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Nanocrystalline Pure and Modified $ZnSnO_3$ Perovskite: A Novel Material for Gas Sensing

Manisha S. Pande [1], V.D. Kapse [2]

Assistant Professor, Department of Physics, Shri Sant Gajanan Maharaj College of Engineering, Shegaon, Maharashtra, India [1]

Assistant Professor, Department of Physics, Arts, Science and Commerce College, Chikhaldara, Maharashtra, India [2]

ABSTRACT: Nanocrystalline powder of pure $ZnSnO_3$ structure and average crystallite size 11.3 nm was synthesized by co-precipitation method. The as-prepared powder sample was characterized by using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Thick films of $ZnSnO_3$ were fabricated by using screen printing technique. Surface modified $ZnSnO_3$ based thick films were fabricated by dipping method which was followed by firing. Surface morphology and elemental analysis of pure and surface modified nanocrystalline $ZnSnO_3$ thick films was studied by using FESEM with EDAX respectively. The response of pure $ZnSnO_3$ and surface modified $ZnSnO_3$ to different oxidizing gases like Cl_2, NO_2, H_2S, SO_2 and CO was investigated. The pure $ZnSnO_3$ exhibited high response response to 100 ppm towards nitrogen dioxide (NO_2) gas at an operating temperature 200^0C. MgO modified $ZnSnO_3$ (5 min), as compared to pure $ZnSnO_3$, demonstrated enhanced response towards NO_2 gas at an operating temperature 200^0C. The selectivity of the sensor elements for various target gases was studied.

KEYWORDS: Nanocrystalline, $ZnSnO_3$, Thick film, X-ray diffraction, Sensor response.

I. INTRODUCTION

Due to the emission of various toxic and hazardous gases, human body suffer from different diseases like lowering of haemoglobin levels, affects the nervous system and may cause mental retardation, headaches, blindness and hypertension. In day today modern life detection of different gases plays a vital role. Gas sensing has become a significant area of research that leads to the development of extremely reactive gas sensing devices able to detect various toxic and hazardous gases. It is supposed that the demand for toxic and deleterious gases is urgent to change human nose. A lot of gas detecting systems have recently been used in process control and laboratory analytics [1-4].

On solid-state gas sensor many types review papers have been published [5-9]. Nitrogen dioxide (NO_2) exposure is now essential target for different crucial processes in an environment. This gas can be very dangerous for human bodies when its concentration in an environment increases hence now a day NO_2 monitoring and controlling is essential. Semiconductor gas sensors (SMO) in the type of thin or thick films, based on metal-oxides like p–n heterojunctions, have been usually reported in the literature for NO_2 detection [10-16]. Basic characteristics of SMO gas sensor are sensitivity, selectivity and durability. In sort to achieve high sensor response and good selectivity, various factors such as nanostructure control, addition of dopant, operating temperature, gas concentration, etc. have been adopted to enhanced the gas sensing properties of SMO gas sensors. In nanostructure particles, a huge portion of the atoms exist at the surface, and therefore, the surface properties exposed to be foremost. The use of nanostructure particles in SMO gas sensors is touching interest in the scientific area [17-20]. Zinc Stannate ($ZnSnO_3$) perovskite has received interest for a variety of applications due to its scientific properties. $ZnSnO_3$ has a perovskite structure of the general formula ABO_3. $ZnSnO_3$ in recent times drawn attention in the research area due to its potential applications in gas sensors, electronic devices, solar cells, plating additives, optoelectronics, etc. [21-25].

In this paper, preparation of pure $ZnSnO_3$ nanocrystalline powder by a simple chemical route, fabrication of $ZnSnO_3$ based thick films and it surface modification by dipping method has been reported. Their gas sensing properties to carbon dioxide (CO_2), carbon-monoxide (CO), nitrogen-dioxide (NO_2), sulphur dioxide (SO_2), chlorine (Cl_2) and hydrogen sulfide (H_2S) were investigated.

II. EXPERIMENTAL DETAILS

2.1. Preparation of nanosized pure $ZnSnO_3$

The synthesis of $ZnSnO_3$ was done by using stoichiometric molar amount of analytically pure grade [$ZnSO_4.7H_2O$] and [$SnCl_4.5H_2O$] aqueous NaOH. The solution was continuously stirred by magnetic stirrer for 1h to obtain a

homogeneous clear solution. Then aqueous NaOH was added drop wise at room temperature under rapid stirring till pH becomes 9. This precipitate was filtered and followed by washing with ethanol and distilled water for several times then precipitate were dried at 120°C in oven. The dried sample was calcined at 800°C for 6 h in muffle furnace to obtain nanoparticles of $ZnSnO_3$.

