Structural And Gas Sensing Properties of Zn Substituted Magnesium Ferrite Nanoparticles Prepared by Sol-Gel Citrate Method

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***Abstract*—Gas-sensing technology has gained significant attention in recent years due to the increasing concern for environmental safety and human health caused by reactive gases. In particular, spinel ferrite (MFe_2O_4), a metal oxide semiconductor with a spinel structure, has emerged as a promising material for gas-sensing applications. In this study, the $Mg_{1-x}Zn_xFe_2O_4$ (MZFO) (with x = 0.2, 0.4, 0.6 and 0.8) nanoparticles were prepared by sol-gel citrate method. The study aimed to explore the effect of substituting Mg with Zn in MZFO on its structural and gas-sensing properties. The spinel phase formation was confirmed using X-ray diffraction pattern. The gas-sensing characteristics of Zn-substituted spinel ferrites at different temperature for CO_2, LPG, NH_3 and ethanol were studied. The nanostructured MZFO exhibited high sensitivity towards CO_2 gas and showed a good response time for CO_2, demonstrating that MZFO can be a good potential candidate for gas-sensing applications.**

***Index Terms*—Gas sensor, Nanomaterial, Response Time, Spinel-Ferrite, XRD.**

I. INTRODUCTION

Metal oxide semiconductor (MOS) gas sensors have become indispensable tools for monitoring environmental pollution, ensuring industrial safety, and safeguarding public health [1]. MOS gas sensors operate by detecting alterations in the electrical conductivity of a semiconducting metal oxide when exposed to a gas [2]. When the MOS sensor comes into contact with the target gas, the gas molecules adhere to the sensor material's surface, resulting in a modification of the sensor's electrical resistance [3]. The extent and direction of the resistance alteration correlate with the gas concentration and its chemical properties.

MOS-gas-sensitive materials can be classified into two categories based on the number of metal ions present in the single-phase metal oxide material: single metal oxides and composite metal oxides. As a semiconducting composite metal oxide material, spinel ferrite has excellent chemical stability, enabling the effective adsorption of various gases [4]. Its inherent catalytic properties stimulate chemisorption processes that result in changes in its electrical resistance when exposed to different gases [5]. This allows for accurate gas detection and measurement. Additionally, spinel ferrite can operate at lower temperatures compared with other gas sensors, which leads to increased energy efficiency [6]. Its high sensitivity [7] and selectivity [8] towards particular gases, coupled with its capacity for miniaturization, make spinel ferrite an optimal material for building reliable, efficient, and compact gas sensors.

Spinel ferrites (AB_2O_4) containing iron oxides are important magnetic compounds and have been studied intensively due to their unique properties such as high Curie temperature [9] high coercivity, large Kerr effect [10] Faraday rotations [11] and insulator-metal transition [12]. Ferrites with these properties can be beneficial in many applications, such as in transformer cores, drug delivery, gas sensors and ferrofluids [13].

Magnesium ferrite ($MgFe_2O_4$) belongs to a class of compounds having the general formula $M^{+2}Fe^{+3}{}_2O_4$ crystallizing with spinel structure (where M represents tetrahedral site and Fe represents the octahedral site)

[14]. The interesting properties of spinel ferrites arise from their ability to distribute the cations among the Tetrahedral (A) and Octahedral (B) sites [15]. For obtaining the specific properties ferrites can be fabricated by substituting various magnetic and non-magnetic ions which greatly affect the magnetic moments, lattice parameters and exchange interactions [16, 17]. Magnesium nano ferrites are the potential materials for various applications due to their high electrical resistivity, low magnetic and dielectric losses [18]. Magnesium ferrite is n-type semi-conductor and also a soft magnetic material. It is used in making of the memory chips for computers, microwaves devices and high-density recording media. Researchers are interested into this because it possesses good photoelectric effect and humidity sensitive properties and it can also be used as moisture gas sensor [19].

The chemical sensing properties of magnesium ferrite have been studied towards various gases like liquefied petroleum gas (LPG), ethanol (C_2H_5OH), carbon monoxide (CO), hydrogen sulphide (H_2S), chlorine (Cl_2) and acetylene [20]. However, chemical sensing properties of complex metal oxides towards weakly reactive gases like carbon dioxide (CO_2) is not well explored. Carbon dioxide is a greenhouse gas, which affects adversely the health and the environment and hence should be monitored. Carbon dioxide sensing is also interesting as it is useful for proximity sensing for incorporating with the indoor air quality maintenance. This requires the installation of CO_2 sensors in large number. However, the currently available commercial sensors are based on infrared optics and are costly.

