

Influence of copper ions on the structure and electromagnetic properties of MgZn ferrite

E. REZLESCU*, L. SACHELARIE^a, N. REZLESCU

National Institute of Research and Development for Technical Physics, Iasi, Romania

^a*University of Medicine and Pharmacy, Iasi, Romania*

The effect of Cu substitution on the properties of magnesium-zinc ferrites sintered at low temperature were investigated. The densification of MgCuZn ferrite is dependent upon Cu concentration in the composition of $Mg_{0.5-x}Cu_xZn_{0.5}Fe_2O_4 + 0.5 MgO$. The sintered ferrite with a density of about 4.5 g/cc and the electrical resistivity greater than $10^8 \Omega \cdot cm$ was obtained at relatively low sintering temperature (1050 °C), for $x = 0.3$. This sintering conditions are suitable for multilayer chip inductor application.

(Received March 15, 2006; accepted May 18, 2006)

Keywords: Ferrites, Resistivity, Shrinkage, Permeability, Density, Saturation magnetization

1. Introduction

MgZn ferrite is considered a candidate material for high frequency engineering ceramics because of its high electrical resistivity, high Curie temperature and low cost. However, for polycrystalline Mg-based ferrites, the densification is a problem because of their high sintering temperature (over 1350 °C) [1,2]. Of course, lowering of the sintering temperature is the objective of every ceramic processor. For totally solid-state sintering, lowering of the temperature requires enhancement of cation diffusion (an exact mechanism may not be known) without increasing the temperature. A common approach to solving this problem is the use of sintering aids. By partial substitution of Mg with Cu ions in MgZn ferrite, it is found that MgCuZn ferrite can be prepared at relatively low sintering temperature with an improved density and without a seriously decreasing of the d.c.resistivity. The copper ions have an significant role in lowering the firing temperature of MgZn ferrite. In a previous paper [3] we reported the preparation of Mg Cu ferrites doped by rare-earths atoms.

In this paper it was investigated the system $Mg_{0.5-x}Cu_xZn_{0.5}Fe_2O_4 + 0.5 MgO$, where $0 \leq x \leq 0.5$. Some effects of Cu substitution for Mg on the properties of MgZn ferrites with magnesia excess were analyzed.

2. Experimental

The materials have been prepared by standard ceramic technology described in [4], using MgO, CuO, ZnO and Fe_2O_3 , of high purity. For sintering experiments, a set of samples were sintered successively at seven temperatures: 800, 850, 900, 950, 1000, 1050 and 1100 °C, 2 h for each treatment. After each sintering experiment the weight and dimensions of the pellets were measured at room temperature to determine the sintered density. Another set of samples (tablets and toroids) were sintered in air, at

1050 °C for 5 h, to explore the effect of copper ions on the physical properties of MgZn ferrite.

All samples sintered at 1050 °C were investigated by means of X-ray, using $FeK\alpha$ radiation to evidence spinel structure. The microstructure was examined by scanning electron microscopy (SEM) on the fracture surfaces of the sintered ferrites. The grain size was determined from micrographs of surface fracture. The d.c. resistivity ρ at room temperature was measured by the bridge method using silver paste contacts. The specific saturation magnetization σ_s was measured at room temperature by a vibrating sample magnetometer in a field of 5 kOe. The initial magnetic permeability μ_i was measured at a frequency of 1 kHz by the bridge method in a field of 5 mOe. From the temperature variation of the initial magnetic permeability, the Curie temperatures T_c were obtained.

3. Results and discussion

3.1. Densification

The influence of the Cu^{2+} ion concentration on the densification of the MgZn ferrite at various sintering temperatures between 800 and 1100 °C is shown in Fig. 1. By incorporating copper into MgZn ferrite high densities were obtained at relatively low firing temperatures. The highest density of about 4.59 g/cm³ was obtained for $x = 0.3$ mol CuO by sintering at 1050 °C. The density of MgZn ferrite without copper is much smaller and requires higher temperatures for densification. Although the detailed atomic mechanism through which CuO improves densification of MgZn ferrites at low temperatures is not very clear at this time, a possible explanation may be the formation of a solid solution. It was supposed that all copper ions enter into the spinel lattice during heating and activate the lattice diffusion. This assumption was

