Synthesis and characterization of Nano-sized Spinel and Orthoferrites and their application as Liquefied Petroleum Gas Sensor

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SUMMARY

Nanoscale materials are the materials having nanometer dimension and the scientific study of these objects, therefore, refers to the materials with sub nanometer dimension and the scientific study of these objects are known as Nanoscience. Nanoscience deals with the novel phenomenon of preparing, measuring its property and manipulating the dimension of an object up to the order of nanometer scale. Nanotechnology deals with using nanomaterials to develop products for practical application and for miniaturization of electronic devices. Nano-materials are the material of nanometer range and the nanometer order dimension can be achieved by constituting atom or molecule of few Angstrom order i.e. 10^{-10}. Nano-materials show enhanced and extraordinary characteristics from their bulk material [1-2]. It's changing extraordinary properties while size reduction, large surface to volume ratio and its application in different field elucidate the properties of nanomaterial. On the size reduction, the material undergoes several electronic transitions and due to which it shows relatively different property from the bulk material. The inverse relation between the particle size and surface area is a key underpinning in nanoscience world. This is due to the enhanced surface area of the material in comparison to the volume and quantum confinement [5]. The maximum number of atoms lies on the surface of the nanoparticle which possesses huge surface energy and causes unstable or metastable stage. So there is a change in its chemical, mechanical, and optical properties resulting in the increase in the surface area per unit mass. This increased surface area made the nanomaterial for versatile application in electronic and technical industry.

Nanomaterials can be synthesized in many ways in strategy synthesis, nature of synthesis, energy sources, and precursor method.

1. **By synthesis strategy,** there are two methods which are commonly used. Top down and bottom up approaches are the two strategies to synthesize nanoparticles. Top down approach is the one-way approach, in which block of material is taken then it is etched or milled into the desired shape. Carvings done on the pillar and breaking down of a block of rock into the

desired figure is an example of the top-down approach. The bottom-up approach is an analytic and universal approach in which smaller subunits (any atom or molecules) are united to make any useful product. Now in today's era, research is more focused on finding the advance bottom-up technique for synthesizing and characterizing nanomaterials range about 1-100 nm range.

2. **By nature of the process,** there are three types of synthesis method; physical, chemical, and biological method. A physical method is a method in which physical states like size, pores, shape and the phase of the material changes.
3. **On the basis of the energy** used as an input, the synthesis processes are categorized in terms of plasma, laser, electron beam, sputtering, ball milling, combustion, supercritical fluid etc.
4. **Precursor method** is widely used classification based on three phase. It is used to synthesize nanoparticles in the solid phase, liquid phase and gas phase [11].

We have been interested in carrying out our investigations with a new material that possess good sensitivity for the LPG concentration at the lower explosive limit (LEL) and beyond, with properties that are stable over time and thermal cycling after exposure to the various species likely to be present in the ambient. On the basis of a literature survey, I found there is no significant work done in the field of design and development of a LPG sensor operable at room temperature. Ferrites show very good surface reactivity and they have temperature dependent surface morphology. Also, they form composites with other metal oxides very easily. Therefore in this thesis, the synthesis of ferrites and their nanocomposites using soft chemical and mechanochemical routes were carried out. After thorough characterization of synthesized materials, these were employed as LPG sensor. In this thesis, the thorough experimental investigation was carried out in order to develop electrical type LPG sensor using thin/thick films of nanosized spinels and orthoferrites.

Requirements of a LPG Sensor

LPG is a combustible gas and it is widely used as a fuel for domestic heating and industrial use. Although it is one of the extensively used gases, it is hazardous. Hence, it is crucial to detect it in its early stages of the leakage and to perform the active suppression. For designing a robust gas sensor, the sensor material should possess following qualities given as under:

- The material should sensitive in lower explosive limit (LEL) for explosive gases.

- The material should have high sensitivity over a wide range of humidity and temperature.
- It should quickly respond to any fast changes in the ambient.
- The sensor material should have rapid response to the variation of gas concentration and good reproducibility of the electrical signal.
- The sensitivity should be independent of the ambient temperature.
- The material should not react with any chemical contaminants present in the application ambient.
- It should show stable characteristics for a long time.
- It should be less portable.
- The construction of the sensor should preferably be simple using IC technology and of low cost.
- The device should be operated by a battery.

