Spinel-Type Nanosized Mixed Ferrite Containing Mg And Zn for Ammonia Gas Sensing

T. R. TATTE[1], V. D. KAPSE[2]

[1]Department of Physics, Govt. Vidarbha Institute of Science & Humanities, Amravati 444604, MH, India
[2]Department of Physics, Arts, Science and Commerce College, Chikhaldara 444807, MH, India
Corresponding Author: truptitatte21@gmail.com

Abstract

Nanosized mixed ferrite $Mg_{1-x}zn_xfe_2o_4$ (x = 0.3) with cubic spinel structure was successfully synthesized by sol-gel route using citric acid as anionic surfactant followed by calcination at 700°C for 2 h. Different characterization techniques have been employed, such as X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Energy dispersive X-ray analysis (EDX) to study the crystallite size, structure and morphology. Fourier Transform Infrared Spectroscopy (FTIR) confirms the formation of $Mg_{0.7}Zn_{0.3}Fe_2O_4$. The mixed ferrite has an grain size ~ 125 nm. These nanoparticles exhibit significantly high response towards ammonia in comparison with ethanol vapor, hydrogen sulfide, hydrogen, liquid petroleum gas, carbon dioxide and chlorine. The gas response towards various gases at their 100 ppm concentrations is investigated at 27–400°c. The results suggest possibility of utilization of the nanosized mixed ferrite, without addition of any precious metal ion, as the ammonia detector.

Keywords: mixed ferrite; nanomaterial; spinel; sensor response

Introduction

Metal oxides based semiconductor gas sensors such as zinc oxide, tin oxide and tungsten oxide have been widely studied for their gas sensing applications; however, presently many other oxides have also been explored for the gas sensing devices. Recently, few reports have appeared on the ferrites as gas sensors [1–8]. Although, ferrites are widely studied for their versatile applications [9–13] however; mostly they are used in the magnetic or electric devices, where the high densities are prerequisite. They have also been reported sensitive towards different gases and humidity wherein; low density and nanosized nature is favored [14,15]. Different spinel ferrites such as $nife_2o_4$, $cdfe_2o_4$, $znfe_2o_4$ and $cufe_2o_4$ have been studied for various gas-sensing applications [2,6,12,14]. Worldwide research efforts are underway to find new applications for ferrites in addition to improving their existing functional properties.

Recent research interests on spinel ferrites are due to their unique optical, electrical, and magnetic properties. These characteristics are strongly dependent on their size, shape, and dispersion [16]. Study of spinel ferriteMFe_2O_4 (where M = Fe, Mn, Zn, Co, Mg, Cu, Ni) nanoparticles has great significance in modern technologies such as contrast enhancement of magnetic resonance imaging, high density data storage, and magnetic carriers for site-specific drugs delivery [17]. Amongst the spinel ferrite families, magnesium ferrite ($MgFe_2O_4$) is a soft magnetic n-type semiconducting material [18, 19]. It has a cubic structure of normal spinel-type and is a soft magnetic n-type semiconducting material, which finds a number of applications in heterogeneous catalysis, adsorption, sensors, and in magnetic technologies.

The gas sensing is a surface phenomenon of gas–solid interaction, where the conductivity of semiconducting oxides can be altered by adsorption of gases from ambient. It is well known that depending upon the morphology and operating temperatures; the oxide surface hold various oxygen

species, such as O^-, O^{2-}. Their number and distribution also plays an important role in the gas sensing characteristics. The literature shows that the metal oxide nanoparticles enhance the sensitivity of a gas sensing material, while the selectivity is achieved by doping on surface or in the volume. However, recently Korotcenkov [20] suggested that the shape control of the nanocrystalline can provide energetically different adsorption sites for the test gases on different crystal facets. Thus existence of large surface to volume ratio in the typical nanostructured material facilitates better response towards specific gases.

Moreover, morphology and particle size of nonmaterial depend upon their method of preparation and sintering temperatures, and hence one can observe different responses towards gases for the similar composition. Synthesis route such as conventional ceramic, sol–gel, co-precipitation and hydrothermal technique [21-23] have been utilized so far for the synthesis of ferrites. These methods have merits and demerits. Ceramic and co-precipitation require high sintering temperatures, and at high temperatures fine particle nature gets lost due to their agglomeration. The presently used sensing devices include, individual nanostructures, multinano structures, MOSFET- based as well thin/thick film sensors. These nano sensor based devices have number of advantages such as high sensitivity, selectivity, fast response and recovery, which set them apart from the conventional gas sensors [3]. However, to our knowledge the ammonia gas-sensing characteristics of Zn doped $mgfe_2o_4$ have been rarely reported in the open literature.

In view of the possibility of finding gas response in the nanostructured mixed ferrite we explored $Mg_{0.7}Zn_{0.3}Fe_2O_4$ as a gas sensing material. It has been synthesized by a sol-gel route, wherein citric acid plays a vital role for anionic surfactant. This effective, environment friendly route is convenient and inexpensive to get ammonia sensitive $Mg_{0.7}Zn_{0.3}Fe_2O_4$.