In the present study, different composition of $Mg_{1-x}Zn_xFe_2O_4$ (x = 0.2, 0.4, 0.6 and 0.8) nanocomposites were prepared by Sol-Gel Citrate method for CO_2 gas sensor. This method is a simple process which speeds up the synthesis of complex materials than the other synthesis methods [21]. Advantages of sol-gel citrate method over the conventional methods are (i) simple and economic method (ii) use of relatively simple equipment (iii) formation of high purity products (iv) good stoichiometric control (v) production of ultra-fine particles with a narrow size distribution (vi) very low processing temperature.

II. EXPERIMENTAL

2.1. Materials

Mg-Zn Nano ferrites having the chemical formula $Mg_{1-x}Zn_xFe_2O_4$ (where x= 0.2, 0.4, 0.6 and 0.8) were synthesized by sol-gel citrate method using magnesium nitrate [$Mg(NO_3)_2.6H_2O$], ferrite nitrate [$Fe(NO_3)_2.9H_2O$], Zinc nitrate [$Zn(NO_3)_2.6H_2O$], citric acid monohydrate [$C_6H_8O_7.H_2O$] and ethylene glycol [$C_2H_6O_2$].

2.2. Synthesis

Calculated quantities of above nitrate salts were dissolved in ethylene glycol and required amount of aqueous citric acid solution was added as chelating agent. The mixture was thoroughly stirred by using a magnetic stirrer at a temperature of about 80ºC for 2 hr to get a homogeneous solution. The mixed solution was then heated in pressure vessel at about 130ºC for 12 hr to obtain a highly viscous gel denoted as precursor. The resultant gel was further heated at a temperature of 350ºC for 3 hr. Finally, the dried powder was ground and was calcined in air at temperature 600ºC for six hr to obtain a spinal phase.

2.3. Characterization

The structural characterization of the synthesized samples was carried out by X-ray diffractometer using Cu Kα radiation (λ=1.5405A^0). The intensity data were collected over a 2θ range of 20–70º. The average crystallite size of the samples was estimated with the help of Scherrer equation using the diffraction intensity of all prominent lines.

2.4. Fabrication of sensor device

For gas sensing properties, the calcinated powder was then mixed with 2% PVA (polyvinyl alcohol) as a binder and 5% ethanol as a solvent to obtain a paste; the resulting paste was coated over a cylindrical alumina tube of length 15mm and diameter 5mm. A small Cr-Al thermocouple was used to sense the operating temperature of the sensor. After coating, the element was sintered at 600ºC for 2 hr in a vertical furnace in order to improve the stability.

The analyte gas was injected into the test chamber through an injection port and the resistance was measured as a function of time till a constant value was attained. Then the chamber was purged with air for about 5 min and the experiments were repeated. The sensor element, with a nichrome heater to provide the necessary temperature and a chromelalumel thermocouple for temperature monitoring is fixed

inside the specimen chamber made of aluminium for studying the gas sensing characteristics. The different test gases are injected into the specimen chamber through an inlet. The output voltage across the sensor element at a 10 V input voltage is taken to determine the resistance of the element.

The gas response (*S*) is defined as the ratio of the change of resistance in the presence of analyte gas (Rg) to that in air (Ra) [22],

$S = \Delta R/Ra = (Ra - Rg) / Ra$ ----------I

The sensor was examined under different reducing gases such as CO_2, LPG, NH_3 and ethanol, whose concentration were fixed at 600 ppm in air. The gas-sensing properties were measured in a temperature range of 50 – 350^{0}C.

III. RESULTS AND DISCUSSION

3.1. XRD Analysis

Figure 1 shows the X-Ray Diffraction (XRD) pattern of $Mg_{0.4}Zn_{0.6}Fe_2O_4$ prepared by sol-gel citrate method, calcined at 600^{o}C for 6 hr. The major peaks with their respective hkl values are (220), (311), (400), (422), (511) & (440). The single-phase cubic spinel structure was indicated from the above peaks provide clear evidence for the formation of the spinel structure of Mg – Zn ferrite.