Liquefied Petroleum Gas (LPG) Sensor

An LPG sensor is a chemical sensor which gives variation in its electrical properties when it interacts with the chemical gas species. The normally LPG are of two type propane (C_3H_8) rich in winters and butane (C_4H_{10}) rich in summer. The reason behind this is propane evaporates at – 44 ºC and butane evaporate at +5 ºC. Small concentrations of other hydrocarbons may also be present The development of gas sensors in particular combustible gases is imperative due to the concern for safety requirements in homes and for the industry. LPG is extensively used in our country but potentially hazardous gas, because its leakage can cause an accident. So it's detection and monitoring of LPG are necessary for domestic appliances to avoid any mishap-pending. Also, it is very important to detect the leakage at the primary level at the LPG gas cylinder's store. If there is a little leakage of gas and if it catches fire by any means, it begins to burn and these burning starts increasing the temperature. Due to which gas inside the cylinders expand and the great explosion takes place. If leakage has been traced at primary level then such type of disasters can be avoided. Hence to avoid the disasters in houses or stores, reliable and cost effective sensing devices are the basic need of the time.

Material selection for the gas sensor fabrication is an important issue. Nanostructured spinel and orthoferrite oxide materials depicted in Table1, attracted the attention of researchers/scientists due to its larger surface to volume ratio and their adsorption efficiency towards polar molecule and hydrocarbons on the surface of crystals. The adsorptions are reasonable so that the desorptions may fast and do not produce any structural change to crystallites. Therefore, they would be proven very good sensor materials. Here we have synthesized nanosized spinel and orthoferrite oxides using sol-gel and co-precipitation method and to perform its detail optical and spectroscopic characterizations. Further sensing investigations would be carried out with the exposure of LPG and other gases.

Table 1. Various types of ferrites on the basis of crystal structure are shown in the table.

S.No.	**Type**	**General Formula**	**Crystal structure**	**Active sites**	**Replacement**
1.	Spinel ferrite	AB_2O_4	Cubic	[A] & [B]	Mn, Zn, Ni, Mg, Co
2.	Garnet	RFe_5O_{12}	Cubic	a, c, and d	Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Lu
3.	Orthoferrite	$RFeO_3$	Perovskite	[A] & [B]	Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Lu
4.	Hexa ferrite	$AFe_{12}O_{19}$	Hexagonal	$12k, 2a, 4f_2, 4f_1, 2b$	Pb, Sr, Ba

Sensor Parameters/ Sensor Attributes of LPG sensor

For optimizing and the performance of any device, it is necessary to know its sensing parameters. % Sensor response, sensitivity, selectivity, stability, response and recovery times, reproducibility and long-term stability are the operating parameters of a sensing device [84-87].

(i) % Sensor Response

Percentage sensor response of a sensor is defined as the ratio of the difference in the resistance of the film in the air and in presence of gas to the resistance in air.

$$\%SR = \frac{|R_a - R_g|}{R_a} * 100$$

(ii) Sensitivity

Sensitivity can be defined as the ratio of the magnitude of response of a sensor to a particular target analyte. There are several definitions of sensitivity depending upon the application. It is defined as the ratio of variation in the resistance of the film in the presence of gas and resistance of the film in air.

$$S = \frac{R_g}{R_a}$$

(iii) Response and Recovery Time

The response time of a sensor is defined as the time taken by the sensor to reach 90% of the final response value. Recovery time is defined as the time taken by the sensor to come to 90% value of the final value.

(iv) Reproducibility and Long Term Stability

Reproducibility of a sensor is defined as the efficiency of a sensor to reproduce the same output for the same amount of measuring input. Stability of a sensor is defined as the efficiency of a sensor to generate the same result after a long time without any change in its sensing parameters.

(v) Selectivity

Selectivity may be defined as the sensor response to a particular gas in a mixture of gases. This parameter defines the specific response of the sensor.

