CHAPTER 1
INTRODUCTION

1.1 SENSORS

A sensor is defined as a device which converts a physical or chemical parameter into an electric signal. It is also defined as a transducer that converts one form of energy concerning which information is sought into another suitable form amenable for further processing [1]. Although sensors of a great variety of types are well established in process industries, agriculture, medicine and many other areas, still the development of sensing materials with high sensing capabilities are proceeding at an unprecedented rate.

In order to characterize sensor performance a set of parameters is used. The most important parameters and their definitions are listed below [2]:

- Sensitivity is a change of measured signal per analyte concentration unit, i.e. the slope of a calibration graph.
- Selectivity refers to characteristics that determine whether a sensor can respond selectively to a group of analytes or even specifically to a single analyte.
- Stability is the ability of a sensor to provide reproducible results for a certain period of time. This included retaining the sensitivity, selectivity, response and recovery time.
- Detection limit is the lowest concentration of the analyte that can be detected by the sensor under given conditions, particularly at a given temperature.
- Dynamic range is the analyte concentration range between the detection limit and the highest limiting concentration.
- Linearity is the relative deviation of an experimentally determined calibration graph from an ideal straight line.
- Resolution is the lowest concentration difference that can be distinguished by sensor.
- Response time is the time required for sensor to respond to a step concentration change from zero to a certain concentration level.
• Recovery time is the time it takes for the sensor signal to return to its initial value after a step concentration change from a certain value to zero.

• Hysteresis is the maximum difference in output when the value is approached with an increasing and a decreasing analyte concentration range.

• Life cycle is the period of time over which the sensor will continuously operate.

The sensor can be categorized into two general groups:

1. Physical Sensors – which are sensitive to physical responses such as temperature, pressure, magnetic field and force. They do not have a chemical interface.
2. Chemical Sensors – Chemical sensor materials rely on a particular chemical reaction for their response.

1.2 CHEMICAL SENSORS

Chemical sensors occur as a result of a chemical interaction or process between the analyte and the sensor device, transform chemical information of a quantitative or qualitative type into an analytically useful signal [3]. The signal from a sensor is typically electronic in nature, being a current, voltage or impedance/conductance change caused by changing analyte composition or quality. An ideal chemical sensor would possess dynamic range and high sensitivity, selectivity and stability, low detection limit, small hysteresis, response time long life cycle and should be sensitive to the measured property only.

Conceptually, every chemical sensor consists of two domains: the physical transducer and the chemical interface layer or receptor domain. At the chemical interface, the analyte interacts chemically with a surface or coating or catalyst that is part of the device and produces a change in physical/chemical properties. These changes are measured by the transducer domain, which monitors this change and generates a proportionally related electrical signal [4].
Sensors are frequently classified and named by their transduction method e.g. conductimetry, potentiometry, amperometry, gravimetry, which includes SAW (Surface Acoustic Wave) and QMB (Quartz Crystal Microbalance) transduction, optical fiber, spectrometric and refractometric), metal oxide semiconductor (heated metal oxide chemiresistive), conductive polymer chemiresistive, polymer composite chemiresistive or capacitive.

**1.3 TYPES OF CHEMICAL SENSORS**

**1.3.1 Electrochemical Sensors (Liquid Electrolyte) [5]**

There are two main sensor classes that use liquid electrolytes: amperometric and potentiometric sensors. The earliest example of an amperometric gas sensor, the clark oxygen sensor was used for the measurement of oxygen in the blood.

The amperometric sensor produces current signal, which is related to the concentration of the analyte by Faraday’s law and the laws of mass transport. The amperometric sensor has an advantage over many other kinds of sensors because it combines small size, low power, high sensitivity, as well as relatively low price. With micro fabrication techniques, the entire sensor can be assembled on a chip or as a part of a μ-TAS (micro fabricated total analytical system).

**1.3.2 Metal Oxide Sensors [6,7,8]**

The heated metal oxide sensor is probably the most investigated and widely produced chemical sensor. The working principle of this type of sensor is that the resistance of the metal oxide changes when it is exposed to the analyte since it reacts with the metal oxide surface and changes its electronic properties. Such devices are sometimes referred to as chemresistors.

**1.3.3 Solid Electrolyte Sensors**

Solid electrolyte sensors are typically designed to operate at high temperature and can operate in either a potentiometric or amperometric mode. An example of a potentiometric sensor is the well known yttria-stabilized zirconia (YSZ) based oxygen sensors that have been widely used for air/fuel ratio control in internal combustion engines. Over the years, two potentiometric designs have evolved; surface-modified solid electrolyte sensors [9,10] and mixed potential sensors [11,12].
In the former, the surface of a solid electrolyte is coated with an auxiliary phase which will react electrochemically and reversibly with the analyte and generate an interfacial potential. In a mixed potential sensor design more than one electrochemical reaction takes place at the electrodes so that a mixed potential is established by competing reactions.

1.3.4 Optical Sensors

In optical sensors there is a spectroscopic measurement associated with the chemical reaction. Optical sensors are often referred to as ‘optodes’ and the use of optical fibres is a common feature, many bio-sensors make use of optical measurements. Absorbance, reflectance and luminescence measurements are used in different types of optical sensors.

1.3.5 Mass Sensitive Sensors

These make use of piezoelectric effect and include devices such as the surface acoustic wave sensors and are particularly useful as gas sensors. They rely on a change in mass on the surface of an oscillating crystal which shifts the frequency of oscillations.

1.3.6 Heat Sensitive Sensors

These are often called calorimetric sensors in which the heat of a chemical reaction involving the analyte is monitored with a transducer such as a themistor or a platinum thermometer. flammable gas sensors make use of this principle. The categories of chemical sensors arranged by their physical principle [4] is shown in Fig. 1.1
1.4 HUMIDITY SENSORS

The measurement and control of humidity the concentration of water vapour in air or other gases is important in many areas, including meteorology, the domestic environment (air conditioners), medicine (respiratory equipment), food production (drying process), industry (paper, textile, electronics and automotive), and agriculture (cereal stocking and green houses) [13]

Humidity sensors are greatly in demand for monitoring and controlling various domestic and industrial surrounding [14,15]. The continuous monitoring and controlling of humidity becomes necessary for high product quality and human comfort [16]. Extensive research work is being carried out even in these present days to obtain highly
sensitive, selective, reliable sensors which are cheap, compact and microprocessor compatible, even though numerous types of solid state humidity sensors are available in the market. The sensors based on resistance and capacitance change are most widely investigated because of their small size and compatibility with electronic circuitry.

The concentration of water vapour can be expressed in various ways. For example, the absolute concentration can be expressed as the ratio of the mass of water vapour present in a mass or volume unit of moist gas (g kg\(^{-1}\) or gm\(^{-3}\)). If the water vapour partial pressure rises to the saturation vapour pressure, a thermodynamic equilibrium exists between water vapour and liquid water at a given total pressure and temperature. This temperature is the dew point (\(t_d\)) or frost point, at which dew or ice is formed on cooling a gas in the range of \(-110^\circ C\) to \(+110^\circ C\). The relative humidity (RH) can be expressed by the ratio of actual vapour pressure to the saturated vapour pressure,

\[
RH\% = \left( \frac{P_{\text{water vapour}}}{P_{\text{saturation}}} \right) \times 100
\]  

(1)

The main methods of humidity measurement are compiled in Table 1.1 and several other techniques have been proposed which use properties of air that change with humidity, such as the transmission of sound waves (acoustic), absorption and emission of ultraviolet light or infrared waves, thermal conductivity and optical refractive index.
Table 1.1 Main Types of Humidity Measurement [13]

<table>
<thead>
<tr>
<th>Sensor Type</th>
<th>Detection Principle</th>
<th>Humidity Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical</td>
<td>Expansion or contraction of organic materials (fibers) with changing humidity.</td>
<td>5 to 100% RH</td>
</tr>
<tr>
<td>Wet- and dry-bulb (Psychrometer)</td>
<td>Comparison of temperature of the gas stream and of a temperature sensor in a porous wet medium chilled by water-vapor evaporation in a rate related to air humidity.</td>
<td>0 to 100% RH, -30 to 100°C t_d</td>
</tr>
<tr>
<td>Dew point hygrometer</td>
<td>Temperature at which condensation of dew or frost takes place on a cooled mirror detected by optical or electrical methods.</td>
<td>-110 to + 110°C t_d</td>
</tr>
<tr>
<td>LiCl-hygrometer</td>
<td>Absorption of humidity increases the conductivity and thus causes self-heating of the sensor to an equilibrium temperature.</td>
<td>-60 to + 100°C t_d</td>
</tr>
<tr>
<td>Electrical impedance</td>
<td>Impedance, resistivity, or capacity change due to water adsorption of porous material like alumina, other oxides, or polymers.</td>
<td>0 to 100% RH, -120 to 80°C t_d</td>
</tr>
<tr>
<td>Coulometric or amperometric</td>
<td>Measuring the electrical energy (current) needed for the electrolysis of water.</td>
<td>1 ppm_v to 1,000 ppm_v</td>
</tr>
<tr>
<td>Spectroscopic</td>
<td>Transmission (emission resp.) change of wet air in the infrared range or ultraviolet light range (Lyman-alpha), change of optical index or transmission of sound or microwaves due to humidity change in air.</td>
<td>1 ppm_v to 100% RH</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>Change of transmission of sound or resonance frequency due to water adsorption in a surface layer of a piezoelectric crystal.</td>
<td>0 to 1,000 ppm_v, -100 to -20°C t_d</td>
</tr>
<tr>
<td>Color change</td>
<td>Color of materials (CoCl₂) varies due to humidity.</td>
<td>20 to 80% RH</td>
</tr>
</tbody>
</table>
A humidity sensor has to fulfil the following requirements to satisfy the widest range of applications [17].

