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Studies on sensing properties of nanostructured Zn_2TiO_4

Jain Gotan H[1], Bongarde Ruturaj R[2], Musale Digvijay B[2] and Nikam Latesh K[2*]

[1]Shreeman P H Jain Science College , Chandwad , Nashik -423101
[2]PDEA'S Baburaoji Gholap College Sangvi, Pune-411027
*Corresponding author: latesh.nikam@gmail.com

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ABSTRACT

Zn_2TiO_4 is functional material having wide applications like sensors, solid oxide fuel cell, thermoelectric material and regenerable catalyst. Hence we have synthesized Zn_2TiO_4 by combustion method at 650 ^{0}C. The as synthesized compounds were characterized by UV-DRS and XRD techniques. The gas sensing properties as synthesized compounds were tested for NH_3, H_2S, Ethanol, CO_2, Cl_2, CO, H_2, and LPG. Nanostructured Zn_2TiO_4 showed maximum sensing response for NH_3 gas at 300 ^{0}C (23.36 ppm) The sensing performance was tested using static gas system.

Keywords Combustion method, Gas sensors, NH_3 and H_2S.

INTRODUCTION

Metal oxides gas sensors are widely used because of their high sensitivity, fast response, low cost stability and accuracy but selectivity is very limited. Zinc titanates has been applied in many fields such as paint, pigments, sensors, photocatalysis etc [1,2]. $ZnTiO_3$ has been applied as gas sensor but use of Zn_2TiO_4 as gas sensors has been less explored. In this work it has been attempted to synthesize Zn_2TiO_4. As synthesized were characterized by UV-DRS, IR, XRD, FESEM and TEM techniques. The gas sensing properties as synthesized compounds were tested for NH_3, H_2S, Ethanol, CO_2, Cl_2 CO H_2, and LPG.

METHODOLOGY

Synthesis of Intermediate for synthesis of Zn_2TiO_4:
Aqueous solution of 0.03 mole (6.5847 g) Zinc acetate and 0.015 mole (5.3118 g) Potassium Titanium oxalate were prepared. Then 30 ml 30 % 20 vol H_2O_2 was added into aqueous solution of potassium titanium oxalate. To the orange color solution formed Zinc acetate solution was added drop wise, yellow precipitate formed during addition of zinc acetate solution. Decolorization of solution part observed after stirring mixture for 6 h which ensures the completion of the reaction . Product obtained was filtered and washed with hot water followed by methanol and kept under IR lamp for 3hr. Then yellow product obtained was dried at 120 ^{0}C for 3 hr.

Synthesis of Zn2TiO4 **by combustion method**.
2.45g intermediate, 1.2 g urea, 3.2 g ammonium nitrate , 4.5 g glycene and 3 g starch are mixed uniformly to form paste. Paste formed was added stepwise into combustion tube at 600 ^{0}C. Burning takes place followed by formation of white residue the bottom. Heating further continued for 2 hrs.

Characterization:
As synthesized intermediates and Zinc titanates were characterized by UV-DRS (Perkin Elmer), XRD (Bruker, D-8)

XRD pattern depicted in figure 1 reveals that as synthesized compound possess tetragonal crystal structure (JCPDS 2002, 86-0158, a= 6.000 A° , b= 8.415 A°)

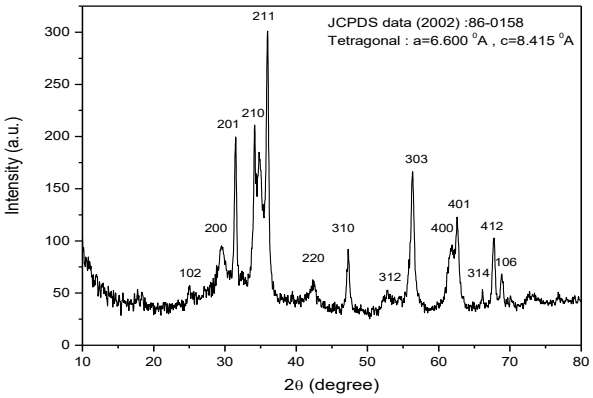

Figure 1: XRD pattern of nanostructured Zn_2TiO_4

UV-DRS absorption spectral study (Figure 2) indicates that band gap of as synthesized nanostructured Zn_2TiO_4 is having band gap 3.19 eV.

