Abstract of the thesis entitled

“Synthesis of pure and modified BaSnO$_3$ for gas sensing”

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ABSTRACT

Synthesis of pure and modified BaSnO₃ for gas sensing

The industrial and private sectors provide a growing market for new sensor materials due to the variety of old and new application areas. Gas sensors are playing an increasingly important role in environmental monitoring, control of chemical processes, remote sensing, in space, agricultural and medical applications. The interest has grown in the development of an electronic "nose," capable of detecting mixed gases and even odors. Instead of analyzing all of the gas constituents by a technique such as gas chromatography, an electronic nose looks for specific patterns or fingerprints of the gas mixture. Such a device generally consists of some chemical sensors, each one sensitive to a specific gas and a pattern recognition system. Various prototypes, based on organic as well as inorganic sensing materials, have appeared in the market. Because of their simplicity and low cost, semiconductor metal-oxide gas sensors stand out among the ones used in multi-sensor arrays. There exists a clear demand for CO₂ concentration monitoring for applications such as the assessment of indoor air quality, food storage and early fire detection.

Most of the natural metallic elements of the periodic table form perovskites with general formula, ABO₃. This wide range of cations, coupled with the possibility of partial substitution, mainly at the B-cation site, results in an abundant diversity of behaviour which leads to a wide variety of applications. Complex perovskite oxides are particularly important since their properties can be tailored for specific applications ranging from superconductivity to oxidation catalysts by suitable doping, oxidation of the hydrocarbon species normally proceeds to completion and CO₂ is produced. Perovskite type oxides with semiconducting behaviour have also shown promise as oxygen sensor. Barium Stannate (BaSnO₃) is a typical compound with a cubic perovskite lattice structure. In the
ambient conditions of temperature and oxygen partial pressure it behaves as a pure, n-type semiconductor below 900°C. Its electrical behaviour can be changed from an insulating one into a conducting one either by substituting lanthanum for barium or by the formation of oxygen vacancies. In both cases a small amount of Sn(IV) atoms are formally reduced into Sn(II) resulting in the formation of a mixed valent oxide. At about the same time, investigations of the properties of Barium Stannate ceramics and Barium Stannate thin films made these oxides suitable for use in semiconductor gas sensor devices at elevated temperatures.

The aforementioned background justifies the need to improve the properties and features of these oxides in order to obtain a more efficient material for gas sensing purposes. Several deposition methods have been used to grow un-doped and doped films such as spray pyrolysis, vacuum evaporation, chemical vapor deposition, magnetron sputtering, pulsed laser deposition, sol-gel and screen printing technique. Screen printing technique was introduced in the later part of 1950’s to produce compact, robust and relatively inexpensive hybrid circuit for many purposes. Later on thick film technique has attracted by the sensor field. Screen printing is viable and economical method to produce thick films of various materials.

A brief summary of the comprehensive report of the thesis and its distribution in different chapters is presented as follows. The thesis consists of seven chapters.

**Chapter 1** is ‘General introduction and literature survey’. This gives the information related to sensors, sensor types, broad literature survey, adsorption studies on semiconducting oxides, different technologies for fabrication of sensors, sensing mechanism and necessity of additives, surface modification technique for sensing and criterion for their selection, synthesis of Barium Stannate etc.
Chapter 2 is ‘Experimental techniques’. This chapter deals with details of physical characterization techniques such as X-ray Diffractometer (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Analysis by X-ray (EDAX), transmission electron microscopy TEM high resolution imaging to determination of size of particles (nano), Thermo-gravimetric Analysis (TGA), FTIR Fourier Transform Infrared spectroscopy for molecular finger print, UV-visible spectroscopy for determination indirect band gap, and technique used for thickness measurement. It also contains details of thick film resistor preparation technique and gas sensing system undertaken for the research work.

Chapter 3 deals with ‘Synthesis, Characterization and micro structural properties of Barium Stannate (BaSnO₃) thick film resistor and its Gas sensing performance: effect of surface modification’. This chapter explains the procedure of synthesis of the said material, thick film preparation, micro-structural properties, modification of thick films using dipping techniques. Electrical characteristics such as variation of current with respect to voltage as well as variation of current with respect to operating temperature were carried out and studied. Pure films in form of screen printed thick film resistors were tested for gas response to various gases such as CO, CO₂, H₂, LPG, C₂H₅OH, Cl₂, O₂, and H₂S at operating temperatures in the range 100-500 °C. Pure film showed temperature dependent gas response property. Effect of surface modification via dipping method were studied and presented. Pure films are then modified by dipping film in aqueous solutions of Aluminum chloride, copper chloride, cadmium chloride, Chromium oxide for different internal of time so as to produce aluminum oxide, Copper oxide, Cadmium oxide, and Chromium(III) oxide respectively on firing at 550 °C for 30 minutes. Films with different dipping time interval were prepared and tested for gas response, response time, recovery time and repeatability. Surface modified films gave the unusual selectivity and sensitivity effects with improving response and recovery time. It was observe that the micro-train ‘e’,
dislocation density ‘\( \rho \)’, and stacking fault probability ‘\( \alpha \)’ decrease with an increase in the annealing temperature. This leads to a reduction in the concentration of lattice imperfections. Crystallite size was found to increase with increase in annealing temperature. When films were surface modified with dipping then in aqueous solution of Aluminum chloride, copper chloride, cadmium chloride, and Chromium oxide for different intervals of time 5, 10, 20, and 30 min. It was observed that the weight percentage of Aluminum, Copper, Cadmium, and Chromium increased with dipping time, reached to a maximum and then decreased with a further increase in dipping time interval. The film with the dipping time of 20 min, 10 min, 5 min and 10 min were observed to be more oxygen deficient when dipped in aq. Solution of AlCl\(_3\), CuCl\(_2\), CdCl\(_2\), and CrO\(_3\) respectively. This oxygen deficiency may make the sample possible to adsorb a large amount of oxygen species. This deficiency leads to maximum response to a particular gas. Unmodified barium stannate shows gas response to NH\(_3\), CO\(_2\), CO (500 °C), and H\(_2\)S(400 °C). Whereas when same films were surface modified gas response was found to shift towards H\(_2\)S (aluminated 20 min. 300 °C, cupricated 10 min. 200°C, chrominated 10 min. 300 °C) and to Chlorine for cadminated 5 min 300°C. Results were interpreted and discussed with the help of XRD, SEM, EDAX and UV spectro-photo meter, and TGA/DTA.