2.2. Fabrication pure and surface modified $ZnSnO_3$ thick films

$ZnSnO_3$ thick films were fabricated on glass substrate by using screen printing technique. The details of fabrication of thick films by using screen printing techniques are already published in our earlier publications [26].

Pure $ZnSnO_3$ thick film was modified by dipping them into a 0.01 M aqueous solution of magnesium chloride ($MgCl_2.6H_2O$) for different intervals of time (5 min). Surface activated films are termed as MgO modified $ZnSnO_3$ thick films. Silver contacts were made for electrical measurements.

2.2. Materials characterization

The XRD patterns were recorded on X-ray diffractometer (PANanalytical X' Pert-Pro) using a Cu-K_α mono chromatized radiation source and filtered in the range $2\theta = 10^o - 90^o$. The average crystalline size (D) was calculated according to the Debye-sheerer equation: $D=K\lambda/B\cos\theta$; where B is the full width at half-maximum intensity of a peak at an angle θ, K is a constant, λ is the wavelength of the X-ray source.

In this investigation FESEM has been done with JEOL JSM -7610F which is operated at 30 kV. The images obtained were used to analysis the particle morphology, film surface topography and grain size etc. In this study, the TEM was recorded by using Hitachi (H-7500) 120 kV is equipped with CCD camera. This instrument has the resolution of 0.36 nm with 40-120 kV operating voltage.

2.3. Test system and gas sensing measurement

To test the gas sensing response, the sensor was loaded into a gas sensing chamber. The concentration within the chamber was increased by adding a particular quantity of gas. Gas mixing is performed via a volumetric method. For designing a gas sensor a variety of factors must be focussed such as the materials sensitivity and material sensitivity. The sensing parameters of the sensor were analysed at different concentrations (ppm) and temperature. The sensing response is given as,

$$S\ (\%) = R_g\text{-}R_a/R_a \times 100$$

Where, R_g is the sensor resistance in the gas, R_a is the sensor resistance in the air.

By using gas sensing setup the fabricated sensors were tested. For absorption of the moisture of material, preheating is necessary condition which gives the stable data collection. The concentration of test gases sensor was tested for the nitrogen dioxide (NO_2), chlorine (Cl_2) carbon mono oxide (CO), hydrogen sulfide (H_2S), sulphur dioxide (SO_2) and nitrogen dioxide (NO_2) gases.

III. RESULTS AND DISCUSSION

3.1. Materials characterization

Figure 1 depicts XRD pattern of nanocrystalline $ZnSnO_3$ powder synthesis by co precipitation method. XRD pattern shows the rhombohedral perovskite structure in accordance with JCPDS card no. 00-052-1381. For $ZnSnO_3$ the characteristic peaks for rhombohedral perovskite structure. XRD pattern of $ZnSnO_3$ shows that all the diffraction peaks can be assigned to rhombohedral $ZnSnO_3$ with lattice parameters a=b=5.283(4) Å and C=14.091(4) Å and $\alpha=\beta=90^o$, $\gamma=120^o$ and volume of cell is 340.66Å^3.

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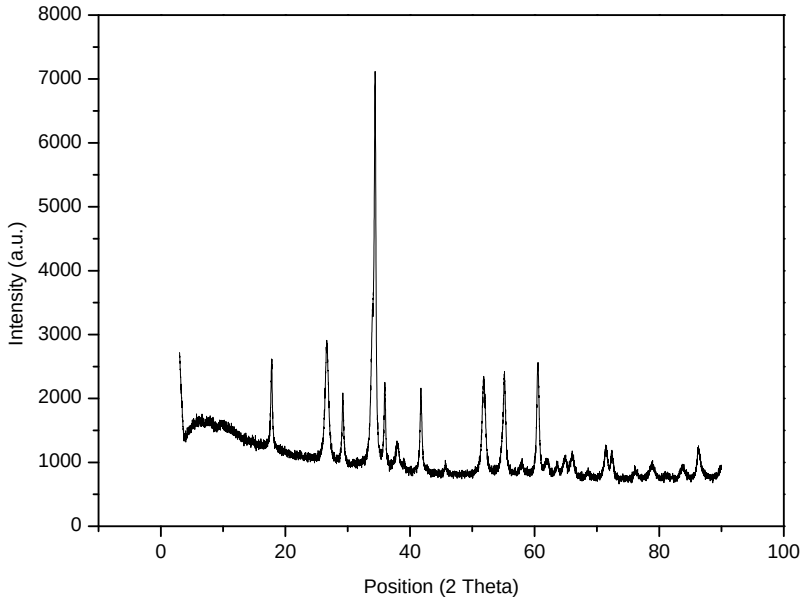