Experimental work

Material and Methods

A sol-gel method has been adopted in order to synthesize nanosized mixed ferrite $Mg_{1-x}zn_xfe_2o_4$. All chemicals were of analytical grade and were used without further purification. Ferrous nitrate, magnesium nitrate, zinc nitrate and citric acid were weighed separately with a ratio 0.5M:0.25M:0.5M. These reagents were dissolved in distilled water and volume made up to 100 ml. The solution mixture was stirred and heated at 60^oc for 3 h and followed by 80^oc, until the mixture changed to gel form. The gel was then dried in an oven at 100^oc for 24 h and followed by calcined in a muffle furnace at 700^oc for 2 h. Taken solid phase sample was grinded in a mortar to make it powder.

Characteristics

X-ray diffraction (XRD) patterns of the nanopowder were obtained with scan rate of $0.02^o\ s^{-1}$ in a 2θ range from 10^o to 80^o, X-ray diffractometer Bruker using Cu Kα radiation (λ = 1.5406A^o) with operating voltage of 40 kv at room temperature and current of 20 ma. The crystallite size was calculated from diffraction peaks according to Scherrer's equation. Fourier Transform Infrared Spectroscopy (FTIR) confirms the formation of $Mg_{0.7}Zn_{0.3}Fe_2O_4$. The FTIR images were recorded using 3000 Hyperion Microscope with Vertex 80 (Bruker,Germany) FTIR system.

Fabrication of sensor and measurement of gas-sensing properties

Appropriate quantity of mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and turpineol was added to the mixture of $Mg_{1-x}Zn_xFe_2O_4$ and a solution of ethyl cellulose (a temporary binder). The mixture was then ground to form paste. The paste obtained was screen printed onto a glass substrate in desired patterns. The thick films so prepared were fired at 500°C for 1 h. The particle

morphology of prepared film was measured by SEM. The SEM images were scanned using JSM-7600F microscope with an accelerating voltage of 0.1 to 30 kV.

The nanostructured $Mg_{1-x}Zn_xFe_2O_4$ oxide powder thick films so prepared and the ohmic contacts were made with the help of silver paste to form the sensing element. The gas sensing studies were carried out on these sensing elements in a static gas chamber to sense ammonia in air ambient. The sensing element was kept directly on a heater in the gas chamber and the temperature was varied from 27 to 400^{o}C. The temperature of the sensing element was monitored by chromel–alumel thermocouple placed in contact with the sensor. The known volume of the ammonia was introduced into the gas chamber pre-filled with air with a micro-syringe so as to yield a desired concentration and it was maintained at atmospheric pressure. The electrical resistance of the sensing element was measured before and after exposure to ammonia using a sensitive digital multimeter. After approximately 90 s, recovery of sensors was studied by opening the chamber to the atmosphere. The performance of the sensing element is presented in terms of gas response (S), which is defined as:

$$S = \frac{R_{air}}{R_{gas}} \qquad (1)$$

Where, R_{air} and R_{gas} are the electrical resistance values of the sensor element in air and in the presence of ammonia gas, respectively.

Result and discussions

XRD analysis

Formation of the desired $Mg_{0.7}Zn_{0.3}Fe_2O_4$ spinel oxide was confirmed by powder X-ray diffraction analysis. X-ray diffraction pattern recorded on $Mg_{0.7}Zn_{0.3}Fe_2O_4$ is as shown in Fig. 1. The analysis of samples shows all the characteristic peaks of ferrite material such as (123), (719), (352), (2031), (547), (184), (185), (537), (826) and (132) reflection planes confirms the clear evidence for the formation of cubic spinel structure of the sample with most intense peak (2031). Figure depicts broad peaks due to the nanosized of particles and the average crystallite size (t) was calculated using Scherrer's formula

$$D = \frac{\kappa\lambda}{B\cos\theta} \qquad (2)$$

Where, D is the average size of the particles, assuming particles to be spherical, k = 0.9, λ is the wavelength of X-ray radiation, B the full width at half maximum of the diffracted peak and θ is the angle of diffraction.

FT-IR analysis

FT-IR spectra of $Mg_{0.7}Zn_{0.3}Fe_2O_4$ nanoparticle are presented in Fig. 2. Vibrations of ions in the crystal lattice are usually observed in the range of 4000 - 400 cm^{-1} in IR analysis. Two main broad metal-oxygen bands are seen in the IR spectra relative to spinel ferrite compounds. The highest one observed in the range 560 cm^{-1}, corresponds to intrinsic stretching vibrations of the metal at the tetrahedral site, whereas the lowest band usually observed in the range 432 cm^{-1}, is assigned to octahedral-metal stretching. The Mg^{2+} ions occupy mainly the octahedral sites but fraction of these ions may be migrated into tetrahedral sites. This would explain the existence of a weak shoulder in the range of 690 –710 cm^{-1}.This confirms that the Mg ferrite has a partially inverse spinel structure.

