

## MgCu NANOCRYSTALLINE CERAMIC WITH $\text{La}^{3+}$ AND $\text{Y}^{3+}$ IONIC SUBSTITUTIONS USED AS HUMIDITY SENSOR

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The partial substitution of La and Y for Fe into nanocrystalline  $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$  compound was studied. The Mg-based ceramics present an attractive set of properties: high electrical resistivity, high Curie temperature and chemical stability.  $\text{Y}^{3+}$  and  $\text{La}^{3+}$  ions affect the structure and magnetic and electric properties of  $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$  compound. These ions increase the grain size and favour the densification of ceramic. The electrical resistivity decreases with incorporation of  $\text{La}^{3+}$  and  $\text{Y}^{3+}$  ions in  $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ .

(Received April 26, 2004; accepted June 3, 2004)

*Keywords:* Ferrites, Humidity sensor, Nanocrystalline materials

### 1. Introduction

Mixed ferrites attracted much attention because of their vast applications in a wide range, from microwave to radio frequencies, such as microwave devices, computer memories and magnetic recording. In many applications, they play a useful role because of their high resistivity and low eddy current losses. During the last years, many oxide ceramics have been investigated as materials for humidity sensors used in automatic humidity controlling systems [1-3]. Basically, ceramic sensors can detect humidity on the basis of the change of the surface electrical conductivity by vapour adsorption.

The partial substitution of La and Y for Fe into nanocrystalline  $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$  compound leads to the compositions  $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_{1.8}\text{La}_{0.2}\text{O}_4$  and  $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_{1.8}\text{Y}_{0.2}\text{O}_4$ , respectively. We selected the Mg-based ceramic because it presents an attractive set of properties: high electrical resistivity, high Curie temperature and chemical stability. It is a light ceramic and the stability of  $\text{Mg}^{2+}$  ions avoids the appearance of  $\text{Fe}^{2+}$  ions. Also, much interest is centered on study of this ceramic as humidity sensitive resistor since it is inexpensive and robust [1, 2].

### 2. Experimental

The samples were prepared by our method of self combustion [3], an improved variant of the method of co-precipitation. According to this method the substances in the reaction are metal nitrates and ammonium hydroxide in polyvinyl alcohol solution. The co-precipitation takes place into a colloidal medium and the reaction that determines the formation of the ferrite is a rapid combustion. The resulted powders were pressed into toroidal and disk shapes.

The chemical formula for the investigated ceramics is  $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_{2-x}\text{R}_x\text{O}_4$ , with  $\text{R} = \text{Y}$  or  $\text{La}$  and  $x = 0$  and  $0.2$ .

Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to investigate the morphology of the microstructure and phase components of the doped and undoped samples.

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Electrical measurements were carried out by a bridge method on disk shape. Specific saturation magnetization was measured by a vibrating sample magnetometer on the torroids and spheres prepared from discs.

Initial magnetic permeability was measured by an inductance bridge on the torroids in a field of 0.4 A/m and the average grain size by the linear intercept technique from micrographs on fracture surfaces.

### 3. Results and discussion

The  $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$  ferrite is used as reference material. X-ray diffraction patterns for all samples are given in Fig. 1. Comparing the XRD spectra (Fig. 1 a-c) it can be concluded that the incorporation of  $\text{La}_2\text{O}_3$  or  $\text{Y}_2\text{O}_3$  in the ferrite composition  $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$  leads to modifications in the phase composition of the ferrite. The pure ferrite is monophasic. The Y- and La-containing compounds are multiphasic. The lattice constant increased from 8.3776 Å to 8.3870 Å and 8.3861 Å by incorporating Y and La respectively.

These crystallographic changes correlate well with the morphological changes displayed in SEM pictures (Fig. 2 a-c). It is clearly observed in Figs. 2 b and c that the  $\text{Y}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  affect drastically the microstructure of MgCu ferrite. An increase in the average grain size and a decrease of the porosity was obtained.