Sensing Mechanism of LPG Sensor

The gas sensing mechanism of ferrites based LPG sensor is based on the surface area of the material at which the LPG molecules adsorb and reacts with pre adsorbed oxygen molecules. When the ferrite is exposed to reducing gas like LPG, it reacts with the chemisorbed oxygen. On interaction with the alkanes of LPG, the adsorbed oxygen is removed forming gaseous species and water. Consequently, the resistance changes, which is due to the change in the width of depletion layer after exposure to LPG. The overall reaction of LPG with the chemisorbed oxygen may take place as shown below:

$$C_nH_{2n+2} + O_2^- \longrightarrow C_nH_{2n}O + H_2O + e^- \text{.....................(iii)}$$

Where C_nH_{2n+2} represent the various hydrocarbons. The formation of the barrier is due to a reduction in the concentration of conduction carriers and thereby, results in an increase in resistance of the sensing material with time. As the pressure of the gas inside the chamber increases, the rate of the formation of such product increases and a potential barrier to charge transport becomes strong which has stopped the further formation of water constituting the resistance constant.

The present thesis is divided into seven chapters. Chapter 1 introduces the materials, methods, characterization tools and describes the object of the present investigation. In view of this, the Chapter 1 deals about the nanoscience and nanotechnology of spinel and orthoferrite materials along with the introduction of LPG sensor. Detailed investigation on nanostructured perovskite type Barium titanate thin film with synthesis, characterization and application as LPG sensor is depicted in Chapter 2. In Chapter 3, the synthesis, characterization and LPG sensing properties of nanostructured hexagonal strontium ferrite thin film is described. Chapter 4 reports the study of liquefied petroleum gas sensing properties of lead-free bismuth sodium titanate prepared by the sol-gel method at room temperature. In Chapter 5, fabrication of perovskite lanthanum ferrite film by sol-gel and its gas sensing properties has been demonstrated. Chapter 6 describes the synthesis of porous Ag-substituted $NiFe_2O_4$ which were applied as LPG sensing material and has been demonstrated. A study of synthesis, characterization and LPG sensing properties of perovskite barium titanate, hexagonal strontium ferrite, lead-free bismuth sodium titanate, perovskite lanthanum ferrite and Ag-substituted $NiFe_2O_4$ is summarized in Chapter 7. This chapter also gives the guidelines for further research work in the field of spinel and orthoferrites materials and their applications as LPG sensor. A study of synthesis, characterization and LPG sensing properties of $BaTiO_3$, $SrFe_{12}O_{19}$, $Bi_{0.5}$ $Na_{0.5}TiO_3$, $LaFeO_3$ and Ag-substituted $NiFe_2O_4$ is summarized as below:

Chapter 1 contains an introductory part of ferrites i.e. Spinel and orthoferrite materials including nanoscience and nanotechnology and its application in the various field. It also focuses on the Gas sensor with a detailed description of LPG sensing mechanism and its attribute. Surface morphology with large surface area and more active sites or interstitial site is an important aspect of gas sensing. Adsorption and desorption are the two phenomena which are responsible for whole sensing mechanism.