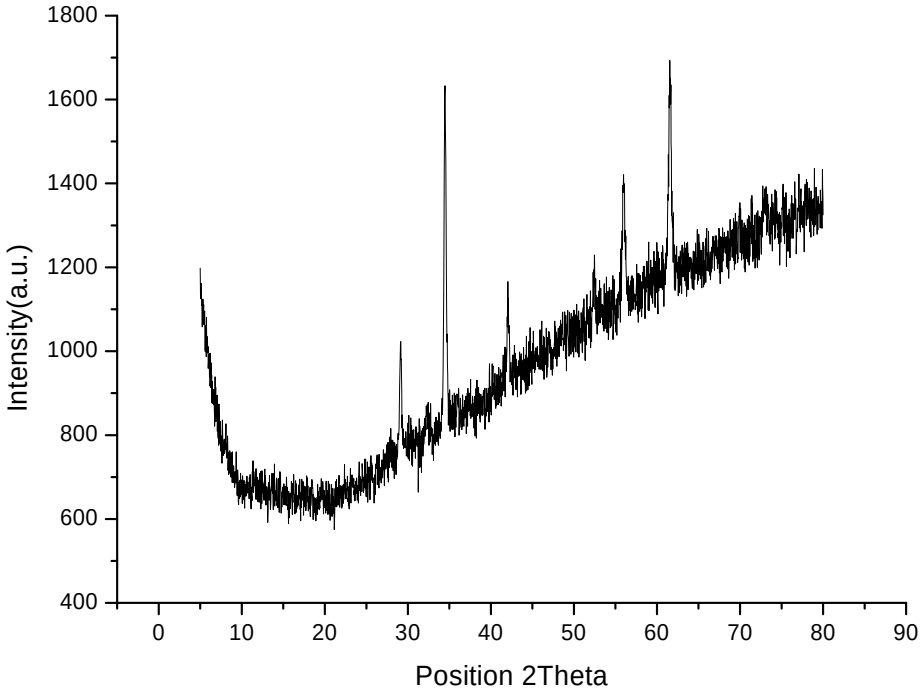
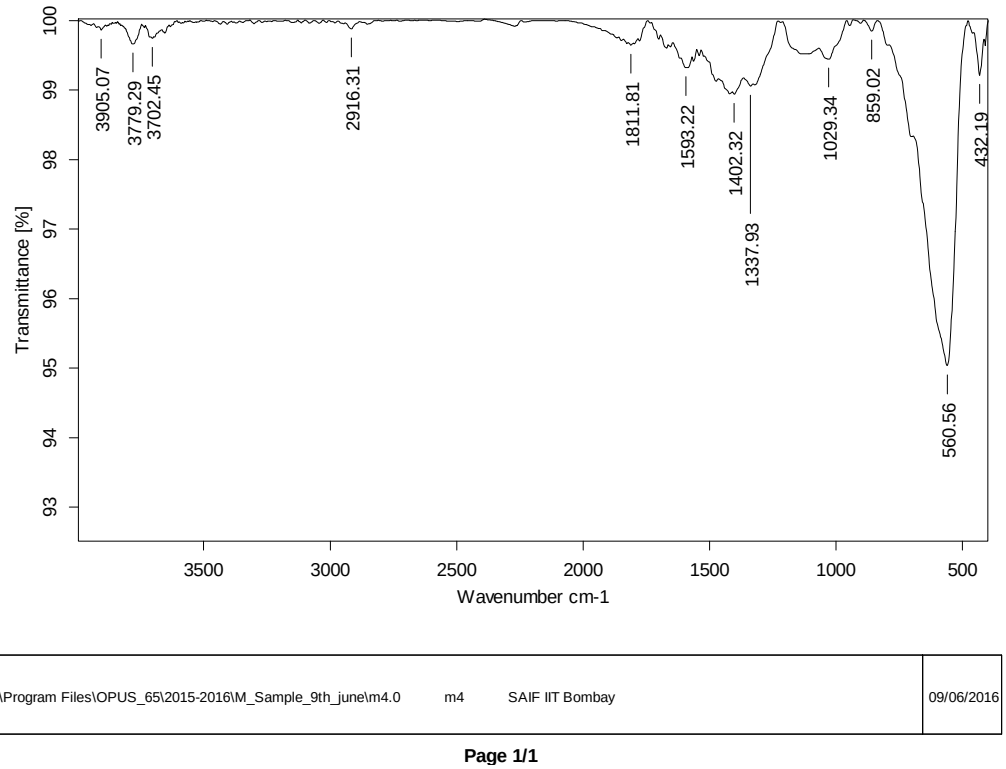


Figure 1. XRD patterns of $Mg_{0.7}Zn_{0.3}Fe_2O_4$ annealed at 700°C.



C:\Program Files\OPUS_65\2015-2016\M_Sample_9th_june\m4.0	m4	SAIF IIT Bombay	09/06/2016

Page 1/1

Figure 2. FTIR spectra of nanosized $Mg_{0.7}Zn_{0.3}Fe_2O_4$.