**Chapter 4** is devoted for ‘Gas sensing performance of Pure Barium Stannate : Effect of doping’. This chapter covers fabrication of thick film resistors, and modification of thick films using doping techniques. Barium Stannate is doped with materials like Sr, and and Ti so as to form materials (\( \text{Ba}_{0.9}\text{Sr}_{0.1})\text{SnO}_3 \) and (\( \text{Ba}_{0.9}\text{Sr}_{0.1})\text{(Sn}_{0.9}\text{Ti}_{0.1})\text{O}_3 \). Films with different doping material were characterized and tested for gas response, response and recovery time, and repeatability. Films were surface modified with aq. Solution of CuCl\(_2\) and CrO\(_3\), upon heating these were converted to CuO and Cr\(_2\)O\(_3\); Modified barium
Stannate films gave the unusual selectivity and sensitivity effects with improving response and recovery time. $(Ba_{0.9}Sr_{0.1})SnO_3$ films (unmodified as well as surface modified) show improved gas response towards $CO_2$ gas. Films of $(Ba_{0.9}Sr_{0.1})(Sn_{0.5}Ti_{0.1})O_3$ improves gas response towards $H_2S$. The results are interpreted and discussed with the help of XRD, SEM, EDAX, UV spectro-photometer, and TGA/DTA.

Chapter 5 presents ‘Synthesis and characterization of Nano crystalline $BaSnO_3$ by Hydrothermal method for gas sensing applications’. This chapter explains the procedure of synthesis of nano crystalline $BaSnO_3$ material by hydrothermal method, its characterization, micro-structural properties, thick film preparation and modification of thick films using dipping techniques. The gas sensing performance of pure and surface modified Barium Stannate $BaSnO_3$ thick film resistor to various reducing gases was included in this chapter. Porosity of nano crystalline $BaSnO_3$ was found to be more as compared to $BaSnO_3$ prepared with solid state reaction, and also porosity was found to be more when material was annealed at 1000 °C. Energy was found to be 3.30 eV. The pure $BaSnO_3$ film was observed to be sensitive to $NH_3$ at 400°C and CO, $CO_2$ at 450°C. When film was surface modified with $TiO_2$ films shift the gas response and selects $H_2S$ at lower temperature (250°C). Surface modification with $Cr_2O_3$ gas response was found to be towards CO at 400°C. The results are interpreted and discussed with the help of XRD, SEM, EDAX and TGA/DTA. This work is presented at ICST 2012 at Kolkata in ‘proceeding of 6th International Conference on Sensing Technology’ at Kolkata (Dec.2012).

Chapter 6 deals with ‘Synthesis and characterization of CdSnO$_3$ as chlorine gas sensor’. This chapter explains the procedure of preparation of CdSnO$_3$ material and its thick film preparation. The gas sensing response of CdSnO$_3$ thick films to various gases was included in this chapter. The film was observed to be sensitive to $Cl_2$ (unmodified
and modified with CdO) gas and it had good selectivity. The gas sensing performance of pure and modified films of CdSnO₃ were studied and presented. The results are interpreted and discussed with the help of XRD, SEM, EDAX and TGA/DTA. The results are interpreted and discussed.

Chapter 7 devoted for ‘Scope for future research’. This chapter explains the use of BaSnO₃ as Dye sensitized solar cell material, limitations of thick film gas sensors related to reproducibility and long-term stability. The nanomaterials could overcome these problems. A brief discussion regarding the possible applications of metal oxides of the type BaSnO₃ as chemical warfare agent is discussed in this chapter.

Annexure gives the information of the publications and paper presented in national/international conferences.
Annexure

- Papers Published/Communicated in International Journal


- Publication In Books


- Papers presented at conferences (International National)


CDAC, Kolkata along with Massey University, New Zealand held at Kolkata, India during 18-21 December 2012.

**Papers presented in conferences (National)**

1) **N. U. Patil**, G. H. Jain, Paper accepted for National conference on Nanomaterials Application and Properties to be held at ASC College, Sonai, University of Pune, Pune, NCNAP2013 (22-23 Feb 2013) (Poster presentation)

2) **N. U. Patil**, G. H. Jain, proceeding of National conference on functional nano materials held at University of Pune, Pune, NC2013 (Poster presentation)


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