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CONDENSED MATTER

GAS SENSING PROPERTIES OF POROUS Cu-, Cd- AND Zn- FERRITES

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Abstract: Some spinel ferrites, MFe_2O_4 (M = Cu, Cd and Zn), having submicron grain sizes (0.1–0.7μm) were prepared by sol-gel-selfcombustion and their sensing properties to reducing gases were investigated. The gas sensing characteristics were obtained by measuring the sensitivity as a function of various controlling factors, like operating temperature, composition and concentration of the gas, and finally the response time. The sensitivities of the three ferrites to reducing gases like acetone, ethanol and LPG were been compared. It was revealed that $CuFe_2O_4$ is the most sensitive to LPG and $ZnFe_2O_4$ is sensitive and selective to ethanol.

Key words: ferrites, gas sensor, structure characteristics, sensitivity, reducing gas.

1. INTRODUCTION

There is an increasing interest in the finding new materials in order to develop high performance solid state gas sensors. Semiconductor metal oxide sensors are an alternative for non expensive and robust detection systems. Spinel-type oxide semiconductors with formula MFe_2O_4 have been reported to be sensitive materials to both oxidizing and reducing gases. Liu et al. [1] reported the high sensitivity of Cd Fe_2O_4 to ethanol vapor, Reddy et al [2] investigated $NiFe_2O_4$ as sensor to detect Cl_2 in air. Chen et al. [3] revealed that $MgFe_2O_4$ and $CdFe_2O_4$ are sensitive and selective to LPG and C_2H_2. Our earlier investigations [4] indicated the promoting effect of Sn ions on the improving the sensitivity of Mg ferrite to acetone gas. The tin in $MgFe_2O_4$ facilitates the oxidation of reducing gas and the occurrence of the oxygen vacancies changing the electrical conductivity. Also, it was found [5] that the Mn addition in Ni ferrite improved sensitivity to acetone. The sensing mechanism of the reducing gases consists in the change of the electrical conductivity resulting from chemical reaction between the gas molecules and adsorbed oxygen onto the metal oxide surface [6, 7].

Taking into account that the sensing phenomena mainly takes places on the material surface, the surface morphology has an essential role on the sensitivity of solid state sensor. In the last years, the nanograined materials offer new opportunities for enhancing the properties and performances of gas sensors. Several research reports [8–10] have confirmed the beneficial effect of nanostructure on the sensor performance.

In this paper, nanopowders of the simple spinel ferrites, $CuFe_2O_4$, $ZnFe_2O_4$ and $CdFe_2O_4$ were prepared by a novel method, sol-gel-selfcombustion [11]. The advantage of this method is that it enables the economic manufacture of a wide range of ceramic nanopowders and the particle size can be controlled by subsequent heat treatments [12]. Also, in this technology, solid state reaction forms separated nanoparticles. The obtained nanopowders were tested for sensing 2 properties to three reducing gases: liquefied petroleum gas (LPG), ethanol (C_2H_5OH) and acetone (CH_3COCH_3). It was concluded that the gas sensitivity considerably depends on the ferrite composition and the gas type to be detected.

2. EXPERIMENTAL

Spinel ferrites of composition MFe_2O_4 (M = Cu, Cd and Zn) were prepared by sol-gel-selfcombustion described in [11]. The analytically pure grade powders of $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, were weighed in the desired proportions and disolved in small amounts of distilled water. Alcohol polyvinyl was added to make a colloidal solution. By adding NH_4OH solution, the pH was adjusted to about 8 and the result was a sol of metal hydroxides and ammonium nitrate. After heating at 120^0C, for 12 hours, the dried gel was ignited in a corner. The combustion wave spontaneously propagates and converts the gel into a loose powder containing very fine crystallites. All residual organic compounds were eliminated by heating the powder at 500^0C for one hour. Then, the combusted powder was compacted into pellets (cilindrical discs), of about 2 mm thickness and 17 mm diameter, at a pressure of 100 MPa. The pellets were treated at 1000^0C for 30 minutes to facilitate solid state sintering followed by furnace cooling of the these.

