CHAPTER II

Principles of Various Characterization Techniques used in the Present Investigation
2.1 Introduction:

This chapter includes different techniques used for characterizations of synthesized oxide materials.

2.2. Thermal analysis techniques:

Thermal analysis techniques are the most powerful experimental tools developed during the last century. In these techniques the changes in the properties of material are followed as a function of temperature when it is heated at the constant predetermined rate under specified ambient atmospheric conditions. The measured properties include mass, energy, dimension, modulus of elasticity, dielectric constant etc. which change with temperature. Each of the thermal technique is identified with the property measured. Several books and monographs are available providing in depth coverage of the techniques [1-6]. TG, DTA, DSC and TD are most commonly and more frequently used thermal analysis techniques. Among these techniques we have used TG and DTA.

2.2.1. Thermogravimetry (TG):

Thermogravimetry is defined as “technique in which the mass of the sample is monitored as a function of temperature or time when it is subjected to a programmed temperature change in specified atmosphere”. A typical TG curve depicting mass loss type reactions is shown in fig.2.1(b). In TG the mass change in the sample is recorded continuously as a function temperature to avoid the possibility of missing any step correspond to the formation of weakly stable intermediates, stable over a limited temperature range. The plot of mass change versus temperature is termed as thermogravimetric or TG curve. A derivative of thermogravimetric curve is termed as DTA and useful in resolving the partially overlapping multistep reactions involving the formation of weakly stable intermediates. The ordinates of DTA plot represents rate of mass change (d∆m/dT) and temperature T is plotted abscissa. fig.2.1(a) represents the DTA curve. fig.2.1 TG curve can be described by characteristic temperatures called the inception temperature (T_i) and the final temperature (T_f). The temperature T_i refers to that temperature at which the cumulative mass change of the sample exceeds the sensitivity of the recording system and the plot begins to show the departure from the horizontal baseline and T_f represents the temperature at which reaction is complete. The difference in the steady baseline before and after the
transformation gives the mass change in DTA is evaluated from the area under the peak.

![DTA and TG curves](image)

**Fig. 2.1: Typical (a) DTA and (b) TG curve.**

Both TG and DTA curves are influenced by several instrumental factors such as heating rate, sample size, ambient atmosphere, type of sample holder and sample characteristics such as particle size etc.[1-3,7].

### 2.2.2. Differential Thermal Analysis (DTA):

DTA is a technique in which the temperature difference (ΔT) between the sample and a thermally inert reference material are continuously recorded as a function of furnace temperature (T_f), or time (t), sample temperature (T_s) and reference temperature (T_r). The schematic diagram of a differential thermal analyzer and typical DTA curve are shown in fig. 2.2 and 2.3 respectively. The initiation temperature represents the temperature where the DTA signal begins to deviate from a steady base line. The extrapolated onset temperature (T_o) corresponding to the point of intersection of the base line with the tangent drawn to the rising part of the DTA curve at the point of maximum slope is often preferred to the initiation temperature.
The peak temperature indicates either the end of the reaction or transformation or the temperature at which the rate of transformation is maximum and finally \( T_f \) denotes the temperature at which the signal returns to the base line. The temperature changes in the sample can be due to enthalpy changes caused by phase transitions, fusion decomposition reaction, oxidation or reduction reactions etc. The nature of the DTA curve and the magnitude of the peak depend on a large number of instrumental factors and also on sample characteristics.
In present investigation Universal V2 4f TA instruments was used. The instrumental factor that influences the DTA signal are the geometry and material of the sample holder, nature of the thermocouple and its location, the heating rate and the atmosphere around the sample. The sample characteristics like the particle size, amount of sample used, its heat capacity, thermal conductivity and packing density also play an important role in affecting the DTA curve. Delineation of phase boundary using DTA is done by measuring evolution or absorption of heat accompanying phase changes, when the sample is heated or cooled at constant rate. The phase changes correspond to the melting and freezing of pure compounds or eutectics.

The DTA instrument requires calibration for both temperature and enthalpy. Several standard materials like pure materials and well characterized compounds have been recommended for these purposes. The melting point of metals like In, Zn, Sn, Sb, Ag and Au and phase transitions in Li₂SO₄, BaCO₃ etc. can be used for temperature calibration. Enthalpy calibration can be done using the heats of solid – solid transitions or fusion of the above materials or organic compounds of high purity.