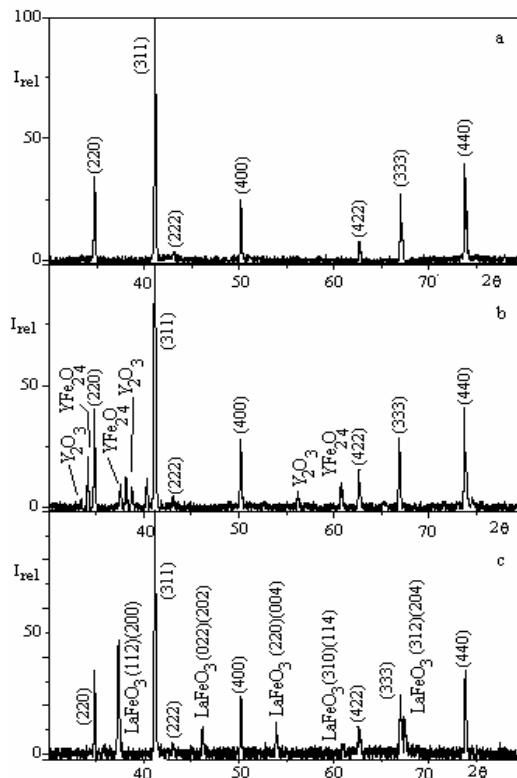


Fig. 1. XRD patterns of samples sintered at 1000 °C: a) MgCu pure ferrite; b) Y-substituted ferrite; c) La-substituted ferrite.

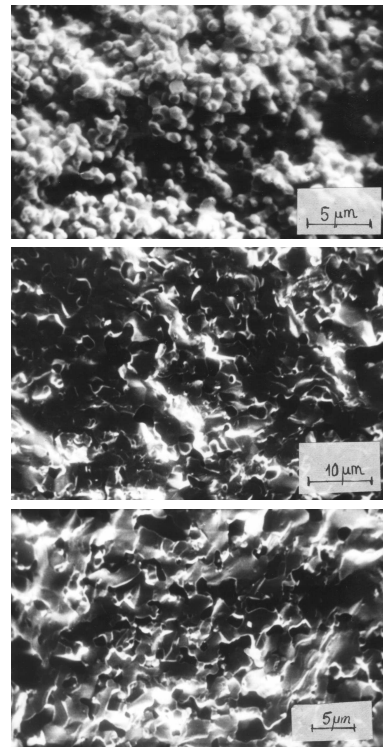


Fig. 2. SEM micrographs for the same samples as in Fig. 1.

In Table 1 are given some structural characteristics for the samples sintered at 1000 °C. From the data given in Table 1 may be concluded:

- The increase of the lattice constant of the spinel phase in the Y and La containing compounds may be due to a few  $\text{La}^{3+}$  or  $\text{Y}^{3+}$  ions entered into octahedral sites of the spinel structure.

- Observed lower values of porosity and higher values of grain size in doped samples indicate that Y<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> enhance sinterability and thereby promote densification as well as grain growth processes. The precise values of solubility of La<sup>3+</sup> and Y<sup>3+</sup> in spinel lattice are not known.

Table 1. Structural characteristics for the samples sintered at 1000 °C.

Substitution	Lattice parameter (Å)	Porosity ( % )	Average grain size D (µm)	Specific surface area S (m <sup>2</sup> /g)
without	8.3796	40	2	1.00
Y	8.3870	33	5	0.34
La	8.3861	27	7	0.22

On can see that the specific area and the average grain size are dependent on the composition. The specific surface area was calculated with formula:

$$S = \frac{s}{vd}, \quad (1)$$

where s and v are, respective, the surface and the volume of the particle and d is the bulk density. The largest value of the specific area was found for the unsubstituted sample, although the particle size is not very small.

Specific saturation magnetization, initial permeability and electrical resistivity, measured at 25 °C, for all samples sintered at 1000 °C are listed in Table 2. One observes the following features:

- The Y<sup>3+</sup> and La<sup>3+</sup> ions decrease the specific saturation magnetization of Mg<sub>0.5</sub>Cu<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> compound. This reveals that a partial incorporation of Y<sup>3+</sup> or La<sup>3+</sup> ions in the spinel matrix can be possible and, thus, a magnetic dilution of octahedral sub-lattice is obtained.
- Even though there is a decrease in saturation magnetization  $\sigma_s$ , the permeability has not shown a corresponding decrease because of the well-developed microstructure.
- The results given in Table 2 indicate that Y<sup>3+</sup> and La<sup>3+</sup> ions strongly influence the bulk resistivity. One can see that electrical resistivity  $\rho$  has a notable lowering when La<sub>2</sub>O<sub>3</sub> or Y<sub>2</sub>O<sub>3</sub> was substituted for Fe<sub>2</sub>O<sub>3</sub>.
- This implies that Y<sup>3+</sup> and La<sup>3+</sup> ions especially act on the grain-boundary related properties. The increase of the grain size, by doping with Y and La, determines a reduction of the grain boundary surface, and as a result, the electrical resistance diminishes.

