DEVELOPMENT OF HIGHLY SENSITIVE AND SELECTIVE $LaFeO_3$ THICK FLIM CHEMIRESISTIVE TRACE FORMALIINE GAS SENSOR

A Dissertation

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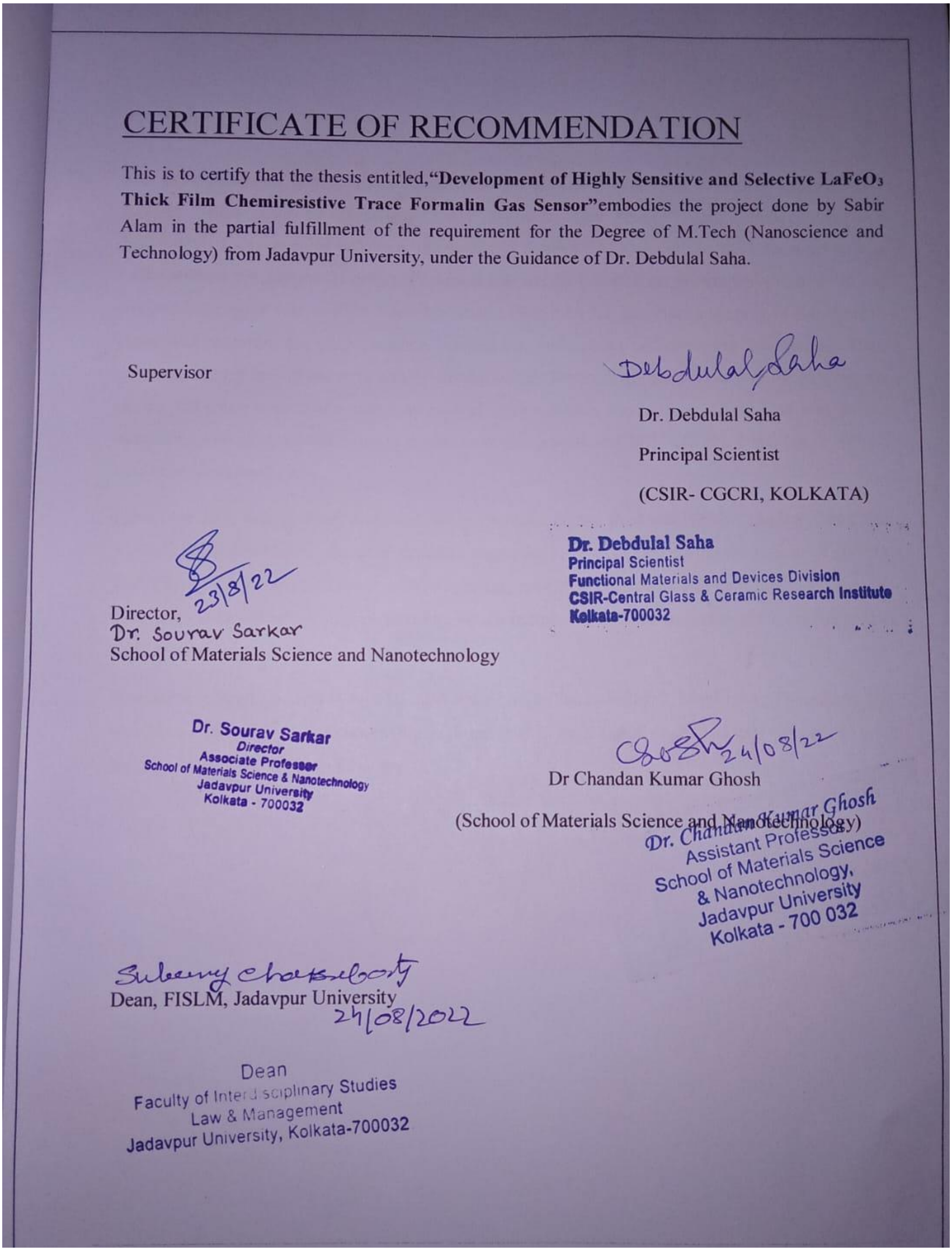

CERTIFICATE OF RECOMMENDATION

This is to certify that the thesis entitled,**"Development of Highly Sensitive and Selective $LaFeO_3$ Thick Film Chemiresistive Trace Formalin Gas Sensor"**embodies the project done by Sabir Alam in the partial fulfillment of the requirement for the Degree of M.Tech (Nanoscience and Technology) from Jadavpur University, under the Guidance of Dr. Debdulal Saha.

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This forgoing thesis is hereby approved as credible study of an engineering subject carried out and represented in a manner satisfactorily to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinion or conclusion drawn therein but approved the thesis only for which it has been submitted.

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I, hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his Master of Technology (Nano Science and Technology) studies during academic session 2020-2022.

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I also declare that, as required by this rules and conduct, I have fully cited and referred all materials and results that are not original to this work.

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Abstract

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List of Abbreviations

CHAPTER 2

2.1 Materials and methods

ABSTRACT

Gas sensor or we can say gas detection instruments are increasingly needed for industrial, health, and safety, environment monitoring and process control. To meet this demand, considerable research into new sensors is underway, including efforts to enhance the performance of traditional devices, such as resistive metal oxide sensor, through nanoengineering. Metal oxide sensor have been utilized for several decades for low cost detection of combustible and toxic gases. However, issues with sensitivity, selectivity, and stability have limited their uses, often in favor of more expensive approaches. Recent advance in nanomaterials provide the opportunity to dramatically increase the response of these materials, as their performance is directly related to exposed surface volume. The recent availability of various metal oxide materials is high surface area nano-powder from, as well as implementation of newly developed nanofabrication techniques, offer tremendous opportunities for sensor manufacturers.

LIST OF SYMBOLS USED ON THIS THESIS

SYMBOLS	SYMBOLS FULL NAME
θ	**Braggs's Angle**
λ	**Wave length of X-ray source**
γ	**Analytic sensitivity of sensor measurement**
D	**Crystallite size of the materials**
β	**Full width at half maximum for diffraction of the materials**
k	**Shape factor of used materials**
h	**Planks constant**
E_g	**Band gap energy**

LIST OF ABBREVIATIONS

ABBREVIATION	FULL NAME
FESEM	**Field Emission Scanning Electron Microscopy**
SEM	**Scanning Electron Microscopy**
XRD	**X-ray Diffraction**
FTIR	**Fourier Transform Infrared Spectroscopy**
XPS	**X-ray Photoelectron Spectroscopy**
PPM	**Parts Per million**
UV-Vis	**UV-Visible Spectroscopy**

CHAPTER 1

1. Introduction

Before we go to our mean topic, we would like to discuss a little-bit about Nano technology. Because here we worked with Nanomaterials, so we must know something about Nanotechnology, Nanomaterials, Nano-particles, etc. and also we know something about ceramic materials its application.

1.1. What is Nanotechnology

- Nanotechnology is the technology of manipulating materials on an atomic or molecular scale especially, to build microscopic devices.

- It is a field of research and innovation concerned with building “things” generally, materials and device on the scale of atoms and molecules. A nanometer is one-billionth of a mater: ten times the diameter of a hydrogen atom. The diameter of a human hair is an average, 80000 nanometers. At such scale, the ordinary rules of physics and chemistry no logger apply. For instance, materials characteristics, such as there, color, strength, conductivity and reactivity, can differ substantially between the nanoscale and the macro. Carbon nanotubes are 100 times stronger then steel but six time lighter.

- Nanotechnology is the use of matter on an atomic, molecular, and supramolecular scale for industrial purposes. The earliest, widespread description of nanotechnology referred to the particular technological goal of precisely manipulating atoms and molecules for fabrication of macroscale products, also now referred to as molecular nanotechnology.

- A more generalized description of nanotechnology was subsequently established by the National Nanotechnology Initiative,Which defined nanotechnology as the manipulating of matter with at least one dimension sized from 1 to 100 nanometers [1]. This definition reflects the fact that quantum mechanical effect are important at this quantum-realm scale, and so the definition shifted from a particular technological goal to a research category inclusive of all types of research and technologies that deal with the special properties of matter which occur below the given size threshold. It is therefore common to see the plural form “nanotechnologies” as well as “nanoscale technologies” to refer to the broad range of research and applications whose common trait is size.

- Nanotechnology is the use of matter on an atomic, molecular, and supramolecular scale for industrial purposes.

- Nanotechnology is science, engineering and technology conducted at the nano scale, which is about 1 to 100 nanometers [2].

A nanometer is one-billionth of a meter

$$1 \text{ nm} = 1/10^9 \text{ m}$$

$$=1\times 10^{-9}\text{m}$$

1.2. History of Nanotechnology

- On December 29, 1959, physicist Richard Feynman gave a radical lecture at an American Physical Society meeting at Caltech titled “**There’s Plenty of Room at the Bottom**”[3].
- Feynman suggested that it should be possible to make machines at a nano-scale that arrange the atoms the way we want and do chemical synthesis by mechanical manipulation.
- This lecture was the birth of the idea and study of nanotechnology.

1.3. What can Nanotechnology do?

Nanotechnology is hailed as having the potential to increase the efficiency of energy consumption, help clean the environment, and solve major health problems. It is said to be able to massively increase manufacturing production at significantly reduced costs. Products of nanotechnology will be smaller, cheaper, lighter yet more functional and require less energy and fewer raw materials to manufacture, claim nanotech advocates. Or we can say, nanotechnology is not simply working at ever smaller dimensions rather working at nanoscale enables scientist to utilize the unique physical, chemical, mechanical and optical properties of materials that naturally occur at that scale [4].

1.4. Where we can use Nanotechnology

We are using Nanotechnology in various field because of there, unusual mechanical, electrical, optical and magnetic properties-

- Carbon Nanotubes
- Medicine
- Information Technology
- Nano robots nano sensors
- Nano computers
- Solar cells
- Paper batteries
- Gas detection device, etc.

1.5. Ceramic Materials

Ceramic materials can be defined as inorganic materials constituted by the combination of metallic and nonmetallic elements whose properties depend on the way in which these elements are linked. Ceramic materials are the more versatile branch of materials. The origin of this versatility lies in the chemical nature of its bonds, science they are mainly constitute by strong ionic and covalent bonds in different proportions. The bonds determine a series of particular properties of ceramic materials among which are relatively high fusion temperature, high modulus, high wear strength, poor thermal properties, high hardness and fragilities combined with tenacities, and low ductility. In addition to the lack of conduction electrons since they are combined forming chemical bonds, they are good electrical insulators [5].

Ceramic materials can be divided into two large group

- Traditional ceramics
- Advanced or technical ceramic

Traditional ceramics can be defined as those that are based on silicates, among which are cement, clay products, and refractories. Traditional ceramics are produced in large volumes and constitute an important market. Traditional ceramic materials are made with raw materials from natural deposits such as clay materials.

The second group, technical or advanced ceramics, is manufactured with artificial raw materials that have undergone an important chemical processing to achieve a high purity and an improvement of their physical

characteristics. Therefore, they are manufactured with more advanced and sophisticated methods. Among them are carbides, nitrides, borides, pure oxides, and a great variety of ceramics with magnetic, ferroelectric, piezoelectric, and superconducting applications, among others.

These ceramics possess excellent mechanical properties under extreme conditions of tension, high wear strength or excellent electrical, magnetic, or exceptional strength to high temperatures and corrosive environments, showing high strength to chemical attack.

1.6 What is sensor?

Sensors are sophisticated devices which can detect and respond to different kind of signals. A sensor converts physical parameter to electrical signal directly. The specific parameter or input could be light, heat, motion, moisture, pressure, or any one of great number of other environmental phenomena. The output is a signal that is transmitted electronically over a network for reading or further processing.

Sensors are used in everyday objects such as touch-sensitive mobile phones, in ATMs, and other useable instruments in daily life. With advance in micromachinery and easy to use micro controller platforms, the use of sensors have increased to large extent in the field of temperature, pressure, moisture measurement etc. Application include manufacturing and machinery, cars, laptops, medical instruments and many other aspects of our day to day life[6].

A good sensor must be

- Sensitive to the measured property
- Insensitive to any other property likely to be encountered in its application, and
- It does not influence the measured property

Common feature of a sensor are as given below:

1. Accuracy- accurate results should be shown with a sensor
2. Environmental condition- usually has limits for temperature/humidity
3. Range- measurement limit of sensor

4. Calibration- essential for most of the measuring devices as the reading changes with time.
5. Resolution- smallest increment detected by the sensor
6. Cost- low cost sensor are preferable
7. Repeatability- the reading that varies is repeatedly measured under the same environment.

Sensors have been classified into many groups such as:

- **Accelerometers** – These are based on the Micro Electro Mechanical sensor **(MEMS)** technology. They are used for patient monitoring which includes pace makers and vehicle dynamic systems.

- **Biosensors** – These are based on electrochemical technology. They are used for food testing, medical care device, water testing, and biological warfare agent detection.

- **Image Sensor** – These are based on the CMOS technology. They are used in consumer electronics, biometrics, traffic and security surveillance and PC imaging.

- **Motion Detector** – These are based on the Infra-Red, Ultrasonic, and Microwave / rater technology. They are used in videogames and simulations, light activation and security detection.

- **Semiconductor Sensors** – These sensors have advantages like high sensitivity, simple operation and are small and compact with low price, whereas it has some disadvantages like difficulty in achieving the desired sensitivity, selectivity and stability.

a. Gas sensor

i. Concept

A typical human nose has 400 types of scent receptors enabling us to smell about 1 trillion different savors. But still many of us do not have the capacity to identify the type or concentration of gas present in our atmosphere. This is where sensors comes in, there are many types of sensors to measure different parametersand a gas sensor is one which comes handy in applications where we have to detect the variation in the concentration of toxic gases in order to maintain the system safe and avoid or caution any unexpected threats. There are various gas sensor to detect gases like formaldehyde, ammonia, oxygen, carbon dioxide, nitrogen, methane, etc. They can also be commonly found in devices that are used to detect the leakage of the harmful gases, monitor the air quality in industries and offices etc. In this thesis hare basically we sense formaldehyde, formaldehyde (HCHO) has been widely used in most of industries including chemical, furniture, textile, construction, printing and cleaning industry which can produce a wide variety of products closely related to people's daily life [1]. Formaldehyde (HCHO) is a gas of colorless and pungent smelling, and can evaporate from products in indoor air and it endangers people's health when the concentration accumulates to a certain degree. When people exposed in formaldehyde atmosphere, headache, nausea, risk of cancer, irritation of the mucous membranes and respiratory tract can be caused once formaldehyde

is inhaled. It was considered as one of the most important air pollutants in the early 1980s and identified as a human carcinogen by the International Agency for Research on Cancer (IARC) till 2004 [2]. Several safety standards towards formaldehyde have been set up. The World Health Organization (WHO) and National Institute for Occupational Safety and Health (NIOSH) have set safe exposure limit of 0.08 ppm and 1ppm to formaldehyde. Thus it is in desperate need of manufacturing sensors having excellent gas-sensing performance towards formaldehyde detecting.