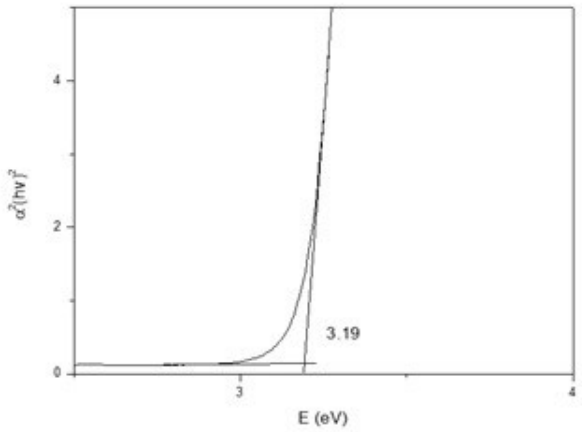

Figure 2: UV-DRS absorption Tauc plot of Zn_2TiO_4

Preparation of Zn_2TiO_4 thick film
The thixotropic paste was formulated by mixing the fine powder of Zn_2TiO_4 with a solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate, terpineol, etc. The ratio of the inorganic to organic part was kept at 75:25 in formulating the paste. This paste was screen-printed[1] on glass substrate in the desired pattern. The films were fired at 550 ˚C for 30 min.

Gas sensing properties of Zn_2TiO_4 thick film
The sensing performance of the sensors was examined using a 'static gas sensing system' explained elsewhere [3].

RESULTS AND DISCUSSION

Basic gas sensing characteristics
The basic gas sensing characteristics of Zn_2TiO_4 thick film was investigated as a function of operating temperature and test gas concentration. In the present studies the films were characterized by various parameters such as sensitivity, selectivity and response and recovery time.

The sensitivity (S) is defined as

$$S = \frac{(Ra - Rg)}{Ra} = \frac{\Delta R}{Ra}$$

where R_g is the resistance in presence of test gas and R_a is the film resistance in dry air, measured at respective temperatures [4,5] . A positive value of *S* implies film resistance decreases on gas exposure and vice versa.

The selectivity or specificity of a sensor towards an analyzing gas is expressed in terms of dimension that compares the concentration of the corresponding interfering gas that produces the same sensor signal. This factor[5] is obtained by

Selectivity = (Sensitivity of the sensor for interfering gas)/(Sensitivity towards the desired gas)

The response time is the time interval over which resistance attains a fixed percentage (usually 90%) of final value when the sensor is exposed to full scale concentration of the gas. A small value of response time is indicative a good sensor.

The recovery time is the time interval, over which resistance reduces to 10% of the saturation value when the sensor is exposed to full scale concentration of the gas and then placed in the clean air. A good sensor should have a small recovery time so that sensor can be used again and again.

Sensitivity of Zn_2TiO_4 thick film to various gases with operating temperature

Figure 3 shows the variation of sensitivity of the Zn_2TiO_4 thick film to various gases (800 ppm) with operating temperature ranging from 50 to 450 °C. For NH_3, the sensitivity goes on increasing with operating temperature, attains its maximum (23.36 ppm) at 300 ˚C and then decreases with a further increase in operating temperature. It is clear from the figure that, the sensor gives the maximum sensitivity to to H_2S (11.87 ppm) at 350 °C and Cl_2 (9) at 300 ˚C. The sensor selects a particular gas at a particular temperature. Thus by setting the temperature, one can use the sensor for particular gas detection. The same sensor could be used for the detection of different gases by operating it at particular temperature for a typical gas. This can be attributed to different chemical re-activities of different gases on the sensor surface. Different gases have different energies for adsorption, desorption and reaction on the metal oxide surface, and therefore the response of the sensor at different temperatures would depend on the gas being sensed.

The amount of oxygen adsorbed (O_2^-, O^-, O^{2-}) on the sensor surface goes on increasing with an increase in temperature, reaches to the maximum and then decreases with a further increase in operating temperature. The response to the gas to be detected follows the same behavior. When a reducing gas comes in contact with the sensor surface, it gets oxidized. The rate of oxidation would be the function of the amount of adsorbed oxygen on the surface and the type of gas to be detected. The larger the rate of oxidation, the larger would be the number of electrons released, and in turn the larger would be the gas response. At higher temperatures (beyond about 300 °C), the amount of oxygen adsorbed would be smaller, leading to a slower rate of reduction of a target gas and, therefore, the smaller gas response.