Fig. 1 : X-ray diffraction pattern of $ZnSnO_3$ powder calcinated at 800°C.

The morphology of synthesized $ZnSnO_3$ nanopowder was examined with the help of transmission electron microscopy (TEM). TEM images of nanocrystalline $ZnSnO_3$ powder calcined at 800°C is shown in figure 2 crystalline size can be revealed 13 nm to 18 nm. The average crystalline size calculated from the XRD data agrees with the TEM results. The small amount of agglomerations is observed in the micrograph.

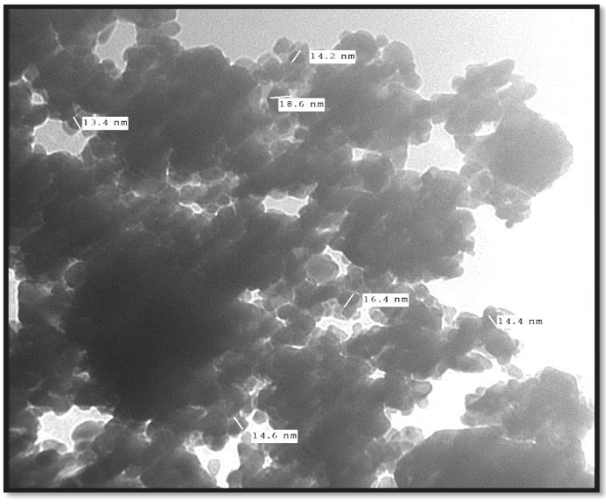

Fig. 2: TEM image of pure $ZnSnO_3$ calcinated at 800°C.

Figure 3 shows the field emission scanning electron microscope (FESEM) images of nanostructured pure $ZnSnO_3$ and MgO modified $ZnSnO_3$ (5 min). FESEM analysed the surface morphology of thick film. Figure 3 shows a few particles are in the range of 22 nm - 32 nm, 36nm - 37 nm and 39 nm - 40 nm could be clearly seen and some agglomerates are formed. Nanostructure and surface area are most main factor that affects the sensor characteristics. High porosity increase surface to volume ratio thus help in getting excellent sensitivity.

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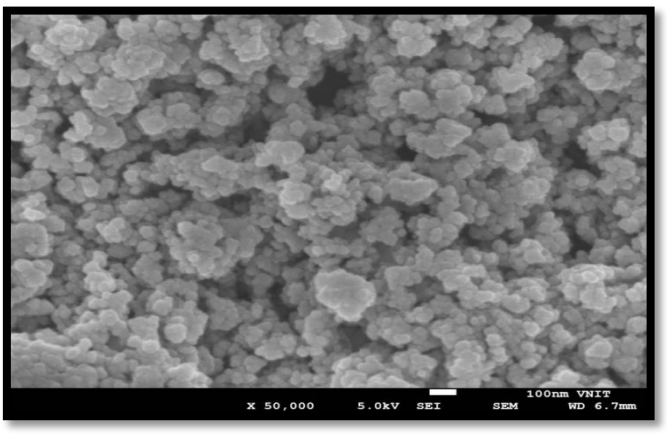
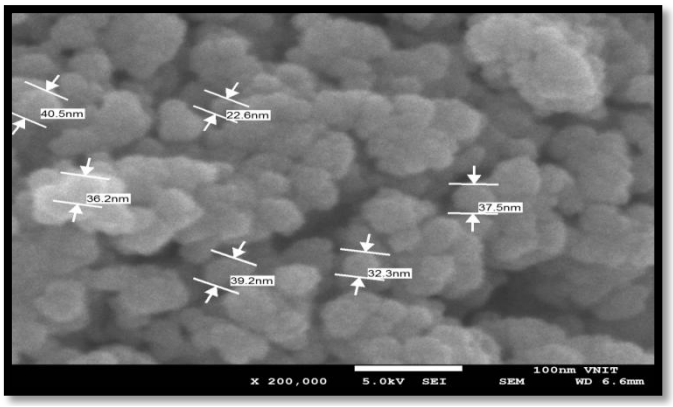


