CARBON DIOXIDE GAS SENSING PROPERTY OF NICKEL SUBSTITUTED ZINC FERRITE

By

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Date Received: 13/11/2018 Date Revised: 14/03/2019 Date Accepted: 01/08/2019

ABSTRACT

The polycrystalline NiZn ferrite have been synthesized by co-precipitation method and characterized by X-ray powder diffraction and FTIR spectroscopy. The FTIR spectra is obtained in the range from 400 cm^{-1} to 4000 cm^{-1}. Absorption bands observed at higher frequencies suggest the existence of significant modes of vibrations. The existence of absorption bands at frequency about 1627 cm^{-1}, 2923 cm^{-1}, and 3437 cm^{-1} are attributed to vibrational modes of triatomic water molecule. The absorption bands, observed at 414 cm^{-1} and 590 cm^{-1}, confirm the formation of the spinel structure. Employing these materials, the sensing elements, were developed on cylindrical glass as substrate. Carbon dioxide (CO_2) gas sensitive electrical properties of the compositions were investigated. The results are attributed to the chemisorption of oxygen species at specific operating temperature. Existence of nano crystallites favors surface phenomenon of adsorption. The materials show n-type conductivity at ambience and depict increase in the resistance due to presence of oxidizing gas. The electrical resistance of sensing elements (RCO_2) was measured for variable concentration of CO_2 gas from 0% to 15%. The RCO_2 increases with increase in CO_2. The sensitivities of the compositions under investigation are also estimated and the result of investigation is discussed here.

Keywords: Spinel Ferrites, X-ray Diffraction, FTIR, Operating Temperature, Electrical Resistance, Gas Sensor.

INTRODUCTION

The ferrite materials of nanostructure exhibit nano particles and very small grains with uniform grain distribution. This leads to increase in the effective surface area, which is an inherent requirement adsorption mechanism (Azad, Akbar, Mhaisalkar, Birkefeld, & Goto, 1992). The gas sensing properties are mostly based on the surface phenomenon such as chemisorption and physisorption. The surface of ferrite materials, at typical operating temperature, reveals chemisorption of the oxygen species needed for physisorption of oxidizing or reducing gases (Abdel-Latif, 2012). The surface of ferrite materials, at typical operating temperature, reveals chemisorption of the oxygen species needed for physisorption of oxidizing or reducing gases. The gas sensing properties of nanostructured thin films of copper ferrites have been investigated by Chapelle et al. (2011). They observed maximum sensitivity at temperature about 280 °C for H_2. They found increase in the resistance due to presence of the H_2 gas (Yamazoe, 2005). They reported that the magnesium ferrites exhibit good sensitivity to the H_2S and ethanol. It was also reported that the zinc ferrites show significant response to the H_2S gas (Xinshu, Yanli, & Jiaqiang, 2002). Reddy, Manorama, and Rao (1999) have synthesized nickel ferrite by using co-precipitation method and investigated the response of the nickel ferrite for various gases. They reported that nickel ferrite is most sensitive to chlorine gas with best selectivity as well. They also demonstrated that the timing parameters such as response time and recovery time are also significant. The gas sensing properties of Lanthanum ferrites were investigated by Kong and Shen (1996) and they reported an increase of resistance of the sensor due to existence of the reducing gas. The response of the sensor is mostly sensitive to the reduction-oxidation reaction with the surface of the sensing material under investigation. The conductance response of the nano crystalline $MgFe_2O_4$ thick films were measured by exposing the films to the reducing gases like methane (CH_4), H_2S, LPG, ethanol (C_2H_5OH) by Liu et al. (2005). Gas sensing properties of MgZn ferrite nano particles were extensively studied by Bharti, Mukherjee, and Majumder (2010) and reported that the composition are sensitive for the carbon monoxide gas. They attributed the properties of electrical conduction to adsorption process. The result of investigation of nickel substituted zinc ferrites for development of CO_2 gas sensor has been presented here.