supported by the lattice parameters measurement. The results of X-ray analysis are given in Table 1. The increase in the lattice parameters with increasing copper content from 8.4060 Å for MgZn ferrite without copper to 8.4120 Å for $x = 0.4$ mol CuO is a prove for solubility of Cu ions in the spinel lattice which determine a change of the Mg ion distribution on A-sites (copper ions prefer the B-sites [5]). Copper radius (0.96 Å) is larger than that of magnesium radius (0.78 Å). The increase of the lattice volume usually increases the diffusion path leading to an increase of the rate of cation interdiffusion in the solid solution in agreement with the lattice diffusion mechanism proposed by Gupta and Coble [6]. Of course, the grain boundary diffusion may play an important role in the grain growth during sintering because the activation energy for lattice diffusion is higher than for grain-boundary diffusion [7]. However, although not conclusive, the sintering of MgZnCu ferrite is strongly suggested to be governed by the two diffusion mechanisms and which of the mechanisms is important may depend on the microstructure evolution.

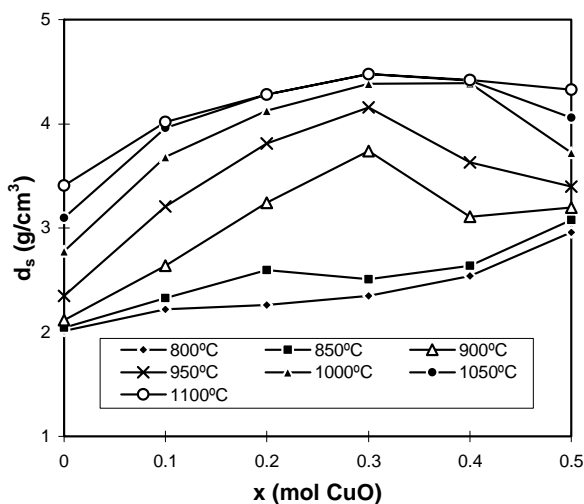


Fig. 1. Effect of Cu-O content on bulk density.

In the case when the CuO would segregate to the grain boundaries, this would retard particle growth further by inhibiting grain-boundary mobility. It is known that the grain growth in porous samples at low temperatures is controlled by grain-boundary mobility according to Greskovich-Lay mechanism of grain growth in porous materials [7]. But, experimental results evidenced an increase in the grain size by incorporating copper (Fig. 2), as a result of interparticle mass transport by diffusion [9].

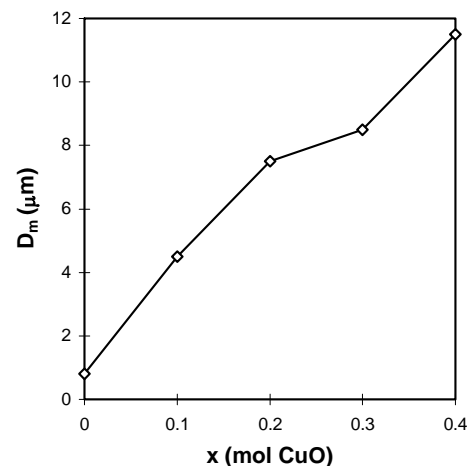


Fig. 2. Effect of CuO content on grain size.

3.2. Effects of Cu²⁺ ions on the magnetic and electrical properties

Fig. 3 shows the variation of the d.c. resistivity ρ versus the Cu content (x) for samples sintered at 1050 °C, for 5 h. This curve provides a clear example of the break in resistivity which occurs beyond a copper to magnesium ratio of 3 to 2. For $x = 0.4$, the resistivity is lower by three orders of magnitude than for $x = 0$, suggesting that the copper ions do increase the conductivity. The noted break in resistivity can be explained by a structural change as copper progressively replaced Mg [10] or by a sudden change in the ordering of copper ions between octahedral and tetrahedral sites beyond a critical copper concentration.

