Porous nickel ferrite for semiconducting gas sensor

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Abstract: The sensitivity to some reducing gases (acetone, ethanol, methane and liquefied petroleum gas-LPG) of doped nickel ferrite, $\text{Ni}_{0.99}\text{Co}_{0.01}\text{Mn}_x\text{Fe}_{2-x}\text{O}_4-\delta$ ($x = 0.01$ and $0.02$), was investigated. Starting from nitrates, as raw materials, the samples were prepared by self-combustion method. The investigations of the samples were carried out by X-ray diffraction, scanning electron microscopy and gas sensitivity measurements of the electrical resistivity. The gas sensitivity largely depends on the composition, temperature and the test gas species. Especially, the mixed ferrite with $\text{Ni}_{0.99}\text{Co}_{0.01}\text{Mn}_{0.02}\text{Fe}_{1.98}\text{O}_4-\delta$ composition is sensitive and selective for the detection of acetone gas.

1. Introduction

Generally, for magnetic or electrical applications, ferrites with high-density are to be used. But, there are many applications, such as gas or humidity sensors, for which lower density and nanosized structures are preferred. As suggested by several authors [1, 2] nanosized grains of sensing materials are preferred to increase the specific surface exposed to gas. The ferrites have demonstrated to be good materials for semiconductor gas sensors [3, 4].

In the present paper, Ni ferrites doped with small amounts of Ca, Co and Mn were investigated as gas sensing material. Ca was added to NiFe$_2$O$_4$, but Co and Mn partial substituted Ni and Fe respectively in Ni ferrite. The incorporation of Co and Mn was made in order to improve the gas sensitivity [5] and to increase electrical resistivity [6]. The sensor elements have been tested to four reducing gases (acetone, ethanol, methane and LPG) and the addition of MnO appears to confer marked sensitivity to acetone.

Lower temperature methods for material synthesis are necessary when the ferrites are to be used as a gas sensor element. The self combustion method was used by us for preparation of ferrite powders [7]. This method offers the advantage to produce ultra-fine, homogeneous and reproducible ferrite powders using aqueous solutions of salts of constituent ions in comparison with ceramic technology.

2. Experimental

Three samples with chemical formula NiFe$_2$O$_4$ + 1 wt% CaO, $\text{Ni}_{0.99}\text{Co}_{0.01}\text{Mn}_{0.01}\text{Fe}_{1.98}\text{O}_4-\delta$ and $\text{Ni}_{0.99}\text{Co}_{0.01}\text{Mn}_{0.02}\text{Fe}_{1.98}\text{O}_4-\delta$ were prepared by sol-gel auto combustion method which is a modified coprecipitation technique. The main feature of this method is the intimate mixing of ions on the atomic level so that the crystallization of ferrite particles can occurs in the process of solid phase diffusion of the cations at relatively low temperatures.

The microstructure of the samples was observed by scanning electron microscopy (SEM). SEM micrographs were carried out on fracture surface of the disks. The resulting ferrite elements were subjected to measurements for the electrical resistance in air and in test gases. For electric measurements, the disks of 2-3 mm thickness were silvered. Electrical resistance was measured by a two-point method.
For sensing measurements, the ferrite disk was mounted on a heater and placed in a glass enclosure capable of controlling the different gas concentrations. The gas sensing was performed in the temperature range from 105°C to 285°C. A chromel-alumel thermocouple placed in the glass chamber indicates the working temperature. As test gases were used: ethanol (C\textsubscript{2}H\textsubscript{5}OH), methane (CH\textsubscript{4}), acetone (CH\textsubscript{3}COCH\textsubscript{3}) and LPG.

The electric resistance of the ferrite sensor in test gases (R\textsubscript{g}) and in pure air (R\textsubscript{a}) was measured respectively, and the gas sensitivity (S) was defined as

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S = \frac{\Delta R}{R_a} = \left| \frac{R_g - R_a}{R_a} \right|
\]

3. Results

By X-ray diffraction it was confirmed that all samples are monophasic. All diffraction peaks correspond to cubic spinel structure. In the XRD spectrum, there are no extra lines due to superior oxidation states of manganese ions as Mn\textsuperscript{3+} or Mn\textsuperscript{4+}, indicating that Mn\textsuperscript{2+} was not oxidized into Mn\textsuperscript{3+} or Mn\textsuperscript{4+}. However, a very weak oxidation of Mn\textsuperscript{2+} to Mn\textsuperscript{3+} or Mn\textsuperscript{4+} can be possible during the slow cooling from 1000°C, but this fact is undetectable by X-ray diffraction. The lattice constant was evaluated to be 8.326 Å. This value is little larger than that for NiFe\textsubscript{2}O\textsubscript{4} (8.320 Å) that attests the incorporation of Co (ionic radius 0.88 Å [8]) and Mn (ionic radius 0.97 Å [8]) dopants in the spinel lattice of Ni ferrite.

The microstructure of the samples can be visualized from scanning electron micrograph of the synthesized materials as in Figure 1. One can observe the presence of macro-agglomerations containing very fine particles (under 0.1 µm). The particle shapes are not well defined. Also, the material is characterized by high porosity (about 40%). The bulk density was evaluated to be 3.11 g/cm\textsuperscript{3}. Many large and small pores are present in the whole material. We assumed that the pores are mainly intergranular because intragranular pores are not observed from SEM photograph.

