

A MODEL OF HUMIDITY SENSOR WITH A Mg-BASED FERRITE

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The microstructure and the humidity sensitivity of $\text{MgFe}_2\text{O}_4 + \text{CaO}$, $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_{1.8}\text{Ga}_{0.2}\text{O}_4$, $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 + \text{KCl}$ and $\text{MgMn}_{0.2}\text{Fe}_{1.8}\text{O}_4$ ferrites were investigated. We have found that the humidity sensitivity largely depends on composition, crystallite size, surface area and porosity. The best results concerning humidity sensitivity were obtained for $\text{MgMn}_{0.2}\text{Fe}_{1.8}\text{O}_4$ ferrite. The Mn ions enhance the humidity sensitivity of the Mg ferrite and assure a fine granulation of ferrite.

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1. Introduction

It is well-known that many porous metal oxides can be used as humidity-sensing materials. The adsorption of water vapor can enhance the surface electrical conductivity and dielectric constant of the metal oxides. There are some major requirements for a good humidity sensor: sensitivity, reversibility, fast response time, long life time, high-humidity selectivity and chemical and thermal stability. In general, the ceramic humidity sensors are more chemically and thermally stable than the polymeric humidity sensors, but not all metal oxides can be used as humidity-sensing materials. The conductance-humidity sensitivity of the ceramic sensors is determined by the material itself, the preparation method, and the sintering conditions. The response time of the ceramic humidity sensor depends on the material properties, porous structure of the sample, and the electrode contact material.

We found that some spinel magnetic oxides (ferrites) are very sensitive to humidity and can be used as humidity sensor element. A great advantage of ferrites is their porosity, which is necessary for a humidity sensor. Another advantage is that the ferrite compositions are characterised by a high resistivity which can very much decrease when the surrounding humidity increases.

The purpose of this study was to investigate the microstructure and humidity sensitivity of four compositions obtained by the substitution or addition of different cations in the original MgFe_2O_4 ferrite. It was determined the effect of dopants on the lattice parameters, porosity, average grain size, electrical resistivity. The humidity characteristics were examined to determine how they changed with the ferrite composition. Polycrystalline spinel ferrites were used for the present investigation.

2. Experimental

Polycrystalline samples with compositions $\text{MgFe}_2\text{O}_4 + 1 \text{ wt}\% \text{CaO}$, $\text{MgFe}_{1.8}\text{Mn}_{0.2}\text{O}_4$, $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_{1.8}\text{Ga}_{0.2}\text{O}_4$ and $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 + 1 \text{ wt}\% \text{KCl}$, were prepared by solid state reaction. The first two ferrites were prepared by self combustion method (SCM) using metal nitrates as precursors [1], and the last two were prepared by standard ceramic technology (CT) using reagent grade Fe_2O_3 , MgO , CuO and ZnO powders.

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After mixing in a ball mill, the powders were compacted in a pellet shape by uniaxially pressing under $5 \times 10^6 \text{ N/m}^2$. The pressed powder pellets (17 mm diameter, 3-4 mm thickness) were sintered in air, at different temperatures between 950 and 1100 °C. During sintering the sample volume extremely shrinks to about 30% of the powder body volume. For every sintering experiment green samples were used. After sintering, the weight and dimensions of the shrunk pellets were measured, at room temperature, to determine sintered density, porosity and volume shrinkage.

The microstructures of the fracture surfaces were examined by scanning electron microscopy (SEM). The grain size was determined by linear intercept method from micrographs of fracture surfaces. The phases analysis was made by X-ray diffraction using $\text{FeK}\alpha$ radiation.

For electrical measurement, the flat surfaces of the pellets were chemically silvered at 600 °C. The a.c. electrical resistance was measured with LCR meter. The variation of a.c. resistance as a function of relative humidity was made at 100 Hz by using a test chamber in which relative humidities ranging from 0 to 98% were obtained above some saturated salt solutions.

3. Results and discussion

Microstructure study is essential for the optimising the properties of ferrites needed for various applications. The diffractograms of the samples indicated the presence of the spinel phase only. The lattice parameter, calculated by X-ray diffraction measurements, was found to depend on the composition.

The SEM micrographs (Fig. 1 a - d) on the fracture surface also evidenced that the structure is dependent on the composition. Each composition is characterized by a typical porous structure and small crystallites without inside pores but many intergrain pores. The finest granulation and a tendency to agglomerated particles were observed in the Mn ions containing sample prepared by self combustion (Fig. 1b). Also, one can observe that the intergranular pores are linked through the large pores. The pore structure should be regarded as interconnected voids that form a kind of capillary tubes. This structure favours the adsorption and condensation of water vapours.