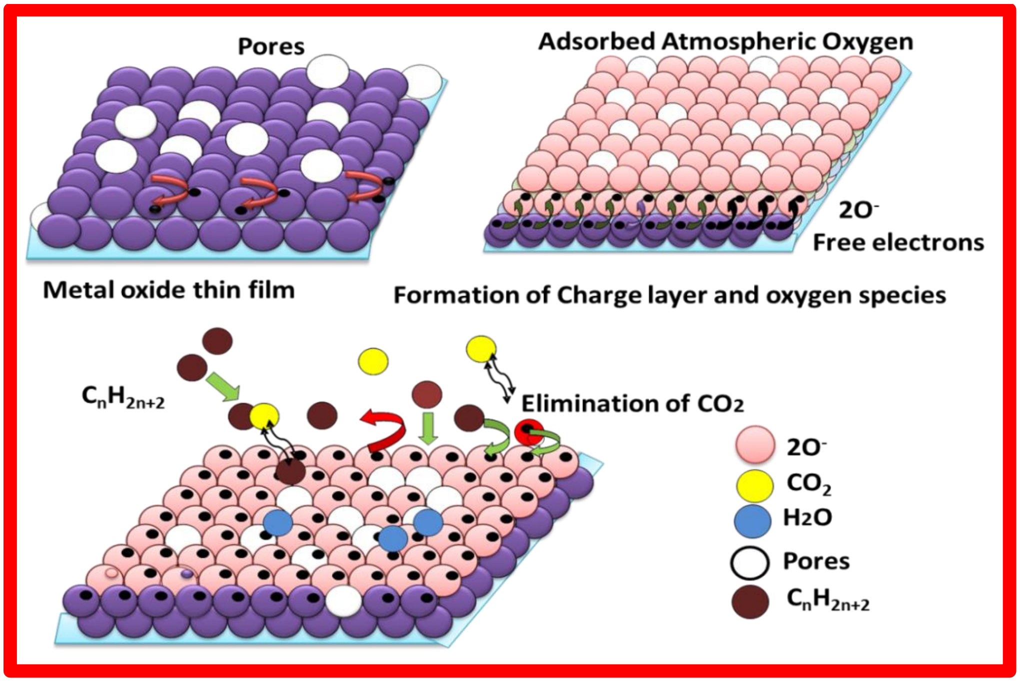

Fig. 1 Sensing mechanism of LPG Sensor

Chapter 2 describes the synthesis and characterization of perovskite Barium titanate thin film and its application as LPG Sensor. In this chapter preparation of nanostructured Barium titanate by the sol-gel method has been presented. The film was prepared by the spin-coating method and further, it was characterized by various characterizing tools. XRD confirmed the perovskite phase of the material. The prepared film was macro-porous which was used as a LPG sensor at room temperature. The sensing characteristic of the film was studied for 0.5 vol. of LPG to 4 vol.% of LPG. The maximum sensitivity was found for 4 vol.% of LPG i.e. 3.50 and % sensor response was found 250.85. Response time was found 30 s and recovery time was found 60 s. The aging effects were also checked after two weeks of sensing and after four weeks and the results were reproducible after this time period also. Graphical Abstract shown in Fig. 2 will give a glimpse of first chapter.