Various ways have been extensively investigated for detecting formaldehyde [7]. For the detection of formaldehyde gas, a series of metal oxides have been reported. In recent study, heterostructure has been considered as an appropriate element to improve the capacity of semiconductor materials for there gas-sensing performance. In this thesis we report for the first time, rGO-$LaFeO_3$based highly selective and stable trace formaldehyde gas sensor. Lanthanum ferrite nanoparticles were prepared by sol-gel synthesis method. The as prepared nano-powders were characterized by multiple sophisticated techniques, viz. X-raydiffraction, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) etc. the as prepared nano-powders prepare a thick film, chemoresistive, type sensor by employing a customized drop coating set up. The sensor shows excellent p-type response towards low ppm formaldehyde. Further, it exhibits negligible cross- sensitivity, fast response and recovery times, and long-term stability. Owing to the excellent sensing performance, long-term stability, and repeatability this sensor is a promising for the detection of formaldehyde gas.

ii. Operating Principles and Sensor Analysis

Sensor analysis is the technique for determination of stimuli from the five (human) senses. The sensory organs can be classified into two sensor types: physical and chemical sensors. The physical sensor measure touch, sight and hearing. The chemical sensors measure olfaction and taste. Olfaction is analyzed in humans during mastication (retro nasal way) or inhalation, while test is analyzed as sweet, salty, sour, or bitter.

The basic principle of chemical sensor analyzed is that chemical compounds readily oxidized or reduce at solid electrodes. This normally results in the deposition of polymeric adherent film on the electrodes. There are electrodes are normally involved in the electrochemical detection of an active analyte; working, reference and counter electrodes. The working electrode serves as transducer, responding to the excitation signal and the concentration of the active analyte, and permitting the flow of electrons or sufficient currents to affect appreciable changes of bulk composition within the ordinary duration of the measurement and permits the observation, measurement and control of potential of the working electrode. The counter electrode merely carries the electrons or current through the cell; no interesting reaction occurs at its surface

Or in short, we can say the ability of a gas sensor to detect gases depends on the chemiresistor to conduct current. The most commonly used chemiresistor is Tin Dioxide (SnO_2) which is an n-type semiconductor that has free electrons (also called as donor). Normally the atmosphere will contain more oxygen than combustible gases [8]. The oxygen particles attract the free electrons present in SnO_2.

As there are no free electrons available output current will be zero. The bellow fig the oxygen molecule (blue color) attracting the free electrons (black color) inside the SnO_2 and preventing it from having free electrons to conduct current.

When the gas sensor is placed in the toxic or combustible gases environment, this reducing gas (orange color) reacts with the adsorbed oxygen particles and breaks the chemical bond between oxygen and free electrons thus releasing the free electrons. As the free electrons are back to its initial state position they can now conduct current, this conduction will be potential the amount of free electrons available in SnO_2, if the gas is highly toxic more free electrons will be available.

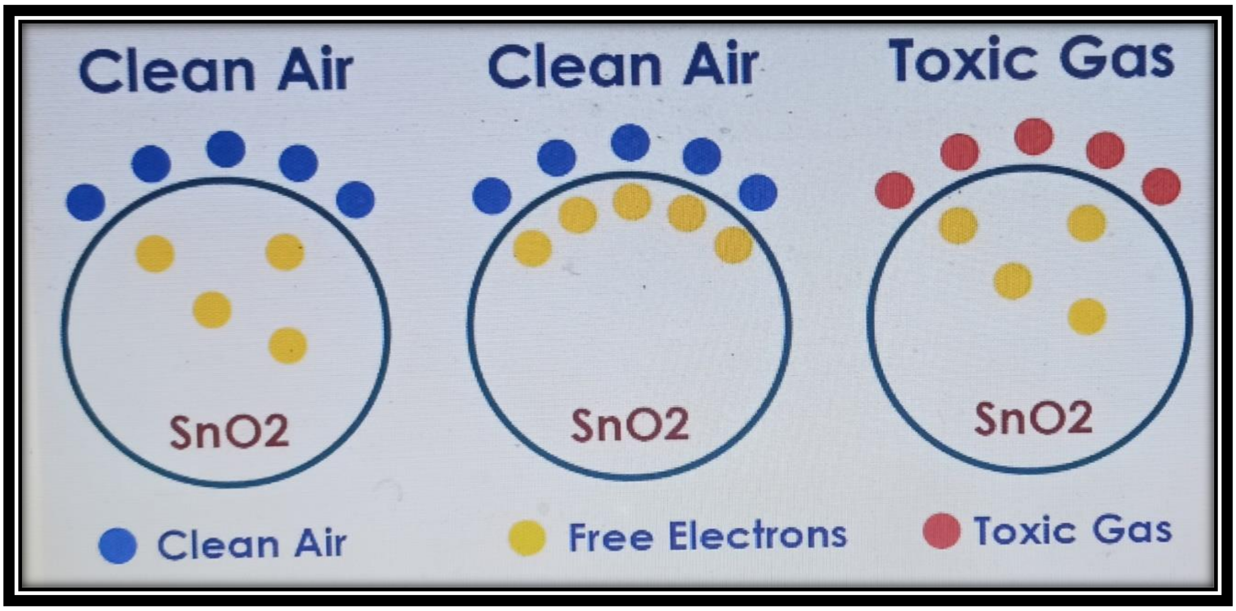


Fig.1. Basic working diagram of gas sensor (adapted from robu.in)

1.7 Classification of gas sensing methods

In order give a clear introduction of sensing principles; this paper classifies gas sensing technologies into two groups: methods based on variation of electrical properties and other properties, as shown in the fig.2.

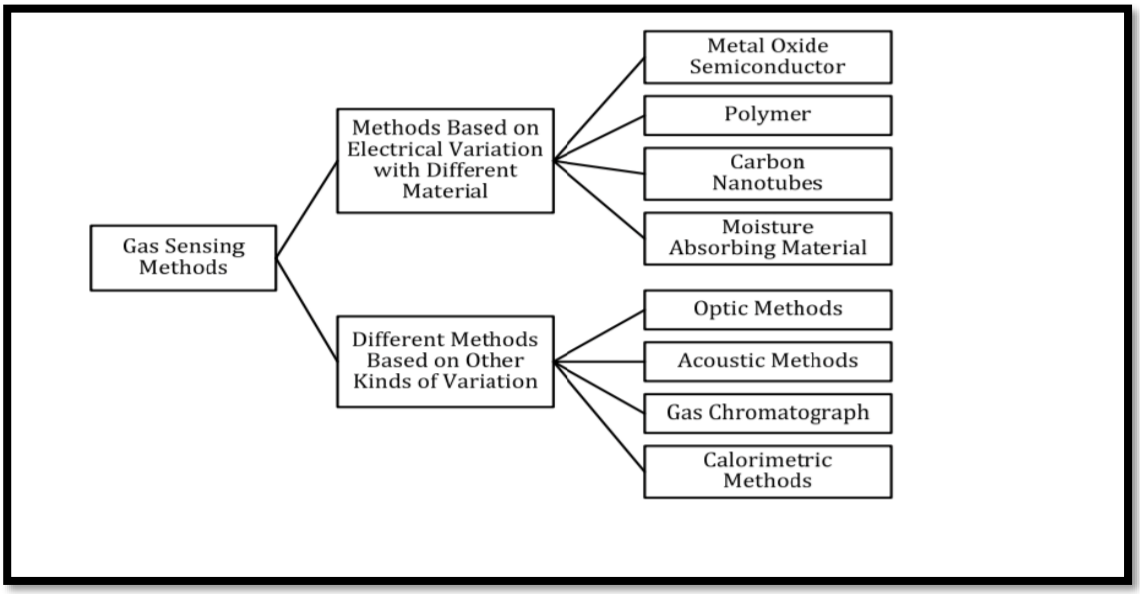


Fig.2. Classification of gas sensing methods

Methods based on variation of electrical properties

Metal Oxide semiconductor

The most common sensing materials are metal oxide semiconductors, which provides sensor with several advantages such as low cost and high sensitivity. Generally, metal oxides can be classified into two types: non-translation and translation [9,4].

The former (e.g., Al_2O_3) contains elements with only one oxidation state since much more energy is required to form other oxidation states, while the latter (e.g., Fe_2O_3) contains more oxidation states. Therefore, translation metal oxides could form various oxidation states on the surface, which is utilized by metal oxide semiconductor as sensing materials, compared to the non-transition one.

More precisely, transition metal oxides with $d^0$and d^{10}electronic configurations could be found in transition metal oxides (e.g., TiO_2, V_2O_5,WO_3) and d^{10} appears in post transition metal concentration are n type semiconductor, there are also a few kinds of p-type semiconductors like NiO_X (usually doped with n type semiconductor like TiO_2) that could be used as gas sensor sensing materials.

It is shown that 10% wt. NiO_x content is needed to convert n type conductivity into p type. The main difference between n type and p type NiO_X doped TiO_2 film is that as temperature increases, the sensitivity of n type towards reducing gases is increased, while that of the p type is decreased therefore p type semiconductors have relatively lower operating temperatures than n type ones.

Sensor based on metal oxide semiconductors are mainly applied to detect target gases through redox reaction between the target gas and the oxide surface. The proces include two steps redox reactions, during which O^- distributed on the surface of the materials would react with molecule with target gases, leading to an electronic variation of the oxide surface and then this variation is transduced into an electrical resistance variation of the sensors [10].

The resistance variation could be detected by measuring the change of capacitance work function, mass, optical characteristics or reaction energy. Metal oxide such as SnO_2, Cr_2O_3, V_2O_5, WO_3 and TiO_2, can be utilized to detect combustible, reducing or oxidizing gases with sensor which are mainly based on the resistance change response to the target gases.

Tin dioxide is the commonly used gas sensing material whose electrical conductivity is dependent on the density of pre-adsorbed oxygen ions on its surface. The resistance of tin dioxide changes according to the variation of gas concentration, liquefied petroleum gas, methane, carbon monoxide and other reducing gases, while the relation between resistance and target gas concentration is nonlinear.

Other metal oxide semiconductor like tungsten trioxide are also widely used for gas sensing. Anodic tungsten oxide applying electrochemical etching of tungsten shows excellent response towards hydrogen and nitrogen oxide. However, the response of pure WO_3 to NH_3 is rather poor and because of the interference from NOx, the selectivity of WO_3 sensors for NH_3 is low [6].

The working temperature of SnO_2 based sensor is 25 ^{0} C to 500 ^{0}C and the best sensing temperature to various gases are different. This could cause potential selectivity problems in applications, because if the temperature deviates too much from the optimal value, other gas components may be more reactive towards SnO_2, leading to poor selectivity. However, if the difference between two temperature is large, a single sensor could also be designed to detect two kinds of target gases at the same time. For example, the optimal sensing temperature of SnO_2 to CH_4 is 400 ^{0}C while that for CO is 90 ^{0}C, which requires a thermostatic cycle of the selective element at the two temperature values so that both gases could be detected by measuring the resistivity of the sensing element during each gas period [11, 5].

The best sensing temperature of another aggressive gas, hydrogen fluoride is different from the above but oxygen is more reactive towards SnO_2 than HF if the temperature is higher than 380 ^{0}C. While the sensitivity of SnO_2 gas sensors could be controlled mainly by temperature, there are several methods that could improve the selectivity of the sensing materials. Selectivity could be improved by doping the sensing film surface with a suitable catalyst material.

Another common method to enhance the selectivity is using sensor arrays based on different sensing elements. A gas sensor array is made up with two or more sensing elements, in order to detect the gas with data of higher dimension. For those with several elements, there is usually a gas recognition circuit for sensor arrays to enhance selectivity.

Sensor based on metal oxide semiconductors have been widely utilized. However, for some sensor, their demand of high operation temperature requires more cost and complicated configurations compered to others working at room temperature, which restricts their development. To solve this problem researchers have come up with some methods such as the utilization of micro-sized sensor elements with micro-heaters fabricated by silicon IC technology and temperature pules operating mode with short heat interval which facilitates the operation of sensor with minimum power consumption. Another problem is the long recovery period needed after each gas exposure, which is not practical for some sensing device like e-noise, and severally restricts their usage in

applications where the gas concentrations may change rapidly. The structural instability and defects of other indicators also limit their filed of application. In conclusion, faced with inherent challenges from their own nature and other kinds of gas sensors, research on sensor based on metal oxide semiconductors should find out some new solutions to overcome their defects. Studies about metal oxide nanostructures could improve gas sensors sensitivity and response time [12].

Polymers

Generally, sensor based on metal oxide semiconductors exhibit significantly greater sensitivity to inorganic gases like ammonia and a few kinds of volatile organic compound like alcohol (C_2H_5OH) and formaldehyde.

However, some other volatile organic compounds which could cause adverse health effects when their concentration over a certain threshold cannot be detected by metal oxide semiconductor-based sensors. These volatile organic compounds could easily be breathed by humans since they are commonly used as ingredients in household products or in an industrial- processes where they normally get vaporized at room temperature therefor it is important to monitor the concentration of these vapors to safeguard the health of residents and workers, such exact requirements need sensing material like polymers.

Although several studies consider polymer- based gas sensing materials applied in detecting inorganic gases like CO_2 and H_2O, they are most frequently used to detect a wide range of volatile organic compounds or solvent vapors in the gas phase, such as alcohols, atomic compounds or halogenated compounds. Like metal oxide semiconductors, when the polymer layer such as its mass and dielectric properties will change upon gas absorption. Specially, the various physisorption mechanisms by which volatile organic compound interact with polymer include dipole interactions and hydrogen bonds [13,8].

