INFLUENCE OF Zn SUBSTITUTION ON THE STRUCTURAL AND GAS SENSING PROPERTIES OF $Co_{1-x}Zn_xFe_2O_4$ NANO-FERRITES

A. V. Kadu[a*], G.N.Chaudhari[b], S.G.Ibrahim[c], N.N.Gedam[d] and S.V.Jagtap[e]

[a*] Department of Chemistry, Prof Ram Meghe College of Engineering and Management, Badnera, Amravati, M.S. India.
[b]Department of Chemistry, Shri Shivaji Science College , Amravati, M.S. India.
[c] Department of Physics , Prof Ram Meghe College of Engineering and Management, Badnera, Amravati, M.S. India.
[d]Department of Chemistry, M. J. F. Commerce, Science Arts College, Bhatkuli, Amravati
[e] Department of Physics , Bar. R.D.I.K.N.K.D., Badnera, Amravati, M.S. India.

Abstract : Polycrystalline samples of $Co_{1-x}Zn_xFe_2O_4$ with stoichiometric proportion (x) varying from 0.2 to 0.8 were synthesized through the sol-gel citrate method. The structure and morphology were characterized by X-ray powder diffraction and Scanning Electron Microscopy. XRD studies revealed the formation of single phase spinel cubical structure. The average particle size of synthesized sample is estimated as from 35 to 40 nm. The gas sensing performance of the unmodified and surface modified films was tested for various gases such as H_2S, Ethanol, LPG and CO. $Co_{0.2}Zn_{0.8}Fe_2O_4$ powder showed large response to 200 ppm ethanol gas at an operating temperature 220^0C. The sensitivity, selectivity of $Co_{0.2}Zn_{0.8}Fe_2O_4$ thick films was measured.

Index Terms **- Gas sensor, $Co_{0.2}Zn_{0.8}Fe_2O_4$, Spinel ferrites , Selectivity.**

1. INTRODUCTION

Metal-oxide semiconductors have been widely investigated for gas sensor applications because of their simplicity, ease of production, low cost and capability of detecting large number of toxic and volatile gases under different conditions [1,2]. Spinel ferrites have been studied extensively due to easy to synthesis and abundant uses in technological and industrial applications [3-5]. The useful properties of the spinel ferrites mostly depend upon the chemical composition, preparation methods, sintering temperature and their distribution i.e. tendency to occupy tetrahedral (A) or octahedral (B) site [6].

$CoFe_2O_4$ has inverse spinel structure with Co^{2+} ions in octahedral sites and Fe^{3+} ions equally distributed between tetrahedral and octahedral sites [7]. Whereas ZnFe2O4 has a normal spinel structure with Zn^{2+} ions in tetrahedral and Fe^{3+} in octahedral sites. Hence, Zn-substitution in $CoFe_2O_4$ may have some distorted spinel structures depending upon the concentration of the precursor solutions. $Co_{0.2}Zn_{0.8}Fe_2O_4$ was prepared by co-precipitation method [8], sol–gel citrate method [9,10], solid-state reaction method [11]. Thick films are suitable for such metal oxide sensors since the gas sensing properties are related to the material surface and the gases are always adsorbed and react with the films surface [12,13]. The development of gas sensors to monitor combustible gases is imperative due to the concern for safety requirements in homes and industries.

The present work deals with the synthesis of nano particles of zinc substituted cobalt ferrite ($Co_{1-x}Zn_xFe_2O_4$ where x= 0.2, 0.4, 0.6 and 0.8) via sol-gel citrate method and characterized using X-ray diffractometry (XRD) and Scanning Electron Microscopy (SEM). The gas sensor based on the nanocrystalline $Co_{0.2}Zn_{0.8}Fe_2O_4$ material shows good sensitivity and selectivity to the Ethanol gas.

2. EXPERIMENTAL DETAILS

2.1. Material Synthesis

The $Co_{1-x}Zn_xFe_2O_4$ where x= 0.2, 0.4, 0.6 and 0.8 nanomaterails were prepared by using citrate sol-gel method [14]. Firstly, $Co(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_2.9H_2O$ were dissolved in deionized water, and proper amount $Zn(NO_3)_2.6H_2O$ was added. Then citric acid was added to the above solution with stirring. The mixed solution was stirred for 1 h and then heated in an 80 ^{0}C water bath until a highly viscous gel was formed. Then ethylene glycol was added under constant stirring to obtain a homogeneous and stable sol. The gels were dried in an furnace at 130 ^{0}C for 14hrs and then cancinied to 700 ^{0}C for 6hrs to obtain the nanoparticles.

