*Research Journal of Chemical Sciences* ISSN 2231-606X
Vol. **5(8),** 7-12, August **(2015)** *Res. J. Chem. Sci.*

# Preparation of Nanocrystalline Spinel-type oxide Materials for Gas sensing applications

**Kapse V.D.**
Department of Physics, Arts, Science and Commerce College, Chikhaldara 444807, Maharashtra State, INDIA

**Available online at: www.isca.in, www.isca.me**
Received 3rd July 2015, revised 7th August 2015, accepted 14th August 2015

## Abstract

*Nanocrystalline $NiFe_2O_4$, $ZnFe_2O_4$, $MgFe_2O_4$, $ZnAl_2O_4$, $CoAl_2O_4$ and $MgAl_2O_4$ with spinel structure and average crystallite size in the range of 8-35 nm, were successfully synthesized by citrated sol-gel technique. The structure and phase identification of the prepared powder samples were characterized by X-ray diffraction (XRD) and microstructure by transmission electron microscopy (TEM). The response of prepared spinel-type oxide materials to various reducing gases like ethanol, liquefied petroleum gas, hydrogen sulfide and ammonia was examined. The sensor response mainly depends on the operating temperature and the test gas species. The reasons for the sensing characteristics of spinel-type oxide based sensor elements were discussed.*

**Keywords:** Spinel-type oxide, X-ray diffraction, ferrite, sensor response, response time.

## Introduction

In recent years, because of increasing apprehension regarding environmental protection and safety, demands for detection and monitoring of toxic and harmful gases have become the issue of concern in the entire world. Different metal oxide semiconductors i.e. ZnO, $SnO_2$ and $Fe_2O_3$ have been researched due to their low-cost and easy sensing technique [1-5]. Conversely, there still exist some drawbacks of them, like very low selectivity of $SnO_2$ and the elevated working temperature of ZnO (400–450$^0$C)[6,7]. Moreover, ZnO exhibited greater sensitivity to various reducing gases. To improve the gas sensing characteristics of these sensors, nanometer-sized materials, which have high surface activity due to their increased surface to volume ratios, have been extensively researched in the field of gas sensors. Also, there are many research publications on the use of materials doping, noble metal additives, filming and oxides multiplicity[8-11]. In some research papers it has been reported that complex oxides made from ferric oxide or aluminium oxide and other oxides demonstrate good sensitivity towards reducing gas[12,13]. Spinel-type oxides with a formula of $AB_2O_4$ (A is a divalent metal and B is a trivalent one) have been reported as a vital complex oxide in field of gas sensors and have been studied for the detection of oxidizing as well as reducing gases. In this paper, ethanol sensing properties of some nanostructured ferrites and aluminates prepared by citrated sol-gel method are presented.

## Material and Methods

$AFe_2O_4$ (A = Ni, Zn, Mg) and $BAl_2O_4$ (B = Zn, Co, Mg) were prepared by citrated sol-gel route. The stoichiometric molar amounts of Ferric nitrate [$Fe(NO_3)_3.9H_2O$], Nickel nitrate [$Ni(NO_3)_2.6H_2O$] and citric acid monohydrate [$C_6H_8O_7.H_2O$] were weighed and mixed with ethylene glycol. The prepared mixture was stirred magnetically at 80$^0$C for 2 h. A transparent solution was obtained after 2 h. Thereafter, this transparent solution was poured to Teflon-lined stainless steel autoclave. The temperature of the autoclave was increased gradually to 125$^0$C and kept for 10 h to obtain gel precursor. Later, the autoclave was allowed to cool naturally to room temperature and the obtained product further heated for 3 h at 350$^0$C in muffle furnace and then milled to a fine powder. Then the obtained powder was calcined at 600 $^0$C for 5 h. In this way, $NiFe_2O_4$ powder was synthesized. $ZnFe_2O_4$, $MgFe_2O_4$, $ZnAl_2O_4$, $CoAl_2O_4$ and $MgAl_2O_4$ powder samples were prepared by following the same procedure. The calcinations temperature for ferrite and aluminate materials was 600$^0$C and 700$^0$C, respectively.

Phase identification of the prepared powder samples was performed by X-ray diffractometer with a Cu Kα radiation (λ = 1.5406Å). The crystallite size ($D_{hkl}$) of the powder sample was calculated using Debye-Scherrer relation, which is given by, $D = K\lambda/B\cos\theta$; Where B is the full width at half-maximum intensity (in radians) of a peak at an angle θ; K is a constant, depending on the line shape profile; λ is the wavelength of the X-ray source. Investigations related to microstructure and morphology of prepared powder samples were carried out by transmission electron microscopy (TEM).