Carbon Nanotubes

Conventional sensing materials like metal oxide semiconductors have to deal with problem of poor sensitivity at room temperature, while carbon nanotubes (CNTs) attract more attention because of their unique properties and have become the most promising material for high-sensitive gas sensors. As a kind of promising sensing material, CNTs, have been found to possess electrical properties and are highly sensitive to extremely small quantities of gasses, such as alcohol, ammonia (NH_3), carbon dioxide (CO_2) and nitrogen oxide (NO_x) at room temperature, while other materials like metal oxides have to be heated by an additional heater in order to operate normally. This high sensitivity eliminates the need of assisting technologies like pre-concentration, and thus contributes to the advantage of low cost, low weight and simple configuration. Besides, CNTs outperform conventional sensing materials in term great adsorptive capacity, large surface area to volume ratio and quick response. Moreover, compared with metal oxide semiconductors that require microfabrication technique power supply when utilize as sensing material, CNTs possess good corrosion resistance and better bandwidth [14].

Moisture Absorbing Material

Moisture absorbing materials could be embedded with RFID tags for detection of water vapor concentration, namely the level of humidity, since their dielectric constant could be changed by the water content in the environment.

If RFID tags are covered with moisture absorbing materials like paper, absorbed water would lead to tag antenna near field ohmic losses thus changing their resonance frequency, which could be detected by RFID readers. For passive RFID tags, the minimum power level offered by the RFID reader to power up the tags is determined by the water concentration, which could be expressed in term of the surrounding air’s humidity.

This procedure could be realized with only one tag, but the distance between tags and readers should be kept constant. An alternating method is utilizing two tags at the same time, of which one is covered with moisture-absorbing material and the other is untouched. In this method a table of the difference in power-up level versus the water concentration is needed. Also method in, sensor like that could be located inside walls or floor of building, mainly in order to prevent costly damage due to mold or decay and it could also be positioned under hidden water pipes for detection of leakage. Other applications detecting humidity levels, like water vapor concentration monitoring for food storage, could also utilize methods like those based on moisture absorbing materials and RFID tags [9].

Moisture absorbing materials could also be used as the RFID tag antenna’s substrate rather than as a tag coverage since its dielectric constant could be controlled by the humidity of the surrounding air, which would cause the variation of antenna’s performance that could be detected by the RFID reader.

The moisture-absorbing material enveloped tags are low cost and suitable for mass production. thus more research in this area can be applied.

a. Sensor Performance Characteristics:

The vital key in the operation of a gas sensor which is detects the presence or concentration of gases in the atmosphere. Based on the concentration of the gas the sensor produce a corresponding potential difference by changing the resistance of the material inside the sensor, which can be measure as output voltage. Based on this voltage value the type and concentration of the gas can be estimated. the type gasthe sensor could depends on the sensing material present inside the sensor.

b. Calibration Curve

Sensor signal is obtained in forms of conductance G, or resistance R. A calibration curve, G=f(C) and R=f(C), is the relationship between the signal response and the stimulus or concentration of the target gas. This could be related as a log-log plot of $(\frac{R_a}{R_g})$ or $(\frac{G_g}{G_a})$ versus C [10].

c. Base Line

A baseline may be defined as the stabilization of sensor of sensor signals when it achieves equilibrium with its environment, there may be large fluctuations of sensor signals before stabilization at the base line; it is essential that this base line be reached before the commencement of tests or measurement.

d. Response and Sensitivity

Sensor response or sensitivity is represented in various forms. Sensor sensitivity, S, is defined as the ratio of change of resistance in test gas ΔR= Ra-Rg, to the value of resistance in air Ra where Rg is the sensor resistance in the presence of the test gas:

$$S\ (\%) = \frac{\mathrm{R_a - R_g}}{\mathrm{R_a}} \times 100 \ldots\ldots\ldots (1)$$

$$S = \frac{R_a}{R_g} = \frac{G_g}{G_a} \geq 1 \ldots\ldots\ldots\ldots (2)$$

Sensitivity of oxidizing gas by an n-type semiconductor or sensitivity of a reducing gas by a p-type semiconductor can be represented as:

$$S = \frac{R_g}{R_a} = \frac{G_a}{G_g} \geq 1 \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Partial sensitivity, m, is the slope of the analytical calibration curve; i.e. the change in the output signal (i.e. the change in the electrical resistance R (ohm) or the change in the electrical conductance G (mho)) for a given change in concentration C (ppm) of the target gas [15,11]. It is the quantitative ability of the sensor to change with the concentration of the target gas.

For reducing gas, m_{red}, is given as:

m_{red} (C) $=-\frac{\delta R}{\delta C}=\frac{\delta G}{\delta C}$ ……………….. (4)

For oxidizing gas, $m_{ox,}$ is given as:

m_{ox} (C) $=\frac{\delta R}{\delta C}=\frac{\delta G}{\delta C}$ …………………... (5)

The partial sensitivity m describes the change in the sensor signal (R or G) due to a specific change in the gas concentration. The higher the value of the sensor sensitivity, the more significant in the change in sensor signal (R or G) instead by a small change in the gas concentration. Science MOX sensors are nonlinear sensors, the partial sensitivity varies with the aging of the sensor due to drifts or concentration effect.

Analytical sensitivity, γ, is a meaningful way to include the precision in the definition of the sensitivity. It is defined as the ratio of the slope, m, of the calibration curve to the standard deviation, σ_s, of the signals (i.e. resistance or conductance) at that sensitivity or concentration:

$\gamma = m / \sigma_s$ …………………… (6)

Where the slope of the calibration curve, m, is taken as the best interpolation of the experimental results, at the targeted gas concentration of interest:

$$m = (\frac{\delta S}{\delta C})x_i \text{ …….. (7)}$$

Where S is the change induced by the presence of the analyte in the measured parameter or specifically:

$S = S_g - S_o$ is represented as $\Delta G = G_g - G_o$ or $\Delta R = R_o - R_g$, X_i denotes the parameters kept constant during the experiment, such as partial pressures of O2 and humidity [12].

The standard deviation, σ_s, of the signals in terms of resistance, σ_g, is given as:

$\sigma_R = \left(\frac{\delta R}{\delta C}\right)\sigma_C$ and $dR = \left(\frac{\delta R}{\delta C}\right)dC$ ………… (8)

The standard deviation of the sensor response represents the uncertainty with which the sensor response can measured, while σ_c is the standard deviation of stimulus represents the precision with which the gas concentration can be determined. Therefore, the analytical sensitivity can be written as:

$\gamma = 1/\sigma_c$………………… (9)

e. Selectivity or specificity

Selectivity is the ability of a sensor to respond to particular gas in the presence of other gases. Selectivity or cross-sensitivity of a sensor, m_{ij} of a sensor compares sensor signal or sensitivity to be monitored (S_i or m_i) to the sensor signal or sensitivity of the interfering stimulus ($S_j$orm_j).

It is ability to concurrently discriminate and uniquely detect a specific target gas in the presence of interfering gases. It is represented as the ratio of sensitivity of the target gas, Si to the sensitivity of the competing gas, S_j:

Selectivity, $m_{ij}(C_i,C_j) = \frac{S_i}{S_j} = \frac{m_j}{m_i}$………… (10)

But, this can be represented in terms of percentage a

% Selectivity, m_{ij} $(Ci,C_j) = \frac{S_i}{S_j} \times 100 = \frac{m_j}{m_i} \times 100$ ……………(11)

f. Detection Time:

The detection time, τ_{det}, is the time taken for the sensor output signal to rise 10% ($\Delta_{10\%}$) above its initial value after applying the target gas in a step function in the bellow fig.3 shows:

Response Time

The response time, τ_{res}, fig.3 describe the time taken for the sensor output signal to reach 90% ($\Delta_{90\%}$) of its saturation value after applying the target gas in a step function.

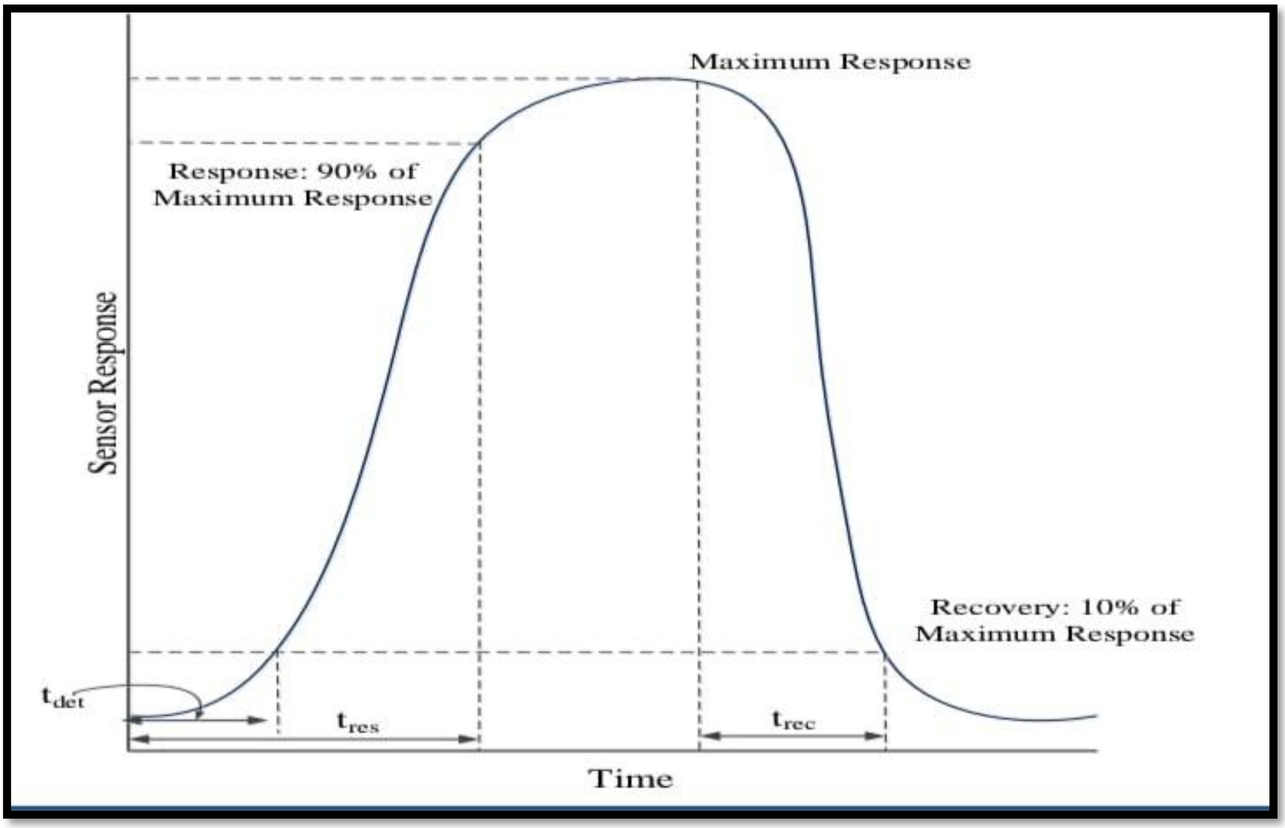


Fig.3. Response and recovery time

The response time, τres, fig.3 describe the time taken for the sensor output signal to reach 90% ($\Delta_{90\%}$) of its saturation value after applying the target gas in a step function.

Recovery or Decay time

The recovery or decay time, τ_{rec} fig.3 is the time taken for the sensor output signal drop to 90% ($\Delta_{90\%}$)

Of its saturation value after switching off the target gas in a step function (i.e. time taken for the sensor response to recover to within 10% above its initial value) [13].

Stability and Long-Term Effect

Stability is the ability of the sensor to maintain it sensitivity and response behavior over a period of time. Depending on the application, the period could be between hours to years. Stability could be expressed in terms of drift in sensor response. The environmental variables and measurement condition must be comparable for good stability values.

Also, it could be defined as the percentage change in conductance in synthetic air over the given time interval:

$$D = \left| \frac{G(t_1) - G(t_0)}{G(t_0)} \right| \times \frac{1}{t_1 - t_0} \text{ ………… (12)}$$

Sensor stability can be distinguished in term of active or passive stability. Active stability or reproducibility refers to sensor characteristics during a certain period of time at working condition, which may include high temperature and the presence of a known analyte. Passive stability is connected with retaining the sensitivity and selectivity during a period of time after some normal storage conditions, such as room temperature and ambient humidity.

Reproducibility:

Reproducibility is a measure of sensor similarity behavior. In order to compere the reproducibility of two sensor batches one can either calculate the mean value and the standard deviation of sensor property for both batches and compare them to calculate the reproducibility Q for each batch. It can calculatedas:

$Q_{x'}$ (C_i) (%) $= \left(\frac{\frac{1}{n}\sum_{k}^{n} R_K}{R_{max}} \mid c_{ij} \right) \times 100$ ………… (13)

Where n is the number of characterized sensor, R_k the sensor response of the sensor k. the reproducibility values range from 0 to 100.

Drift:

Sensor drift represent the random temporal variation in the signal behaviour when it is exposed to the same analyte under identical condition. This effect is attributed to the functions of the environmental variables and measurement conditions, such as gas concentration (Ci), relative humidity and operation temperature of the surrounding atmosphere and measurement time (Δt), system sampling non-specific adsorption, variations on flow rate, thermo-mechanical degradation and poisoning. All of these factors can modify both the baseline and the sensitivity of the sensors, and produce different responses and alters over time for the same target gas concentration, resulting in poor sensor repeatability, especially during the commencement and concluding phase of the experiment [13].

Mathematically, drift is represented as:

$D (C_i,\Delta_t) \partial R/\partial t \mid^{Ci}_{\Delta t}$………… (14)

In terms of percentage, it can be represented as:

$\tau(C_i,\Delta_t)$ (%) = $[(1/n)\sum_{i=1}^{n} Ri/R_{max} \mid^{Ci}_{\Delta t}] *100$ ……… (15)

Where n is the number of measurement, R_{max} the maximum sensor response value of the determined sensor response values Ri. To be able to compare drift values of different sensors, the environmental variables and measurement conditions must be compareable.

CHAPTER 2

EXPERIMENTAL SECTION

2.1 MATERIALS AND METHODS

a. Materials

- Lanthanum (III) Nitrate [$La(NO_3)_3.6H_2O$] (Mw =433.01 g/mol)

- Iron Nitrate [$Fe(NO_3)_3.9H_2O$] (Mw =403.01 g/mol)

- Citric Acid [$C_6H_8O_7$] (Mw =210.14 g/mol)

b. Synthesis of $LaFeO_3$ Nanopowder

$LaFeO_3$ nanopowders were prepared by sol-gel reaction route. 4.33 gm of La $(NO_3)_3$. $6H_2O$, 4.04 gm of Fe $(NO_3)_3$. $9H_2O$, and 4.10 gm of citric acid all the material we take and put on the beaker which is filled with 150 ml of DI water and then we dissolve it perfectly with the help of spinot.