The surface morphology of the heat treated pellets was analysed using a scanning electron microscope (Tesla-BS340). The grain size was appreciated from SEM micrographs using the linear intercept method [13]. Porosity was calculated with relation

$$P = 1 - \frac{d}{d_x}, \tag{1}$$

where $d = m/V$ is bulk density determined from dimensions and mass and $d_x = 8M/Na^3$ [14] is the theoretically density (M is the molecular weight, N is the Avogadro's number and a is the lattice parameter). The mass of the samples was measured using a digital balance and the volume was calculated by measuring the sample dimensions. The specific surface area was determined using equation [15, 16]

$$A = \frac{s}{vd} = \frac{6}{dD_m}, \tag{2}$$

were s and v are the particle surface and volume respectively, d is the bulk density and D_m is the average grain size. The number 6 is the shape factor. It is assumed that the particles of a specimen have the same size and the same shape.

For electric measurements, two silver electrodes were applied on a face of the ferrite disc, as in Fig. 1. The electrical resistance was measured by a two-point method with a digital LCR meter at 100 Hz. For gas sensing measurements, the sensor element (ferrite disc) was provided with a heater and the assemble heatersensor element was introduced in a glass chamber (2 dm^3). The test gases were injected with high precision syringes into the glass chamber. The measurements were done in the temperature range from 150^0C to 400^0C. A cromel-alumel thermocouple located in close proximity of the sensor element was used to measure the operating temperature.

The resistance of the ferrite sensor placed into the measuring chamber was measured at fixed temperatures, both in air and in the presence of the test gas. The sensitivity S was calculated with the relation

$$S = \frac{\Delta R}{R_a} = \frac{R_a - R_g}{R_a} \tag{3}$$

were R_a is the ferrite resistance in air and R_g is the resistance in the test gas at a given temperature.

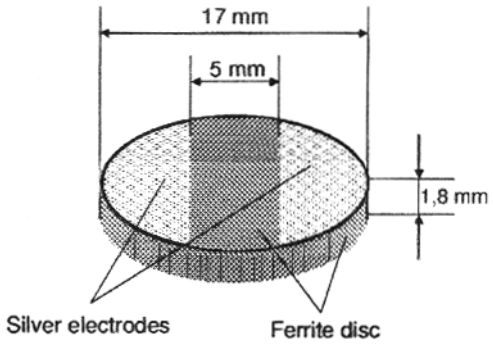

Fig. 1 – Design of ferrite sensor with silver electrodes.

Taking into account the thermal inertia of ferrites, all measurements were carried out under the thermal stabilization conditions. All date were collected at least 30 minutes after gas exposure. After each change of the test gas, the sensor element was activated by submitting it to heat treatment at 500°C for 15 minutes in order to form the intial structure and its thermodynamically stabilize. Heat cleaning of the samples was found to be necessary for better and reproducible sensitivity.

3. RESULTS AND DISCUSSION

3.1. STRUCTURE RESULTS

SEM images (Fig. 2) of the three ferrite compositions were made before exposing to test gas. Each ferrite is characterized by a porous structure and submicron grains.The porosity is entirely intergranular, the pores are interconnected to form pore channels. Since the pores are channeled and do not have well-defined shape, it is dificult to give a particular dimension of the pores.

It is evident that the morphology is dependent on the ferrite composition. Even though all samples were prepared under identical conditions, the grain size was not the same for all ferrites. This is probably due to different rate of the solid state cation diffusion during the sintering at 1000^0C. Except for $CuFe_2O_4$, the other ferrites have rounded grains and a homogeneous grain size distribution, between 100 and 300 nm. $CuFe_2O_4$ exhibits large faceted crystallites (700 nm). Also, a tendency towards agglomerations is observed due to the small size of the ferrite particles prepared by sol-gel-selfcombustion.

The structural characteristics are summarized in Table 1. One can see that $ZnFe_2O_4$ is characterized by the smallest grain size (100 nm), the highest porosity (48.4 %) and largest active surface (22.2 m^2/g) towards test gases.

Table 1

Structural characteristics for the studied ferrites

Ferrite	Bulk density d (g/cm^3)	Porosity p (%)	Average grain size D_m (nm)	Surface specific area A (m^2/g)
$CuFe_2O_4$	3.6	32.8	700	2.4
$CdFe_2O_4$	3.3	45.5	300	6.0
$ZnFe_2O_4$	2.7	48.4	100	22.2