- Good sensitivity in a wide humidity range
- Quick response
- Good reproducibility
- No hysteresis
- Fitness to circuitry
- Tough durability and long life
- Resistant to contaminants
- Insignificant dependence on temperature
- Simple structure and low cost

1.4.1 Applications of humidity sensors

The applications of humidity sensors are widespread covering domestic electric appliances, automobiles, medical services, various industries and agriculture. The applications of humidity sensors are represented in Table 1.2. Numerous humidity sensors based on different transduction and fabrication techniques have been reported in the literature [18-21]. The purpose of adopting humidity sensors and the operation conditions are quite different depending on the field of application, each field requiring a specific humidity sensor. Hence, the growing demand for accurate reliable sensors has led to the investigation and development of various kinds of humidity sensors.

1.4.2 Different Types of Humidity Sensors

According to the measurement units, humidity sensors are divided into two types: Relative Humidity (RH) sensors and absolute humidity (moisture) sensors. Most humidity sensors are relative humidity sensors, which is further classified into ceramic, semiconductor and polymer humidity sensors. Two types of absolute humidity sensors or hygrometers available are solid moisture sensor and mirror chilled hygrometer [22].

The materials used in humidity sensors exploiting variations of electrical parameters were earlier roughly classified into three groups: electrolytes, organic polymers and ceramics [17].
Table 1.2 Applications of humidity sensors

<table>
<thead>
<tr>
<th>Industry</th>
<th>Application</th>
<th>Operating Temp (°C)</th>
<th>Humidity Range (% RH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domestic electric appliance</td>
<td>Air conditioning system</td>
<td>5 - 40</td>
<td>40 – 70</td>
</tr>
<tr>
<td></td>
<td>Drier for clothing</td>
<td>80</td>
<td>0 – 40</td>
</tr>
<tr>
<td></td>
<td>Microwave oven</td>
<td>5 - 100</td>
<td>2 – 100</td>
</tr>
<tr>
<td></td>
<td>VTR</td>
<td>-5 - 60</td>
<td>60 – 100</td>
</tr>
<tr>
<td>Automobile Medical service</td>
<td>Car Windows</td>
<td>-20 - 80</td>
<td>50 – 100</td>
</tr>
<tr>
<td></td>
<td>Medical apparatus</td>
<td>10 - 30</td>
<td>80 – 100</td>
</tr>
<tr>
<td></td>
<td>Incubator</td>
<td>10 - 30</td>
<td>50 – 80</td>
</tr>
<tr>
<td>Industry</td>
<td>Textile mill (spinning)</td>
<td>10 - 30</td>
<td>50 – 100</td>
</tr>
<tr>
<td></td>
<td>Drier for ceramic powder</td>
<td>5 - 100</td>
<td>0 – 50</td>
</tr>
<tr>
<td></td>
<td>Dehydrated food</td>
<td>50 - 100</td>
<td>0 – 50</td>
</tr>
<tr>
<td></td>
<td>Electric device manufacturing</td>
<td>5 - 40</td>
<td>0 – 50</td>
</tr>
<tr>
<td>Agriculture Measurement</td>
<td>Forcing culture</td>
<td>5 - 40</td>
<td>0 – 100</td>
</tr>
<tr>
<td></td>
<td>Thermo-hydrostatic chamber</td>
<td>-5 - 100</td>
<td>0 – 100</td>
</tr>
<tr>
<td></td>
<td>Radio-sonde</td>
<td>-5 - 40</td>
<td>0 – 100</td>
</tr>
<tr>
<td></td>
<td>Hygrometer</td>
<td>-5 - 100</td>
<td>0 – 100</td>
</tr>
</tbody>
</table>

1.4.2.1 Lithium Chloride Humidity Sensor

The electrolyte humidity sensor using LiCl was developed by Dunmore in 1938 was used for over 40 years, being the only electric moisture-sensing device available at the time. It operated on the principle that lithium chloride solution immersed in a porous binder changes its ionic conductivity depending on the relative humidity of the surrounding atmosphere air [14,17].

However this sensor showed slow response time and was unable to be operated in very humid environments or in the presence of ammonia or organic solvents. Other materials were thus studied to be used in those environments where the LiCl sensor was not suitable.
1.4.2.2 Ceramic Humidity Sensors

Ceramics, in particular metal oxides, have shown advantages in terms of their mechanical strength, their resistance to chemical reaction and their thermal and physical stability. Ceramic have been studied for use in humidity sensors mainly as porous sintered bodies, prepared by traditional ceramic processing, in order to allow water vapour to pass easily through the pores and water condensation in the capillary-like pores between the grain surfaces. Ceramic materials possess a unique structure consisting of grains, grain boundaries, surfaces and pores which makes them suitable for chemical sensors when they have a controlled microstructure [23].

Compacts with a given microstructure can be produced by controlling the different steps of the ceramic production process. The modification of the microstructure and the chemical composition of ceramic materials permits both performance optimization in sensors exploiting their electrical properties and tailoring to specific requirements. The problems for ceramic humidity sensors are mainly related to their need for periodic regeneration by heat cleaning to recover their humidity sensitive properties, commercial sensors based on ceramic sensing elements were equipped with a heater for regeneration [24]. The surface related phenomena of humidity sensing by ceramics make these materials less resistant than polymers to surface contamination because of their porous structure.

A number of investigations have been carried out for humidity sensors utilizing porous ceramic elements [20,25-29]. Various humidity-sensing mechanisms and operating principles have been identified for ceramics. The type of conduction may be ionic or electronic [30]. Most current humidity sensors are based on porous sintered bodies of ionic-type humidity-sensitive ceramics.

In the first type (which is the proton type) ceramic element exhibit ionic conductivity in a humid atmosphere due to adsorption followed by capillary condensation of water vapour. The second type utilises the sensitivity of some semiconducting materials to water vapour, in which electronic conductivity changes with water chemisorption [31].
1.4.2.3 Ionic-Type Ceramic Humidity Sensors

$\text{Al}_2\text{O}_3$ was one of the most favourable ceramic sensing materials due to its independent of temperature at nearly all range of relative humidity from 25°C to 80°C [32]. In addition to capacitive and resistive sensors, sensing devices based on $\text{Al}_2\text{O}_3$ like MISFETS (Metal Insulator Semiconductor Field Effect Transistors), were fabricated and some of them have very good linear response. Many of the present $\text{Al}_2\text{O}_3$ humidity sensors are fabricated through anodisation. Because of its low cost and easy process, anodic $\text{Al}_2\text{O}_3$ has great priority over other ceramics [33]. Cathodically grown aluminium hydroxide or hydrated $\text{Al}_2\text{O}_3$ was also used as humidity sensing materials.

L. Chow et.al. reported the use of anatase TiO$_2$ prepared by sol-gel method for humidity sensing applications [34]. Because of its protonic conducting devising mechanism doping with alkali ions improved the conductivity of TiO$_2$ [35,36]. Bilayered TiO$_2$/SnO$_2$, TiO$_2$/Al doped ZnO, and ZrO$_2$/SnO$_2$ were reported to have less hysteresis than pure TiO$_2$, Al-doped ZnO and ZrO$_2$ [37-39].

The ionic-type humidity sensors utilise the decrease in impedance due to water adsorption. A resistive type humidity sensor based on MgCr$_2$O$_4$- TiO$_2$ was developed for practical use in microwave ovens [24,25]. A ceramic sensor based on ZnCr$_2$O$_4$- LiZnVO$_4$ was developed for used in air conditioners by Yokomizo et. al. [40]. The use of porous La$_2$O$_3$-TiO$_2$-V$_2$O$_5$ glass ceramics has recently been proposed for humidity sensors [41,42]. Multifunctional sensors are an interesting group capable of detecting other parameters in addition to humidity, such as gas concentration or temperature [43-45]. Other potential multifunctional sensor materials have been studied [46,47]. One of the advantages of ceramic materials is that porous films can be produced using thick film technology [48,49]. Many different materials have also been studied in thick-film form, using films prepared by screen printing or by dipping as coatings on substrate with electrodes [50].

1.4.2.4 Electronic-Type Ceramic Humidity Sensors

Semiconductor humidity sensors using metal oxides were proposed for this purpose [51], although some ionic conductor ceramics are also able to detect humidity at high temperatures. As the operating temperature of the sensors based on semiconductors
is much higher than that of water physisorption, the observed change in electrical conductivity is based on the chemisorption of water molecules.

The demand for humidity sensors able to operate at temperatures higher than 100°C led to the development of humidity-sensing devices based on different detection mechanisms. In this case, the sensitivity to humidity is a result of electronic conduction: when water molecules are chemisorbed on semiconducting oxides, their resistivity varies, decreasing or increasing according to the type of semiconducting oxides. Semiconductor humidity sensors such as SnO₂, In₂O₃, Sr₁₋ₓLaₓSnO₃, ZrO₂ – MgO and ZnO – Y₂O₃ have been reported in the literature [22].