Place the solution beaker on magnetic stirrer spinot and add HNO_3 solution drop by drop by adjusting the hating rate to 80^0C. After 5 hour the brown colour sol was obtained [15].

By continue heating to next 30 min the solution has converted to gel then we stop magnetic stirrer. And we take the beaker and put it on oven and kept it at 120^0 C temperature overnight [16].

Next the blackish powder is calcined at 900^0 C for 5 hoursto obtain $LaFeO_3$nanopowder. And then we take the material and send it to some of this material for characterization, to cheek the material synthesis is done properly or not, that’s why we cheek first its XRD [17].

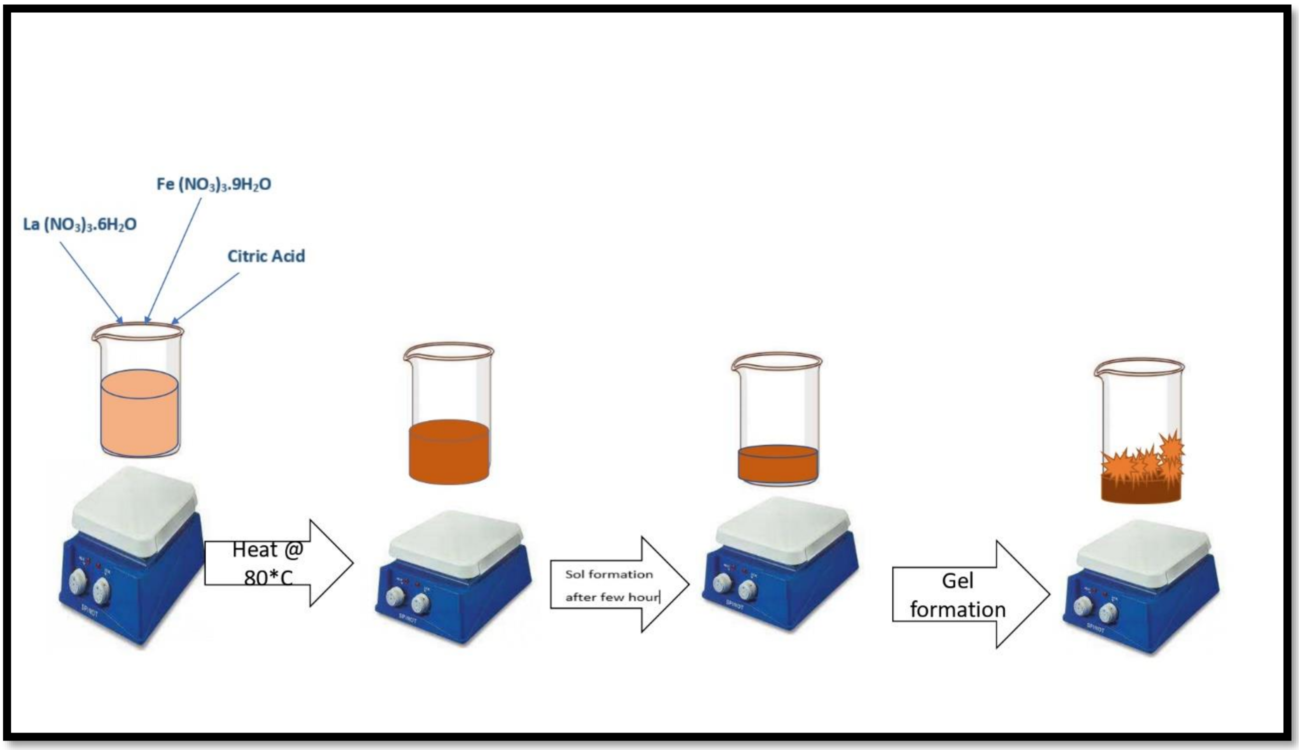


Fig.1. Schematic illustration sol gel methods

c. Fabrication on Lanthanum ferrite nanopowder based sensor:

A Taguchi type sensor module is fabricated using the as prepared $LaFeO_3$nanopowder. Firstly, a 3.5 mm long sensor substrate was cut from a long, hollow, and cylindrical α-alumina tube (1 mm outer diameter, and 0.5 mm inner diameter).The substrate was cleaned sequentially with hydrochloric acid (35 % E-mark), DI water, acetone and dried.Thereafter [18]. Then the substrate was electrode by applying conducting gold paste on its two ends and Pt wire as lead wires were connected to these electrodes. The electrodes were then cured at 900°C for 1 hour. The distance between two electrodes was maintained as 3 mm. the substrate thus prepared was hooked to a drop coater (ref. ©,fig-2) which can rotate the sensor around its axis at an rpm of 10. Meanwhile, 0.5g of the as prepared $LaFeO_3$nanopowder was pestled with IPA into an agate mortar until drop coating consistency was achieved (ref. (A) and (B), fig. 2). Thereafter, 5 μL of the paste was dropped onto the rotating α-alumina substrate. The rotating motion uniformly coats the drop onto the substrate surface (ref. (D) fig. 2). Then a nichrome wire (resistance 24 ohm) was inserted into the hollow core of the sensor (ref. (E), fig. 2) and the sensor was mounted on a six-pin plastic socked by spot-welding the Pt electrode leads and the heater to these six pins (ref. (F), fig. 2). Finally, a plastic cap with double mesh (200 mesh each) was push-fitted on this socket (ref. (H), fig. 2). This sensor module was used for all sensor measurements [19].

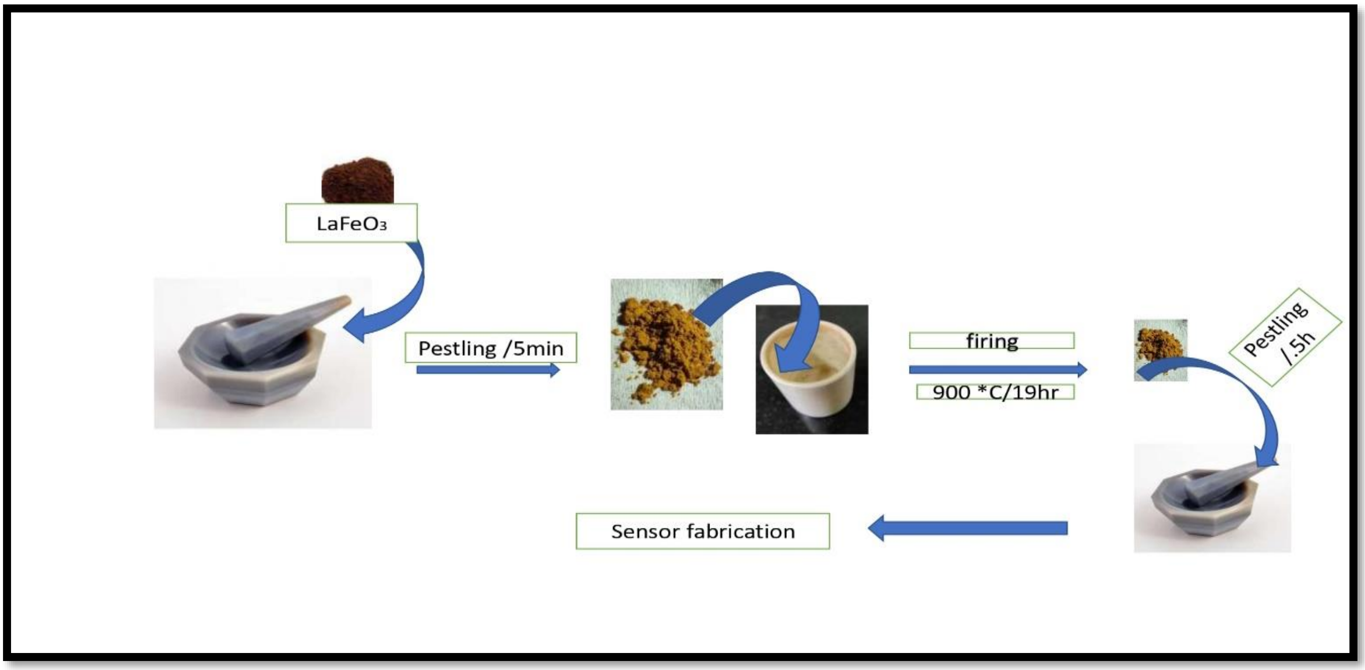


Fig.2. Schematic illustration of drop coating material prepared

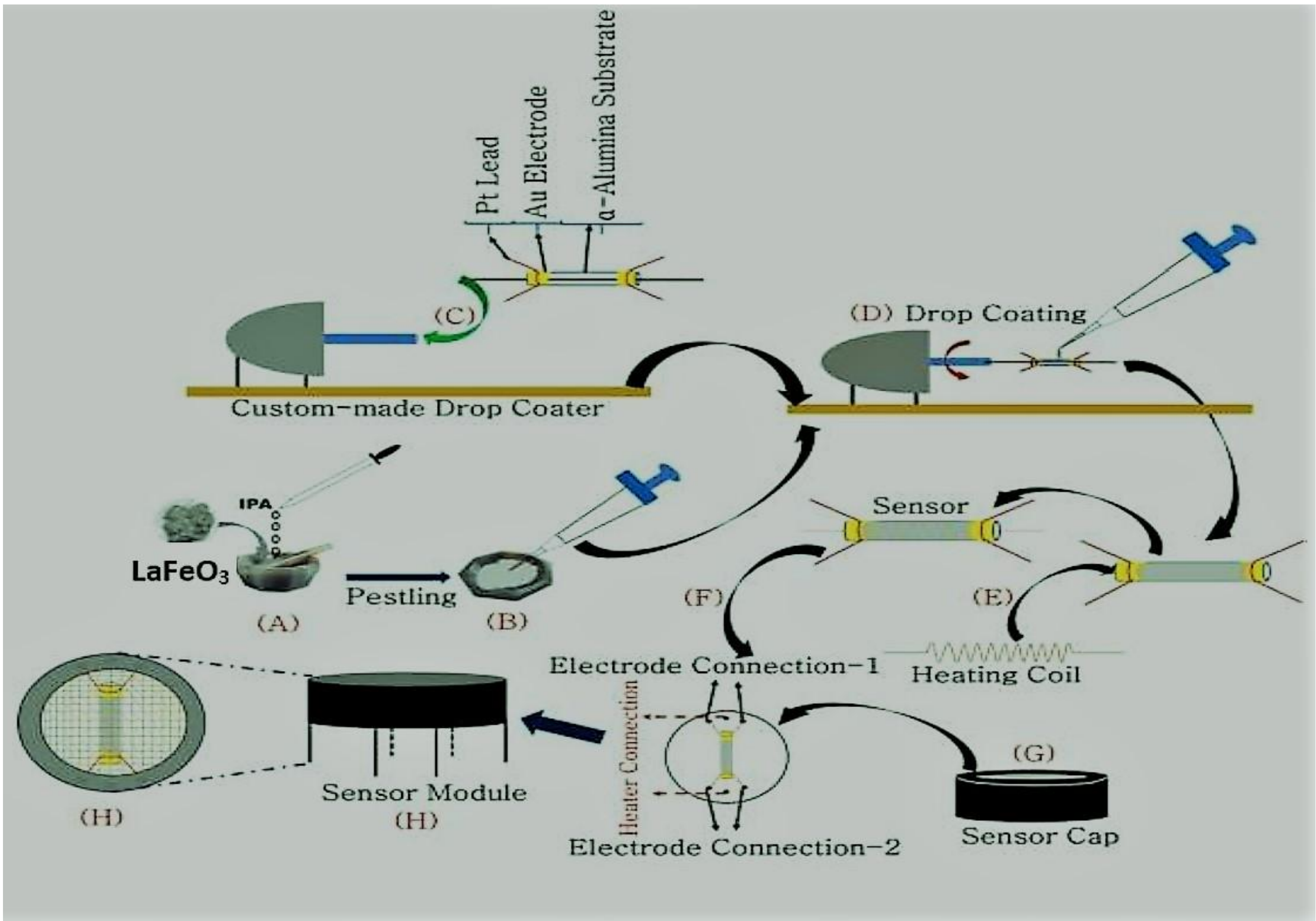


Fig.3. Schematic illustration of the step by step fabrication of $LaFeO_3$Nanopowder based Taguchi type sensor.

d. Preparation of trace formalin vapor and sensor measurement setup:

After several measurement it was conformed that the resistance of the as prepared $LaFeO_3$ sensor chances in response to trace formalin gas in a repeatable fashion. Trace formalin gas of different concentrations, viz. 100 ppm, 50 ppm, 10 ppm, 5 ppm, 3ppm, 1 ppm, and 0.5 ppm were prepared by desiccator dilution method. Required volume of formalin aqueous solution (25%) was poured into a large desiccator designated as the mother desiccator and sufficient time was allowed for complete vaporization, and homogenization of the formalin gas throughout the mother desiccator [20]. Thereby, a high concentration of formalin gas prepared in the mother desiccator. Small volumes of high concentration formalin gas were syringed out of it and syringed into a different smaller desiccator [21].

Thereafter, we waited for 24 hours to allow homogeneous mixing of the formalin gas inside the desiccators. Thus, different lower concentration of formalin gas, ranging from 0.5 ppm to 100 ppm are prepared. The desiccator dilution technique is governed by the following equation,

$$V_1 \times C_1 = v_2 \times c_2 \ldots\ldots\ldots\ldots \quad (1)$$

Where V_1 is the volume of the mother desiccator, C_1 is the concentration of formalin gas in the mother desiccator, v_2 is the volume of small desiccator and c_2 is the concentration of formalin gas small desiccator.

The as prepared sensor was mounted on a sensor base which connects the heating coil to a DC voltage source (Keysight make, E3530A) and the electrodes to a digital multimeter (34470A, Keysight make).