1. Gas Sensing Mechanism

Gas sensing is the realization of surface phenomenon, wherein the phenomenon of chemisorption and physisorption are ensured. When the sensing element is heated to the sufficient temperature, the adsorption of the oxygen at the crystallographic sites of surface of the grains of polycrystalline material takes place. This is called as the chemisorption of the oxygen to form ionic species, such as O^-, O_2^-, and O^{2-}, which acquired electrons from the conduction band of the surface material. The adsorption mechanism can be described through reaction path (Herrán, Mandayo, & Castano, 2009; Sadek, Choopun, Wlodarski, Ippolito, & Kalantar-zadeh, 2007).

$$O_{2(gas)} \Leftrightarrow O_{2(Adsorbed)}$$

$$O_{2(Adsorbed)} + e- \Leftrightarrow O_2-$$

$$O_2- + e- \Leftrightarrow 2O-$$

$$O- + e- \Leftrightarrow O^{2-}$$

Thus, three types of oxygen ionspecies may be formed at the surface of the sensing element. The operating temperature favours the formation of these ionic species. These oxygen ions, O_{2-}, $O,^-$ and O^{2-} are stable below 100 °C, in between 100 °C to 300 °C and above 300 °C, respectively (Ghimbeu, Lumbreras, Siadat, & Schoonman, 2010). The electron transfers from conduction band of the sensing element to the chemisorbed oxygen results into decrease in the concentration of electrons, the charge carriers, of the sensing element. Therefore, for n-type semiconducting metal oxides, an increase in the resistance of the sensor is observed (Wetchakun et al. (2011). Moreover, in case of p-type metal oxides, the transfer of electrons results into formation of the holes at valence band and it favours the electrical conduction. This reveals the decrease in the resistance of the sensor film. The operating temperature plays a vital role on the adsorption and desorption rate of the oxygen ion at surface of the ferrite film. Moreover, this also depends upon the nature of the gases to be sensed. As per the properties, generally, the gases could be classified into two groups such as oxidizing gases and reducing gases. The gases such as NO_2, NO, N_2O, CO_2, etc., are oxidizing gases. However, the gases such as NH_3, H_2S, CH_4, ethanol, acetone, etc., are come under the group of reducing gases.

When the sensing element of the ferrite material is exposed to the oxidizing gases such as Co_2, it reacts with chemisorbed O^- ion at the surface of the film. The oxidation reaction between metal oxide and oxidizing gas follow the reaction paths (Zhang, Liu, Qi, Li, & Lu, 2009)

$$CO_{2(gas)} + e- \quad CO_{2-(Adsorbed)} \qquad (1)$$

$$CO_{2-(Adsorbed)} + O- + 2e- \quad CO_{(gas)} + 2O^{2-} \qquad (2)$$

The adsorbed O- ions play an interesting role of assisting the oxidizing ions to take electrons from surface of the ferrite films, which results into reduction in the concentration of electrons. Hence, resistance of the sensor increases with increase in the concentration of oxidizing gas molecules. This is for n-type metal oxide thick films. Therefore, the gas sensing response for oxidizing gas is normally defined as $S = (R_a/R_{og})$, where R_{og} is the resistance in presence of the oxidizing gas and R_a is the resistance at ambient condition for pure and dry air.

This adsorption significantly depends upon operating temperature. During temperature range from 200 °C to 350 °C, the adsorption favours. However, for higher temperature, the desorption of the species occurs, which results into decrease in the sensitivity of the sensor to the test gas.

2. Experimental Details

The ferrite materials belong to technologically important class of magnetic oxides. It exhibits interesting structural, electrical, and magnetic properties. These intrinsic properties are strongly dependent on the chemical compositions, method of preparation, preparation conditions, sintering time, rate of sintering, sintering temperature, microstructural features, doping of the foreign ions, particle size, particle distribution, etc. (Dias, Moreira, Mohallem, & Persiano, 1997; Qu et al. 2006). By controlling these parameters, the ferrites $Ni_xZn_{1-x}Fe_2O_4$ (x = 0.2, 0.4, 0.6, and 0.8) synthesized by using co-precipitation method. The compositions were characterized X-ray powder diffractometry and FTIR spectrophotometry. Deploying cylindrical glass tube as a substrate, the thick film is deposited on the surface of the tube by using screen printing technology. The sensing materials should be operated at elevated temperature. For this purpose, a separate heating element was designed and installed along the axis of the sensor.