2.3. X-Ray Diffraction (XRD) analysis:

The X-ray diffraction technique is most extensively used for characterization of different crystalline solids. The position and intensities of X-ray diffracted by a crystalline solid can provide a lot of information such as crystals structure, composition of solids, particle size, evidence of decomposition, polymorphism, preferred orientation, disorder and so on. X-rays are a form of electromagnetic radiation of very short wavelength ranging from 1 to 100 Å. X-rays are produced when high speed electrons are suddenly stopped by solid object. These rays are generated with the help of X-ray tube the electrons are produced by an electrically heated tungsten filament and accelerated towards the target by applying a large potential difference between filament and target. These high speed electrons are stopped by the atoms of the target resulting in X-rays being produced from the surface of target. Pure transition metals having atomic number such as Mo, W, Cr, Fe, Mn and Cu are used as target materials. The electron on hitting the target has sufficient energy to displace an electron from target atom. This produces an unstable ion and electron the outer shell drops into vacant position. This transition is accompanied by the emission of a characteristic photon of a definite wavelength known as X-ray.
The phenomenon of diffraction occurs when light is passed through a narrow slit or grating consisting of parallel slits. In a crystal, different atoms and molecules are arranged in different planes in a systematic and repetitive manner. These inter-planar distances are of the same order of magnitude as the wavelength of the characteristic X-rays emitted by target. Hence the crystal planes act as a diffraction grating to the X-ray and diffraction occurs.

The necessary condition for X-ray diffraction to occur is represented by Bragg’s equation 2.1.

\[ n \lambda = 2d \sin \theta \]  

Where \( n \) is integer (1, 2, 3, 4, …) called order of refraction, \( \theta \) is glancing angle of incident X-ray beams on crystal surface, \( d \) is inter-planar spacing between crystals planes and \( \lambda \) is the wavelength of X-rays.

The path difference between the two monochromatic parallel beams after diffraction can be shown to be \( 2d \sin \theta \) and can be seen from the ray diagram presented in fig. 2.4.

When narrow X-ray beam strikes the surface of the crystal like NaCl at glancing angle \( \theta \), it means array of ions in parallel planes AA, BB, separated by distance ‘d’. The incident ray LM is reflected as MN from the plane AA, and the incident ray PQ is reflected as QR from the plane BB and so on. The second ray PQR has to travel a longer path than the first ray LMN, the extra path being SQT which from geometry of the crystal planes and the laws of optical reflection is just \( 2d \sin \theta \). If the two reflected rays are to be in phase to reinforce each other, the path difference has to be an integral multiple of \( \lambda \), the X-ray wavelength. Diffraction would only occur if the Bragg’s equation is obeyed for a particular family of planes. Although the crystal contains a number of families of plane it would be mere chance that particular family was at the correct angle \( \theta \) to satisfy the Bragg’s equation. If the crystal is rotated, then sooner or later a position would be reached when the particular family of planes would satisfy Bragg’s condition.
Fig. 2.4: Schematic representation of Bragg’s law.

In the powder XRD Pattern, the intensity of the diffracted beam is plotted against 2θ. The relative intensity of reflections depends upon the atomic number of atoms, the arrangement of atoms within the unit cell, the unit cell volume of diffracting crystal and the absorption of X-rays by crystal. In X-ray diffraction pattern from the position of the reflection observed size and shape of unit cell can be determined. There are two different ways of obtaining X-ray diffraction data 1. X-ray powder photograph by employing the powder camera and 2. X-ray powder diffraction pattern employing powder diffractometer. The diffractograms were recorded within the range of 20 between 10° and 100°. For cubic spinel structure the interplaner distance ‘d’, the lattice constant ‘a’ and the Miller indices (hkl) of reflecting planes are related [8] by the equation 2.2

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]

2.2

Where, \( a \) = Lattice parameter

In cubic system lattice parameter can be obtained by using following equation 2.3,

\[
a = \frac{\lambda}{2 \sin \theta} (h^2 + k^2 + l^2)^{1/2}
\]

2.3

Knowing the value of lattice parameter (a) and the indices (hkl) interplaner distance (d) for other planes were calculated by usual procedure.
2.3.1. X-ray Powder photograph:

In this technique, one obtains the complete spectrum and the results of the diffraction are visible on the film after development. The intensity data obtained by this method is much more accurate as all the planes in the crystal are exposed to X-ray radiation repeatedly. The powder photograph of X-ray diffractogram serves as fingerprint in the identification of the compound. Although the film techniques are capable of producing X-ray powder diffraction data, it is time consuming. In addition to long exposure times and time spent in processing the film, it takes several hours to measure the pattern and perform the subsequent calculations for derivation of $\theta$ and d values.