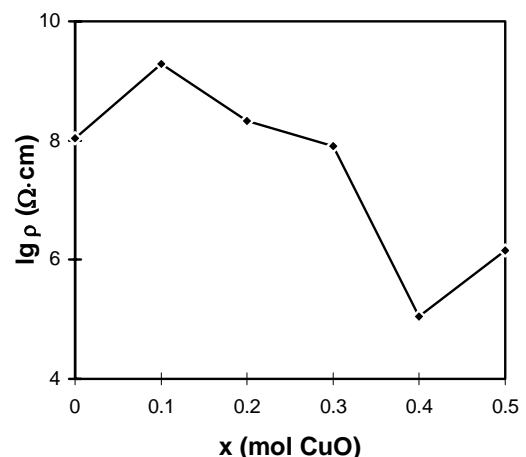


Fig. 3. Effect of CuO content on resistivity.

Table 1. X-ray analysis for samples sintered at 1050 °C for 5 h.

x (mol CuO)	a (Å)	Standard deviation	Identified crystalline phases
0.0	8.4060	0.0006	spinel phase
0.1	8.4075	0.0005	spinel phase
0.2	8.4080	0.0017	spinel phase, trace of non-identified second phase
0.3	8.4080	0.0012	spinel phase, trace of non-identified second phase
0.4	8.4120	0.0011	spinel phase

Another explanation for the increase in the conductivity with increasing content of Cu^{2+} ions may be attributed to the fact that in the case of MgCuZn ferrite on B-sites there are Fe^{3+} and Cu^{2+} ions which can change between the +2/+3 and the +1/+2 states, respectively, thus providing a greater number of hoppings on the B-sites. Also, we think that an important factor, which cannot be neglected, is the microstructure, taking into account the change in the lattice parameter for $x > 0.3$ (Table 1).

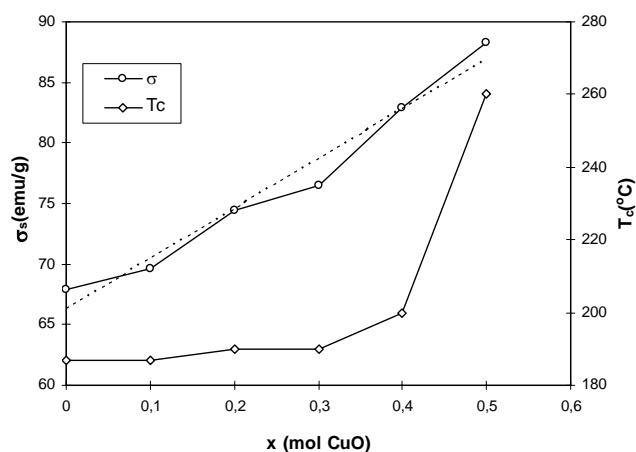


Fig. 4. Effect of Cu-O content on saturation specific magnetization and Curie temperature.

Fig. 4 shows the influence of the Cu^{2+} ion concentration on the specific saturation magnetization and Curie temperature. One can remark that the specific magnetization increases nearly linear with increasing copper concentration; the σ_s values can be expressed as

$$\sigma_s = 45.75 x + 64.60 \quad (\text{emu/g}).$$

It is known that the Mg ferrite is a spinel with an inversion degrees of about 0.8 [2], with the following cation distribution:



where brackets denote B-sites. In the MgZn ferrite, the stable Zn^{2+} ions occupy the A-sites only. By substituting of

Mg^{2+} ions with Cu^{2+} (which has a magnetic moment of $1 \mu_B$) on the octahedral sites (B-sites), an increase of the magnetization of B sublattice takes place leading to the increase of the saturation magnetization of the ferrite.

