

## **Chapter III**

# **Fabrication and Characterization of La<sub>2</sub>CuO<sub>4</sub> Nanoparticle Based NO<sub>x</sub> Gas Sensors**

### III.1. Introduction

Metal oxide semiconductor gas sensor with finer microstructures are ideal candidates for low range detection because of its larger contact surface area between gas-solid interface. From the view point of today's demand, development of sensors, suitable for low range detection are necessary because of increase in environmental pollutants from different industrial exhaust and automobiles. There are already some legislation<sup>1</sup> based on low limit values for CO, NO<sub>x</sub> and HCs from automotive emission. Several earlier investigations reported that sensitivity and response time depends on gas concentration profile.<sup>2</sup> The dependence of sensitivity at different range of gas concentration with the pore size distribution of the sensing electrode of YSZ based Potentiometric sensor has been studied in this investigation. Two theories have been proposed to explain the working mechanism of the potentiometric sensors: Mixed Potential Theory and Differential Electrode Equilibria Theory. Among them, Mixed Potential Theory originates from corrosion theory,<sup>3</sup> in which a pair of reduction and oxidation (redox) electrochemical reactions occur simultaneously to establish an equilibrium and there by produces a corrosion potential. This concept was first introduced in order to address potentiometric responses that deviated from the Nernst Equation.<sup>4-12</sup> According to Mixed Potential Theory, multiple gas reactions simultaneously come to equilibrium over the electrodes and each electrode establishes a mixed potential based on the equilibrium and rates of these reactions. For a NO sensor, the following equations represents the corresponding redox reactions:



Since it measures the equilibrium level of NO, cannot describe NO sensing accurately. There are two limitations in Mixed Potential Theory, one of them is that NO does not come to thermodynamic equilibrium at sensor operating conditions because of the kinetic limitations and other is that at least one of the electrodes in a sensor must be a semiconducting material. To overcome these discrepancy Wachsmann et al. introduced the idea of Differential Electrode Equilibria<sup>13</sup> to the gas sensing mechanism which is a more inclusive theory that takes into account multiple contributions as a cause for the difference in potential between two electrodes. Besides them additional contributions, namely the adsorptive and catalytic properties of

semiconducting oxides, including  $\text{La}_2\text{CuO}_4$ , have been thoroughly studied to potentiometric sensitivity in  $\text{NO}_x$  sensors. Upon adsorption of gas, semiconductors exhibit a change in Fermi Energy which lies between the valence and conduction bands and tends to bend under development of charge on the surface due to the adsorption.<sup>14</sup> Since Fermi Level is the localized electrochemical potential of electrons ( $\mu_e = E_F$ ), the output (i.e. the difference between two electrodes) of a potentiometric sensor is affected by this phenomenon. Mixed Potential Theory that occurs over electrodes also does not take account for gas phase catalysis. So, sensitivity of semiconducting gas sensors in potentiometric mode can be explained with adsorption kinetics.

Earlier investigations with Potentiometric gas sensors indicate that electrode's microstructure affect the sensitivity and response time of the sensor<sup>15-17</sup> due to a large number of adsorption sites of microstructure electrode element which increases the surface to bulk ratio of microstructure electrode that extend the surface charging into the core of the microstructure. In previous work it was reported that response time decreases with microstructure of electrodes.<sup>18</sup> The  $\text{NO}_x$  sensors based on YSZ as a solid electrolyte has been reported in many publications.<sup>19-27</sup> From literature survey it has been observed that there are various sensors for  $\text{NO}_x$  detection in the form of  $\text{Cr}_2\text{O}_3|\text{YSZ}|\text{Pt}$ ,<sup>28</sup>  $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3|\text{YSZ}|\text{Pt}$ ,<sup>29</sup>  $\text{NiO}|\text{YSZ}|\text{Pt}$ ,<sup>30,31</sup>  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3|\text{YSZ}|\text{Pt}$ ,<sup>23</sup>  $\text{La}_2\text{CuO}_4|\text{YSZ}|\text{Pt}$ ,<sup>32</sup>  $\text{CuO}|\text{YSZ}|\text{Pt}$ ,<sup>33</sup> possess maximum range of detection 500 ppm, 20–1000 ppm, 10–400 ppm, 0–500 ppm, 50–400 ppm, 10–100 ppm respectively. But dependence of electrode's pore size with range of detection of a sensor is not discussed properly yet. Here we will discuss how detection of ultra-low ppm range is possible by using nano-crystalline microstructure electrode.