2.3.2. X-ray powder Diffractometer:

In powder diffractometer it is possible to scan the whole spectrum as well as only the part of spectrum of interest. The intensity data obtained by this method is less accurate as compare to that from the photographic method. In contrast, the powder diffractometer can produce data in less than half an hour and is less time consuming.

Typical layout of powder diffractometer is shown in fig. 2.5. A flat specimen is mounted on a turntable around which moves a detector. As the sample rotate, the angle $\theta$ between the incident beam and sample changes. Whenever Bragg’s condition is fulfilled, X-rays are reflected to the detector. The detector is connected to the specimen table and geared in such a way that when the table rotates through $\theta$ degrees, the detector rotates through 2 $\theta$ degrees. This results in the detector being always in the correct position to receive rays reflected by sample. To record the diffraction pattern, the detector is positioned at or near $0^\circ$ on the graduated 2 $\theta$ scale, and then driven by a motor at constant speed e.g. $2^\circ$ per minute. Alternatively, the detector may be driven clockwise from about $170^\circ$. The X-rays reaching the detector are registered and displayed on a paper chart recorder as a series of peaks.
A typical diffraction pattern is shown in fig.2.6. Such a pattern is referred as diffractometer trace. A linear intensity scale is used in recording the trace. Also 2θ degree scale is print automatically. If only approximate intensities are required e.g. for qualitative phase analysis, it is normal practice to measured the peak height above the background in mm and to scale the values up or down such that the tallest peak has a value of 100. If the accurate values of intensities are required e.g. for quantitative phase analysis, the peak areas have to be measured.
angles, d values and intensities in the form of count per second. For accurate intensity measurement the instrument is set stationary so that the detector is receiving diffracted X-rays correspond to a particular peak. The intensity is then measure over a selected length of time using counting circuitry built into the instrument.

The details of working, application and instrumentation are discussed in several books [9-10]. In the present study Philips Analytic X-ray B.V. (PW-3710 Based Model) Advanced X-ray diffraction was used for the optimization of conditions for the preparation of various mixed oxides.

2.3.3. Identification of substances by X-ray diffraction:

The X-ray diffraction technique has proved invaluable in identification of thousands of crystalline phases. This is due to a finger-print type patterns displayed by each sample which is characteristic of that sample. Thus by matching the patterns of a known compound, unknown can be identified. This system was devised by Hanawalt [11]. He selected the fundamental quantity that is ‘d’ spacing of lattice plane forming each line instead of 2θ. Since more than one substance can have the same or nearly same ‘d’ values, Hanawalt characterized each substance by ‘d’ values of its three very strong lines. A data bank consisting of d-spacing and intensities of different peaks recorded in the XRD patterns are listed along with the ‘hkl’ Miller indices for each plane. Left-top of each card lists ‘d’ values of three very strong lines of a compound. In addition, other parameter like type of unit cell, length of a, b and c axis and the angle between them are also available in the compilation for each compound. Data for several thousand new compounds are each year to the existing data bank which is generally referred to as JCPD (Joint Commission on Powder Diffraction) data file. The X-ray pattern recorded for the compound is compared with that available in JCPD file for its identification. A typical card for LaFeO₃ is reproduced and presented in Table 1.
Table: 1 Typical JCPD card for TiO$_2$

<table>
<thead>
<tr>
<th>2θ</th>
<th>Int</th>
<th>h</th>
<th>k</th>
<th>l</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>65</td>
<td>701</td>
<td>10</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>2θ</td>
<td>Int</td>
<td>h</td>
<td>k</td>
<td>l</td>
</tr>
<tr>
<td>2θ</td>
<td>Int</td>
<td>h</td>
<td>k</td>
<td>l</td>
</tr>
<tr>
<td>2θ</td>
<td>Int</td>
<td>h</td>
<td>k</td>
<td>l</td>
</tr>
</tbody>
</table>

