

The influence of the heat treatment on the humidity sensitivity of magnesium nanoferrite

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In this work, we reported on a large improvement of the humidity sensitivity of pure magnesium ferrite by the modification of the surface granulation and material's morphology, based only upon the change of the thermal treatment parameters (temperature and time). Humidity sensitivity of MgFe_2O_4 was studied in the range 0 %-98 % RH. The studied samples were prepared by a new method, the precursor method of self-combustion. The nanometer powder was obtained that was pressed in disc shape and then subjected to heat treatments. The spinel structure of the ferrite compound was confirmed by the presence of XRD peaks. The morphology was studied by a high resolution scanning electron microscopy (SEM). The best results were obtained by an optimum thermal treatment in air at 1000°C for 30 minutes. This ferrite is characterized by good humidity sensitivity for large humidity interval, between 0 % RH and 98 % RH, and a short response time of about 70 seconds. These results are of high importance for applications.

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1. Introduction

In the last years the nanograined materials offer new opportunities for enhancing the performances of water vapor sensors. Spinel-type oxide semiconductors are an alternative for inexpensive and robust humidity detection systems. The sensing mechanism consists in the change of the electrical resistivity resulting from chemical reaction between water molecules and the metal oxide surface. Surface granulation and morphology have an essential role on the humidity sensitivity of solid-state sensors [1,2]. Previously, we reported an increase of the humidity sensitivity of magnesium spinel nanoferrite (MgFe_2O_4) by doping with Sn [3].

In this work, we achieved a large improvement of the humidity sensitivity of pure magnesium ferrite by modifying the granulation and material's morphology, based only upon the change of the thermal treatment parameters (temperature and time) without Sn addition.

The samples were prepared by self-combustion method (precipitation in a colloidal environment followed by self-combustion) followed by heat treatments [4,5]. The main advantages of self-combustion method powders over the conventional powders (physical mixtures of oxides) are molecular scale homogeneity, nanosized granulation, enhanced reactivity (lower heat treatment temperatures), and controlled grain size by subsequent heat treatments [6].

For comparison, the magnesium ferrite obtained by heat treatment at 1100°C for 4 hours was used. By lowering the temperature and time of the heat treatment we obtained samples having a finer granulation and larger surface area contributing to both the improvement of the humidity sensitivity and shortening the response time.

Magnesium ferrite is an oxygen deficient material at lower sintering temperature [7] as well as porous, which is

desirable for humidity sensing. Since defective sites on the surface are highly reactive due to unsaturated bonds [8,9] induce the dissociation of the water vapors. Researchers worked on this material in order to increase its sensitivity and shortening the response time by synthesizing nano-size particles [10,11].

In this work, the lowering of sintering temperature and treatment duration in magnesium nano-ferrite decreased the grain size from 500 nm to 100 nm, increased intergranular porosity, surface activity hence humidity sensing. It showed a linear humidity response curve at RH values between 0 % and 98 %.

2. Experimental

Ferrite samples MgFe_2O_4 were prepared by self-combustion method followed by heat treatments, starting from metal nitrates as raw materials. Preparing method includes:

- solution of metal nitrates $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2$ in deionized water,
- polyvinyl alcohol addition to make colloidal solution,
- stirring at 80°C ,
- NH_4OH addition to adjust pH to about 8,
- drying at 120°C ,
- self-combustion,
- precalcination of combusted powder at 500°C .

The reactions can be schematized as follows [12]:

- $2 \text{Fe}(\text{NO}_3)_3 + \text{Mg}(\text{NO}_3)_2 + 8 \text{NH}_4\text{OH} \rightarrow 2 \text{Fe}(\text{OH})_3 + \text{Mg}(\text{OH})_2 + 8 \text{NH}_4\text{NO}_3$;
- $2 \text{Fe}(\text{OH})_3 + \text{Mg}(\text{OH})_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{MgO} + 4 \text{H}_2\text{O}$;
- $\text{Fe}_2\text{O}_3 + \text{MgO} \rightarrow \text{MgFe}_2\text{O}_4$.

The resulting powders were mixed in a ball mill and compacted by biaxial pressing in a stainless steel die. The pressed pellets (17 mm diameter, 2-3 mm thickness) were

sintered in air, at 1100 °C and 1000 °C for various times, from 240 minutes to 30 minutes. For every sintering temperature, we used green samples. After each sintering, the weight and dimensions of the pellets were measured, at room temperature, to determine sintered density and porosity [3].

The micro morphology of the samples was examined by a high-resolution scanning electron microscope VEGA-TESCAN. The grain size was determined by linear intercept method [13] from SEM micrographs on the fracture surfaces. Spinel structure of the ferrite compound was confirmed by XRD peaks presence using DRON-2 diffractometer and CuK_α radiation.

For electrical measurements, the flat surfaces of the pellets were polished and porous chemically silvered at 500 °C. The a.c. electrical resistance was measured by a two-point method with LCR meter at 100 Hz.

