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Nanocomposite $ZnNb_2O_6$ Thick Film as Room Temperature Liquefied Petroleum Gas (LPG) Sensor

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Abstract In the present work, thick film of zinc niobium oxide was prepared by screen printing technology and its LPG sensing properties were investigated. The structural and surface morphological characterizations of the material were analyzed by using X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The minimum crystallite size of $ZnNb_2O_6$ calculated from Scherrer's formula was found to be 25 nm. SEM images exhibit the porous nature of sensing material with a number of active sites. The average size of pores of nanocomposite $ZnNb_2O_6$ was found to be 4 µm. The LPG sensing properties of the film were investigated at room temperature 26°C for different vol% of LPG. The variations in electrical resistance of the film were measured with the exposure of LPG as a function of time. The maximum value of sensitivity was found 4.8 for 4 vol. % of LPG. These experimental results show that **$ZnNb_2O_6$ nanocomposite** is a capable material for LPG sensor.

Keywords: *Sensor, morphology, sensitivity, nanomaterial, pores, LPG*

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1. Introduction

Liquefied petroleum gas (LPG) sensor has become the interesting topic of research today in observation of fundamental research as well as industrial applications. Metal oxide semiconductors are useful for the detection of combustible gases by a change in the surface conductivity due to exposure of gases. *n*- Type semiconducting materials such as stannous oxide, zinc oxide, titanium dioxides are promising materials for gas and humidity sensors [1-9].

$ZnNb_2O_6$ is a highly insoluble and thermally stable source suitable for glass, optic, and ceramic applications. An ideal gas sensor should have the ability to discriminate different gases, and for this purpose ZnO and $ZnNb_2O_6$ are most promising materials.

Basic requirement for the sensor is its change in electrical conductivity with exposure of LPG to surface of semiconducting oxides which depends on their band gaps, surface morphology, size, diffusion rate of gas and specific surface area [10]. The semi-conductive properties of metal oxides represent the basis for their use as gas sensors, since the number of free charge carriers within the metal oxide and thus its electrical conductivity reversibly depends on the interactions with the ambient gas atmosphere [11].

For sensor application of nanostructured materials the charge transfer either results from adsorption or chemisorptions of gas molecules at the sensor surface, or from diffusion of the gas into the bulk of the sensor material [12]. Since the sensing mechanism is based on the chemisorptions reaction that takes place at the surface of the metal oxide, so increasing specific surface area of the sensitive film leads to more sites for adsorption of surrounding gases.

The sensing mechanism of the reducing gases consists in the change of the electrical resistance resulting from chemical reaction between the gas molecule and adsorbed oxygen on the metal oxide surface [13,14,15]. The state and amount of the oxygen adsorbed on the surface of materials are strongly dependent on the microstructure of the materials, namely, specific surface area, particle size as well as surface morphological structure. As the sensing phenomenon mainly takes place on the surface of sensing element, the surface morphology has an essential role on the sensitivity of sensor. Also, the sensitivity of the sensor depends on the method used to produce nanoparticles, with the efficiency of the chemical sensor increases as particle size decreases [2].

2. Synthesis of Material

ZnO was prepared by conventional precipitation method [1]. Powder of niobium oxide was chemically mixed with pure zinc oxide in 100 mL isopropyl alcohol as a solvent. Both solutions were mixed properly and stirred for 2 h. Some drops of poly ethylene glycol-400 (PEG-400) was added which works as capping agent and prevents the grain growth during precipitation process. After that the solution is sonicated for 20 minutes using ultrasonic machine and after vigorous stirring for 8 h, it

was filtered and dried. Later $ZnNb_2O_6$ nanocomposite in the form of powder was obtained.

2.1. Fabrication of Thick Film

A thick film of the sample was prepared by screen printing method on taking glass as a substrate. For this purpose, the synthesized powder was dissolved in isopropyl alcohol and this was sonicated for 15-20 min. The sonicated solution was stirred at 80°C for 6 h. Then the paste of material was formed. This paste was used for fabrication of thick film using screen printing technology. Took the paste of sample and it was screen printed on glass substrate. The resulting film was drying at 120°C for 4 h. This drying procedure stabilizes the film. Further the film was annealed at 400°C which converts the film as sensing material. The film was almost uniform and the thickness of the film was found 2 μm measured by Accurion variable angle spectroscopic ellipsometer (Nanofilm EP3 Imaging). Further we took the silver paste and deposited it on opposite sides of the film for signal registering.

Two Ag wires were inserted in top of the film. The resistance was measuring using Keithley Electrometer [Model: 6514]. Sensing films with silver contacts was used for LPG sensing measurements.

