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Beneficial effect of small MgO content on some physical properties of a CuZn ferrite

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Ferrite samples having the general formula $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ were prepared using standard ceramic method. The structure characterization was made using X-ray diffraction and scanning electron microscopy. The effect of Mg^{2+} ion concentration, $0 \le x \le 0.5$, on the mechanical and magneto-electric properties of the ferrites is investigated. It is found that the mechanical, magnetic and electrical properties depend on the Mg concentration. From the sintering experiments carried out between 800 and 1100 ^{0}C it was established that a small Mg concentration, of 0.2, is sufficient to promote sintering at low temperature (1050 ^{0}C) and to yield a dense material (4.5 g/cm^3). High electrical resistivities were obtained for x = 0.2 – 0.5. Mechanical properties are improved.

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1. Introduction

Ferrites are very important in applications as inductor cores due to their high resistivities, high Curie temperatures and chemical stability. Since the material parameters of the ferrites are found to be sensitive to the preparation method, sintering temperature and time, type and content of the substitutions or additions, microstructure and porosity, a lot of studies have been done on these problems [1-4]. Recent studies [5, 6] have demostrated the influence of the rare earth ion substitutions (Sm, Nd) on the magnetic and electrical properties of Cu-Zn ferrite. It was found that a small amount of rare earth substituent (x=0.02) can improve magnetization and permeability of CuZn ferrite.

In the present work we investigate the effects of Mg^{2+} ions which progressively replace Cu^{2+} ions in the oxide compound $Cu_{0.5}Zn_{0.5}Fe_2O_4$. The work is focused on the intrinsic properties such as density, hardness, resistivity, saturation magnetization, Curie temperature, initial permeability, of the stoichiometric oxide compound $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$, $0.0 \le x \le 0.5$. One remarkable aspect of the magnesium oxide is its ability to control the grain growth in a polycrystalline material [7, 8]. Indeed, magnesium ion has a fixed valence, of +2, and thus it prevents the occurrence of divalent iron (an essential requirement to obtain high resistivity).

Details on the changes in morphology together with the role of MgO substituent on the densification during the sintering process at various temperatures of the $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ are presented. All results concluded that the role of MgO in CuZn ferrite is a grain growth inhibitor and and a microstructural stabilizer.

2. Experimental details

Polycrystalline ferrites with the chemical formula $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) were prepared by standard ceramic technique. The chemical constituents, MgO, CuO, ZnO and Fe_2O_3, of high purity, were mixed together in an agate ball mill for 2 hours. The resulting powders were dry-pressed into pellets and toroids in a stainless-steel die under a pressure of about 5×10^7 N/m^2 without any lubrificant. The pressed pellets (17 mm diameter, 5-6 mm thickness) and toroids (16 mm outside dameter, 8 mm inside diameter, 4 mm thickness) were sintered in air. For sintering experiments, a set of pellets were sintered successively between 800 and 1100 ^{o}C, 4 hours for each experiment. After each sintering experiment, the weight and dimensions of the pellets were measured at room temperature to determine bulk densities. Another set of samples (tablets and toroids) were sintered at 1050 ^{o}C for 5 hours, to explore the effect of Mg ions on the intrinsic properties of CuZn ferrite.

The phase composition of the samples sintered at 1050 ^{o}C was identified by X-ray diffraction (XRD) using FeKα radiation. The X-ray analysis confirmed the cubic structure of the samples in spite of the presence of the Jahn Teller cation (Cu^{2+}). Microstructural studies have been performed by scanning electron microscopy (SEM). The average grain size D_m was determined from SEM images, by the linear Mendelson intercept method [10].

The DC resistivity ρ at room temperature was measured on the pellets by the bridge method using silver-paste contacts. The specific saturation magnetization σ_s was measured at room temperature on the spheres prepared from toroids 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 on the toroids by an inductance bridge in a field of 5 mOe.

The Vickers microhardness H_V were measured by a Vickers diamond indent at 50 g load and a loading time of 15 seconds. The calculated hardness for each specimens was the mean value of five indentations with a standard deviation in the range of 3 to 6%.

3. Results and discussions

In this paper several relevant results are presented. Fig.1 shows the variation of the sintered density d of $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ ferrites with sintering temperature and magnesium content. One observes that the highest density, of about 4.5 g/cm^3 is obtained for small Mg content, x = 0.2, by sintering at 1050^{0}C. For larger Mg contents the density lowers.