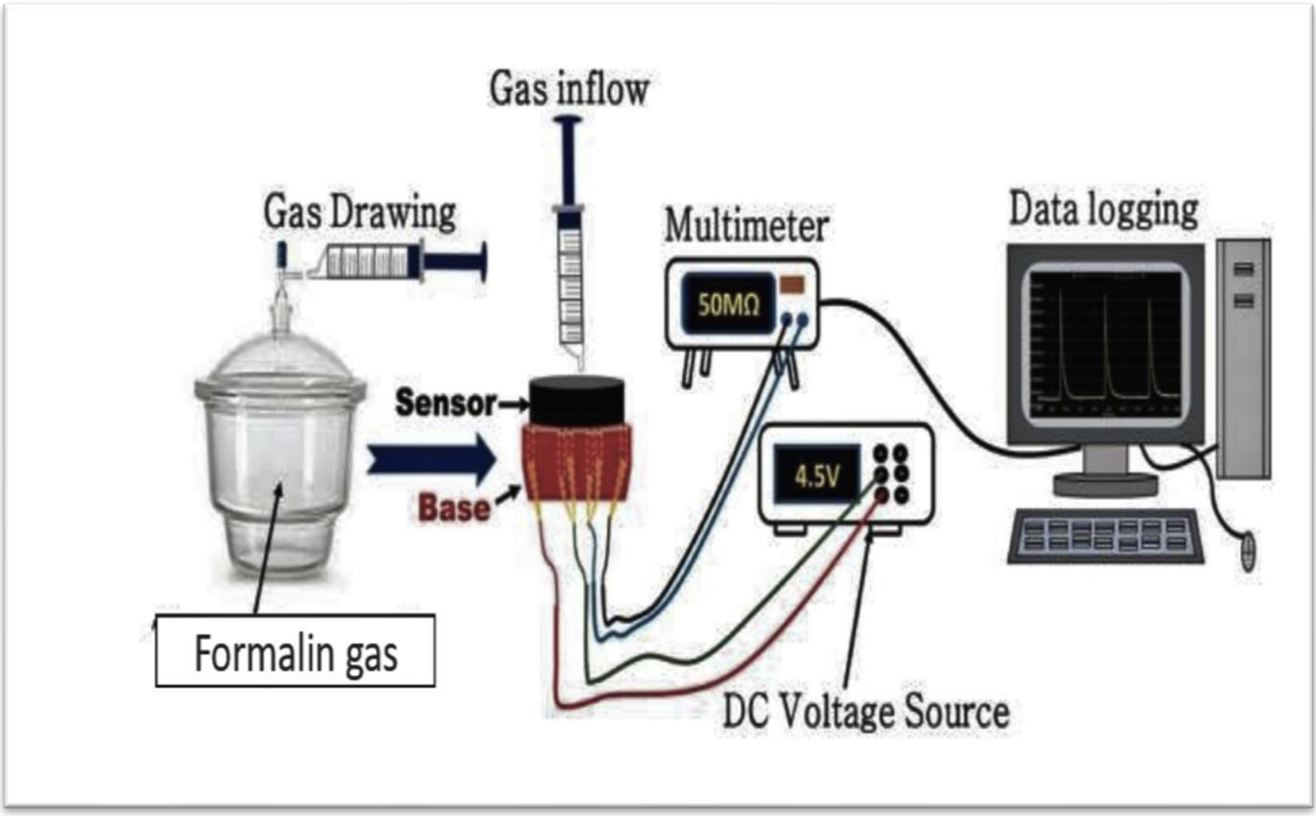


Fig.4. Schematic representation of the $LaFeO_3$ sensor-based trace formalin measurement setup.

Different DC voltages were applied across the heating coil to heat up the sensor to various elevated temperature. The multimeter measures the resistance of the sensor and change of it. The sensor was allowed to achieve a stable base resistance before data recording at a particular temperature [22].

A data logging software allied to the multimeter records the change in resistance of the sensor and a graphical user interface allows the visualization of the change. A schematic illustration of measurement setup is shown in fig.3.

2.2 CHARACTERIZATION TOOLS USED IN THE EXPRIMENT

To check the purity, arrangement, properties and functional group identification of sample which is used as a sensing layer for the gas sensor, some characterization were done in the present investigation like FESEM, XPS, XRD, RAMAN Spectroscopy, FTIR, UV-VIS Spectroscopy [23].

a. Scanning Electron Microscopy (SEM)

A scanning electron microscopy (SEM) is a type of electron microscope that produce a largely magnified image of a sample by scanning it with a high-energy beam of electrons in a raster scan pattern instead of light. The electrons interact with the atoms producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity [24].

b. FESEM (Field Emission Scanning Electron Microscope)

A FESEM is microscope that works with electrons (particles with a negative charge) instead of light.

These- electrons are liberated by a field emission source. The object is scanned by electrons according to zig-zag pattern. FESEM is used to visualize very small topographic details on the surface or entire or fractioned objects. The FESEM images in this research work has been taken with Field Emission Electron Microscope [25].

c. Powder X-ray Diffraction Technique

X-ray diffraction is a non-destructive analytical method for identical method for identification and quantitative determination of various crystalline forms, known as 'phases' of compound present in powder and solid samples. In the present study the room temperature powder X-ray diffraction (XRD) was carried for phase identification using a Philips X-ray diffraction (PE1730) with CuKα (1.54 A^0)radiation at a 2θ scan rate of 2^0 per minute [26].

This technique allows identifying and studying crystalline materials by using the phenomenon of diffraction.

Basic Principle

X-rays are electromagnetic radiation are typically generated by bombarding a metal with high energy electrons [27]. The high energy electron must penetrate through the outer electron shells and interact with the inner-shell electrons.

If more than a critical amount of energy is transferred to an inner shell electron, that electron is rejected; i.e. it escapes atoms.

The attractive field of the nucleus, leaving a hole in the inner shell and generates ionized atoms. The ionized atom returns almost to its lowest energy by filling in the missing electron with one from the outer shells. It is this transition which is accompanied either by the emission of an X-ray or an Auger electron [28].

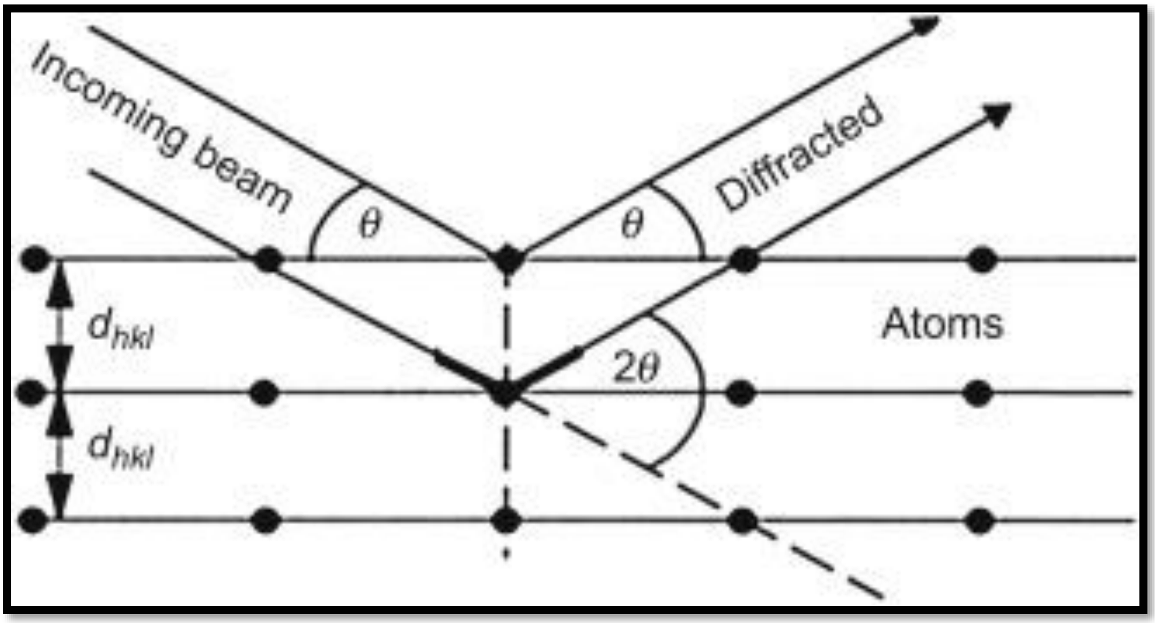


Fig .5. Schematic diagram of X-Ray Diffraction (adapted from veqter.co.uk)

X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering, and the electron is known as the scatterer. Although these cancel one another out in the most directions through destructive interference, they add constructively in a few specific directions, determined by equation bellow

Bragg's law:

$$2d\sin\theta = n\lambda$$

Here, D= spacing between diffracting planes

θ = incident angle

n = any integer

λ = wavelength of the beam.

(n=0.29 or Cu-Ka radiation = 1.5404Å)

The XRD Characterizations were done with **Philips X-ray diffractometer (PW1730) in CGCRI.**

d. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transformation Infrared Spectroscopy is mathematical technique used to get the infrared spectrum of the absorption or emission of a solid, liquid or gas sample. In this technique, a high resolution data is collected over a wide spectral range and the time domain signal is converted into a frequency domain signal with the use of Fourier transform [29]. The advantage of Fourier Transform over dispersive spectrometer is that the intensity is measured over a very narrow range of wavelength in case of Dispersive Spectrometer. In this experimental work FTIR Fourier transform-infrared (FT-IR) measurement was done on a Perkin Elmer-Spectrum two. The goal of any absorption Spectroscopy is to measure how well the sample can absorb light at each wavelength. In case of dispersive spectroscopy, the technique used involves passing a monochromatic beam o light through the sample and measure the amount of light that is absorbed and the process is repeated for each wavelength. UV-Visible Spectroscopy uses this method. The FTIR Spectroscopy, rather than using a monochromatic light, uses a beam of light containing many frequencies of light at once and measure the amount of absorption of that beam by that sample [30]. Then the beam is modified such that it contains different combination of frequencies that give the second data point. The process is repeated a number of times and the computer is used to infer the result of the absorption at all the wavelengths. This beam is produced by a broadband light source that contains the whole spectrum of wavelength to be measured. The infra-red portion of the electromagnetic spectrum is divided into three regions [31]. The near IR region consisting of wave number ranging from 14000 to 4000 cm^{-1} can excite overtone or harmonic vibrations. The mid-infrared portion ranging 4000 to 400 cm^{-1} corresponds to the fundamental vibrations and the far infrared region is used to study rotational spectroscopy. The basic of this spectroscopy also lies in the fact that molecules absorb light of frequencies according to their structure. The absorption occurring at there resonant frequencies matches with there vibrational frequency. Now for the mid IR region, High temperature heated silicon Carbide element is used as the source. For this range, pyroelectric detectors are used [32].

Advantages of FT-IR

Some of the major advantages of **FT-IR** over the dispersive technique include:

- **Speed**
- **Sensitivity**
- **Mechanical Simplicity**
- **Internally Calibrated**

e. Raman Spectroscopy:

Raman spectroscopy (RS) is a versatile method for analysis of wide range of forensic samples. It resolves most of limitations of other spectroscopic techniques. It can be used for both qualitative as well as quantitative purpose. Qualitative analysis can be performed by measuring the frequency of scattered radiations while quantitative analysis can be performed by measuring the intensity of scattered radiations[44,47]. In this experiment the **RAMAN** spectra were obtained using a **Renishaw in via Reflex micro Raman spectrometer** with an argon ion (514nm) laser [33].

e. UV-Visible Spectroscopy:

UV- spectroscopy is type of absorption in which light of ultra-violet region (200-400 nm) is absorbed by the molecule. Absorption of the ultra violet radiations results in the excitation of the electrons from the ground state to higher energy state. The energy of the ultra violet radiations that are absorbed is equal to the energy difference between the ground state and higher energy states

($\Delta E = h\nu$).

Generally, the most favoured transition is from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). For most of the molecules the lowest energy occupied molecular orbital, which correspond to sigma bonds [34].

Applications of UV spectroscopy:

- **Detection of functional group**
- **Detection of extend of conjugation**
- **Identification of unknown compound**
- **Determination of configurations of geometrical isomers**
- **Determination of the purity of a substance**

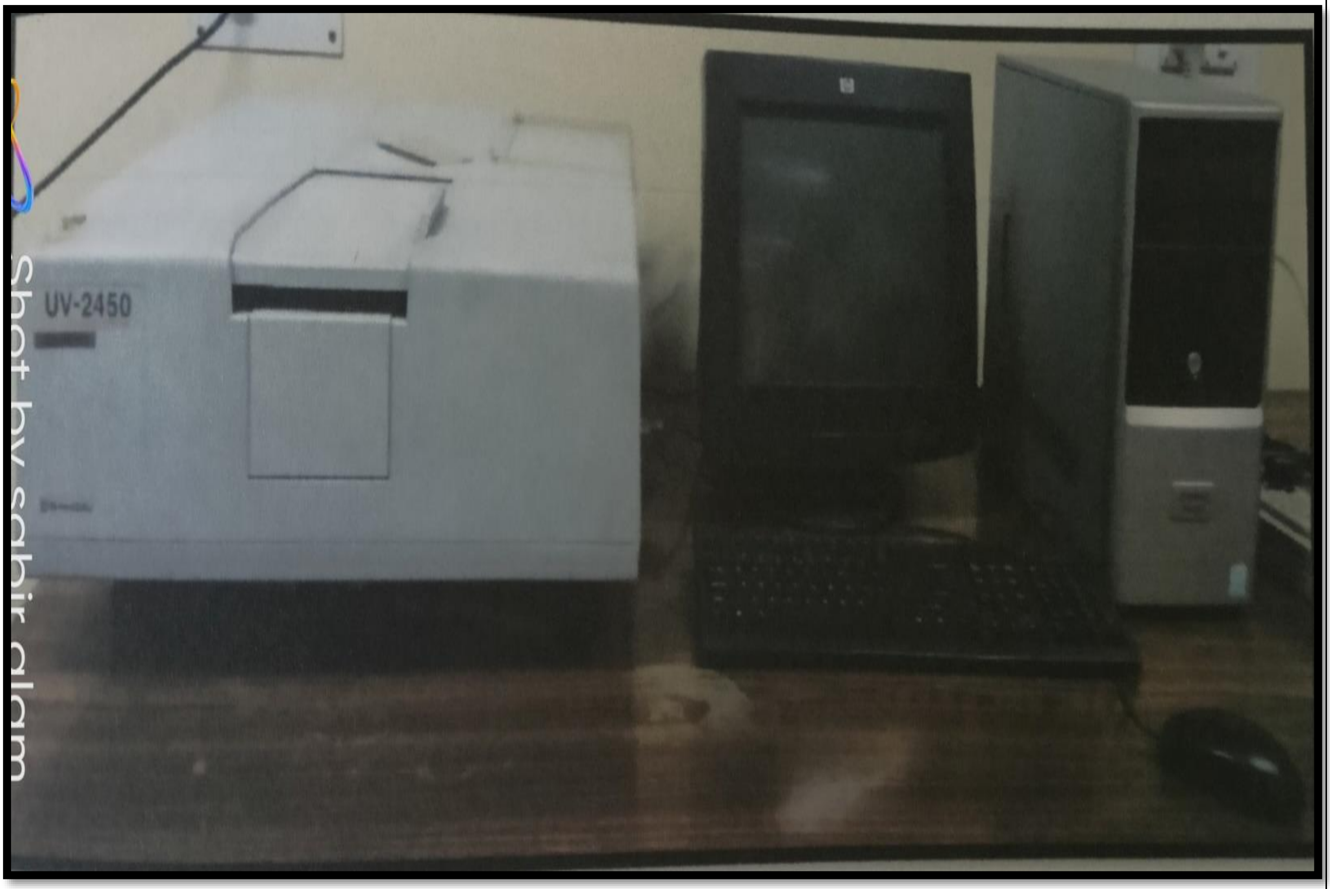


Fig. 6. UV Spectrometer used for measurement at CGCRI

f. X-Ray Photo electron Spectroscopy (XPS)

Photoelectron spectroscopy (PES) is a technique used for determining the ionization potentials of molecules. PES comprises of two separate techniques for quantitative and quantitative measurements. They are ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS).

