectrum can be observed. The PL spectroscopy is used to study properties of the material such as band gap, recombination mechanisms, oxygen vacancies, impurity levels etc. [48].

![A schematic representation of PL spectrophotometer set up.](image)

**Fig. 2.12** *A schematic representation of PL spectrophotometer set up.*

A typical fluorescence spectroscopy setup is shown in Fig. 2.12. The light beam from source passes through excitation monochromator which select the required wavelength from continuum source generally xenon lamp. The radiations fall on the sample. This incident light excites the material under study and its de-excitation causes photoluminescence, which is emitted in all directions. The emitted light arrives at the detector after passing through an optional emission monochromator [45] which scan the spectrum of the sample. Generally, an emission spectrum is recorded, where the sample is irradiated with appropriate wavelength and the intensity of the fluorescence emission is recorded as a function of wavelength. To record an excitation spectrum, the emission monochromator is set at the desired wavelength,
generally the emission maximum. The excitation monochromator is scanned. The fluorescence of a sample can also be monitored as a function of time, after excitation by a flash of light. This technique is called time resolved fluorescence spectroscopy. It gives lifetime of excited states. A Perkin Elmer LS-55 fluorescence spectrometer is used for this thesis work to recording the fluorescent emission spectra of Ti$_{1-x}$Cr$_x$O$_2$ and Ti$_{1-x}$Co$_x$O$_2$ (x = 0.00, 0.03, 0.05 and 0.07) NPs at the Department of Applied Physics, AMU, Aligarh.

2.3.10 Transport Measurement

The electrical transport properties, specifically dielectric properties, have been carried out as a function of frequency and temperature.

2.3.10.1 Dielectric Setup

Basically, dielectric properties of the synthesized samples were studied using LCR meter (Agilent - 4285A) with two-probe setup as shown in Fig. 2.13 at the Department of Applied Physics, AMU, Aligarh. Frequency dependent dielectric properties in the range 75 kHz - 5 MHz at room temperature and temperature dependent dielectric properties from room temperature to 450 °C at constant frequencies can be performed using this setup.
For dielectric measurement, the samples of diameter 12.9 mm with thickness 1.2 mm, were palletized and were sintered at 450 °C for 6 hrs. The pallets were coated on opposite faces with silver paste to form a parallel plate capacitor with the synthesized product acting as dielectric medium. There are various quantities for explaining dielectric properties.

2.3.1 Dielectric Constant

The response of materials in an alternating electric field is characterized by a complex dielectric constant ($\varepsilon^*$) defined as

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$  \hspace{1cm} (2.8)

where, $\varepsilon'$ and $\varepsilon''$ are the real and imaginary part of the dielectric constant respectively. The real part of the dielectric constant $\varepsilon'$ is associated with the ability of a material to store energy in the electric field inside material. The imaginary part $\varepsilon''$ is associated with the ability of the material to absorb or dissipate energy. The value of frequency dependent real part of the dielectric constant ($\varepsilon'$) has been calculated using the expression [49]

$$\varepsilon' = \frac{C_p d}{\varepsilon_o A}$$  \hspace{1cm} (2.9)

where, $C_p$ is the capacitance of the material in Farad (F); $\varepsilon_o = 8.854187 \times 10^{-12}$ F/m is permittivity of free space; A is the cross sectional area of the flat surface and $d$ is the thickness of pellet. The imaginary part of dielectric constant, $\varepsilon''$, can be calculated from the equation

$$\varepsilon'' = \varepsilon' \tan\delta$$  \hspace{1cm} (2.10)

where, $\tan\delta$ is the dielectric loss.

2.3.2 Dielectric Loss

The dielectric loss factor ($\tan\delta$) is the ratio of the imaginary and real parts of dielectric constant and it is expressed by equation,

$$\tan\delta = \frac{1}{2\pi f \varepsilon_o \varepsilon' \rho}$$  \hspace{1cm} (2.11)

where, $f$ is the frequency of the applied ac field and $\rho$ is the resistivity of the dielectric material. The dielectric loss occurs due to lagging of the polarization behind the applied a.c. field as well as by the impurities and imperfections in the crystal lattice.
The material density also plays a crucial role in the difference of dielectric constant. High porosity and low density results in low dielectric constant and dielectric losses [50].

### 2.3.10.4 A.C. Conductivity

The electrical conductivity is a measure of a material’s ability to conduct an electric current. The total electric conductivity of any system is the sum of the d.c. conductivity and a.c. conductivity and is written by the following relation [49]

\[
\sigma = \sigma_0(T) + \sigma(\omega, T) \tag{2.12}
\]

where, \(\sigma_0(T)\) is termed as d.c. conductivity which is frequency independent part. The second term, \(\sigma(\omega, T)\), is temperature as well as frequency dependent function, and it is related to the dielectric relaxation caused by the localized electric charge carriers or due to the hoping between the two ions. However, the a.c. conductivity is investigated as a function of angular frequency of applied field \((\omega = 2\pi f)\) using the relation [50]

\[
\sigma(\omega, T) = \sigma_{ac} = \varepsilon_0 \varepsilon' \omega \tan \delta \tag{2.13}
\]

### 2.3.11 Magnetic Measurements

The study of magnetic properties of materials is a basic requirement for understanding magnetism in condensed matter physics. There are so many techniques for knowing magnetic properties of the material under study. To verify the presence of the magnetic phase and the kind of magnetic order, field dependent magnetization (M-H) of the synthesized samples was investigated using vibrating sample magnetometer (VSM) and superconducting quantum interference device (SQUID) magnetometer. Temperature dependent magnetization (M-T) measurement was also performed with the SQUID magnetometer.