Enhancement of humidity sensitivity of SrSnO₃ was achieved by partially substituting the A-site element of SrSnO₃ with La³⁺ ions, and best results were obtained for the composition Sr₀.⁹₅La₀.₀₅SnO₃. The effect of the sintering temperature on the humidity sensitivity of Sr₀.⁹₅La₀.₀₅SnO₃ was reported. An electronic-type humidity sensor based on ZrO₂-MgO has been developed by Nitta et.al. SnO₂ showed electronic conductivity at rather low temperature (even at room temperatures) [52–55]. Most reported SnO₂ sensors are only sensitive to RH higher than 30% [56–58]. When this sensor was exposed to an atmosphere containing a given gas at high temperature in the range 400-700°C, reverse chemisorption becomes dominant and the sensor electrical conduction changes with gas chemisorption.

A couple of methods were developed for fabrication of rough and porous In₂O₃ layers that were sensitive to moisture. In₂O₃ humidity sensors none of the reported was able to sense relative humidity lower than 25% [59–62]. Homogeneously mixed and sintered ZnO-Y₂O₃ was found to be a humidity-sensitive semiconductor. Doping with Li⁺ at 900°C showed linear behaviour in the entire humidity range from 5% to 98% RH at room temperatures.

1.4.2.5 Solid-Electrolyte Type humidity Sensors

In recent years humidity control at high temperatures has become more important for several industrial applications, such as drying processes and combustion control systems. Humidity sensors operating in the temperature range 100–300°C are required for the control of humidity in drying ovens. Solid electrolytes have also been studied for this purpose.
Proton conductors have been used for humidity sensing at high temperature [63]. High proton conductivity, good stability at operating temperatures, low electronic conductivity and good mechanical properties are the requirements of the materials to be used as proton conductors in high-temperature electrochemical sensors [63].

SrCeO$_3$ and BaCeO$_3$ based perovskite type oxides are stable and efficient proton conductors at temperatures above 400$^\circ$C. A humidity sensor using SrCe$_{0.95}$Yb$_{0.05}$O$_3$ has been studied in temperature range 600-1000$^\circ$C [64]. A humidity sensor using amino acid, which is a proton conductor, has been investigated for operation at medium temperature, measuring the variations of impedance with water-vapour pressure.

1.4.2.6 Polymer-based Humidity Sensors

Polymeric humidity sensors have been widely studied in research and applied in industry for more than thirty years. Most of the sensors are based on porous polymer film thinner than millimetres and their sensing principle is quite similar to that of ceramic sensors. The film is filled with micro-pores for water vapour condensation and some of the measurable physical properties change due to water absorption. Traditionally, according to sensing mechanisms, polymeric humidity sensors are divided into two fundamental categories: resistive type and capacitive type [65]. The former responds to moisture variation by changing its conductivity while the latter responds to water vapour by varying its dielectric constant. Almost all of the humidity sensors based on polymers operate at room temperature, due to polymer’s high sensitivity to heat.

In the recent years, in addition to the traditional quaternary ammonium and sulfonate compounds [66–70], polymers containing phosphonium have been developed for humidity sensing. More importantly, copolymers and mutually reactive copolymers have also been studied for humidity sensing [71].

1.4.2.7 Polyelectrolyte-based Resistive Sensors

Polyelectrolyte are polymers with electrolytic groups, which could be salts, acids and bases. Based on functional groups, humidity-sensitive polyelectrolytes are fundamentally divided into three major categories: quaternary ammonium salts [66–68], sulfonate salts [69,70] and phosphonium salts [71,72–74]. To absorb moisture, the polyelectrolytes are usually prepared as porous thin films.
As shown in Fig. 1.2, Cl\(^-\) is a counter ion in poly(dimethyl diallyl ammonium chloride), while Na\(^+\) is a counter ion in poly(sodium p-styrene sulfonate). Apparently, the mobility of the counter ions in polyelectrolytes is very high. An important problem encountered in adopting these polymers to humidity sensors is water resistivity. Polymer electrolytes are generally hydrophilic and soluble in water, so that they have a poor durability against water or dew condensation. This problem has been mitigated by cross-linking reagent and/or copolymerizing hydrophilic monomers with hydrophobic monomers.

Many other copolymers have been investigated. Examples are crosslinked copolymers prepared from styrene sulphonate, a vinyl polymer and N, N-methylene (bis-acrylamide) (a cross linking reagent) or from styrene sulphonate and polyvinyl chloride, a copolymer of sodium styrene sulphonate and 2-hydroxy ethyl methacrylate. Sensitivity, stability and reliability are of course dependent upon the chemical structure of the polymers.

![Chemical structures](image)

**Fig. 1.2 Two typical polyelectrolytes**

### 1.4.2.8 Conducting/Semiconducting Polymers

In polymers and single molecules, sometimes double bond and single bond may occur alternately along the main chain. This structure is called conjugation, which is a key for semi conductive and conductive polymers. A conjugation structure existing along the entire main chain with universal conjugation.

![Conjugation structure](image)

**Fig. 1.3 Poly(p-Phenyl Vinylene), a typical conducting polymer with universal conjugation.**
Conductive polymers were first reported in 1977 [75]. As conducting polymers, polyaniline (PANI) and its derivates have been found to be humidity sensitive for a long time [76–78]. Poly (p-diethyl benzene) or PDEB was reported as a conducting polymer due to its long-chain conjugated structure by M. Yang et. Al. M.Yang et al. [79] also reported the investigation of other conducting polymers such as Poly(propargyl benzoate) (PPBT), p-diethyny/benzene-co-propargyl alcohol and ethyl benzene-co-propargyl alcohol (copolymer) for humidity sensing [80].

1.4.2.9 Hygrometric Humidity Sensors

Transduction from air humidity via the mechanical domain is one of the oldest techniques known. A device designed by Gerlehch and Sager [81–83] consists of a silicon/polysilicon membrane with a hygroscopic polyimide layer on top. In this device, polymer-doped silicon is used as the piezo resistive material. As the air humidity increases the polyimide swells due to the adsorption of water vapour. Due to differences in expansion coefficients of silicon/polysilicon and polyimide, the bending of the membrane structure is changed and latter is measured with the integrated piezoresistors. They are placed where the bending of the membrane is maxima and hence the signal is large, i.e. near the ridges.

A hygrometric device with an optical input and output was reported [84]. This device uses a mirror fixed in between one fixed hair bunch while the other is connected to a metal sheet. When the humidity changes, the strain in the hair pull the metal sheet up or down, thereby changes the window area. In turn, this causes a change in transmitted light and hence a change in the output current of the photodiode, compared to capacitive or conductance type devices, this shows an improved long-term stability and less temperature dependency.

1.4.2.10 Gravimetric Humidity Sensors

The most widely known gravimetric humidity sensor is the quartz crystal microbalance (QCM) [85]. Thin plates of piezoelectric quartz have resonance frequencies in this MHz range, when coated with hygroscopic layer, the change in frequency acts as a measure for the humidity. By using a non-coated reference resonator, cross sensitivities of pressure and temperature can be minimized. Properties such as response time, sensitivity and hysteresis of tile QCM are largely dependent on the applied
hygroscopic film. A few interesting devices have been recently reported, e.g. with fullerene layers, with sol-gel produced silica coatings.

**1.4.2.11 Optical Humidity Sensors**

Information about air humidity can be achieved by studying the various parameters associated with electromagnetic wave such as amplitude, polarisation, frequency or by the phase of the wave. Optical techniques make use of the absorption wavelength of water, when light is passed through a gas. The absorption of certain wavelengths provides information about the adsorbed water which can change both the polarisation and the amplitude of an incident optical signal. Mitschke used a fiber optic sensor where light is passed through a fiber and received by a sensor [85].

**1.4.2.12 Piezo Electric Materials as Sensors**

Piezoelectric materials have been used for acoustic wave sensors. Here, an electric field is applied to a piezoelectric material via metal electrodes to induce ultrasonic acoustic waves. Piezoelectric devices based on lead zirconate titanate (PZT) were studied extensively for humidity sensing. PZT replaced barium titanate as the piezoelectric material of choice for most applications later on.

For surface-acoustic-wave (SAW) devices, piezoelectric substrate materials (such as lithium niobate, lithium tantalite or quartz crystals) and thin films of oriented zinc oxide or aluminium nitride were used [86].

**1.4.2.13 Negative Temperature Coefficient Thermistors**

Negative temperature coefficient thermostors resistors have also been widely produced for over thirty years and are primarily employed as sensors for temperature measurement and control and as nonlinear circuit elements for voltage regulation or temperature compensation.

Spinel solid solutions in the oxide system Ni-Mn-Co-Cu, has been used in devices. Materials in this system possessed high temperature coefficient, had excellent stability and was readily sintered in an air atmosphere [86].
1.5 WATER-ADSORPTION ON OXIDE SURFACES (CONDUCTION MECHANISM)

The electrical properties of ceramics change because of water-adsorption processes on their surface, which permit their use as humidity sensors. As dry oxides are kept in contact with humid air, water molecules chemisorb on the available sites of the oxide surface, mainly at the neck parts of crystal grains, by a dissociative mechanism to form two hydroxyl ions for each water molecule; from each water molecule, the hydroxyl group adsorbs on metal cations present in the surface layer of the grains, which possess high local charge density and a strong electrostatic field, and the proton reacts with an adjacent surface $O^{2-}$ ion to form a second OH$^-$ group.

The chemisorbed layer, once formed, is not further affected by exposure to humidity. When the first layer of water molecules is formed, subsequent layers of water molecules are physically adsorbed on the first hydroxyl layer. The physisorbed water easily dissociates to form $H_3O^+$ because of the high electrostatic fields in the chemisorbed layer. The first layer of physisorbed water molecules is characterized by double hydrogen bonding of a single water molecule. The physisorption changes from monolayer to multilayer as the water-vapour pressure increases. Water molecules in the succeeding physisorbed layers are only singly bonded and form a liquid-like network.