An experimental arrangement is shown in Figure 1 to study the electrical resistance (R_g) of the sensing element by exposing to the CO_2 gas in percentage unit (%). The operating temperature is controlled by controlling current through heating element (HH). The operating temperature is optimized by studying temperature dependent sensitivity for CO_2 gas. The gas sensitive resistance (R_{CO2}) of the sensing element is measured with respect to variable concentration of CO_2 gas. The digital meter is used for resistance measurement. The Resistance against concentration of CO_2 data is employed for further interpretation.

Figure 1. Experimental Arrangement

3. Results and Discussion

X-ray diffractograms of compositions of $Ni_xZn_{1-x}Fe_2O_4$ were obtained from x-ray powder diffractometer and depicted in Figure 2. It shows well defined reflections which supports the confirmation of spinel structure (Patil, Pawar, Tilekar, & Ladgaonkar, 2016; Ladgaonkar, Patil, & Tilekar, 2013). Using Debye-Scherrer relation, values of particle size are calculated for each of the reflections. The particle diameter varies from 35 nm to 75 nanometer.

For further confirmation, FTIR spectroscopy is employed and materials under investigation are characterized. As depicted in Figure 3, the FTIR spectra for the compositions $Ni_xZn_{1-x}Fe_2O_4$, for (x =0.80) shows significant absorption bands, ν_1 and ν_2, at frequency about 570 cm^{-1} and 428 cm^{-1}. Three absorption bands ν_4, ν_5 and ν_6 at higher frequencies were also observed. The absorption band observed at frequency (ν_4) about 3440 cm^{-1} can be attributed to the bending of the O-H bond. The existence of C-H is reflected by the absorption band at frequency (ν_5) about 2920 cm^{-1}.

4. CO_2 Gas Sensitive Electrical Properties

The prepared thick film sensors of the compositions $Ni_xZn_{1-x}Fe_2O_4$ are exposed to the CO_2 gas of variable concentration from 0.1% to the 15% and resistance of the sensing element (R_{CO2}) in MW, is measured at constant operating temperature (T_{op}).

In the beginning, the operating temperature is optimized by studying operating temperature dependent sensitivities of compositions. The temperature at which the

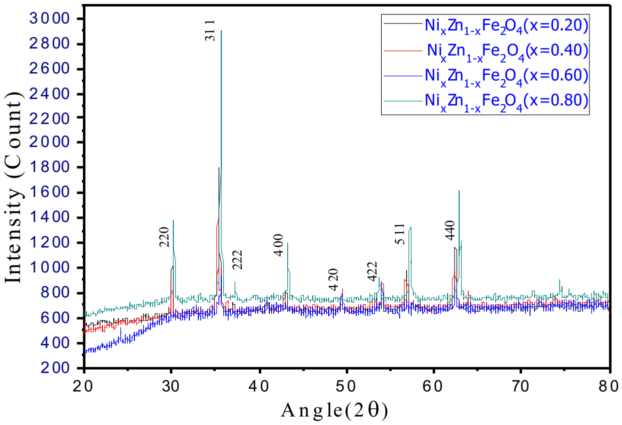
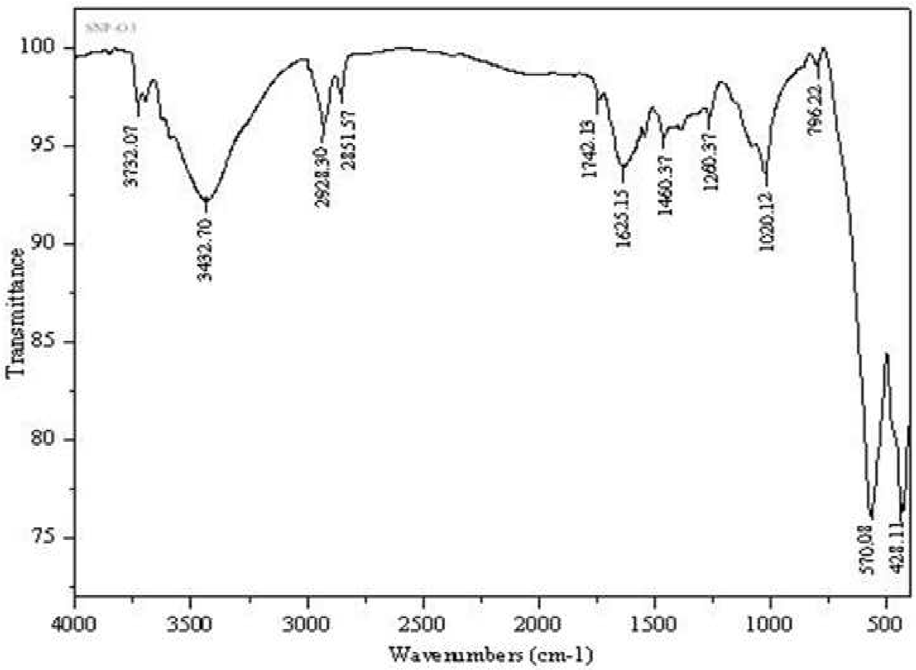


