CHAPTER II
REVIEW OF LITERATURE

2.1. INTRODUCTION

Different materials in the forms of thick or thin films, powder or pellet and gels are being prepared by many methods for various technological applications. Devices or components made in thin film forms have advantages over the bulk materials because of low cost of production, high reliability, superior performance, extreme compactness and corresponding reduction in size and weight, low power consumption etc. Hence materials in thin film forms are preferred much for fabricating devices.

Also, there has been an increasing interest in the preparation of nanocrystalline thin film materials owing to their electrical, optical, mechanical and gas sensing properties being superior to those of conventional coarse granular structures [1-4]. The surface to bulk ratio for a nanocrystalline material is much greater than for a material with large grains, and hence the nanocrystalline material yields a large interface between the solid and a gaseous medium, increasing the gas sensitivity [5,6]. In the following section a brief literature survey relating the methods of preparation of oxides of lithium are described.
2.1.1. PULSED LASER DEPOSITION (PLD) METHOD

PLD has many advantages in the fabrication of thin films such as high deposition rate, easy control over film thickness, capability of reactive deposition in ambient gases and transferring nearly the original stoichiometry of a bulk target to the deposited film [7].

By using this technique several lithium based thin film battery materials such as LiCoO$_2$ and LiMn$_2$O$_4$ [8,9] have been prepared. In the preparation of lithium phosphorous oxynitride (LiPON) film [10] the experimental set-up consisted of a stainless vacuum chamber equipped with a rotating holder for the Li$_3$PO$_4$ target. The Li$_3$PO$_4$ target was prepared by compressing Li$_3$PO$_4$ powder into a pellet of 13 mm diameter, and was sintered at 600$^\circ$C for 2 hrs. 355 nm laser beam provided by the third harmonic of a Q-switched Nd : YAG laser was focused and irradiated onto a rotating Li$_3$PO$_4$ target at an angle incidence of 45$^\circ$. The pulsed laser repetition rate and pulse width were 6 ns and 10 Hz respectively. The laser energy was measured by a power meter with a pyroelectric detector. The Si substrate was placed at a distance of 5 cm away from the Li$_3$PO$_4$ target. Before deposition the vacuum chamber was evacuated and then filled with N$_2$ gas through a needle valve. LiPON film was formed by the nitridation of Li$_3$PO$_4$ during reactive pulsed laser ablation. Similarly Li$_3$PO$_4$ thin film was prepared in an oxygen gas ambient.
XRD shows crystalline nature of Li$_3$PO$_4$ and amorphous nature of LiPON thin films. SEM studies show that the films exhibit a glassy phase without any pinhole or crack. But the presence of coagulated droplets on the surface makes the film surface rough. Formation of particulates or droplets is one of the recognized disadvantages of PLD. Thus quality of the film depends strongly on the laser fluence, the ambient gas pressure and the target-substrate distance as well as the nature of target.

2.1.2. REACTIVE RF SPUTTERING METHOD

The RF sputtering method is suitable for making reproducible thin films from various target materials such as metals and oxides in a relatively short time and with controlled film thickness.