To study the gas sensing behavior, as-prepared powder samples were mixed separately with α-terpineol as a binder to form pastes. After that prepared pastes were correspondingly coated as a gas sensing film onto $Al_2O_3$ tube substrate with gold wire electrodes for good ohmic contacts at each end. To evaporate the α-terpineol, the sensor element was annealed at 400$^0$C for 1

h. Then, the sensors were kept at $350^0$C for 10 days in air before use. The sensor element, with Ni-Cr heating coil to provide the necessary temperature and a chromel-alumel thermocouple (TC) for indicating the operating temperature, was placed in the glass chamber to investigate the gas sensing properties. The static gas-sensing unit was used to investigate the sensing performance of the fabricated sensor elements. To measure the gas sensing characteristics, desired volume of the test gas was injected into a glass chamber and mixed with air. The concentration of LPG and $NH_3$ was 500 ppm each whereas it is 50 ppm each for $H_2S$ and $C_2H_5OH$. The electrical resistance of the sensor was calculated in the presence as well as in the absence of different test gases. The sensor response to a test gas (S) is defined as the ratio $R_a/R_g$, where, $R_a$ is the sensor resistance in air and $R_g$ is the sensor resistance in the presence of a test gas.

## Results and Discussion

Figure-1 and figure-2 presents the X-ray diffraction patterns for prepared $AFe_2O_4$ (A = Ni, Zn, Mg) and $BFe_2O_4$ (B = Zn, Co, Mg) powders. Every one of the powder samples have single-phase spinel-type structure with *d*-spacing values consistent with those found in the JCPDS files ($NiFe_2O_4$: 00-010-0325; $ZnFe_2O_4$: 01-073-1963; $MgFe_2O_4$: 01-073-1720; $ZnAl_2O_4$: 01-074-1136; $CoAl_2O_4$: 01-073-0238 and $MgAl_2O_4$: 01-074-1133). The average crystallite sizes, according to the Debye-Scherrer formula, of $NiFe_2O_4$, $ZnFe_2O_4$, $MgFe_2O_4$, $ZnAl_2O_4$, $CoAl_2O_4$ and $MgAl_2O_4$ powder samples were found as ~23, 17, 25, 22.4, 23.4 and 10 nm, respectively. In case of ferrite samples and aluminate samples, it was minimum for $ZnFe_2O_4$ and $MgAl_2O_4$ respectively.

Figure 3 illustrates TEM photographs of the prepared powder samples. As it can be seen that the results estimated from TEM photographs were in concurrence with those calculated by using Debye-Scherrer formula as per XRD experiments.

Figure-4 shows the sensor response (S) of ferrite samples to ethanol as a function of operating temperature. It is important to note here that each of the curves demonstrates a highest sensor response to ethanol corresponding to an optimum operating temperature. The best sensor response to 50 ppm ethanol was observed for $ZnFe_2O_4$ and $MgFe_2O_4$ at $325^0$C and for $NiFe_2O_4$ at $300^0$C. Figure-5 shows the sensor response (S) of aluminate samples to ethanol as a function of operating temperature. The sensor response to ethanol was found to decrease in the order $CoAl_2O_4$ > $ZnAl_2O_4$ > $MgAl_2O_4$. Furthermore, optimal operating temperature was found to increase in the order $CoAl_2O_4$ (150 $^0$C) < $ZnAl_2O_4$ (175 $^0$C) < $MgAl_2O_4$ (225 $^0$C).

The observed optimal operating temperatures are used to study the selectivity and response-recovery characteristics of gas sensors. The gas sensing mechanism belongs to the surface-controlled type[14]. The sensor response to target gas depends on various parameters like crystallite size, surface state, porosity, thickness, oxygen adsorption, charge mobility, lattice defects, etc. Generally, the sensor response is higher for the smaller crystallite size[14]. The higher working temperature of $ZnFe_2O_4$ and $MgFe_2O_4$ sensor probably needs supplementary excitation for the sensors to demonstrate reasonable response towards ethanol at lower operating temperature.