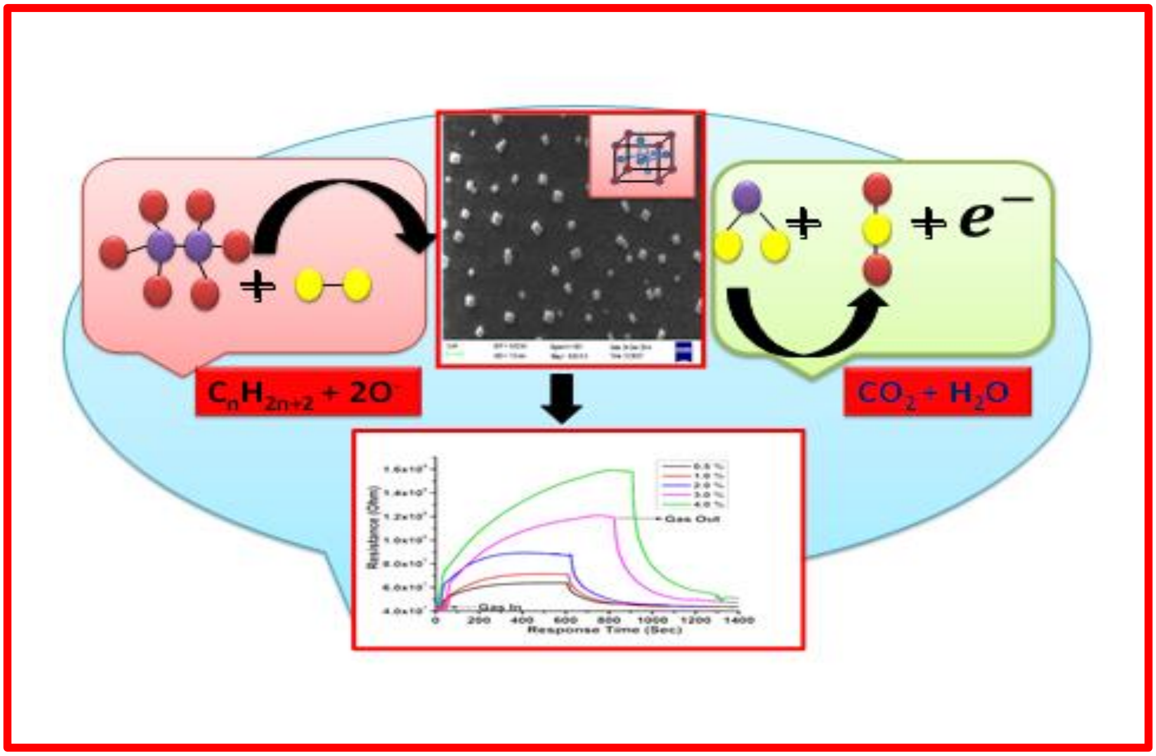

Fig. 2 Graphical Abstract of Barium titanate as LPG Sensor

Chapter 3 includes the detection of liquefied petroleum gas below lowest explosion limit (LEL) using nanostructured hexagonal Strontium ferrite thin film. In this chapter, we prepared hexagonal structured material by using co-precipitation method to reduce the size of the particle and better sensing response. We prepared the bulk amount of powder by this method and annealed it at high temperature 900 ºC to get the hexagonal phase of the ferrite. Hexagonal phase has four active sites which will give better LPG sensing response as LPG sensing depends on adsorption and desorption phenomenon. The minimum calculated size of the particle was found 18 nm. Sensitivity was found as 7 and % Sensor response as 602. Response time was found 40 s and recovery time was found 120 s. The Graphical Abstract of the work reported in this chapter is shown in Fig 3.