For the humidity sensing measurements the sensor element (porous silvered ferrite disc) was placed in a thermostatic enclosure at 20 °C and exposed to different values of relative humidity. RH ranging 0 % to 98 % was obtained using ten saturated salt solutions as the humidity generation source [3].

After each change of the humidity, the sensor element was exposed to the new humidity for 2 minutes before measuring the new resistance.

The humidity response times were obtained by monitoring the resistance changes when the relative humidity varied from 53 % to 98 % and from 98 % to 53 % RH for the sample treated 4 h at 1100 °C, respectively from 0 % to 53 % and from 53 % to 0 % RH for the sample treated for 30 min. at 1000 °C.

3. Results and discussion

X-ray diffraction (XRD), scanning electron microscopy (SEM) and density measurements were used to analyze the structure of samples. The diffractograms (Fig.1) of two samples indicated the presence of a single phase of the spinel structure, without secondary crystalline phases. The thermal treatment of 30 min. at 1000 °C is sufficient for complete synthesis of this ferrite. The lattice parameter, calculated by X-ray diffraction measurements, was evaluated to be $8.406 \pm 0.0005 \text{ \AA}$ and X-ray density, d_x , was found to be 4.92 g/cm^3 .

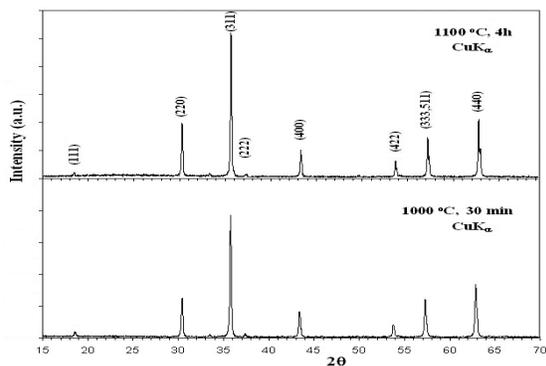


Fig.1. X-ray diffractograms for samples MgFe_2O_4 heat treated at 1100 °C/4h and 1000 °C/30min.

SEM micrographs (Fig.2 a, b, c) on the fracture surfaces of the samples evidenced the dependence of the microstructure on the sintering temperature and duration of the treatment.

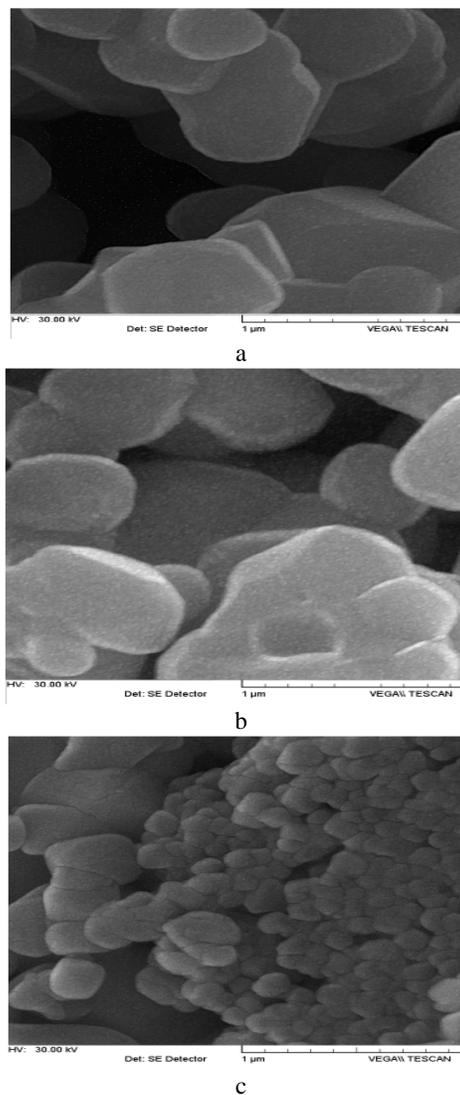


Fig. 2. SEM micrographs for the studied samples (MgFe_2O_4) (a) 1100 °C/4h, (b) 1000 °C/4h, (c) 1000 °C/30min.

Generally, all the samples are characterized by a fine granulation. The average grain sizes are within the range 0.1 μm (Fig.2 c) to 0.5 μm (Fig.2 a). The ferrite particles being small, a tendency towards agglomerations can be observed. One can also remark the change of the grain shape from rounded to faceted crystallites and pore coarsening when increasing sintering temperature from 1000 °C to 1100 °C. Large pores, above 1 μm in diameter, distributed along the grain boundaries and between the grains boundaries are necessary for rapid response of sensor, because the water adsorption rate is controlled by diffusion rate of water vapors. These structures indicate

that the investigated ferrites can easily exhibit adsorption and condensation of water vapors. Furthermore, the porous structure is an advantage in discouraging fracture due to thermal shock.