The experimental curve and simulated curve in this study both provide proofs of S-type nature of sensitivity with gas concentration with a definite shift in sensing range with average pore size of sensing layer. Microporous  $\text{La}_2\text{CuO}_4$  based  $\text{NO}_x$  sensor also exhibit higher sensitivity at low gas concentration and low range(ppm) detection capability.

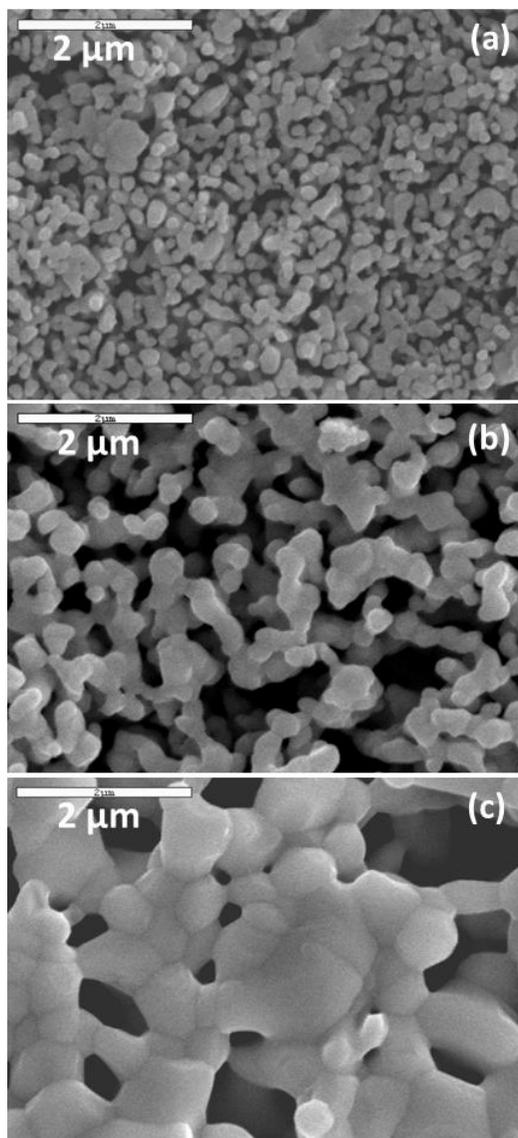
### **III.2. Background and Objectives**

Although a large number of different oxides have been investigated for their gas sensing properties, commercially available gas sensors are mainly made of  $\text{SnO}_2$  in the form of thick film, porous pellets or thin films. The effects of the microstructure, namely, ratio of surface area to volume, grain size and pore size of the metal oxide particles, as well as film thickness of the

sensor are well recognized. Lack of long-term stability and selectivity has until today prevented a widespread diffusion of this type of sensors. Gas sensors are employed in many applications including monitoring emissions from vehicles and other combustible processes, detection of toxic and combustible gases, Breadth analysis for medical diagnosis, and quality control in chemicals, food and cosmetic industries. Recently, by the application of Nanostructured sensing elements, issues like sensitivity and selectivity were reported by earlier workers and encouraging results were found. Higher sensitivity at lower concentration of gases is expected using sensing surface with finer microstructure. In this investigation, we propose, a systematic study of response with nano-structured sensing element which is expected to enhance the range of measurement up to ppb level.

### **III.3. Present work: Result and Discussion**

Powder sintered at 750 °C, 800 °C and 1000 °C exhibit tiny, intermediate and macro grains respectively (reveals from Figure III.1). Again, it was observed from earlier literature that pores were usually comparable to their grain sizes.<sup>34</sup> With increasing sintering temperature, grains as well as pores began to fuse together,<sup>35</sup> produces a reduction of total porosity of the sensing material because of decreased surface area and modified surface structure.<sup>36</sup> In this regard, we optimized the sintering temperature at 1000 °C for macro pore and that sintered at 750 °C to yield micro pore, while 800 °C to yields mesoporous sensing surface.