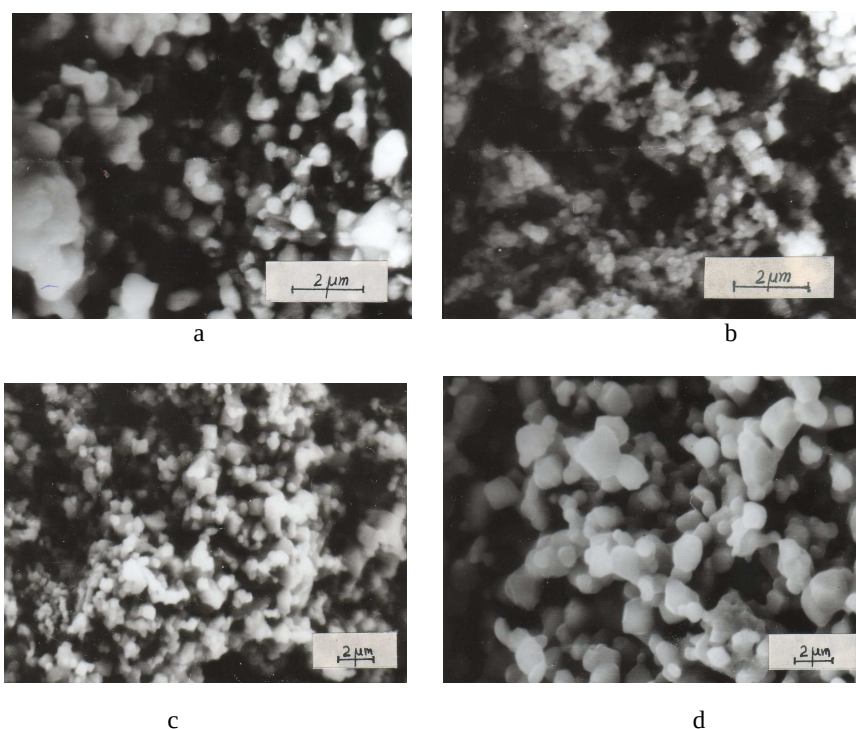


Fig. 1. SEM micrographs for ferrites: a) $\text{MgFe}_2\text{O}_4 + 1 \text{ wt\%CaO}$, sintered at 1100 °C for 4 hours ; b) $\text{MgFe}_{1.8}\text{Mn}_{0.2}\text{O}_4$, sintered at 1000 °C for 20 minutes; c) $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 + 1\% \text{ KCl}$, sintered at 1050 °C for 4 hours; d) $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 + 1\text{wt\% KCl}$, sintered at 1100 °C for 4 hours.

The structural characteristics of the specimens investigated in this paper are summarized in Table 1. Because the intragranular porosity is absence, the specific surface area can be calculated with formula [2]

$$S = \frac{s}{vd},$$

where s and v are particle surface and volume, respectively, and d is the bulk density (It is assumed that all particles have the same size and the same shape). From the Table 1 one can see that the Mn substituted ferrite is characterized by the highest specific area and the smallest values for grain size and bulk density.

The investigation of microstructure is very important to obtain an useful humidity sensor with a high humidity sensitivity wide range measurement and short response time.

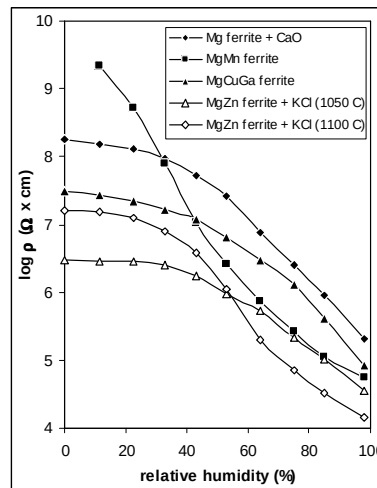


Fig. 2. The resistivity-humidity characteristics for the investigated.

Table 1. The structure data.