A planar-magnetron-type RF sputtering apparatus was used to form thin film of LiMn$_2$O$_4$, which is used as an electrode for rechargeable micro batteries [11]. A sputtering target, 2 inch in diameter and 6 mm thickness was made by cold pressing LiMn$_2$O$_4$ powder. LiMn$_2$O$_4$ powder was prepared by the solid-state reaction of stoichiometric amounts of lithium hydroxide monohydrate (LiOH.H$_2$O) and electrolytic manganese dioxide at 800°C in air for 24 hrs [12]. For cold pressing, 1 weight percent of polyvinyl alcohol (PVA) was used as a binder. After mixing, they were pressed into disks. Quite robust targets could be obtained by sintering in air at 900°C for 12 hrs. The target was placed on
the lower electrode and 2.5x2.5 cm$^2$ Pt/Ti/SiO$_2$ substrates were attached to the upper electrode. The distance between the target and the substrates was about 35 mm. The chamber was evacuated to base pressure of 3 x 10$^{-3}$ torr and back filled to 0.01 torr with a gas mixture of Ar with 5% oxygen. 150W RF power (7.4W/cm$^2$) was used and the substrates temperature was 100 - 150°C during deposition. Films about 0.2micron thickness were obtained after sputtering for 40 min. (50 Å/min). The as-deposited films were amorphous but crystallized into spinel structure [13-21] by rapid thermal annealing in an oxygen atmosphere. Similarly Li doped SnO$_2$ film as oxygen gas sensor material [22] were formed on Al$_2$O$_3$ substrate from the target of SnO$_2$ (1Vol % Li). The sputter deposition was made in an atmosphere of argon with 30% of oxygen. XRD analysis showed that the film are polycrystalline in nature.

2.1.3. SOL-GEL METHOD

Because of the simplicity of operation and various advantages like (i) ambient temperature of sol preparation and gel processing (ii) high purity of precursors;(iii) product homogeneity;(iv) low temperature of sintering and (v) good control on particle size [23], sol-gel processing has proved to be very popular in recent times for the preparation of inorganic materials.
Thin film of LiMn$_2$O$_4$ used as an electrode in micro batteries was obtained by sol-gel method [24]. Lithium acteylactetonate (LiCH$_3$CO-CHCOCH$_3$) and manganese acetylactonate [Mn(CH$_3$COCHCOCH$_3$)$_3$] were dissolved in 1-butanol and acetic acid, having a molar Li/Mn ratio of 1/2. This solution was mixed by stirring for 24 hrs and then was degassed by ultrasonic cleaner for 5 min. at room temperature in a glove box filled with purified Ar gas. After this the sol was filtered with polytetrafluoroethlyene (PTFE) membrane whose average pore size was 0.2 micron.

The resulting sol was spin-coated on Pt substrate at 5000 rpm for 30 s and then dried at 350°C over 15 min. to evaporate solvents and organic materials. The spin-coating and drying processes were successively repeated to control the film thickness. Finally the crystalline LiMn$_2$O$_4$ film was obtained by annealing the as-deposited film at 800°C for 4 hrs in air. SEM studies showed that the film thickness to be about 120 nm. The film was clearly identified by XRD and Inductively Coupled Plasma Analysis shows that the film is composed of a single lithium-excess phase with the cubic-spinel structure.

Ceramic thin film of TiO$_2$-K$_2$O-LiZnVO$_4$ as humidity sensor material was prepared by sol-gel method [25]. Tetrabutyl titanate was used as titania precursor, and acetylacetone as a stabilizer. The matrix sol was prepared by mixing tetra-butyl titanate with
acetylacetone, absolute ethanol, distilled water and an acid catalyst (HNO₃ 65%) in molar ratio of 1 : 1 : 21 : 16 : 0.11. Solutions containing K, Zn, Li and V were then prepared by adding calculated amount of CH₃COOK, Zn(CH₃COO)₂ and LiVO₃ (made from LiOH and NH₄VO₃), to the tetrabutyl titanate mixed solution and stirring for about 2 hrs. The film was deposited on Al₂O₃ substrate at a withdrawal speed of 25 cm/min. The film thus obtained was dried at 100°C for 1 day, and then heat-treated at 600°C for 30 min. with a heating rate of 20°C/min. The surface composition of the film determined by X-ray photoelectron spectroscopy shows that the dopants of K, Li, Zn and V are enriched on the film surface. But the bulk composition of the films determined by chemical analysis shows that Ti : Li : Zn : V : O are in the molar ratios of 1 : 0.04 : 0.1 : 0.1 : 2.42. SEM studies show that the film is compact and continuous, with crystalline grains and with a film thickness of about 1.2 micron.