2.2. Characterization Techniques

The synthesized samples were characterized for their structure and morphology by X -ray powder diffraction (XRD; Siemens D5000) and Scanning electron microscopy (SEM) images were performed on a JEOL JEM-6700F microscope operating at 5 kV. The X-ray diffraction data were recorded by using CuK_α radiation (1.5406 A^0). The intensity data were collected over a 2θ range of $10–70^0$.

The gas-sensing properties of prepared $Co_{1-x}Zn_xFe_2O_4$ powders were studied for reducing gases such as H_2S, Ethanol, LPG and CO whose concentration were fixed at 1000 ppm in air. The gas sensitivity (*S*) was defined as: $S = (Ra - Rg)/Ra = \Delta R/Ra$; where, *R*a and *R*g are the resistance of sensor in air and the test gas, respectively. The gas-sensing properties were measured in a temperature range of 50 – 350^0C.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD diffraction patterns of the $Co_{0.2}Zn_{0.8}Fe_2O_4$ nanoparticles calcinied at 700 ^{0}C. The diffraction peaks show the reflection planes (220),(311), (400), (422), (551) and (440) which are consistent with the standard powder diffraction reported from XRD library code (00-052-0279) and no other metal oxides could be identified. XRD studies revealed the formation of single phase spinel cubical structure. The diffraction peaks become sharper when the calcinations temperature increased. It can be said that all samples formed the spinal phase with a face centered cubic structure (f.c.c). The particle size of the ferrite nanoparticles has been estimated from the XRD plane (311) by the Scherrer's formula d = 0.9 λ/β cosθ, where d is the average particle size in nm, β is the FWHM of the intensity measured in radians, λ is the X-ray wavelength and θ is the Bragg angle. The average particle size increased from 35 nm to 40 nm.

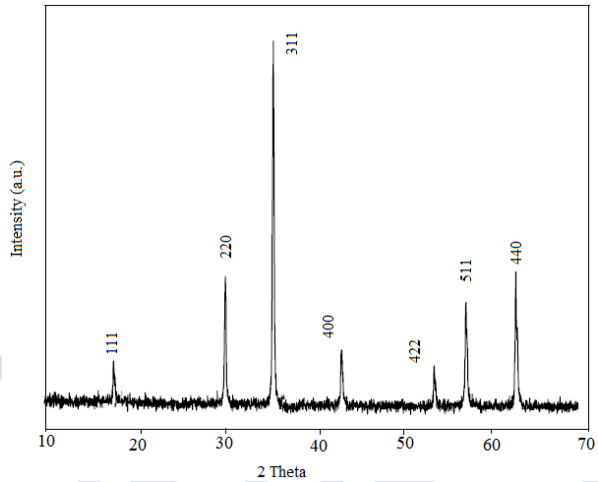

Figure 1. X-ray Diffraction pattern of $Co_{0.2}Zn_{0.8}Fe_2O_4$ nanoparticles calcinied at 700 ^{0}C

Surface morphology of the sensing element was analyzed using Scanning Electron Microscope unit. SEM image of $Co_{0.2}Zn_{0.8}Fe_2O_4$ nanoparticles calcinied at 700 ^{0}C is shown in **Figure 2**. It exhibits that the grown samples consist of irregular grains having more space as pores. Each grain is uniformly distributed over the surface. The sample have an inhomogeneous dispersion of particle sizes, ranging from less than 500 nm.

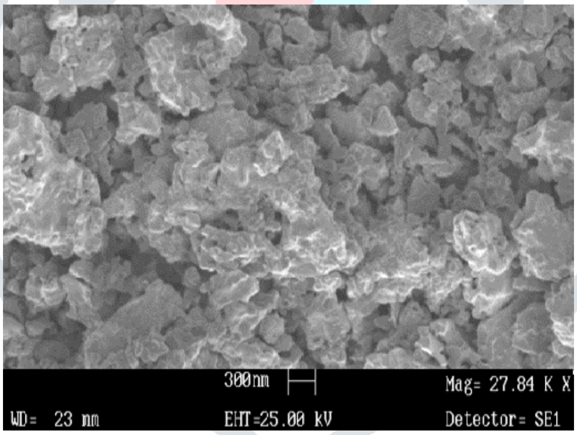

Figure 2. SEM image of $Co_{0.2}Zn_{0.8}Fe_2O_4$ nanoparticles calcinied at 700 ^{0}C