Figure 2. X-ray Diffractograms for Composition of $Ni_xZn_{1-x}Fe_2O_4$



Figures 3. IR Absorption Spectra of the Composition $Ni_xZn_{1-x}Fe_2O_4$(x=0.80)

sensitivity of the material found maximum is called operating temperature and presented in Table 1. For optimization of operating temperature, concentration of CO_2 is kept constant and values of electrical resistance are measured. After determination of operating temperature, the CO_2 sensitive electrical properties are investigated. The electrical resistance (R_{CO2}) is measured for variable concentration of carbon dioxide gas from 0.1% to 15% by deploying CO_2 gas chamber and plotted. The graphs of observed resistance of sensing material against concentration of CO_2 gas (in %) are depicted in Figure 4.

From Figure 4 it is found that the sensing element for x=0.20 and 0.40, that is $Ni_{0.20}Zn_{0.80}Fe_2O_4$ and $Ni_{0.40}Zn_{0.80}Fe_2O_4$ ferrites show significant sensitivity for CO_2 gas and for x=0.60 and 0.80, less sensitive to the CO_2 gas. Employing expression (3), the sensitivity, S_G, (in %) are estimated for composition of NiZn ferrites. The sensitivity is defined as relative change in the measuring value of the parameter (Umar & Hahn, 2010; Zhang et al., 2009).

$$S_G = \frac{R_{CO2} - R_a}{R_{CO2}} \times 100\ \% \qquad (3)$$

R_a is the resistance of the sensing element for ambient condition.

It is found that the resistance of the sensing element increases with increase in the concentration of CO_2 gas. This nature of the graph can be attributed to the fact that the CO_2 gas is an oxidizing gas. When it comes in contact with the chemisorbed oxygen species, it takes electron from the conduction band. The reaction mechanism is given in expressions (1) and (2). Due to this, the concentration of electrons of the conduction bands decreases, which results into decrease in the electrical current and increase in the resistance R_{CO2}, due to increase in the concentration of CO_2, is observed.

On inspection of Figure 4, it is found that out of four compositions, the compositions for x = 0.20 and 0.40 are more sensitive to the carbon dioxide gas. Therefore, it is suggested that for development of the sensor for CO_2 gas, the composition x = 0.20 and 0.40 are most suitable.