SEM analysis

Fig. 3 shows SEM image of the nanosized spinel $Mg_{0.7}Zn_{0.3}Fe_2O_4$. The SEM technique was employed for finding morphology of the powder; it shows formation of the agglomerated particle having size ~ 125 nm. SEM pictures show that the samples exhibit large grains structure having regular morphology (polygons) with the presence of soft agglomerations.

Energy dispersion X-ray analysis

The elemental composition of synthesized $Mg_{0.7}Zn_{0.3}Fe_2O_4$ nanoparticle has been investigated by the energy dispersion X-ray analysis (EDX). Fig. 4 shows EDX patterns of the nanosized spinel $Mg_{0.7}Zn_{0.3}Fe_2O_4$. From the EDX spectrum, the presence of Mg, Zn, Fe and O has been confirmed and EDX results reveal almost the same ratio of Mg/Zn/Fe for the synthesized nanoparticle as they were actually added during synthesis process.

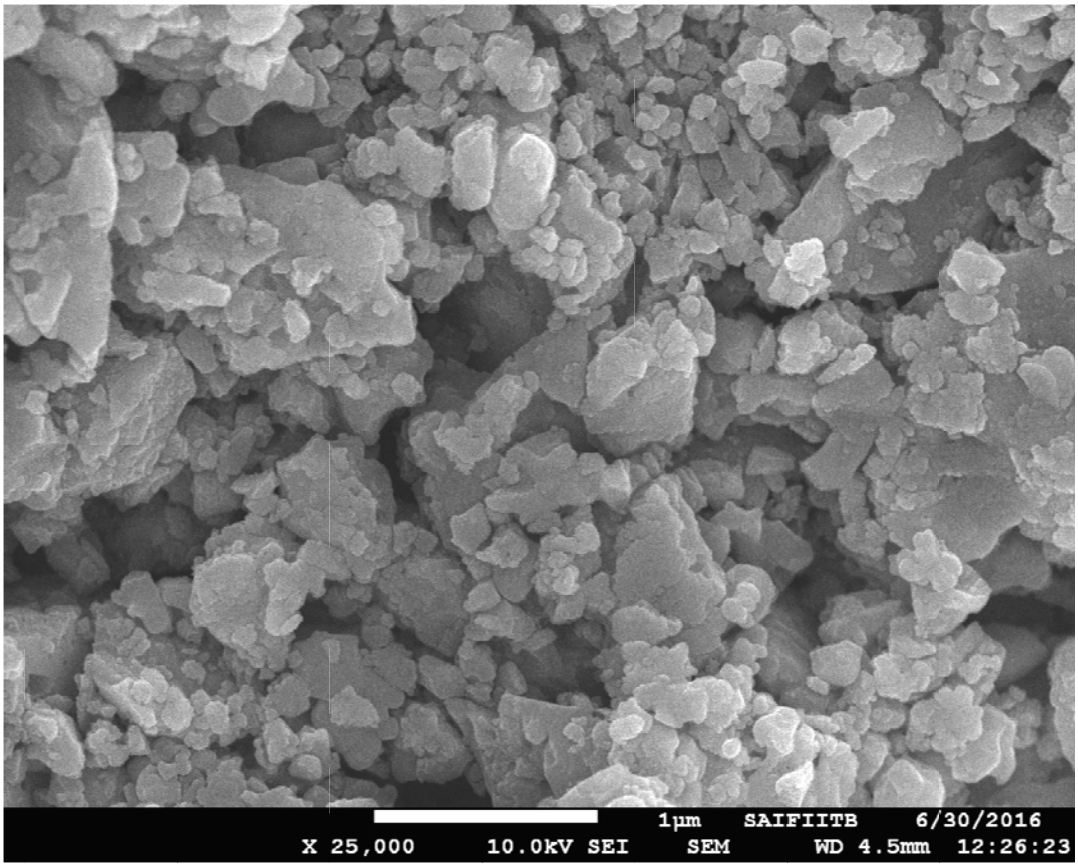


Figure 3. SEM image of nanosized $Mg_{0.7}Zn_{0.3}Fe_2O_4$.

Gas sensing properties

To investigate gas-sensing properties, the crystalline nanosized $Mg_{0.7}Zn_{0.3}Fe_2O_4$ powder was made in the form of thick films. The prepared films were then subjected for studying their sensitivity and selectivity at the different controlled temperatures towards various gases in the dynamic setup

The gas response (S) against various reducing gases is shown in Fig. 5. The bar graph shows that this material is highly selective towards ammonia as compared with the other reducing test gases. On the bar graph, the time required for sensing of each gas with their 100 ppm concentration is mentioned. All the gases such as hydrogen, LPG, hydrogen sulphide, CO_2, Cl_2 and ethanol vapors show response (S)

below 5 while ammonia shows 23.26, moreover it requires remarkably less time for sensing as compared with other reducing gases. Fig. 6 shows response (S) towards ammonia at various operating temperatures which indicates 200°C as the optimum temperature for the gas response.

