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Gas sensitivity of nanocrystalline nickel ferrite

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Nanometer-sized materials, which have high surface activity due to their small particle size and enormous surface area, have been widely studied in the field of gas sensors in recent years. The samples were obtained by self-combustion 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

In technologies where ferrites are to be used for magnetic or electrical applications, high-density materials are generally required and the ferrites are often prepared by high temperature solid-state reactions between finely ground powders. Although most applications of ferrites as ceramic materials require high densities to achieve the desired properties, there are many applications for which lower densities and high surface area are preferred [1]. Spinel-type oxides with a general formula of AB_2O_4 are important mixed oxides in gas sensors, and have been investigated for the detection of both oxidizing and reducing gases [2]. In particular, nickel ferrite as a p-type semiconducting oxide has show to be a very good sensor to detect oxidizing like chlorine [1], whereas nickel ferrite prepared by the hydrazine method showed an n-type semiconducting behaviour [3-5].

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 [6,7].

In our previous papers [4,8,9] we have shown that various ferrites with various doping elements are sensitive to gases and/or humidity.

In the present study, nickel ferrite doped with small amounts of calciu, cobalt and manganese was investigated as gas sensor. In an attemp to improve the sensitivity and impart selectivity, nanoparticles of nickel ferrite have been partly repaced with Co and Mn on place of Ni and Fe, respectively. 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

Two samples with chemical formula $NiFe_2O_4$+1wt%CaO and $Ni_{0.99}Co_{0.01}Mn_{0.01}Fe_{1.99}O_4$ 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 ^{o}C 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.

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 has been already described in our earlier publication [4].

Gas sensing properties were investigated at various operating temperatures from 105 to 305 ^{o}C. The experiments were performed with four test gases: LPG, ethanol, methane and acetone. The sensitivity, S, is defined as the ratio:

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

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. 1 shows the powder X-ray diffractogram for the sample treated at 1000 ^oC 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.

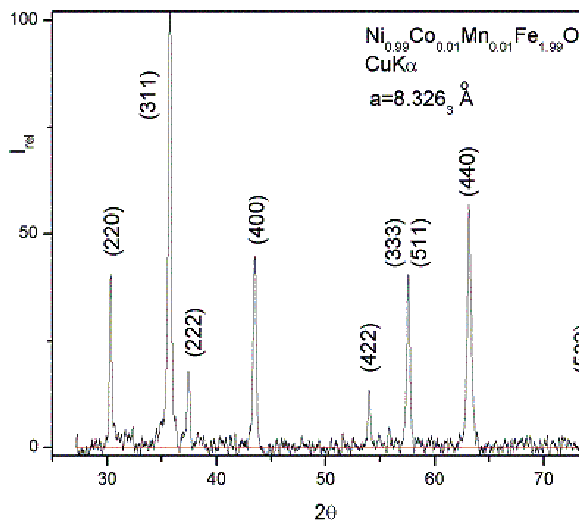

Fig. 1. Powder X-ray diffractogram for the sample calcined at 1000 ^oC in air for 30 minutes.

The external morphology of the sample can be visualized from the scaning electron micrograph of the synthesized material as in Fig. 2. 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 3.40 g/cm^3. Many large and small pores are present in all material.

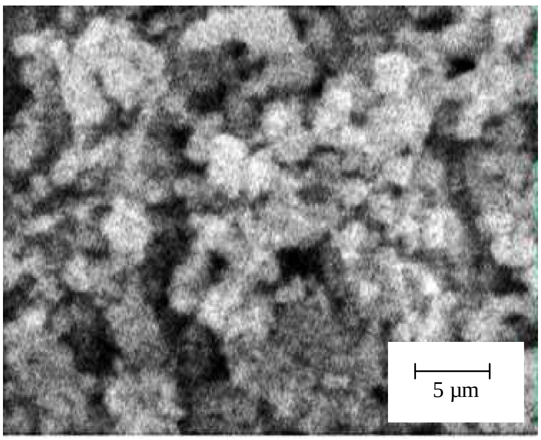

Fig. 2. SEM micrograph for the studied sample.

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. 3). The investigation was limited to the temperature interval of 105 to 305 ^oC. 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 [2].