Photoelectron Instrumentation

The main goal in either UPS or XPS is to gain information about the composition, electronic State, chemical state, binding energy, and more of the surface region of solids.There are a few basics common to both techniques that must always be present in the Instrumental setup.

- **A radiation source:** The radiation sources used in PES are fixed energy radiation sources. XPS - sources from x-ray while UPS sources from a gas discharge lamp.

- **An analyzer:** PES analyzer are various types of electron energy analyzers.

- **A high vacuum environment: PES** is rather picky when it comes to keeping the surface of the sample clean and keeping the rest of the environment free of interferences from things like gas molecules. The high vacuum is almost always an ultra-high vacuum (UHV) environment.

When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical deflection analyzer which the photoelectrons pass through before they are collected at the collector slit [37].

Working Principle of XPS

A surface is irradiated with X-rays (commonly Al Kα or Mg Kα) in vacuum. When an x-ray photon hits and transfers this energy to a core-level electron. It is emitted from its initial state with a kinetic energy dependent on the incident X-ray and binding energy of the atomic orbital from which it originated. The energy and intensity of the emitted photoelectrons are analyzed to identify and determine the concentrations of the elements present. These photoelectrons originate from a depth of <10 nm therefore the information obtained is from within this depth.

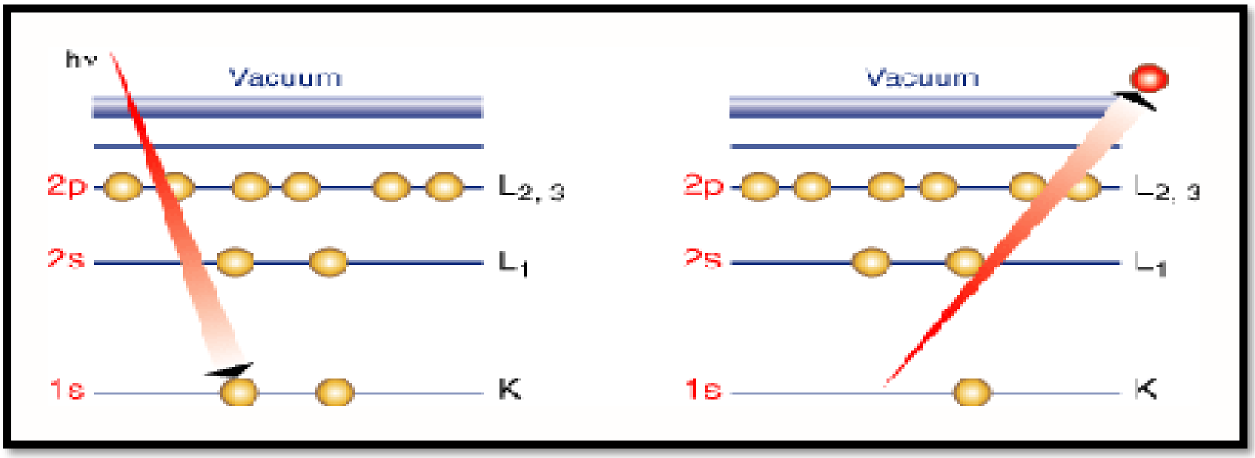


Fig. 7. Schematic representation of photoemission principle.

Each prominent energy peak on the spectrum corresponds to a specific element. In the spectrum below, there is a peak at 284.6 electronvolts (eV), which corresponds to carbon, and a peak at 532.5 eV, which corresponds to oxygen, therefore, this sample contains carbon (C) and oxygen (O).

Besides identifying elements in the specimen, the intensity of the peaks can also tell how much of each element is in the sample. Each peak area is proportional to the number of atoms present in each element. The specimen's chemical composition is obtained by calculating the respective contribution of peak area. By applying relative sensitivity factors and appropriately integrating peak area, it can be determined that the sample below is 25 percent oxygen and 75 percent carbon [38].

By studying the energy of the peak, it can also be determined if the surface of this material corresponds to a C-O single bonds (ethers, alcohols) or a much stronger C=O double bond (carboxylates, ketones). Core level shifts are important in determining valence states in metals, Transition metal oxides, and actinide materials.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. RESULTS AND DISCUSSION

a. X-ray Diffraction Analysis (XRD)

X-ray diffraction analysis is used for characterization of nanopowder of any size, and the observed change in position of diffraction picks are used to make conclusions on how crystal structure and cell parameter change with the in nanoparticles size and shape.

The crystalline phase of prepared Lanthanum Ferrite ($LaFeO_3$) particles was characterized by X-ray diffraction pattern which matched very well with JCPDS card no 04-783. No shift peaks and appearance of extra peaks were observed. This conformed that the material calcined at 900^0 C temperature result in forming pure cubic phase of Lanthanum ferrite ($LaFeO_3$)

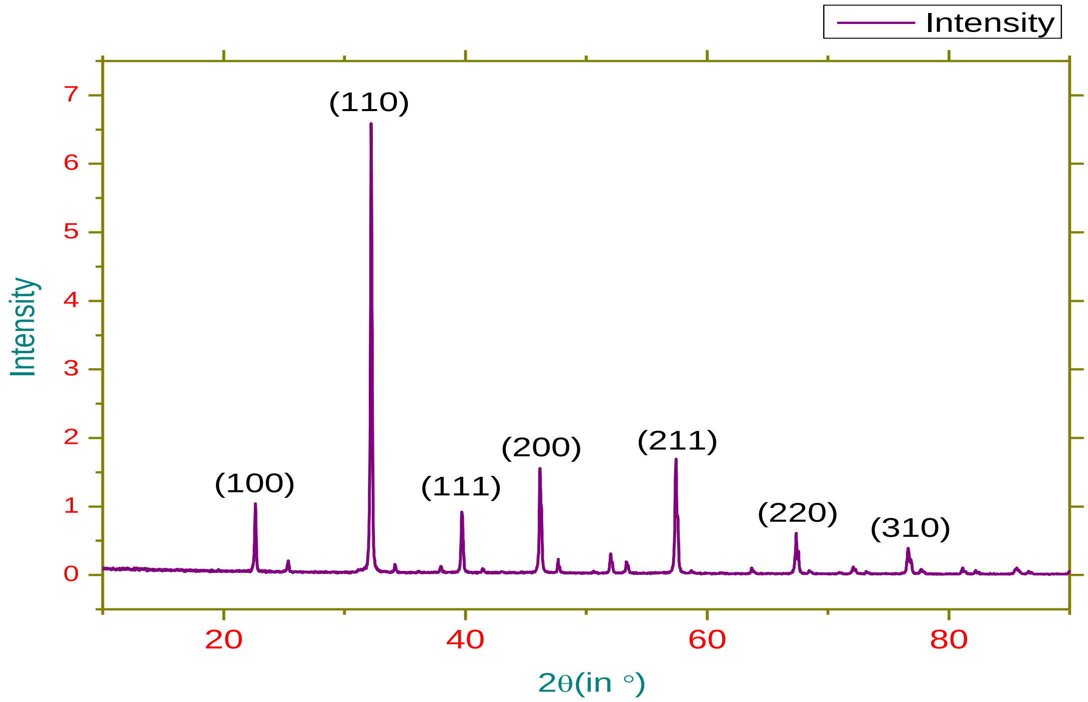


Fig.1. XRD of lanthanum ferrite

The average crystallite size was calculated to be 39.93 nm using Debye Scherer's formula is given by

$$D = k\lambda/\beta \mathrm{Cos}\theta$$

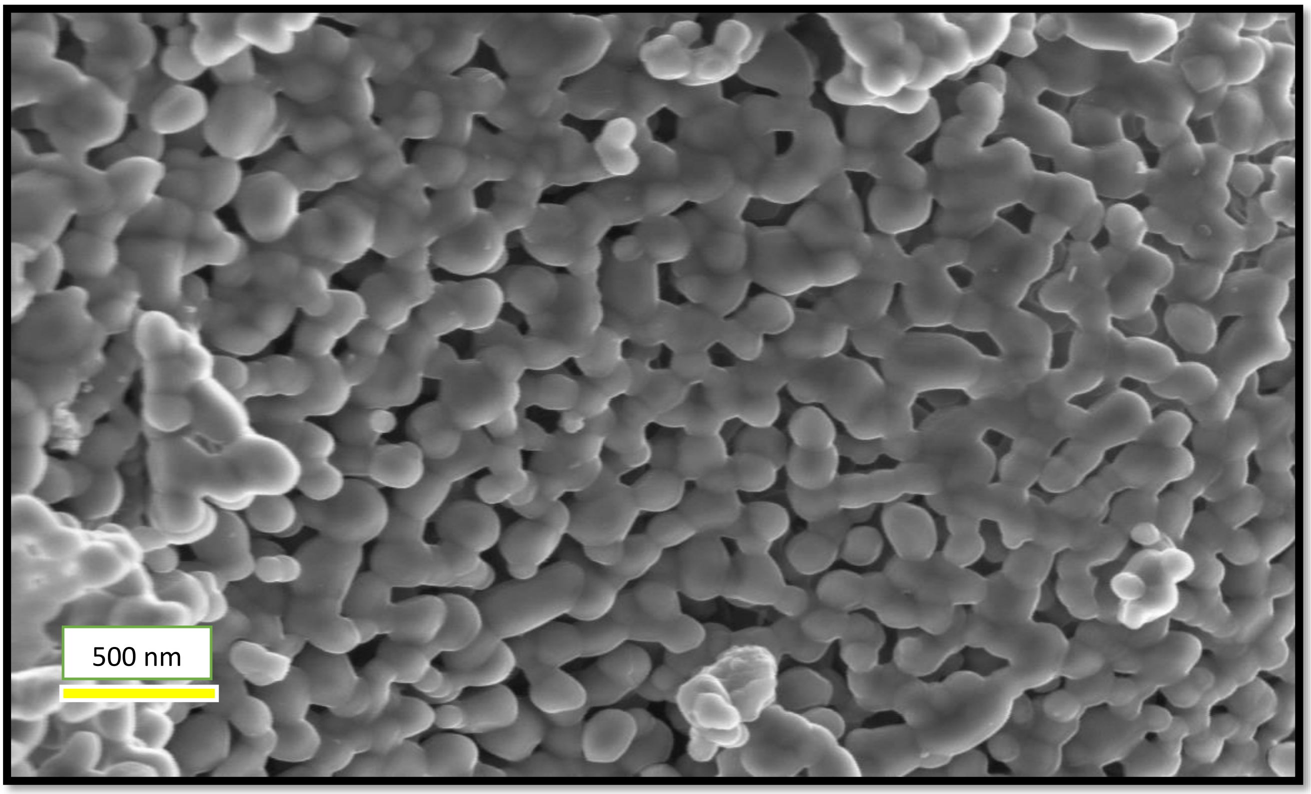
Where D is crystallites size, K is shape factor (hare 0.89), λ is the wavelength of X-ray source (hare 0.15406 nm) β is the full width of the diffraction peak at half maximum for the diffraction angle 2θ

(FWHM), and θ is the Bragg angle [39]. The indexed X-ray diffraction pattern of the prepared LaFeO3 nanopowder is shown in fig.1.

b. Field Emission Scanning Electron Microscope (FESEM)

Field emission scanning electron microscope (FESEM) study was conducted to determine the particle size and morphology of the as prepared Lanthanum Ferrite ($LaFeO_3$) nanoparticle fig.2. shows a typical micrograph at a magnification of 50,000.

It appears that the particles are almost spherical in shape and the particle size is in the range of 100 to 500 nm. However, due to agglomeration it is rather difficult to accurately determine the particle size and morphology from this image.



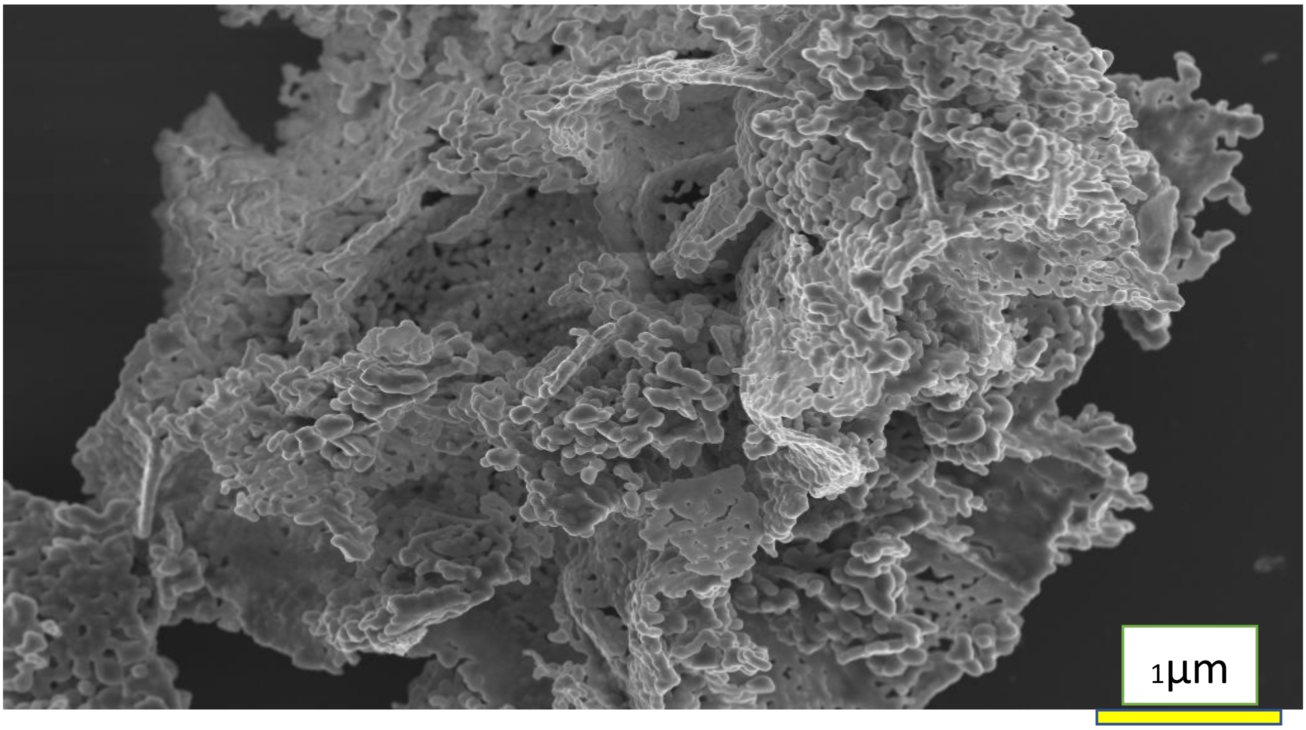


Fig.2. FESEM images

Alao in the fig.3. shows the EDX spectrum of the as prepared nanopowder. It is clearly shows the presence of La, Fe, and O as should present in Lanthanum Ferrite. The product of C and Ca is attributed to the C coated Ca grid used.