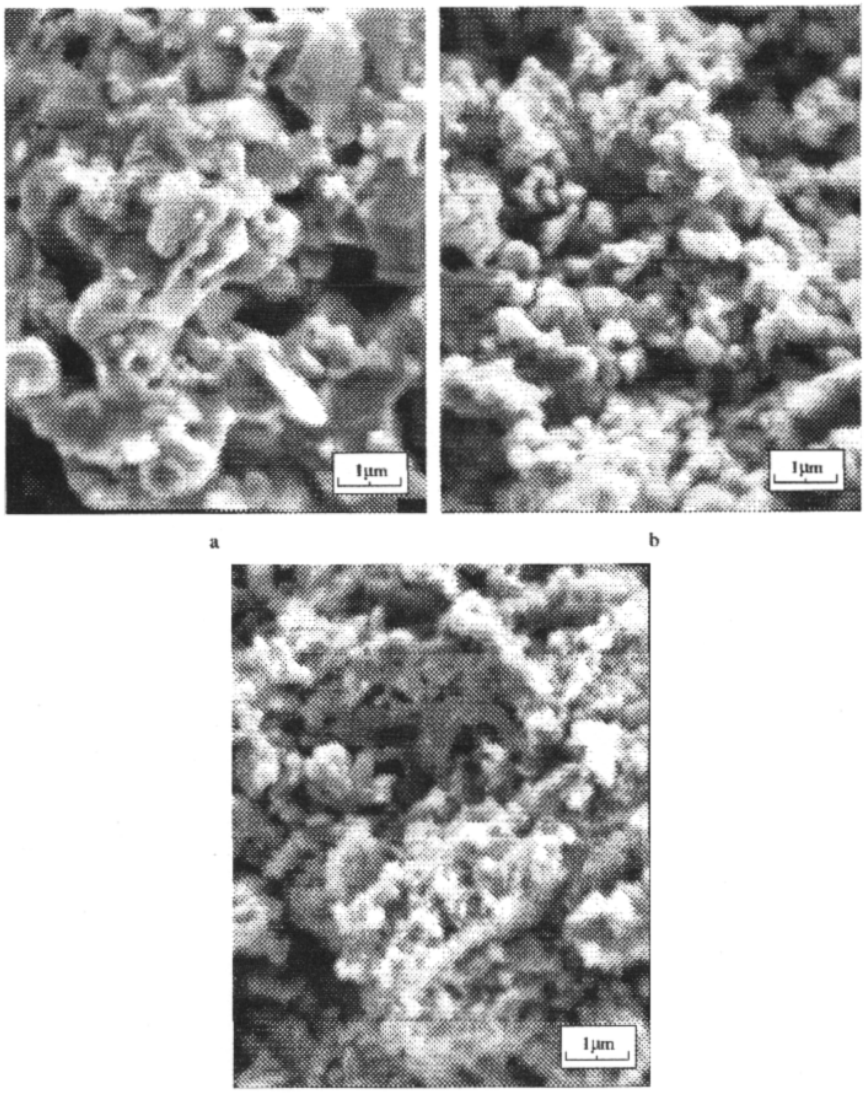

Fig. 2 – SEM micrographs of the $CuFe_2O_4$(a), $CdFe_2O_4$(b) and $ZnFe_2O_4$(c) ferrites. Enlargement × 8000.

3.2. GAS SENSING RESULTS

Figures 3, 4 and 5 illustrate the sensitivity variation towards acetone, ethanol and LPG vapors of the three simple ferrites as a function of operating temperature. At least three samples of each ferrite composition were tested, but in all figures are

shown the results for only one sample from each ferrite type, since no large difference between the sensors of the same ferrite type was observed. Sensitivity measurements was performed at temperatures higher than 150^0C. At lower temperatures the electrical response to the test gases was low because elevated temperatures are required to change the oxidation state and conductance of ferrite. Several features can be drawn from these figures:

1) Each of the curves shows a maximum of the sensitivity corresponding to an optimum operating temperature of the sensor element. For $CdFe_2O_4$ and $ZnFe_2O_4$ the sensitivity maximum appears at 350^0C and for $CuFe_2O_4$ it appears at 300^0C. Therefore, the ferrite sensors have need of thermal excitation to response to the investigated gases.

2) There are large differences in the sensitivity values to various gases of the three ferrites. $CuFe_2O_4$ shows a good sensitivity to all gases (Fig. 3). $CdFe_2O_4$ is sensitive to alcohol and less sensitive to LPG and acetone (Fig. 4). $ZnFe_2O_4$ is sensitive to alcohol and exhibits a poor response to acetone and LPG (Fig.5).