From Figure 4, it is also found that at and above typical

$Ni_xZn_{1-x}Fe_2O_4$	Operating Temperature (°C)	Sensitivities S_G (%)	Saturation limit of Co_2 gas in %
0.20	180	70.26	8
0.40	190	24.56	9
0.60	220	18.14	7
0.80	180	13.69	6

Table 1. Operating Temperature, Sensitivities and Saturation Limit for Sensing Element

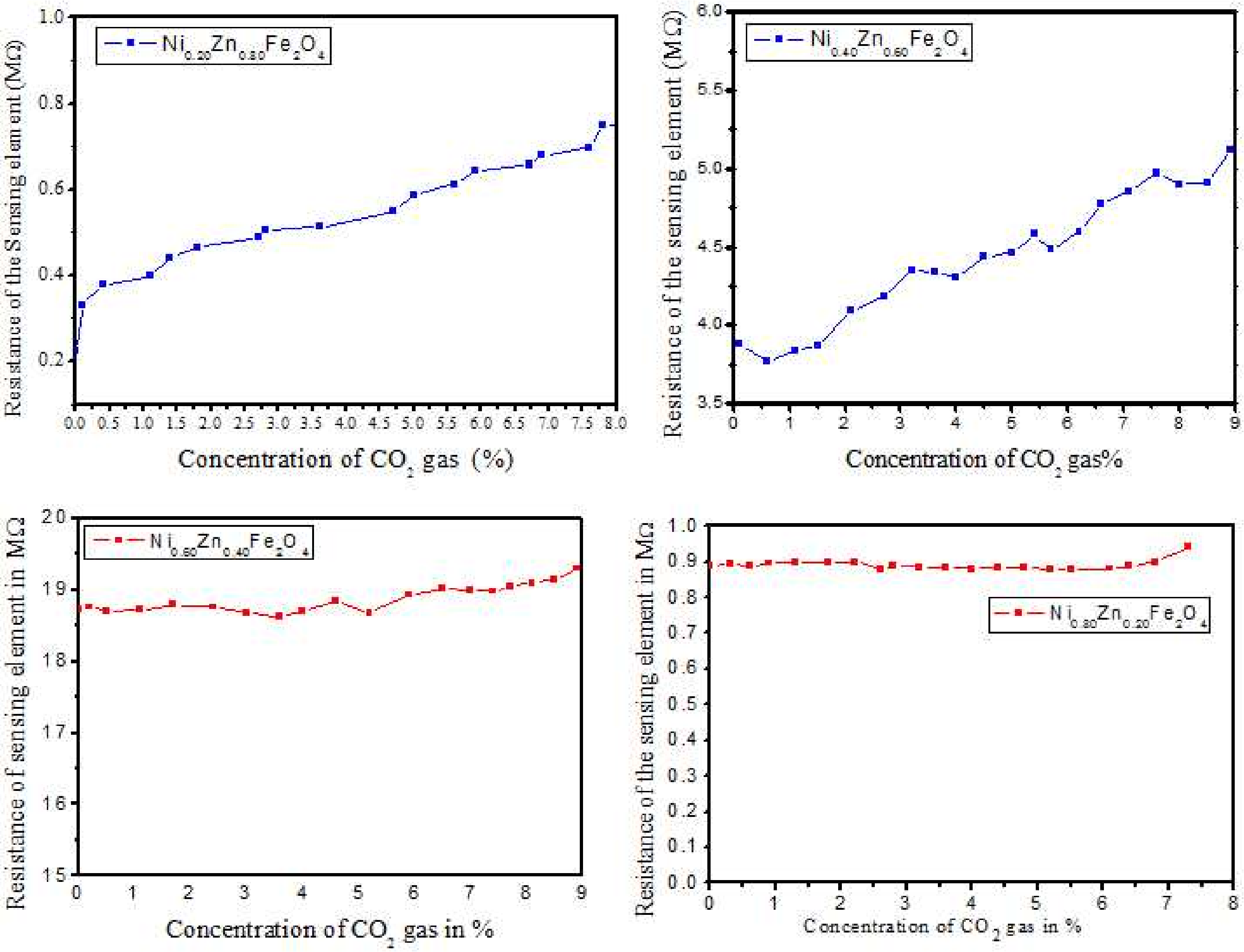


Figure 4. Resistance of Sensing Element, RCO_2, in MW, Against Concentration of CO_2 Gas in %

limit of the CO_2 gas, saturation in the resistance value takes place. It is known that the chemisorptions of oxygen species favours at typical range of operating temperature (Barsan, Schweizer-Berberich, & Göpel, 1999; Bârsan & Weimar, 2003). At typical operating temperature, the concentration of oxygen species are constant. Therefore, the saturation of chemisorptions takes place. Therefore, after typical concentration of the CO_2 gas, the saturation in the response is observed. Along with the sensitivities, the saturation levels are also depicted in Table 1.