(a)



(b)

Fig.3 : FESEM images of nanocrystalline (a) pure $ZnSnO_3$ (g) MgO modified $ZnSnO_3$ (5min) based thick films.

3.2. Gas sensing properties

The gas sensing properties of pure and modified $ZnSnO_3$have been studied towards CO, Cl_2, SO_2, H_2S and NO_2. The gas sensing property studied for various concentration of NO_2 gas at operating temperature 200^oC. Both adsorption and combustion of the oxidizing gases occur on the surface of the sensors.

The response of the $ZnSnO_3$ film towards NO_2 was measured at different operating temperature and results are shown in figure 4. From figure it is clearly seen that the sensor response of $ZnSnO_3$ towards NO_2 gas increase with the increasing temperature and reaches to a maximum value. And thereafter it decreases with the increasing operating temperature. From figure, it can be observed that $ZnSnO_3$ exhibited maximum response 25 to 100 ppm NO_2 at 200^oC.

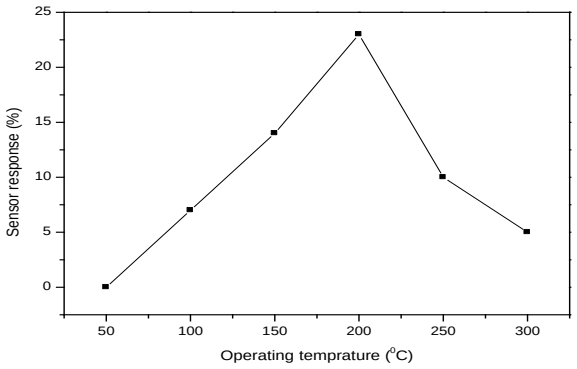


Fig. 4: Sensor response of $ZnSnO_3$ based thick film sensor towards NO_2 gas.

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Sensor response of pure $ZnSnO_3$ to different oxidizing gases like nitrogen dioxide (NO_2) , Chlorine (Cl_2), carbon monoxide (CO), sulpur dioxide (SO_2) and reducind gas hydrogen sulfide (H_2S) at 200°C operating temperature were studied. It is observed that the sensing responses to different gases go through maxima at different operating temperature. For 100 ppm NO_2 sensor response maximum at 200°C as compared to other test gases. The responses of pure $ZnSnO_3$ to NO_2, Cl_2, CO, SO_2, and H_2S at 200°C is shown in figure 5.

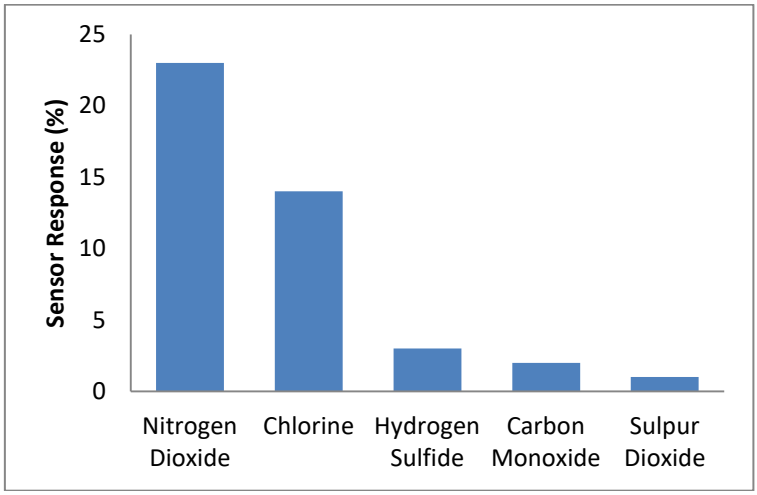

Fig. 5 : Sensor response of $ZnSnO_3$ towards different gases at 200°C.