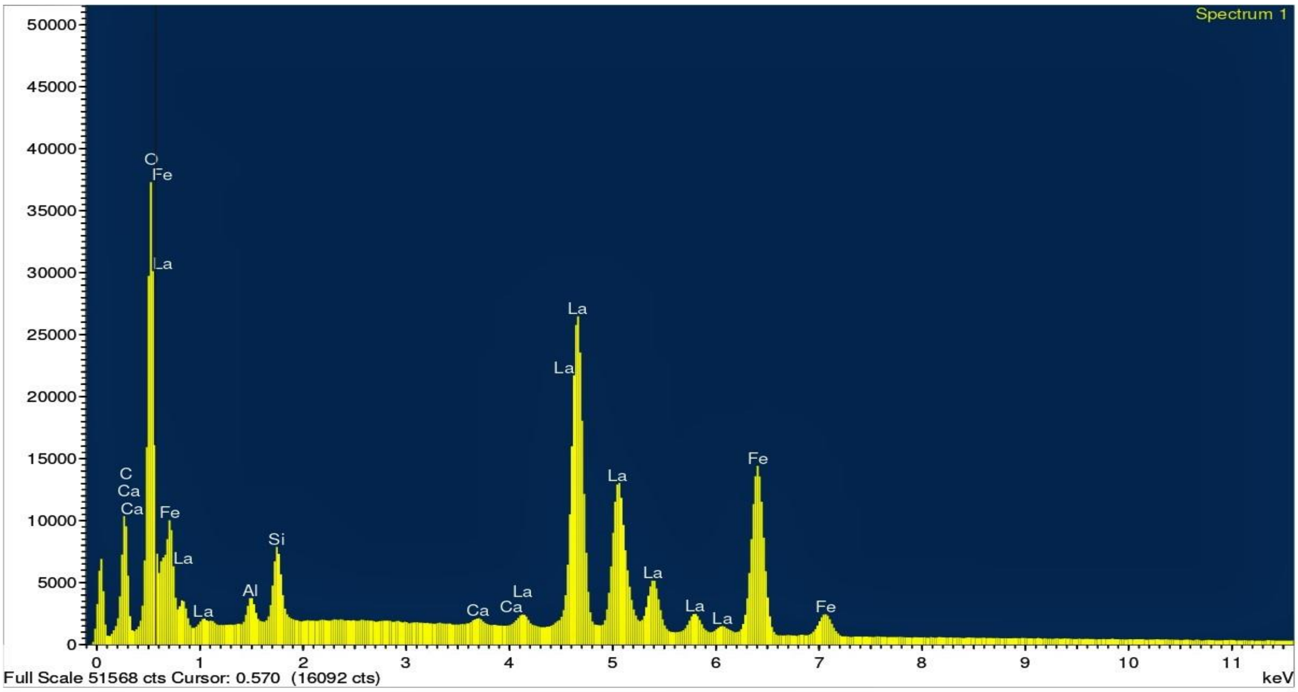


Fig.3. Schematic representation EDX

c. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Room temperature FTIR band was recorded in the range of 0 to 4000 cm^{-1} in the transmittance mode to investigate the presence of characteristics functional groups and bonds in the synthesized sample [40].

Typical Fourier transform of Lanthanum ferrite shown in the fig.10. from spectrum it is clear that several transmission bands are assigned in the prepared material.

The peaks at 400 cm^{-1} and 544 $cm^{-1}$are attributed to the vibration of Fe-O bond and La-O bonds respectively. The bands in the region 580 cm^{-1} to 670 cm^{-1} are found due to the stretching modes of BO_6 octahedra of Perovskite structure of ABO_3. The peaks around 1054 cm-1 and 1384 cm^{-1} can be attributed to the presence of carbonates.

This result is very significant for conformation of carbonate traces ceramics due to elimination of CO_2. The transmission band assigned at 1628 cm-1 are attribute to the C=0, H-0-H, bending vibration of the water molecule and nitrate groups respectively.

The complexation process between citric acid and metal ion’s was conformed by transmission band 3462 cm-1 also shows the splitting of stretching asymmetric mode of metal carbonates.

In present of Perovskite structure, the Fe-O bonds of the BO6 units dominate the spectroscopic behavior, i.e. FeO_6 octahedral dominates over 12 coordinated La-O units. These, result fully agreed with the XRD analysis.

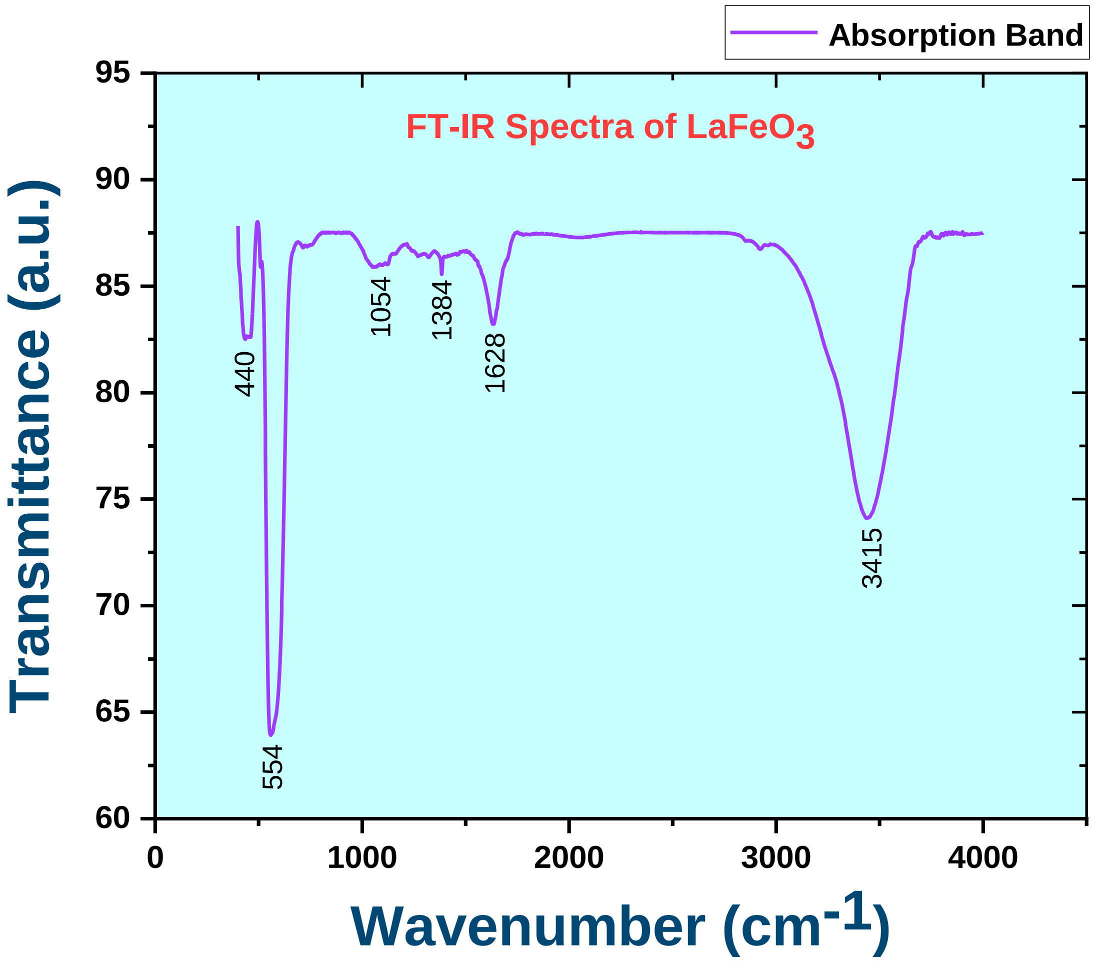


Fig.4. Schematic representation FTIR Lanthanum Ferrite

d. UV-VIS Absorption Spectroscopy

In this context, optical properties of the Lanthanum Ferrite ($LaFeO_3$) were investigated by UV-Vis spectroscopy in the wave range from 300 nm to 800 nm. Show in the fig.5. shows the UV-Vis absorption spectrum of prepared $LaFeO_3$ dispersed in isopropanol. It is known that the size and morphologies greatly affect the optical properties of semiconductor nanomaterials. As show in the fig.5, the absorption edge of the lanthanum ferrite ($LaFeO_3$) is observed at the wavelength of about 561 nm, which be attributed to the band gap absorption lanthanum ferrite [41].

Also, this deduces that synthesized Lanthanum Ferrite ($LaFeO_3$) is a visible light active compound. It has been found that Lanthanum Ferrite ($LaFeO_3$) is visible light photocatalytic active due to its unique optoelectronic properties and narrow band gap [42]. The strong absorption can generally be related to the electronic transition from the valence band to conduction band. Consequently, this indicates that the Lanthanum Ferrite ($LaFeO_3$) prepared by this method could be a kind of photocatalysis and magneto-optical devices. Using the absorption data the energy band gap was estimated by Truc's relationship equation 1:

$$\alpha h\nu = k\,(h\nu - Eg)^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where k is the probability parameter for the transition, also the constant k is a measure of the disorder of the material, α is the absorption coefficient, ν is frequency, h is Planck's constant, Eg is the optical band gap of material. The energy band gap of the obtained Lanthanum Ferrite ($LaFeO_3$) can be estimated to be 2.57 eV according to equation (1). On the other hand, energy band gap can be also determined by the following relationship equation (2). According to the Literature, the relationship between the energy band gap and λ_{onset} can be expressed as following [43]:

$$Eg = 1243/\lambda_{onset} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where Eg is the band gap energy (eV) and λ is wavelength (nm) of the edge in the spectrum. The energy band gap according to the equation (2) is 2.49 eV which is close to the above mentioned value (Eg =2.57 eV) derive from the absorption onset value.

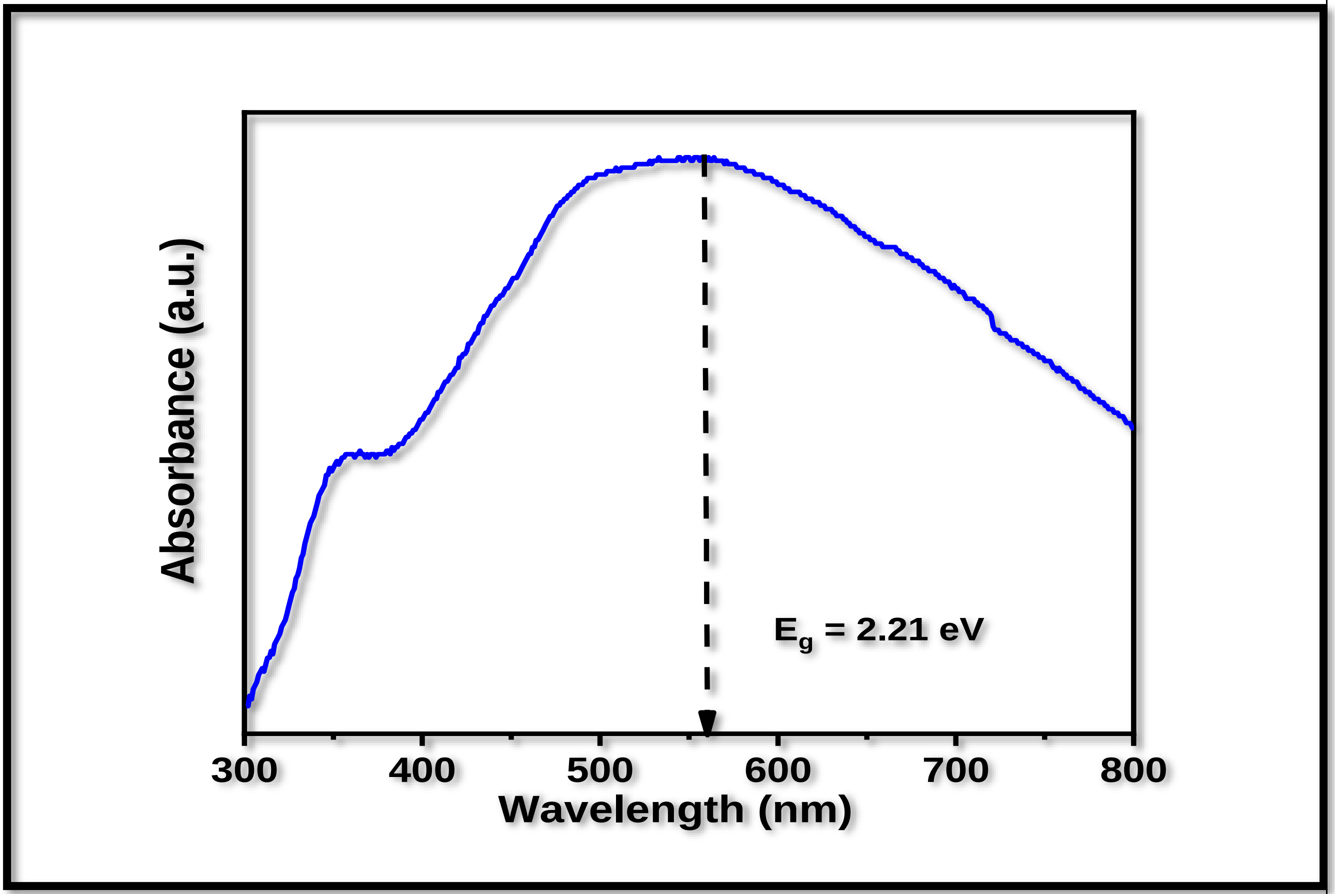


Fig.5. Schematic representation UV-Vis Lanthanum Ferrite.

e. Operating Temperature vs Response of Lanthanum ferrite sensor:

Different DC voltage were applied across the heating coil inside the sensor to generate these operating temperature, we basically applied the different voltage source ranging from 2.5 volts to 5 volts and hence its corresponding temperature ranging about from 70^0C to 390^0C. when we increase the voltage then temperature also increase in the heating coil of the sensor. It is of utmost importance that the operating of a chemoresistance gas sensor is optimizes carefully. The as prepared Lanthanum Ferrite sensor showed a p-type response towards formalin vapor at different operating temperatures ranging from 150^0C to 350^0C.