The sensitivities of the three ferrites towards the three reducing gases at optimum operating temperature and fixed gas concentration (150 ppm) are compared in Fig. 6. It is surprising that $CuFe_2O_4$ element has good sensitivity to all test gases, although this ferrite has the largest grain size and the smallest porosity (see Table 1). Moreover, $CuFe_2O_4$ is the most sensitive element to LPG gas (Fig. 6). An explanation for the high gas sensitivity and low selectivity of $CuFe_2O_4$ would be the formation of Cu^{1+} ions during the reducing gas oxidation. We recall that the electrical conduction in ferrites is mainly attributed to the electron hopping between Fe^{2+} and Fe^{3+} ions distributed on the octahedral (B) sites in the spinel structure [14]. In the inverse spinel $CuFe_2O_4$, Cu^{2+} ions prefer octahedral sites and Fe^{3+} ions are distributed on both octahedral (B) and tetrahedral (A) sites. The occurence of the Cu^{1+} ions on the octahedral sites can provides a greater number of hoppings ($Fe^{2+} \leftrightarrow Fe^{3+}$, $Cu^{1+} \leftrightarrow Cu^{2+}$) on B sites and the gas response will increase.

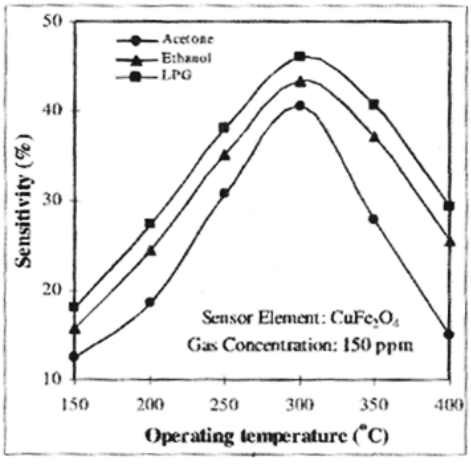

Fig. 3 – Variation of gas sensitivity as a function of operating temperature for $CuFe_2O_4$ sensor element.

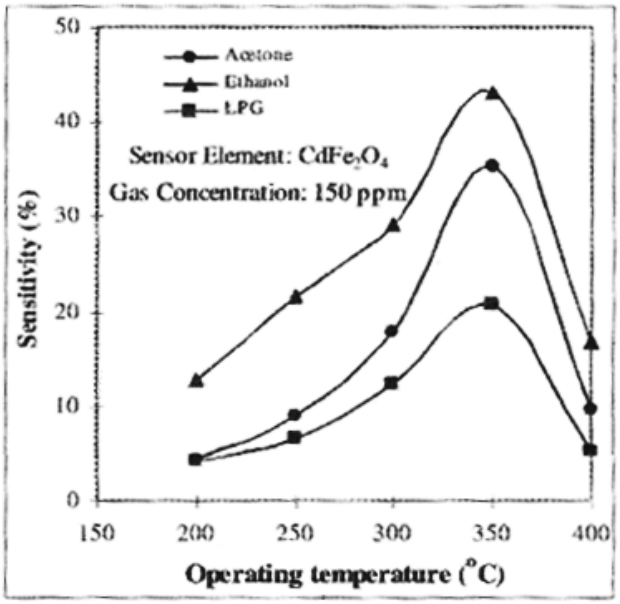

Fig. 4 – Variation of gas sensitivity as a function of operating temperature for $CdFe_2O_4$ sensor element.

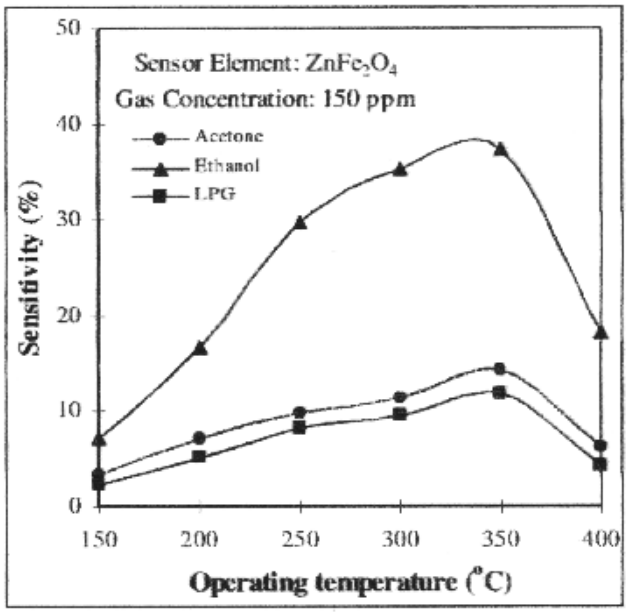

Fig. 5– Variation of gas sensitivity as a function of operating temperature for $ZnFe_2O_4$ sensor element.