Therefore, singly bonded water molecules are able to form dipoles and to reorient freely under an externally applied electric field, resulting in an increase in the dielectric constant. Physisorption of water molecules can take place at temperatures lower than 100°C. At higher temperatures, chemisorption of water molecules is only responsible for changes in the electrical conductivity of ceramics. Surface hydroxyl group start to desorb at about 400°C. The interaction between the porous structure and water must also be considered. The presence of open porosity permits water condensation in the capillary pores. The quantity of condensed water depends on the available pore sizes and their distribution. It is possible to evaluate the pore radius at which capillary condensation occurs at different temperatures (T) by using the Kelvin equation:

$$r_K = \frac{2\gamma M}{\rho RT \ln(P_s/P)}$$ (2)
where \( r_K \) is the Kelvin radius, \( P \) is the water-vapour pressure, \( P_s \) is the water-vapour pressure at saturation, and \( \gamma \), \( \rho \) and \( M \) are the surface tension (72.75 dyn cm\(^{-1}\) at 20 °C), density and molecular weight of water, respectively. The water condensation takes place in all the pores with radii up to \( r_K \), at given temperatures and water-vapour pressures. The smaller the \( r_K \), the lower the temperature, the more easily condensation occurs. The rh sensitivity of a ceramic oxide is therefore related to the number of water molecule adsorption [15].

![Grotthuss mechanism – protons tunnel from one water molecule to another via hydrogen bonding](image1)

**Fig. 1.4** Grotthuss mechanism – protons tunnel from one water molecule to another via hydrogen bonding [15]

![Four stages of adsorption](image2)

**Fig. 1.5** Four stages of adsorption [87]

1. Chemical adsorption of water molecules on activated sites
2. Formation of an adsorption complex
3. Formation of surface hydroxyl groups with the metal
4. Adsorption of another \( \text{H}_2\text{O} \) molecule between the neighbouring surface hydroxyl groups
1.6 STRUCTURE OF PEROVSKITES

Important classes of mixed metal oxides are known as perovskites. The perovskites have the general formula $\text{ABX}_3$ in which the 12 coordinate hole of $\text{BX}_3$ is occupied by a large A ion. The X ion is most frequently $\text{O}^{2-}$ or $\text{F}^-$. Perovskite itself is named after the naturally occurring oxide mineral $\text{CaTiO}_3$ and the largest class of perovskites are those with the anion as oxide. In its ideal form, the perovskite structure is cubic with each A cation surrounded by twelve X anions and each B cation surrounded by six X anions. In fact, the perovskite structure may also be described as a cubic close packed array of A and oxide ions (arranged such that each A-type cation is surrounded by twelve $\text{O}^{2-}$ ions from the original close-packed layers) with B cations in all the octahedral holes that are formed from six of the oxide ions, giving $\text{B}_{m/4}\text{A}_{n/4}\text{O}_3$ equivalent to $\text{ABO}_3$. This breadth of perovskites is widened by the observation that solid solutions and non-stoichiometry are also common features of the perovskites structure, as in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ and $\text{SrFeO}_{3-y}$. Some metal rich materials adopt the perovskite structure with the normal distribution of cations and anions partially inverted.
The perovskite structure is often observed to be distorted in such a manner that the unit cell is no longer centrosymmetric and the crystal develops an overall permanent electric polarization as a result of ion displacement [89].

### 1.6.1 Perovskite Materials

Perovskite materials exhibit many interesting and intriguing properties from both the theoretical and the application point of view. Colossal magneto resistance, ferroelectricity, superconductivity, charge ordering, spin dependent transport, high thermo power and the interplay of structural, magnetic and transport properties are commonly observed features in this family. These compounds are used as sensors and catalyst electrodes in certain types of fuel cells and are candidates for memory devices and spintronics applications [90].

Many superconducting ceramic materials (the high temperature superconductors) have perovskite-like structures, often with 3 or more metals including copper and some oxygen positions left vacant. One prime example is yttrium barium copper oxide which can be insulating or superconducting depending on the oxygen content. This material is being considered as a replacement for platinum in catalytic converters in diesel vehicles [91].
1.6.2 Properties and applications of Perovskites materials

Perovskites find technical application in ceramics, refractories and electronics, as well as possible hosts for nuclear waste. Table 1.3 lists the properties and applications of some commonly investigated perovskites.

Table 1.3 Properties and applications of few perovskite

<table>
<thead>
<tr>
<th>Property</th>
<th>Application</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical property</td>
<td>Electro optical modulator, laser host, switch, second harmonic generator</td>
<td>(Pb,La) (Zr,Ti)O₃, YAlO₃, LiNbO₃, KNbO₃</td>
</tr>
<tr>
<td>Ferroelectric/Piezoelectric</td>
<td>Piezoelectric transducer, P.T.C. thermistor, Electrostrictive actuator</td>
<td>BaTiO₃, Pb(Zr,Ti)O₃, Pb(Mg,Nb)O₃</td>
</tr>
<tr>
<td>Magnetic property</td>
<td>Magnetic bubble memory, ferromagnet</td>
<td>GdFeO₃, LaMnO₃</td>
</tr>
<tr>
<td>Electrical and Dielectric property</td>
<td>Multilayer capacitor, Dielectric resonator Thinfilm resistor</td>
<td>BaTiO₃, BaZrO₃</td>
</tr>
<tr>
<td>Ionic conducting</td>
<td>Solid electrolyte</td>
<td>(La,Sr) (Ga,Mg)O₃₋δ</td>
</tr>
<tr>
<td>Proton conducting</td>
<td>SOFC electrolyte, hydrogen sensor</td>
<td>BaCeO₃, SrCeO₃, SrZrO₃, (La,Sr)Mn O₃₋δ</td>
</tr>
<tr>
<td>Mixed conducting</td>
<td>SOFC electrode</td>
<td>BaPrO₃, LaCoO₃</td>
</tr>
<tr>
<td>Super conducting</td>
<td>Superconductor</td>
<td>Ba(Pb, Bi)O₃</td>
</tr>
<tr>
<td>Catalytic property</td>
<td>Catalyst</td>
<td>LaFeO₃, La(Ce,Co)O₃</td>
</tr>
</tbody>
</table>

1.7 LANTHANUM ORTHOFERRITE (LaFeO₃)

Lanthanum orthoferrite, LaFeO₃, is one of the most common perovskite-type oxides and has an orthorhombic perovskite structure with space group Pbnm [92]. LaFeO₃ consists of FeO₆ octahedra units with La³⁺ ions inserted between these units. The atomic positions in the unit cell have been determined by X-ray diffraction on small twinned single crystals [93]. In this structure Fe³⁺ ions are located at the centers of slightly distorted O²⁻ octahedral. The Fe³⁺ ions are coupled antiferromagnetically to six
Fe$^{3+}$ nearest neighbours via Fe-O-Fe super exchange and exhibit G-type antiferromagnetic ordering like all the other rare earth perovskites [94]. It has been assumed that the magnetic moments point along the crystallographic a direction because such is the case with all the other members of the series at high temperatures.

LaFeO$_3$ first in the series of rare earth orthoferrites, exhibit like all of its members, an orthorhombically distorted perovskite structure with space group Pbnm. Lanthanum ferrite, LaFeO$_3$, crystallises in the orthorhombic space group Pbnm at temperatures below ~ 1273 K. At temperature above 1273 K, it has rhombohedral structure with space group $R\overline{3}c$. The crystal structure of LaFeO$_3$ is shown in Fig. 1.8

![Orthorhombic Perovskite Unit Cell](image)

**Fig. 1.8 Orthorhombic Perovskite Unit Cell**  
Blue, Yellow and Red respectively A cations, B cations and oxygen ions.

AFeO$_3$ oxides (the so-called orthoferrites) belong to a relevant class of weak ferromagnetic materials with interesting magnetic-optical properties [95]. The magnetic structure in orthoferrites can be conventionally described by two interpenetrating pseudo-cubic face centred sub-lattices in which each Fe$^{3+}$ ions is surrounded by six O$^{2-}$ ions. This results in a collinear arrangement of the two sub-lattices, giving an antiferromagnetic ordering. However, the FeO$_6$ octahedra can be tilted to different degrees depending on the size of the rare-earth cation, leading to a net magnetic moment [96,97].
Bulk LaFeO$_3$ is known to be antiferromagnet with a Neel temperature $T_N$ of 740°C [98]. It has much practical interest for electroceramic applications due to their attractive mixed conductivity displaying ionic and electronic defects. The mixed ionic-electronic conductivity of LaFeO$_3$ exhibits a linear response to oxygen pressure and provides oxygen sensor applications [99]. Moreover, LaFeO$_3$ nanoparticles exhibited good photocatalytic properties under visible light irradiation [100,101].

1.8 METHODS OF SYNTHESIS OF LANTHANUM FERRITES

Conventionally solid-state oxide reaction method was used for preparation of LaFeO$_3$. This conventional route was employed due to simplicity and low manufacturing cost. The method results in single phase of perovskite. However, it is associated with drawbacks such as diffusional constraint to synthesis, results into slow kinetics and high temperatures results in uncontrolled particle size and lower surface area. Alternative routes to solid-state reaction method are wet chemical synthesis methods such as, coprecipitation, combustion, sol-gel methods, etc. In all these wet chemical synthesis methods, pure phase formation can be accelerated, as it involves mixing of elements at atomic level and lower calcinations temperatures. In addition to this, it is possible to have controlled particle size, morphology, and improvement in surface area. Based on the varied applications different synthesis methods have been used by different researchers. A number of attempts have been made for synthesis of LaFeO$_3$, for different purposes.