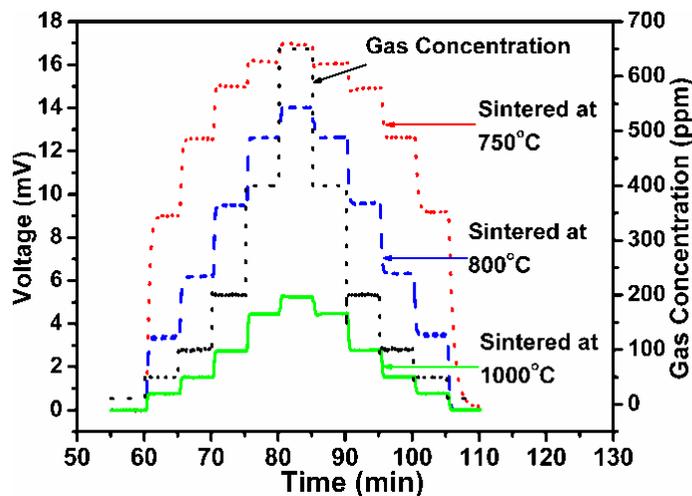


**Fig.III.1.** Typical SEM images of prepared  $\text{La}_2\text{CuO}_4$  nanoparticles sintered at (a) 750 °C, (b) 800 °C and (c) 900 °C.

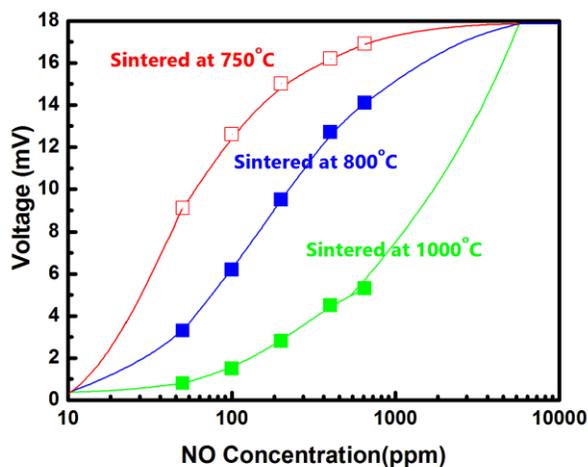
### **III.3.1. Change of response magnitude with gas concentration**

The NO gas response of the potentiometric sensing element has been shown in Figure.III.2 where the response voltage is presented with changing gas concentrations in steps of 0, 50, 100, 200, 500 and 650 ppm. Under exposure of 650 ppm NO gas on the three types of porous sensing surfaces, gas response at a fixed temperature (450 °C) are different in magnitude and it is maximum for sensor which exhibit tiny pore, sintered at 750 °C and is minimum for that which exhibit macropore, sintered at 1000 °C. However, under close observation it was seen that the

sensitivity is not always same and it indicates a larger variation at the beginning for micropores and smaller variation at the beginning for macropores. In order to understand the variation more closely, the sensitivity of three types of sensing surfaces are plotted in Figure III.3.



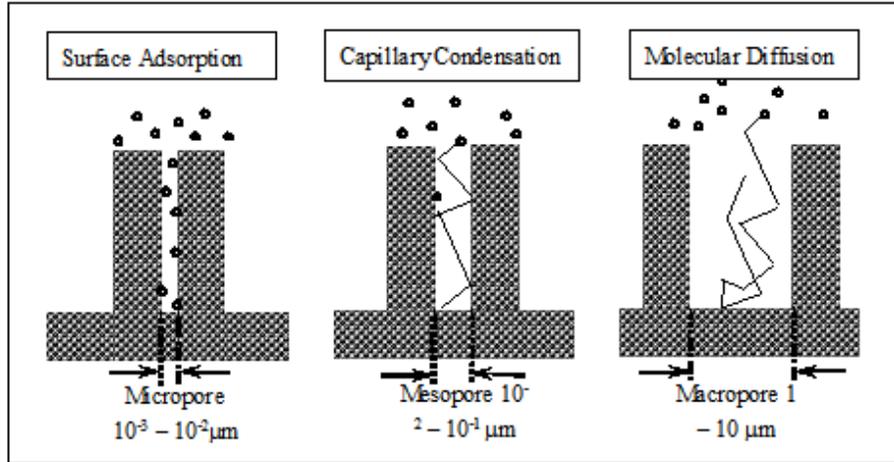
**Fig.III.2.** Voltage response of three different types of prepared  $\text{La}_2\text{CuO}_4$  nanoparticles sintered at 750 °C, 800 °C and 900 °C with step change in gas concentration