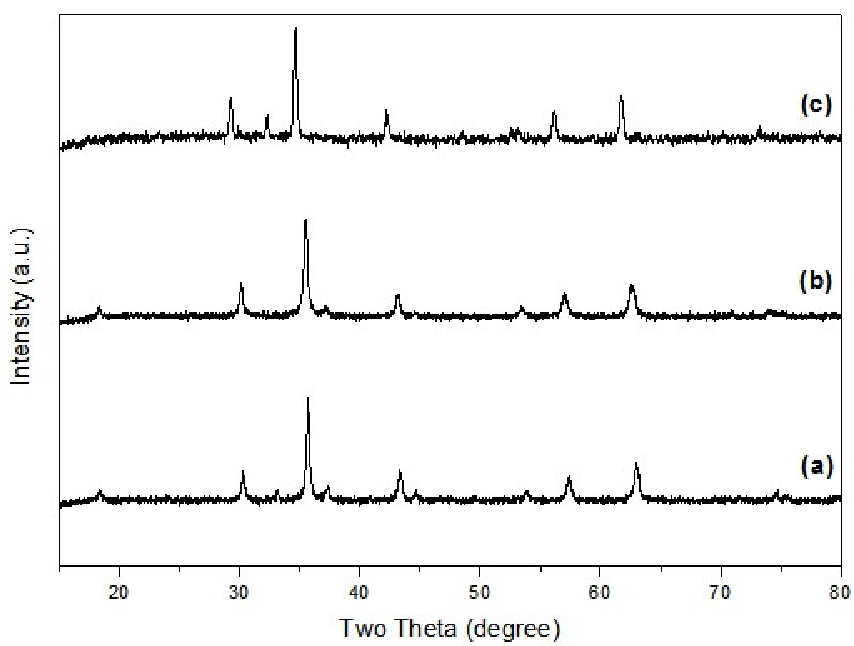


**Figure-1**
**XRD patterns of (a) $NiFe_2O_4$, (b) $ZnFe_2O_4$, (c) $MgFe_2O_4$ powder samples calcinated at $600^0$C**

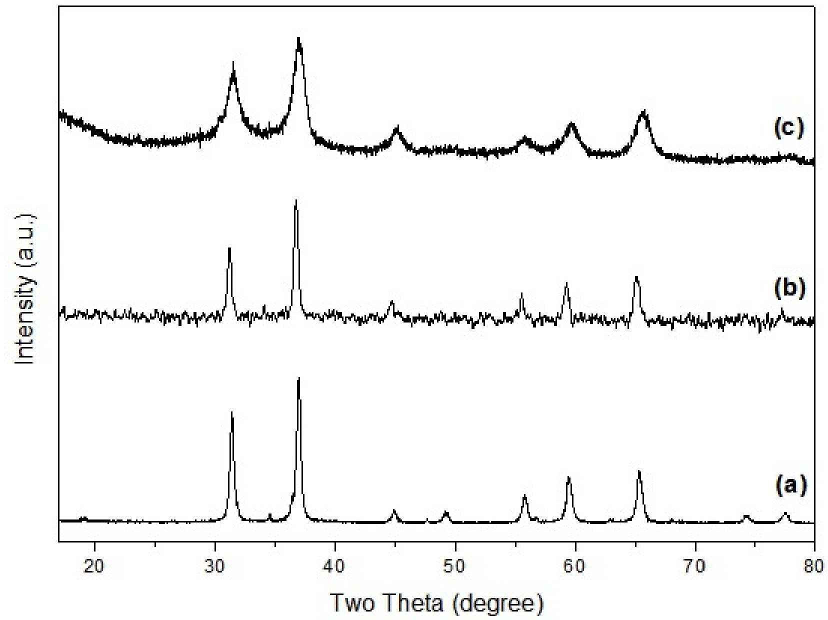


**Figure-2**
**XRD patterns of (a) $ZnAl_2O_4$, (b) Co $Al_2O_4$, (c) Mg $Al_2O_4$ powder samples calcinated at $700^0$C**

Response and recovery times are the significant parameters of gas sensor, which are defined as the time reached to 90% of the final signal. The response time and recovery time for investigated ferrites and aluminates are depicted in table-1. From all the obtained results of investigated ferrite materials, $MgFe_2O_4$ sensors exhibited a high response and rapid response behavior to ethanol as compared with $ZnFe_2O_4$ and $NiFe_2O_4$. Likewise, amongst investigated aluminates, $CoAl_2O_4$ based sensors exhibited a good response and quick response and recovery to ethanol as compared with the other two.

To study the selective behavior of $MgFe_2O_4$ and $CoAl_2O_4$, their response towards $NH_3$, LPG and $H_2S$ were also determined (table-1). $MgFe_2O_4$ and $ZnAl_2O_4$ showed high response to ethanol as compared with other tested gases indicating good selectivity of these sensors.