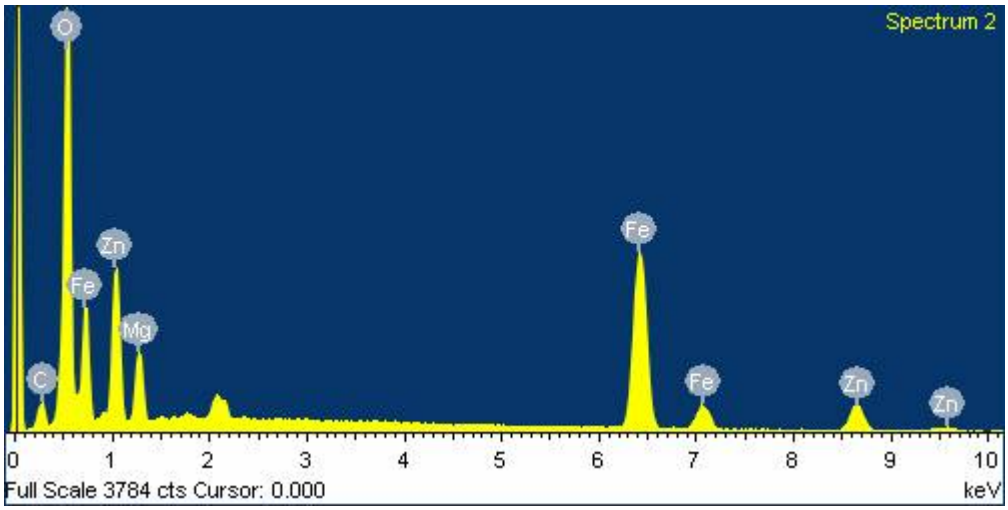


Figure 4. EDX spectrum for nanosized $Mg_{0.7}Zn_{0.3}Fe_2O_4$.

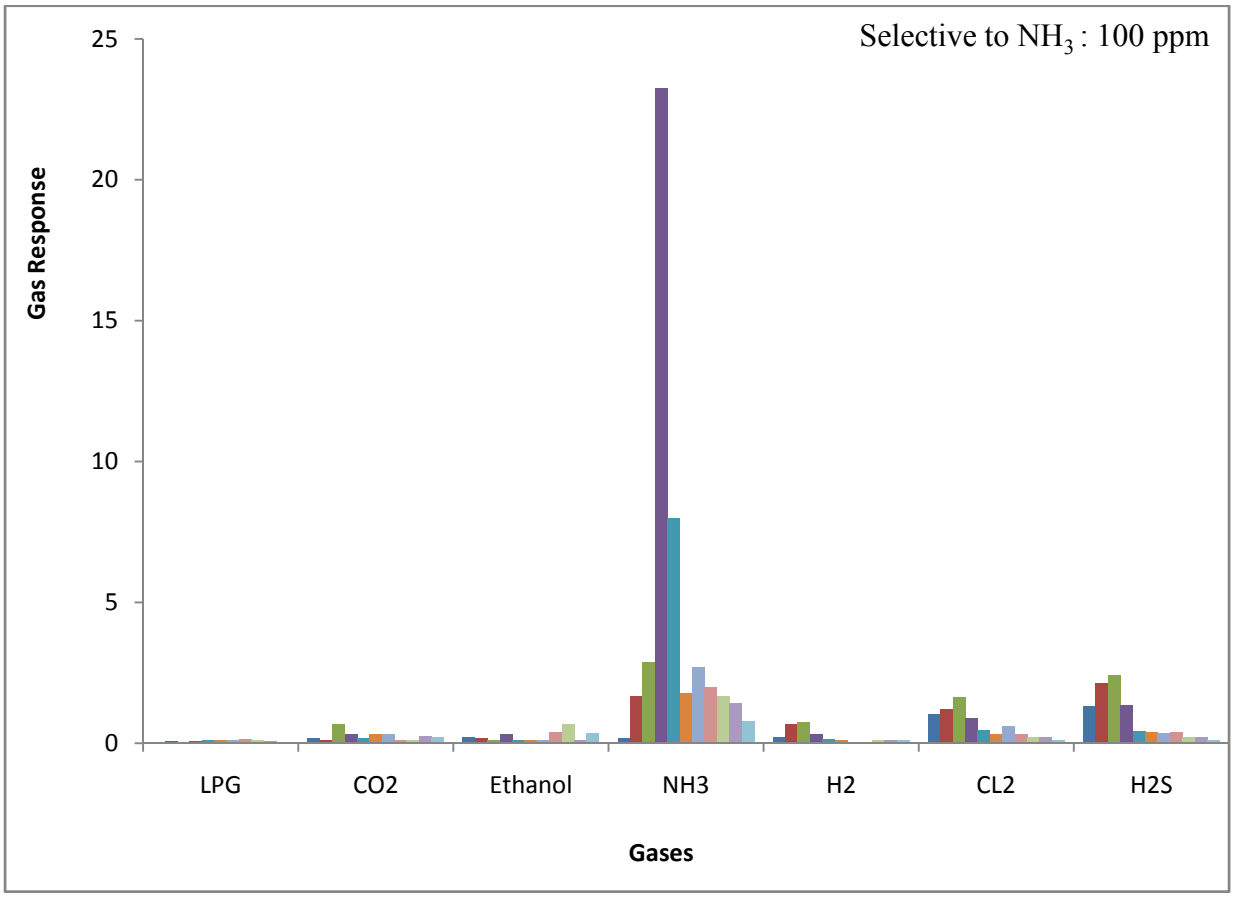


Figure 5. Response of nanosized spinel $Mg_{0.7}Zn_{0.3}Fe_2O_4$ towards 100 ppm of various gases at 200°C.