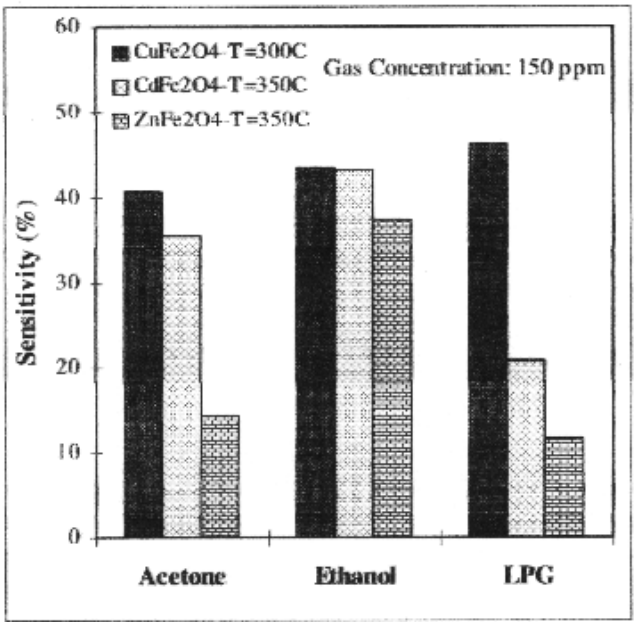

Fig. 6 – Bar diagram for maximum sensitivities to test gases of $CuFe_2O_4$, $CdFe_2O_4$ and $ZnFe_2O_4$ ferrites.

One the other hand, from Figs. 4–6 one can remark that all ferrites have better sensitivity to ethanol vapor. The improved sensitivity to ethanol vapor is related to the interaction of OH^- groups with porous ferrites acting as a reducing agent and generating free electrons into the semiconductor ferrites. Ferreira et al. [17] investigated the detection mechanism of ethanol using porous hydrogenated silicon (SiO:H) thin films and concluded that the reduction /oxidation of OH^- group from ethanol and the SiO bonds are involved and responsible for the creation of extra free electrons for conduction when the material is in the presence of the ethanol.

$ZnFe_2O_4$ ferrite shows not only enhanced sensitivity to ethanol (C_2H_5OH) but also exibits high selectivity to ethanol by the decreasing sensitivity to LPG and acetone (Fig. 5). The sensitivity maximum to ethanol of $ZnFe_2O_4$ ferrite is over three times larger that that to LPG or acetone. The surprising high selectivity to ethanol could be explained by a stronger interaction between ethanol molecules and Zn ferrite components. Previously, it was reported [18] the detection of ethanol using ZnO. The high ethanol selectivity of $ZnFe_2O_4$ without using a catalyst is one of the characteristics of ultrafine particle ferrite and additional investigations are required to clarify this problem.

It was also investigated the behavior of the gas sensitivity of $ZnFe_2O_4$ as a function of gas concentration when it stepwise increased from 0 to 150 ppm, at fixed operating temperature 350^0C (Fig. 7). For low gas concentrations

(25–100 ppm) the gas sensitivity increases with increasing gas concentration. For higher concentrations (above 100 ppm) the gas sensitivity tends to a constant value. Also, the gas sensitivity largely depends on the gas type. This is remarkably higher to ethanol. The sensitivity to ethanol concentration of 100 ppm was 0.38 whereas to acetone and LPG is of about 0.1. The same measurements were repeated after one month, but the results were reproducible within the deviation limits of ± 5%. These results demonstrate that the simple ferrite, $ZnFe_2O_4$, is sensitive and selective for the detection of ethanol vapor and it may use for fabrication of ethanol vapor detector, but its high operating temperature, of 350^0C, is not favorable from commercial point of view.

Fig. 8 shows the plot of the response characteristics to ethanol (ethyl alcohol) and LPG vapor for $ZnFe_2O_4$ and $CuFe_2O_4$ sensors, respectively. The response time required for the gas sensitivity to attain 90% of its maximum value is of about 3 minutes for $CuFe_2O_4$ and 2 minutes for $ZnFe_2O_4$, whereas the recovery time during the sensitivity fallen to 10% of its maximum value is longer, of about 4 minutes for the two ferrites. The faster response of $ZnFe_2O_4$ material was ascribed to higher porosity and finest granulation (see Fig. 2c). The response and recovery times of the sensors towards other gases showed similar results and therefore these are not shown here.