## Conclusion

In summary, different nanocrystalline spinel-type oxide materials containing Ni, Zn, Mg, and Co were successfully prepared by citrated sol-gel technique. The gas sensing characteristics of spinel-type ferrite based sensor indicate that $MgFe_2O_4$ sensor exhibits the highest response with good selectivity and speedy response-recovery behavior to ethanol at $325^0$C, which is mainly because of its smaller crystallite size. While, in case of ethanol sensing properties of spinel-type aluminate samples, $CoAl_2O_4$ sensor demonstrates the maximum response, very good selectivity and rapid response behavior to ethanol at $150^0$C.

**Table-1**
**Sensor response of $NiFe_2O_4$, $ZnFe_2O_4$, $MgFe_2O_4$, $ZnAl_2O_4$, $CoAl_2O_4$ and $MgAl_2O_4$ to ethanol at optimal operating temperature. The response-recovery time and sensor response to other tested gases at optimal operating temperature for ethanol**

| Sample | Operating temperature ($^0$C) | Sensor response at optimal operating temperature | | | | Response –Recovery time to 50 ppm ethanol | |
|---|---|---|---|---|---|---|---|
| | | $H_2S$ | $NH_3$ | $C_2H_5OH$ | LPG | Response time (s) | Recovery time (s) |
| $NiFe_2O_4$ | 300 | 2.1 | 0.6 | 6.4 | 2.7 | 88 | 220 |
| $ZnFe_2O_4$ | 325 | 2.5 | 0.2 | 9.1 | 3.1 | 40 | 72 |
| $MgFe_2O_4$ | 325 | 4.8 | 0.8 | 12.4 | 6.3 | 26 | 48 |
| $ZnAl_2O_4$ | 175 | 0.2 | 0.4 | 8.2 | 0.2 | 22 | 54 |
| $CoAl_2O_4$ | 150 | 0.2 | 1.3 | 10.4 | 0.1 | 15 | 40 |
| $MgAl_2O_4$ | 225 | 1.1 | 0.5 | 9.0 | 0.4 | 28 | 62 |