3. Characterizations of $ZnNb_2O_6$

3.1. Scanning Electron Microscopy (SEM)

Figure. 1(a), 1(b) and 1(c) show Scanning Electron Micrographs of thick film of $ZnNb_2O_6$ nanocomposite at different scales i.e. 300 nm, 1 μm and 10μm respectively. The SEM images reveal that prepared film have clusters of crystallites over the entire surface of the material. The porosity of the material is an imperative parameter regarding gas sensing point of view as the film has a number of active sites. A close look at scanning electron micrographs reveals material is porous in nature therefore; the prepared film adsorbs more gas through the surface which causes changes in the resistance of the sensing film. The average size of pores was calculated by using Scanning Electron Micrographs. The average size of pores of nanocomposite $ZnNb_2O_6$ was found to be 4 μm.

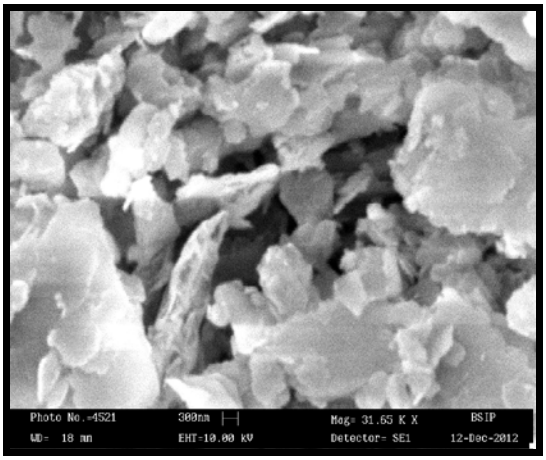

Figure 1 (a). Scanning electron micrographs of thick film of $ZnNb_2O_6$ nanocomposite at 300 nm scale

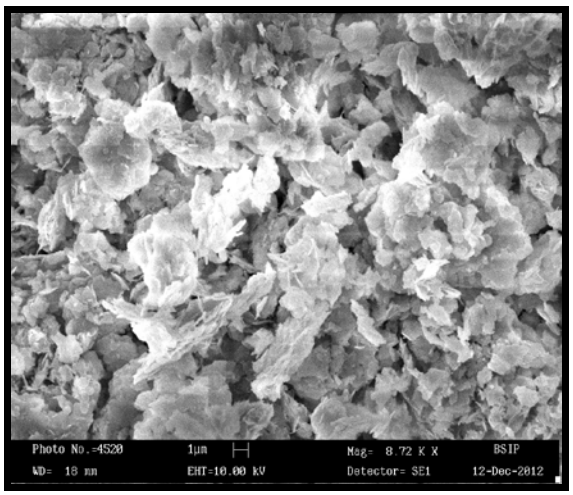

Figure 1 (b). Scanning electron micrographs of thick film of $ZnNb_2O_6$ nanocomposite at 1 μm scale

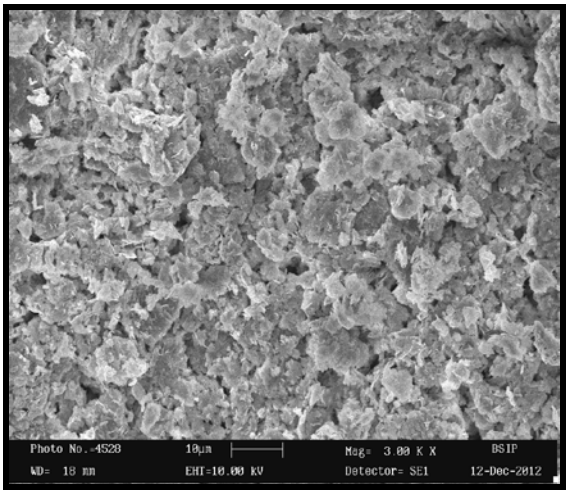

Figure 1 (c). Scanning electron micrographs of thick film of $ZnNb_2O_6$ nanocomposite at 10 μm scale

3.2. X-Ray Diffraction

X-Ray diffractions show extent of crystallization of the sample. The average crystallite size (D) of the sensing material can be calculated by the Debye-Scherrer's formula, which is given by

$$D = K\lambda / \beta\cos\theta$$

where K= 0.94 is Scherrer's coefficient, which depends on the shape of the crystallite and the type of defects present, λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the angle of diffraction. Figure 2 shows the XRD patterns of samples prepared at room temperature shows that the synthesized material is pure and less crystalline.

XRD patterns of the zinc niobium oxide composite prepared at room temperature reveals that the sensing material consists of larger peaks of $ZnNb_2O_6$ along with a few peaks of Nb_2O_5 and ZnO. The average value of crystallite size of $ZnNb_2O_6$ calculated from Scherrer's formula is found to be 25 nm.