2.1.4. ELECTROSTATIC DEPOSITION (ESD) METHOD

ESD [26-32] enables to form uniform and dense film of Spinel LiMn₂O₄ battery material [33-35]. In this method a high dc voltage of 12 KV was applied between a metal capillary nozzle (inner diameter 0.8 mm) and an electrically conductive substrate consisting of a circular gold flag with a geometric surface area of 0.2 cm². A precursor solution 25 mM LiNO₃ + 50 mM Mn(NO₃)₂ in
ethanol was pumped through the metal capillary nozzle at a rate of 2 ml/hr. Owing to electrostatic force, the precursor solution was atomized at the orifice of the nozzle and consequently a spray was generated and deposited as a thin layer of thickness of 0.1 micron on the substrate. The substrate was placed 2.5 cm below the orifice of the capillary nozzle on a hot plate heated to 400°C. The film was left on a hot plate to anneal for 1hr. The thickness of the ESD films can be varied by varying the salt concentration, the solution flow rate and the deposition time [34]. In the ESD process, a charged aerosol of the reactants is generated and directed to the heated substrate under an electric field. The solvent evaporation process has been found to influence the morphology of the film [26]. At a low temperature chosen, the solvent evaporation process onto the substrate is generally quite slow and helps to form a relatively denser film.

2.1.5. POWDER METHOD

Fine powders of Li$_{1-x}$Mn$_{2-x}$O$_4$ battery material [36] were synthesized by a nitrate route based on Lux-flood principle. The method involves the reaction of MnSO$_4$·H$_2$O with an excess of lithium nitrate from a nitrate bath. The reaction consists of three steps namely dehydration, oxidation and lithiation. In dehydration step I, H$_2$O is released between temperature 150°C and 180°C[37]. During step II the simultaneous formation of a dark powder and evolution of a brown gas is observed corresponding
to the oxidation of manganese. The normal LiNO₃ melting point of 263°C was found to be depressed to about 240°C. [38]. Finally step III corresponds to the insertion of Li in MnO₂ with initial formation of the spinel phase Li₄Mn₅O₁₂ followed by a transition to Li₂MnO₃. The preparation of powder can be summarized into the following reaction scheme.

\[
\begin{align*}
\text{Mn}^{2+} + 2\text{NO}^3 & \rightarrow \text{MnO}_2 + 2\text{NO}_2 \\
5 \text{MnO}_2 + 4\text{LiNO}_3 & \rightarrow \text{Li}_4\text{Mn}_5\text{O}_{12} + 4\text{NO}_2 + \text{O}_2 \\
\text{Li}_4\text{Mn}_4\text{O}_{12} + 6\text{LiNO}_3 & \rightarrow 5\text{Li}_2\text{MnO}_3 + 6\text{NO}_2 + \frac{3}{2} \text{O}_2
\end{align*}
\]

The overall reaction is then

\[
\text{MnSO}_4\cdot\text{H}_2\text{O} + 4\text{LiNO}_3 \rightarrow \text{Li}_2\text{MnO}_3 + 4\text{NO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + \text{Li}_2\text{SO}_4.
\]

The products of each step were subsequently annealed at 700°C to form LiMn₂O₄ spinel. To obtain pure LiMn₂O₄ or variant LiₓMn₂ₓO₄, the final composition can easily be tuned by varying the reaction temperature or the reaction time. XRD and Atomic Absorption Analysis for sample composition show that the extent of lithiation is greater for samples prepared at higher temperatures. TEM studies show that the grain size is one to two orders of magnitude smaller than LiMn₂O₄ powders made from standard solid-state reaction [39,40].
2.1.6. POWDER MATERIAL BY CITRATE GEL METHOD

Powders of lithium manganese oxides for batteries were prepared by the citrate gel method [41-43]. A mixture of LiNO$_3$(20mMol); Mn(NO$_3$)$_2$(40mMol) and citric acid(60mMol) was dissolved in water. The resulting aqueous solution was then concentrated to give a sol and further dried in vacuum to yield amorphous gel. The gel was then crushed and calcined at 600 to 800°C for 4 hrs. The heating and cooling rates were fixed at 1 and 0.5°C/min. respectively. X-ray powder diffraction analysis of the prepared powders indicated a spinel structure with no discernable impurities. However the diffraction peaks were broader for the powders calcined at lower temperature. Many oxygen-rich defect spinels are observed in Li-Mn-O system [44] due to lower calcined temperature.