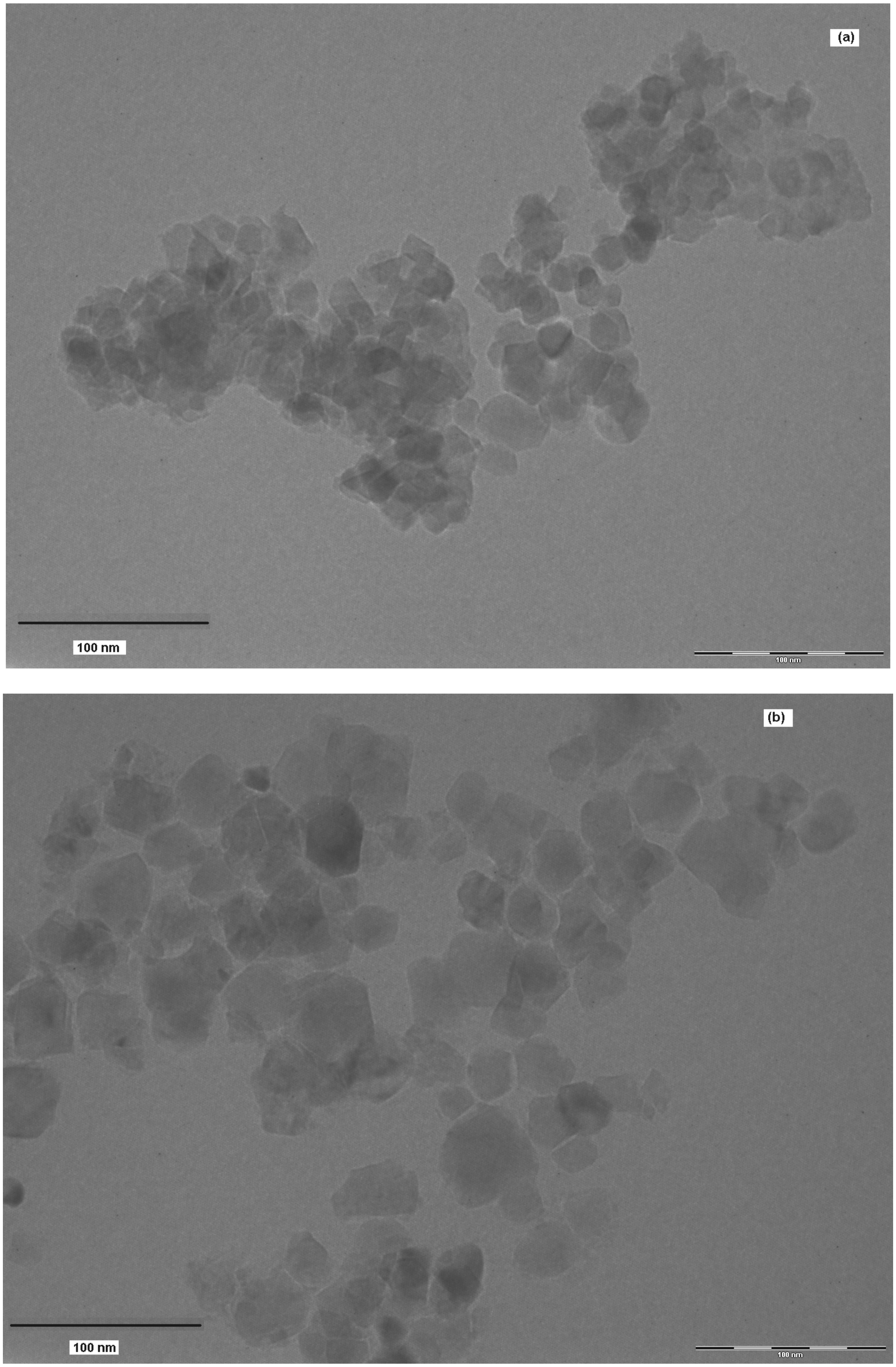


**Figure-3**
**TEM photographs of (a) $MgFe_2O_4$ and (b) $CoAl_2O_4$ powder samples calcinated at 600 $^0C$ and 700 $^0C$ respectively**

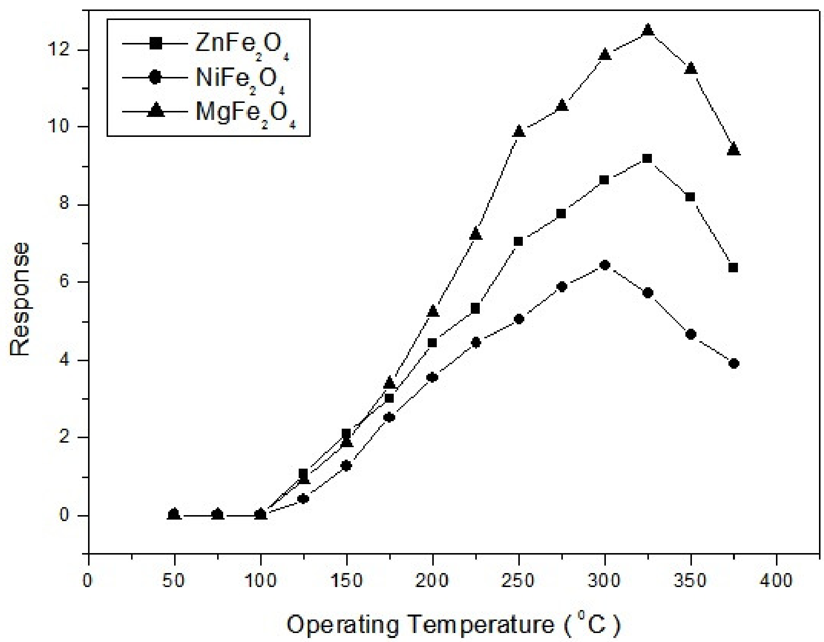


**Figure-4**
**Sensor response of (a) $NiFe_2O_4$, (b) $ZnFe_2O_4$ and (c) $MgFe_2O_4$ to ethanol at different operating temperatures**