Sample	Sintering	Resis- tivity ρ ($\Omega \times \text{cm}$)	Bulk density d (g/cm^3)	Poro- sity p (%)	Average grain size D_m (μm)	Specific surface area S (m^2/g)	Lattice para- meter (nm)
$\text{MgFe}_2\text{O}_4 + 1 \text{ wt\%CaO}$	1100 °C, 4 h, SCM	1.4×10^8	2.29	51	0.3	8.73	0.8401
$\text{MgFe}_{1.8}\text{Mn}_{0.2}\text{O}_4$	1000 °C, 20 min, SCM	$>2 \times 10^9$	2.18	54	0.1	27.52	0.8421
$\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_{1.8}\text{Ga}_{0.2}\text{O}_4$	950 °C, 4 h, CT	1.1×10^8	2.38	55	-	-	0.8375
	1000 °C, 4 h, CT	2.8×10^7	2.5	50	1.2	2.0	0.8374
$\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 + 1 \text{ wt\% KCl}$	1050 °C, 4 h, CT	1.05×10^7	2.53	49	0.5	4.7	0.8406
	1100 °C, 4 h, CT	1.14×10^6	2.54	47	1.0	2.4	0.8388

The resistivity-humidity characteristics of the investigated specimens are shown in Fig.2. It is seen that the largest slope of the $\log \rho$ vs. RH curve is for Mn substituted Mg-ferrite. This means that this material exhibits the best characteristics in which the restivity decreased markedly with an increase of the relative humidity up to 88% because of capillary condensation of water vapours in all the pores. In this case, the resistivity was found to decrease by four orders of magnitude with

increase of humidity. In contrast, the resistivity of the other samples has marked sensitivity at relatively large humidities only, above 33% RH. These show a low sensitivity over the humidity range from 0% to 33% and, therefore, are unsuitable for use as humidity sensor for low humidities. It is seen from Fig. 2 that the humidity sensitivity of MgZn ferrite + KCl increases with a decrease in sintering temperature because the pore size distribution and grain size (surface area) change with the sintering conditions (see Fig. 1 c,d and Table 1). Indeed, the electrical resistance at the grain contact region decreases with the grain growth that explains the smaller value of ρ for sample sintered at 1100 °C.

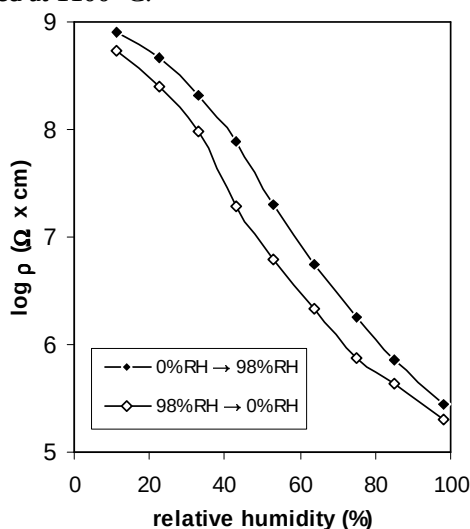


Fig. 3. The reproducibility of humidity-resistivity characteristics for Mn doped Mg ferrite.

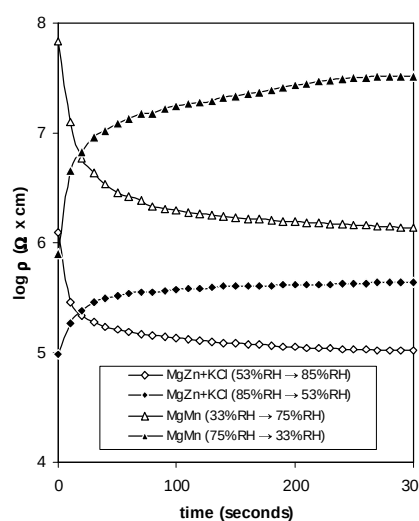


Fig. 4. Humidity response characteristics of $\text{MgFe}_{1.8}\text{Mn}_{0.2}\text{O}_4$ ferrite (above) and $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite + 1 wt% KCl (below).

It was examined reproducibility of the resistance-humidity characteristics for Mn doped Mg ferrite, when the RH was increased from 0% to 98% and then decreased from 98% to 0% (Fig. 3).

The response time of the electrical resistivity to humidity changes is shown for two samples only, in Fig. 4. The Mn doped Mg ferrite element which had a greater number of micropores below 1 μm in diameter (Fig.1b), showed rather long response time to humidity changes but its resistivity changed remarkably, over five minutes (Fig. 4). By contrast, the MgZnferrite + KCl element sintered at 1100 °C, which had few micropores below 1 μm in diameter, showed short response time to humidity changes and its resistance changes accompanying humidity changes were much smaller than for Mn doped element. Pores larger than 1 μm are necessary for short response time in agreement with Seiyama et al [3].

4. Conclusions

The $\text{MgFe}_{1.8}\text{Mn}_{0.2}\text{O}_4$ prepared by self combustion method is promising, judging from the humidity sensitivity, measurability and mechanical strength. However, the response time for this element is not yet a satisfactory value and further investigation must be made to shorten the response time by reduction of the thickness of the element.

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