**Fig.III.3.** Voltage response of three different types of prepared  $\text{La}_2\text{CuO}_4$  nanoparticles sintered at 750 °C, 800 °C and 900 °C with gas concentration at 450 °C

### III.3.2. Sensitivity with pore size

Actually, with the increase in pore size following three types of diffusion occur at sensing material such as surface diffusion, Knudsen diffusion and molecular diffusion respectively,<sup>36</sup> which are responsible for gas sensing at different types of porous surfaces. For microporous material, pore sizes are too small to adsorb multiple layers of gas molecules and also, the pore edges are sharp. Due to these factors, the gas adsorption or surface forces are dominant so that adsorbed gas molecule cannot escape from force field of the surface. Due to small volume of pores, saturation of gas adsorption occurs at lower gas concentration ranges. This variation can be explained with the help of diffusion theory in nano porous media.<sup>37</sup> On the other hand, for mesoporous range, as the pore sizes are comparatively larger, capillary forces dominate over surface forces for their sensitivity in which pore condensation occur after multilayer adsorption of gas on the sensing material, as a result free volume of a mesopore decreased slowly than micropore after sorption treatment.<sup>38,39</sup> Again, from literature survey, Nitrogen adsorption isotherm for active charcoal showed that Nitrogen uptake at low relative pressure was mainly due to filling of micropores.<sup>40</sup> So, in case of mesoporous surface, sensitivity is smaller than that for microporous sensor in the low concentration range. The reason behind this may be due to an increased number of van der-waals interactions between gas molecules inside the confined space of capillary. For macro pore, molecular diffusion is responsible for their sensitivity,<sup>39</sup> in which transport properties of gas molecules through the macro pore is large but gas adsorption capacity is very small, and in this case interaction between gas molecules is significantly larger than the interaction between gas molecule to pore wall, that's why it exhibits a smallest sensitivity among them as shown in Fig III.4.



**Fig III.4.** Schematic diagram of gas diffusion through different porous sensing surface.

This can be explained with the concept of mean free path length. The gas diffusion coefficient is related linearly with its pore diameter as given in equation.

$$D_K = \frac{4}{3} r \sqrt{\frac{2RT}{\pi M}} \quad (3)$$

By using this diffusion constant and by solving the diffusion equation, one can estimate the amount of gas adsorbed ( $C_A$ ) inside the sensing surface.

$$\frac{\partial C_A}{\partial t} = D_K \frac{\partial^2 C_A}{\partial x^2} - k C_A \quad (4)$$

$$C_A = C_{AS} \frac{\cosh\left[(L-x)\sqrt{\frac{k}{D_K}}\right]}{\cosh\left[L\sqrt{\frac{k}{D_K}}\right]} \quad (5)$$

Where,  $C_{AS}$  is the gas concentration outside the sensing layer, and  $L$  and  $x$  is the thickness of sensing layer and the diffusion length respectively. The different range of detection for micro, meso and macro-porous sensing surface can be explained with the help of this gas concentration profile inside this sensing surface, which again depends on pore size (from Equation 3) as well as surface reaction and rate of diffusion on surface of sensing material.<sup>41,42</sup> The gas concentration reduces with decrease in pore diameter. For micropores, volume of gas adsorbed is sufficiently low. This results in the gas molecules to reside closely near the sensing surface and further diffusion is restricted, reducing the chances of multilayer adsorption. Since micropores are in the

range of <1 nm, so it is assumed that a small concentration of target gas is sufficient to fill the pore.<sup>43</sup> Hence saturation region in this case came earlier than meso and macro-porous surfaces.

For macro-porous surfaces, the amount of gas adsorbed in sensing layer is sufficiently large, increasing the collision probability between gas molecules, results in lowering of mean free path

length  $\lambda_M = \frac{2kT}{\pi d^2 P}$ , where d and P are the pore diameter and pressure concentration of applied

gas. So, a large number of multilayer adsorption is required to fill up the pore volume of the sensing material. In macro pores, diffusion occurs mainly by bulk or molecular diffusion mechanism in which diffusion coefficient is inversely proportional to square of its pore diameter as given in Equation (6) below,

$$D_M = \frac{2}{3} \sqrt{\frac{kT}{\pi m}} \frac{kT}{\pi d^2 P} \quad (6)$$

So, with increasing pore diameter, rate of diffusion decreases and as a result high concentration of target gas is required to fill all the pores of bulk region. For this reason, saturation occur at high concentration range of the target gas.