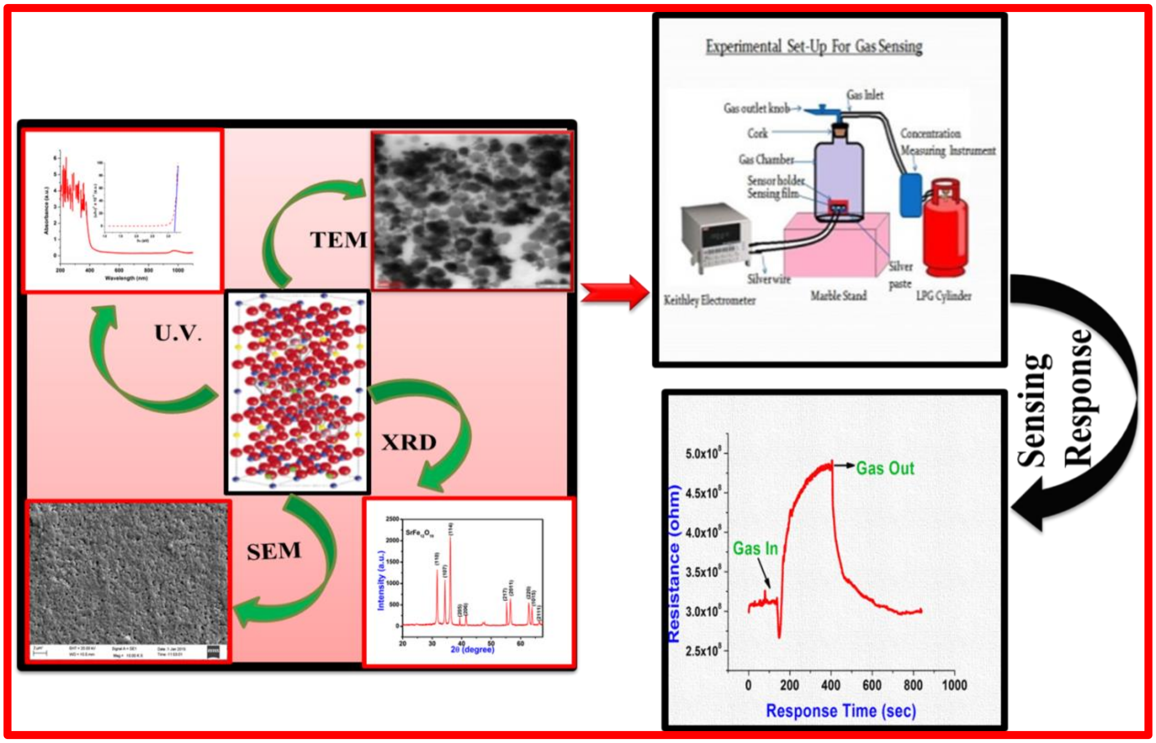

Fig. 3 Graphical Abstract of Strontium ferrite as LPG Sensor

Chapter 4 comprises of the study of Liquefied Petroleum Gas sensing properties of lead-free Bismuth sodium titanate prepared by sol-gel method. In this chapter, we again used the sol-gel method to replace Barium sites by some other material in Barium titanate. So we substituted Barium by Bismuth and Sodium at A-site to study its change in behaviour. Hence Bismuth sodium titanate was synthesized by using the sol-gel technique with a reduced size which belongs to orthoferrite family. The minimum crystallite size by XRD was found ~ 9 nm. The energy band gap was observed as 5.4 eV. Sensitivity was found 215 and % sensor response was found 115.4. Response time was found 22 s which was lesser than the previously reported response time. Graphical Abstract of BNT as LPG Sensor is presented by Fig.4.

Chapter 5 deals with the fabrication of perovskite Lanthanum ferrite film by sol-gel route and its gas sensing properties. The particle size was reduced to 8 nm and bandgap was found 5.3 eV. TEM revealed the particle size as 2.8 nm. Gas sensing properties were observed and the response time of this sensor was found as 12 s for 0.25 vol.% LPG and recovery time was 14 s. Maximum sensitivity was found as 3.3 for 3.5 vol.% LPG. Graphical Abstract of BNT as LPG Sensor is shown in Fig.5.