LaFeO$_3$ is synthesized by many methods. There are various types of methods to process LaFeO$_3$ which can be classified into four types:

a) Co-Precipitation Method  
b) Solution combustion synthesis (SCS)  
c) Sol-Gel Technique  
d) Sol-gel auto combustion method

1.8.1 Co-Precipitation Method

Co-precipitation is an attractive method of producing ferrites because of increased homogeneity, purity and reactivity over other methods. The chemical species most frequently used are the hydroxides, oxalates, and carbonates. A useful method of preparing ferrites has been developed by the co-precipitation of preferred combinations of
metal carbonates and hydroxides. These combinations give powders of predictable compositions, low impurity levels and optimum particle sizes and reactivities. Some of the variables which are controlled are pH, temperature, rates of addition and degree of agitation. The method is used to prepare NiZn, MgMn, and MnZn ferrites. Control of composition and impurity level is achieved by proper choice of raw materials and processing techniques.

In this method, soluble salts of the desired metal cations are dissolved (usually in water) and co-precipitation is achieved by heating or by addition of a precipitating agent resulting in the formation of insoluble salts. Carbonate precursors, calcite type solid solutions are used for the synthesis of complex mixed metal oxides. Hydroxide, nitrate and cyanide solid solutions can also be used. Co-precipitation depends on similar solubility of metal salts, similar precipitation rate and formation of solid solution. Successful preparation by calcinations may depend on similar decomposition temperatures for the metal precursors, structural similarity and compatibility of the oxides. Mixed metal precursors can also be used to produce ceramic oxide powders.

![Flow chart for the powder preparation using a co-precipitation route](image-url)

**Fig. 1.9 Flow chart for the powder preparation using a co-precipitation route**
Stoichiometric amounts of comprising oxides and/or carbonates were first dissolved in nitric acid solution by stirring on a hot plate. After the complete dissolution of these component oxides and/or carbonates, this solution was added dropwise into a stirred ammonia solution at 80°C. A white precipitate was formed at a pH value around 9. The resulting precipitate was then aged for 24h on the hot plate and evaporated in the oven at 150°C. Calcination was subsequently carried out for the dry precursor powder.

In another type of preparation, aqueous solutions of lanthanum nitrate and iron nitrate were prepared separately and mixed together in 1:1 molar ratio. The prepared solution was dropped slowly into 50% ammonia solution to form precipitate. After complete precipitation the resultant brown precipitate was aged for 24 h. Subsequently precipitate was dried at 120°C for 12 h. In order to prepare crystalline LaFeO₃ perovskite dried precursor was subjected to calcination by using a predefined heating cycle. This specific heating cycle, with relatively slow heating rates and long holds at temperatures, is important in phase formation of perovskite with retaining higher surface area.

The reactions for co-precipitation method could be described as given below:

\[
\text{La(NO}_3\text{)}_3 + \text{Fe(NO}_3\text{)}_3 + \text{NH}_4\text{OH} \rightarrow \text{La(OH)}_3 + \text{Fe(OH)}_3 + \text{NH}_4\text{NO}_3
\]

\[
\text{La(OH)}_3 + \text{Fe(OH)}_3 \rightarrow \text{LaFeO}_3
\]

According to the reactions given above, nitrates are precipitated in the form of hydroxides, respective hydroxides undergo reactions and yield required perovskite product.

S. Nakayama prepared LaFeO₃ perovskite-type oxide [102] from the thermal decomposition of a co-precipitated precursor, La(OH)₃ and Fe(OH)₃. The formation of the LaFeO₃ perovskite oxide by co-precipitation was clearly recognized at calcining temperatures above 800°C.

Wankassama Haron, prepared nano-LaCoO₃ through low calcination temperature [103], La(NO₃)₃.6H₂O and Co(NO₃)₂.6H₂O were used as starting materials. The precursor that was obtained after the addition of the precipitating agent was calcined at 900°C for two hours yielding high purity perovskite phase of LaCoO₃.
The \( \text{Mg}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 \) polycrystalline spinel ferrites were prepared by the oxalate co-precipitation method \cite{104}. The high purity starting materials \( \text{MgSO}_4\cdot7\text{H}_2\text{O} \), \( \text{CdSO}_4\cdot8\text{H}_2\text{O} \) and \( \text{FeSO}_4\cdot7\text{H}_2\text{O} \) were used for preparation of the samples. These chemicals were weighed in desired stoichiometric proportion and dissolved in distilled water. The precipitating reagent was ammonium oxalate. The resultant precipitate was the solid solution of cadmium oxalate, magnesium oxalate, and ferrous oxalate. The precipitate along with solution was digested on sand bath for one hour for it to settle down at the bottom of the beaker. The co-precipitated product \( \text{Mg}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 \) was dried and pre-sintered.

Nickel ferrite spinel nanoparticles of very small size were prepared by co-precipitation techniques \cite{105}. Crystallite size of the particles increased with annealing temperature. The co-precipitation derived particles had irregular shape and very small particle size with a wide size distribution. Appropriate amount of ferric nitrate and nickel nitrate were dissolved in sufficient amount of de-ionized water. In order to control the pH, sodium hydroxide, which acts as the precipitating agent was added to the solution kept under constant stirring. The resulting precipitate was annealed to form the ferrite nanoparticles.

1.8.2 Solution combustion synthesis (SCS)

Solution combustion synthesis (SCS) is an effective method for the synthesis of lanthanum ferrite materials and has been used in the production of various ceramic powders for a variety of advanced applications. Ceramic oxide powders at the nanoscale using SCS can be prepared by the combination of metal nitrates (oxidizers) in an aqueous solution with a fuel (e.g., glycine, urea, Hexamethylene tetraamine (HMTA), hydrazides). Glycine and urea, in particular, are suitable fuels because they are amino acids that can act as a complexing agent of the metal ion in the solution and also serve as fuel for the synthesis of nanocrystalline metal oxides. This method can directly produce the desired final product, although in some cases, a subsequent heat treatment of the synthesized powder is needed to promote the formation of the required phase. The properties of the resulting powders (crystalline structure, amorphous structure, crystallite size, purity, specific surface area and particle agglomeration) depend heavily on the adopted processing parameters.
Solution combustion synthesis (SCS) is a simple, suitable and fast process for synthesizing the variety of nano sized materials in the range (1-100 nm). This process depends on the volume or layer-by-layer self-propagating combustion modes. This process is not only for synthesizing nanosized oxide materials but also allows standardized doping of suggestive amounts of rare-earth contamination ions in a single step.

Using solution combustion method various possible oxides structures could be prepared such as perovskite (e.g. LaFeO$_3$), spinel (e.g. MgAl$_2$O$_4$), garnet (e.g. Y$_3$Fe$_5$O$_{12}$), hexa ferrite (e.g. SrFe$_{12}$O$_{19}$) etc. The latest developments in SCS technique have paved way for several material applications.

G.Venkaiah et al. prepared lanthanum ferrite nanopowdered sample by solution combustion [106]. In this technique, stoichiometric amounts of La(NO$_3$)$_3$.6H$_2$O and Fe(NO$_3$)$_3$.9H$_2$O were mixed together in aqueous medium with glycine solution(NH$_2$CH$_2$COOH). Glycine to total metal ion concentration was varied between two and three. The solution was ignited rapidly upto a certain temperature (eg.200°C). On ignition, vigorous fumes of CO$_2$ and N$_2$ were formed, with elimination of water. The ignition temperature helps in the formation of the perovskite. Resulting product was subjected to further calcination to synthesize the targeted product.

The equation representing the reaction is given below:

$$3\text{La(NO}_3\text{)}_3 + 3\text{Fe(NO}_3\text{)}_3 + 10\text{C}_2\text{H}_5\text{NO}_2 \rightarrow 3\text{LaFeO}_3 + 25\text{H}_2\text{O} + 20\text{CO}_2 + 25\text{N}_2$$

Todd Striker and James A. Ruud investigated the effect of fuel choice on the aqueous combustion synthesis of lanthanum ferrite and lanthanum manganite [107]. High-surface area, nanocrystalline powders of two closely related perovskite oxides, LaFeO$_3$ and LaMnO$_3$, were produced by aqueous combustion synthesis using two different fuels. LaMnO$_3$ powders synthesized using glycine fuel had a higher surface area and a smaller crystallite size than when synthesized using ethylene glycol fuel. However, the opposite was observed for LaFeO$_3$ powders, where a higher surface area and a smaller crystallite size was obtained using ethylene glycol. The effect of the fuel type on the powder properties was attributed to the combustion characteristics, such as the rate of temperature increase and maximum measured temperature, and the mode of combustion synthesis. The lower surface area LaFeO$_3$ and LaMnO$_3$ powders had higher rates of temperature
increase, which is characteristic of a volume combustion synthesis mode. The high-surface area LaFeO$_3$ powder produced using ethylene glycol fuel, in contrast, had a lower rate of temperature increase, representative of a self-propagating high-temperature synthesis mode. Differential thermal analysis showed that the mode of combustion correlated to the delayed reaction of the iron nitrate oxidizer with the ethylene glycol fuel. For the combustion synthesis of multication complex oxides, each fuel–oxidizer reaction is important for predicting the combustion characteristics and the resulting powder properties [108,109].