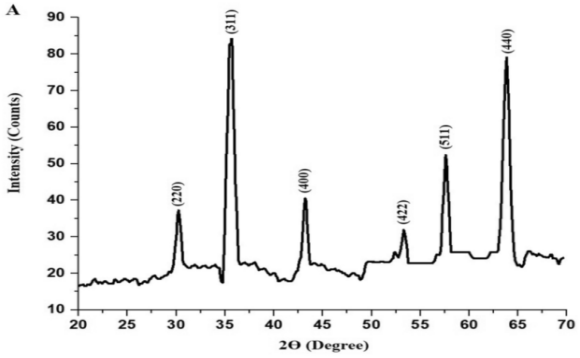

Fig 1: XRD patternof $Mg_{0.4}Zn_{0.6}Fe_2O_4$, calcined at 600^{o}C for 6 hr

The crystallite size (D) was calculated for all the composition using maximum intensity peak from Scherrer's formula and it was found to be 40 nm.

Crystallite size, $D = 0.91\lambda / \beta Cos\theta$ ---------- II

Where, λ = wavelength of X-Ray; β = Full width half maximum (radians); θ = Bragg's angle at the peak position.

3.2. Gas sensing measurement

Since the response of gas sensors is greatly influenced by operating temperature, we have investigated the sensor response (*S*) as a function of operating temperature for undoped $MgFe_2O_4$ nano powder calcined at 600^{o}C for 6 hr for various reducing gases like ethanol, LPG, CO_2 and NH_3 at 50–350^{o}C, as shown in Figure 2.

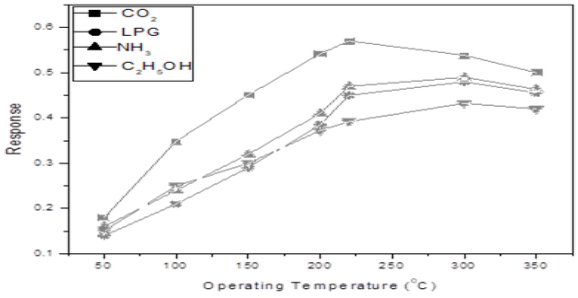

Fig. 2: Response vs operating temperature for undoped$MgFe_2O_4$, calcined at 600^{0}C.

It is clear from the figure that the response goes on increasing with increase in operating temperature, attains its maximum and then decreases with further increases in operating temperature. The sensor characteristic shows higher response for CO_2 gas as compared to LPG, ethanol and NH_3 at an operating temperature 220^{o}C.

In order to improve the gas response properties, a great variety of atoms or additives are introduced in the base sensing semiconductor. Figure 3 shows the gas response as a function of different amount of Zn doped $MgFe_2O_4$ ($Mg_{1-x}Zn_xFe_2O_4$; x = 0.2, 0.4, 0.6 and 0.8) calcined at 600^{0}C. Four samples were studied as CO_2 gas sensor.

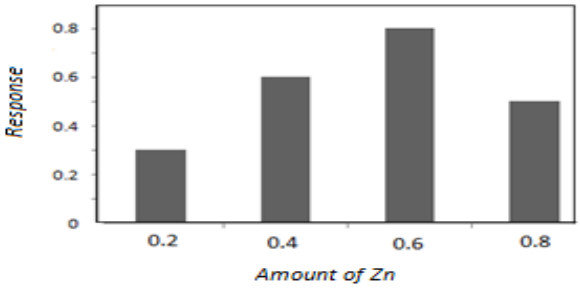

Fig 3: Sensor Response of $MgFe_2O_4$ doped with different amount of Zn (a) x=0.2, (b) x=0.4, (c) x=0.6and (d) x=0.8

The response to CO_2 gas goes on increasing with increasing amount of Zn. The largest response for $Mg_{0.4}Zn_{0.6}Fe_2O_4$ (x = 0.6) was obtained due to more available sites for the oxygen to be adsorbed and in

turn to oxidize the test gas. The decrease in response may be due to the insufficient number of sites available on the surface. The partial replacement of Mg by Zn ion results in decrease in grain size, which results in larger density of grain boundaries, which increases film's effective exposure area to the ammonia gas. The chemical composition of the semiconductor is also a key parameter that influences their sensing performance. In fact, composition by itself can affect the microstructure and, thus determine the sensing properties.

Selectivity is the ability that a gas sensor to distinguishes between different kinds of gases. Figure 4 illustrates the gas response of $Mg_{0.4}Zn_{0.6}Fe_2O_4$ at different operating temperature. It is evident from the figure that the sensor was highly selectivity to CO_2 gas against LPG, NH_3 and ethanol at 180^0C.