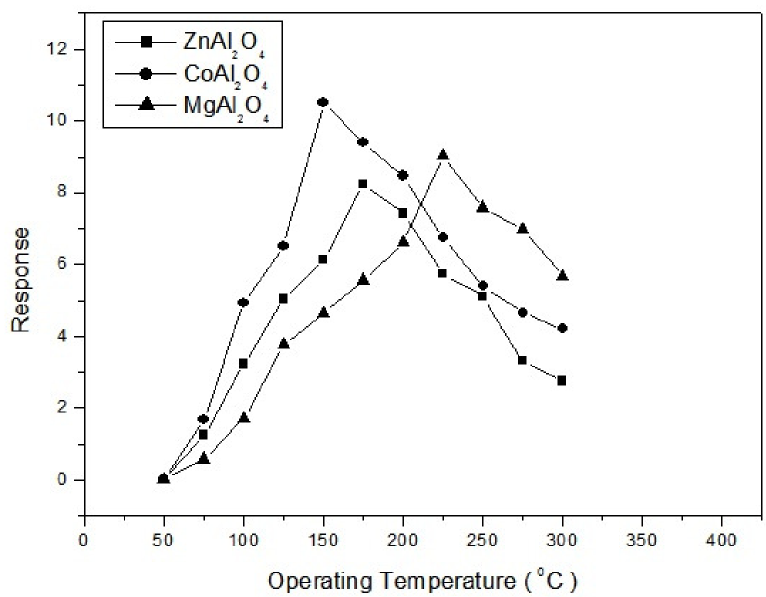


**Figure-5**
**Sensor response of (a) $ZnAl_2O_4$, (b) $CoAl_2O_4$ and (c) $MgAl_2O_4$ to ethanol at different operating temperatures**

## Acknowledgements

VDK gratefully acknowledges the financial support from the University Grants Commission (U.G.C.), New Delhi, India through the Minor Research Project No. F. 47-762/13(WRO).

## References

**1.** Waitz T., Becker B., Wagner T., Sauerwald T, Kohl C.D. and Tiemann M., Ordered nanoporous $SnO_2$ gas sensors with high thermal stability*, Sens. Actuators B*, **150(2)**, 788-793 **(2010)**

**2.** Shao Changjing, Chang Yongqin and Long Yi, High performance of nanostructured ZnO film gas sensor at room temperature, *Sens. Actuators B*, **204**, 666-672 **(2014)**

**3.** Mangamma G., Jayaraman V., Gnanasekaran T. and

Periaswami G., Effects of silica additions on $H_2S$ sensing properties of $CuO–SnO_2$ sensors**,** *Sens. Actuators B,* **53(3),** 133-139 **(1998)**

4. Jin W.X., Ma S.Y., Tie Z.Z., Jiang X.H., Li W.Q., Luo J., Xu X.L. and Wang T.T., Hydrothermal synthesis of monodisperse porous cube, cake and spheroid-like α-$Fe_2O_3$ particles and their high gas-sensing properties, *Sens. Actuators*, B, **220**, 243-254 **(2015)**

5. Cantalini C., Faccio M., Ferri G., Pelino M., The influece of water vapour on carbon monoxide sensitivity of α-$Fe_2O_3$microporous ceramic sensors, *Sens. Actuators B*, **19**, 437-442 **(1994)**

6. Barsan N., Schweizer-Berberich M. and Göpel W., Fundamental and Practical Aspects in the Design of Nanoscaled SnO2 Gas Sensors, *Fresenius J. Anal. Chem.*, **365**, 287- 304 **(1999)**

7. Seiyama T., Futata H., Era F. and Yamazoe N., Detection of gases by an activated semiconductive sensor, *Mater. Sci.*, **8**, 63-65 **(1972)**

8. Xu J., Shun Y., Pan Q. and Qin J., Sensing characteristics of double layer film of ZnO, *Sens. Actuators B*, **66**, 161-163 **(2000)**

9. Zakrzewska K., Radecka M. and Rekas M., Effect of Nb, Cr, Sn additions on gas sensing properties of $TiO_2$ thin films, *Thin Solid Films*, **310**, 161-166 **(1997)**

10. Miyata T., Hikosaka T. and Minami T., High sensitivity chlorine gas sensors using multicomponent transparent conducting oxide thin films, *Sens. Actuators B*, **69,** 16-21 **(2000)**

11. Zakrzewska K., Mixed oxides as gas sensors , *Thin Solid Films*, **391**, 229-238 **(2001)**

12. Zhang Jie, Song Ji-Ming, Niu He-Lin, Mao Chang-Jie, Zhang Sheng-Yi and Shen Yu-Hua, $ZnFe_2O_4$ nanoparticles: Synthesis, characterization, and enhanced gas sensing property for acetone, *Sens. Actuators B*, **221**, 55-62 **(2015)**

13. Vijaya Judith, Kennedy L. John, Sekaran Bayhan G.M. and William M. Albert, Preparation and VOC gas sensing properties of Sr(II)-added copper aluminate spinel composites, *Sens. Actuators B*, **134 (2)**, 604-612 **(2008)**

14. Xu J., Pan Q., Shun Y. and Tian Z., Grain size control and gas sensing properties of ZnO gas sensor, *Sens. Actuators B*, **66**, 277-279 **(2000)**