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ON THE POSSIBILITY OF THE USE OF A NICKEL FERRITE AS SEMICONDUCTING GAS SENSOR

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Polycrystalline nickel ferrite doped with cobalt and manganese was invetigated for gas sensing applications. The samples were obtained by selfcombustion method and were studied using powder X-ray diffraction and scanning electron microscopy. It was investigated the sensitivity of the electrical resistivity to acetone, ethanol, methane (CH_4) and liquefied pertroleum gas (LPG). It is observed that the gas sensitivity depends on the temperature and the test gases to be detected.

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1. Introduction

It is known that the electrical resistivity of a semiconducting oxide can be modified by adsorbtion of gases from the ambient [1]. This property has been used in semiconductor sensors for the detection of inflammable and toxic gases [2-4]. The semiconductor gas sensors offer good advantages with respect to other gas sensor devices (such as spectroscopic or optic systems), due to their simple implementation, low cost and good reliability for real-time control systems [5].

In recent years the ferrites have demonstrated to be good materials for gas sensing applications [6]. In the present study, nickel ferrite doped with cobalt and manganese was investigated as gas sensor. The self combustion method was used for preparation because the followings two advantages: (1) heat generated in the exothermic reaction accelerates the process and (2) the resulting magnetic powder is fine grained with grain size smaller than that of the starting powders. Grain size and pore structure have a major effect on the properties in polycrystalline materials and their full characterization should be the first step in the study of materials. Also, the microstructure has a major role in the performance of a ceramic sensor. We examined the microstructures of the end products by SEM to obtain quasi-three dimensional information on the grain shape, size and pore sizes. It was investigated the variation of the electrical resistance in the presence of four gases: acetone, ethanol, methane and liquefied petroleum gas. Detailed results on the microstructure and the gas sensing propertiers are given in the paper.

2. Experimental

The chemical formula of the investigated ferrite composition is $Ni_{0.99}Co_{0.01}Mn_{0.02}Fe_{1.98}O_4$. The samples were prepared by self combustion method using metal nitrate and ammonium hydroxide as raw materials. The coprecipitation of the metal hydroxides takes place into a colloidal medium. By a quick combustion takes place the calcination of metal hydroxides and the reaction between metal oxides. The obtained powder was pressed into disk shapes and subjected to thermal treatment at 1000^0C for 30 minutes. The microstructure and phase composition were performed by SEM and X-ray powder difraction (XRD). Average grain size was determined by the linear intercept technique from SEM micrograph on fracture surface.

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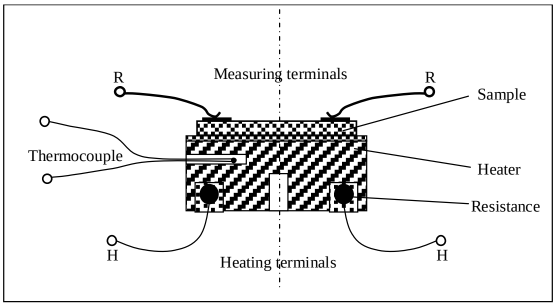

Fig. 1. The assembly for measuring the gas sensitivity of the sample.

The disk samples were silvered in order to measure the electrical resistance. For the gas sensing measurements, the sensor element (ferrite disk) was mounted on a heater and placed in a glass chamber capable of controlling the different gas concentrations. The schematic of the sensor assembly is shown in Fig. 1. Gas sensing properties were investigated at various operating temperatures from 125 to 285^{0}C. The experiments were performed with four test gases: LPG, ethanol, methane and acetone. The sensitivity, S, is defined as the ratio

$$S = \frac{\Delta R}{R_a} = \frac{|R_a - R_g|}{R_a} ,$$

where R_a and R_g are the sensor resistances in air and in presence of the test gas, respectively.

3.Results and discussion

3. 1. Structural properties

Fig. 2 shows the powder X-ray diffractogram for the sample treated at 1000^{0}C in air for 30 minutes. All the peaks belong to the spinel ferrite. No other separate phase oxides could be identified by X-ray diffraction. The lattice constant was found to be 8.326±3 Å. The slight increase of the lattice constant of $NiFe_2O_4$ (8.320 Å) by doping with Co and Mn indicates the incorporation of the dopants in the spinel lattice of Ni ferrite.

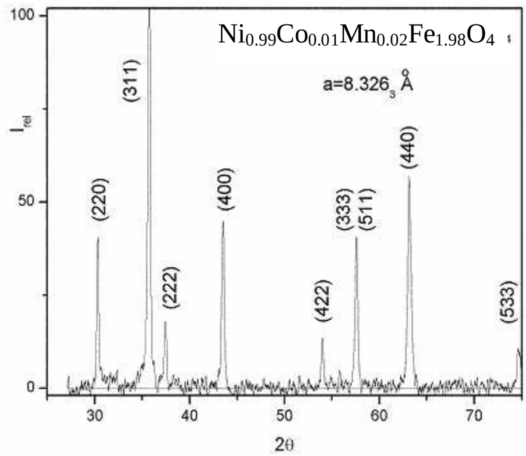

Fig. 2. X-ray diffractogram for the studied sample.