#### 2.3.11.1 Vibrating Sample Magnetometer (VSM)

VSM is the equipment for the determination of the magnetic properties of magnetic samples [51]. Foner developed the VSM in the late 1950s [51]. It is based on Faraday’s law induction according to which an e.m.f. is induced in a conductor by time varying magnetic flux. An illustration of VSM is shown in Fig. 2.14 [52].
Fig. 2.14 Schematic block diagram for the VSM setup.

In this setup, a magnetized sample vibrates sinusoidal at small constant amplitude with respect to stationary pick-up coils. When a magnetic material is subjected to a homogeneous magnetic field, a dipole moment is induced in the sample, which is made to vibrate perpendicular to the uniform magnetic field of an electromagnet. An electrical signal is induced in pick-up coils around the sample [52]. From measurement of this voltage, the magnetic properties of sample can be determined because the induced voltage is proportional to induced magnetic moment in the sample under investigation. To get the magnetic moment of the sample, a second voltage is induced in the reference coil by a vibrating reference sample using same transducer. The sample and reference are driven synchronously by a common transducer. The phase and amplitude of the resulting voltages are directly related. Two signals are given to two inputs of a differential amplifier to cancel the effects of amplitude and frequency of vibration. The output of the differential amplifier is a function of only the magnetic moment of the sample [52, 53]. It is applied to lock-in amplifier, where it is compared with a reference signal, and is also applied to transducer which oscillates the sample [53]. Therefore, the output signal is proportional to amplitude of the magnetic moment. This signal is then amplified and used in two different ways. One part is fed back to the movable plate assembly of the
vibrating capacitor and second part is applied to the output display circuits, where the amplitude of the moment is recorded. The effect of the feedback is to adjust automatically the signal to required level to maintain the capacitor output signal at the same level as the signal pickup coil.

In the present study, the VSM set up (at Department of Physics, Himachal Pradesh University, Shimla, India) was used for the measurement of magnetic field dependent magnetization (M vs H) of Ti$_{1-x}$Cr$_x$O$_2$ and Ti$_{1-x}$Co$_x$O$_2$ (x = 0.00, 0.03, 0.05 and 0.07) NPs at room temperature.

### 2.3.11.2 Superconducting Quantum Interference Device (SQUID)

A common use of Josephson junction is in SQUID. It consists of closed superconducting loop including one or two Josephson junctions in the loop's current. SQUID is capable of resolving changes of external magnetic field of $10^{-15}$ tesla. It does not detect directly the magnetic field from the sample. Its function as highly linear current to voltage converter. SQUID magnetometer can be used to measure small magnetic moment of the order of $10^{-6}$ emu [54]. In this magnetometer, a magnetic sample passes through a set of sensing coils which are superconducting coils separated by thin (> 30 Å) insulating layers (Fig. 2.15) called Josephson junctions. Cooper pairs in superconductors could tunnel through an insulating layer between the superconductors [55]. The pair tunneling constitutes a super current below the critical current and no voltage is developed across the junction. However, a voltage appears for currents greater than the critical value. The presence of the thin insulating layer typically restricts the value of the super current flowing in the coil to a value less than $10^{-5}$ A.

Most of the low T$_C$ SQUIDs are made from Niobium thin films that have a transition temperature around 9.25 K and are also mechanically very stable. Tunnel junctions are patterned from Nb/AlO$_x$/Nb trilayers in which an AlO$_x$ barrier is formed by oxidization of a few nanometers of aluminum [56]. Fig. 2.15 shows a schematic of a Josephson junction.
Fig. 2.15 Schematic diagram of SQUID and Josephson junction consisting of two superconductors separated by thin insulating layers.

There are two types of SQUIDs. The RF SQUID based on the AC Josephson effect contains a single Josephson junction inserted into a superconducting loop, while, the DC SQUID, based on the DC Josephson effect, has two Josephson junctions connected in parallel on a superconducting loop and is operated in the voltage state with a current bias. The sample is placed in a superconducting pick-up coil that is connected to the actual SQUID. Since the magnetic flux through a superconducting ring is quantized, the sample will induce a super current in the pick-up coils that will keep the flux at a constant value.
In the present study field dependent magnetization (M-H) at 300 K and temperature dependent magnetization (M-T) measurements of Ti$_{1-x}$Cr$_x$O$_2$ and Ti$_{1-x}$Co$_x$O$_2$ (x = 0.00, 0.03, 0.05 and 0.07) NPs. (details are in Chapter 4 and 6) were performed using SQUID magnetometer (MPMS SQUID VSM - 050, Quantum design, USA) at Department of Physics, University of Calcutta, Kolkata, India.
References


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