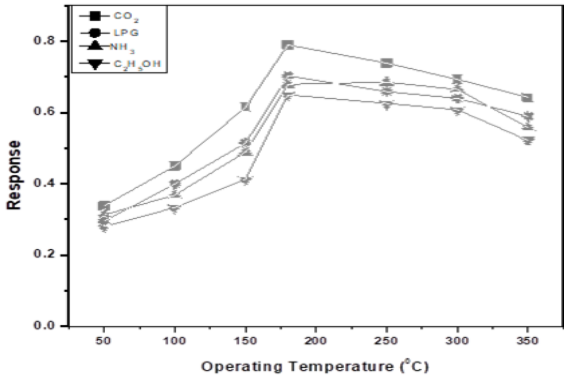

Fig 4: Response to different reducing gases of $Mg_{0.4}Zn_{0.6}Fe_2O_4$ as a function of op. temp.

The high response to CO_2 gas can be attributed to the surface modification by Zn over $Mg_{0.4}Zn_{0.6}Fe_2O_4$ film. The improved selectivity is possibly explained as follows: When O^{2-}, is adsorbed on the $Mg_{0.4}Zn_{0.6}Fe_2O_4$ surface, it traps electron(s) from the body of the n-type semiconductive $Mg_{0.4}Zn_{0.6}Fe_2O_4$ due to the strong electronegativity of the oxygen atom to produce negatively charged chemisorbed oxygen such as O_2^-, O^- and O^{2-}. As the result, the concentration of electrons in the n-type $Mg_{0.4}Zn_{0.6}Fe_2O_4$ decreases and hence the resistance of the material increases.

Figure 5 shows the dependence of gas response of the $Mg_{0.4}Zn_{0.6}Fe_2O_4$ sensor on the concentration level of CO_2 at 180ºC. It is clear from the graph that with the increase in the concentration, the response increases linearly up to 200 ppm of CO_2, after that it saturates. The graph also indicates that at low concentration response has a linear relationship with concentration because there may be sufficient number of available surface states to act on CO_2 vapour. After 200 ppm level of CO_2, the curve flattens because there would not be enough ionosorbed oxygen species to contribute to detecting mechanisms.

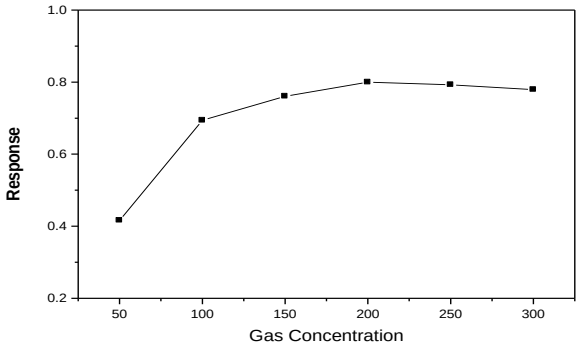

Fig 5: Response of $Mg_{0.4}Zn_{0.6}Fe_2O_4$ to CO_2 gas of different concentration at an operating temperature 180ºC.

Figure 6 shows the response time of the sensor at 180ºC. The response time in this case is ~ 40 sec. It was observed that the response time comes to saturated at 55 sec. It suggests that after this time there is no more O^- species left to react with the ammonia vapour. It also indicates that by increasing the surface area i.e., increasing the grain size of the film, one can increase the response time.

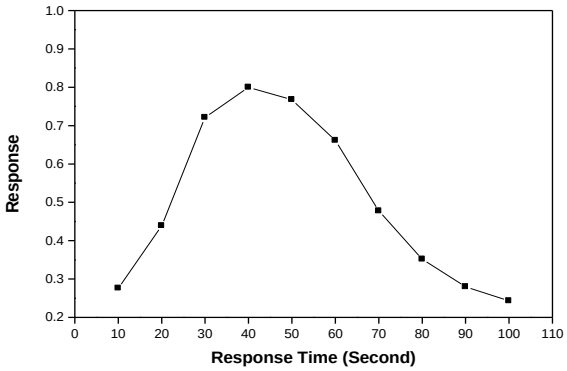

Fig 6: Response characteristics of $Mg_{0.4}Zn_{0.6}Fe_2O_4$at 180ºC.

IV. CONCLUSION

Nanocrystalline $Mg_{0.4}Zn_{0.6}Fe_2O_4$ thick film gas sensor was prepared by sol-gel citrate method. XRD of $Mg_{0.4}Zn_{0.6}Fe_2O_4$ calcined 600^0C for 6 hr showed good

crystalline quality with a grain size 40 nm. It was also found that $Mg_{0.4}Zn_{0.6}Fe_2O_4$ sensor exhibited excellent gas response and selectivity for CO_2 gas at 180^0C. The sensor is very promising for CO_2 gas detection with a response time in second range.

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