2.1.7. POWDER MATERIAL BY SOL-GEL METHOD

The LiNi$_{1-y}$Co$_y$O$_2$ (0≤Y≤0.3) and Li$_{1-x}$CoO$_2$ as battery electrode were synthesized by sol-gel procedure [45-47]. Nickel acetate, cobalt acetate and lithium carbonate were dissolved in acetic acid, and the solution was refluxed. Small amounts of water and hydrogen peroxide were then added, and the solution was refluxed further until it became clear. The solution was then dried to produce a transparent gel and the gel was decomposed at 400°C for 10 min. and then fired at 750-800°C for 24 hrs in a flowing oxygen atmosphere. LiCoO$_2$ was synthesized by a solid-
state reaction between lithium carbonate and Co₃O₄ in air at 900°C for 24 hrs. Chemical oxidation of lithium in LiNi₁₋ₓCoₓO₂ and in LiCoO₂ was carried out at room temperature in both aqueous and non-aqueous media. In the aqueous medium, the sample powder was stirred with aqueous sodium perdisulfate for 3 days [48]. During this reaction, LiNi₁₋ₓCoₓO₂ undergoes an oxidation yielding Li₁₋ₓNi₁₋ₓCoₓO₂. The product was then filtered and washed several times with water to remove the unreacted Na₂S₂O₈ and the by-products Na₂SO₄ and Li₂SO₄. In the case of non-aqueous medium, the samples were stirred with an acetonitrile solution of the oxidizer NO₂PF₆ for 2 days and the products formed were washed with acetonitrile [49,50] to obtain Li₁₋ₓCoO₂. XRD studies show that LiNi₁₋ₓCoₓO₂ had the rhombohedral layer structure of α-NaFeO₂.

2.1.8. COPRECIPITATION METHOD

The Li(Ni₁₋ₓMgₓ)₂(0 ≤ y ≤ 0.4) battery material [51,52] were synthesized by co-precipitation method in aqueous solution. Solution containing Ni(NO₃)₂ and Mg(NO₃)₂ in (1-y)/y molar ratio was prepared. The solution was added while stirring to a solution of 1M LiOH and 3M NH₄OH. An excess of lithium was used in order to compensate for lithium loss during the calcination process and thereby to limit any lithium deficiency of the as-synthesized samples. Blue green coprecipitates were obtained and the remaining water and ammonia were removed in a rotary...
evaporator at 70°C under primary vacuum. The resulting products were then dried for 20 hrs at 110°C in air. The ground mixtures were heated under a flow of dry oxygen for 5 hrs at 700°C and 850°C to form single-phase material. XRD lines are quite narrow, indicating good crystallinity of the material.

2.1.9. SPRAY PYROLYSIS TECHNIQUE

Spray pyrolysis technique is simple and inexpensive and hence requires less capital to deposit thin films over large areas for mass production [53] than other conventional techniques.

Spray pyrolysis was used as early as 1910 to obtain transparent oxide films. Chamberlin et al [54-56] developed the technique to deposit sulphide and selenide films. Spray pyrolysis [57-58] involves spraying of a solution usually aqueous containing soluble salts of the constituent atoms onto a heated substrate. Various geometries of the spray set-up are employed [59-63] including an inverted arrangement in which large droplets and precipitates are prevented from reaching the substrate resulting in films of better quality. Better quality doped tin oxide films were prepared by spraying appropriate combinations of respective chloride compounds [64,65]. In all cases O₂ is the most common and convenient oxidizing agent, but it is normally helpful to add dilute solutions of ethanol, methanol [66] propanol [67,68] or butyl acetate [69,70] in the precursor solution. These solvents
have high volatility and low surface tensions and they yield comparable results.