The zinc niobium oxide nanocomposite having 25 nm crystallite sizes provide large surface to volume ratio hence the ability for exposure of gas through the surface of the film increases which enhance the sensitivity of gas sensor.

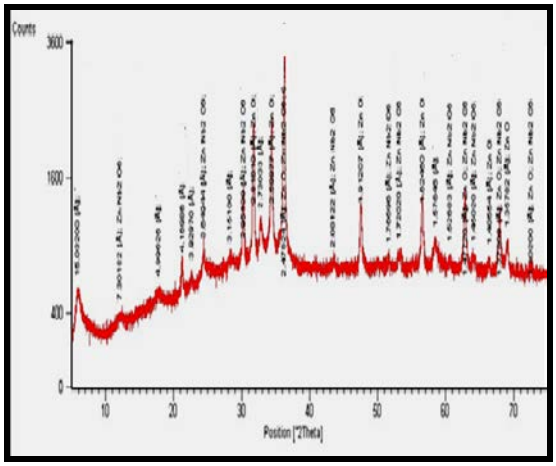

Figure 2. X-Ray Diffraction of synthesized $ZnNb_2O_6$ nanocomposite prepared at room temperature

4. Gas Sensing Measurements

The schematic diagram of LPG sensing set-up is shown in Figure 3 (a). The sensing film was inserted between the silver electrodes inside the glass chamber having two knobs. One knob is associated with the concentration measuring system (gas inlet) and other is an outlet knob for releasing the gas. Concentration measuring system is shown in Figure 3 (b), which consists of a glass bottle containing double distilled water, which is saturated with LPG, in order to avoid the possibility of dissolution of inserted gas. At the top of the bottle, the measuring tube (pipette) is connected by vacuum seal. The cock I is connected to the LPG cylinder and cock II is connected to the inlet of the gas chamber. When the cock I is opened, the LPG from the cylinder is filled in the glass bottle and an equivalent amount of water is displaced in the measuring pipette. When the cock II is opened, a desired amount of gas e.g. 1, 2, 3 vol.% and onwards is entered in the gas chamber. Before passing the LPG in the chamber, the gas chamber with resistance measuring holder was stabilized for 10-15 minutes.

The stabilized resistance of the film was taken as stabilized resistance in the presence of air (R_a). Now this was exposed with LPG and variations in resistance with the time for different vol % of LPG were recorded by using Keithley electrometer (Model: 6514).

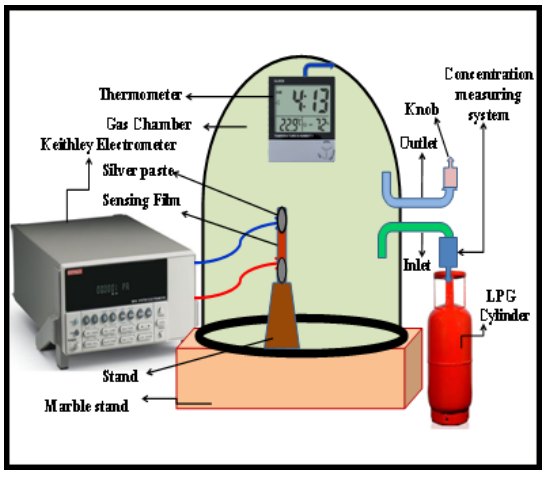

Figure 3 (a). Experimental-set-up

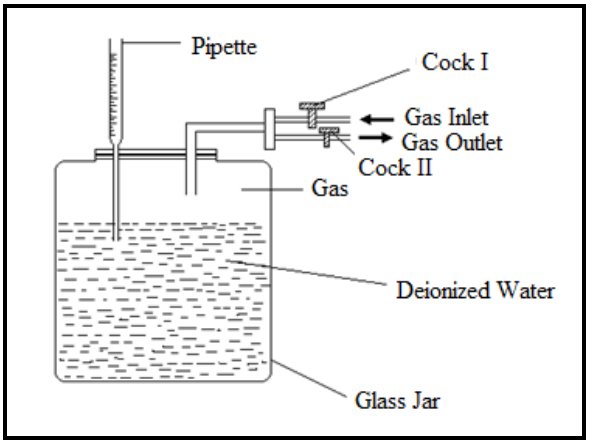

Figure 3 (b). Concentration measuring system

Sensitivity of the LPG sensor is defined as the change in resistance in the presence of gas (R_g) to the resistance in presence of air (R_a) that is

$$S = R_g / R_a$$

Figure 4 illustrates variations in resistance of the film with time after exposure for different vol.% of LPG at room temperature. Curve for 1 vol% of LPG show small variation in resistance with time after exposure. Curve for 2 & 3 vol% of LPG exhibits improved response and has better sensitivity than 1 vol%. Further, for 4 vol% of LPG resistance increases sharply with time after exposure up to 1000 s and then become constant.