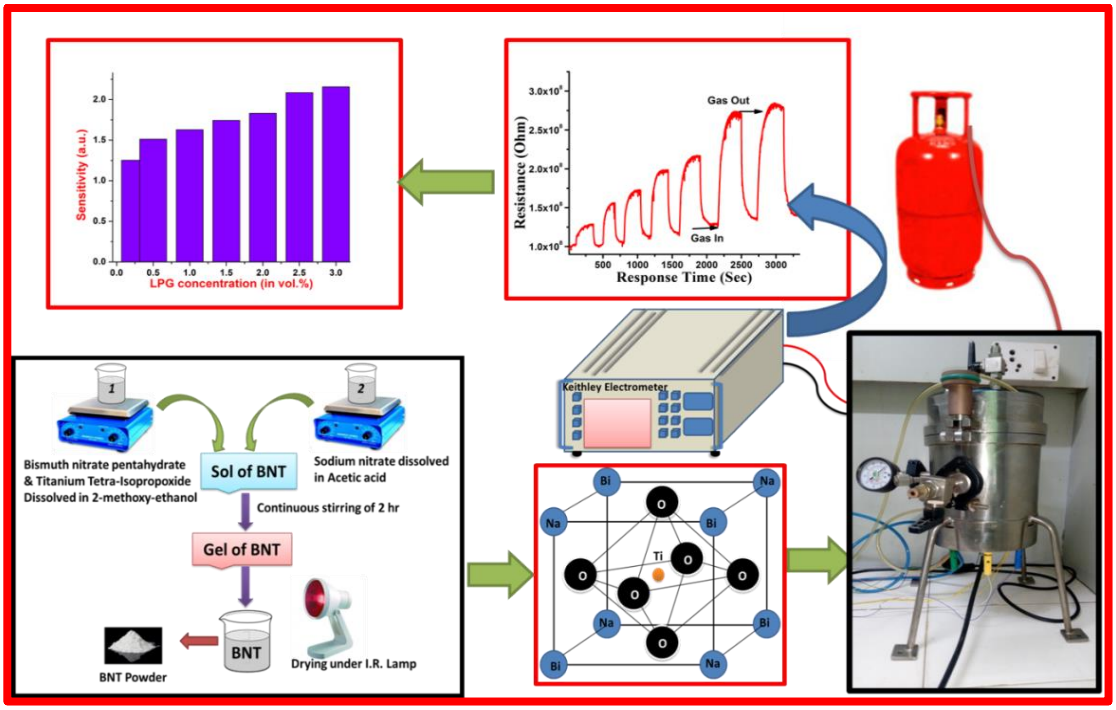

Fig.4 Graphical Abstract of BNT as LPG Sensor

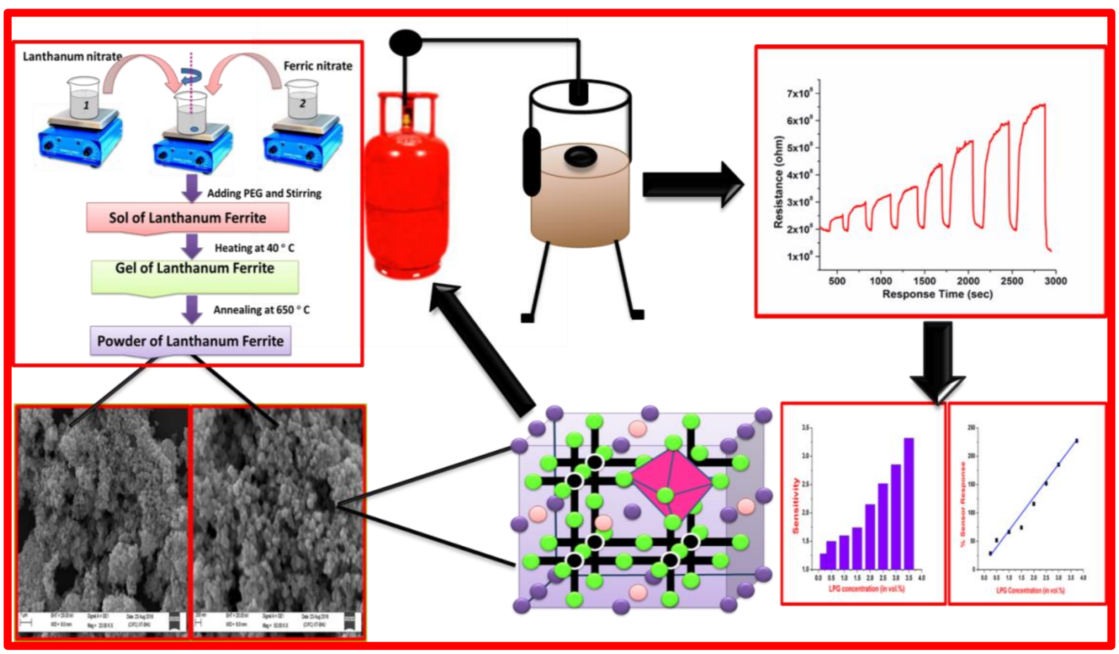

Fig.5 Graphical Abstract of Lanthanum ferrite as LPG sensor

Chapter 6 reports the Ag substitute Nickel spinel ferrite and further its application as LPG sensor below LEL. The comparisons in their microstructures were observed by SEM. Micrographs obtained, exhibited the better surface morphology of 0.45 Ag-substituted nickel ferrite than 0.2%

Ag-substituted nickel ferrite. As Ag-substitution increases, the porosity of material was found to be increased. XRD revealed the crystalline phase of Ag-substituted nickel ferrite. Similarly, there was a change in energy bandgap from 5.3 to 5.4 eV and also the optical behaviour of the samples. The maximum sensitivity was found 2.57 and 4.57 with % sensor response of 157.8 and 357.14 for 4 vol.% of LPG. The investigated LPG sensor produced a repeatable curve one after the other experiment hence this sensor was more reliable and a next step towards the development of a LPG sensor at commercial scale. Graphical Abstract of Ag substituted Nickel ferrite as LPG sensor is presented in Fig.6.