Table 2. Saturation magnetization, initial permeability and electrical resistivity, measured at 25 °C, for all samples sintered at 1000 °C.

Substitution	Saturation magnetization, $\sigma_s$ (emu/g)	Initial permeability, $\mu_i$	Electrical resistivity, $\rho$ (Ω·cm)
without	25.5	4.5	$1.73 \times 10^6$
with Y	21.2	10.4	$3.71 \times 10^2$
with La	19.8	8.8	$1.40 \times 10^4$

The humidity sensitivity of the electrical resistance is given in Fig. 3. The resistance of the samples sintered at 900 and 950 °C is sensitive to humidity change independent on composition.

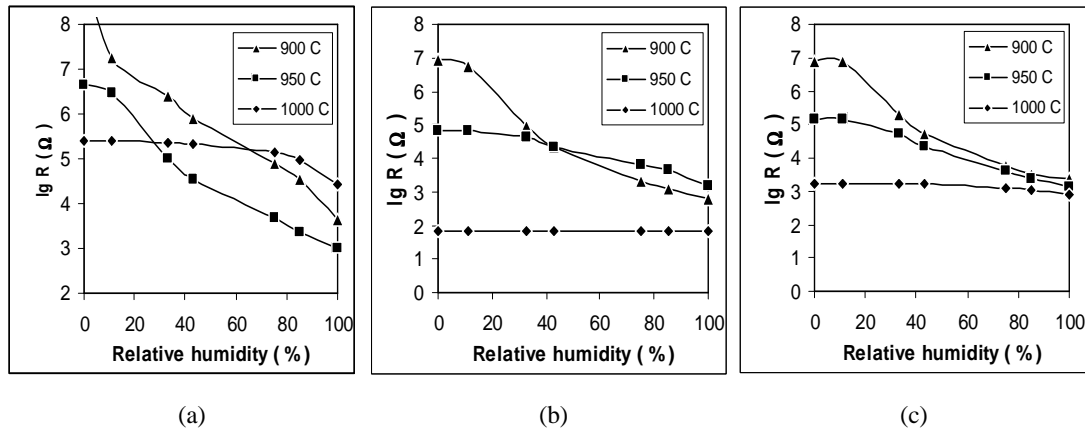


Fig. 3. Humidity-resistivity characteristics for the same samples as in Fig. 1.

By sintering at 1000 °C, the resistance of the substituted samples shows almost humidity independent behaviour caused by a better densification and the presence of the closed pores which hinder the interaction of H<sub>2</sub>O with ceramic. However, it must be mentioned that the sintering at low temperature is not advantageous for these ceramics because unsatisfactory mechanical properties can be obtained.

#### 4. Conclusions

The impact of Y<sup>3+</sup> and La<sup>3+</sup> ions on the structure and magnetic and electric properties of Mg<sub>0.5</sub>Cu<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> compound are summarized as follow:

- The compounds Mg<sub>0.5</sub>Cu<sub>0.5</sub>Fe<sub>1.8</sub>Y<sub>0.2</sub>O<sub>4</sub> and Mg<sub>0.5</sub>Cu<sub>0.5</sub>Fe<sub>1.8</sub>La<sub>0.2</sub>O<sub>4</sub> are multiphase, whereas the Mg<sub>0.5</sub>Cu<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> is singlephase.
- These ions increase the grain size and favour the densification of ceramic.
- A decrease of saturation magnetization was obtained due to a slight solubility of Y<sup>3+</sup> and La<sup>3+</sup> ions in the spinel matrix.
- The electrical resistivity decreased with incorporation of La<sup>3+</sup> and Y<sup>3+</sup> ions in Mg<sub>0.5</sub>Cu<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>. The reduction of the grain boundary area appears to be responsible for diminishing of the resistivity of these samples.

#### References

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