

HUMIDITY-SENSITIVE ELECTRICAL RESISTIVITY OF MgFe_2O_4 AND $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$ POROUS CERAMICS*

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Pure and Sn substituted Mg ferrites have been prepared by sol-gel autocombustion method. This method offers the advantage to prepare ultra-fine, homogeneous and reproducible ferrite powders using aqueous solutions of constituent ions (metal nitrates) salts. Sn ion partially substituted Mg ion to improve the humidity sensitivity of Mg polycrystalline ferrite. The phase composition and lattice parameters were determined by X-ray diffraction (XRD), and the effect of Sn substitution on the granular structure was investigated by scanning electron microscopy (SEM). We have found that Sn ions affect crystallite size, surface area and porosity. Sn ions assure a nanocrystalline structure of $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$ ferrite. The average grain size changes from 500 nm to 100 nm by partial substituting Mg with Sn ions in MgFe_2O_4 . Also, Sn ions enhance the humidity sensitivity of Mg ferrite. For Sn substituted ferrite, the electrical resistivity decreases by about three orders of magnitude, from $10^9 \Omega\cdot\text{cm}$ to $10^6 \Omega\cdot\text{cm}$ when the relative humidity increases from 11% to 85%. These results show that the promoting effect of Sn ions on humidity sensitivity of Mg ferrite can be related with the changes in porosity and specific surface area. Further investigations are necessary to shorten response time to humidity variations.

Key words: humidity sensor, magnesium ferrite.

1. INTRODUCTION

During the last years, many kinds of ceramic oxides have been investigated actively as humidity sensing materials [1–4]. Humidity sensors based on semi-conducting oxides have certain advantages compared to other types of humidity sensors, such as low cost, simple construction, small size and ease of placing the sensor in the operating environment. Basically, a ceramic sensor can detect humidity on the principle of measuring a change in the resistance by water vapor adsorption.

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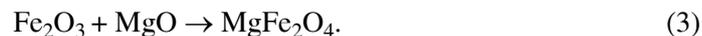
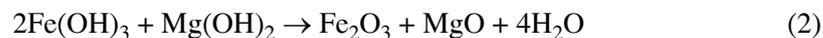
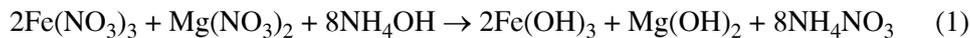
Seki *et al.* [5] have reported the utilization of ferrites for water vapors detection as humidity sensitive active elements. Because the ferrites behave as a n type semiconductor, conductivity will be increased in the presence of water vapor. Much interest was focused on Mg ferrite owing to its high electrical resistivity and high porosity.

In this work we study the influence of Sn ion on morphology, electrical properties and humidity sensitivity of MgFe₂O₄ ferrite.

2. EXPERIMENTAL

2.1. PREPARING SENSOR MATERIAL

Two ferrite compositions were prepared: MgFe₂O₄ (sample AG1) and Mg_{0.9}Sn_{0.1}Fe₂O₄ (sample AG2). We have applied a new procedure for preparing precursor nanopowders which is a combination of sol-gel technique with self-combustion [6, 7]. By using selfcombustion, an external heat source is absent, the thermal energy is provided by the fast exothermic reaction and the product obtained is a finely divided powder. As starting materials we used metal nitrates, ammonium hydroxide and polyvinyl alcohol. The analytically pure grade powders of metal nitrates, were weighed in the desired proportions and dissolved with small amounts of water. An aqueous solution of 10% polyvinyl alcohol was added to make a colloidal solution. Then, small amounts of NH₄OH solution (25% concentration) were added to adjust pH to about 8. By coprecipitation a sol of metal hydroxides and ammonium nitrate were formed. By mixing with a magnetic stirrer for 5 to 10 min, we obtained the viscous gel. This was dried at 120°C for 12 h and then was ignited in a corner. A combustion wave spontaneously propagates through the dried gel and converts the hydroxides into metal oxides and the synthesis between oxides begins to form spinel structure. Due to rapid heating and cooling by the passage of a combustion wave from the point of ignition throughout the solid compact, a powder containing very fine crystallites were obtained. The reactions which take place can be schematized as follows:



The as-prepared powder was compacted in a disk shape, by uniaxial pressing at a pressure of 200 MPa. The compacts were treated at 1100°C for 4 h, in a furnace. After slow cooling in the furnace, the mass and dimensions of the disks were measured to determine the experimental density, d (density = mass / volume) and porosity, p , by the formula

$$p = 1 - \frac{d}{d_x}, \quad (4)$$

where d_x is the theoretical density

$$d_x = \frac{8M}{N \cdot a^3}, \quad (5)$$

where M is the molecular weight, N is Avogadro's number and a is the lattice constant. The phase composition of the sintered pellets was identified by X-ray powder diffraction (XRD). The microstructure was examined using a scanning electron microscope (SEM). In order to obtain high resolution scanning electron microscopy (SEM) pictures, the samples were coated with an ultra thin silver layer of 30 nm. The average grain size was determined by the linear-intercept technique from micrographs on the fracture surface of the samples. The specific surface area was calculated using the following equation [8]

$$A = \frac{s}{v \cdot d}, \quad (6)$$

where s and v are the particle surface and volume, respectively and d is the experimental density. (It is assumed that all the particles have the same size and the same shape).

2.2. MEASURING PROCEDURE

To measure the electrical properties of the samples, silver electrodes were applied to opposite faces of the disks (about 1.8 mm thickness and 17 mm in diameter). The alternating current electrical resistance was measured by a two-point method, with a digital LCR meter, at 100 Hz.

For the humidity sensing measurements the sensor element (ferrite disc with silver electrodes) was placed in a thermostated enclosure and exposed to different relative humidities. Relative humidities ranging 11% to 98% were obtained using saturated salt solutions as the humidity generation source. A list of saturated salts and their constant humidity values is given in Table 1 (From the Handbook of Chemistry and Physics).

Table 1

Relative humidity RH above saturated salt solutions at 20°C

Salt	LiCl	K(C ₂ H ₃ O ₂)	MgCl ₂	K ₂ CO ₃	Mg(NO ₃) ₂	CoCl ₂	NaCl	KCl	K ₂ SO ₄
Relative Humidity (%)	11.3	22.7	33.1	43.2	53.0	64.0	75.7	85.1	97.6

The experimental arrangement for humidity sensing measurement and the ferrite sensor element are shown in Fig. 1 a and b. The resistance of the sensors was measured in dry air (about 0% RH) as well as in different humidities. The elements were mounted in a setup in which up to three sensors can be electrically connected. The enclosure was sealed with a lid to minimize leaking. At least three samples of each composition are tested, but in presented curves, only one result from each sensor composition is shown, since no difference between the samples of the same composition was observed. During the measurements, the temperature was kept at 20°C. After each change of the humidity, the sensor element was exposed to the new humidity for 2 minutes, before to measure the new resistance.

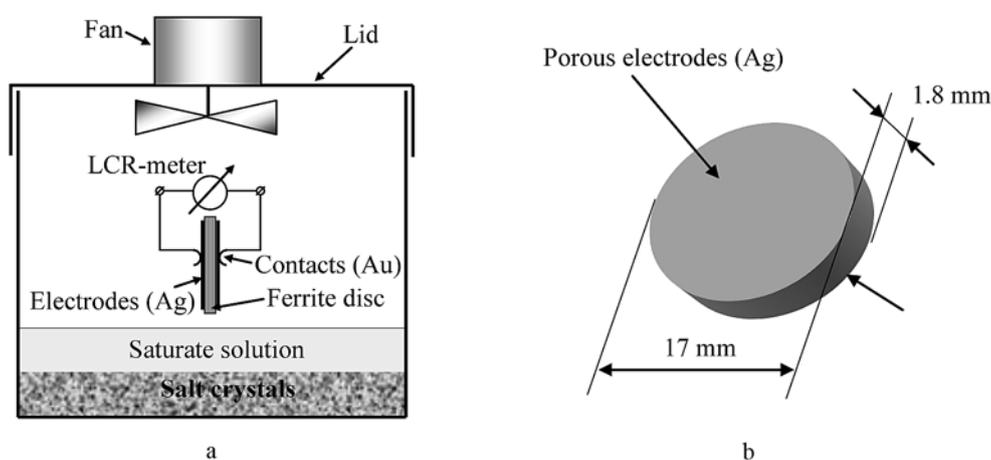


Fig. 1 – Experimental arrangement for gas sensing measurements: a) measurement enclosure; b) design of ferrite sensor with silver electrodes.