The detailed mechanism of different gases inducing the different resistance change observed is not completely understood at present. The structural features of the nanoscale ferrite complicate the sensing activities, as it involves size, crystallite shape, phase composition, mixed valence and its surface architecture. In the gas sensing mechanism adsorbed O^- and O^{2-} species play important role which in turn depends upon the temperature and oxidation states of the surface ions. The selectivity shown by nanosized $Mg_{0.7}Zn_{0.3}Fe_2O_4$ towards ammonia in comparison with LPG can be attributed to the higher electron affinity of ammonia towards the acidic ferrite surface. At the same time presence magnesium on the surface also increases the acidity therefore may hinder affinity towards LPG and thereby reduce the LPG sensitivity.

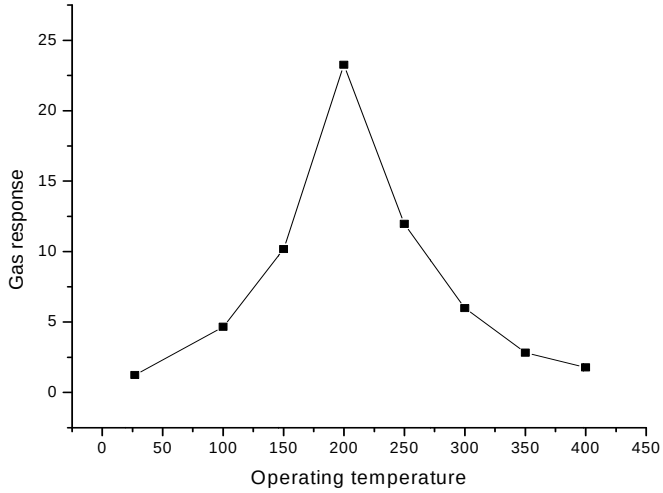


Figure 6. Response of nanosized spinel $Mg_{0.7}Zn_{0.3}Fe_2O_4$ towards ammonia at the different operating temperatures.

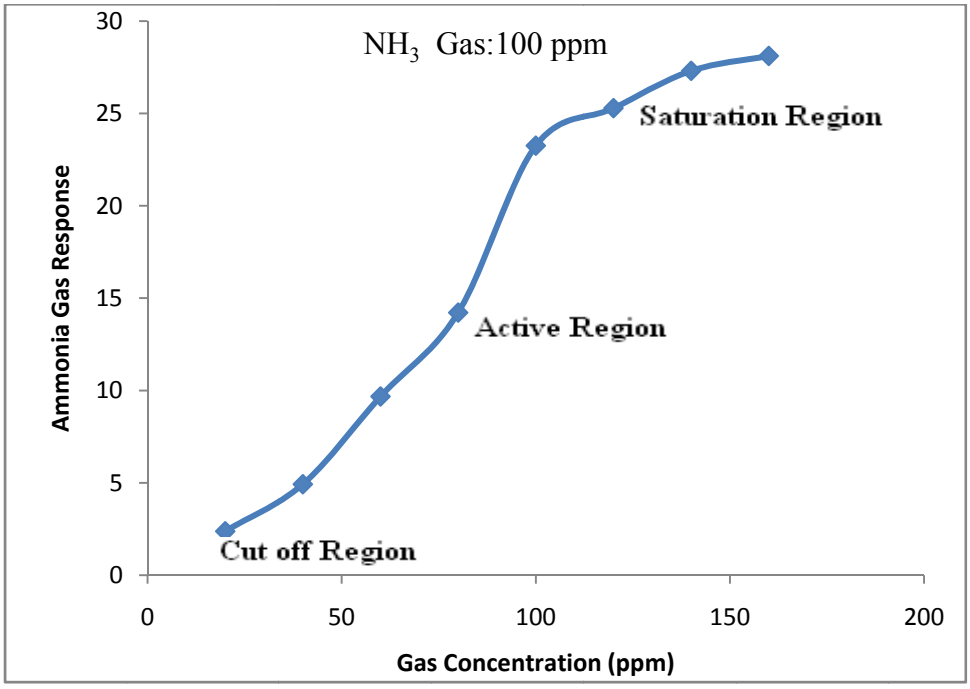


Figure 7. Response towards various concentrations (ppm) of ammonia.