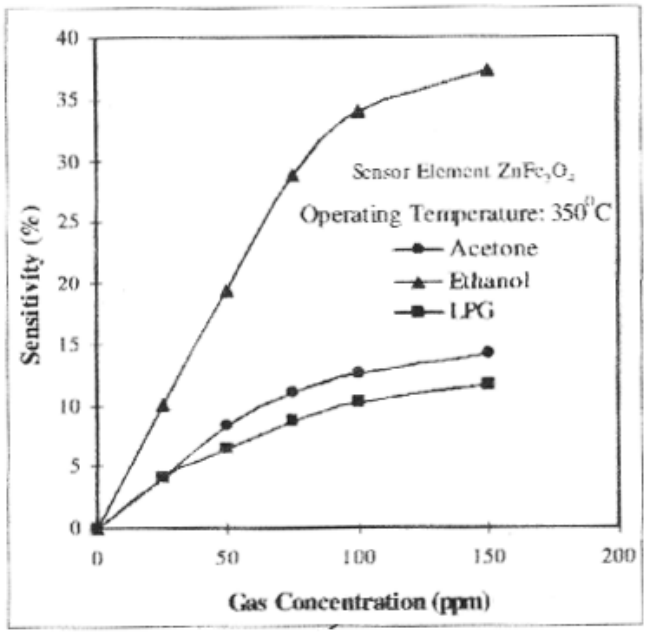

Fig. 7 – Gas sensitivity *versus* gas concentration of $ZnFe_2O_4$ sensor element.

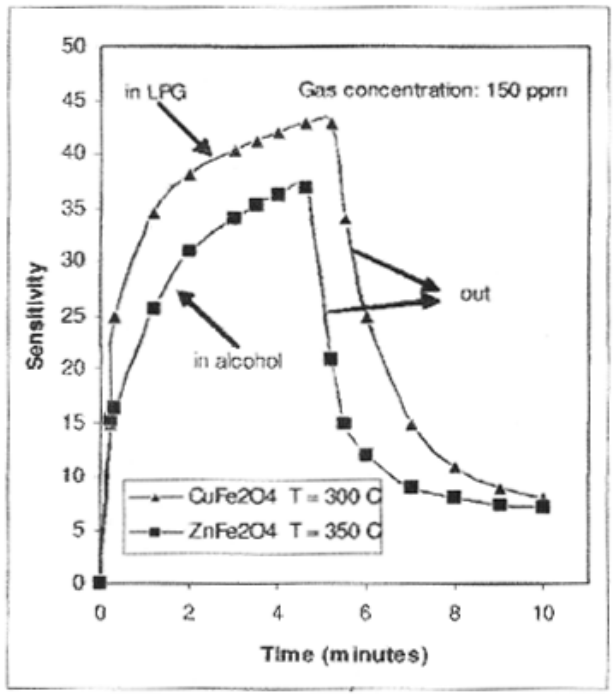

Fig. 8 – Response characteristics to LPG for $CuFe_2O_4$ and to ethanol for $ZnFe_2O_4$.

4. CONCLUSIONS

$CuFe_2O_4$, $CdFe_2O_4$ and $ZnFe_2O_4$ ferrites were prepared by sol-gel-selfcombustion technology and tested for sensing properties to ethanol (ethyl alcohol), LPG and acetone. The grain sizes of the samples obtained in the present work are in the range 0.1 to 0.7 μm which are much smaller than those for the samples prepared by conventional ceramic method.

By gas sensitivity measurements it was found that $CuFe_2O_4$ has a good sensitivity to reducing gases at optimum working temperature of 300^0C. Better sensitivity to LPG of $CuFe_2O_4$ can not be explained by morphology changes. $ZnFe_2O_4$, having the highest porosity and the largest surface area, is sensitive to ethanol only. A probable explanation for selective sensitivity to ethanol and negligible sensitivity to other gases can be the strong interaction between ethanol molecules and the components of the Zn ferrite.

The main conclusion from the obtained results is that the interaction of the spinel ferrites with reducing gases is a more complicated mechanism including the removal of lattice oxygen, modification of the oxidation state and creation of new bonds between ions.

These results are preliminary. Further studies aim at the improving of sensor's performance characteristics with respect to: sensitivity, response time, durability and to establish the exact role of Cu ion for improving the gas sensitivity of $CuFe_2O_4$. Mössbauer studies would be beneficial in observing the change in the oxidation state of Cu ion in the presence or absence of reducing gases.

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