The humidity response times were obtained by monitoring the resistance changes when the relative humidity was varied from 53% to 98% and from 98% to 53%. To examine stability of the sensors the humidity-resistivity characteristics at 20°C, between 11% and 98% RH were measured after 5, 10 and 25 days and no important changes were observed. In fact, the sensor resistance slightly increased in room atmosphere after aging.

3. RESULTS AND DISCUSSION

3.1. STRUCTURE ANALYSIS

Fig. 2 shows the X-ray diffractograms of samples. It is evident that only pure ferrite is monophasic. The XRD lines belonging to the spinel structure are

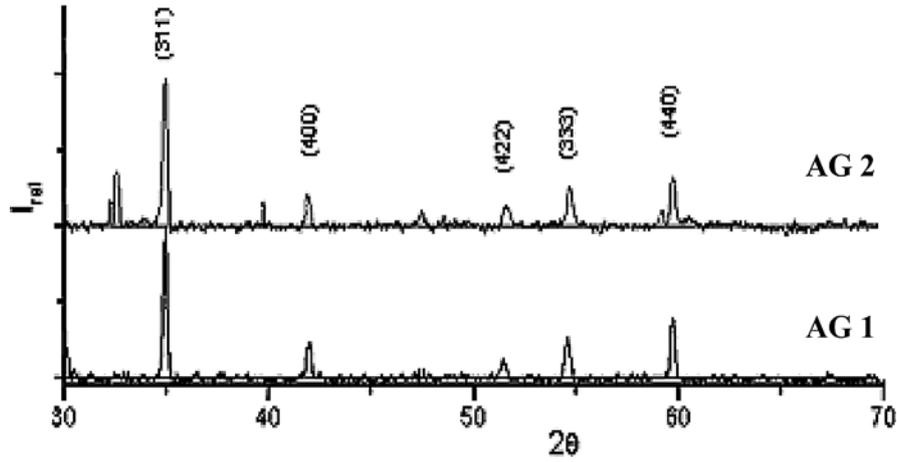


Fig. 2 – X-ray diffraction patterns of studied samples: AG1 – MgFe_2O_4 ; AG2 – $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$.

presented with “Miller” indices. The Sn ion induces a foreign phase. This new phase has not yet been identified. Judging from the peak height, it seems that a large amount of foreign phase is present in the sample containing Sn (AG2). The presence of the foreign phase can suggest a solubility limit of Sn^{4+} ions in the spinel lattice due to its radius (0.083 nm) [9]. It is known that the degree of replacement of the host cations by the other ions in the host lattice depends on the cationic radius of the substituents [10].

The values of lattice constant for cubic spinel structure of the investigated samples are listed in Table 2 (column 3). The lattice constant of Sn doped ferrite does not differ so much from that of the undoped one. This fact reveals a good crystalline structure of spinel type.

Table 2

Structural data for ferrites sintered at 1100°C

Sample symbol	Cationic substituent	Lattice constant (nm)	Average grain size D_m (μm)	Porosity (%)	Specific surface area A (m^2/g)	Pore size distribution (μm)
AG1	No	0.8354	0.50	45.8	5.0	0.15 ~ 1.00
AG2	Sn	0.8352	0.10	51.6	23.8	0.30 ~ 2.20

Morphology of the sample can be visualized from SEM micrographs on the fracture surfaces of the synthesized materials, as in Fig. 3 (a and b). Each composition is characterized by a porous structure and submicron rounded grains. It is evident that the structure of the Mg ferrite is affected by substitutions. The SnO_2 incorporation produced radical changes in microstructure (Fig. 3b).