2.3.4. Calculation of crystallite size (t):

The full width at half maxima (FWHM) was used to calculate the crystallite size by using the Scherrer’s formula in equation 2.4.

\[ t = \frac{0.9 \lambda}{\beta \cos \theta} \]

Where \( \beta = \text{FWHM} \times \pi/180 \)

2.4. Energy Dispersive X-Ray analysis (EDX):

There are four primary components of the EDS setup:

1) Beam source
2) X-ray detector
3) Pulse processor
4) Analyzer

EDX is an analytical technique used for the elemental analysis or chemical characterization of a sample. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit with charged particles. To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons, or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell.
while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

Accuracy of EDX spectrum can be affected by many variants. EDX detectors cannot detect presence of elements with atomic number less than 5, meaning that EDX cannot detect H, He, Li, or Be[12]. Differing the over-voltage of the EDX will result in different peak sizes and raising over-voltage on the EDX will shift the spectrum to the larger energies making higher-energy peaks larger while making lower energy peaks smaller. Also many elements will have overlapping peaks (eg. Ti Kβ and V Kα, Mn Kβ and Fe Kα.). The accuracy of the spectrum can also be affected by the nature of the sample.

2.5. Scanning Electron Microscope (SEM):

Scanning electron microscopes are equipped with a cathode and magnetic lenses to create and focus a beam of electrons and since the 1960s they have been equipped with elemental analysis capabilities. A detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them into an analyzer for data display and analysis.

Most methods of analysis give an average composition of a sample. However, the properties of many solids, depend not only on the average composition, but also on the composition of the individual grain boundaries, etc. The scanning electron microscope is suitable to study the samples at microscopic levels [17]. A scanning electron microscope operates at lower electron beam current. The instrument produces electron images of specimens surface of up to X160000 magnification with resolution better than 100 Å. SEM’s are fitted with energy dispersive X-ray spectrophotometers. This technique primarily designed to provide well resolved high magnification of specimen’s surface. SEM is primarily concerned with surface topography. This technique is preferred for the investigation of shape, size and surface texture. It also helps in determination of micro cracking in fractured ceramic and study of diffusion and corrosion of alloys. SEM is used to study the localized
enrichment in bones, tissues and membranes which may be related to body function or disease.

This SEM technique is used in the study of surface morphology of the sample. For SEM studies, samples are mounted on stubs with double-sided adhesive tape. The samples, which are very sensitive to electron beam cause artifacts and also create focusing problems in the SEM. To avoid charging, the sample specimen is generally coated with a thin layer (250-300Å) of conducting material. Coating of sample allows observation of a specimens topography, undisturbed by flare and distortion caused by thermal effects and insufficient grounding. Coating such as gold, gold-palladium and carbon are often used because highly conducting, easy to apply and can be applied on the specimen in the form of thin film either by evaporation or sputtering. The sample is placed in an evacuated chamber and scanned by an electron beam.

![Interaction of the electrons beam with the specimen](image)

**Fig. 2.7: Interaction of the electrons beam with the specimen**

Interaction of electron beam with the specimen produces a variety of physical phenomena such as 1. emission of secondary electrons SE, 2. reflection of backscattered electrons BSE, 3. Characteristic X-ray emission, 4. emission of Auger electrons, 5. cathode luminescence CL, 6. conduction of current, 7. charging from induced voltage IV or absorbed electrons AE, 8. electron transmission, and 9. hest generation fig.2.7. Out of these, SE and BSE are the most important for constructing SEM images and X-ray emission analysis used in elemental analysis of the selected
part of the sample. Secondary electrons SE are low energy electrons 5 to 20 eV emitted from the specimen surface as a result of metallic collisions between primary (incident) electrons PE and electrons within the specimen. These are originated from within 2 to 30 nm on the surface and generate highly resolved images. Back scattered electrons BSE are PE., which have been reflected from the sample. The PE can undergo multiple collisions prior to exiting from the specimen; therefore BSE have energies over a broad range (15 to 25 kV). BSE are collected less efficiently than SE, and they yield images with poorer resolution. The efficiency of BSE reflection is a function of atomic number (Z) of the specimen atoms; thus the contrast of BSE images depends on elemental composition. BSE emerge from relatively deeper penetration (0.1 to 5 μm) The penetration depth of all electrons is affected by elemental composition, specimen density ect. BSE images of heavy –versus light element phase, or mixtures of species, show dramatic contrast differences that are representative of elemental heterogeneity [18].