The control parameters in the spray pyrolysis method are, the temperature of the substrate, the solution composition, the carrier gas, solution flow rate, the deposition time and the nozzle to substrate distance and angle. Viguie and Spitz [71] have investigated the role of the substrate temperature in determining the exact mechanism of film formation which in turn affects the micro structure of the film. Films grown at low temperature show amorphous nature and those at higher temperature are polycrystalline [71].

Review of literature shows that there has been very little work done on the preparation of lithium oxide compounds in thin film form by spray pyrolysis method. However this simple and inexpensive method has been employed to produce many oxide [72-78] materials. Hence in the present work this method is adopted. Detailed experimental setup procedure are described in chapter IV.

2.2. METAL OXIDE SEMICONDUCTOR GAS SENSOR

There is a need to monitor all aspects of the environment in real time in order to minimize environmental pollution and to enhance our health and safety. During the past years metal oxide semiconductors (SnO₂ the most common) were used as gas sensors due to the dependence of their electrical conductivity on
the ambient gas composition [79,80]. This phenomenon is based on two types of processes.

The first one involves bulk process where the oxide defect chemistry equilibrates with the ambient oxygen pressure, determining the carrier concentration and consequently the bulk electrical conductivity. The second one involves surface process where chemisorption of oxygen capture electrons from the oxide, producing a depletion region near the surface and diminishing the surface conductivity. Reduction of the chemisorbed oxygen by gases such as CO or H₂ leads to an opposite effect. Generally, the sensing mechanism of metal oxide semiconductor gas sensors is dominated by bulk processes at high temperatures (above 600°C) and by surface processes at low temperatures (below 400°C) [79,80].

The selectivity, operating temperature and response time of semiconductor based gas sensor depend on various parameters which have been extensively analysed:

1) Intrinsic behaviour relating to defect chemistry (oxygen vacancies are found to be the main defect) [81,82]

2) Morphological properties (namely specific surface area, grain size and porosity) [83,84]

3) Specific chemical sensing reactions and catalytic effects at the grain and boundary surface [82-85]
4) Influence of suitable additives, dopants and catalyst [86-88]

5) Use of suitable measuring techniques (fixed/pulsed operating temperature) [89-91]

6) Geometry and nature of the electrical electrodes [92-95].

There has been considerable interest in recent years in thin film based gas-sensing materials [96-99]. In comparison with conventional sintered bulk gas sensors, thin film gas-sensing materials have good sensitivity, optimum operating temperature and selectivity. In addition, materials in the form of thin film are well suited to integrate into micro sensor devices [100-101]. Also, the development of thin film deposition techniques based on chemical processes is of great interest in the field of gas sensors as an alternative to the physical deposition ones [102,103].

The effect of the addition of different metallic particles on the gas sensing metal oxides has been widely studied [104-109]. This influence has formally been classified as chemical and electronic sensitization mechanisms. In the electronic mechanism, the reaction with the gas molecules takes place on the surface of the induced clusters and not with the metallic oxides. These clusters change their charge state which induces a variation of the surface barrier height consequently leading to a conductance change on the base oxide. In this case, the base
semiconductor has only a transducer role and changes are induced in the additive particles by their interaction with the gas.

In the chemical mechanism, the semiconductor itself acts as a chemical catalyst. Now, the additive role is to increase the reaction rate of the gas molecules, which are firstly adsorbed on the metallic clusters and, later, moved to the oxide surface. Pd as metallic surface additive typically acts by an electronic mechanism, whereas Pt is supposed to lead to the chemical one [110,111].

In the following section a brief literature survey relating the gas sensing properties of lithium based compounds are discussed.