Conclusion

The compositions $Ni_xZn_{1-x}Fe_2O_4$ polycrystalline spinel nanoferrites were synthesized by chemical route and characterized with standard tools. The diffractograms reveal the formation of the single phase compositions without any ambiguity. On characterization, it is found that the compositions are cubic spinels with F3dm space group symmetry. Using Debye-Scherer relation, the particles size of compositions is estimated and it is in the range from 35 nm to 75 nm. The results of investigation of gas sensitive electrical properties, reveal the suitability of the materials for development of carbon dioxide gas sensor. The behavior of electrical conductivity is attributed to the contribution of charge carriers due to adsorption. The materials are n-type metal oxides and depict increase in the resistance due to presence of carbon dioxide gas. The sensitivities are also estimated. From results obtained, it can be concluded that the compositions of NiZn ferrites, $Ni_{0.2}Zn_{0.8}Fe_2O_4$ and

$Ni_{0.4}Zn_{0.6}Fe_2O_4$ are most suitable for development of carbon dioxide gas sensor.

References

[1]. Abdel-Latif, I. A. (2012). Fabrication of nano-size nickel ferrites for gas sensors applications. *Journal of Physics*, 1(2), 50-53.

[2]. Azad, A. M., Akbar, S. A., Mhaisalkar, S. G., Birkefeld, L. D., & Goto, K. S. (1992). Solid-state gas sensors: A review. *Journal of the Electrochemical Society*, 139(12), 3690-3704. https://doi.org/10.1149/1.2069145

[3]. Bârsan, N., & Weimar, U. (2003). Understanding the fundamental principles of metal oxide based gas sensors; the example of CO sensing with SnO_2 sensors in the presence of humidity. *Journal of Physics: Condensed Matter*, 15(20), R813-R839. https://doi.org/10.1088/0953-8984/15/20/201

[4]. Barsan, N., Schweizer-Berberich, M., & Göpel, W. (1999). Fundamental and practical aspects in the design of nano scaled SnO_2 gas sensors: A status report. *Fresenius' Journal of Analytical Chemistry*, 365(4), 287-304. https://doi.org/10.1007/s002160051

[5]. Bharti, D. C., Mukherjee, K., & Majumder, S. B. (2010). Wet chemical synthesis and gas sensing properties of magnesium zinc ferrite nano-particles. *Materials Chemistry and Physics*, 120(2-3), 509-517. https://doi.org/10.1016/j.matchemphys.2009.11.050

[6]. Chapelle, A., Yaacob, M. H., Pasquet, I., Presmanes, L., Barnabé, A., Tailhades, P., ... & Kalantar-Zadeh, K. (2011). Structural and gas-sensing properties of CuO–CuxFe_3– xO_4 nanostructured thin films. *Sensors and Actuators B: Chemical*, 153(1), 117-124. https://doi.org/10.1016/j.snb.2010.10.018

[7]. Dias, A., Moreira, R. L., Mohallem, N. D., & Persiano, A. C. (1997). Microstructural dependence of the magnetic properties of sintered NiZn ferrites from hydrothermal powders. *Journal of Magnetism and Magnetic Materials*, 172(1-2), L9-L14. https://doi.org/10.1016/S0304-8853(97)00134-0

[8]. Ghimbeu, C. M., Lumbreras, M., Siadat, M., & Schoonman, J. (2010). Detection of H_2S, SO_2, and NO_2 using electrostatic sprayed tungsten oxide films. *Materials Science in Semiconductor Processing*, 13(1), 1-8. https://doi.org/10.1016/j.mssp.2010.01.001