The SEM itself or in conjugation with energy-dispersive X-ray (EDX) or wavelength-dispersive-X-ray spectrometry (WDS) is an extremely important tool for characterizing the size and morphology of microscopic specimens and in obtaining the following information in the materials prepared under varying experimental conditions.

**Topography:** The surface features of an object, it’s texture.

**Morphology:** The shape, size and arrangement of the particles making up the samples

**Composition:** The elements and compounds the sample is composed of and their relative ratios.

**Crystallographic Information:** The arrangement of the atoms in the specimen and their degree of order.

The details of the working, instrumentation and applications of SEM are discussed in various books on the subject [10,17]. In the present investigation JEOL (Model 840) Scanning Electron Microscope was used for the characterization of mixed oxide powder for microstructure and morphological characteristics
2.6. Transmission Electron Microscopy (TEM):

TEM is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through fig. 2.8. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution and semiconductor research [19]. At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material.

Fig.2.8: Schematic diagram of TEM.
At higher magnifications, complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.

The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolving power greater than that of light in 1933 and the first commercial TEM in 1939.

Electrons, Theoretically the maximum resolution $d$, that one can obtain with a light microscope has been limited by the wavelength of the photons that are being used to probe the sample in equation 2.5, $\lambda$ and the numerical aperture of the system, $NA$ [20].

$$d = \frac{\lambda}{2n \sin \alpha} \approx \frac{\lambda}{2 NA} \tag{2.5}$$

Early twentieth century scientist’s theorized ways of getting around the limitations of the relatively large wavelength of visible light (wavelengths of 400–700 nanometers) by using electrons. Like all matter, electrons have both wave and particle properties (as theorized by Louis-Victor de Broglie), and their wave-like properties mean that a beam of electrons can be made to behave like a beam of electromagnetic radiation. The wavelength of electrons is found by equating the de Broglie equation to the kinetic energy of an electron. An additional correction must be made to account for relativistic effects, as in TEM an electron’s velocity approaches the speed of light $c$, shown in equation 2.6.

$$\lambda_e \approx \frac{h}{\sqrt{2m_0E\left(1 + \frac{E}{2m_0c^2}\right)}} \tag{2.6}$$

Where, $h$ is Planck's constant, $m_0$ is the rest mass of an electron and $E$ is the energy of the accelerated electron. Electrons are usually generated in an electron microscope by a process known as thermionic emission from a filament, usually tungsten, in the same manner as a light bulb, or alternatively by field electron emission. The electrons are then accelerated by an electric potential (measured in volts) and focused by electrostatic and electromagnetic lenses onto the sample. The
transmitted beam contains information about electron density, phase and periodicity; this beam is used to form an image.

From the top to down, the TEM consists of an emission source, which may be a tungsten filament, or a lanthanum hexaboride (LaB$_6$) source. For tungsten, this will be of the form of either a hairpin-style filament, or a small spike-shaped filament. LaB$_6$ sources utilize small single crystal. By connecting this gun to a high voltage source (typically ~100-300 kV) the gun will, given sufficient current, begin to emit electrons either by thermionic or field electron emission into the vacuum. This extraction is usually aided by the use of Wehnelt cylinder. Once extracted, the upper lenses of the TEM allow for the formation of the electron probe to the desired size and location for later interaction with the sample.

Manipulation of the electron beam is performed using two physical effects. The interaction of electrons with a magnetic field will cause electrons to move according to the right hand rule, thus allowing for electromagnets to manipulate the electron beam. The use of magnetic fields allows for the formation of a magnetic lens of variable focusing power, the lens shape originating due to the distribution of magnetic flux. Additionally, electrostatic fields can cause the electrons to be deflected through a constant angle. Coupling of two deflections in opposing directions with a small intermediate gap allows for the formation of a shift in the beam path, this being used in TEM for beam shifting, subsequently this is extremely important to STEM. From these two effects, as well as the use of an electron imaging system, sufficient control over the beam path is possible for TEM operation. The optical configuration of a TEM can be rapidly changed, unlike that for an optical microscope, as lenses in the beam path can be enabled, have their strength changed, or be disabled entirely simply via rapid electrical switching, the speed of which is limited by effects such as the magnetic hysteresis of the lenses.