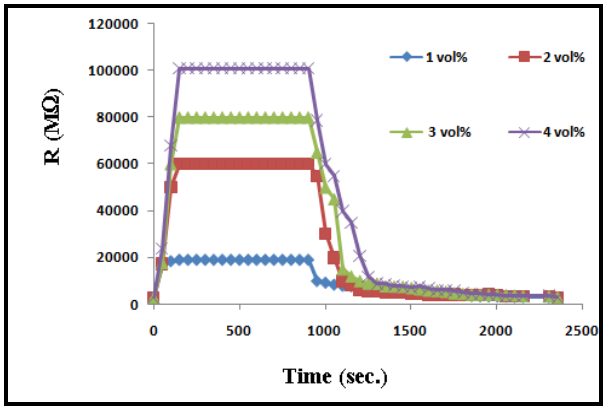

Figure 4. Variations in resistance of $ZnNb_2O_6$ nanocomposite with time after exposure for different vol% of LPG

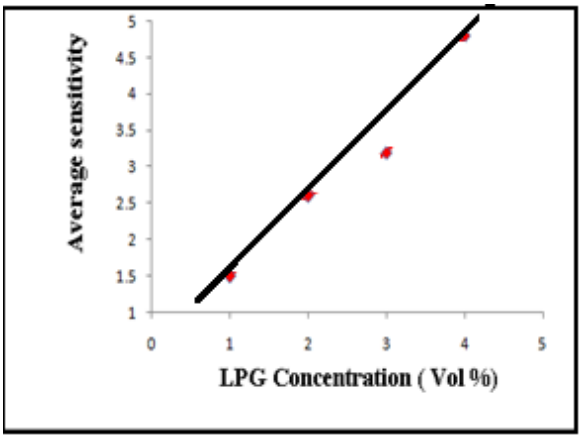

Figure 5. Variations of average sensitivity of $ZnNb_2O_6$ nanocomposite with different concentrations of LPG

Figure 5 exhibits the variations of average sensitivity with concentration of LPG and it was found that as the concentration of LPG (in vol%) increases, the average sensitivity of sensor increases linearly upto vol% of LPG later it increases slowly. The linear increment of the sensitivity of the sensor is a significant factor for device fabrication. The maximum sensitivity was obtained for 4 vol% of LPG and is ~ 4.8.

The gas sensing mechanism of $ZnNb_2O_6$ nanocomposite based sensor belongs to surface controlled type, i.e. resistance change is controlled by surface area and the amount of chemisorbed oxygen. LPG consists of CH_4, C_3H_8 and some hydrocarbon. In each composition, the reducing hydrogen species are bound to carbon atom therefore LPG dissociates into the reactive reducing components hardly on the surface of the sensing element. As LPG exposed to sensing element, the conductivity decreases due to adsorption of oxide and release of more electrons that contribute to enhance current. It was observed that as the concentration of LPG increases, the average sensitivity increases linearly in the beginning and later it becomes saturated. The linear relationship between sensitivity and gas concentration may be attributed to the availability of sufficient number of sensing sites on the film to act upon the LPG. The low concentration implies a lower surface coverage of gas molecules, resulting in a lower surface reaction between the surface adsorbed oxygen species and the gas molecules. The increase in LPG concentration increases the surface reaction due to a large surface coverage. Further increase in the LPG concentration does not increase the surface reaction and eventually saturation takes place.

Thus, the maximum sensitivity was obtained at higher concentration of LPG i.e. 4 vol.%. The linearity of average sensitivity for the LPG suggests that the screen printed $ZnNb_2O_6$ nanocomposite film can be reliably used to monitor the LPG over this range of concentration As the lower explosive limit (LEL) for LPG is 4.0 vol. % [16] therefore, response is measured up to 4.0 vol. % in order to detect the LPG below LEL for safety requirement.

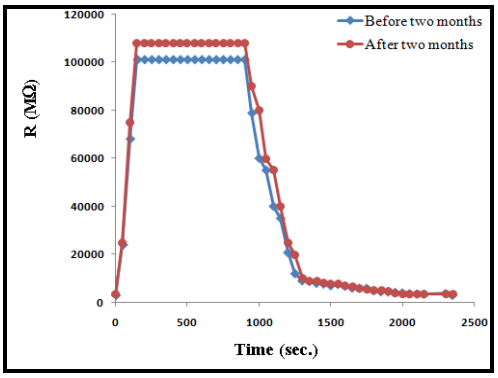

Figure 6. Reproducibility curve of sensor after two month

Figure 6 shows the reproducibility curve of sensor after two month. It was found that after two month, it performs 90% of its initial performance.