In mesopore region, both the surface reaction as well as capillary forces are responsible for their wide detection range. In this case, the pore size is in intermediate range and so the volume of gas adsorbed will also be intermediate. Again, from Equation (5), it can be observed that the adsorbed gas concentration ( $C_A$ ) decreases from surface after few diffusion layers. So, adsorption starts at higher gas concentration than microporous surface and saturation occurs after a small number of multilayer adsorption. Here the mean free path length for mesopore

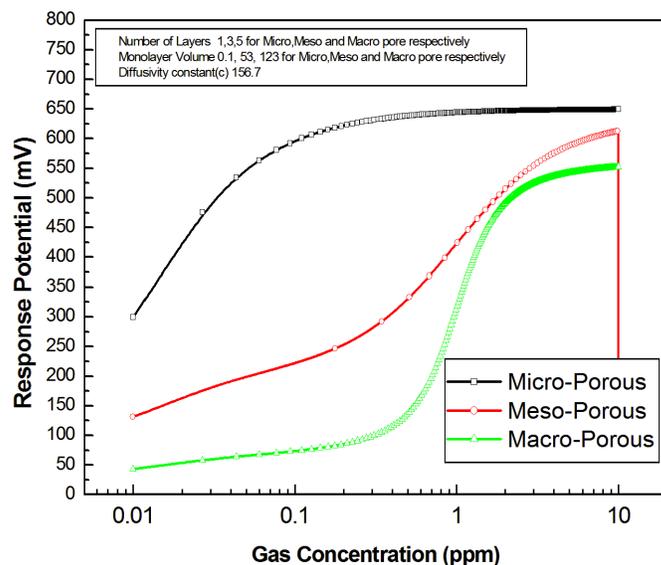
is  $\lambda_m = \frac{1}{\sqrt{2\pi\sigma^2}} \frac{V}{N_A}$ , where V is the gas molar volume at particular pressure and  $\sigma$  is the

molecular cross section. In this case, collision probability between gas molecules are lower compared to collision probability with pore walls.

The profile of distribution of adsorbed molecules in subsequent layers can be obtained from Langmuir's isotherm equation for monolayer adsorption.<sup>44</sup> Considering evaporation in one layer and condensation in subsequent layer, the Langmuir's isotherm equation can be modified for nth layer as.

$$v = \frac{v_m cx}{(1-x)} \left[ \frac{1 - (n+1)x^n + nx^{n+1}}{1 + (c-1)x - cx^{n+1}} \right] \quad (7)$$

Where,  $v$  is the volume of gas adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer,  $x=P/P_0$  and  $n$  is the number of layers of adsorbent  $v_m$  is the volume of the adsorbed gas in a monolayer of adsorbent. With the help of equation 7, the s-type nature of our experimental graph could be simulated and is presented in Figure III.5.



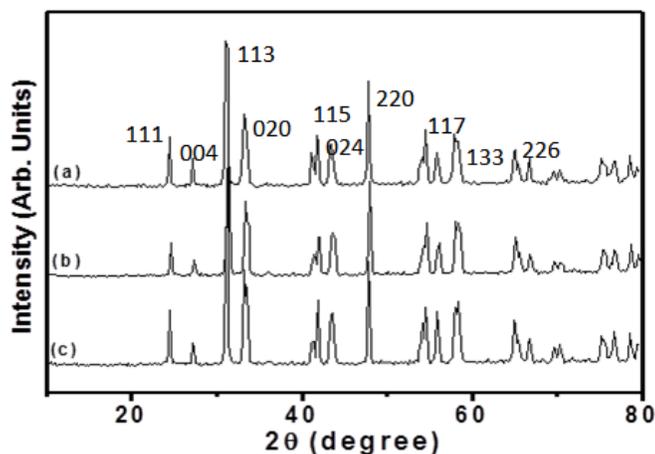
**Figure III.5.** Simulation of the sensitivity range for small, medium and large sized pores of sensing material.