The response S of the sensor at a particular operating temperature is given by:

$$S = R_{HCHO}/R_{air}$$

Where RHCHO is the resistance of the sensor when exposed to formalin gas and Rair is the resistance of the sensor in the air.

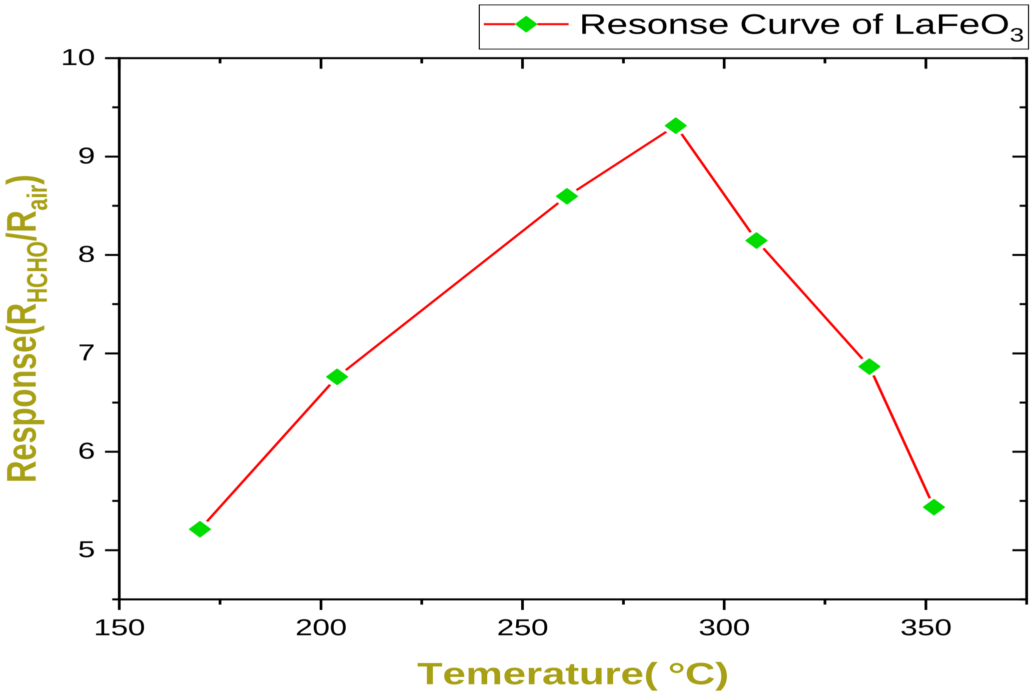


Fig.6. Schematic representation Temperature vs response plot.

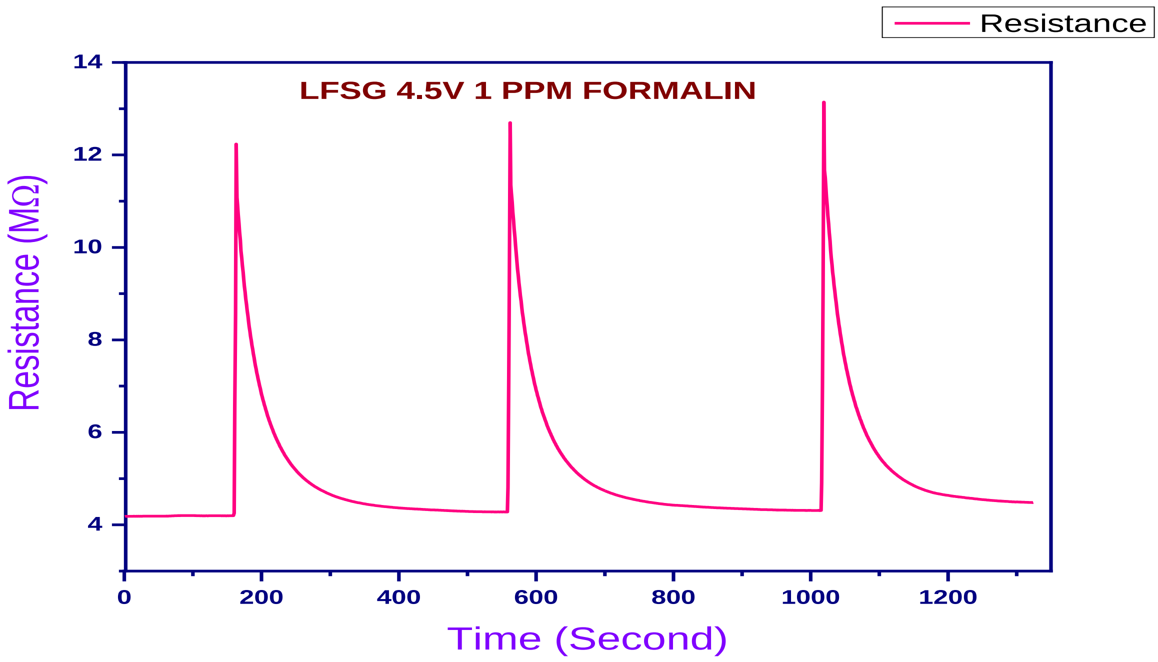
Fig.6 shows the response of the sensor towards 1 ppm formalin at different operating temperatures ranging from 150^0C to 350^0C. It is observed that maximum response is obtained at around 300^0C. Bellow this temperature the number of conduction band electrons at the sensor surface available for trapping by the atmospheric oxygen is low for an appreciable response. However , above this temperature the desorption rate of the target analyte supersedes the adsorption rate of it resulting in reduction in response [44].

f. Gas sensing Response of Lanthanum Ferrite Sensor:

Gas sensing response of Lanthanum Ferrite sensor showing fig. 7. The dynamic response curve of the sensor to various trace concentration of formalin vapor ranging from 1 ppm to 10 ppm shows in the fig.7. The sensor exhibited response of 3.25, 8.12, 10 folds to 1ppm, 5ppm, 10ppm, of formalin gas respectively at nearly 300^0C or at applying voltage 4.5 volts. Clearly, the resolution (difference) in response towards trace concentrations of formalin is excellent.

That means when we increase the gas concentration sensor response also increase. When we further, to test the repeatability of the sensor three consecutive measurement were taken at each concentration of formalin gas its picks looks like same as before and number of folds also give same also before, so we can say this sensor have good repeatability [45].

That’s means, it can be clearly seen that the three response peaks corresponding to each concentration of formalin match well. This confirms repeatability of the sensor. Further, the sensor exhibits the first response and recovery time, rendering it suitable for real time application.



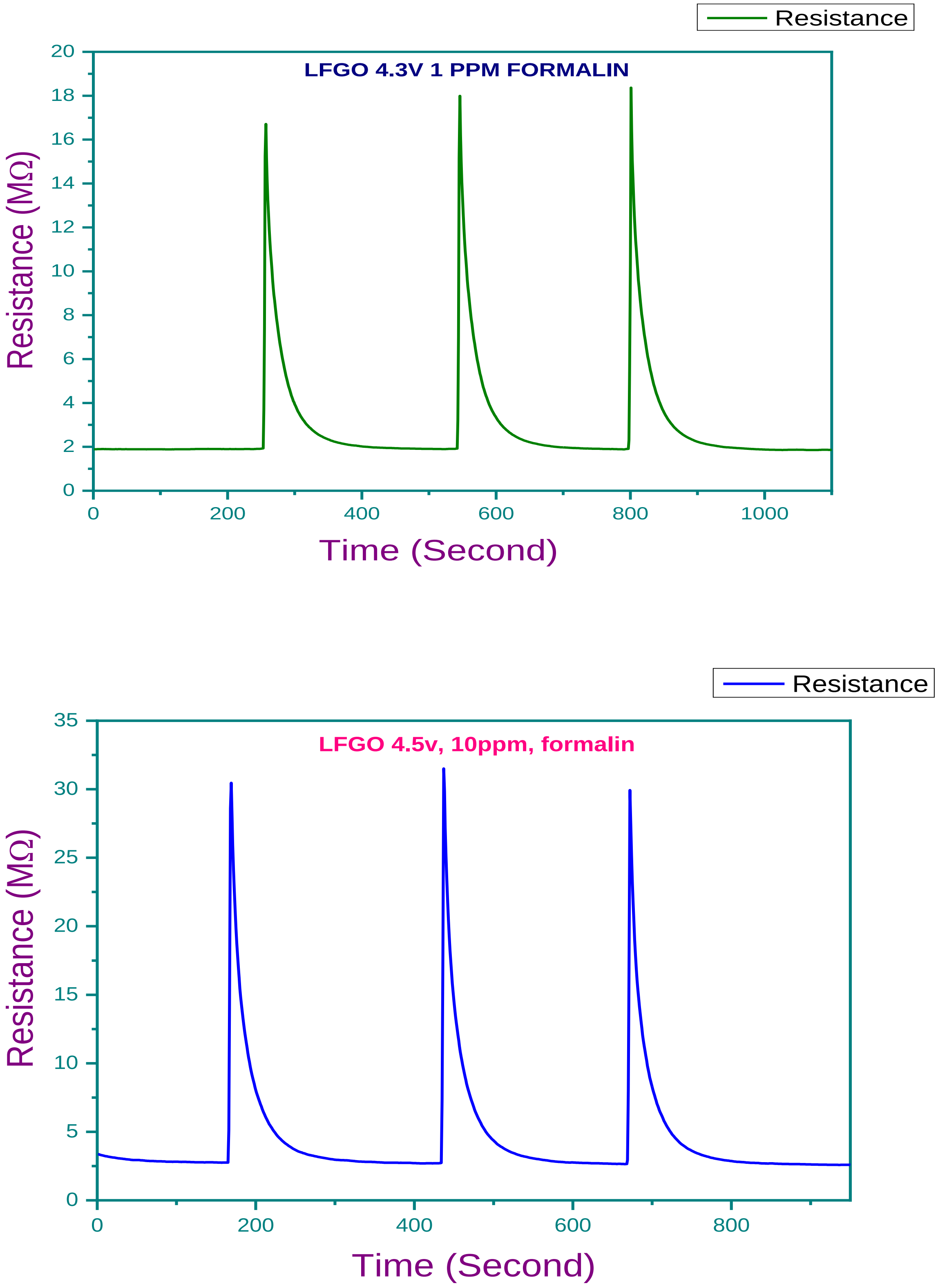


Fig.7. Gas sensing response of Lanthanum Ferrite sensor

g. Sensing Mechanism of the Lanthanum Ferrite:

In this study, the sensing mechanism of Lanthanum ferrite ($LaFeO_3$) is interpreted by the change in resistance that is originated from the reaction between target gas molecules and the chemisorbed oxygen species on the material surface. The ion exchange mechanism also shows a guiding significance for our discussion on the sensing mechanism [46].

The resistance is determined by the carrier concentration of materials, which is a decisive factor in the gas response. When the sensor based $LaFeO_3$ are exposed to air oxygen molecule will be adsorbed accumulation layers (HAL) near the $LaFeO_3$ surfaces, which results in an increase of the hole concentration of LaFeO3 and a decrease of its resistance. In contrast, when the sensors based on LaFeO3 are exposed to reductive gases, the gas molecules will react with the chemisorbed oxygen, the captured free electrons will be released back to the conduction band and causes a decrease of the hole concentration of LaFeO3 by electron hole recombination, which will narrow the thickness of the hole accumulation layer, inducing the increase of resistance. The sensing mechanism can be explained by the following chemical reaction:

$$O_2\ (gas) \longrightarrow O_2(ads)$$

$$O_{2(ads)} + 2e^- \longrightarrow 2O^-_{(ads)}$$

$$HCHO_{(ads)} + 2O^-_{(ads)} \longrightarrow CO_{2(gas)} + H_2O_{(gas)} + 2e^-$$

The cubic structure has rich pores and a large surface area, which can provide a large amount of active site for gas adsorption [47]. In addition, the change of the hole concentration may be the key factor for enhancing the gas response. According to the previous research by kim et al, the gas response can be written as bellow:

$$S_g = R_g/R_a = P_a/P_g = P_a/P_a\text{-}\Delta p$$

Where in Rg and Ra are the resistance of the sensor in the target gas and air, Pg and Pa are the hole concentration in target gas and air, respectively, and Δp = Pa- Pg is the variation of the gas. Accordingly, when the hole concentration at the hole accumulation layer of a p-type oxide semiconductor in air becomes lower, the injection of electrons will lead to a relatively higher variations in the resistance, and eventually improve the gas response, which indicates that electronic compensation can be utilized to improve the gas response of a gas sensor [48].

CONCLUSION

Nanostructured Lanthanum ferrite (LaFeO3) was successfully prepared by sol-gel synthesis method. X-ray diffraction study conformed the formation of Lanthanum Ferrite nanocomposite and its average crystallite size was found to be 39.93 nm. The uniform distribution of particles of Lanthanum Ferrite and large number of pores act as gas adsorption sites. The energy band gap of Lanthanum Ferrite is found to be 2.49 eV.

From FESEM we observed that the Lanthanum Ferrite particles size is 100 to 500 nm. The development sensor of Lanthanum Ferrite is p-type in nature and shows high response to different concentration of formalin vapor, viz~ 3.25 folds to 1 ppm formalin vapor, ~ 8.12 folds to 5 ppm formalin vapor and ~ 10 folds to 10 ppmformalin vapor and we also see the lanthanum ferrite gas sensor have fast response and recovery time.

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