In Fig. 7 response towards higher concentrations of ammonia is shown, which indicates that $Mg_{0.7}Zn_{0.3}Fe_2O_4$ responses as low as 20 ppm of ammonia and the response increases linearly with its concentration. Fig. 8 shows ammonia response and recovery (as the change in resistance) with reference to time. The nanosized $Mg_{0.7}Zn_{0.3}Fe_2O_4$ senses 100 ppm of ammonia with response characteristic was good, the resistance of the sensor obviously increased, and the response time was quick and the recovery time was fast. To find the reproducibility ammonia was again introduced which showed similar responses, indicating the reproducible nature of its response. The sensor was measured about its responses to 100 ppm ammonia in a month the results are shown in Fig. 9. From the 1st day to the 6th day, the response decreased slowly. After the 6th day, it kept constant almost. On the whole, it indicates that the $Mg_{0.7}Zn_{0.3}Fe_2O_4$ at 700^0C sensor possesses a very good stability.

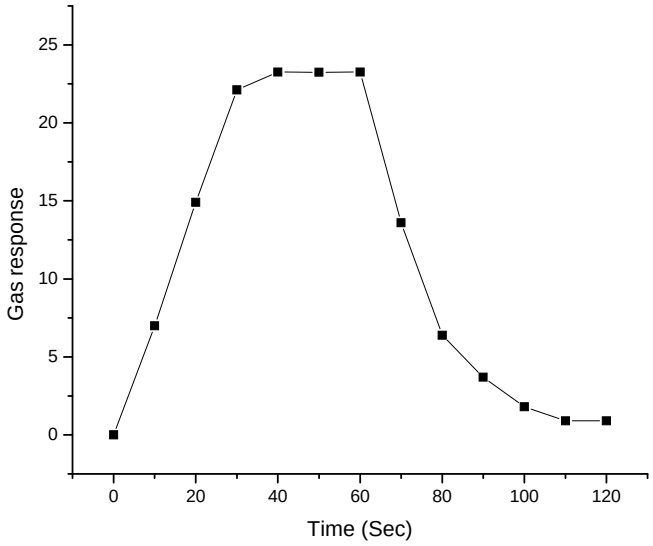


Figure 8. Response and recovery characteristics of $Mg_{0.7}Zn_{0.3}Fe_2O_4$ to 100 ppm ammonia.

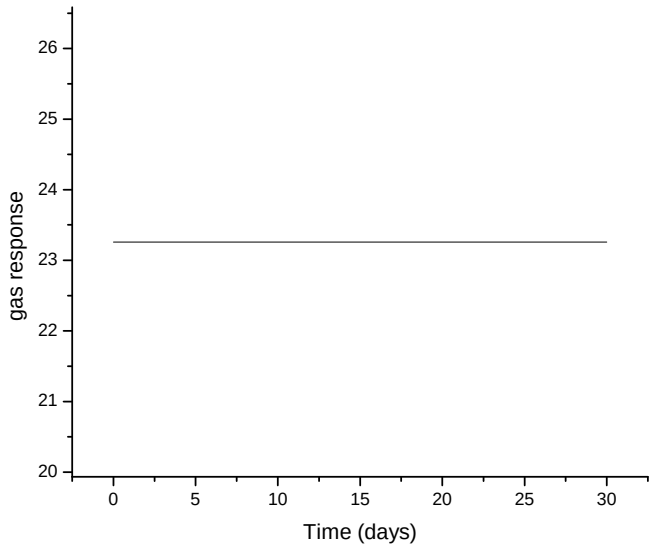


Figure 11. Long-time stability curve of $Mg_{0.7}Zn_{0.3}Fe_2O_4$ sensor.

Conclusion

Nanopowder of $Mg_{0.7}Zn_{0.3}Fe_2O_4$ was synthesized using less expensive, environment-friendly and low temperature sol-gel route using citric acid as anionic surfactant occurring at a temperature 700^oC. SEM analysis validated the structure of final powder with the grain size ~ 125 nm. The nearly cubical shaped morphology with the isolated nanoparticles shows potential of this simple method. The sensor based on the pure $Mg_{0.7}Zn_{0.3}Fe_2O_4$ nanomaterial showed selective response towards 100 ppm of ammonia at 200^oC operating temperature with a response time of few seconds and good reproducibility.

Acknowledgements

I would like to thank Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology (I.I.T.), Bombay for carrying out FT-IR, SEM-EDAX and TEM-ED characterizations and Department of Physics, Vidyabharati Mahavidhyalaya, Amravati for providing the XRD facility.