2.2.1. Li-DOPED IRON OXIDE THIN FILM HUMIDITY SENSOR

The humidity response of the undoped iron oxide film and Li doped iron oxide film has been reported [102]. The resistance of Li doped iron oxide decreases strongly with the exposure to increasing relative humidity (RH), showing a variation of about five order of magnitude between 10 and 90%. However the resistance of the film at low (<10%)RH is a parameter of utmost important because values higher than 10^7 ohms limits the practical use of devices based on resistive films. A strong response variation was noted in the range of low humidity (10-30%) where the surface conduction was due to the chemisorption of water molecules on the film surface which donates electrons to
the conduction band [112]. This suggests that the addition of Li ions strongly favours the increase of the number of chemisorption sites for water molecules due to its small size and high local charge [113]. The more Li ions the sensor contains, more is the chemisorbed water molecules and smaller the sensor resistance. Above 30% RH, physisorbed layer begin to be formed and a proton hopping mechanism is likely to be responsible for the conduction up to 70% RH. Further for the Li-doped films, in particular for the high loading Li-films capacitance increases at low RH, confirming that the humidity sensing mechanism of Li-doped iron films prepared by Liquid Phase Deposition is of ionic-type [114].

2.2.2. Li\(^+\) MODIFIED CaPbTiO\(_3\) THIN FILM HUMIDITY SENSOR

Li\(^+\) modified CaPbTiO\(_3\) based homogeneous thin film was prepared by sol-gel process for humidity sensor [115]. Ca\(^{2+}\) doped PbTiO\(_3\) sample sintered at 950°C/1 hr showed high sensitivity in the wide range but it cannot still be used for sensor purposes due to its poor linear characteristic. Therefore, lithium was doped to enhance the sensitivity and linearity. The doping of 0.5-1 mol% Li\(^+\) in CaPbTiO\(_3\) film sensor has enhanced the sensitivity by two orders of magnitude. There is a reasonable assumption that the increase of the sensitivity with Li\(^+\) doping may be due to higher charge density of Li\(^+\) ions which highly polarize the adsorbed water molecules. This in turn provides
more free $\text{H}^+$ or $\text{H}_2\text{O}^+$ ions for conduction, thus decreasing resistance [116,117]. The highest sensitivity and best linear behaviour has been achieved in the samples sintered at 850°C for 1 hr with 0.5% and 1.0 mol% Li$^+$ doping.

Humidity-resistance of a thick film shows a minimal hysteresis. The response times are about 8 and 15 s for moisture adsorption and desorption processes, respectively. Although the response time of desorption is longer, there is no negative effect on the application of the sensor. The sensitivity depends on the frequency at which the resistances are measured. At 100 Hz, $\log R$ is linear with humidity for a high sensitivity which is more than four orders of magnitude over the whole relative humidity range tested. Higher the frequency lower is the sensitivity in the humidity range. It has been found that there exists a little drift of resistance even after a long time (1 month), showing the properties of the prepared film to be stable and confirming the ion-type sensing mechanism.

2.2.3. Li-DOPED SnO$_2$ THIN FILM OXYGEN SENSOR

Thin films of SnO$_2$ and Li doped SnO$_2$ deposited by reactive sputtering with the same growth parameter for oxygen sensor have been reported [118]. The electrical conductivities of pure and Li doped SnO$_2$ at room temperature in a synthetic air flow were equal to $10^{-5}$/ohm-cm in both cases and there was no
remarkable change in electrical conductivity of the SnO$_2$ film due to introduction of lithium.

Conductivity of the films increases when $10^4$ ppm of oxygen in a nitrogen flow is introduced in the test chamber. The response times (defined as the time necessary for the conductance to decrease up to 90% of the final value in oxygen) towards 1% of oxygen in a nitrogen flow at 500°C are equal to 15 and 3 s for pure and Li doped SnO$_2$ films respectively, while the recovery times of the films are equal to 20 and 35 s respectively.

The sensitivity of Li doped SnO$_2$ thin film was about 10 times higher than the sensitivity of the undoped film and a minimum was observed at about 430°C. The position of the minimum of oxygen sensitivity with respect to temperature seems to coincide with the positions typical of desorption of the species O$^-$ or O$_2^-$ from the SnO$_2$ surface [119], when the semiconductor is placed in an atmosphere containing oxygen. The increase of oxygen sensitivity at temperatures higher than 500°C seems to be due to the incorporation of oxygen in the material lattice.

Thus lithium acts as a catalyst for reactions of chemisorbed oxygen. Lithium doped SnO$_2$ is suitable to be employed as a material for oxygen sensing in the concentration range between 0.1 and 21% O$_2$ in nitrogen.
2.2.4. Li DOPED ZnO SPUTTERED THIN FILM OXYGEN SENSOR

The oxygen gas-sensing characteristics of sputtered undoped and Li-doped ZnO films has been reported [120]. The introduction of Li as dopant in ZnO causes a strong increase of resistivity and leads to the formation of two deep donor levels which are 0.38 and 0.81 eV respectively below the conduction band, while the undoped film shows two levels at 0.16 eV and 0.48 eV. The electrical conductance decreases at high temperatures due to the surface chemisorption of oxygen. The higher sensitivity to O$_2$ is observed for Li doped ZnO films, since oxygen atoms are more strongly bonded to the lattice in Li-doped ZnO thin films, where Li$^+$ replaces Zn$^{2+}$ in the lattice, as reported by Egashira et al [121]. The response time of undoped films, necessary to reach 63% of the final value is between 70 to 100 s at 450°C, while for Li-doped films at the same temperature it is 10-15 s. The recovery times of the pure and doped films are 300-400 and 50-70 s respectively. The great difference between adsorption and desorption times are due to bulk effect of the film.

2.2.5. CO$_2$ DETECTION USING LITHIUM BASED SOLID ELECTROLYTE

A CO$_2$ sensor prepared by LiTi$_2$(PO$_4$)$_3$ + 0.2Li$_3$PO$_4$ sintered material as a solid electrolyte and Li$_2$CO$_3$ + Li$_2$O mixture as a detecting electrode has been reported [122]. The measured emf
shows good agreement with the calculated emf for CO₂ gas content from at 650°C. This CO₂ sensor work quite well even in an atmosphere contaminated with NO₂ or SO₂(<20ppm) with a very small variation in emf. The sensing ability greatly depends on lithium sulphate formation on the detecting electrode surface. Also presence of water vapor does not interfere with the CO₂ detection (>1000ppm). The sensor also operate well for CO₂ at 350°C, when an Li₂CO₃-K₂CO₃-Na₂CO₃ eutectic mixture is applied as the detecting electrode.

2.2.6. GAS SENSING PROPERTIES OF LiTaO₃

Lithium tantalite (LiTaO₃) has been proved to be pyroelectric material responding to H₂, HCl and NH₃ gases [123-125]. The principle involves measuring the thermal evolution of solid-gas interaction on the large surface covered by suitable membranes. Thin plates of LiTaO₃ single crystal covered on both surfaces by thin chromium-gold layers (in order to ensure surface electrical conductivity) were coated by spinning with different acid membranes, such as nonanoic acid(CH₃(CH₂)₇-COOH) and ethanesulfonic acid(CH₃CH₂-SO₃H), in order to compare their ammonia sensitivities. In both the cases the temperature behaviours due to ammonia-membrane interactions for different concentrations of ammonia, rise rapidly and decay slowly as by the time integration of the pyroelectric responses. However the decay time depends on the thermal capacity of both the sensor

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and the environment. The variation of temperature of the film is about 0.05°C and few degrees centigrade in the ammonia range of a few ppm to thousands of ppm.
2.3. REFERENCES


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