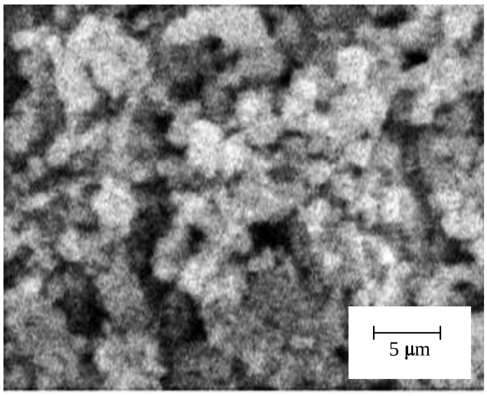

Fig. 3. SEM micrograph for the studied sample.

Scanning electron micrographs for the sample is presented in Fig.3. This figure shows that sample consists primarily of irregularly shaped of 1 to 6 μm aggregates of fine (0.1 μm) particles. It can be seen that the crystallite size of the sample is extremely fine, on the order 100 to 500 nm. The material is characterized by high intergranular porosity (about 40%). The bulk density was evaluated to be 3.11 g/cm^3. Many large and small pores are present in all material.

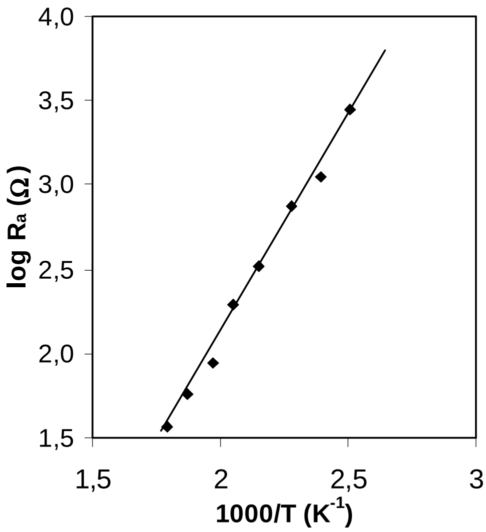

Fig. 4. Log R_a vs.1/T for studied sample.

The gas sensitivity depends largely on the microstructure, such as grain size, surface area and pore size.

3.2. Electrical properties

a. Electrical properties in dry air. It was investigated the temperature variation of the electrical resistance (Fig. 4). The investigation was limited to the temperature interval of 125 to 285^{0}C. The log R_a vs. 1000/T (K^{-1}) graph shows a linear decrease of the log R_a with increasing the temperature. In the investigated temperature interval, R_a decreases by two orders of magnitude. The increase in the conductivity with temperature must mainly regarded as due to the thermally activated mobility of the carriers (electrons or holes) rather than to a thermally activated generation of these. The value of the activation energy (0.5 eV) is in agreement with those reported for other ferrites [6].

b. Gas sensing properties. Fig. 5 shows the gas sensing measurements for liquefied petroleum gas (LPG), methane, ethanol and acetone at various temperatures between 125 and 285 ^{o}C. It is clear from the graph that the sensitivity of the ferrite to acetone is the best, whereas the ferrite is almost insensitive to methane. As expected the sensitivity increases with increasing the operating temperature and reaches a maximum value around 230 ^{o}C and decreases further with temperature. The maximum sensitivity to ethanol and LPG is much lower. There is a sligth reduction in the operating temperature for LPG detection from 230 to 210 ^{o}C, which can be seen in Fig. 5. Usually, the gas sensing mechanism depends on the work temperature, because this mechanism is thermally activated [1].

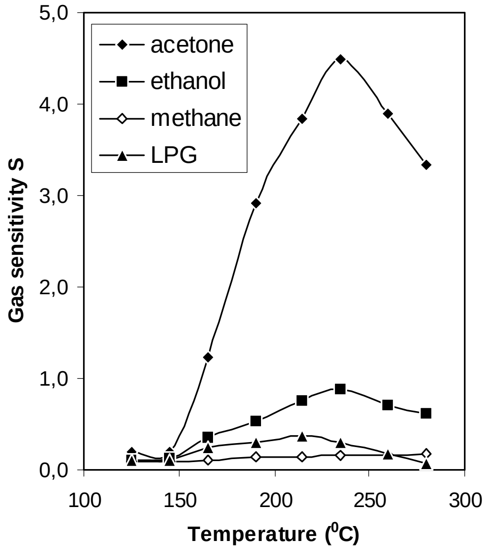

Fig. 5. Gas sensing of the ferrite.

4. Conclusion

Sensitivity studies on $Ni_{0.99}Co_{0.01}Mn_{0.02}Fe_{1.98}O_4$ ferrite for LPG, acetone, methane and ethanol have shown that the electrical resistivity of this ferrite, prepared by selfcombustion, is more sensitive to acetone and its sensitivity depends on the temperature.

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