The structural characteristics of the specimens are summarized in Table 1. The surface area A_{sp} was calculated with formula [14]

$$A_{sp} = \frac{S}{v \cdot d} = \frac{6}{d \cdot D_m} \quad (1)$$

where S and v are the surface and volume of the ferrite particle, D_m is the average particle size and d is the bulk density. (It was assumed that all the crystallites have the same size and the same shape). One can see that the sintering parameters strongly influence the structural parameters. The specific surface area and porosity of the specimens decrease with increasing sintering temperature and duration, whereas the average grain size and sintered bulk density increase with increase sintering temperature. The largest specific surface area, $22.5 \text{ m}^2/\text{g}$, was found for the samples treated 30 min. at 1000°C , about 100 nm. (see Fig.2c).

Table 1. Structural data for the studied samples MgFe_2O_4 .

Sintering temperature/time ($^\circ\text{C}/\text{hours}$)	Sintering density d (g/cm^3)	Average grain size (nm)	specific surface area A_{sp} (m^2/g)	Porosity (%)
$1100^\circ\text{C}/4\text{h}$	2.75	500	5.0	45.8
$1000^\circ\text{C}/4\text{h}$	2.6	400	8.5	46.5
$1100^\circ\text{C}/30\text{min.}$	2.13	100	22.5	50.6

The humidity variation of the electrical resistivity was also investigated. The $\log \rho$ vs. relative humidity RH characteristics is shown in Fig. 3 for samples sintered for 4 hours at 1100°C and 30 minutes at 1000°C . The graphs clearly show that the electrical resistivity decreases with increasing relative humidity from 0 % to 98 % RH. At relative low humidity, lower than 70 % RH, the sample treated 4h at 1100°C shows smaller sensitivity. The sample treated 30 min. at 1000°C shows greater sensitivity and good linearity (better than magnesium nanoferrite doped with Sn) [3] for RH values between 0 % and 98 %. This behavior of resistivity shows that the larger specific surface area and porosity result in a better humidity response curve at values between 0 % and 98 % RH.

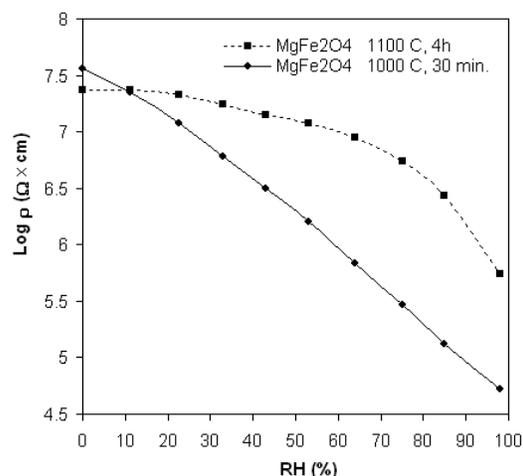


Fig. 3. The resistivity – humidity characteristics for the MgFe_2O_4 samples sintered 4 hours at 1100°C and 30 minutes at 1000°C .

The response time of the electrical resistivity to humidity changes was investigated for two samples and is shown in Fig. 4. The ferrite sintered 30 min. at 1000°C , characterized by higher porosity and a larger specific surface area, shows a shorter response time (70 – 140 seconds) than the ferrite treated 4h at 1100°C (5-7 minutes). Larger opened pores, cca. $1 \mu\text{m}$, are necessary for short response time, in agreement with Seiyama et al. (1983).

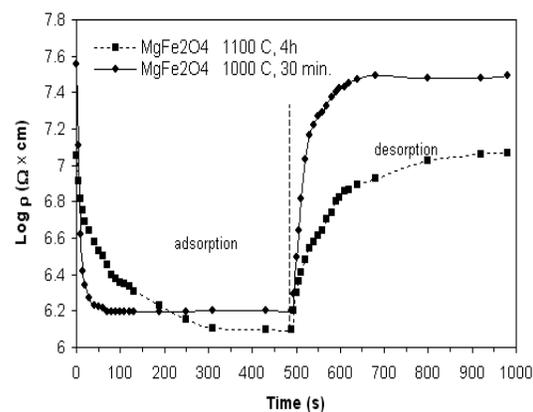


Fig. 4. Humidity response characteristics for MgFe_2O_4 samples sintered 4 hours at 1100°C (from 53% -98% and 98%-53% RH) and 30 minutes at 1000°C (from 0%-53% and 53%-0% RH).

4. Conclusions

The simple MgFe_2O_4 ferrite prepared by self-combustion method, annealed at 1000°C for 30 minutes is a promising humidity sensor material, considering its humidity sensitivity, chemical and thermal stability, mechanical strength and reduced producing cost.

In the humidity range between 0 % and 98 % RH, their electrical resistivity drops exponentially by over three orders of magnitude with increasing humidity.

Due to large porosity of samples and very small average grain size, a short response time (70-140 seconds) was obtained.

The best results were obtained by optimum thermal treatment in air, without modifying the composition of the material.

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