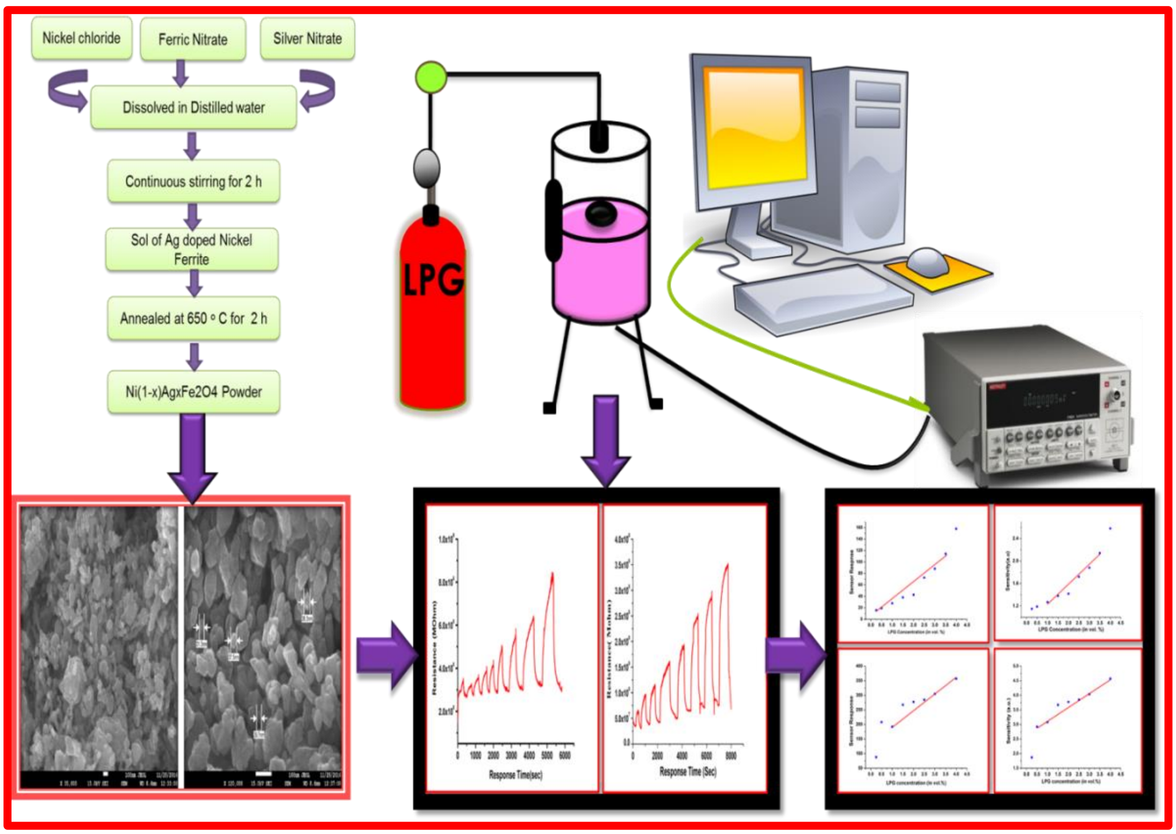

Fig.6 Graphical Abstract of Ag substituted Nickel spinel ferrite as LPG sensor

A chapter wise sketch of the Thesis including the sensing materials, dopants, bandgap, sensitivity, crystallite size, average grain size, pore size is depicted in Table 1.

Chapter No.	Materials	Method of Preparation	Band Gap (eV)	Particle Size	Sensitivity/ % Sensor Response	Response time
Chapter 1	Introduction	………...	…………	…………	………….	…………
Chapter 2	$BaTiO_3$	Sol-gel	3.9 eV	11 nm	3.50/ 250.85	30 s
Chapter 3	$SrFe_{12}O_{19}$	Chemical Precipitation	3.2 eV	18 nm	7.02/ 602	40 s
Chapter 4	$Bi_{0.5}Na_{0.5}TiO_3$	Sol-gel	5.4 eV	9 nm	2.15/ 115.4	22 s
Chapter 5	$LaFeO_3$	Sol-gel	5.3 eV	8 nm	3.31/ 231	12 s
Chapter 6	Ag-substituted $NiFe_2O_4$	Sol-gel	5.3 & 5.4 eV	6 nm & 7 nm	2.57/ 157.89 & 4.57/ 357.15	10 s & 30 s
Chapter 7	Conclusion and future Scope	………….	…………	…………	………….	…………

Table 1 A chapter wise sketch of the Thesis

From the Table 1, we infer that the Ag-substituted $NiFe_2O_4$ is an excellent material for LPG sensing application at room temperature and using this material a commercialized model of LPG sensor applicable for both indoor and outdoor detection may be designed.