References

[1]. L. Satyanarayana, K. M. Reddy, V. M. Sunkara, "Nanosized spinel $NiFe_2O_4$: a novel material for the detection of liquefied petroleum gas in air", Mater. Chem. Phys., vol. 82, pp. 21–26, 2003.
[2]. T. S. Zhang, P. Xing, J. C. Zhang, L. B. Kong, "Ethanol-sensing characteristics of cadmium ferrite prepared by chemical coprecipitation," Mater. Chem. Phys., vol. 61, pp.192–198, 1999.
[3]. Y. Liu, H. Wang, Y. Yang, Z. Liu, H. Yang, G. Shen, R. Yu, "Hydrogen sulfide sensing properties of $NiFe_2O_4$ nanopowder doped with noble metals," Sens. Actuators B, vol. 102, pp. 148–154, 2004.
[4]. L. Satyanarayan, K. M. Reddy, S. V. Manorama, "Synthesis of nanocrystalline $Ni_{1-x}Co_xMn_xFe_{2-x}O_4$: a material for liquefied petroleum gas sensing," Sens. Actuators B, vol. 89, pp.62–67, 2003.
[5]. L. Satyanarayan, K. M. Reddy, S. V. Manorama, "Nanosized spinel $NiFe_2O_4$: a novel material for the detection of liquefied petroleum gas in air," Mater. Chem. Phys., vol. 82 (1), pp.21–26, 2003.
[6]. C. V. Gopal Reddy, S. V. Manorama, V. J. Rao, "Semiconducting gas sensor for chlorine based on inverse spinel nickel ferrite," Sens. Actuators B, vol. 55, pp. 90–95, 1999.
[7]. N. Rezlescu, N. Iftimie, E. Rezlescu, C. Doroftei, P. Popa, "Semiconducting gas sensor for acetone based on the fine grained nickel ferrite," Sens. Actuators B, vol. 114, pp.427–432, 2008.
[8]. C. Xiangfeng, J. Dongli, Z. Chenmou, "The preparation and gas-sensing properties of $NiFe_2O_4$ nanocubes and nanorods," Sens. Actuators B, vol. 123, pp. 793–797, 2007.
[9]. M. Sugimoto, "The past, present, and future of ferrites," J. Am. Ceram. Soc., vol. 82, pp.269–280, 1999.
[10]. K. Raj, B. Moskowitz, R. Casciari, "Advances in Ferro fluid technology," J. Magn. Magn. Mater., vol. 149, pp.174–180, 1995.
[11]. R. D. McMichael, L. J. Shull, L. J. Swartzendruber, R. H. Bennett, R. D. Watson, "Magnetocaloric effect in super paramagnets," J. Magn. Magn. Mater., vol. 11, pp. 29–33, 1992.
[12]. J. Azadmanjiri, S. Ebrahimi, H. Salehani, "Magnetic properties of nanosize $NiFe_2O_4$ particles synthesized by sol–gel auto combustion method," Ceram. Int., vol. 33, pp.1623–1625, 2007.
[13]. S. Ziemniak, L. Anovitz, R. Castelli, W. Porter, "Magnetic contribution to heat capacity and entropy of nickel ferrite ($NiFe_2O_4$)," J. Phys. Chem. Solids, vol. 68, pp.10–21, 2007.
[14]. E. Comini, M. Ferroni, V. Guidi, G. Fagila, G. Martinelli, G. Sberverglieri, "Nanostructured mixed oxides compounds for gas sensing applications," Sens. Actuators B, vol. 84, pp.26–32, 2002.
[15]. H. Ogawa, A. Abe, M. Nishikawa, S. Hayakawa, "Electrical properties of tin oxide ultrafine particle films," J. Electochem. Soc. Solid-State Sci. Technol., vol. 128, pp. 2020–2025, 1981.

[16]. J. Hu, T. W. Odom, C. M. Lieber, "Chemistry and physics in one dimension: synthesis and properties of nanowires and nanotubes," *Accounts of Chemical Research*, vol. 32(5), pp. 435–445, 1999.

[17]. Z. L. Wang, Y. Liu, Z. Zhang, "*Handbook of Nanophase and Nanostructured Materials*," vol. 3, Kluwer Academic/Plenum, New York, NY, USA, 2003.

[18]. R. J. Willey, P. Noirclerc, G. Busca, "Preparation and characterization of magnesium chromite and magnesium ferrite aerogels," *Chemical Engineering Communications*, vol. 123, pp. 1–16, 1993.

[19]. N. Sivakumar, A. Narayanasamy, J.-M. Greneche, R.Murugaraj, Y. S. Lee, "Electrical and magnetic behaviour of nanostructured $MgFe_2O_4$ spinel ferrite," *Journal of Alloys and Compounds*, vol. 504(2), pp. 395–402, 2010.

[20]. G. Korotcenkov, "Gas response control through structural and chemical modification of metal oxide films: state of the art and approaches," Sens. Actuators B, vol. 107, pp.209–232, 2005.

[21]. S. Bida, P. Sahub, S.K. Pradhanc, "Microstructure characterization of mechanosynthesized nanocrystalline $NiFe_2O_4$ by Rietveld's analysis," Physica, vol. 39, pp.175–184, 2007.

[22]. J. Miki, M. Asanuma, Y. Tachibana, T. Shikada, "A highly effective countermeasure for the deactivation of the $NiO–NiFe_2O_4–Na_2O$ catalyst for phenol synthesis," Appl. Catal. A, vol. 143, pp.215–222,1996.

[23]. X. Huang, Y. Choi, "Chemical sensors based on nanostructured materials," Sens. Actuators B, vol. 122, pp.659–671, 2007.