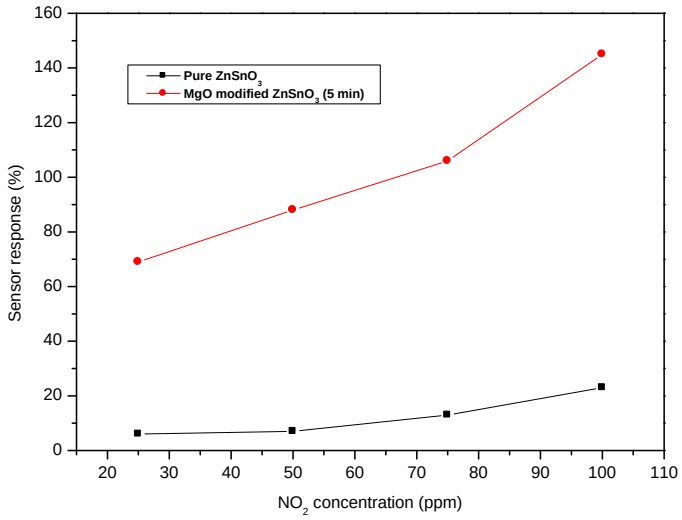

Fig. 6 : Sensor response of pure $ZnSnO_3$ and MgO modified $ZnSnO_3$ (5 min) based thick film sensor as a function of NO_2 concentration.

Figure 6 reveal the relationship between the response of pure $ZnSnO_3$ and MgO modified $ZnSnO_3$ (5 min) to different NO_2 concentration. It can be seen that MgO modified $ZnSnO_3$ (5 min) exhibits the excellent response 100 ppm NO_2 at 200°C. Excellent response of MgO modified $ZnSnO_3$ (5 min) towards NO_2 due to enhancement of surface adsorption property. The gas sensing mechanism of $ZnSnO_3$ film and NO_2 gas is established by a potential barrier form. Number of majority charge carriers at the boundary of gas and solid reduces as the electrons are taken from ionized donors through conduction band hence there is formation of a surface barrier for electrons. Due to enhance of the number of oxygen ions on the surface the additional oxygen adsorption is inhibited. It is noted that, there is sudden enhancement in the resistance of $ZnSnO_3$thick film due to exposure of NO_2 gas molecules. Such increased in the resistance of $ZnSnO_3$ thick film due to the adsorption of NO_2 gas on the surface of $ZnSnO_3$ thick film as well as the successive reactions between them. $ZnSnO_3$ is n-type semiconductor, once it interacts with oxidizing gas i.e. NO_2

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which is electron accepter then adsorption of oxygen leads to detaching of electrons. So there is decrease in charge carrier density of $ZnSnO_3$, which enhanced the potential barrier height. As the electrons density (majority carrier) of $ZnSnO_3$ gets decreased due to electron accepting nature of NO_2 gas which leads to decrease in the conductivity of material and hence sensors resistance increases.

IV. CONCLUSION

Co-precipitation method was used to synthesis nanocrystalline powder $ZnSnO_3$ powder samples with different preparation parameters followed by calcination at 800°C. This synthesis method is simpler and more capable compared to some of the other techniques. The precursor on heating yields nanocrystalline $ZnSnO_3$ particles. The effects of the preparation parameters, such as the reaction time and temperature, precipitation agents, calcinations temperature and time on the formation of composites were investigated. Nanoparticles were characterized by an different experimental techniques. XRD patterns showed the formation of nanocrystalline rhombohedral structure of prepared samples. The crystallite size were calculated by Scherrer formula which is found to be 11.3 nm. The average crystallite size of sample estimated from XRD analysis concurs with TEM investigation. Nanocrystalline pure and modified $ZnSnO_3$ thick films were fabricated by screen printing technique on glass substrate and by dipping method surface of $ZnSnO_3$ was modified by MgO. By using scanning electron microscopy with energy dispersive X-ray analysis (FESEM), the surface morphology confirm the $ZnSnO_3$ modified by MgO. The gas sensing property of $ZnSnO_3$ towards different gases like Cl_2, NO_2, H_2S, SO_2 and CO was studied. $ZnSnO_3$ thick film sensor exhibited maximum response to 100 ppm NO_2 at 200°C with quick response. The enhancement in the sensing response of MgO modified $ZnSnO_3$ (5 min) attributed to its smaller crystallite size.

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