1.8.3 Sol-Gel Technique

Among the available wet chemical methods, the sol-gel process is undoubtedly the simplest and the cheapest one. The method is based on the phase transformation of a sol obtained from metallic alkoxides or organometallic precursors. The advantages of the sol-gel methods are its versatility and the possibility to obtain high purity materials, the composition is perfectly controlled. The sol-gel process is a wet chemical technique for the fabrication of nanocrystalline material (typically a metal alkoxide) starting from a chemical solution containing colloidal precursors(sol). Typical precursors like metal alkoxides and metal chlorides are used. It can be used in ceramic manufacturing processes, as an investment casting material or as a means of producing very thin films of metal oxides for various purposes.

1.8.3.1 Fundamentals of sol-gel processing

The sol-gel synthesis process involves the hydrolysis and the condensation of metal alkoxide(M(OR)\textsubscript{n}), where M is the metal, O the oxygen, R the organic group. Since the metal alkoxide and the water are insoluble in each other, they are dissolved in a common alcoholic solvent in order to carry out the reaction. The alkoxide group(OR), being highly electronegative, creates a partial positive charge on the central metal atom. On the other hand, in the water molecule, there exists a partial negative charge on the oxygen atom. As a result, metal alkoxides are highly reactive to water. The water molecule attacks the central atom, which results in the hydrolysis of the alkoxide.

The hydrolysis and the condensation reactions are generally described as:

\[
\begin{align*}
\text{Hydrolysis:} & \quad M(OR)_4 + 4H_2O \rightarrow M(OH)_4 + 4ROH \\
\text{Condensation:} & \quad M(OH)_4 + M(OH)_4 \rightarrow (OH)_3M-O-M(OH)_3 + H_2O
\end{align*}
\]
The kinetics of the hydrolysis and the condensation reactions are governed mainly by the ratio (R) of molar concentrations water to alkoxide. In general, low R-value (<3) is suitable for thin film formation while large R-value (>3) generate powder particles, forming a stable colloidal suspension of oxide nanoparticles (sol) is hence essential. This stable sol is then used for producing either nanocrystalline powder by removing the solvent by heating or nanocrystalline thin films, spin coating and dip coating techniques have been extensively used for producing quality thin films.

1.8.3.2 Advantages of Sol-gel process [110,111]

Sol-gel technique, as a method for synthesizing nanocrystalline materials for sensing, offers several advantages:

- The sol-gel technique is simpler and cheaper than other methods
- It allows an easy coating of large and complex shaped substrates
- The process is inexpensive with respect to the initial investment of the production plant and the running cost
- It produces no perturbation of devices in the case of deposition on top
- It offers easy control of film thickness and porosity
- It can produce ultrafine films
- It is a low temperature process
- Large surface area can be obtained on both films and powders
- It can easily modify the composition with uniformly dispersed dopants which in turn can enhance the sensitivity
- Particle size can be controlled through careful control of the film calcination temperature good porosity and improved surface to volume ratio can be achieved.
1.8.4 Sol-gel auto combustion method

The synthesis of nano LaFeO$_3$ with an orthorhombic structure by sol gel auto-combustion method using citric acid (C$_6$H$_8$O$_7$) as a complexing reagent, La(NO$_3$)$_3$.6H$_2$O and Fe(NO$_3$)$_3$.9H$_2$O as metal precursors was reported by K.M. Parida et al. [108]. According to the stoichiometric composition, specified amount of Fe(NO$_3$)$_3$.9H$_2$O, La(NO$_3$)$_3$.6H$_2$O and citric acid were dissolved in distilled water. The molar amount of citric acid was equal to total molar amount of metal nitrates in solution. Ammonium hydroxide was slowly added to adjust the pH to 7.0 and also to stabilize the nitrate citrate sol. Then the solution was kept stirred continuously at 60°C. Afterwards, the stabilized nitrate citrate sol was poured into a tray and heated slowly to 130°C. The change in viscosity and colour was observed as the sol turned into a brown, puffy, porous dry gel, which on further heating automatically gets ignited as a result of thermally induced oxidation reduction reaction. Finally, the solid dry gel is formed by auto-ignition. The solid dry gel is then activated at different temperatures from 500 to 900°C for 2 h.
LaCo$_{0.6}$Fe$_{0.4}$O$_3$ (LCFO) [112] nano powder was prepared by polymeric precursor method using La(NO$_3$)$_3$.6H$_2$O, Co(NO$_3$)$_2$.6H$_2$O, Fe(NO$_3$)$_3$.9H$_2$O, citric acid, ethylene glycol, nitric acid and deionised water. The precursor solution was prepared by mixing metal nitrates, citric acid, nitric acid and deionised water, ethylene glycol was added to the mixture. The solution was ultra-sonicated for complete dissolution of metal cations in solution. After suitable heat treatment and dehydration of the boiled solution, decomposition resulted in enormous swelling, produced foam and after auto combustion, there was formation of fine black powders. The precursor powder (xerogel) was well ground with an agate mortar and calcined at different temperatures.
1.9 LITERATURE REVIEW

Humidity sensitivity of \( \text{Mg}_{1-x}\text{Li}_x\text{Fe}_2\text{O}_4 \) (0.0 \( \leq x \leq 0.6 \)) samples prepared by solid-state reaction of inorganic precursors was investigated by R.K.Kotnala et al. Specimens prepared by this method were confirmed to exhibit spinel structure by X-ray diffraction studies and FT-IR spectral absorption peaks observed in mid IR spectroscopic analysis at \( v_1 = 580–600 \text{ cm}^{-1} \) and \( v_2 = 400–436 \text{ cm}^{-1} \). Distribution of nano-size grains was observed by scanning electron micrographs. It was observed that the grain size further decreased from 200 nm to 110 nm with substitution of lithium ions. The sensitivity factor increased from 165 for pure magnesium ferrite to 2080 for lithium substitution in the range 10–80% RH. The shortest response time was measured to be 180s for the \( x = 0.4 \) composition sample. The purpose of substituting smaller \( \text{Li}^+ \) ions for \( \text{Mg}^{2+} \) ions was to create more defects and porosity in the structure. The results suggested that lithium ion substitution enhanced the formation of smaller grains of magnesium ferrite, leading to an increase in surface area and improved humidity sensing properties. It was observed that the distribution of wide-open pores shortened the response time. The humidity responses of the samples were examined on the basis of microstructure and conduction mechanism of such porous spinel ferrite materials [113].

The electrical resistance relative to the water absorption of humidity sensors made from \( \text{Ni(Al,Fe)}_2\text{O}_4\text{-TiO}_2 \) ceramic was investigated by L.Wu et al. [114]. The ceramic body formed a spinel structure after sintering and exhibited a porous structure. Porous ceramics easily absorb and desorb water vapour through the pores, and the electrical conductivity is enhanced by water absorption. In this ceramic system the conduction mechanism was found to be ionic. The \( \text{Ni(Al,Fe)}_2\text{O}_4\text{-TiO}_2 \) porous ceramic had a high humidity activity, short response time for humidity detection (less than 40s) and high stability. The highest sensitivity among the specimens studied was found in \( \text{Ni(Al}_{0.875}\text{Fe}_{0.125})\text{O}_4\text{-5 mol}\% \text{ TiO}_2 \).

Humidity–sensitive electrical conductivity of \( \text{MgFe}_2\text{O}_4 \) and \( \text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4 \) porous ceramics were reported by N. Rezlescu et al. [115]. Pure and Sn substituted magnesium ferrites were prepared by sol-gel auto combustion method. Tin ion partially substituted magnesium ion to improve the humidity sensitivity of magnesium polycrystalline ferrite. The phase composition and lattice parameters were determined by
X-ray diffraction (XRD) and the effect of tin substitution on the granular structure was investigated by scanning electron microscopy (SEM). Tin ions affected the crystallite size, surface area and porosity. Tin ions further enhanced the humidity sensitivity of magnesium ferrite.

Thick films of Cu-doped lanthanum strontium ferrites were prepared by screen printing for humidity detection at room temperature by A.Cavalieri et al. The prepared powders were first characterized by X-ray diffraction, scanning electron microscopy and B.E.T. The thick films were heat treated at 800, 900 and 1000°C for 1h and all the compositions proved to be effective in humidity sensing and presented a good reproducibility between several measurements. In particular, the application of La$_{0.8}$Sr$_{0.2}$Fe$_{1-x}$Cu$_x$O$_3$ based solid-state sensors was envisaged, for example in industrial processes and in air-conditioning systems for the automatic regulation of living environments, where it is important to evaluate partial water pressure [116].

The humidity sensing properties of nanocrystalline α-Fe$_2$O$_3$ in the range from room temperature up to 100°C, and the variation of electrical resistance with grain size and temperature was investigated by P.Chauhan et al. [117]. The nanocrystalline α-Fe$_2$O$_3$ films were prepared by sol-spinning process. The grain size and microstructure of these films was controlled by varying the annealing temperatures. The sol process is a chemical process in which independent control over material can be achieved easily. The advantages of the sol-process are good composition control and homogeneity, low processing temperature and low cost. The fabrication of thin film sensors is based on integrated circuit technology and has many potential advantages such as good uniformity, low power consumption, low cost, higher reliability in mass production, micro-miniaturization and integration. The reaction between water and lattice iron was found to be reversible, suggesting the reusability of films.

Mixed ionic and electronic conducting (MIEC) oxides have potential applications as sensors, as oxygen separation membranes, in membrane reactors for syn gas production, and as cathodes for solid oxide fuel cells. La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-\delta}$ or LSCF is a well-known MIEC oxide which enjoys a greater degree of mechanical and chemical stability than other mixed conducting oxides, and hence has been studied extensively. Substituting Sr and Co on the La and Fe sites decreases the high-temperature phase stability of LaFeO$_{3-\delta}$ and the material becomes highly oxygen deficient at elevated
temperatures and reduced oxygen partial pressures. Hence R.Sundaram et al. investigated the humidity dependent DC conductivity on the well-known oxygen deficient mixed conductor La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3.5}$. The compound exhibited good sensitivity to moisture, linearity in the entire RH range and narrow hysteresis [118].