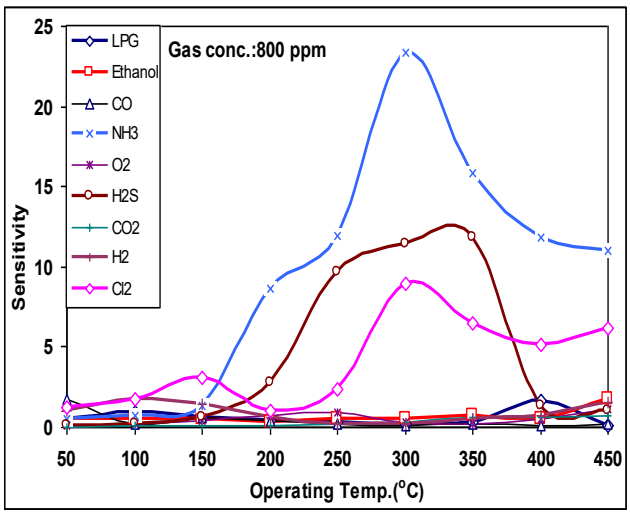

Figure.3 Variation of sensitivity with operating temperature.

Variation in sensitivity with NH_3 gas concentration

The dependence of the sensitivity of the Zn_2TiO_4 thick film on the H_2S concentration at an operating temperature 300^{0}C is shown in figure 4. It is observed that the sensitivity increases linearly as the NH_3 concentration increases from 100 to 800 ppm and then decreases with further increase in the H_2S concentration. The linear relationship between the sensitivity and the NH_3 concentration at low concentrations may be attributed to the availability of sufficient number of sensing sites on the film to act upon the NH_3. The low gas concentration implies a lower surface coverage of gas molecules, resulting into lower surface reaction between the surface adsorbed

oxygen species and the gas molecules. The increase in the gas concentration increases the surface reaction due to a large surface coverage. Further increase in the surface reaction will be gradual when saturation of the surface coverage of gas molecules is reached. Thus, the maximum sensitivity was obtained at an operating temperature of 300 °C for the exposure of 800 ppm of NH_3. The linearity of the sensitivity in the low NH_3 concentration range (100-800 ppm) suggests that the Zn_2TiO_4 thick film can be reliably used to monitor the concentration of NH_3 over this range.

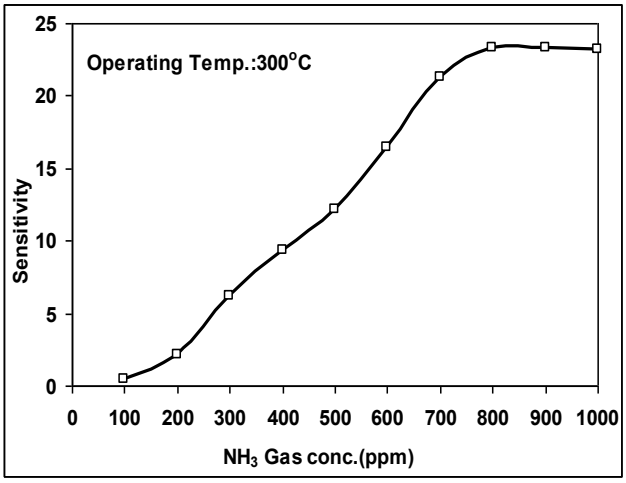

Fig. 4: Dependence of the sensitivity of the Zn_2TiO_4 thick film on the NH_3 concentration at 300 °C

Selectivity of Zn_2TiO_4 thick film for various gases

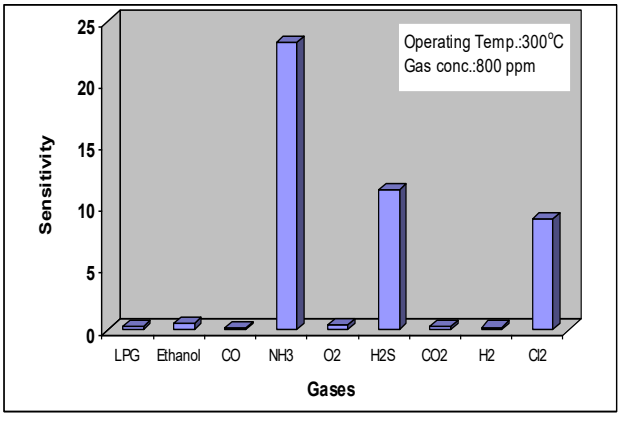

Figure 5. Selectivity of Zn_2TiO_4 thick film for various gases.