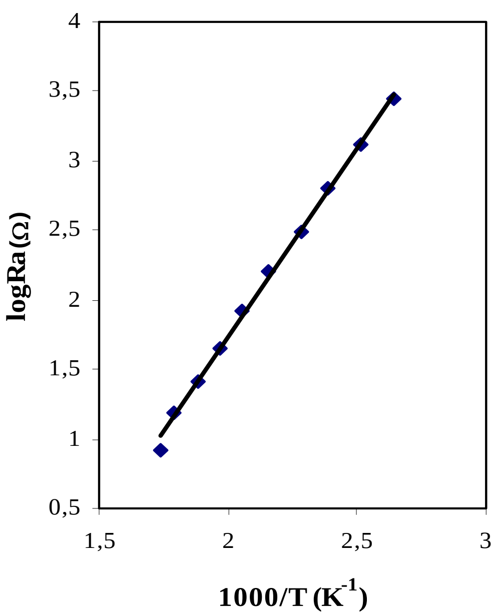

Fig. 3. Log R_a vs.1/T for the studied sample.

b. Gas sensing properties

Fig. 4 shows the gas sensing measurements for all samples, in acetone atmosphere, at various operating temperatures. The following observations can be made: the nickel ferrite doped with calciu is practically insensitive to acetone and for the mixed ferrites containing Mn and Co, the gas sensitivity depends on the operating temperature and Mn content.

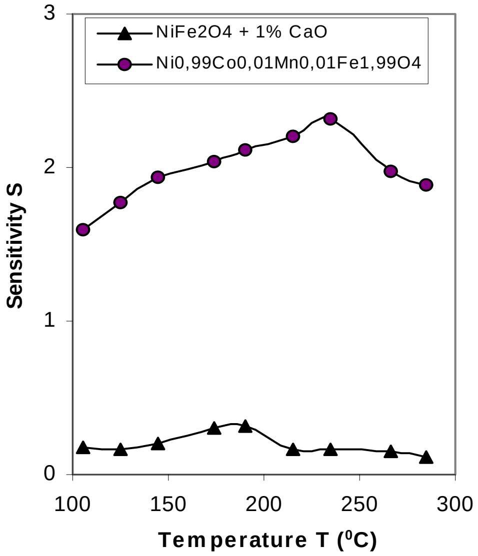

Fig. 4. Sensitivity versus operating temperature for studied samples in acetone gas.

Fig. 5 shows the gas sensing measurements for liquefied petroleum gas (LPG), methane, ethanol and acetone at various temperatures between 105 and 305 °C. It is clear from the graph that the sensitivity of the ferrite to acetone and LPG 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: 235 °C for acetone, 285 °C for LPG, 180 °C for ethanol and methane and decreases further with temperature. In the operating temperature 105 – 235 °C the sensitivity for LPG detection is lower after which increases significance having a maximum value around 285 °C and can be seen in Fig. 5.

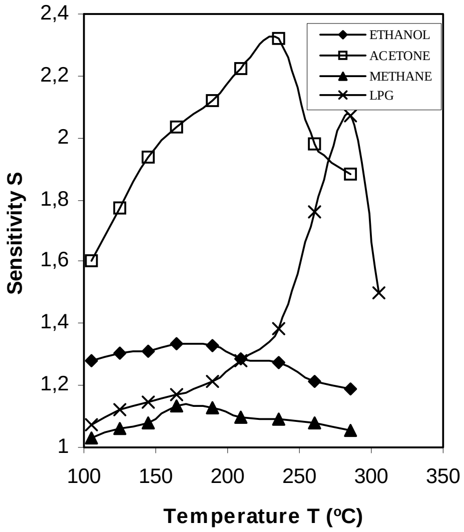

Fig. 5. Sensitivity vs sample temperature for some reducing gases.

Satyanarayana was showing that same composition for nickel ferrite ($Ni_{0,99}Co_{0,01}Mn_{0,01}Fe_{1,99}O_4$), but prepared by the hydrazine method have high sensitivity of LPG, with a maximum value around 230 °C. Usually, the gas sensing mechanism depends on the work temperature, because this mechanism is thermally activated [3].

4. Conclussion

The sensitivity studies to four gases (LPG, acetone, methane and ethanol) were carried out on two samples based on Ni – ferrite prepared by selfcombustion.

Studies on $Ni_{0.99}Co_{0.01}Mn_{0.01}Fe_{1.99}O_4$ ferrite for these gases have shown that the electrical resistivity of this ferrite, prepared by self-combustion, is more sensitive to acetone and LPG, and its sensitivity depends on the temperature. The optimized operating temperature, of 235 °C for this compound ($Ni_{0.99}Co_{0.01}Mn_{0.01}Fe_{1.99}O_4$) is favorable for the commercial development of acetone sensors.

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