[9]. Herrán, J., Mandayo, G. G., & Castano, E. (2009). Semiconducting $BaTiO_3$-CuO mixed oxide thin films for CO_2 detection. *Thin Solid Films*, 517(22), 6192-6197. https://doi.org/10.1016/j.tsf.2009.04.007

[10]. Kong, L. B., & Shen, Y. S. (1996). Gas sensing properties and mechanism of $CaxL_{1-x}FeO_3$ ceramics. *Sensors and Actuators B: Chemical*, 30(3), 217-221. https://doi.org/10.1016/0925-4005(96)80052-9

[11]. Ladgaonkar, B. P., Patil, S. N., & Tilekar, S. K. (2013). Development of Ni-Zn ferrite based smart humidity sensor module by using mixed signal programmable system-on-chip. *Applied Mechanics and Materials*, 310, 490-493. https://doi.org/10.4028/www.scientific.net/AMM.310.490

[12]. Liu, Y. L., Liu, Z. M., Yang, Y., Yang, H. F., Shen, G. L., & Yu, R. Q. (2005). Simple synthesis of $MgFe_2O_4$ nanoparticles as gas sensing materials. *Sensors and Actuators B: Chemical*, 107(2), 600-604. https://doi.org/10.1016/j.snb.2004.11.026

[13]. Patil, S. N., Pawar, A. M., Tilekar, S. K., & Ladgaonkar, B. P. (2016). Investigation of magnesium substituted nano particle zinc ferrites for relative humidity sensors. *Sensors and Actuators A: Physical*, 244, 35-43. https://doi.org/10.1016/j.sna.2016.04.019

[14]. Qu, Y., Yang, H., Yang, N., Fan, Y., Zhu, H., & Zou, G. (2006). The effect of reaction temperature on the particle size, structure and magnetic properties of coprecipitated $CoFe_2O_4$ nanoparticles. *Materials Letters*, 60(29-30), 3548-3552. https://doi.org/10.1016/j.matlet.2006.03.055

[15]. Reddy, C. G., Manorama, S. V., & Rao, V. J. (1999). Semiconducting gas sensor for chlorine based on inverse spinel nickel ferrite. *Sensors and Actuators B: Chemical*, 55(1), 90-95. https://doi.org/10.1016/S0925-4005(99)00112-4

[16]. Sadek, A. Z., Choopun, S., Wlodarski, W., Ippolito, S. J., & Kalantar-zadeh, K. (2007). Characterization of ZnO nanobelt-based gas sensor for H_2, NO_2, and hydrocarbon sensing. *IEEE Sensors Journal*, 7(6), 919-924. https://doi.org/10.1109/JSEN.2007.895963

[17]. Umar, A., & Hahn, Y. B. (2010). Metal oxide nanostructures and applications. *American Scientific Publishers*, 3, 31-52.

[18]. Wetchakun, K., Samerjai, T., Tamaekong, N., Liewhiran, C., Siriwong, C., Kruefu, V., ... & Phanichphant, S. (2011). Semiconducting metal oxides as sensors for environmentally hazardous gases. *Sensors and Actuators B: Chemical*, 160(1), 580-591. https://doi.org/10.1016/j.snb.2011.08.032

[19]. Xinshu, N., Yanli, L., & Jiaqiang, X. (2002). Simple synthesis of $MgFe_2O_4$ as gas sensing materials. *Chin. Funct. Mater*, 33, 413.

[20]. Yamazoe, N. (2005). Toward innovations of gas sensor technology. *Sensors and Actuators B: Chemical*, 108(1-2), 2-14. https://doi.org/10.1016/j.snb.2004.12.075

[21]. Zhang, T., Liu, L., Qi, Q., Li, S., & Lu, G. (2009). Development of microstructure In/Pd-doped SnO_2 sensor for low-level CO detection. *Sensors and Actuators B: Chemical*, 139(2), 287-291. https://doi.org/10.1016/j.snb.2009.03.036

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