Optics:

The lenses of a TEM allow for beam convergence, with the angle of convergence as a variable parameter, giving the TEM the ability to change magnification simply by modifying the amount of current that flows through the coil, quadrupole or hexapole lenses. The quadrupole lens is an arrangement of electromagnetic coils at the vertices of the square, enabling the generation of a lensing
magnetic fields, the hexapole configuration simply enhances the lens symmetry by using six, rather than four coils.

Typically a TEM consists of three stages of lensing. The stages are the condenser lenses, the objective lenses, and the projector lenses. The condenser lenses are responsible for primary beam formation, whilst the objective lenses focus the beam down onto the sample itself. The projector lenses are used to expand the beam onto the phosphor screen or other imaging device, such as film. The magnification of the TEM is due to the ratio of the distances between the specimen and the objective lens image plane. Additional quad or hexapole lenses allow for the correction of asymmetrical beam distortions, known as astigmatism. It is noted that TEM optical configurations differ significantly with implementation, with manufacturers using custom lens configurations, such as in spherical aberration corrected instruments, or TEMs utilizing energy filtering to correct electron chromatic aberration.

Display:

Imaging systems in a TEM consist of a phosphor screen, which may be made of fine (10-100 μm) particulate zinc sulphide, for direct observation by the operator. Optionally, an image recording system such as film based or doped YAG screen coupled CCDs. Typically these devices can be removed or inserted into the beam path by the operator as required.

2.7. UV-visible spectroscopy:

The UV-Vis Spectroscopy is known to be very sensitive and useful technique for the identification of the electronic state of the metal atom and the measurement of absorbance of the colored compounds. The electronic spectra of the lanthanide ion doped mixed metal oxide were recorded on a Systronic UV-Vis double beam AU-2700 UV-visible spectrophotometer in the range 190 to 1100 nm. Quartz cell with 10 mm size was used. The radiant energy sources are the deuterium lamp for the ultraviolet region and a tungsten lamp for the visible region. A cell containing the pure solvent was used as reference. All the measurements were made at room temperature.
2.8. Surface area measurement by adsorption method:

Adsorption occurs when the clean solid surface is brought into the contact with a gas. The forces involved in the adsorption process are physical or chemical corresponding to physisorption and chemisorptions respectively. The physisorption is a spontaneous process, its magnitude is dependent on the nature of the system, the surface area and porosity of absorbent material. It also depends on the condition of measurement such as pressure, temperature and concentration. It is therefore possible to employ physisorption measurement of surface area of solids provided that the other variables can be controlled. Most procedures for surface area determination are based on the evaluation of monolayer capacity \( n_0 \) (amount of gas or solute require to cover the surface with single layer of absorbed molecules). To obtained the surface area \( A \), it is necessary to know the effective molecular area \( (a_m) \) of the absorbate, which form monolayer on the absorbent surface.

The amount of gas absorbed is determined with 1) Volumetric method, which involves the amount of gas removed from the gas phase or ii) a gravimetric method, which involves the determination of the increase in mass of absorbent. The adsorption isotherm is constructed by adsorbing a gas on adsorbent surface. Prior to determination of adsorption isotherm all previously adsorbed material must be removed (out gassed) from the adsorbent surface. This is achieved by out gassing or flushing the adsorbent with inert gas at elevated temperature. The low temperature adsorption of nitrogen is generally recommended technique in all the standard methods proposed for the determination of surface area by gas adsorption [13] Nitrogen isotherms at 77 K are usually determined volumetrically and routine measurements are carried out with fully automated instruments. Details of adsorption isotherm are explained in reference