Gas-sensing experiments are performed at different operating temperatures in order to find the optimum operating condition for ethanol gas detection. Figure. 3 shows the relationship between the different operating temperatures and the responses of the sensors to 200 ppm ethanol gas. As can be seen in **Figure. 3**, as operating temperature increases, the gas response increases and its reaches to maximum at 220 ^{0}C, and then decreased rapidly with increasing the operating temperature. The similar tendencies are commonly observed for all the five samples such as undoped and Zn doped $CoFe_2O_4$ where Zn= 0.2, 0.4, 0.6 and 0.8 nanoparticles. Therefore, 220 ^{0}C is chosen to be the operating temperature for further examine the properties of the gas sensor. Moreover, the 0.8 wt% Zn-doped $CoFe_2O_4$ sensors show the maximum response of about 35 at 220 ^{0}C which indicate that the addition of Zn is beneficial to the ethanol gas sensing of $CoFe_2O_4$ sensors.

It is well known that response and recovery characteristics are an important indicator to evaluate the performances of gas sensors. **Figure. 4** shows the gas response versus time cures of pure and Zn-doped $CoFe_2O_4$ sensors to 200 ppm ethanol gas. It can be seen that although the response values increase signally by doping Zn, the response and recovery times change slightly. This phenomenon suggests that doping Zn may increases the sensing reaction between materails and ethanol gas. The response and recovery times of 0.8 wt% Zn-doped $CoFe_2O_4$ nanomaterials sensors are about 6 and 20 s, respectively.

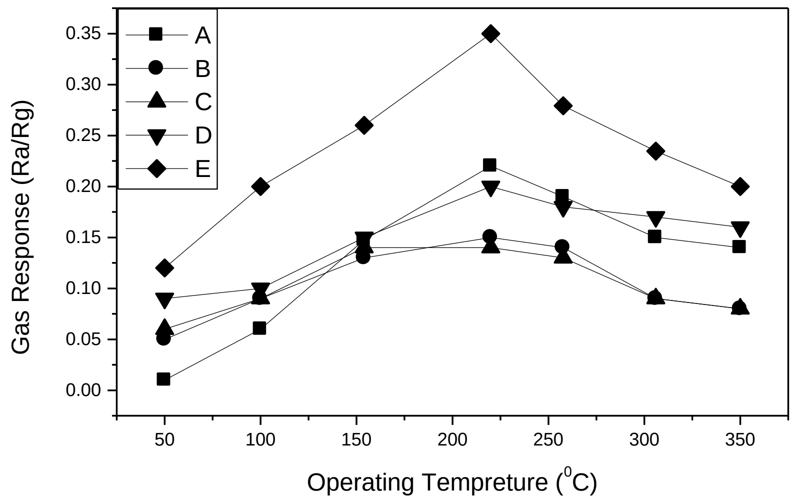

Figure 3: Gas Response of $CoFe_2O_4$ doped with different amount of Zn (A) X=0, (B) x=0.2, (C) x=0.4, (D) x=0.6 and (E) 0.8

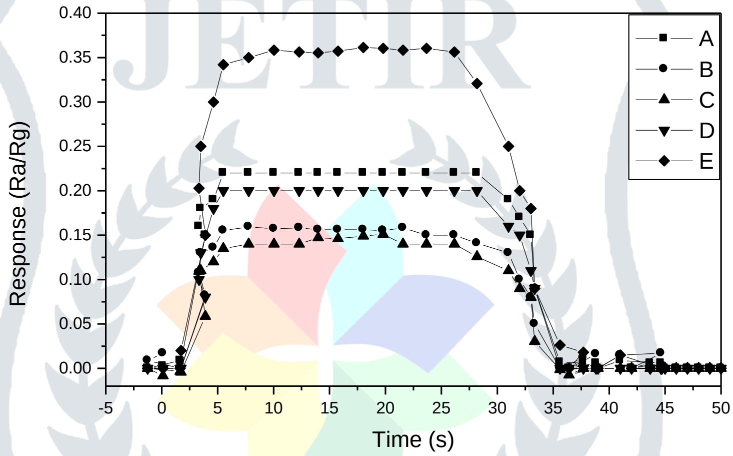

Figure 4: Response characteristics of $CoFe_2O_4$ doped with different amount of Zn (A) X=0, (B) x=0.2, (C) x=0.4, (D) x=0.6 and (E) 0.8 at 220ºC.