It is observed from figure 5 that the Zn_2TiO_4 thick film gives maximum sensitivity to NH_3 (800 ppm) at 300 °C. The films showed highest selectivity for NH_3 against all other tested gases: H_2S, LPG, Cl_2, CO, CO_2, O_2, H_2 and ethanol.

Response time and recovery time

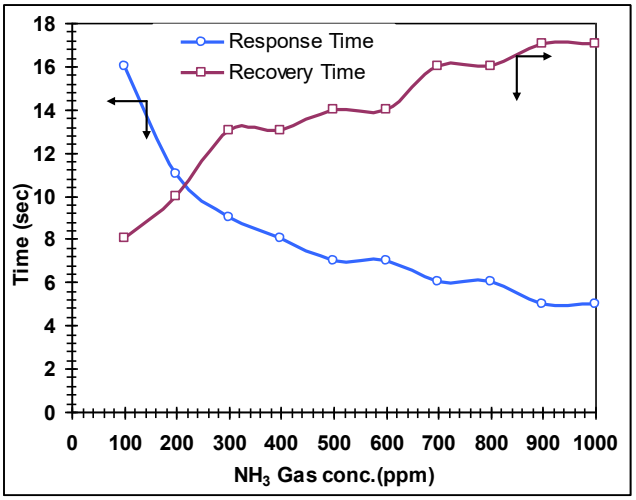

Figure 6. Variation of response and recovery time with concentration of NH_3.

Figure 6 shows the response and recovery time vs concentration of NH_3. It is revealed that response time decreased from 16 sec to 5 sec when NH_3 concentration is increased from 100 ppm to 1000 ppm. This may be due to the presence of sufficient gas molecules at the interface for reaction to occur. From the same graph, it is found that for higher concentrations of NH_3, the recovery time was long. This may be due to the reaction products are not leaving from the interface immediately after the reaction.

Gas sensing mechanism

It is known that atmospheric oxygen molecules are adsorbed on the surface of n-type semiconductor oxides in the forms of O^- and O^{2-} thereby decreasing the electronic conduction. Atmospheric oxygen molecules take electrons from the conduction band to be adsorbed as O^-. The reaction is as follows:

$$O_{2\,(g)} + 2e \rightarrow 2O^- \quad (1)$$

When reducing gas molecules like NH_3 reacts with negatively charged oxygen adsorbates, the trapped electrons are given back to conduction band. The energy released during decomposition of adsorbed ammonia molecules would be sufficient for electrons to jump up into the conduction, causing on increase in the conductivity of the sensor. The possible reaction is:

$$2NH_3 + 3O^- \rightarrow 3H_2O + N_2 + 3e^- \quad (2)$$

For this reaction to proceed to the right hand side, some amount of activation energy has to be provided thermally. An increase in operating temperature surely increases the thermal energy so as to stimulate the oxidation of NH_3 (Eq. (2)). The reducing gas (NH_3) donates electrons, therefore the resistance decreases, or the conductance increases[6]. This is the reason why the gas response increases with operating temperature. The point at which the gas response reaches maximum is the actual thermal energy needed for the reaction to proceed. However, the response decreases at higher operating temperatures, as the oxygen adsorbates are desorbed from the surface of the sensor[7]. Also, at high temperatures the carrier concentration increases due to intrinsic thermal excitation and the Debye length decreases. This may be one of the reasons for the decreased sensitivity at high temperatures[8]. As the species are desorbed from the surface, oxygen is adsorbed again. As a result, the initial resistance of the film would decrease and the overall change in the resistance on the exposure of gas would be smaller leading to lower sensitivity to the target gas.

CONCLUSION

Sensing performance of Zn_2TiO_4 thick film sensor was observed to be maximum for NH_3 amongst gas tested. The optimum temperature for maximum sensing of NH_3 gas was found to be 300 ^{0}C. The sensor showed good selectivity to NH_3 gas against LPG, H_2, C_2H_5OH, CO, CO_2 and Cl_2 gases.

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Conflicts of interest: The authors stated that no conflicts of interest.

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