To explain the exponential rise in sensitivity at very low gas pressure range, following factors may be responsible. It is highly probable that some surface complex containing carbon, hydrogen, and oxygen remained at the sensing surface. These can decompose into  $CO_2$ ,  $CO$ , and  $H_2$  by continued thermal treatment. Some of this complex could be removed during the outgassing at  $450\text{ }^\circ\text{C}$ , but an appreciable portion always remained in the adsorbent. The presence of this residual complex could have a major influence on the observed steady-state pressure in the range of very low pressures. The experimental results suggest that one of the factors responsible for the behaviour observed at low pressures may be directly related to the residual complex. Another factor of influence is associated with the diffusion of gas molecules at low pressures. Because of the intricate structure of the porous material, more time is required for the adsorbate to locate the adsorption sites of minimum potential energy which reduces the surface coverage. A similar argument may be valid in connection with surface diffusion phenomena.

This helps to explain the fact that even relatively well out gassed adsorbents (400 °C for 16 hour) required long periods to attain equilibrium in the low-pressure range.<sup>45</sup> With larger pore sizes, this equilibration time should be much larger. More and more be the gas pressure, the equilibration time became faster.

### III.3.3. Experimental Details

In this study to fabricate a sensor ,tape cast YSZ (20mm×10mm×0.15mm) was taken as substrate and  $\text{La}_2\text{CuO}_4$  as one of the electrode which were prepared through Auto-ignition technique,<sup>46</sup> where nitrate salts of constituent elements were taken and citric acid was added in appropriate proportion and subsequently heated with thorough mixing to form a gel, which was burnt to ashes which depends on the citrate-nitrate ratio, and was the key parameter in determining the powder morphology and the prepared  $\text{La}_2\text{CuO}_4$  were calcined in air at 750 °C, 800 °C and 1000 °C and mixed with appropriate amounts of solvents and ball-milled for 10 hours. The slurry thus obtained was screen-printed on one face of the substrate and Pt was pasted on the other. Thin platinum wires were connected to both the electrodes using Pt paste for ohmic contact. Finally, after drying of the printed electrode slurry, the sensor was sintered at appropriate temperature. The synthesized nanoparticles were characterized by X-ray diffraction (XRD) (Figure III.6) and scanning electron microscopy (SEM) (Figure III.1), which revealed that the particle size of the prepared nano materials increases with increasing the annealing temperature. The phase identification of all three perovskite oxides showed only the peaks of orthorhombic perovskite-type  $\text{La}_2\text{CuO}_4$  phases.



**Figure III.6.** X-ray diffraction pattern for the prepared  $\text{La}_2\text{CuO}_4$  nanoparticles sintered at (a) 750 °C, (b) 800 °C and (c) 900 °C.

Prepared  $\text{La}_2\text{CuO}_4$  perovskite-based sensor was systematically evaluated for NO reduction activity in Nitrogen ( $\text{N}_2$  as carrier gas and the sensing experiments were carried out in a gas-flow system with a controlled heating facility. The sensors were exposed to step change of 50, 100, 200, 400 and 650 ppm of the NO gas to be sensed, in simulated combustion environment, at the total flow rate of 300 ml/min, in the temperature range between 400 and 700 °C. Electromotive force (EMF) measurements were performed between the two electrodes of the sensors using a Keithley 2400, digital voltmeter. During the EMF measurements, the electrode with the oxide coating was always kept at the positive terminal of the electrometer and both the electrodes were exposed to the same gas environment.

#### **III.4. Conclusion**

In conclusion, this study shows that the sensitivity of different microstructures are different in magnitude and they exhibit a shift in detection range, which has got definite correlation with pore size of the sensing layer. Larger pores have got higher sensitivity at higher concentration of gas whereas smaller pores have higher sensitivity at lower concentration of gas. Considering adsorption in one layer and condensation in subsequent layers and mean free path of gas molecules, we simulated the sensitivity profile. Simulation shows S-type nature of sensitivity with gas concentration with a definite shift in sensing range with average pore size of sensing layer. It was concluded that very large pore diameter reduced the adsorption sites and very small pore diameter reduced the probability of penetration. So, for the detection of higher concentrations one may use sensing material with larger pores and for low ppm detection one may use the sensor with micro pores.

#### **III.5. Reference**

References are given in BIBLIOGRAPHY under chapter III page no. 92-94.