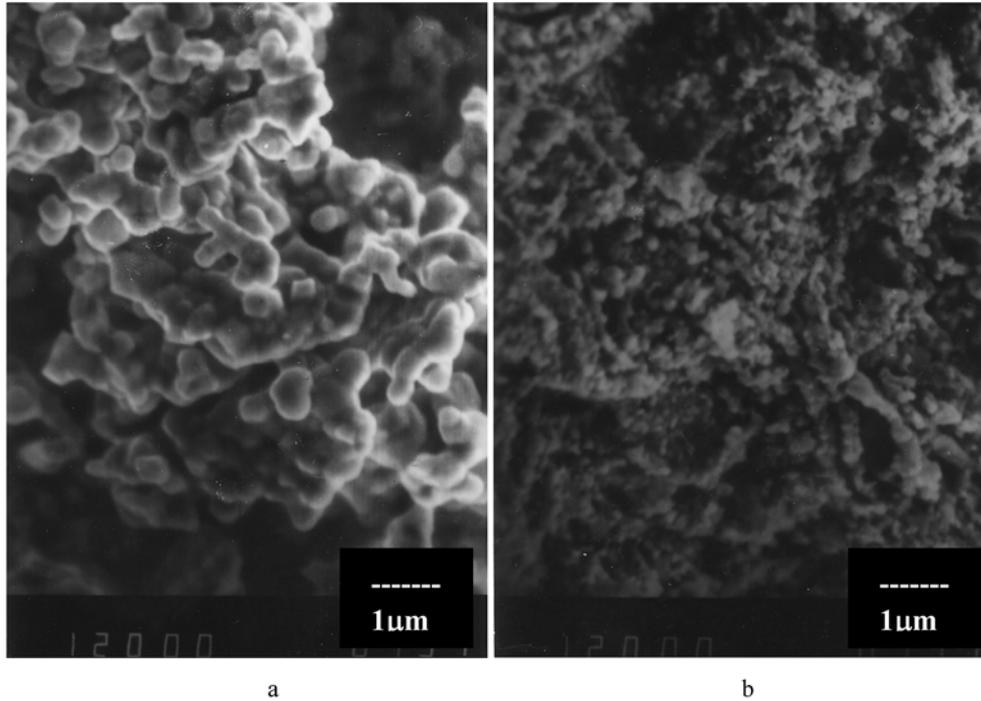


Fig. 3 – SEM micrographs of studied ferrites: a) AG1 – MgFe_2O_4 ; b) AG2 – $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$.

A substantial decrease in the grain size from 500 nm to about 100 nm and the formation of the grain bridges around the interconnected pores can be observed in Fig. 3b. It is possible that the presence of the foreign phase in the Sn-containing samples inhibits the grain growth.

The structural data are summarized in Table 2. One can see that the Sn doped sample (AG2) has higher porosity, of 51%, larger specific area, of about $24 \text{ m}^2/\text{g}$ and a wide pore size distribution. A larger specific area implies a much more active surface towards water vapor and thus the sensitivity of the resistivity to humidity will be increased. Also, large pores are necessary for a rapid response; these can easily exhibit adsorption and condensation of water vapor [1].

3.2. SENSOR PROPERTIES

The effect of the partial substitution of Mg^{2+} with Sn^{4+} in MgFe_2O_4 on the electrical resistivity-humidity characteristics was also investigated as shown in Fig. 4. The following two observations can be made:

– The measurements show an increase in ρ with about two orders of magnitude, from $10^7 \text{ } \Omega\cdot\text{cm}$ to $10^9 \text{ } \Omega\cdot\text{cm}$ as tin partially replaces magnesium in MgFe_2O_4

ferrite. One can suppose that partial substitution of octahedral Mg ions by tetrahedral Sn ions localizes the octahedral Fe^{2+} ions and thus, the number of the electronic jumps between Fe^{2+} and Fe^{3+} ions (hopping conduction mechanism in ferrites) decreases [11]. Moreover, microstructure (porosity, grain size, structural defects) has a great role on the electrical resistivity. Smaller grains implies an increase of the grain boundary surface which normally account for high resistivity of a polycrystalline material.

– The humidity sensitivity depends upon the microstructure. The larger the specific surface area and porosity of the specimens the more water vapors can be physically adsorbed, resulting in a larger decrease of the resistivity. One can see from Fig. 4 that the Sn-substituted ferrite (AG2) is more sensitive to humidity change. Its electrical resistivity decreases by about three orders of magnitude, from $10^9 \Omega\cdot\text{cm}$ to $10^6 \Omega\cdot\text{cm}$ when the relative humidity increases from 11% to 85%.