2.8.1. The BET Method:

The Brunaur-Emmett-Teller (BET) gas adsorption method (32) is most widely used method for determination of the surface of fine powder and porous materials. The BET equation 2.7 is used in its linear form.
Where \( n \) is amount of gas adsorbed at \( P/ P_0 \), \( n_m \) is monolayer capacity and \( c \) is an empirical constant. It is important to recognize that there should be linear relation between \( P/n \ (P_0-P) \) and \( P/ P_0 \), BET surface area \( A \) is calculated if the amount of gas needed to form a monolayer is known, using the equation.

\[
A \text{ (BET)} = n_m N a_m
\]

Where \( n_m \) is monolayer capacity, \( N \) is Avogadro’s number and \( a_m \) is the average area occupied by the absorbate molecule in the complete monolayer. Nitrogen monolayer at 77 K in close packed liquid state \( a_m \ (N_2)=0.162 \) nm\(^2\). For wide range of non-microporous adsorbent the use of this value \( (a_m) \) gives BET area which shows good arrangement to the surface area determined by other methods. In the present work BET nitrogen adsorption technique was used to find out the surface area of mixed oxides.

2.9. I-V Characteristic:

A current–voltage characteristic is a relationship, typically represented as a chart or graph, between an electric current and a corresponding voltage, or difference. In electronics, the relationship between the DC current through an electronic device and the DC voltage across its terminals is called a current–voltage characteristic of the device. Electronic engineers use these charts to determine basic parameters of a device and to model its behavior in an electrical circuit. These characteristics are also known as I-V curves, referring to the standard symbols for current and voltage.

A more general form of current–voltage characteristic is one that describes the dependence of a terminal current on more than one terminal voltage difference; electronic devices such as vacuum tubes and transistors are described by such characteristics.[14-18] The simplest I–V characteristic involves a resistor, which according to Ohm's Law exhibits a linear relationship between the applied voltage and the resulting electric current. However, even in this case environmental factors such
as temperature or material characteristics of the resistor can produce a non-linear curve.

2.10. Thermoelectric power (TEP) measurement:
Thermoelectric power measurements of annealed (100 °C) thin films were carried out under the condition of maximum temperature difference and minimum contact resistance. The temperature difference of the ends of the samples was measured with Chromel–Alumel thermocouple placed in such a way so as to touch the sample ends. The thermoelectric voltage or seebeck voltage developed across the sample and the temperature of the ends was read on Testronix microvoltmeter and Meco-801 digital multimeter respectively. Set of the values of thermoelectric voltage at various temperatures thus obtained were plotted against the respective absolute temperatures. Thermo-emf measurements have also been carried out to determine the type of conduction.

2.11. Powder and paste preparation:
Synthesized powder was ground in an agate paste mortar to ensure sufficiently fine particle size. The fine powder was calcined at fixed temperature, in air and re-ground. The thixotropic paste was formulated by mixing the resulting fine powder with a solution of ethyl cellulose (temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and turpineol. The ratio of inorganic to organic part was kept as 75:25 in formulating the paste. The paste was then used to prepare thick film of the material [19].

2.12. Thick film preparation:
The thixotropic paste was screen printed on a glass substrate in desired patterns. The films prepared were fired at 550 °C for 24 h. These films were surface modified by dipping them into a 0.01M aqueous solution of cupric chloride for different intervals of time and were dried at 80 °C followed by firing at 550 °C for 24 h in air ambient. The CuCl₂ dispersed on the films was oxidized in firing process, and sensor elements with different mass% of materials were obtained. Silver contacts were made by vacuum evaporation for electrical measurements [20].

2.12.1 Technology:
To prepare s, the thixotropic paste of functional material is formulated and printed onto an insulating substrate in a definite pattern. The technique involves screen printing followed by firing process. For technology, paste of the functional material is
prepared with the use of some temporary organic binder [21-22]. A proper permanent binder is used along with the functional material to achieve adhesion of a film to the substrate. The paste is screen-printed on an insulating substrate (e.g. alumina), which can stand at higher temperatures, to get definite pattern. The printed film is dried under an IR lamp to remove the temporary organic binder and then it is fired at a higher temperature with a definite time-temperature profile to obtain stability and better adhesion of the film to the substrate [23].

2.13. Thickness Measurement (Talystep Method):

Film thickness was observed to be in the range from 20 to 35 µm. The reproducibility of film thickness was achieved by maintaining the proper rheology and thixotropy of the paste.
2.14. References:


