Synthesis, characterization and low temperature carbon monoxide sensing performance of alkaline earth metal incorporated tin oxide

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By

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Certificate

This is to certify that the thesis entitled" Synthesis, characterization and low temperature carbon monoxide sensing performance of alkaline earth metal incorporated tin oxide" has been carried out by Debojyoti Sinha in Central Glass and Ceramic Research Institute, Council of Scientific and Industrial Research during the academic session 2021-2022 in partial fulfillment of the requiremenst for the award of degree of Master of Technology in Nano Science and Technology in Jadavpur Univeristy West Bengal. This document is a bonafide record of the work carried out by the candidate.

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I hereby declare that the thesis entitled *"Synthesis, characterization, and low temperature carbon monoxide sensing performance of alkaline earth metal incorporated tin oxide"* submitted for the award of degree of Master of Technology in Nano Science and Technology of Jadavpur University is based on the original work done by me under the guidance of Dr. Susmita Kundu, Principal Scientist, Functional materials and devices division CGCRI Kolkata and Dr. Chandan Kumar Ghosh, Assistant Professor ,Jadavpur University. I also declare that I have followed all the principles of academic honesty, have not misrepresented or fabricated or falsified any facts/data in my submission and the work presented in this thesis has not been included in any other thesis submitted previously for the award of any other degree.

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Dedicated To My

Parents &Teachers

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Abstract

Since from the onset of industrial revolution which brought tremendous changes in the life style of every individual in this planet a major concern regarding these changes to make more sustainable in near future has started to rise. Due to rapid use of renewable energy resources for technological developments induced significant amount of harmful pollutants in the atmosphere. These pollutants are not only harmful for the environment but also prove very much fatal to all human beings. These pollutants include some gases for ex. CO, CO_2 etc and different volatile organic compounds for ex. ethylene, benzene, formaldehyde etc. Among all these gases the thing which makes carbon monoxide one of the most fatal gases is due it its colorless and odorless behavior. As the atmospheric pollution has started to rise at an alarming rate in recent years, detection of these harmful and flammable gases are the subjects of growing interest for researchers worldwide.

Detection of this gas is very important for pollution control, protection of individuals as well as environment. Scientist and researchers worldwide are working on several mechanisms through which gases can be detected for ex. infrared spectroscopy, mass spectroscopy, semiconductor gas sensors and others. Among these metal oxide semiconductor based gas sensors are at higher advantage because of their low fabrication cost, easy availability, wide variation of detectable target gases etc. Along with advantages there are also certain disadvantages associated with metal oxide semiconductor sensors for example, high response time, low cross sensitivity etc. Therefore in order to overcome certain disadvantages associated with these sensors we have to either select the most appropriate material for the sensing of any particular target gas or we have use some noble techniques by which we can enhance the properties of any metal oxide ready to make it suitable for gas sensing.

In this quest of finding a proper semiconductor material for carbon monoxide sensing at an ambient temperature in this present work we have first synthesized sol gel based nanocrystalline pristine SnO_2 for sensing purpose. The preliminary result shows that sensitivity of SnO_2 based gas sensor is not very high at ambient temperature. Then in order to improve sensing performance of SnO_2 gas sensors we have chose to incorporate alkaline earth metal ions(Ca^{2+},Ba^{2+},Sr^{2+})in tin oxide matrix and detailed sensing performance was studied. The primary reason of incorporation is to improve the surface characteristics of SnO_2 by creating more lattice sites for oxygen adsorption which can enhance the sensing of the metal oxide.

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CHAPTER 1

1 Introduction

1.1 Introduction

From the inception of industrial revolution i.e. from 18th century living standards of humans has increased significantly. This revolution introduced some major changes in the way of living and working thus transforming the society remarkably. Some major technological changes that were introduced through industrial revolution were (1) Rapid exploration and usage of non-renewable energy resources to meet energy demands of rapidly increasing population (2) Innovation of more and more sophisticated machines and technologies, one such as heat engines that can be used both in production as well as other sectors to make the lives easy etc. [1]. As we know everything in this world comes with some cost unfortunately this was also not an exception. This rapid technological developments throughout the globe since then has resulted in degradation of our environment. Due to rapid use of non-renewable energy resources (fossil fuels i.e coal, petroleum etc) from last century for production of energy, has resulted in excessive release of hazardous gases and chemicals in the environment. These gases include CO_2, CO, NO etc.[2] which are not good for the environment as well creatures living in to sustain for long time. Among them carbon monoxide is one of the major one. In this present work we have developed nonmaterial based a sensing module to detect this gas effectively.

1.2 Carbon Monoxide (CO)

Carbon monoxide is a colorless, odorless, toxic gas [3]. This gas is also inflammable in nature and slightly denser than air.CO is the simplest member of oxycarbon family. Each molecule of CO contains one carbon atom and one oxygen atom connected through a triple bond Fig-1.

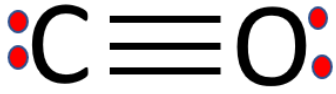


Fig 1- Atomic Structure of carbon monoxide

Human activities have lead towards significantly increase in the level of CO in the environment. Some of the major sources of CO gas are (i) Incomplete combustion of fossil fuel used in the vehicles [4] (ii) Emission from power generating plants using non-renewable energy resources

[5] (iii) Wastage from chemical industries using CO gas as an industrial gas to manufacture alkenes, aldehydes [7,6] etc.

1.2.1 Necessity of CO gas detection-

CO results in poisoning inside body of any human individual if inhaled above prescribed limit. This CO poisoning is caused as soon as CO enters in the body. As soon as CO enters the body it first reacts with red blood cells (hemoglobin) present in the blood to form carboxyhemoglobin. This carboxyhemoglobin then in turn further restricts red blood cells to react with oxygen and result in deficiency of oxygen in the blood. Due to this deficiency it causes heavy damage to health such as cardiac dysfunction, left ventricular systolic dysfunction, myocardial infarction and some other health problems also for example : headache, vomiting, inertia, weakness, hypotension, coma, inflammation of existing diseases, confusion, nausea, depression, hearing problems,[8] etc. occur. Whether it's a small amount of CO is inhaled for long period of time or large amount of CO for short period of time both cases can kill any person. Due to these all reasons CO is also known as **"the silent killer**". According to WHO the prescribed limit of exposure to this gas for any human is 6ppm for 8hr and 29ppm for 1 hr [9]. In this context it is the need of the hour to fabricate a device that can real time monitor this gas from environment effectively and efficiently to protect the environment as well as to make humans aware of any dangerous situation.

1.3 Sensor-

Sensor is a device that can detect as well as respond to some specific types of physical changes in the environment. These changes can be for example-light, moisture, temperature; heat etc. In general Sensor is a form of transducer that converts input signals from one energy domain to electrical domain for the purpose of measurement. These output electrical signals are further processed by computing machines to convert them to human-readable manner [10]. Sensors are generally the fundamental components of bigger security systems installed in industries for monitoring purposes, which can be controlled by microprocessors and microcontrollers.

Types of Sensors-

Sensors are of different types depending on their application as well as their mode of operation. However they are broadly categorized under following groups-

1. Active and Passive Sensor-Active sensors are those sensors which require an external stimulus in the form of input signal for excitation and give output according to that. On the other hand passive sensors are termed as sensors that don't require any external input for output generation.
2. Analog and Digital Sensor-Analog sensor are the sensors that produce output in analog form i.e. usually voltage in correspondence to the quantity which is to be investigated. On contrary digital sensors generate output in form of digital or discrete signals.
3. The third classification is purely based on conversion phenomena i.e. from input signal to output response. The most common types in this category are- Photoelectric, Thermoelectric, Electrochemical etc.
The following are some examples of different types of sensors used for various monitoring purposes-
1.Temperature sensor, 2-Proximity Sensor, 4.Pressure sensor, 5.Touch sensor, 6.Color sensor, 7.Humidity sensor, 8.Position sensor, 9.Gas sensor, 10.PIR sensor, 11.IR sensor, 12.Microphone(Sound sensor) etc.

1.4 Gas Sensors

Gas sensors are the sub-class of sensors that can detect both the presence and concentration of any particular gas present in the atmosphere in which it is installed. These sensors generally interact with the target gas, due to which there are certain changes in their sensing material properties [11]. These changes are then transmitted in form of electrical signals in order to detect the presence of target gas.

1.5 Application of Gas Sensor-

The major concern over health and to prevent any sudden unforeseen situations, detection and monitoring of any hazardous gas and toxic pollutants leaking in the atmosphere has to be monitored carefully over the time. In this regard a gas sensor serves out dual purpose; it helps us both in detection as well as measurement of various toxic gases present in the environment for regular monitoring purposes. In general Semiconductor and Catalytic Sensors are used for detection purposes and Electrochemical, Galvanic types are used in both detection as well as measurement purposes. With an increased demand in health and safety concerns these gas sensors are widely installed in industries and homes depending on their application. Some of these gas sensors along with their applications which are widely used are-

- A CO sensor helps to check any sudden leakage of CO gas in the atmosphere to prevent any dangerous situation. These sensors are widely installed in homes and industries to check any excess CO emission.
- Ammonia detectors [12] are primarily used in livestock and poultry farms to check any excess build-up of ammonia gas which is poor for health.
- Breath Analyzers are primarily used to check the breath of on road vehicle drivers for detection of any excess alcohol consumption above drink and drive limit [13]. These sensors are also deployed in manufacturing utilities, semiconductor industries using various solvents for various manufacturing process.
- CO_2 sensor are installed in industries, offices, schools, homes to monitor the level of carbon dioxide in these facilities and make humans inside those facilities aware of any dangerous situation.
- Ethylene sensors are primarily used in food industries to check freshness of fruits and fishes in order to maintain the standard food quality [14].
- VOC (Volatile Organic Compounds) sensors are used in medical industries majorly in instruments which are used for detection of various diseases of humans. These sensors can also be integrated with air ventilation and cleaning system to monitor the quality of air. Therefore these sensors are also very much in demand for airline industries, hospitality industry etc.

1.6 Sensor Parameters-

To compare among various types of similar sensors available in market few parameters are evaluated and checked carefully before installation. Few of the parameters are listed below.

- **Response-**When any gas sensor is exposed to particular target gas, there are some changes in its physical properties which is termed as Response of that sensor.
- **Selectivity**-It is defined as the ability of any gas sensor to detect the target gas accurately from a mixture of gases present at same concentrations.
- **Sensitivity**-It is defined as the response rate of any gas senor upon exposure to unit concentration of target gas. It is in general the relationship between input signal and output electrical signal.

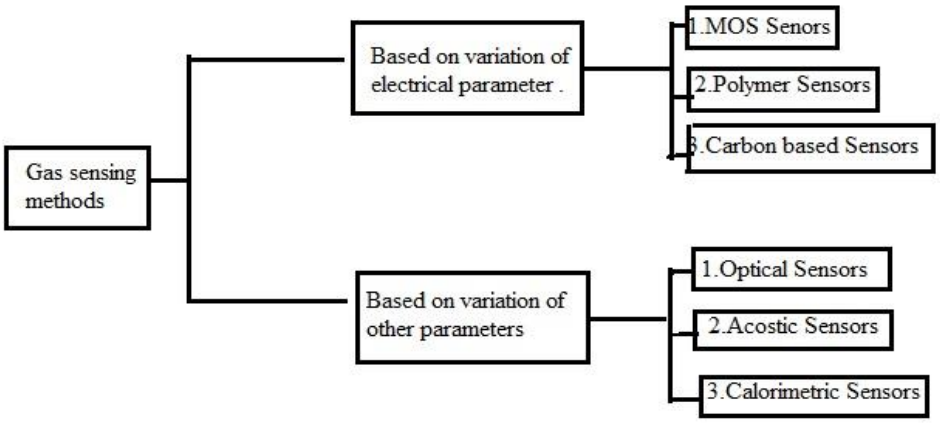
- **Operating Temperature**-Operating temperature of any gas sensor is defined as the maximum temperature at which sensor is able to show maximum sensitivity upon exposure to that particular target gas.
- **Response Time**-It is defined as the time taken by the sensor to respond when exposed to the target gas.
- **Stability**-The degree to which any gas sensor is able retain its output characteristics over the time, keeping concentration level of target gas constant to which it is exposed.
- **Recovery Tine**-It is termed as the time taken by any gas sensor to return to its initial state (90%) after step removal of target gas which it is under investigation.

For an ideal sensor it must satisfy following criteria.

- ✓ High sensitivity and selectivity.
- ✓ Faster response and recovery time.
- ✓ High reproducibility and long term stability.
- ✓ Lowe power consumption
- ✓ Low fabrication and operation cost

1.7 Classification of gas sensor based on sensing mechanism-

Classification of gas sensors can be done on the grounds of various factors for example, sensing mechanism, sensing materials, detection means, conversion phenomena etc. Based on purely gas sensing mechanism gas sensors are classified under two categories shown in below figure-



1.7.1 Sensors based on variation of electrical parameters-

In this group, sensing of any gas is primarily indicated through change in electrical properties for example, field resistance, field emission current, dielectric properties etc of the gas sensing material used inside the sensor. Therefore through measuring any change in electrical properties of the sensing material, respective gases can be detected.

(i) Semiconductor Sensors-

Semiconductor sensors generally use metal-oxide based sensing thick films onto Si-micro-machine substrate (micro sensors) for sensing purpose Fig2.. This substrate contains electrodes that measure the resistance of the sensing layer, and a heater that heats the sensing layer to 200 ℃ to 400 ℃ .The sensor responds to changes in the composition of the ambient atmosphere with change in resistance of the sensing layer. Large number toxic and explosive gases can be detected, even at very low temperature and concentration with the help of this sensor. This sensor can detect wide range of gases, includingCO, NO, NH_3, etc.

Fig2.-Semiconductor Sensor

Advantages of MOS sensor-

1. Low operation and fabrication cost.
2. Wide range of target gases
3. Response time is low.

Disadvantages of MOS sensor-

1. Relatively low sensitivity and low selectivity.
2. High energy consumption
3. Sensitive to environmental changes.

(ii.) **Polymer sensors**-

Polymer sensors are generally made up of polymer layers. When these layers comes in contact with the target gas, the physical properties of the polymer layers such as its mass and dielectric properties will change upon gas absorption which in turn will help in detection of the gas. These sensors have greater sensitivity towards VOC like alcohol and formaldehyde [15-16] which are used in several household appliances, products and may get vaporized at room temperature. If these gases are inhaled by humans then may cause serious health problems thence polymer sensors are of great use for this purpose.

Advantages -

1. Highly sensitive
2. Low operation and fabrication cost
3. High sensitive'
4. Simple and portable structure

Disadvantages -

1. Poor selectivity.
2. Highly instable in nature.

(iii.) **Carbon based Sensors**-

Carbon nanotubes (CNTs) have been extensively researched by scientists all across the globe as a promising element for highly sensitive gas sensor. CNTs can be used as gas sensing materials in conventional resistive gain measurement and even in field emission current measurement configuration [17]. CNTs acts as sensing materials in pressure, flow thermal, gas, optical,mass, position, stress, strain, chemical and biological sensor.

Advantages -

1. Lower response time.
2. Low weight.
3. Great adsorptive capacity.

Disadvantages-

1. Highly complicated and complex fabrication process
2. High manufacturing cost.

1.7.2 Methods based on variation of other kind of parameters-

In this group sensing of any gas primarily depends on some other properties example, light adsorption spectrum, thermal conductivity etc of the gas.

(i) Optical Sensors-

Sensing of any gas by means of optical method is very much accurate as well as complex process. Optical based sensors works on the concept of absorption and emission spectroscopy. These sensors generally consists of a light emitting element, a photo detecting element, a gas sensing element responding to light and a filter for picking up fluorescence or phosphorescence. These precise wavelengths of fluorescence of any specific gases are then matched with those data found from the HITRAN database [18]. Apart from basic principle of absorption spectroscopy there are also many other types of spectroscopy involved in gas sensing now a day's ex. Differential Optical Absorption Spectroscopy (DOAS), Raman Light Detection and Ranging (LIDAL) ,Intra-Cavity Absorption Spectrometry (ICAS), Differential Absorption LIDAR (DIAL) etc. Infrared (IR)-source gas sensors based on optical spectroscopy are most widely used in industry. This sensor works on the principle that each and every gas has its own infrared fingerprint i.e. every gas has its own infrared absorption property. This type of sensor generally consists of three parts-IR source, gas chamber and detector. First IR source emits infrared rays of various wavelengths inside chamber consisting of the target gas. The target gas then absorbs the rays of specific wavelength and then optical filter is used to screen out all radiation except for the wavelength that is absorbed by the target gas. Therefore in this way target gas can be detected by this sensor.

Advantages-

1. High Accuracy
2. Operating area is very broad
3. Modular size
4. Insensitive to environment changes

Disadvantages-

1. Manufacturing cost is very high.
2. Complex working procedure.

(ii) Acoustic Sensors-

Acoustic based sensing devices are majorly used in telecommunication industry primarily in various radio stations. The very first acoustic based sensing device was fabricated by King in 1964.As the name suggest these sensors works principle of detection of acoustic or mechanical wave.These sensors are very much rugged in quality and highly reliable. Whenever any acoustic or mechanical wave travels through any gas there is some change in its speed, amplitude etc. The measured change in gas velocity can be useful in finding many gas properties such as concentration of gas which is directly proportional to the time difference of sound propagation [19],to identify any particular gas from a mixture with the help of some thermodynamic equations[20]. An acoustic based sensor generally contains a receptor which transforms the output response into electrical signal. This type of device generally contains some piezoelectric material to generate the acoustic wave. There are different types of this devices based on propagation of acoustic waves. Acoustic based devices find many application gases sensing technology also.

Advantages-

1. Low operation cost
2. Service period is very high
3. Can be installed in harsh environment.

Disadvantages-

1. Selectivity is poor
2. Highly sensitive to environment changes.

(iii) Calorimetric Sensors-

Calorimetric sensors or pellistors are solid state devices used for detection of combustible gases.The basic principle behind these sensors is these are one of the widely used types of sensors for gas sensing application. This type is mainly used for sensing of those gases whose thermal conductivity is very high compared to that of air[21]. These sensors primarily usesmall pellets for gas sensing application. These pellets are made up of catalyst loaded ceramic surface which changes its resistance in the presence of different gases.Now on calculating the amount of

change in resistance will help in identifying the gas .There are primarily two types of pellistors used one is of Catalytic type and other is of thermal conductive type.

Catalytic Sensors-In catalytic type the heat released due to burning of combustible gas on the surface of the catalyst is monitored and measured carefully for gas sensing purpose. The most common type of catalyst used in these sensors is generally made up of platinum.It is one of the most used sensors in industries for detection of toxic gases. These sensors help in detection of gases at relatively low temperature [22]. However one of the major problems associated with them is that sometimes due to presence of some unknown impurities in gas leads to catalytic poisoning which further drastically reduce the sensor performance.

Thermal conductive sensors-This type of sensor generally rely on the monitoring of heat dissipation of the gas sensing element in the presence of target gas[23].In this method target gas is first injected into the gas chamber having a calorimeter fixed at the center. This calorimeter is then generally heated to a certain temperature.As the gas flows inside the chamber the temperature of calorimeter decreases due to certain loss of heat. This loss of heat in general gives us idea about the thermal conductivity of the gas which in order helps in identification.

Advantages-

1. High stability
2. Sensitivity is very good

Disadvantages-

1. High risk of catalyst poisoning and explosion.
2. Fabrication cost is somewhat on the higher side.

1.8 Metal Oxide Semiconductor (MOS) Sensor-

MOS sensors are one of the most widely studied sensors throughoutthe world nowadays. In the year 1953, Brattain et al. first demonstrated that due to change in components of surrounding atmosphere the atoms and molecules interacting with semiconductor surfaces changes the surface properties of semiconductor materials such as its conductivity and sensitivity. Later in the year 1962, Seiyama et al. first fabricated metal oxide semiconductor based gas sensor which was the pioneering work in this field. This sensor solved the problem of toxic gas detection with the help of absorption principle of the gas sensing material. The early-metal oxides based sensors faced many unpleasant characteristics such as high cross sensitivity, sensitivity to humidity, high

drift etc Since then several researches have been carried out all over the world to develop new technology, new materials to detect gases.

Metal Oxide Semiconductors are widely used in detection of various toxic, combustible, reducing oxidizing gases etc by conductive measurements. Metal oxides are capable of showing semiconducting, insulating and conducting nature due to being composed of both positive metallic ions and negative oxygen ions. The right choice of metal oxide for a particular gas sensing primarily depends on its compositional structure .Thus different structures of metal oxide are used in different types of gas sensing. Based on electronic structure of any metal oxide, they are broadly classified under two categories-

1. Non-Transition-metal oxide which includes NiO,Cr_2O_3, etc.

2. Transition-metal oxides, which are further divided into two groups (i) Pre-Transition Metal Oxides ex. (Al_2O_3) and (ii) Post-transition metal oxides ex (ZnO, etc)

Transition metal oxides generally have electronic configuration as $d_n$and d_{n+1}ord_{n-1}.Due to this atomic configuration they can easily change to different oxidation states [24] which helps in many application ex gas sensing, water filtration etc. Among this category pre transition metal oxides (Al_2O_3 etc) are generally inert in nature and have large band gap. As a result of which they are not suitable for gas sensing application due to difficulty in formation of electrons and holes. Transition metal oxides with electronic configuration either d_0 ex TiO_2 andWO_3[25] and configuration d_{10}exZnO and SnO_2 are relatively stable and can be utilized in various gas sensing application. Along with stable electronic forms these MOS also posses different physical or structural forms such as nanocomb, nanoneedle, nanosheets, nanowire, nanocubes, nanofilmsetc which makes them very much suitable element in gas sensing application. Thus small physical size of MOS based gas sensors makes them very attractive in compact devices. Along with this they are also capable of operating in real time thus making them suitable in LPG leakage detection alarm. MOS based gas sensors also have good sensitivity and selectivity which in turn is helpful for various Green House Gas such as (CO_2, NO etc) sensing. Another advantage of Metal Oxides for CO sensing is that they can be synthesized by various techniques ex. Sol-gel method, Hydrothermal method, Chemical Vapor Deposition, Thermal evaporation, Spray pyrolysis etc according to the requirement.

1.9 Gas Sensing Mechanism-

Gas sensing mechanism generally explains how electrical parameters of sensors change due to the presence of gas.MOS sensors generally detect gasesdue to change in its electrical parameters caused by the gas. There are many theories regarding gas sensing by any metal oxides but among them the most accepted theory focuses mainly on the relationship between the material and the gas therefore it is relatively macroscopic in nature. This theory also helps us in better understanding of interaction between any metal oxides with the gas with proper analytic explanations. There are several models under this theory for ex. absorption/desorption model, the bulk resistance control mechanism and the gas diffusion control mechanism. Among all this models absorption/desorption model is most famous and widely accepted.

1.9.1 Adsorption/Desorption Model-

This model is mainly based on the physical/chemical absorption of gas onto the surface of any metal oxide resulting in change in the resistance of the material caused due to variation in its surface charge concentration. Modern researches on sensing are mainly based on this mechanism as its explanations are very analytical. The most accepted absorption/desorption model is oxygen adsorption model Fig-3 due to its simple and easy explanations.

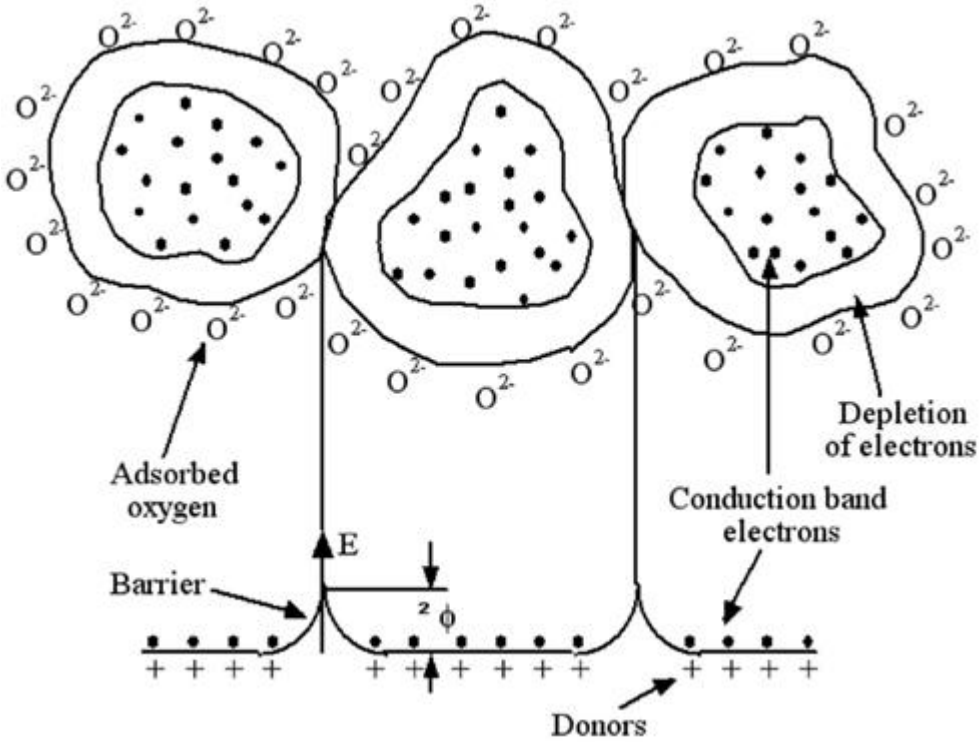


Fig-3. Energy band diagram at grain boundary of SnO_2 crystal.

Oxygen Adsorption Model-This model is primarily based on the change in surface resistance of any metal oxide due to adsorption of oxygen species through its surface during sensing. In most of the metal oxide semiconductors there exists oxygen vacancies on the surface of atom and majority charge carriers in them are mainly electrons. Whenever any metal oxide semiconductor sensor is heated at certain temperature in air, oxygen is chemisorbed on the surface of the oxide in the form of O^{2-}, O^{-}, O_2^{-} depending on the operating temperature. These oxygen species will now absorb electrons form the conduction band and will transform into negative species (eqn 1-4). Due to consumption of electrons from conduction band a depletion layer or space charge conduction area is formed. This formation of depletion layer further leads to reduction in conductivity and thus sensor resistance increases accordingly.

$$O_2(g) \rightarrow O_2(ads) \quad \ldots\ldots\ldots\ldots(1)$$

$$O_2(ads) + e^- \rightarrow O_2^-(ads) \quad \ldots\ldots\ldots\ldots\ldots(2)$$

$$O_2(ads) + e^- \rightarrow 2O^-(ads) \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$O^-(ads) + e^- \rightarrow O^{2-}(ads) \ldots\ldots\ldots\ldots\ldots(4)$$

Due to formation of negatively charged oxygen species likeO^{2-},O^{-},O_2^{-}leads to increase in electron depletion layer. These negatively charged oxygen species will now startgradually diffusing and covering all the grain boundaries which in turn will further increase the resistance offered towards the electrons flowing across the grain boundaries. Now when any target gas (reducing or combustible ex.CO,H_2 etc) passes through the sensor this gas first reacts with the highly chemisorbed oxygen species present on the surface and then undergoes redox type of reaction(5). Due to this redox reaction electrons from the highly negative oxygen species are re-released back into the conduction band as a result of which the electron depletion layer shrinks. As the depletion layer starts shrinking the flow of electrons through adjacent grains becomes smooth again and sensor resistance starts decreasing accordingly.

$$RG(g) + O(ads) \rightarrow RGO(g) + e^- \ldots\ldots\ldots..(5)$$

The resistance(R) of any sensor is given in (6) as –

$$R = R_o \exp\left(\frac{E_b}{KT}\right) \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Here R_0 is a gas constant,E_b is the barrier voltage, K denotes Boltzmann constant and T is temperature.

Now by calculating the resistance of the sensor in normal air, as well as in the presence of the target gas and putting them together in the mathematical function(7 or 8) will give us sensor sensitivity.

The sensitivity of any sensor is calculated using either of the following equations-

For n-type response:

$$S = \frac{R_a - R_g}{R_a} * 100 \text{.....(7)}$$

For p-type response:

$$S = R_a / R_g \text{.....(8)}$$

Here R_a is the sensor resistance in air at particular temperature and R_g is the resistance of the sensor in the presence of gas at the same temperature.

1.10 Methods to improve the sensing performance of MOS gas sensors-

As we have seen in adsorption/desorption model that sensing mechanism primarily revolves around the amount of oxygen adsorbed by the surface of metal oxide thus creating more electron deficiency. The more the deficiency of electrons, more the redox reaction will take place between gas molecules and negative oxygen species hence better and improved sensing. To improve the sensing performance we have to employ some techniques or methods that will create more gas adsorption sites, construct more oxygen vacancy, and thus directly increasing the surface activity to catalyze the reaction. Some of the techniques and process commonly used worldwide to increase sensitivity are explained below.

1.10.1 Formation of Oxide Heterojunctions -

We know that principle behind MOS based gas sensing is that whenever any metal oxide comes in contact with any gas, the molecules of the gas reacts with its surface atoms thus changing its conductive properties. Metal oxide semiconductors are one of the widely studied materials worldwide for gas sensing now a days. To choose any particular metal oxide for sensing application first we have to check various parameters of that oxide like its sensitivity, selectivity, response time, etc in the presence of the gas. In this regard many oxides are good in various parameters but not in all of them as a result of which they are overall not very suitable for sensing application. In order to make these metal oxides more efficient and suitable for sensing, changing their chemical composition by combining them with two or more metal oxide is one of the techniques. In this process instead of forming only binary oxides of a particular

metal, ternary, quaternary or complex oxides are formed which in turn will improve the sensing characteristics. In complex metal oxides presence of heterojunction barrier between different oxides leads to formation of more adsorption sites which enhances better sensing[26]. Also this width of the heterojunction layer in the presence of target gas can be controlled chemically. Overall the formation of heterojunctions results in more adsorption and reaction sites which in turn will increase the catalytic activity and sensitivity of the sensor. Complex metal oxides based on different metals combined together are generally more sensitive than their individual component[27,28] as a result many researchers worldwide today are now focused on forming composite oxides such as $SnO_2 - ZnO$,$Fe_2O_3 - ZnO$ etc and putting them use under different applications.

1.10.2 Surface modification by using noble metals additives-

The conductive response of any metal oxide senor is determined by the efficiency of the catalytic reaction taking place between the target gas and the surface atoms of metal oxides. The more the catalytic reaction taking place the more efficient is sensing. However most of the metal oxides for ex. TiO_2, ZnO,SnO_2 , Cu_2O, Ga_2O_3, $Fe_2O_3$are very poor in catalytic activity. As a result of which sensors made up of pure metal oxides show very poor sensitivity. If we somehowcan enhance the catalytic activity of these metal oxides the sensing performance of them can be increased significantly. As we know noble metals acts as high effective oxidation catalysts and they also have very high work function, therefore surface modification of MOS with noble metals can increase their sensitivity. This phenomenon is known as **electron sensitization**[29-31]. Whenever any noble metal is doped in MOS the electrons from the conduction band of Metal oxide starts traversing from the conduction layer of MOS to the noble metal. Due to this an interface dipole moment is formed in the direction of traversing of electrons. This dipole moment will further prevent electron hole recombinations which in turn will increases the gas response of the MOS and thus sensitivity. There are wide varieties of method including, Impregnation, sol-gel, sputtering and thermal evaporation for introducing noble metals additives into metal oxide substrate.

1.10.3 Alternate Metal Atom Doping-

It is one of the techniques of increasing gas sensing performance by any metal oxide. In this method we primarily dope a metal in some metal oxide to enhance its sensing performance. When some metal heteroatom is doped in metal oxide some metal heteroatom will replace base

metal atom whichfurther leads to reduction in grain size of metal oxide [32,33].This reduction in grain size of metal oxide will further result in increase in electron depletion layer, more adsorption sites, gas diffusion paths[34] through which gas comes in contact with the oxide surface which will eventually improve the gas sensing performance of MOSs.

1.10.4. Metal oxide nano-particles in sensing-

We know that a nano is about on billionth of a meter. Therefore any material whose particle size ranges between 1 to 100 nanometre can be declared as nanomaterial. These particle are very small in size, cannot be detected with human eye and exhibit significantly different physical and chemical properties. The reason behind their characteristics is that whenever size of any particle approaches atomic scale the ratio between its surface area and volume starts increasing. As a result of which the materials surface atoms starts dominating the material performance. For this reasons researchers worldwide are extensively studying nanoparticles and their application in gas sensing. The sensitivity of any material depends on the reaction between the surface atoms of that material and the target gas. The more the interaction the more is the sensitivity. Therefore any nanoparticle due to their very small size, catalytic activity on their surface on inducing of target gas compared to any other bulk material as a result sensing performance increases. Therefore the sensor consisting of any nanoparticle show generally high sensitivity and recent reports on nano-structured material on gas sensing application also further confirmed that suing nanoparticle as active material can significantly enhance the sensor performance.

1.10.5. High energy crystal facets for sensing-

Catalytic activity between any gas and metal oxide primarily occurs on the surface of the metal oxide, therefore metal oxides with different electronic structure exhibit different surface properties as a result different sensing performance. In these context crystals with higher energy facets have better applications in gas sensing purposes as they have more gas adsorption sites compared to that of normal crystals [35,36,37]. These high energy crystal facets facilitate more charge transfer between the gas and the oxide when the gas reacts on the surface of the oxide. As a result of this phenomenon MOS with high energy crystal facets exposure exhibit very good performance in the field of photocatalysis [38,39] as well as in sensing.

1.10.6. Temperature modulation -

The motive of any gas sensor is to detect the correct gas accurately in any environment. Therefore improving the sensitivity of any sensor should be given a very high priority. In this context temperature plays a very vital role. As sensing by any metal oxide sensor depends on the amount of oxygen species chemisorbed on its surface. Therefore heating any sensor above its atmospheric temperature enhances its sensing performance as more oxygen species gets adsorbed on the surface. Therefore in this case a self heating element connected with a sensor helps to increase its surface temperature thus facilitating better sensing without any extra power source.

1.11 N-type metal oxides in Carbon monoxide sensing-

Metal Oxide Semiconductors are primarily of two types n-type and p-type .The n-type nature of MOS is due to the fact that majority charge carrier in this type are primarily electrons and minority charge carrier are holes as a result conductivity of n-type is completely based on the presence of electrons. On the other hand p-type semiconductors are ones who have hole as majority charge carriers and electron as minority charge carrier and their conductivity primarily depends on the presence of holes. These two types of MOS due to their opposite and distinctive characteristics find suitable in various application for ex. in gas sensing, 3d printing etc depending on the mechanism behind respective application. For example in sensing of CO gas (reducing in nature) the widely accepted mechanism is based on adsorption/desorption model. According to this mechanism the type of metal oxide chosen for theCO gas sensor should have adequate oxygen vacancies; gas diffusing sites etc present in the lattice so that adequate sensing can takes place. As in n-type metal oxides majority charge carriers are free electrons which indirectly signify adequate oxygen deficiency in the lattice as a result these metal oxides at the start of sensing adsorb oxygen form air which leads to decrease in their conductivity and increase in their resistivity. Due to presence of this adequate chemisorbed oxygen species on the surface of metal oxide the resistance of oxide is high at the beginning .Now on application of the CO gas this gas reduces the oxide by reacting with chemisorbed negative oxygen species thus re-releasing electrons back into the conduction band, reducing barrier energy and eventually decreasing sensor resistance. Therefore n-type metal oxides are very promising material for CO gas sensing. However there are various n-type metal oxide which includes-ZnO,

SnO_2, TiO_2, In_2O_3, WO_3, CeO_2, CuO, etc but choice among them should be done carefully after looking their crystal structure, band gap energy, surface to volume ratio etc.

1.11.1 SnO_2based CO sensor-

$SnO_2$is a typical n-type surface sensitive metal oxide with band gapof 3.6 eV at 300K[40].It has a melting point of 1630 can and also have a density of around 6.95 gcm^{-3}at 300k.SnO_2 is also insoluble in water.In everySnO_2 crystal each atom of tin is surrounded by six oxygen atoms and each oxygen atom is surrounded by three atoms of tin. At room temperature the SnO_2 crystal is of tetragonal structure. In this structure Sn^{4+}ions occupy the top and center of the tetrahedron and O^{2-}ions occupy specific positions within the structure. The three crystal axes form an angle of 90° with each other, with the lattice parameters of a = b = 4.737 Å, c =4.8 Å[41] Fig-4 respectively

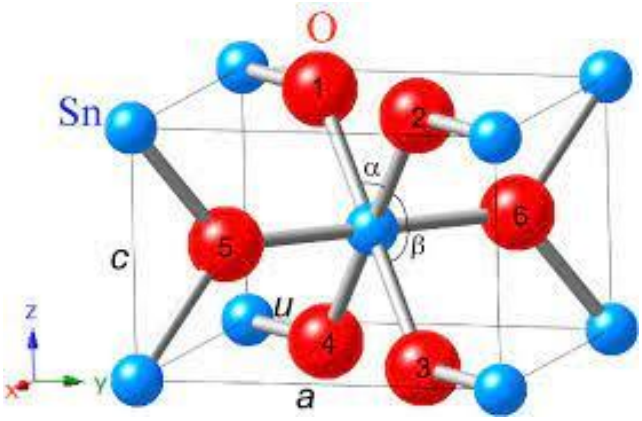


Fig4.- Molecular structure of SnO_2

Traditionally SnO_2 has been used in several applications for ex-photo-catalyst[42], thin film transistor, biosensors[43,44],UV sensors[45,46],humidity sensors[47,48], batteries[49,50,51], gas sensors[52],etc due to its high chemical stability, fast response, large excitation binding energy and non toxic in nature. Gas sensing bySnO_2 is mainly based on change in its surface resistance caused due to change in surface electron concentration after adsorption of gas. This change in resistance can then be then converted to electrical signals through proper transformation and COgas can be detected.

As sensing of any gas by a metal oxide primarily depends on its morphology. Therefore crystal structure is of great concern for the researchers. If microstructure of any metal oxide changes its sensing performance also varies accordingly. There are various procedures reported through which we can synthesis different SnO_2 microstructure. Some of thesemethods include,

hydrothermal method[53,54], sputtering[55,56], solvo-thermal process[57], sol-gel method[58,59], wet chemical process[60], electrospining[61,62] , spray-pyrolysis[63,64], and etc.

From last few decades SnO_2based gas sensors are widely used in CO gas sensing (Table-1) applications due to its stable microstructure, easy to synthesis and good adsorption performance.

Sensing Material	Synthesis procedure	CO(concentration) ppm	Response Time(Sec)	Working Temperature(℃	Sensor Response	References
SnO_2 QD	Sol-gel method	1000	NA	300	47^a	[65]
SnO_2	Sol-gel	50	NA	220	55^a	[66]
SnO_2QD	Sonochemistry	1000	NA	225	147^a	[67]
SnO_2thin film	Sputtering	150	NA	300	34^b	[68]
SnO_2thin film	Spray pyrolysis	260	NA	350	50^b	[69]
SnO_2:Ag	Spray pyrolysis	1000	NA	300	9.5^a	[70]
SnO_2:Pd	Conductance Oxillation waveform	170	NA	200	2.3^a	[71]
SnO_2:Pd	Hydrolysis	1000	NA	300	2.75^h	[72]
SnO_2:Pd	Hydrothermal	200	NA	100	7^a	[73]
SnO_2:Pt	Screen printing	200	NA	220	2.1^a	[74]
SnO_2:Pt	Sol-gel	100	NA	280	22^c	[75]
SnO_2:Pd,Pt	Wetchemical	100	NA	275	35^a	[76]
SnO_2: Au	Sputtering	1000	NA	400	22.8^a	[77]
$ZnO: SnO_2$	Electrospinning	300	NA	300	65^a	[78]
$Ni - SnO_2$	Screen printing	50	6	375	40^a	[79]
$CeO_2: SnO_2$	Sol-gel	2800	NA	400	90^b	[80]
$La_2O_3: SnO_2$	Sputtering	75	NA	350	213.7^a	[81]

Table1-CO gas sensing performance by SnO_2 sensor

Here a= (R_a/R_g) , b= $([R_a-R_g]/R_a,\%)$, c=$([R_a-R_g]/R_a$ where $R_a$is the resistance of sensor in air and $R_g$is the resistance of sensor in presence of CO gas

However some major concerns associated with thissensors are that they are only capable of sensing CO gasof high concentration (above 100ppm) at higher temperatures (above$100^{\circ}C$) only. Unfortunately the above sensing characteristics of any sensor are not desirable for real time monitoring of CO gas at any concentration [63-67].Along with that sensing performed at high temperatures gradually decays the performance of the sensor from time to time which is again one of the drawbacks. According to some researches these drawbacks are due to lack of oxygen adsorption sites present on the surface of each molecule of SnO_2. Hence researchers worldwide are working to find noble techniques through which sensing performance of SnO_2 can be enhanced. In this context if somehow surface property of SnO_2 is altered i.e. by creation of more oxygen adsorption sites its sensitivity can be improved. To alter the surface property of the metal oxide there are some methods. One such popular method is to dope the metal oxide with appropriate element is accepted worldwide.

In the above context to find the appropriate choice amongnumerous elements present on earth to be doped in $SnO_2$to form composite material is very difficult. Among different choices there are various works reported where noble metals (Ag, Au, Pt, Pd etc) are dopedin SnO_2[68-75] to form composite and then sensing is performed. The major reason behind doping of noble metal is that noble metals acts as very high oxidation catalyst which can in turn enhance the sensitivity of the sensor, but unfortunately in all the above works the working temperature of the sensor as well as concentration of the gas which was sensed was well over our threshold limits which is strictly undesirable. In this regard researchers have also tried to dope some other transition metal ex. Zn[76],Ni[77],La[79],Ce[78] in SnO_2 to form some ternary or complex oxides for CO sensing purpose but in this cases also working temperature of these composite oxide sensors where still above 100℃ which was again not desirable.

1.11.2 Alkaline earth metal incorporated SnO2-

Alkaline earth metals are present on the 2nd group of the periodic table. These are one of the most widely found elements on this planet in the form of alumina silicate, sulphite materials etc. Alkaline earth metals are highly basic and reactive in nature. Due to these natures of these metals they are widely used in various applications for ex.gas sensing[80], photo-catalyst [81], energy storage purpose etc.

As we know metal oxide gas sensors are of great advantage due to their less cost of fabrication, easy availability etc. However they also suffer from the problem of high working temp which gradually decrease their sensing performance from time to time. In this context alkaline earth metals are one of the most promising dopant in metal oxides for gas sensing purpose. Doping of alkaline earth metal in metal oxide creates certain types of surface defects such as creation of absorption sites, oxygen vacancies which enhance the sensing performance of metal oxides. As the one of the most important requirement for metal oxides to sense any gas at ambient temperature is creation of more oxygen vacancies in the lattice, therefore in this context when an alkaline metal is doped in metal oxide due to ionic mismatch between radius of metal oxide ion and alkaline earth metal ions it can inhibit the growth of metal oxide ion and enhance the surface morphology of the metal oxide, which in turn can provide more gas adsorption sites in the lattice thus improving sensing performance. The other advantages of doping in alkaline earth metal ion is due to highly basic in nature can modify the pH of the metal oxides heterojunctions which in turn can greatly affect adsorption and desorption character of any material which can in turn improve selectivity of the sensing material.

Doping of SnO_2 with elements other than noble metals or some transition metals for CO gas sensing applications are relatively less found. In this context very few works are done on adding alkaline earth metals with SnO_2 for CO sensing. Table-2 shows performance of some Ca doped SnO2 sensors in CO gas sensing application.

Sensing Material	Synthesis procedure	CO(concentration) ppm	Response Time	Working Temperature(℃	Sensitivity	References
Ca-Pt-Catalysed SnO2	Sputtering	500	NA	270	NA	[82]
Ca- SnO2	Sono-chemical	30	NA	350	NA	[83]

Table2- CO gas sensing performance by Ca doped SnO2 sensor

In the first work [82] shown in Table-2 surface of SnO_2 got covered with excessive clusters of Ca which resulted in degradation of sensor performance. But further in the second work [83] in Table-2 Ca doped SnO_2 sensor was prepared using sonochemical method. This sensor was able to detect low concentration of CO gas (30ppm).The main reasons behind this performance was

that when Ca is doped in SnO_2 the it modifies the crystalline structure of the metal oxide by increasing the surface area of the metal oxide[84] as well as making the surface of the metal oxide more rough[85]. This increased rough surface of the metal oxide then allows more non laminar movement of gas on it thus facilitating more chemisorptions of CO gas molecule at high temperatures only. Thus in the above case they have achieved the low detection limit (30ppm) of CO gas using Ca doped SnO_2 at high temperatures, it was also reported that the sensor suffers from the problem of cross-sensitivity. In order to overcome this problem incorporation of SnO_2 with different weight percentages of Ca as well as other alkaline earth metals i.e Ba, Sr should be performed in similar terms with the above reference[83] using different synthesizing techniques and then their sensing performance needs to be analyzed carefully for further modifications.

In the above context there are several method reported through which we can synthesize alkaline earth metal doped SnO_2.Some of these methods are hydrothermal method [86,87],sol-gel technique[88],wet-chemical procedure[89] etc

1.12 Motivation

This is need of the hour to develop a sensor that can be used in real time monitoring of CO gas of any concentration level and at ambient temperature present in the atmosphere to protect human beings and surrounding environment. Traditionally the CO sensors developed to detect CO from atmosphere usually operate at very high temperature (100-300℃) [64-67] and also show poor sensitivity for low concentration of gas which is undesirable. In order to make those traditional sensors work at normal temperature we have to constantly heat them. This leads to developing an extra heating mechanism that can heat the sensor to make it function properly. The fabrication of this heating device is very complex as well as very costly business and also leads to decrease in sensors' lifetime. Therefore there is an urgent need to develop a carbon monoxide sensor that can normally detect this gas at ambient temperature without any external source.

This thesis work primarily focuses on developing a CO sensor that can detect low concentration of CO gas at normal temperature along with showing good sensor characteristics i.e selectivity, sensitivity etc.

Proposed work-

On the basis of literature survey we have observed that there are several metal oxides i.eTiO_2, ZnO,SnO_2 , C$u_2O$which aretraditionally used as sensing material in different carbon monoxide sensors. However the major drawback associated with these binary metal oxides is that they

show poor selectivity and sensitivity at room temperature. Recently several research works are going on throughout the world to overcome these challenges. There is a lot of scope to research to carry out in this emerging field. With this perspective in the present proposed work we have selected tin oxide as most promising sensing material and in this work we have planned to synthesize a tin oxide nanomaterial doped with alkali earth metal (Ca,Ba,Sr) of various weight percentages to fabricate differentCO gas sensors and then compared their performance to find the most optimal one. This addition of alkali earth metal in metal oxide increase the sensitivity of the sensor and makes the sensor detect low concentration of gas at room temperature as well. Therefore to achieve the aim of this thesis following objectives have been taken into consideration:

1. To synthesis different weight percentage of alkali earth metal like Ca, Ba, and Sr incorporated SnO_2powder using sol-gel technique.
2. Characterization of the above synthesized powder using different techniques such as X-ray diffraction (XRD), FESEM, Fourier transform infrared spectroscopy (FTIR) etc
3. Fabrication of Taguchi type sensing modules using the synthesized nano-crystalline powders.
4. Detection as well as comparison of sensing performance of all the fabricated sensors.

1.13 References-

1. H.K.Mohajon;First industrial revolution creation of new global human era. Journal of social sciences and humanities.2019

2.ShuibingWang[ac]GuijianLiu[a]MingjianYi[b]XuemeiHuang[b]HongZhang[c]XingyuanHong[c]The characteristics of particulate matter during an air pollution process revealed by joint observation of multiple equipments

3.EsaKariVakkilainen, 2 - Solid Biofuels and Combustion,Steam generation from biomass.2017

4.Varon, J.; Marik, P.E.; Fromm, R.E., Jr.; Gueler, A. Carbon monoxide poisoning: A review for clinicians. J. Emerg. Med. 1999, 17, 87–93. [CrossRef]

5.Raub, J.A.; Mathieu-Nolf, M.; Hampson, N.B.; Thom, S.R. Carbon monoxide poisoning—A public health perspective. Toxicology 2000, 145, 1–14. [CrossRef]

6. Respiratory Health–Air Pollution, Boston University School of Public Health. Available online:http://sphweb.bumc.bu.edu/otlt/MPHModules/PH/RespiratoryHealth/RespiratoryHealth7.html (accessed on 28 September 2018).

7. Harper, A.; Croft-Baker, J. Carbon monoxide poisoning: Undetected by both patients and their doctors. Age Ageing 2004, 33, 105–109. [CrossRef] [PubMed]

8. Goldstein, M. Carbon monoxide poisoning. J. Emerg. Nurs. 2008, 34, 538–542.

9. http://www.euro.who.int/__data/assets/pdf_file/0005/74732/ E71922.pdf.

10.Bhagwati Charan Patel, G R Sinha and Naveen Goel; Introduction to sensors , Advances in Modern Sensors.

11.T.singh,U.bonne;Gas sensors, Reference module in material science and material engineering(2017)

12.DongwookKwak,Yu Lei,RadenkaMaric ;Ammonia gas sensor a comprehensive review,Talanta, 1 November 2019, Pages 713-730

13.BertilHök, HåkanPettersson, Annika Jonsson, SjoerdHaasl, Breath Analyzer for Alcolocks and Screening Devices, IEEE Sensors Journal · February 2010

14.Mworia, E. G.; Yoshikawa, T.; Yokotani, N.; Fukuda, T.; Suezawa, K.; Ushijima, K.; Nakano, R.; Kubo, Y., Characterization of ethylene biosynthesis and its regulation during fruit ripening in kiwifruit, Actinidiachinensis ‘Sanuki Gold’. Postharvest Biology & Technology 2010, 55 (2), 108-113

15. Hatfid, J.V.; Neaves, P.; Hicks, P.J.; Persaud, K.; Travers, P. Towards an integrated electronic nose using conducting polymer. Sens. Actuators B 1994, 18, 221–228.

16.Shrivas, A.G.; Bavane, R.G.; Mahajan, A.M. Electronic nose: A toxic gas sensor by polyaniline thin film conducting polymer. In Proceedings of International Workshop on Physics of Semiconductor Devices 2007(IWPSD 2007), Mumbai, India, 16–20 December 2007; pp. 621–623.

17. Yang, L.; Rongwei, Z.; Staiculescu, D.; Wong, C.P.; Tentzeris, M.M. A novel conformal RFID-enabled module utilizing inkjet-printed antennas and carbon nanotubes for gas-detection applications. IEEE Antennas Wirel. Propag. Lett. 2009, 8, 653–656.

18. The HITRAN Database. Available online: http://www.cfa.harvard.edu/hitran/ (accessed on 16 April 2012).

19. Shan, M.; Li, X.; Zhu, C.; Zhang, J. Gas concentration detection using ultrasonic based on wireless sensor networks. In Proceedings of the 2nd International Conference on Information Science and Engineering (ICISE), Hangzhou, China, 4–6 December 2010; pp. 2101–2106.

20. Jacobson, S. New developments in ultrasonic gas analysis and flowmetering. In Proceedings of IEEE International Ultrasonics Symposium, Beijing, China, 2–5 November 2008; pp. 508–516.

21. e2V. Available online: http://www.e2v.com (accessed on 16 April 2012).

22. Caucheteur, C.; Debliquy, M.; Lahem, D.; Megret, P. Catalytic fiber bragg grating sensor for hydrogen leak detection in air. IEEE Photonics Technol. Lett. 2008, 20, 96–98.

23. Tardy, P.; Coulon, J.R.; Lucat, C.; Menil, F. Dynamic thermal conductivity sensor for gas detection. Sens. Actuators B 2004, 98, 63–68

24. M. M. Arafat, A.S.M. A. Haseeb, S. A. Akbar, M. Z. Quadir, In-situ fabricated gas sensors based on one dimensional core-shell TiO_2-Al_2O_3 nanostructures. Sens. Actuators B Chem. 238 (2017) 972-984.

25.Sovandeb Sen, SouravMaity, Susmita Kundu, Fabrication of Fe doped reduced graphene oxide(rGO) decorated WO_3 based low temperature based ppm level gas sensor. Unveiling sensing mechanism by impedance spectroscopy. Sensors and Actuators B: Chemical June 2022

26. R. Ma, X. Zhao, X. Zou and G. Li, Enhanced formaldehyde sensing performance at ppb level with Pt-doped nanosheet-assembled In2O3 hollow microspheres, J. Alloys Compd., 2018, 732, 863–870

27. J. M. Walker, S. A. Akbar and P. A. Morris, Synergistic effects in gas sensing semiconducting oxide nano-heterostructures: A review, Sens. Actuators, B, 2019, 286, 624–640.
28. Y. Wang, Y. Zhou, C. Meng, Z. Gao, X. Cao, X. Li, L. Xu, W. Zhu, X. Peng, B. Zhang, Y. Lin and L. Liu, A highresponse ethanol gas sensor based on one-dimensional TiO2/V2O5 branched nanoheterostructures, Nanotechnology, 2016, 27, 425503.
29. X. Yang, H. Fu, Y. Tian, Q. Xie, S. Xiong, D. Han, H. Zhang and X. An, Au decorated In2O3 hollow nanospheres: A novel sensing material toward amine, Sens. Actuators, B, 2019, 296, 126696.
30. D. H. Kim, T. H. Kim, W. Sohn, J. M. Suh, Y. Shim, K. C. Kwon, K. Hong, S. Choi, H. Byun, J. Lee and H. W. Jang, Au decoration of vertical hematite nanotube arrays for further selective detection of acetone in exhaled breath, Sens. Actuators, B, 2018, 274, 587–594.
31. Y. Shim, D. H. Kim, H. Y. Jeong, Y. H. Kim, S. H. Nahm, C. Kang, J. Kim, W. Lee and H. W. Jang, Utilization of both-side metal decoration in close-packed SnO2 nanodome arrays for ultrasensitive gas sensing, Sens. Actuators, B, 2015, 213, 314–321.
32. H. Chen, J. Hu, G. Li, Q. Gao, C. Wei and X. Zou, Porous Ga–In Bimetallic Oxide Nanofibers with Controllable Structures for Ultrasensitive and Selective Detection of Formaldehyde, ACS Appl. Mater. Interfaces, 2017, 9, 4692– 47000
33.G. K. Mani and J. B. B. Rayappan, Influence of copper doping on structural, optical and sensing properties of spray deposited zinc oxide thin films, J. Alloys Compd., 2014, 582, 414–419.
34.G. K. Mani and J. B. B. Rayappan, ZnO nanoarchitectures: Ultrahigh sensitive room temperature acetaldehyde sensor, Sens. Actuators, B, 2016, 223, 343–351.
35. Z. Wang, J. Xue, D. Han and F. Gu, Controllable Defect Redistribution of ZnO Nanopyramids with Exposed {101¯1} Facets for Enhanced Gas Sensing Performance, ACS Appl. Mater. Interfaces, 2015, 7, 308–317.
36. R. Wu, F. Tian, Z. Liu, X. Xue, J. Zhang and J. Zu, CH4 activation and sensing on hexagonal WO3 (001) and (110) surfaces, Appl. Surf. Sci., 2019, 481, 1154–115
37.J. Liu, G. Chen, Y. Yu, Y. Wu, M. Zhou, H. Zhang, C. Lv, Y. Zheng and F. He, Controllable synthesis of In2O3 octodecahedra exposing {110} facets with enhanced gas sensing performance, RSC Adv., 2015, 5, 44306–44312.

38. Z. Xie, N. Han, W. Li, Y. Deng, S. Gong, Y. Wang, X. Wu, Y. Li and Y. Chen, Controllable Facet-dependent gas sensing properties of Cu2O crystals, Phys. Status Solidi A, 2017, 214, 1600904.

39. G. Zhu, X. Yu, F. Xie and W. Feng, Ultraviolet light assisted heterogeneous Fenton degradation of tetracycline based on polyhedral Fe3O4 nanoparticles with exposed high-energy {110} facets, Appl. Surf. Sci., 2019, 485, 496– 505.

40.SovandebSenSusmitaKundu Reduced graphene oxide (rGO) decorated ZnO-SnO2: A ternary nanocomposite towards improved low concentration VOC sensing performance

41. Matthias Batzill, Ulrike Diebold, Review the surface and materials science of tin oxide, Prog. Surf. Sci. 79 (2005) 47–154

42.J. Liu, Y. Li, X. Huang, Z. Zhu, Tin oxide nanorod array-based electrochemical hydrogen peroxide biosensor, Nanoscale Res. Lett. 5 (2010) 1177.

43. A.J. Haider, A. Jasim Mohammed, S.S. Shaker, K.Z. Yahya, M. Haider, Sensing characteristics of nanostructured SnO2 thin films as glucose sensor, Energy Procedia 119 (2017) 473–481

44.J. Liu, Y. Li, X. Huang, Z. Zhu, Tin oxide nanorod array-based electrochemical hydrogen peroxide biosensor, Nanoscale Res. Lett. 5 (2010) 1177.

45. A.J. Haider, A. Jasim Mohammed, S.S. Shaker, K.Z. Yahya, M. Haider, Sensing characteristics of nanostructured SnO2 thin films as glucose sensor, Energy Procedia 119 (2017) 473–481

46. P. Sharma, S. Sawyer, A High Responsivity SnO2 Hollow Nanospheres Based Ultraviolet Photodetector, IEEE), Piscataway, NJ, 2016.

47.M.-L. Lu, T.-M. Weng, J.-Y. Chen, Y.-F. Chen, Ultrahigh-gain single SnO2 nanowire photodetectors made with ferromagnetic nickel electrodes, NPG Asia Mater. 4 (2012) 26.

48.M. Parthibavarman, V. Hariharan, C. Sekar, High sensitivity humidity sensor based on SnO2 nanoparticles synthesized by microwave irradiation method, Mater. Sci. Eng. C 31 (2011) 840–844.

49.W. Li, J. Liu, C. Ding, G. Bai, J. Xu, Q. Ren, J. Li, Fabrication of ordered SnO2 nanostructures with enhanced humidity sensing performance, Sensors 17 (2392) (2017).

50. L. Zhu, H. Yang, D. Jin, H. Zhu, Hydrothermal synthesis of SnOnanoflakes as anode materials for lithium ion batteries, Inorg. Mater. Appl. Res. 43 (2007) 1307–1312.

51. R. Demir-Cakan, Y.-S. Hu, M. Antonietti, J. Maier, M.-M. Titirici, Facile one-pot synthesis of mesoporous SnO2 microspheres via nanoparticles assembly and lithium storage properties, Chem. Mater. 20 (2008) 1227–1229.

52. S.Y. Son, S.-A. Hong, S.Y. Oh, Y.-C. Lee, G.-W. Lee, J.W. Kang, Y.S. Huh, I.T. Kim, Crab-shell biotemplated SnO2 composite anodes for lithium-ion batteries, J. Nanosci. Nanotechnol. 18 (2018) 6463–6468.

53. Kiyoshi Fukui, Sachiko Nishida, CO gas sensor based on Au–La2O3 added SnO2 ceramics with siliceous zeolite coat, Sens. Actuators B Chem. 45 (1997) 101–106.

54. A. Chiorino, G. Ghiotti, M.C. Carotta, G. Martinelli, Electrical and spectroscopic characterization of SnO2 and Pd-SnO2 thick films studied as CO gas sensors, Sens. Actuators B Chem. 47 (1998) 205–212.

55. SoichiTabata, KatsukiHigaki, Hisao Ohnishi, Takuya Suzuki, Kenji Kunihara, Mitsuo Kobayashi, A micro machined gas sensor based on a catalytic thick film/SnO2 thin film bilayer and a thin film heater Part 2: CO sensing, Sens. Actuators B Chem. 109 (2005) 190–193.

56.P.-J. Chen, H.-T. Jeng, Phase diagram of the layered oxide SnO: GW and electron-phonon studies, Sci. Rep. 5 (16359) (2015).

57. Kang Wanga, Tianyu Zhao, Gang Lian, Qinqin Yu, Chunhong Luan, Qilong Wang, Deliang Cui, Room temperature CO sensor fabricated from Pt-loaded SnO2 porous nanosolid, Sens. Actuators B Chem. 184 (2013) 33–39.

58.L. Fan, S. Chen, S. Peng, Effects of different adsorbed species on ultrafine CO sensors, Sens. Actuators B Chem. 50 (1998) 220–226.

59.Xi-Tao Yin, Xing-Min Guo, Selectivity and sensitivity of Pd-loaded and Fe-doped SnO2 sensor for CO detection, Sens. Actuators B Chem. 200 (2014) 213–218

60.M. Schweizer-Berberich, J.G. Zheng, U. Weimar, W. Gopel, N. Bsan, E. Pentia, A. Tomescu, The effect of Pt and Pd surface doping on the response of nanocrystalline tin dioxide gas sensors to CO, Sens. Actuators B Chem. 31 (1996) 71–75

61. Ehsan Nikan, Abbas Ali Khodadadi, YadollahMortazavi, Highly enhanced response and selectivity of electrospun ZnO-doped SnO2 sensors to ethanol and CO in presence of CH4, Sens. Actuators B Chem. 184 (2013) 196–204.

62.Joong-Ki Choi, In-Sung Hwang, Sun-Jung Kim, Joon-Shik Park, Soon-Sup Park, UnyongJeong, Yun Chan Kang, Jong-Heun Lee, Design of selective gas sensors using electrospunPd- doped SnO2 hollow nanofibers, Sens. Actuators B Chem. 150 (2010) 191–199.

63. G.S. Korotchenkov, S.V. Dmitriev, V.I. Brynzari, Processes development for low cost and low power consuming SnO2 thin film gas sensors (TFGS), Sens. Actuators B Chem. 54 (1999) 202–209.

64. E. Brunet, T. Maier, G.C. Mutinati, S. Steinhauer, A. Kock, C. Gspan, W. Grogger, Comparison of the gas sensing performance of SnO2 thin film and SnO2 nanowire sensors, Sens. Actuators B Chem. 165 (2012) 110–118.

65. S. MosadeghSedghi, Y. Mortazavi, A. Khodadadi, Low temperature CO and CH4 dual selective gas sensor using SnO2 quantum dots prepared by sonochemical method, Sens. Actuators B Chem. 145 (2010) 7–12.

66. Sumanta Kumar Tripathy, Bhabani Prasad Hota, Carbon monoxide sensitivity of tin oxide thin film synthesized by sol gel method, Afr. Review Phys. 7 (2012) 0047.

67. S. MosadeghSedghi, Y. Mortazavi, A. Khodadadi, Low temperature CO and CH4 dual selective gas sensor using SnO2 quantum dots prepared by sonochemical method, Sens. Actuators B Chem. 145 (2010) 7–12.

68. M. Di Giulio, G. Micocci, R. Rella, p. Siciliano, A. Tepore, Properties of reactively sputtered tin oxide films as CO gas, Sensors. Sens. Actuators B Chem. 23 (1995) 193–195.

69. E. Brunet, T. Maier, G.C. Mutinati, S. Steinhauer, A. Kock, C. Gspan, W. Grogger, Comparison of the gas sensing performance of SnO2 thin film and SnO2 nanowire sensors, Sens. Actuators B Chem. 165 (2012) 110–118

70. G. Korotcenkov, B.K. Cho, L.B. Gulina, V.P. Tolstoy, Gas sensor application of Ag nanoclusters synthesized by SILD method, Sens. Actuators B Chem. 166–167 (2012) 402–410.

71. Kyoung Ran Han, Cheng Kim, Keon Kang, Jin He, He Jngwen Desk, Study on sensing properties of tin oxide CO gas sensor with low power consumption, Sens. Actuators B Chem. 81 (2002) 182–186.

72. A. Chiorino, G. Ghiotti, M.C. Carotta, G. Martinelli, Electrical and spectroscopic characterization of SnO2 and Pd-SnO2 thick films studied as CO gas sensors, Sens. Actuators B Chem. 47 (1998) 205–212.

73. Qingji Wang, Chen Wang, Hongbin Sun, Peng Sun, Yongzhi Wang, Jun Lin, Lu. Geyu, Microwave assisted synthesis of hierarchical Pd/SnO2 nanostructures for CO gas sensor, Sens. Actuators B Chem. 222 (2016) 257–263

74. M. Di Giulio, G. Micocci, R. Rella, p. Siciliano, A. Tepore, Properties of reactively sputtered tin oxide films as CO gas, Sensors. Sens. Actuators B Chem. 23 (1995) 193–195.

75. A. Cabot, J. Arbiol, J.R. Morante, U. Weimar, N. Barsan, W. Gopel, Analysis of the noble metal catalytic additives introduced by impregnation of as obtained SnO sol–gel nanocrystals for gas sensors, Sens. Actuators B Chem. 70 (2000) 87–100

76.M. Schweizer-Berberich, J.G. Zheng, U. Weimar, W. Gopel, N. Bsan, E. Pentia, A. Tomescu, The effect of Pt and Pd surface doping on the response of nanocrystalline tin dioxide gas sensors to CO, Sens. Actuators B Chem. 31 (1996) 71–75.

77.O. Wurzinger, G. Reinhardt, CO-sensing properties of doped SnO2 sensors in H2-rich gases, Sens. Actuators B Chem. 103 (2004) 104–110.

78.Ehsan Nikan, Abbas Ali Khodadadi, YadollahMortazavi, Highly enhanced response and selectivity of electrospun ZnO-doped SnO2 sensors to ethanol and CO in presence of CH4, Sens. Actuators B Chem. 184 (2013) 196–204

79.Kwon-Il Choi, Michael Hubner, Alexander Haensch, Hyo-Joong Kim, Udo Weimar, NicolaeBarsan, Jong-Heun Lee, Ambivalent effect of Ni loading on gas sensing performance in SnO2 based gas sensor, Sens. Actuators B Chem. 183 (2013) 401–410.

80. A. Khodadadi, S.S. Mohajerzadeh, Y. Mortazavi, A.M. Miri, Cerium oxide/SnO2-based semiconductor gas sensor with improved sensitivity to CO, Sens. Actuators B Chem. 80 (2001) 267–271.

81. J.Y. Choi, T.S. Oh, CO sensitivity of La2O3-doped SnO2 thick film gas sensor, Thin Solid Films 547 (2013) 230–234

82. K. Steiner, U. Hoefer, G. Kiihner, G. Sulz, E. Wagner, Ca- and Pt-catalysedthinfilm SnO2 gas sensors for CO and CO2 detection, Sens. Actuators B 24–25 (1995) 529–531

83.Saptarshi Ghosh, MousumiNarjinary, Amarnath Sen, RajibBandyopadhyay, Somenath Roy, Fast detection of low concentration carbon monoxide using calcium-loaded tin oxide sensors, Sensors and Actuators B: Chemical,2014

84. 2. Ilager, D.; Shetti, N.P.; Malladi, R.S.; Shetty, N.S.; Reddy, K.R.; Aminabhavi, T.M. Synthesis of Ca-doped ZnO nanoparticles and its application as highly efficient electrochemical sensor for the determination of anti-viral drug, acyclovir. J. Mol. Liq. 2020. [CrossRef]

85. Water, W.; Yang, Y.-S. The influence of calcium doped ZnO films on Love wave sensor characteristics. Sens. Actuators A Phys. 2006, 127, 360–365

86. Lu ZG, Liu JF, Tang Y, Li YD (2004) Hydrothermal synthesis of CaSnO3 cubes. InorgChemCommun 7(6):731–733. doi:10.1016/ j.inoche.2004.03.030

87.Lu WS, Schmidt H (2005) Hydrothermal synthesis of nanocrystalline BaSnO3 using a SnO2xH2O sol. J Eur Ceram Soc 25(6): 919–925. doi:10.1016/j.jeurceramsoc.2004.04.010

88. Azad AM, Hashim M, Baptist S, Badri A, Haq AU (2000) Phase evolution and microstructural development in sol-gel derived MSnO3 (M = Ca, Sr and Ba). J Mater Sci 35(21):5475–5483

89. Cerda J, Arbiol J, Diaz R, Dezanneau G, Morante JR (2002) Synthesis of perovskite-type BaSnO3 particles obtained by a new simple wet chemical route based on a sol-gel process. Mater Lett 56(3):131–136

CHAPTER 2

2 Experimental details and Characterization techniques

2.1 Synthesis Techniques-

Nanomaterials are the materials whose size lies in the range of 1 to 100nm. Due to rapid advancement in various technology sectors demand for nanomaterial has skyrocketed. Nanomaterials due to their extremely small size having high surface area to volume ratio and other properties find suitable in various applications. However these properties of any nanomaterial primarily depend on how they are synthesized. Hence it is a great challenge to synthesize any nanoparticle according to the requirement. In this context researchers and scientist have came up with different synthesis techniques which are summarized together in a single chart given below Fig-1.

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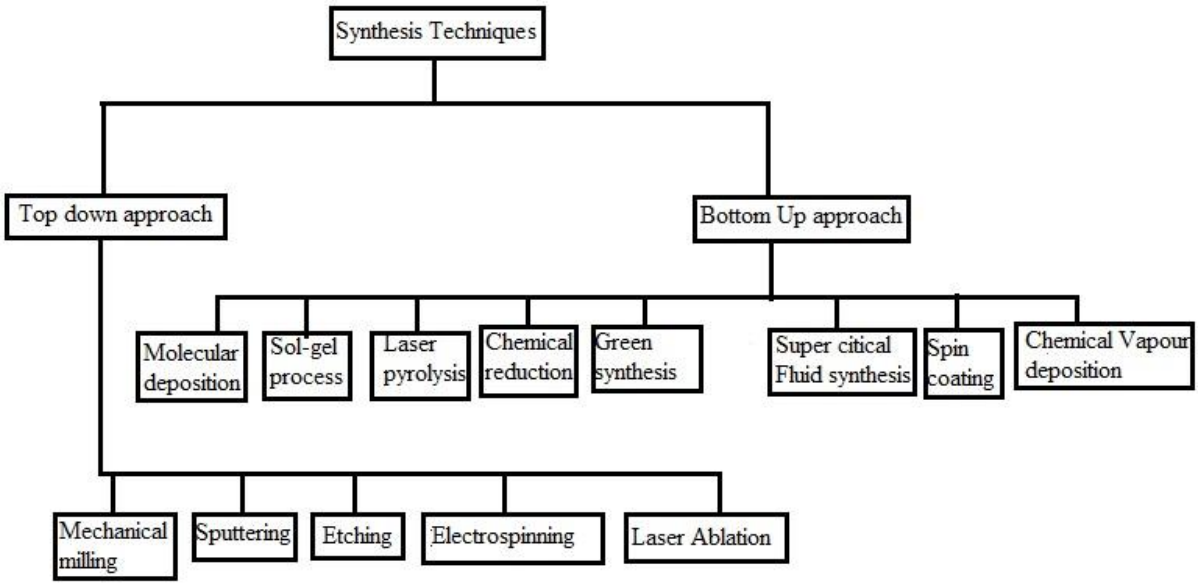


Fig1. Various methods for synthesis of nanomaterials

In general synthesis of any nanomaterial is done by following any of the two approaches [1].

(i) Top-down approach, (ii) bottom up approach.

i. Top-down approach-As the name suggests in this approach bulk materials are broken down continuously to obtain a nanomaterial. Various synthesis methods through which it is achieved are

1. Mechanical milling [2], 2 Sputtering[3], 3.etching[4], 4.electrospinning[5], 5.laser ablation[6]

ii. Bottom-up approach-This approach is just opposite to that of top-down approach. In this approach spontaneous arrangement of molecules are achieved with the help of physical and chemical forces acting at near equilibrium to obtain a stable nanostructure[7].Various synthesis methods which fall under this category are-

1.Sol-gel process[8] 2.Molecular deposition[9], 3.Laser pyrolysis[10] 4.Chemical vapor deposition[11] 5.Green synthesis[12] ,6.Spin coating[13] 7.Chemical reduction,8.Super critical fluid synthesis[14]

Among all these methods sol-gel process is considered one of the easiest techniques to synthesis nanoparticle due to its simple steps as well as economical due to less requirement of costly equipments.

2.2 Sol-gel Process-

Sol-gel is considered one of bottom-up approaches used for synthesizing any nanoparticle[8]. The reason behind its name is that precursors are first transformed to sol and then that sol is finally converted to some complex structure commonly known as gel. To synthesis any nanomaterial using this process some easy steps are followed. In the first step solid precursors are hydrolyzed with the help of some solvent ex. water, alcohol etc to form a solution which is left to age. In the following step due to ageing of the solution poly-condensation of the solvent takes place which results in the formation of large numbers of hydroxo- (M–OH–M) or oxo- (M–O–M) bridges which increases the viscosity of the solution and decrease the distance between colloidal particles. After ageing is completed the solution is dried in order to remove the solvents present and as a result gel like substance is formed. In the last step gel is calcined at very high temperature to obtain the nanoparticle. In general sol-gel technique is mainly used to synthesis high standard doped and undoped metal-oxide nanoparticle as the ouput from this process is very homogenous in nature and doping can be done in very trace level.

In the present work we have selected the sol-gel process to synthesis the pristine and alkaline earth metal ions incorporated tin oxides.

Materials Used

In this experiment Tin (IV) chloride ($SnCl_4.5H_2O$), nitrates of alkali earth metals i.e.$Ca(NO_3)_2$,$Ba(NO_3)_2$,$Sr(NO_3)_2$, were used as precursor salts and ethanol as a solvent. All these chemicals used were of analytical grade.

2.2.1 Procedure for synthesis of SnO_2

At first the base material, pristine tin oxide was prepared. In this process calculated amount of $SnCl_4.5H_2O$ as a solid metallic precursor and ethanol as a solvent was first taken in a small beaker and following steps were followed Fig-2.till formation of SnO_2 nano-crsytalline powder.

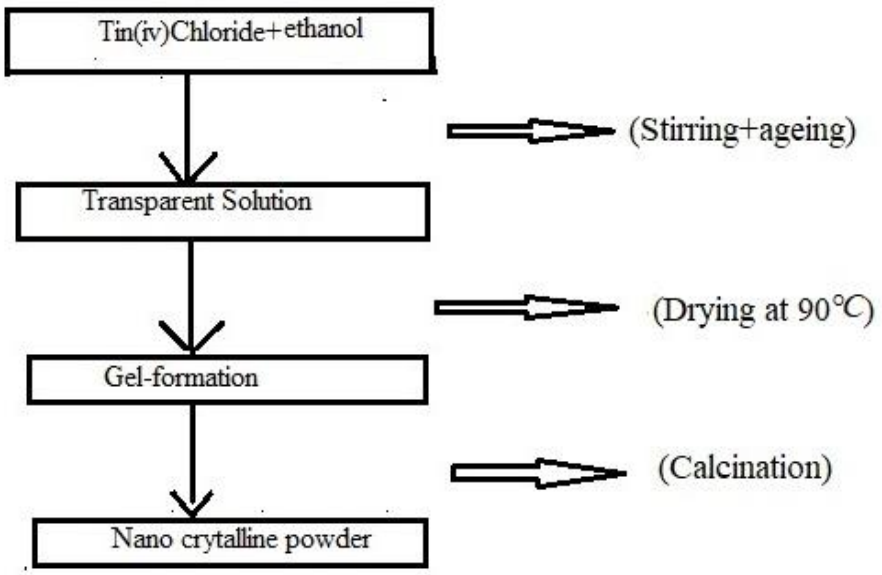


Fig 2 .Flowchart for synthesis of SnO_2

2.2.2 Procedure for synthesis of (Ca, Ba, Sr) doped SnO_2

To form (Ca ,Ba ,Sr) doped SnO_2 calculated amount of $SnCl_4.5H_2O$, nitrate of each alkali earth metals as solid metallic precursors and ethanol as a solvent were first taken in a small beaker and following steps were followed Fig-3 to obtain the nano-powder.

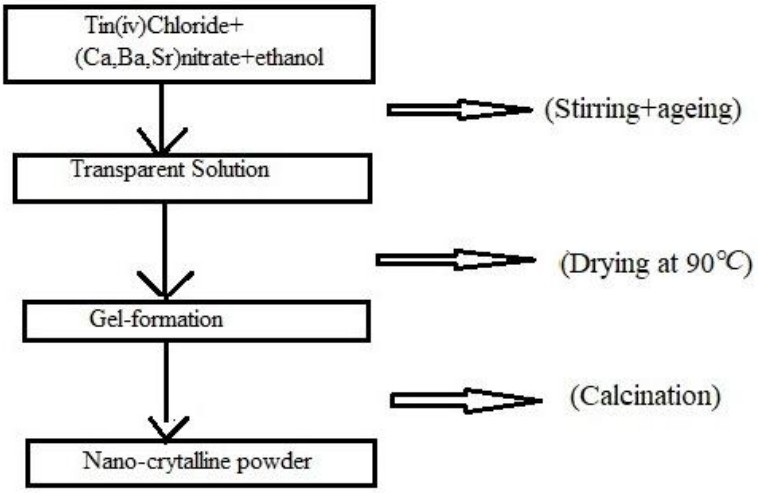


Fig 3.Flowchart for synthesis of alkaline earth metal doped SnO_2

In this study we have varied the concentrations of Ca(II), Ba(II) and Sr(II) ions as 2,4 and6wt% The Following table represent the nomenclature of the as prepared nanocrystalline powders

Incorporating Metal ion	Concentration (wt%)	Sample Identification
Ca(II)	2	2CS
	4	4CS
	6	6CS
Ba(II)	2	2BS
	4	4BS
	6	6BS
Sr(II)	2	2SS
	4	4SS
	6	6SS

2.3 Characterization Techniques-

Characterization is done in order to find information of certain distinctive features or their compositional i.e their shape, size, behavior etc present in them. Characterization is very important before implementation of any nanoparticle in an application. In this present work different characterization techniques such as Gravimetric Analysis (TGA), X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, Field Emission Electron Microscopy (FESEM),UV-visible spectroscopy, BET surface area and pore size measurement etc are discussed briefly.

2.3.1 Thermo gravimetric Analysis (TGA)

Thermo gravimetric analysis or thermal gravimetric analysis is an important characterization technique used in characterization of a nanomaterial. It works on the principle that with change in temperature, molecular weight of any material changes. Thermal analyzers are the devices which are used for carrying out the analysis.

In this analysis sample is heated in a known environment (Air,CO_2 etc) at a controlled rate. Due to gradual increase in heating of the sample there is certain change in the weight of the sample which is recorded as function of time. This plot between the change in weight of the sample with respect to temperature which is also known thermo gravimetric curve or thermo gram is used to get details about different materials from which the sample is constituted.[15].

This analysis primarily relies on high degree of precision in three measurements: weight, temperature and change in temperature.TGA is commonly employed in research and testing fileds to determine characteristics of materials such as polymers etc ,to determine degradation temperature, absorbed moisture content of materials, the level of inorganic and organic components present in any material, decomposition point of explosives etc

In this present work, the thermo gravimetric analysis (TGA) was carried out by heating 10 to 25 mg of powder sample in an alumina pan upto 1000 under ambient environment at a heating rate of 10 ℃/min using TGA-50/50H and DTA-50 Shimadu Japan.

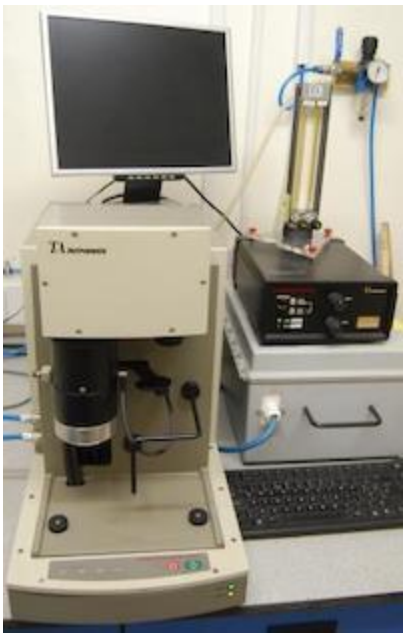


Fig4. Thermo gravimetric analyzer

2.3.2 X-ray Diffraction technique (XRD)-

Full form of XRD is X-ray diffraction. XRD is one of the powerful tools used in industry and research purpose for the study of any nanomaterials [16] .It is also known as X-ray powder diffraction because the material analyzed using this technique is generally ground down to very finite powder form. With the help of this tool we can identify different phases of the crystal present in that material which in order help us to study about crystallographic structure of a material.

As the name says x ray diffraction we make use of x-rays for this process. This method is based on constructive interference of monochromatic x-rays and the sample. In this process X-rays which are produced using cathode tube are first filtered through filter to produce monochromatic radiation, then this wave of radiation are directed towards the sample. Due to interaction of these x-rays with the sample diffracted rays of various wavelengths are generated and by collecting these diffracted rays we can analyze the sample structure [17].

Atoms are building block of every material in this universe. When any material is bombarded with x-rays beams of certain wavelength some of the rays get transmitted and some gets diffracted. This phenomenon was studied further by Sir William Henry Bragg and Sir William Charles Bragg and they came up with their new law known as Braggs Law, for which they received Nobel Prize in physics in the year 1915.

Bragg's law is termed as."*For every diffracted beam there exists a set of crystal lattice planes such that the diffracted beam appears to be specularly reflected from those set of planes*"[18]. According to this law whenever any crystalline material is bombarded with any incident X-ray of certain wavelength the rays gets scattered i.e. some of it gets transmitted and some of it gets reflected. These reflected rays are formed due to first constructive interference of scattered rays and then reflection of the resultant form a particular set of planes. In this context for any set of rays to interfere constructively the path length difference must be equal to any integer multiple of their wavelength. As a result when this interference occurs a diffracted beam of x-ray will leave the crystal at an angle equal to the incident angle.

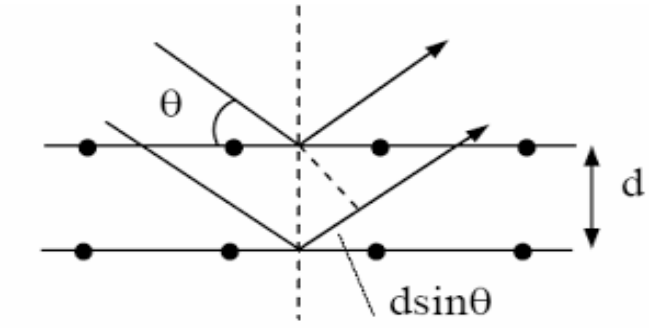


Fig5. X-rays Scattering

In general context, the relation between the wavelength of incident ray, the spacing between crystal lattice planes, incidence angle was given by Bragg's mathematical relation[19]i.e

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

Here n is representing an integer ,λ is wavelength ,d is the spacing between surfaces and theta is the angle between radiation and surface.

Bragg's law helps us to calculate the general spacing between crystal lattice planes which in order. This further helps up in characterization and identification of the crystal. Identification is practically carried out through systemic comparison of the obtained spectrum with a standard one, taken from any X-ray powder data file catalogues, published by the American Society for testing and materials (JCPDS).

2.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR stands for Fourier Transform Infrared Spectroscopy. It is combination of two terms one is Fourier transform that is a mathematical tool to do conversions from time domain to frequency domain and other is Infrared Spectroscopy which is all about studying the interaction between infrared light and matter[20]. It is one the analytical method used for identifying the

structure of any unknown material by finding all types of covalent bonds present in them. It is based on the principle of Infrared spectroscopy [21]. Infrared spectroscopy is the measurement of interaction of infrared radiation with matter by absorption, emission, reflection. It is also one of the important tools used for purpose of identification of any unknown specimen in the field of material science and nanotechnology.

Infrared radiation is an electromagnetic radiation composed of infrared light of different wavelengths. In infrared spectroscopy, infrared lights of different wavelength generating from a source made of silicon carbide element are made to fall over the sample. On collision of these rays with any sample some of it gets reflected and some gets transmitted. We know most of the chemical samples are generally composed of covalent bonds and these bonds are not static in nature. These bonds have characteristics frequency at which they start vibrating. These vibrations are of many types. Whenever an IR of particular wavelength falls and if the frequency of IR matches with that of characteristics frequency of any bond the waves gets absorbed and the bonds start vibrating. As a result of these phenomena that light of particular wavelength gets lost from the radiation. The transmitted waves which passes through the sample are now collected using detector and by analyzing the transmittance of the transmitted wave we can generally find the type of bond present in it which in order helps to characterize any sample.

FTIR spectroscopy method is an up gradation of traditional IR spectroscopy to get more accurate structure of unknown sample. For FTIR spectroscopy we use Michelson Interferometer which is made of 3 components beam splitter, mirrors (fixed and movable). The rays generated from the source first strikes splitter .The splitter then splits the beam and send it towards two mirrors. The mirrors then reflect the beam and send it towards the sample. On adjusting the position of the movable mirror we can create path difference between these two reflected waves, this path difference leads to interference either constructive or destructive. The reflected wave coming from these mirrors after interference strikes the sample and finally after striking the transmitted wave is detected using detector. The detector after detecting the wave sends output in the form of interferogram. This interferogram is a plot between outputsignal intensity and time. Now with the help of Fourier transform theseinterferogram is then converted to FTIR spectra. This FTIR Spectra is a plot between wave number and signal intensity. Now with the help of these FTIR spectra we can determine structural composition of any crystal

2.3.4 Raman Spectroscopy-

Raman spectroscopy is one of the non-destructive spectroscopic techniques used to detect chemical structure,morphology of any sample. It is primarily based on inelastic scattering of photons which is commonly known as Raman scattering.

Whenever any monochromatic light is made to fall over any liquid sample it gets scattered. This scattering occurs due to interaction between light and various chemical molecules of the sample. As vibration energy of individual molecules of the sample are different it results in majorly two different types of scattering in the first type the frequency of scattered is equal to that of the incident light which is known as Rayleigh Scattering. In the second type of scattering the frequency of the scattered light is different from that of incident one and is known as Raman Scattering (Fig6.). This scattering of light from molecules with a change in frequency is called as Raman Effect. Let frequency of incident light be ϑ and frequency of scattered light as ϑ'.If frequency of the scattered light is less than that of incident light (i.e$\vartheta'.<\vartheta$)it is called as Stokes Raman scattering and if frequency of scattered light is greater than that of incident light it is called as Anti-Stokes Raman scattering($\vartheta'> \vartheta$).

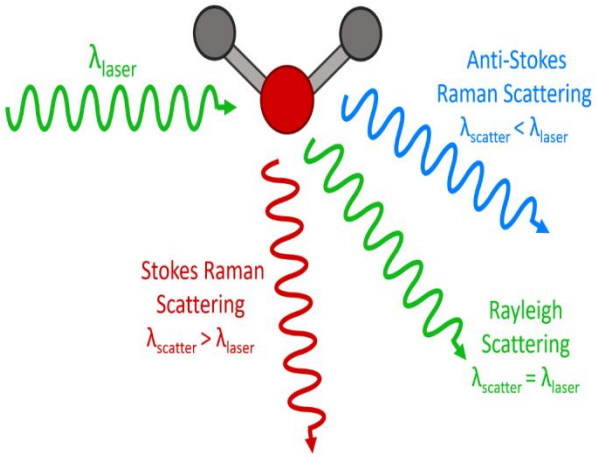


Fig6. Raman Scattering

This change in frequency between the incident and scattered light is defined as Raman shift. The calculated amount of shift represents some functional groups or molecules. For every molecule or functional this shift is different. Raman Spectroscopy is a very good analysis technique as it gives information about certain vital characteristics of a sample i.e its structure, composition, stability etc.

2.3.5 Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscope is a type of electron microscope (Fig7) that images the sample surface by scanning it with a high energy beam of electrons. Apart from conventional light microscope which uses light source SEM uses electron beam.SEM also has more than 300 times the depth of field compared to light microscope which means better resolution.

The SEM works on the principle that when a beam of electrons strike the surface of any sample and interact with the atom of the sample, signals in the form of secondary electrons, backscattered electrons, and characteristics x-rays are generated which contain information about the sample topography and composition.

A typical SEM contains an electron gun which is fitted with tungsten filament cathode to emit electron beams. This electron beam is now focused by one or two condenser lenses to spot about 0.4-5nm in diameter. This beam now passes through pairs of scanning coils or pairs of deflector plates. These deflector plates deflect the beam in the x-axis and y-axis so that beam can scan over a rectangular area of the sample surface.

When an electron beam collides with the sample it causes ionization of the sample. Due to this ionization of the sample the electrons which are loosely bound from surface tends to release out from the surface in form of secondary electrons. Along with secondary electrons there is also generation in back scattered electrons, auger electrons and characteristics X-rays in the SEM column. Now a detector catches all electrons released due to collision in the column and produces an electronic signal corresponding to that. This electronic signal is now amplified and converted into image that can be seen on the screen [22].

Fig7. Scanning Electron microscope

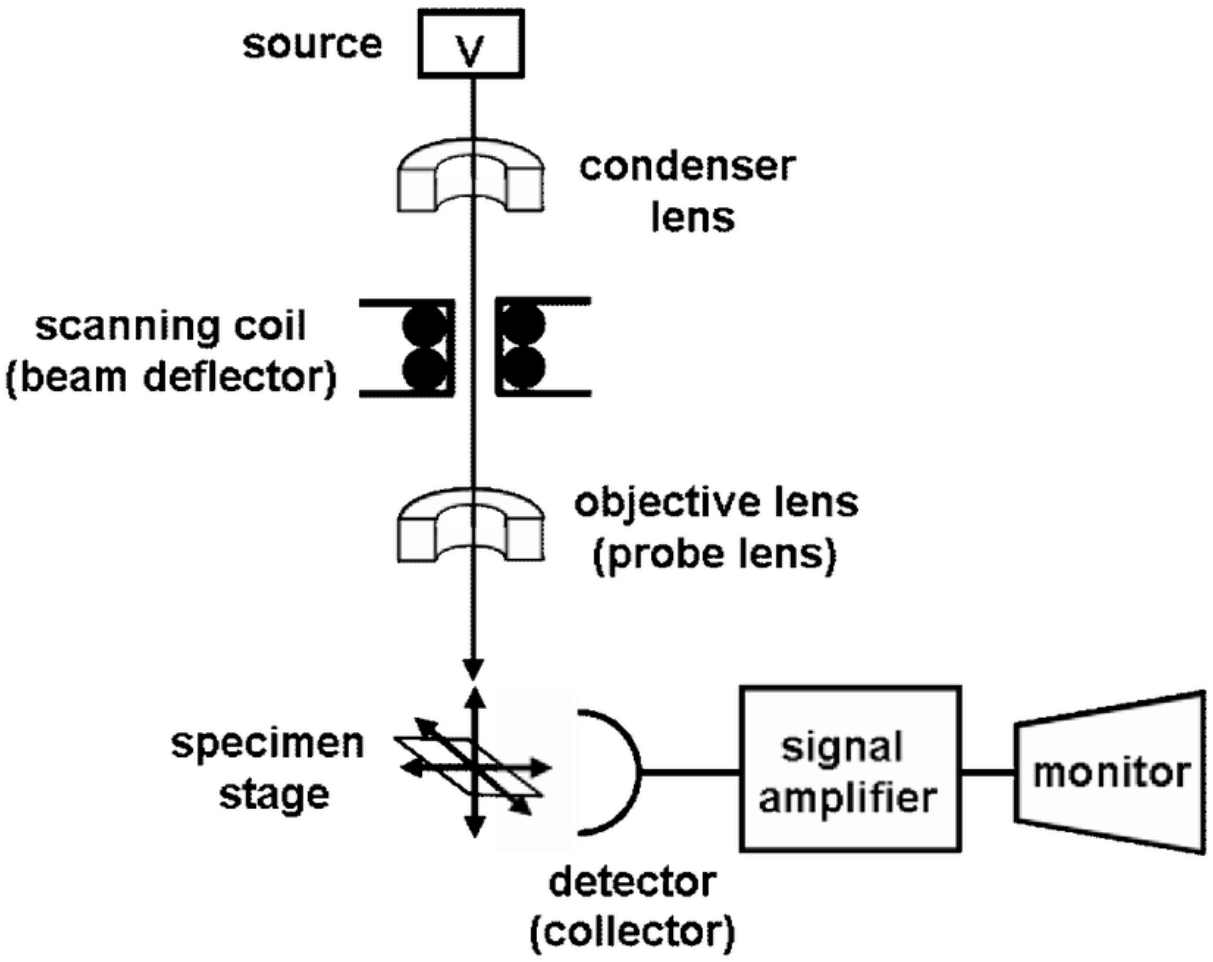


Fig8. Schematic representation of SEM instrument

SEM's gives topographic details of any sample hence with this we can generally characterize any sample. Therefore SEM's are generally used in various industries like medicine, food processing for research purpose.

2.3.6. Transmission Electron Microscopy (TEM)

Full form of TEM is Transmission Electron Microscope. It is a device through which we can get to know about internal microstructure of any sample [23]. It is capable of magnifying any object up to 2 million times. It is one of the important tools used in the field of nanotechnology. It was invented by German physicist "Ernst Ruska" for which he received Nobel Prize in physics in the year 1986.

Inside TEM electron beams are made to fall on the sample present inside the column for interaction. On interaction of electron beam with the sample gets transmitted and strikes a fluorescent screen and produces a high resolution sample image.

TEM works on the same principle as the light microscope but it uses electron beam instead of light beam (photon beam) to produce an image. As De' Broglie wavelength of electrons are smaller compared to photons so TEM is capable of producing high resolution images that can reveal finest details of internal structure of sample.

A typical TEM contains an electron gun at the top of the column from which electron beam is released. This beam now passes through electromagnetic lens .When passing through electromagnetic lens this beam gets converge. This converged beam finally falls on the sample which is placed on the sample tray. This high energy converged beam when passes through the sample under investigation it gets distorted i.e. some gets scattered and some transmitted. This transmitted beam then passes through the projector lens. This projector lens then diverges the collected transmitted beam. This diverged transmitted beam then falls on the fluorescent screen present at the bottom of the chamber and produces a light signal corresponding to that. This light signal gives 2-d image of the specimen. This image is then modified and processed by the computer to be seen on the screen [24,25].

Fig9. Transmission electron microscope

2.3.7 UV-Visible Spectroscopy

This type of spectroscopy is one of the other analytical tools used in characterization of any sample. It works on the principle of spectrometry. This technique is primarily based on

adsorption of light of a particular wavelength by any sample to get information about the substituent present inside it. We know that when light of certain wavelength falls over any sample it results in excitations of electrons from ground state to excited state which in turn leads in creation of adsorption spectra corresponding to each molecule. With the help of these adsorption spectra we can characterize any material. In UV-vis spectroscopy we make use of Ultra Violet rays for characterization process.

In this technique there is a light source from where UV light gets emitted is made to fall on the sample. When Ultra violet rays falls on sample some gets absorbed and some gets transmitted. Let the ratio of light entering the sample be I_0 and intensity of transmitted light be I. This ratio between intensity of entering light and transmitted light is defined as transmittance (T).And the absorbance (A) by any sample is defined as negative logarithm of transmittance and given by following equation

$$A=-\log (T)$$

This absorption follows Beer-Lambert law[26]. According to this law absorbance of any sample at a given wavelength is proportional to the molar attenuation coefficient, path length and concentration of absorbing substance. The Absorbance under this case is defined as

$$A= \varepsilon * l * C$$

Where ε is the molar attenuation coefficient, l is the path length and C is theconcentration of absorbing substance

Fig10. UV-Visible spectrometer

2.3.8. BET Surface area measurement

The surface of a material is a dividing line between a solid and its surrounding. Surface area affects, for example, dissolution rates of pharmaceutical, the activity of industrial catalysts and the processing of most powders and porous materials.

The tendency of all solid surfaces to attract surrounding gas molecules gives rise to process called gas sorption. Monitoring of gas sorption process provides a wealth of useful information about the characteristics of solids such as surface area and pore size.

Before performing a surface area analysis or pore size measurement, solid surfaces must be free of contaminants such as water and oils. Surface cleaning is often carried out by placing a sample of the solid in a glass cell and heating it under the vacuum. Once clean the sample is brought to a constant temperature by means of an external bath, typically a dear flask containing a cryogen like liquid nitrogen. Then small amount of gas are admitted in steps into the evacuated sample chamber.

Brunauer-Emmett-Teller (BET)[27] theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material.

The concept of the theory is an extension of Langmuir theory, which is theory for monolayer adsorption, to multilayer adsorption with the following hypothesis: (i) gas molecules physically adsorb on a solid in layers infinitely, (ii) there is no interaction between each adsorption layer, and (iii) the Langmuir theory can be applied to each layer. The resulting BET equation

$$\frac{1}{\vartheta[(\frac{\rho}{\rho o})-1]} = \frac{c-1}{\vartheta c}\left(\frac{\rho}{\rho o}\right) + \frac{1}{\vartheta_m c}.$$

Here, ρ and ρ_o are the equilibrium and the saturation pressure of adsorbents at the temperature of adsorption,ϑ is the adsorbed gas quantity and ϑ_m is the monolayer adsorbed gas quantity, c is the BET constant.

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right).$$

Where,E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction.

This BET method is widely used in surface science for the calculation of surface area of solids by physical adsorption of gas molecules. The total surface area is S_{Total} and the specific surface area S_{BET} are given by

$$S_{Total} = \frac{(\vartheta_m N s)}{V}.$$

$$S_{BET} = \frac{S_{Total}}{a}.$$

2.4 References-

1. Nadeem Baig, IrshadKammakakam and Wail Falathab: Nanomaterials: a review of synthesis methods, properties, recent progress, and challenges: Mater. Adv., 2021, 2, 1821

2. Thakur Prasad Yadav, Ram Manohar Yadav, Dinesh Pratap Singh: Mechanical Milling: a Top Down Approach for the Synthesis of Nanomaterials and Nanocomposites, Nanoscience and Nanotechnology

3. K Ma, JY Feng, ZJ Zhang - Improved photoluminescence of silicon nanocrystals in silicon nitride prepared by ammonia sputtering, Nanotechnology, 2006

4. CC Welch, DL Olynick, Z Liu… -, Formation of nanoscale structures by inductively coupled plasma etching, … Micro-and Nano …, 2013

5.SChen,RLi, XLi, JXie - Electrospinning: An enabling nanotechnology platform for drug delivery and regenerative medicine, Advanced drug delivery reviews, 2018

6. K Chacón-Madrid, MAZ Arruda, Internal standard evaluation for bioimaging soybean leaves through laser ablation inductively coupled plasma mass spectrometry: a plant nanotechnology approach: Journal of Analytical Atomic Spectrometry, 2018

7. W.W. Gerberich, ... W.M. MookTHE BOTTOM-UP APPROACH TO MATERIALS BY DESIGN, , in Nano and Microstructural Design of Advanced Materials, 2003

8. S Sen, S Kundu , Reduced graphene oxide (rGO) decorated ZnO-SnO2: A ternary nanocomposite towards improved low concentration VOC sensing performance, - Journal of Alloys and Compounds, 2021

9.Y Zhao, X Sun, Molecular layer deposition for energy conversion and storage, ACS Energy Letters, 2018

10. R Alexandrescu, F Dumitrache, I Morjan,TiO2 nanosized powders by TiCl4 laser pyrolysis, Nanotechnology 2004

11. M Meyyappan, A review of plasma enhanced chemical vapour deposition of carbon nanotubesJournal of Physics D: Applied Physics, 2009

12.VA Basiuk, EV BasiukSpringer, Green processes for nanotechnology, 2015

13. H Schlicke, JH Schröder, M Trebbin, .Freestanding films of crosslinkedgoldnanoparticles prepared via layer-by-layer spin-coating,Nanotechnology,2011

14. MKM Lane, JB Zimmerman ,Controlling metal oxide nanoparticle size and shape with supercritical fluid synthesis, Green Chemistry, 2019

15.Ming-ming Chen Chapter 12 - Thermal Analysis

Springer,Berlin,2001.

16. H. Saka, Electron Microscopy of Crystals. Uchidarokakuho, Tokyo, 1997

17.P.M.A.Sherwood,Carbons and Graphites: Surface Properties of

18.Utz Kramer,X-Ray Fluorescence Spectrometers*,1999 Elsevier Ltd

19. Delphine D Le Pevelen, Small Molecule X-Ray Crystallography, Theory and Workflow

20. S. N. Ghosh, IR Spectroscopy

21. Norman B. Colthup, Infrared Spectroscopy.

22.Lu X, Yao S, He M. Raman spectroscopic determination of salinity of ore-forming fluid inclusions. Geosci Front 2001;8(4):429e33

23. William K. Ovalle and Patrick C. Nahirney .Eye and Adnexa,Netter's Essential Histology, 19, 459-480

24. D.B. Williams and C.B Carter, Transmission Electron Microscopy. Plenum Press, New York & London, 1996

25. B. Howe and J.M. Howe,Transmission Electron Microscopy and Diffractiometry of Materials.

26.MarietaL.C.PassosMafaldaC.SarraguçaM.LúciaM.F.S.SaraivaT.PrasadaRaou Spectrophotometry | Organic Compounds, Encyclopedia of analytical Science (3rd edition) 2019

27.SoubantikaPalchoudhury,MohammedBaaloushaJamie,R.LeadCharacterizationof anomaterials in Complex Environmental and Biological Media

CHAPTER 3

3.Result and Discussion

3.1. Material Characterizations

3.1.1 TG analysis

The following figure is representing TG analysis of 4CS and 4BS samples. The given TG plot of Ca(II) incorporated tin oxide (4CS) shows three distinct steps. In the first step there is a sharp weight loss of around 58% in the temperature range from room temperature to 310˚C. In step 2 it is seen as weight loss of around 14% from 310 to 530˚C the final step i.e. from temperature 530˚C till 800˚C there is seen a weight loss of around 20%. The initial weight loss in TG curve might be due to desorption of adsorbed water and different chemical ions from the sol. The second weight loss was due to decomposition of hydroxyl groups (O-H) present in the matrix. The third weight loss might be due to the phase transformation. In case of Ba(II) incorporated tin oxide (4BS), two distinct step of weight loss was observed. The weight loss upto temperature ~200^{o}C due to desorption process and the afterward loss was due to decomposition of hydroxide groups to the nanocrystalline oxide powders[1]. After 400^{o}C there was no significant change was observed corresponding to phase transformation. For Sr(II) added sample(4SS) similar pattern of mass loss was observed as per 4BS so not shown here.

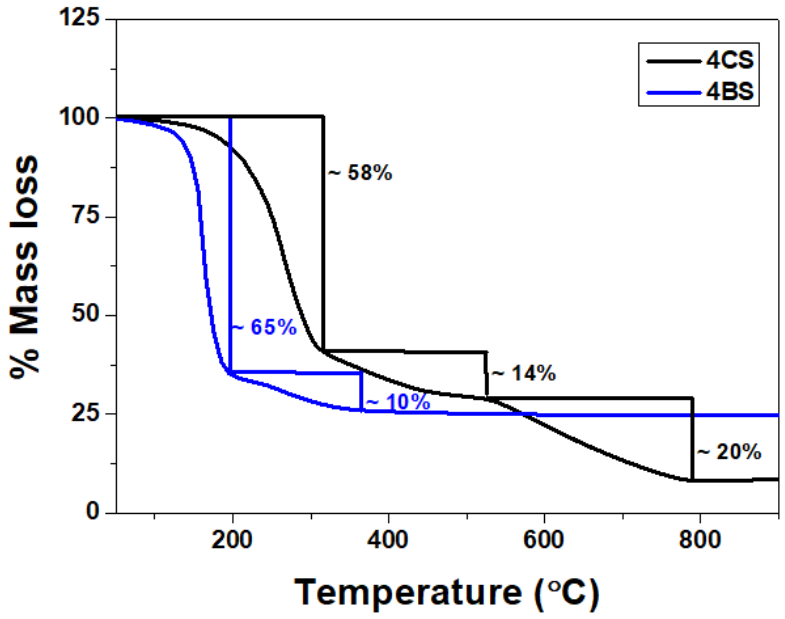


Fig1: TG analysis of 4CS, 4BS

3.1.2 XRD analysis

Addition of alkaline earth metal ions inSnO_2 matrix introduces can leads to two phenomena, one is occupying of substitutional sites these metal ions might replace some Sn^{4+} ions. As the ionic radius of these alkaline earth metal ions are larger compared to Sn^{4+} ions there might be only nominal substitution. Another possibility is to inhibit the crystalline growth of the tin oxide.

In pristine SnO_2 we observed (Fig.2) some diffraction peaks corresponding to the tetragonal structure of SnO_2 (JCPDS 78-1063) centered at 26.84, 29.75, 31.58, 33.95 and 51.99 degrees indexed as (112), (113), (021), (006), and (118) [1]respectively. The XRD pattern of 4CS clearly showed that there were some peaks at 22.6 and 32.2 degrees corresponding to (002) and (200) planes of calcium stannate (JCPDS No. 77-1797). Due to presence of these peaks the intensities of peaks corresponding to SnO_2 have diminished. From the fig is showing clearly how the intensities of peaks of tin oxide are decreasing with increasing in the alkaline earth metal weight percentage. Due to presence of CaO there is some shift in peak position in SnO_2 which is also observed from the given XRD pattern.