The humidity sensing property of nanocrystalline spinel Ni$_x$Cu$_{0.8-x}$Zn$_{0.2}$Fe$_2$O$_4$ ferrite systems was investigated by V.Jeseentharani et al., using the standard ceramic route. The spinel structure of the compounds was confirmed by X-ray diffraction studies. The samples were subjected to humidity sensing studies by solid-state electrical conductance method. One of the composites had the highest $S_f$ (sensitivity factor) due to larger surface area and porosity of the sample. Good response and recovery characteristics was exhibited by the sample which showed the highest $S_f$ [119].

Perovskite-type lanthanum strontium ferrite ceramics were synthesized in an oxygen atmosphere using the solid phase reaction method. The resistance versus relative humidity (r.h.) characteristics as well as the dielectric and complex impedance spectra were investigated by Z.J.Li et al. [120]. The experimental results were treated by a non-Debye model, and the equivalent circuit parameters were calculated. The model separated the samples into three regions: crystal grain, grain surface and electrode surface. The electrode surface resistance $R_{eo}$ decreased with increasing r.h., but the grain resistance $R_g$ was not affected by water vapour.

Pure and Sn$^{4+}$ and/or Mo$^{6+}$ substituted Magnesium ferrites with compositions Mg$_{1-x}$Sn$_x$Fe$_{2-y}$Mo$_y$O$_4$ ($x = 0.00, 0.10$ and $y = 0.00, 0.02$) have been prepared by sol–gel auto combustion method by N.Rezlescu et al. [115]. The ceramic samples were sintered at 1100°C for 4 h. The phase composition and lattice parameters were determined by XRD, while effect of tin and molybdenum substitutions on the granular structure was studied by SEM. Experimental results revealed that some physical properties are in close relation with the structural changes induced by the presence of tin and Molybdenum ions. The humidity sensitivity of the electrical resistivity largely depended on composition, crystallite size, surface area and porosity. The best results concerning humidity sensitivity were obtained for Mg$_{0.9}$Sn$_{0.1}$Fe$_2$O$_4$ ferrite. The tin ions enhanced the humidity sensitivity of the magnesium ferrite and assured a nanocrystalline structure of this ferrite.
Oxide compounds, \( \text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_{2-x}\text{M}_{x}\text{O}_4 \), in which \( M = (\text{La}, \text{Ga}, \text{Y}) \) and \( x = (0 \text{ and } 0.2) \), were prepared by self combustion method and studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electric measurements by E.Rezlescu \textit{et al.} The XRD analysis evidenced that the compounds containing \( \text{Y}^{3+} \) and \( \text{La}^{3+} \) ions are pluriphasic, whereas the others are monophasic. An increase in average grain size and a decrease in the porosity in the \( \text{Y} \)- and \( \text{La} \) substituted compounds were observed from SEM images. The electrical resistivity decreased by \( \text{La} \) and \( \text{Y} \) incorporation and increased by \( \text{Ga} \) incorporation. The porous \( \text{Ga} \) containing ferrite was the most sensitive to humidity change for this ferrite the resistivity response time to humidity change was shorter.

Humidity sensitive properties of pure and \( \text{K}^+ \) doped nanocrystalline \( \text{LaCo}_{0.3}\text{Fe}_{0.7}\text{O}_3 \) thick film sensors was investigated by Z.Wang \textit{et al.} The humidity sensitive thick films were prepared by screen printing on ceramic substrates with interdigitated electrodes. It was found that pure \( \text{LaCo}_{0.3}\text{Fe}_{0.7}\text{O}_3 \) showed sensitivity only in the relative humidity (RH) above 54%. The addition of alkali \( \text{K}^+ \) was beneficial for improving the humidity sensitive properties of the sample. The best results were obtained for 2 wt.% \( \text{K}_2\text{CO}_3 \)-doped sample, which exhibited excellent linearity in the whole humidity range of 11-95% [122].

The microstructure and humidity sensitivity of \( \text{Cu}_{x}\text{Zn}_{1-x}\text{Fe}_2\text{O}_4 \) ferrites doped with 0.05 and 0.1 wt% of magnesium chloride (\( \text{MgCl}_2 \)) prepared by standard ceramic route have been studied by Nishat Begum \textit{et al}. Microhardness, bulk density, porosity and water absorption properties were studied. It was found that the humidity sensitivity depends on composition and porosity. Dependence of electrical resistivity on composition, temperature and humidity was also investigated. Electrical resistivity decreased with the increase of temperature, humidity and molar weight of copper oxide (CuO) content but increased with \( \text{MgCl}_2 \) doping. It was concluded that the Cu-Zn ferrite with low \( \text{MgCl}_2 \) doping could be a suitable candidate for a humidity sensitive material [123].

A ceramic thick film humidity sensor, produced from Mn Zn ferrite, was investigated by K.Arshaka \textit{et al}. The proposed sensing mechanism was a combination of proton hopping, hydronium diffusion and vacancy donor traps releasing electrons into the conduction band. The sensor structure comprised of a two-layer device; the first layer was an interdigitated conductor and the second layer was a 30 m thick sensing layer. The
effects of sintering the sensing pastes in air and vacuum were reported. The air-fired sample exhibited the highest humidity sensitivity and the lowest temperature sensitivity. The vacuum-fired sample had the lowest humidity sensitivity and the highest temperature sensitivity. The sensitivity results indicated that the air-fired sample had the best potential for use in humidity sensing applications [124].

Polycrystalline soft ferrite samples were prepared with chemical formula, \( \text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4 \) \( (x = 0.30; 0.50; 0.70; 0.80 \text{ and } 0.90) \) doped with controlled amount of lithium chloride (LiCl) by standard ceramic technique by A.Y.Lipare et al. The samples were characterized by XRD, IR absorption techniques. X-ray diffraction studies of the compositions reveal formation of single-phase cubic structure. The values of lattice constant decrease as doping percentage of LiCl is increased from 0.01% to 0.10%. Temperature dependent \( dc \) resistivity was carried out in the temperature range from 300 to 800 K. From the compositional study, it was found that the dielectric constant shows decreasing trend with increasing both zinc concentration as well as doping percentage of lithium chloride [125].

Polycrystalline soft ferrites, \( \text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4 \) \( (x = 0.30, 0.50, 0.70, 0.80 \text{ and } 0.90) \), doped with controlled amount of calcium chloride (CaCl\(_2\)) were prepared by standard ceramic route and studied for a.c. susceptibility by A.Y.Lipare et al. X-ray diffraction studies of the compositions revealed formation of single-phase cubic spinel. The values of lattice constant increased as doping percentage of CaCl\(_2\) increased from 0.01% to 0.05% and afterwards decreased slightly. The presence of chlorine ions is confirmed by absorption peak in far IR spectra near 650 cm\(^{-1}\) for all the samples. The variation of a.c. susceptibility with temperature showed the existence of single domain structure for \( x = 0.3 \) and exhibited transition from single domain to multi domain structure with increased Ca\(^{2+}\) contents from 0.01 to 0.1%. The composition, \( x = 0.5 \), showed multi domain structure independent of Ca\(^{2+}\) content [126].

J.Shah et al. investigated the addition of cerium oxide to MgFe\(_2\)O\(_4\) at concentrations of 2 wt%, 4 wt% and 6 wt% in the precursor, while preparing the samples by a ceramic method. All samples were highly resistive of the order of mega ohms at room temperature and humidity. The spinel phase present in the samples is confirmed by X-ray diffraction (XRD). The relative humidity generated is in the range from 10% RH to 90% RH at 25°C. The addition of cerium oxide in the spinel lattice increases the
intergranular porosity, distribution of pore size and open pores. The porosity increases from 2.5% to 26%. With the addition of cerium oxide the sensitivity at low RH increases and shows a better linearity than that of pure magnesium ferrite [127].

The role of gallium and lanthanum ions which partially substituted iron in Mg$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ ferrite on the microstructure and electrical sensing properties was studied by E.Rezlescu et al. Polycrystalline samples of mixed ferrite Mg$_{0.5}$Cu$_{0.5}$Fe$_{2-x}$M$_x$O$_4$ with $x = 0$ or 0.2 and M=La or Ga, were prepared by the ceramic technique. X-ray diffraction patterns of the samples sintered at 1000°C were recorded for the determination of the various phases present in the samples. The scanning electron microscopy (SEM) was used to analyse the microstructure. Average grain size was determined using linear intercept methods [128].

The effect of Cu substitution on the properties of magnesium-zinc ferrites sintered at low temperature were investigated by N. Rezlescu et al. The densification of MgCuZn ferrite is dependent upon Cu concentration in the composition of Mg$_{2.5-x}$Cu$_x$Zn$_{0.5}$Fe$_2$O$_4 + 0.5$MgO. The sintered ferrite with a density of about 4.5 g/cm$^3$ and the electrical resistivity greater than 10$^8$ Ω cm was obtained at relatively low sintering temperature (1050°C), for $x = 0.3$. This sintering condition is suitable for multilayer chip inductor application [129].