![Figure 1](image-url)

Electrical resistance measurements in air, at room temperature, indicated very high values, over 10\textsuperscript{8} Ω. The small amounts of CaO, CoO or MnO contribute to the increase of the resistance of Ni ferrite [6]. Because the gas sensitivity measurements were performed in the temperature interval 105°C – 285°C, we investigated the temperature variation of the electrical resistance. There is a lowering of R\textsubscript{a} by two orders of magnitude in the mentioned temperature interval. This decrease was attributed to thermally activated mobility of the carriers (electrons and holes).

Figure 2 shows the gas sensing measurements for all samples, in acetone atmosphere, at various operating temperatures. The following observations can be made:

1. The Ni ferrite doped with Ca is practically insensitive to acetone;
2. For the mixed ferrites containing Mn and Co, the gas sensitivity depends on the operating temperature and Mn content. The sensitivity increases with increasing temperature and reaches a maximum value corresponding to an optimum operating temperature. For Ni$_{0.99}$Co$_{0.01}$Mn$_{0.01}$Fe$_{1.99}$O$_{4-\delta}$ sample there is a slow increase in the sensitivity to the maximum value of 2.2 at optimized operating temperature of 235°C, whereas for Ni$_{0.99}$Co$_{0.01}$ Mn$_{0.02}$Fe$_{1.98}$O$_{4-\delta}$ sample, the sensitivity significantly increases with an increase of the temperature up to 215°C. Above 215°C, the sensitivity decreases. The value of the maximum sensitivity (4.5) is twice than in ferrite containing less Mn.

From the above experiments it was concluded that the transition metal oxide, MnO, acts only as a catalyst to enhance the sensitivity to acetone gas.

It was investigated the sensitivity of the sample Ni$_{0.99}$Co$_{0.01}$Mn$_{0.02}$Fe$_{1.98}$O$_{4-\delta}$ to other reducing gases such as methane, ethanol and LPG (Figure 3). For these experiments, the ferrite sample was heated to about 300°C and was exposed to gases during the cooling. It is clear that this material is the most sensitive to acetone gas and less sensitive to the others.

The sensitivity of the two mixed ferrites containing Mn and Co to the four gases is compared in Figure 4. The sensitivity values correspond to the optimized working temperature for the two ferrite sensors, 215°C and 235°C. The gases have been taken as saturated vapours. The bar diagram from Fig.6 clearly shows that the incorporation of Mn in Ni ferrite confers marked sensitivity to acetone. Moreover, the increase of the Mn amount improved the selectivity to acetone by decreasing the sensitivity to other reducing gases. We concluded that the compound Ni$_{0.99}$Co$_{0.01}$Mn$_{0.02}$Fe$_{1.98}$O$_{4-\delta}$ is sensitive and selective for the detection of acetone. The sensitivity of this compound to acetone can be explained by the involvement of a possible reaction of acetone with ferrite surface leading to an increase of the resistance.
It was investigated the response time for the high sensitive ferrite to acetone. The response characteristic of the sensor element in presence of acetone gas is shown in Fig.5. The time taken by the sensor element to reach 90% of the maximum sensitivity at optimised operating temperature (215°C) is found to be about 3 minutes. The time taken by the sensor to come back once the acetone is removed was found to be longer, of 5.5 minutes. The response time was too long since this is controlled by the diffusion rate of gas vapour through the micropores. Further investigations are necessary to short the response time.

4. Conclusions
The sensitivity studies to four reducing gases (acetone, ethanol, methane and LPG) were carried out on three samples based on Ni-ferrite prepared by selfombustion method.

The results presented in this paper clearly show a high selectivity of the sample Ni0.99Co0.01Mn0.01Fe1.99O4-δ to acetone. The optimum detecting temperature, of 215°C, for this compound is favorable for the commercial development of acetone sensors. The sensitivity to methane, ethanol and LPG remains low even though the Mn content increases.

Further studies are necessary to elucidate the exact role of Mn which is responsible in improving the sensitivity of NiFe2O4 to acetone, and to can propose a plausible explanation on gas sensing mechanism of Mn doped Ni-ferrite to acetone.

References
[1] Shimizu Y and Egashira M 1999 MRS Bulletin 24 18
[2] Xu C, Jun T, Miura N and Yamazoe N 1990 Chemical Letters 3 441
[3] Cher N S, Yang X J, Liu E S and Huang J L 2000 Sensors and Actuators B 66 178
[4] Comini E, Ferroni M, Guidi V, Fagila G, Martinelli G and Sberverglieri G 2002 Sensors and Actuator B 84 26
[5] Yamazoe N, Kurokawa Y and Seiyama T 1993 Sensors and Actuators B 4 283
[6] Rezlescu E, Sachelerie L, Popa P D and Rezlescu N 2000 IEEE Transactions on magnetics 36 3962
[7] Popa P D and Rezlescu N 2000 Romanian Reports in Physics 52 769
[8] Shannon R D 1976 Acta Crystallographica A 32 751