5. Conclusion

We have successfully synthesized $ZnNb_2O_6$ nanocomposite via hydrothermal precipitation method. It was found that the sensing film of material works as a good LPG sensor at room temperature and maximum average sensitivity of this sensor is found 4.8 for 4 vol % LPG. As detection of Liquefied petroleum gas is very important for disaster management purpose that's why this study is quite appreciable for commercial applications. Good sensitivity, reproducibility and stability demonstrate the promise of this sensor for LPG determination in the industrial and environment monitoring. Thus, this study demonstrates the possibility of utilizing $ZnNb_2O_6$ nanocomposite film as a sensing element for the detection of LPG.

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References

[1] R Srivastava, B C Yadav, C. D. Dwivedi, R. Kumar, Comparative Study of Moisture Sensing Properties of ZnO nanomaterials through hydroxide route by mixing drop wise and Sudden *Sens. Trans. J.* 80, 1295, 2007.

[2] D R Patil, L A Patil, Room temperature chlorine gas sensing using surface modified ZnO thick film resistors, *Sens. Actuators B: Chem.* 123, 546, 2007.

[3] A M More, J L Gunjakar, C D Lokhande, Liquefied petroleum gas (LPG) sensor properties of interconnected web-like structured sprayed TiO_2 films, *Sens. Actuators B: Chem.* 129, 671, 2008.

[4] Richa Srivastava and B.C. Yadav**,** Nanaostructured ZnO, ZnO-TiO_2 and ZnO- Nb_2O_5 as solid state humidity sensor**,** *Advanced Material Letters*, 3, 197, 2012.

[5] V R Shinde, T P Gujar, C D Lokhande, LPG sensing properties of ZnO fims prepared by spray pyrolysis method: Effect of molarity of precursor solution *Sens. Actuators B: Chem.* 120, 551, 2007.

[6] D R Patil, L A Patil, G H Jain, M S Wagh, S A Patil, Surface Activated ZnO Thick Film Resistors for LPG Gas Sensing, *Sens. Trans. J.* 74, 874, 2006.

[7] B. C. Yadav, R. Srivastava and Anuradha Yadav, Nanostructured Zinc Oxid Synthesized via Hydroxide Route as Liquid Petroleum Gas Sensor, *Sensors and Materials* 21, 87, 2009.

[8] G N Chaudhari et al *Indian Journal of Physics*, Sensitivity and selectivity of chemically modified nanosized SnO_2 based CO sensors, 79, 1157, 2005.

[9] G T Lamdhade, S S Yawale, S P Yawele, TiO_2- MgO Mixed Oxide Humidity Sensors, *Indian Journal of Physics* 76, 399, 2002.

[10] S C Yeow, W L Ong, A S W Wong, G W Ho, Template-free synthesis and gas sensing properties of well- controlled porous tin oxide nanospheres, *Sens. Actuators B*, 143 295, 2009.

[11] N Barsan, U Weimar, Understanding the fundamental principles of metal oxide based gas sensors; the example of CO sensing with SnO_2 sensors in the presence of humidity *J. Phys. Condens. Matter* 15, R813, 2003.

[12] N Yamazoe, K Shimanoe, Receptor Function and Response of Semiconductor Gas Sensor *J. Sens.* Article ID 1 875704, 2009.

[13] N Barsan, U Weimar, Conduction Models in Gas-Sensing SnO_2 Layers: Grain-Size Effects and Ambient atmosphere Influence *J. Electrocer*., 7, 143, 2001.

[14] Y. Xiaojuan, C. Naisheng, S. Shuifa, L. Ersheng and H. Jinling, Preparation, characterization and gas sensitive properties of nano-crystalline Cr_2O_3- Fe_2O_3 mixed oxides, Sci. in China 41, 442, 1998.

[15] G. Sberveglieri, L.E. Depero, M. Ferroni, V. Guidi, G. Martinelli, P. Nelli, C. Perego and L. Sangletti, A novel method for the preparation of nanosized TiO_2 thin films, *Advan. Mater.* 8, 334, 1996.

[16] B.C. Yadav, A. Yadav, T. Shukla and S. Singh, Experimental investigations on solid state conductivity of cobaltzincate nanocomposite for liquefied petroleum gas sensing, *Sens. Lett.* 7, 1, 2009.