The sensitivity to some reducing gases (acetone, ethanol, methane and liquefied petroleum gas—LPG) of calcia doped nickel ferrite (NiFe$_2$O$_4 + 1$%CaO) and cobalt and manganese doped nickel ferrite, Ni$_{0.99}$Co$_{0.01}$Mn$_x$Fe$_{2-x}$O$_{4-δ}$ ($x = 0.01$ and 0.02), was investigated by E.Rezlescu et al. Starting from nitrates, as raw materials, the samples were prepared by self combustion method. The nano sized powders were obtained by quick combustion. After a 30 min heat treatment at 1273 K of the compacted powder in a disc shape, some investigations of the ferrite disks were carried out by X-ray diffraction, scanning electron microscopy and measurements of the electrical resistivity sensitivity to the four test gases. The response time was studied, too. The gas sensitivity largely depends on the composition, temperature and the test gas species. The ferrite compounds doped with Co and Mn were selective to detect reducing gases at low operating temperature. The mixed ferrite with Ni$_{0.99}$Co$_{0.01}$Mn$_{0.02}$Fe$_{1.98}$O$_{4-δ}$ composition was sensitive and selective to acetone gas [130].
Magnetic and humidity sensing properties of nanostructured Cu$_x$Co$_{1-x}$Fe$_2$O$_4$ synthesized by auto combustion technique was studied by S. Muthurani et al. Magnetic nanomaterials (23-43 nm) of Cu$_x$Co$_{1-x}$Fe$_2$O$_4$ ($x = 0.0, 0.5$ and $1.0$) were synthesized by auto combustion method. The crystallite sizes of these materials were calculated from X-ray diffraction peaks. The band observed in Fourier transform infrared spectrum near $575$ cm$^{-1}$ in these samples confirm the presence of ferrite phase. Conductivity measurement showed the thermal hysteresis and demonstrated the knee points at $475^\circ$C, $525^\circ$C and $500^\circ$C for copper ferrite, cobalt ferrite and copper-cobalt mixed ferrite respectively. Among these ferrites, copper ferrite exhibits highest sensitivity for humidity [131].

Nanostructured zinc-copper mixed ferrite synthesized by sol-gel method was investigated for LPG sensing by Anuj Jain et al. XRD patterns of different compositions of zinc copper ferrite, Zn$_{1-x}$Cu$_x$Fe$_2$O$_4$ ($x = 0.0, 0.25, 0.50, 0.75$), revealed single phase inverse spinel ferrite in all the samples synthesized. With increasing copper concentration, the crystallite size was found to be increased from 28 to 47 nm. The surface morphology of all the samples studied by the scanning electron microscopy exhibited porous structure of particles throughout the samples. The pellets of the samples are prepared for LPG sensing characteristics. The sensing is carried out at different operating temperatures ($200, 225$, and $250^\circ$C) with the variation of LPG concentrations ($0.2, 0.4$, and $0.6$ vol%). The maximum sensitivity of $55.33\%$ was observed at $250^\circ$C operating for the $0.6$ vol% LPG [132].

Humidity sensitivity of metal ferrite nanoparticles [MFe$_2$O$_4$, M(II) = Co, Cu, Mg, Ni and Zn] prepared by solid-state reaction of inorganic precursors was studied by V. Jeseentharani et al. The process was convenient, environmentally-friendly, inexpensive and efficient. The spinel structure of the compounds prepared by this method was confirmed by XRD and FT-IR studies. The surface morphology was observed by scanning electron microscopy, and the surface area was analysed by the nitrogen adsorption/desorption study by the Brunauer-Emmett-Teller (BET) method. All the samples were subjected to dc electrical conductivity studies at room temperature. The resistance measurements as a function of relative humidity in the range of $5-98\%$ and the sensitivity factor ($S_f = R_{5\%}/R_{98\%}$) were calculated. Among all the metal ferrites, zinc ferrite (ZnFe$_2$O$_4$) possessed the highest humidity sensitivity factor of $2895 \pm 85$, whereas
the other compounds possessed a very low sensitivity factor. The response and recovery times of ZnFe$_2$O$_4$ were 330 and 80 s [133].

Pellets of MgFe$_2$O$_4$ were prepared by sintering, at different temperatures, powders prepared either by solid-state reaction between MgO and Fe$_2$O$_3$, or by the thermal decomposition of hydroxide mixtures, co-precipitated from magnesium and iron nitrate solutions with an Mg/Fe ratio of 1:2 by G.Gusmano et al. Mercury porosimetry, specific surface area measurements and scanning electron microscopy were used in order to determine the main microstructural characteristics of the pellets. Electrochemical impedance spectroscopy (EIS) was used to correlate the humidity-sensitive electrical response of the pellets with their microstructure, in particular with total open porosity and pore-size distribution. EIS measurements showed a close correlation between their relative humidity dependence of the electrical resistance and the microstructure of the sintered bodies. Good reproducibility and a fast response time to humidity variations, evaluated from d.c. measurements, were also observed [134].

I. Petrila et al. investigated the effect of partially substitution of iron with tungsten on the properties of copper–zinc spinel ferrite for humidity sensors application. The copper–zinc–tungsten Cu$_{0.5}$Zn$_{0.5}$W$_{0.3}$Fe$_{1.7}$O$_4$ spinel ferrite was prepared using a sol–gel auto combustion technology. The ferrites samples were treated for 30 min at 800°C, 1000°C and 1200°C, respectively. X-ray diffraction and scanning electron microscopy were performed in order to identify phase compositions and crystallites structure. The electric properties of the Cu$_{0.5}$Zn$_{0.5}$W$_{0.3}$Fe$_{1.7}$O$_4$ spinel ferrites heat-treated at different temperatures and humidity conditions were characterized and analyzed. As an application of the material the characteristics of resistive and capacitive humidity sensors were analyzed using Cu$_{0.5}$Zn$_{0.5}$W$_{0.3}$Fe$_{1.7}$O$_4$ ferrite as active material [135].

A. B. Gadkari et al. prepared nanocrystallite Mg-Cd ferrite samples by oxalate co-precipitation method. The XRD revealed single phase cubic spinel nature of materials. The crystallite size lies in the range of 27.79 to 30.4 nm. DC electrical resistivity decreases with increasing temperature indicating the semiconductor behavior. The DC electrical resistivity increases and the Curie temperature decreases with increase in cadmium content. All the samples show decrease in resistivity with increase in relative humidity. All the samples were humidity sensitive in low humidity range (40 to 70 %). The electrical resistivity of Cd substituted samples decreased by three order of magnitude,
when %RH increased from 40%RH to 90%RH. The response and recovery time of all the samples were in the range 200-300 sec. The shorter response time was 240 s for composition $x = 0.4$ [136].

**O. F. Caltun et al.** investigated the influence of the manganese substitution on the magnetostrictive coefficient of ferrite samples with compositions of $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$ where $x$ ranged from 0 to 0.6. The samples were made using standard powder ceramic technique. Microstructures of the samples were characterized using a scanning electron microscope. The spinel structure and the presence of residual phases were checked by X-ray diffraction analysis. Saturation magnetization, Curie temperature and magnetostriction measurements were performed on the samples to determine the influence of the substitution. By adjusting the manganese content and the sintering process it was concluded that the material properties could be optimized for use in magnetomechanical stress sensors [137].

Richa Srivastava, explored the synthesis of nanocomposite NiFe$_2$O$_4$-Fe$_2$O$_3$-NiO and its relevance as liquefied petroleum gas sensor. The prepared material was characterized using Scanning electron microscope and X-ray diffractometer. The X-ray diffraction revealed the formation of nickel ferrite along with ferric and nickel oxides. The average crystallite size of material was found to be 4.62 nm. SEM images exhibit the porous nature of sensing material with a number of active sites. Thick film of material was fabricated using screen printing techniques and was investigated with the exposition of liquefied petroleum gas. Variations in resistance of the film with time for different concentrations of LPG recorded at room temperature (28°C). The maximum value of sensitivity was found 5733 for 4 vol.% of LPG. These experimental results showed that the synthesized nanocomposite material was a promising material for LPG sensor [138].

The sensing properties of the humidity sensor made of composite material of nanocrystalline lanthanum ferrite (LaFeO$_3$) and polymer quaternary acrylic resin are investigated by J. Wang et. al., polymer quaternary acrylic resin is compared with those of nanocrystalline lanthanum ferrite, including the sensitivity, the hysteresis, and the response and recover times. The measurement frequency influences both the linearity of the curves of resistance via relative humidity (RH) and the relation between capacitance and RH. By coating the ethyl cellulose on the humidity sensor as protecting films, the
water resistance property of the sensor is improved. Humidity sensing mechanisms of the sensors are discussed [139].

1.10 SCOPE OF THE WORK

- Nanocrystalline lanthanum–metal ferrites (LaM\textsubscript{x}Fe\textsubscript{1-x}O\textsubscript{3-δ}, where \( x = 0, 0.2, 0.4, 0.6, 0.8, 1, M=\text{Sr, Mg, Ca, Ba and Co} \) were prepared by sol-gel method as humidity sensor material.
- The lanthanum–metal ferrites were characterized by different analytical techniques such as Thermal Analysis (TG/DTA), Fourier Transform-Infrared Spectroscopy (FT-IR), Powder X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, Scanning electron microscopy (SEM) and Electron Dispersive X-ray Energy Analysis (EDAX).
- An investigation of electrical conductance and humidity sensing studies of lanthanum–metal ferrite nanocrystalline compounds were carried out.
- Response and recovery time and stability were evaluated for the lanthanum–metal ferrite compounds which showed the highest sensing factor.
- The temperature–dependent electrical conductance studies were carried out to obtain the energy of activation of the nanocrystalline compounds of lanthanum–metal ferrites.