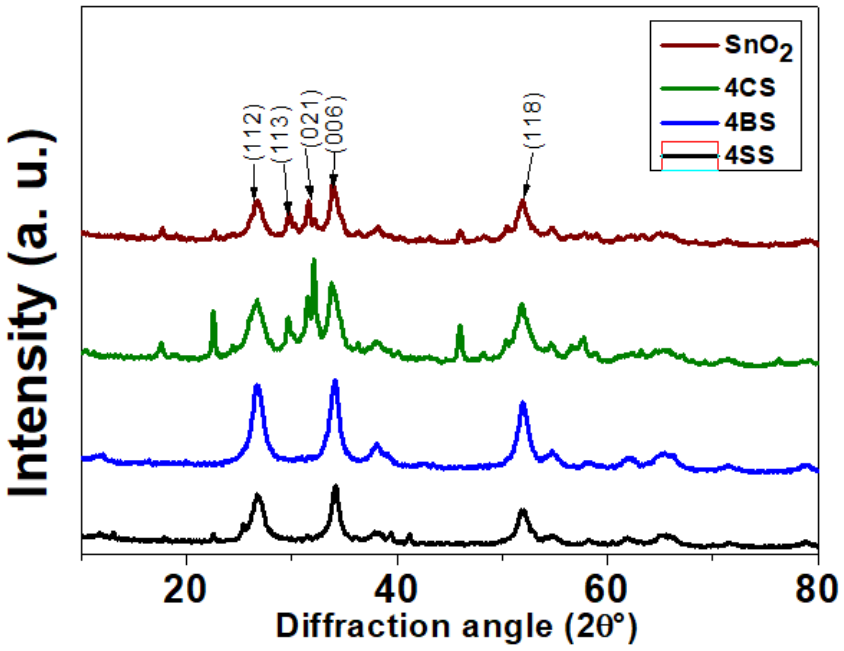


Fig2: XRD pattern of pure SnO_2, 4CS,4BS, 4SS

When barium is added in tin oxide some due to ionic size mismatch between barium and tin, barium ions may either occupy certain substitution sites in tin oxide matrix or may get disperse at the grain boundaries of SnO_2. From the XRD pattern, we can see that the diffraction peaks at 2θ values were at 26.48, 33.73, 37.97, 51.71, 54.97, 57.76, 61.94, 64.72, 66.11 and 71.45. All the diffraction peaks can be indexed as (110), (101), (111), (211), (220), (002), (310), (112), (301) and (202) respectively against the tetragonal rutile structure of SnO_2 (JCPDS 41-1445) only. Therefore the absence of any peak corresponding to barium oxide can be attributed as its low abundance in the matrix which is below detection range of XRD.

From the XRD pattern of Sr^{2+}added SnO_2we can see that the presence of diffraction peaks at 2θ values were at 26.48, 33.73, 37.97, 51.71,54.97, 57.76, 61.94, 64.72, 66.11 and 71.45. The observed peak positions were then matched with the reference (JCPDS part no. 041-1445)[2] and were correlated with different crystal planes (110), (101), (200), (111), (211), (220), (002), (310), (112), (301) and (202) of SnO_2 respectively. Therefore the absence of any peak corresponding to strontium oxide can be attributed as its very less presence in the matrix which is below detection range of XRD. However, as the concentration of added Sr2+ exceed 4 wt.% they probably started to accumulate across the grain boundary zone and that's for significant peak indexed as (200) and (003) observed -in the XRD pattern of 6SS.

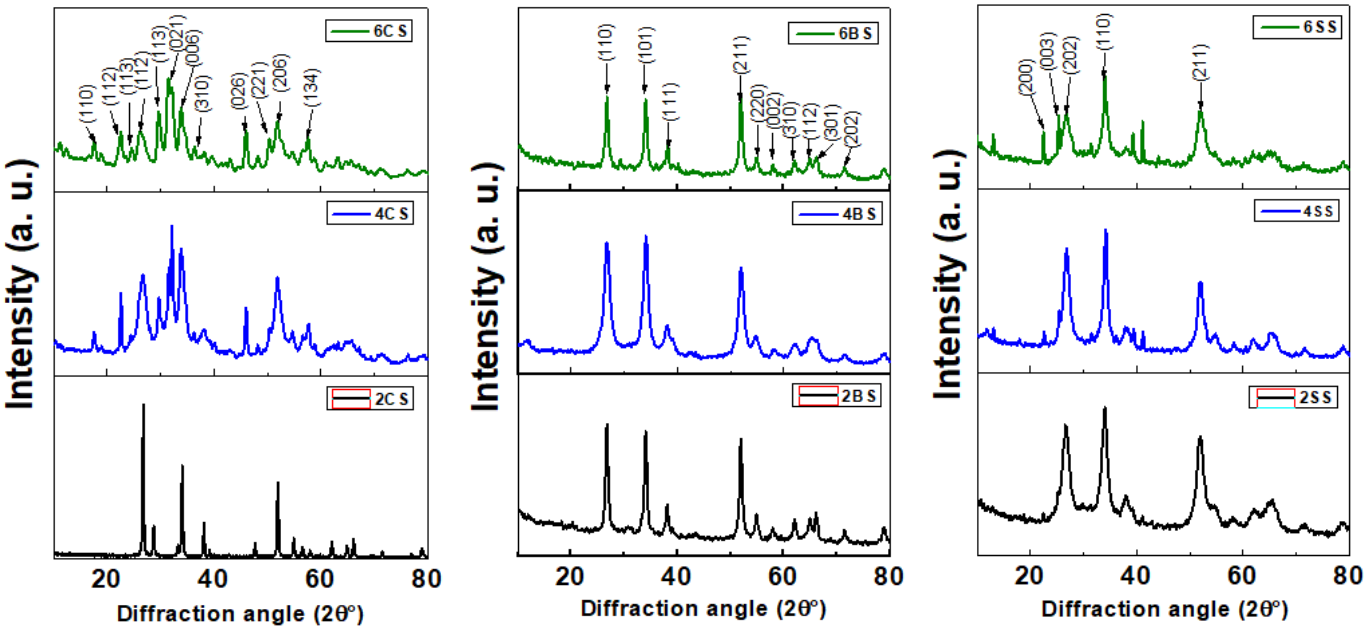


Fig3: XRD pattern of (a) 2, 4, 6 CS, (b). 2, 4, 6 BS, (c).2, 4, 6 SS

3.1.3 FTIR analysis

The FTIR transmission spectra of samples 4CS, 4BS and 4SS are shown in figure-4. A broad peak at 3440 cm^{-1} was attributed to stretching vibrations of -O–H coming from atmospheric moisture adsorbed in it. The peaks at 1633 cm^{-1} signified stretching vibration of -C=C- bond. There were some weak signals in the range 1200 – 1450 cm^{-1} could be correlated to bending vibration of O–H group. These bands were due to organic trace impurities, left over during calcinations process. All the other peaks below 1000 cm^{-1} were mainly associated with different metal oxide stretching vibrations. The peaks observed in that range were due to the vibration of M–O (in this case Sn-O) surface cation – oxygen bonds vibration and stretching vibration of M-O-M (in this case Sn-O-Sn).

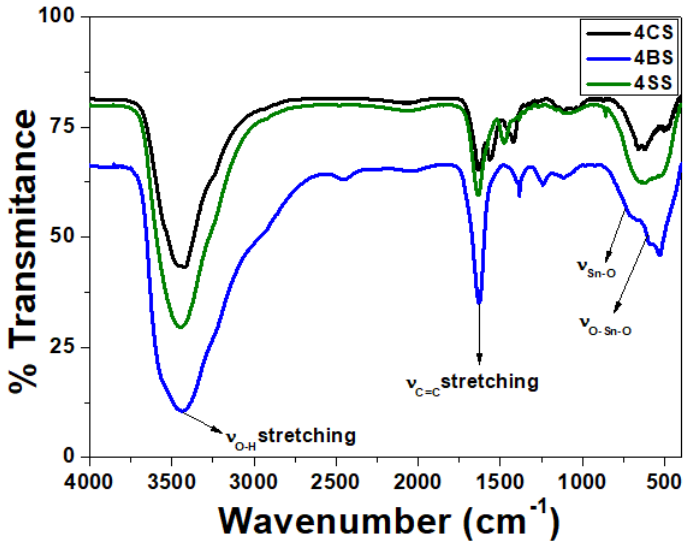


Fig4: FTIR spectra of 4CS, 4BS, 4SS

3.1.4 Raman Spectra analysis

The Raman spectrum of a typical Ca incorporated tin oxide (4CS) is shown in the figure-5. The spectrum shows presence of several peaks at 165, 259, 334, 459 and 643 cm^{-1}. Among these, the band at 165 cm^{-1} is due to O-Sn-O bending vibration[3]. The characteristics peaks present at 259, 334, and 459 cm^{-1} were representing symmetric vibration of SnO_2 molecule. The stretching mode of SnO_2 was present at 643 cm^{-1}.

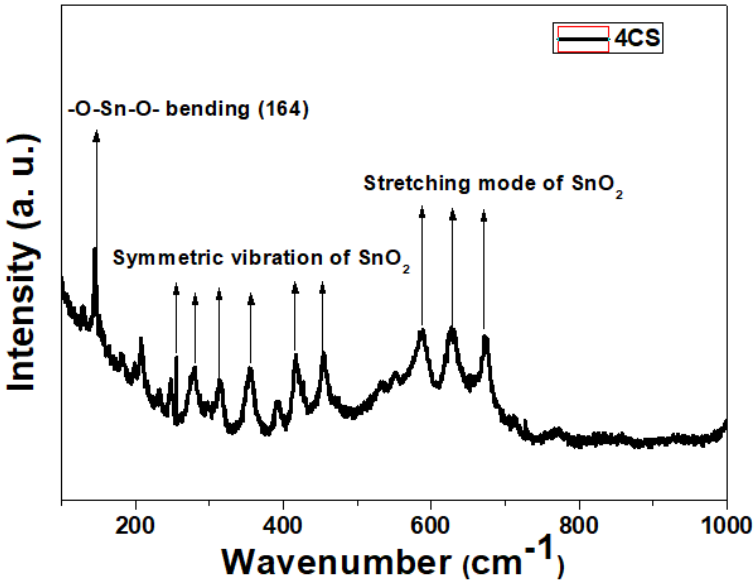
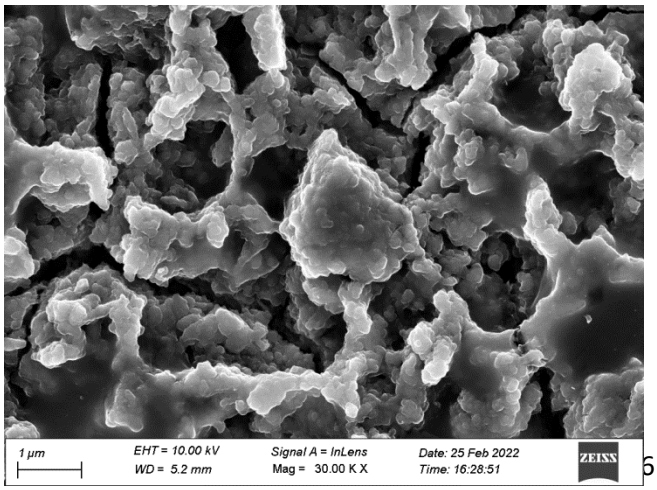
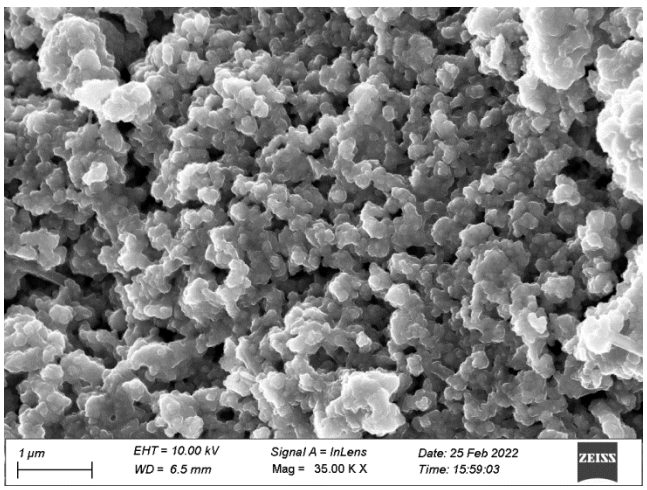


Fig5: Raman spectra of 4CS

3.1.5 FESEM analysis

FESEM images of 4CS, 4BS and 4SS samples calcined at 650℃ are shown in the following figures to study about their surface morphology. From the images we can see presence of agglomerated spherical particles with nano-scale pores composed of nano-sized individual particles. These porous structures enhances facilitate diffusion of experimental CO gas on the sensing material surface of the samples thus favoring the reaction between surface molecules and gas which directly contributes towards better gas sensing response and simultaneous faster response and quick recovery times.





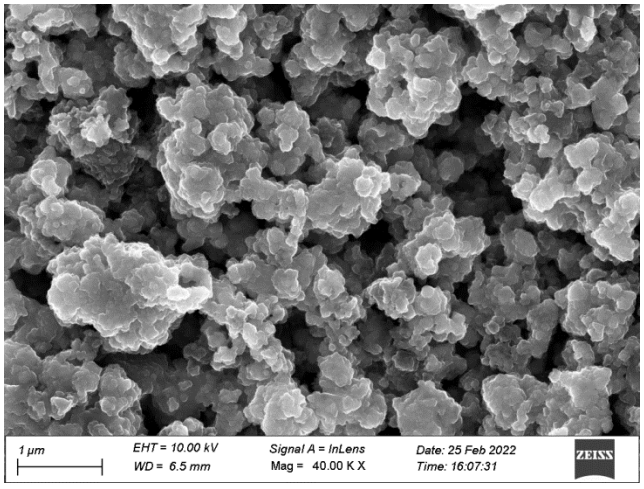


Fig5: FESEM images of 4CS, 4BS, 4SS

3.1.6 UV-Visible spectra analysis

The following figure 6 is showing the absorption spectra of the4CS, 4BS and 4SS samples recorded in the range 200 to 800 nm. The occurrence of these peaks was primarily due to the transfer of excited electrons from the valence band to the conduction band on the application of UV rays. From the figure it was clearly seen that the absorption peaks of tin oxide primarily at ~290 cm^{-1}. Upon addition of alkaline earth metal ions (Ba and Sr ions) in SnO_2 matrix the peaks blue shifted probably due to the perturbation originated in the pristine SnO_2 lattice by the presence of metal ions. This observation also inferred of decreasing the particle size of SnO_2, inhibited by the presence of alkaline metal ions. In case of Ca loaded tin oxide, some anomaly observations was found. This is probably due to presence of some Ca stannate phase in the sample. Detailed understanding of the phenomena required detailed analysis further.

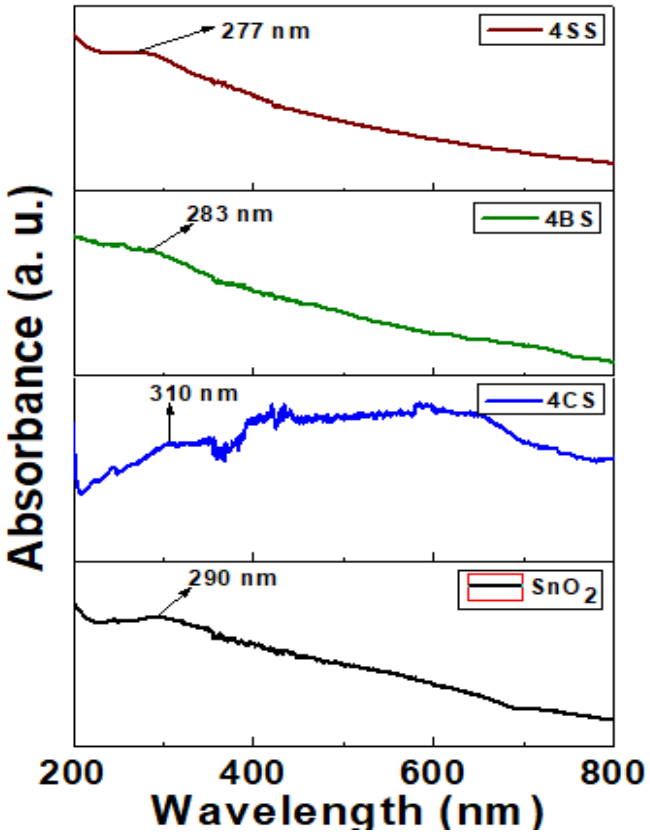


Fig6: UV-visible spectra analysis of SnO_2,4CS, 4BS, 4SS

3.1.7 BET Surface area analysis

The porous inner architecture of the nanocomposite 4CS was measured using nitrogen adsorption-desorption isotherm. The N2 sorption isotherms and corresponding pore size distribution curve (inset) have been presented in Fig. N_2 adsorption/desorption isotherm shows sharp capillary uptake at low P/P_0 and at high N_2 partial pressure, there was a pronounced hysteresis. The isotherm exhibited a type IV isotherm (according to IUPAC convention). This proved the highly textural properties of the nanocomposites. The BET surface area of 4CS was ~ 12.08 m^2/g. The pore size distribution plot of 4CS showed the pore size distribution in a wide range of ~ 3 nm to ~ 16 nm with the peak centered at ~ 4.26 nm and the measured pore volume was 0.024 cc/g.

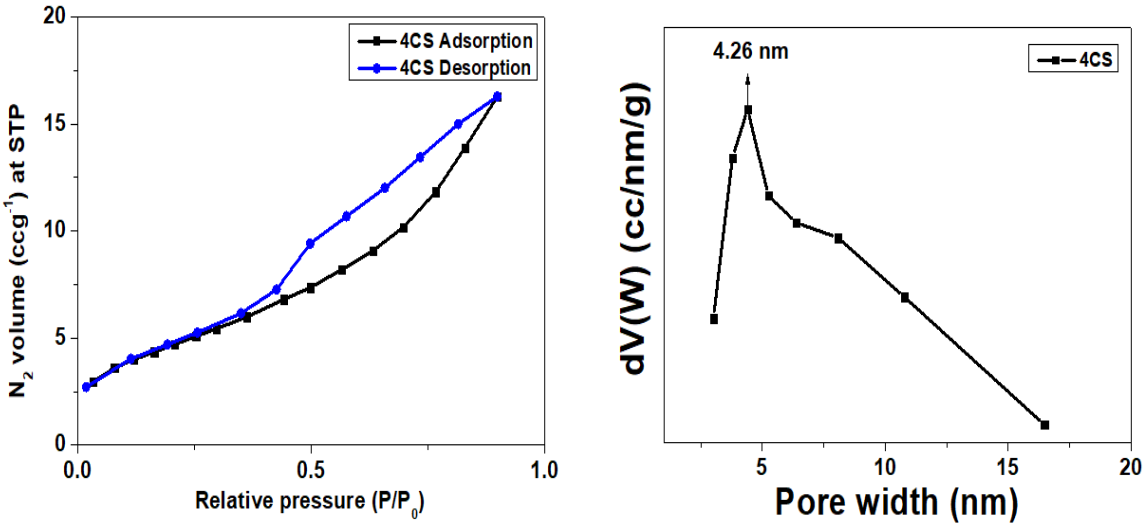


Fig7: Surface area analysis of 4CS

3.2 Gas sensing performance study

Optimization of operating temperature of a sensor is very much essential for its proper functioning and energy saving point of view. With the fabricated sensors the base resistance i.e resistance of the sensor at an open atmosphere was recorded over a range of temperature started from room temp to 150°C. All the three sensors 4CS, 4BS, and 4SS showed measurable base resistance in mega-ohm range at room temperature. Henceforth the further gas sensing performance study carried out at room temperature only.

The sensing responses of all the fabricated sensors were measured in presence of 35ppm CO. In presence of CO all the sensors showed a p-type sensing response i.e. increase of base resistance value in presence of experimental gas. In case of room temperature sensing, due to presence of abundant moisture in atmosphere there develops a secondary layer of water molecules on the sensing material surface. Now, when the sensing material exposed to experimental gas molecules then there initiates a chemical reaction between the hydroxyl groups of the secondary layer and gas molecules and further reacted with the sensing material.

All of the sensors exhibited a good repeatability to the CO pulse at the optimized experimental conditions. It was observed that 4 wt% alkali metal addition in SnO2 matrix delivered

maximized sensing response and beyond that the sensing response diminished might be due to the accumulation of metal ions across the grain boundary.

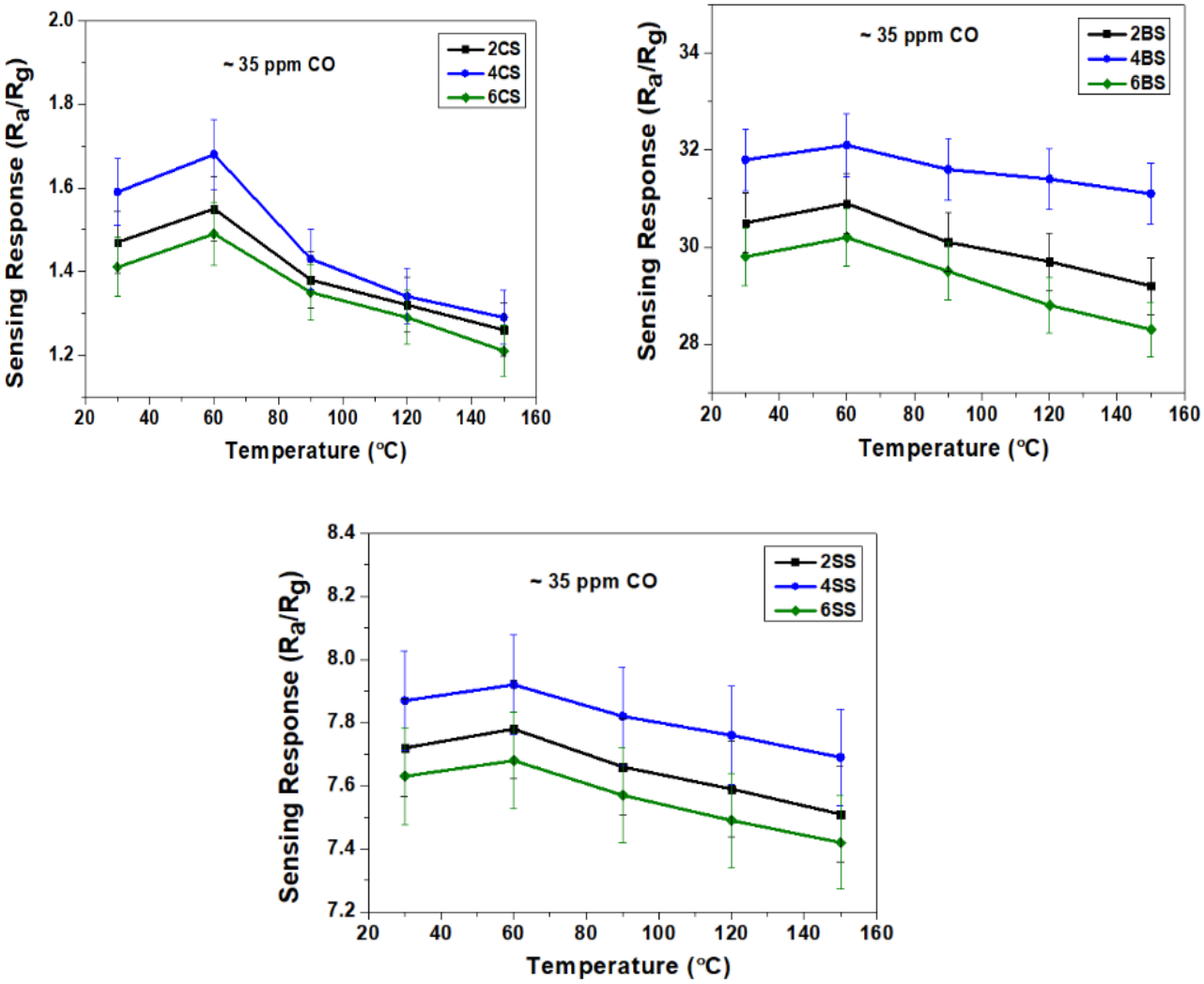


Fig8: Change of sensing responses with temperature of the sensors

For 4CS sensors we observed a sensing response of ~ 1.78 in presence of ~ 35ppm CO. The corresponding response and recovery time was ~ 20sec and ~ 90sec respectively. For 4SS sensor we obtained the improved sensing response of ~ 7.8 with the response time of ~ 10 sec and recovery time of ~ 30 sec. This sensing response increased by many folds for 4BS sensor under identical experimental conditions as well the response and recovery time also shorted. For 4BS sensors ~ 31.8 sensing response was obtained with the same response time of ~ 10sec and fastest recovery time of ~ 20 sec.

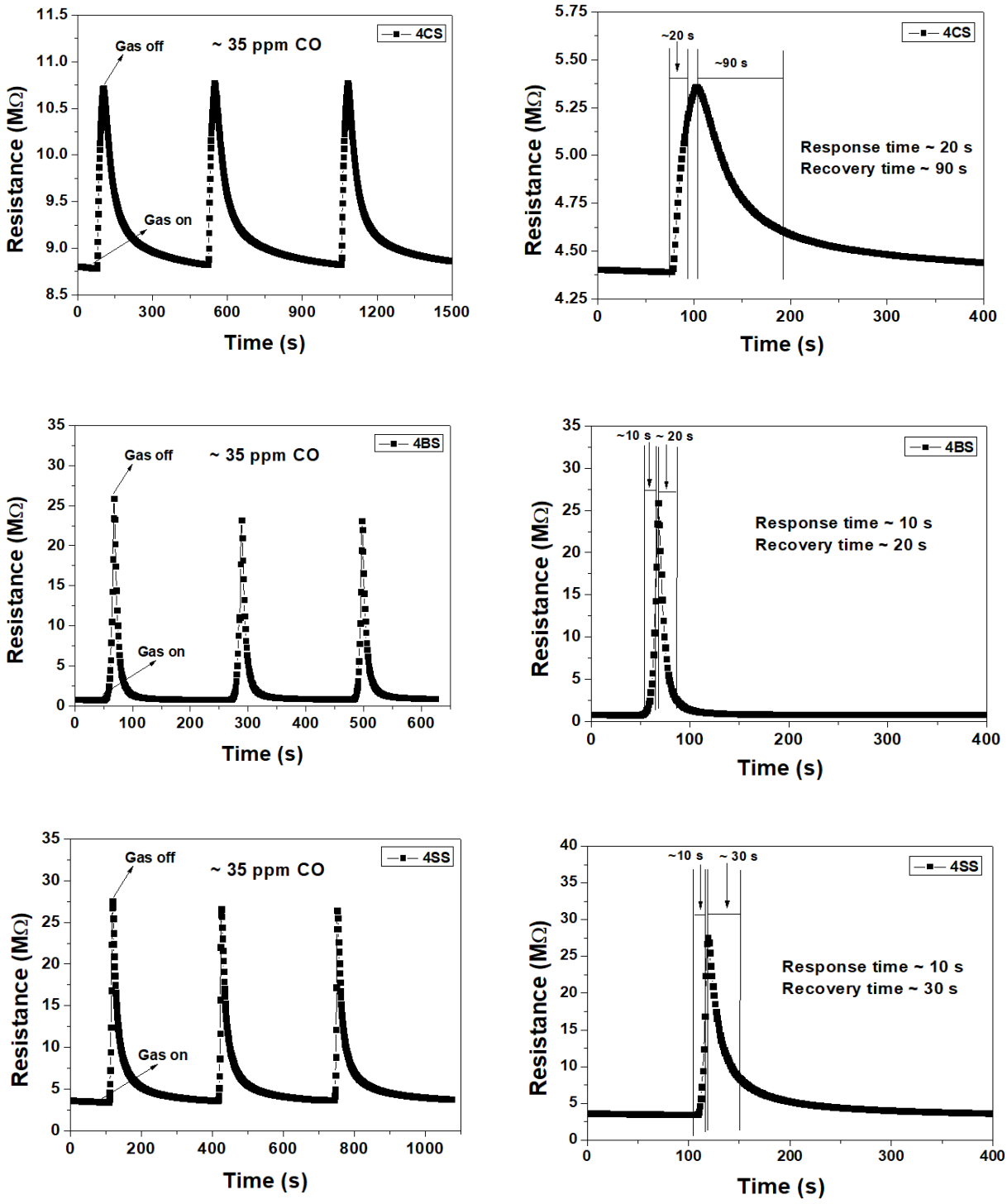


Fig9: Sensing response and response and recovery time of 4CS, 4BS, and 4SS

The 4BS sensor deployed for cross sensitivity measurement in presence of other interfering volatile organic compounds like ammonia, ethanol, methane, formaldehyde etc.of around 30 ppm concentrations. There we obtained a good selectivity for CO in comparison to other mentioned VOCs under similar optimized working conditions of the sensor.

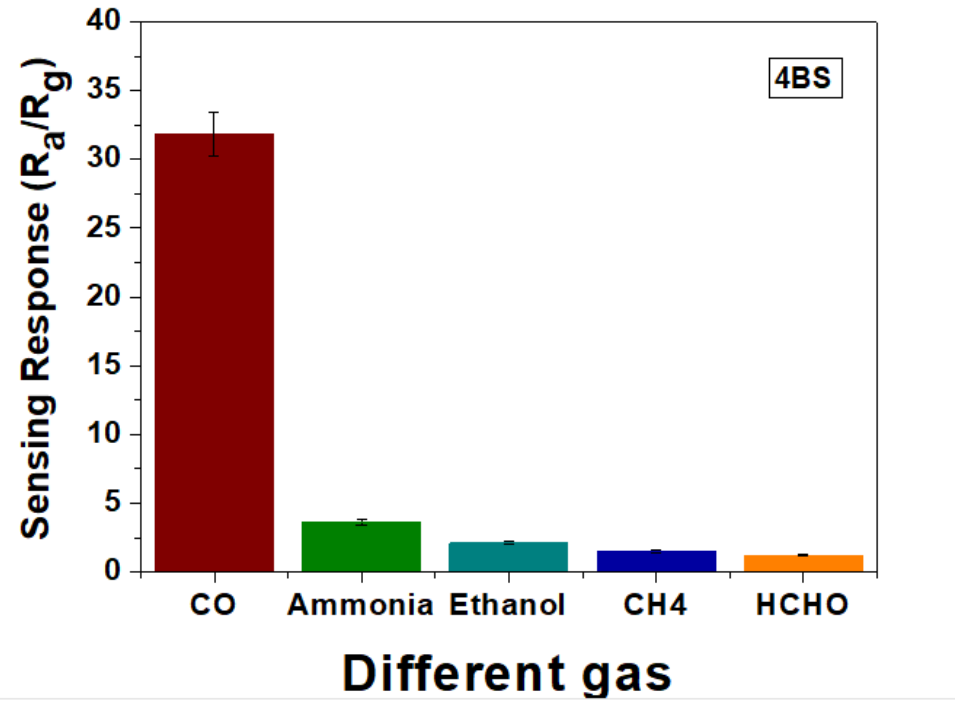


Fig10: Selectivity test of 4BS

From the obtained sensing performance results it could be ensured that the fabricated 4BS sensor would be a promising material for room temperature CO sensing applications.

3.3 References

1. Saptarshi Ghosh, MousumiNarjinary, Amarnath Sen, RajibBandyopadhyay, Somenath Roy, Fast detection of low concentration carbon monoxide using calcium-loaded tin oxide sensors, Sensors and Actuators B: Chemical,2014

2. Ziqiao Jiang a , Tingting Jiang , Jinfeng Wang , Zhaojie Wang , Xiuru Xu , Zongxin Wang , Rui Zhao , Zhenyu Li , Ce Wang ,Ethanol chemiresistor with enhanced discriminative ability from acetone based on Sr-doped SnO2 nanofibers, Journal of Colloid and Interface Science 2015

3. Balamurugan Muthukutty, Alagumalai Krishnapandi, Shen-Ming Chen,* Manickavasagan Abinaya, and Arumugam Elangovan Innovation of Novel Stone-Like Perovskite Structured Calcium Stannate (CaSnO3): Synthesis, Characterization, and Application Headed for Sensing Photographic Developing Agent Metol, ACS sustainable chemistry and engineering .

CHAPTER 4

4.1 Summary-

Detecting gases and determining their concentration has constantly been on rise since few years. The demand for more sustainable and healthy environment has lead researchers worldwide to shift their focus on gas sensors. In this context gas sensors using metal oxide semiconductors, primarily SnO_2 has been one of the most widely investigated material since last few decades.Using metal oxides in gas sensors have several advantages for example, low fabrication cost, highly robust in nature etc However in recent years instead of relying on any single and simple binary oxide, focus has been shifted towards developing other metal oxides also or using noble techniques to make ternary or complex metal oxides, for the purpose of gas sensing. Gas sensors incorporating metal oxide nanomaterials are also highly focused worldwide for the purpose of gas sensing. The main advantage of using any nanoparticle in gas sensing is that due its high surface area to volume ration it facilitates better diffusion gas on the surface of the sensing material hence increasing the sensitivity of the sensor.

In recent years the efforts of researchers and scientists worldwide were primarily aimed at developing sensors which has (i) high sensitivity and selectivity and (ii) work at low temperatures. Keeping in view all the above objectives in this present thesis we have divided our work in primarily two sections in the first section we have first tried to synthesize some pure as well as doped SnO_2nanomaterials and then in the second part we have characterized them as well checked sensing performance of all those synthesized materials to find the most suitable one for the detection of Carbon Monoxide.

In the first section for the synthesis purpose we have used Sol-gel technique. Some basic advantages for using this technique are (i) low operation cost (ii) steps incorporated are very simple. After synthesis of a material we characterized them by different techniques like XRD, FTIR, Raman spectroscopy, FESEM, UV-visible spectroscopy, and BET surface area measurement. After that, the synthesized nanocomposites were used to fabricate the Taguchi type sensor modules. The fabricated sensors were used to study the gas sensing performances. All the sensors were operable at room temperature and in ambient condition. Among them 4BS sensor showed maximum p-type sensing response of ~ 31.8 in presence of ~ 35 ppm CO. Simultaneously, the 4BS sensor also demonstrated fastest response and recovery time of ~ 10 s and ~ 20 s. Beside this the sensor also exhibited a superior selectivity to CO at optimized working condition.

4.2 Future Scope of the work

During this short time period of M.Tech thesis work it was hardly possible to clearly understand all the challenges and queries encountered in the literature survey and experimental works .Although after a thorough literature study, in order to develop a suitable optimized CO sensor, pristine SnO_2 material functionalized with different alkali earth metal ions like Ca^{2+}, Ba^{2+}, and Sr^{2+}. Different characterization techniques have been used for details characterizations of synthesized nanomaterials. Then after Taguchi type sensors fabricated by using the synthesized nanomaterials. The sensors were deployed to study the sensing performance in presence of CO (~35 ppm) gas. The sensors demonstrated a good sensing response with rapid response and recovery time as well as a considerable selectivity towards CO in presence of other interfering gases. Despite of that, there is a scope of further investigation in this work for obtaining better perspectives.

- All the synthesized nanomaterials needed to be characterized thoroughly and their sensing performances should be studied in details.
- The sensing performance of the fabricated sensors required to be recorded in presence of further low concentration of CO.
- The stability profile of the sensor should be studied.
- The versatility of the sensor needed to be improved by its miniaturization on different flexible substrates.
- The ground level application and its comparison with different market available CO sensors should be done.
- Finally, a probable prototype/device would be fabricated.