In comparison with Sn substituted ferrite, the unsubstituted ferrite (AG1) is sensitive to high relative humidities only, over 75%. It is thought that Sn ions have preferable effects on the sensitivity to water vapors (humidity).

The response rate of the electrical resistance due to humidity change was examined also. The humidity response characteristics to variation in RH from 53% to 98% and from 98% to 53% for MgFe_2O_4 (AG1) and from 0% to 53% and from 53% to 0% for $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$ (AG2) are shown in Fig. 5. The response

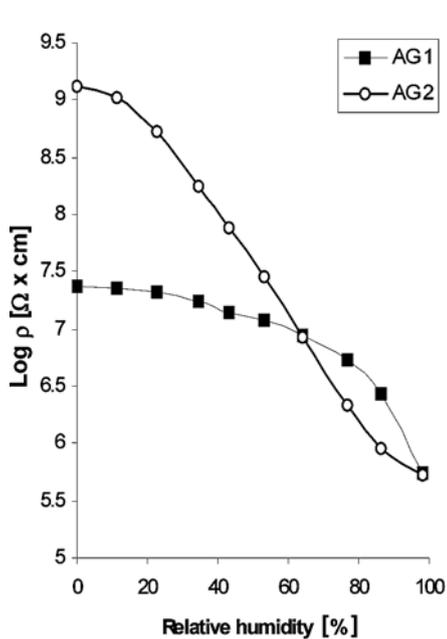


Fig. 4 – The resistivity-humidity characteristics for the investigated samples.

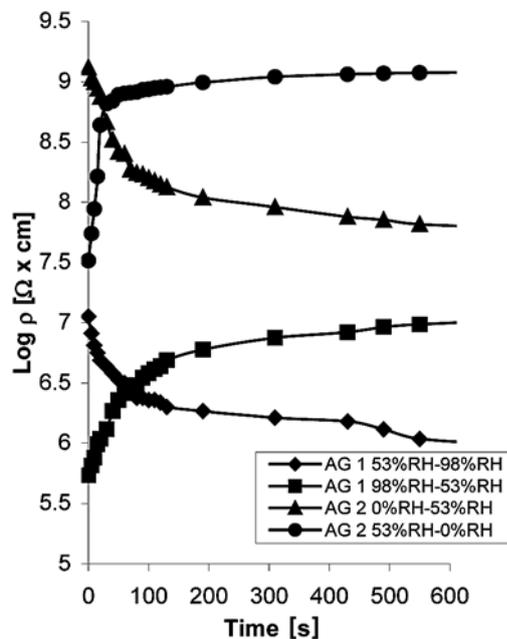


Fig. 5 – Humidity response characteristics for AG1 and AG2 samples.

time of MgFe_2O_4 (AG1) is of about 5 minutes to attain a steady state value of the resistivity, whereas the response time for $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$ (AG2) is shorter, of about 3 minutes. These results may suggest that the adsorption or desorption rate of water vapors is controlled by the diffusion rate of these through the micropores which in its turn is dependent on the pore size distribution. Large micropores, above $0.5 \mu\text{m}$, are necessary for rapid response to humidity changes. The MgFe_2O_4 element, which has a great number of micropores below $0.5 \mu\text{m}$ in diameter (Fig. 3a), showed a longer response time to humidity changes.

4. CONCLUSIONS

The $\text{Mg}_{0.9}\text{Sn}_{0.1}\text{Fe}_2\text{O}_4$ porous ceramic exhibits a better humidity sensitivity in comparison with MgFe_2O_4 . Its electrical resistivity changed remarkably, by three orders of magnitude, when the relative humidity increased from 11% to 98%. Also, this ceramic element exhibits a shorter response time. However, the response time is not yet satisfactory.

These results show that the promoting effects of Sn ions on humidity sensitivity of Mg ferrite can be related with the changes in porosity and grain size (specific surface area).

Further investigations are necessary to shorten response time, without any decrease in humidity sensitivity, and to explain the role of Sn^{4+} substituent which is responsible for the enhancement of the humidity sensitivity of Mg ferrite.

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