To further investigate the sensitivity of the 0.8 wt% Zn-doped $CoFe_2O_4$ nanomaterials, the sensor is exposed to different concentration of ethanol gas at 220 ^{0}C as shown in **Figure. 5**. It can be easily found that the sensor reveals as a liner response value to ethanol in the range of 1–200 ppm. Above 200 ppm, the response becomes steady slowly, which indicates that the sensor becomes more or less saturated.

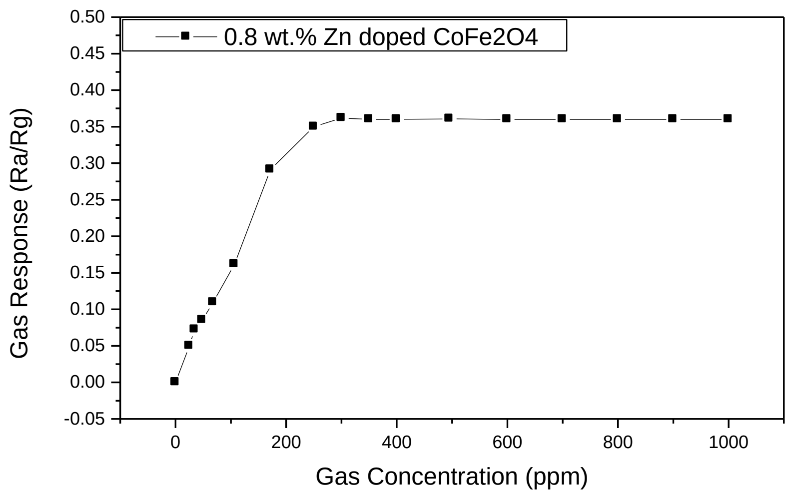

Figure 5: Response of 0.8 wt% Zn-doped $CoFe_2O_4$ to Ethanol gas of different concentration at an operating temperature 220^{0}C.

The selective test of 0.8 wt% Zn-doped $CoFe_2O_4$ nanomaterials based sensor toward to 200 ppm H_2S, Ethanol, LPG and CO are conducted at 220 ^{0}C. As demonstrated in **Figure. 6**, the sensor shows less sensitive to H_2S, and almost no response to the other typical interference gases at the same temperature. However, the response of 0.8 wt% Zn-doped $CoFe_2O_4$ nanomaterials to 200 ppm ethanol gas is 35. This indicates that the 0.8 wt% Zn-doped $CoFe_2O_4$ nanomaterials based sensor has good selectivity to ethanol gas.

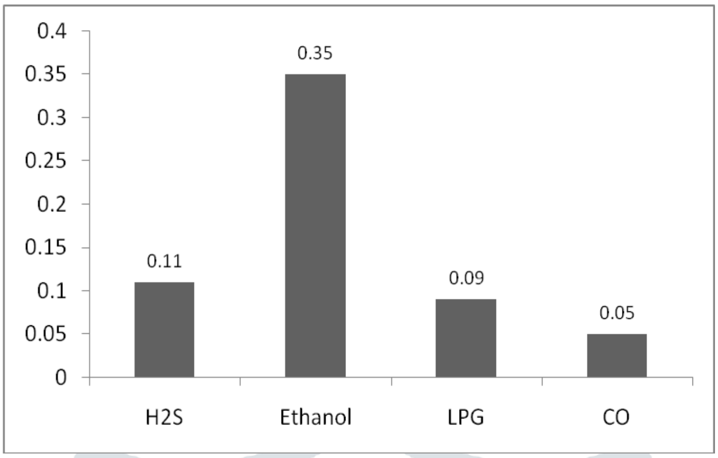

Figure 6: Response to different reducing gases of 0.8 wt% Zn-doped $CoFe_2O_4$ as a function of operating temperature.

4. CONCLUSION

$Co_{1-x}Zn_xFe_2O_4$ where x= 0.2, 0.4, 0.6 and 0.8 nanoparticles thick film were prepared by sol-gel citrate method. XRD of $Co_{0.2}Zn0_{.8}Fe_2O_4$ calcined 700^{0}C for 6 h showed good crystalline quality with a grain size 35-40 nm. XRD studies also revealed the formation of single phase spinel cubical structure. It was also found that $Co_{0.2}Zn0_{.8}Fe_2O_4$ sensor exhibited excellent gas response and selectivity for ethanol gas at 220^{0}C. The sensor is found to exhibit good selectivity towards Ethanol gas against H_2S, CO and LPG. The sensor is very promising for ethanol gas detection with a response time in second range.

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