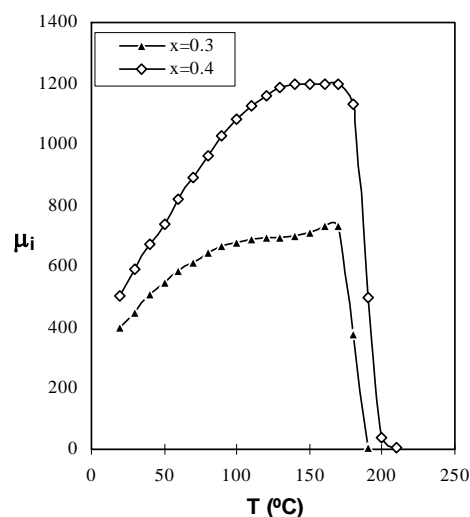
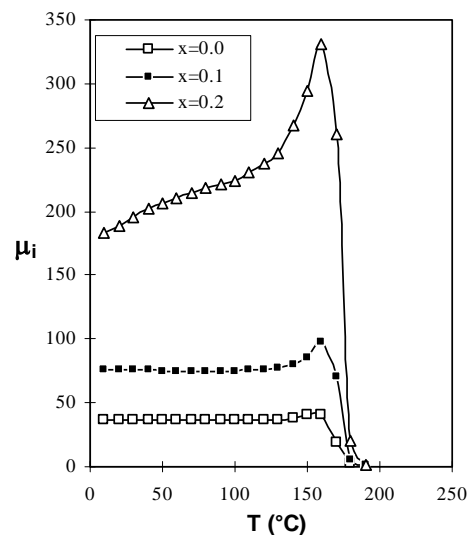


Fig. 5. Temperature dependence of initial permeability for samples sintered at 1050 °C.

Also, the increase of T_c for $x > 0.3$ is probably due to strengthening of the A - B interaction as a result of the change of the inversion degrees. Similar observations have also been reported by Singh et al [8] during investigation of the system $\text{Cd}_{1-x}\text{Cu}_x\text{FeCrO}_4$.

The influence of the copper ions on the permeability and its thermal dependence was studied (Fig. 5). One can remark from Fig. 6 a good thermal stability of initial permeability for $x = 0$ and $x = 0.1$ over a large temperature range. For larger copper content μ_i increases, but the plateau in the $\mu_i - T$ curves narrows. The shape of $\mu_i - T$ curves strongly depends on the preparation conditions since these ferrites are in polycrystalline form. Further investigations will be necessary in order to clarify the

factors affecting the permeability and its temperature dependence.

4. Conclusions

These preliminary investigations indicate the followings:

a) The incorporation of copper oxide into MgZn ferrite activates the lattice diffusion and make possible to reduce the sintering temperature.

b) The properties of these compounds are controlled by the copper content. The optimum content of CuO was appreciated to be $x = 0.3$, which is sufficient to promote sintering at low temperature (1050 °C) and to yield a good density (4.5 g/cm³).

c) The d.c. resistivity of this series exhibits a marked decrease for $x > 0.3$, from $10^8 \Omega \cdot \text{cm}$ to $10^5 \Omega \cdot \text{cm}$.

d) The development of low sintering temperature ceramics will reduce energy consumption and environmental pollution and enables the ceramics to be co-fired with less expensive metals in multilayer devices.

References

- [1] D. M. Liu, *J. Mat. Sci.* **29**, 1507 (1994).
- [2] J. Smit, H. P. J. Wijn, *Les Ferrites*, Dunod, Paris, 1961.
- [3] N. Rezlescu, E. Rezlescu, F. Tudorache, P. D. Popa, *J. Optoelectron. Adv. Mater.* **6**(2), 695 (2004).
- [4] N. Rezlescu, E. Rezlescu, P. D. Popa, M. L. Craus, L. Rezlescu, *J. Mag. Mag. Mat.* **182**, 199 (1998).
- [5] A. B. Naik, S. A. Patil, J. J. Powar, *J. Mater. Sci. Lett.* **7**, 1034 (1988).
- [6] T. K. Gupta, R. L. Coble, *J. Am. Ceram. Soc.* **51**, 521 (1968).
- [7] J. E. Burke, *J. Am. Ceram. Soc.* **40**, 80 (1957).
- [8] C. Greskovich, K. W. Lay, *J. Am. Ceram. Soc.* **55**, 142 (1972).
- [9] F. F. Lange, B. J. Kellet, *J. Am. Cer. Soc.* **72**, 735 (1989).
- [10] G. Singh, V. S. Darshane, *J. Mat. Sci.* **29**, 1540 (1994).

*Corresponding author: hellen@phys-iasi.ro