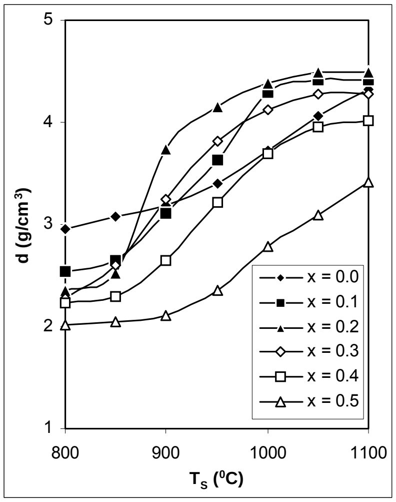

Fig. 1. The variation of the sintered density d of $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ *ferrites with sintering temperature* T_s *and magnesium content x.*

The detailed mechanism through which a small Mg content incorporated in a CuZn ferrite improves the densificationn is not very clear at this time. It was assumed that Mg ions dissolve in the spinel lattice during the sintering. The decrease of the lattice parameter from 8.4120 Å for x = 0.1 to 8.4060 Å for x = 0.5 in agreement with the smaller ionic radius of Mg^{2+} (0.86 Å) than that of Cu^{2+} (0.87 Å) [11] supports this assumption. A smaller lattice volume implies an increase of the rate of cation interdiffusion in the solid solution in agreement with the lattice diffusion mechanism proposed by Gupta and Coble [12]. Of course, the grain boundary diffusion may also play an important role, taking into account that the activation energy for grain-bounadry diffusion is smaller than that for lattice diffusion. But, at larger Mg concentrations it is possible that MgO forms $MgFe_2O_4$ as a second phase on the grain boundaries which could limit grain growth [13], resulting in smaller grains. In Fig. 2 are given the density *d* the average grain size, D_m, determined from SEM images as a function of Mg content for samples sintered at 1050 ^{o}C. The SEM images on the fracture surface of the samples revealed important differences between the structures of the samples.

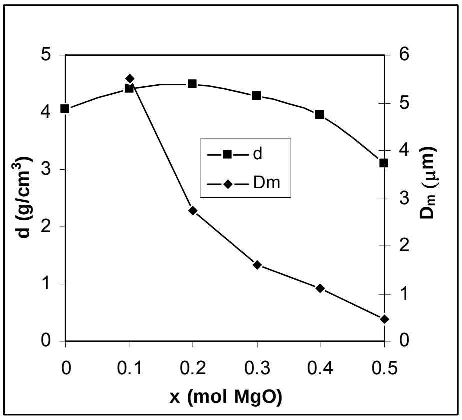

Fig. 2. Average grain size D_m *and density d as a function of Mg content for* $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ *ferrites sintered at 1050* ^{0}*C*

In Fig. 3 (a,b) are shown two microstructures: (a) of the sample with x = 0.2 which has the highest density (4.5 g/cm^3) and (b) of the sample with x = 0.5 having the lowest density (3.1 g/cm^3) by sintering at 1050 ^{o}C. It is evident that MgO leads to a finer, more uniform structure and higher porosity. Therefore, the microstructure modifications cannot be neglected in the densification process.

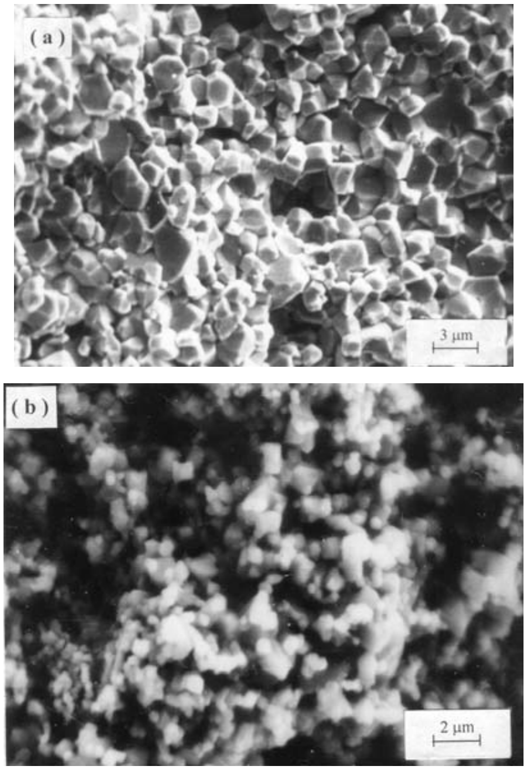

Fig. 3. SEM microraphs of (a) $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ *and (b)* $Mg_{0.5}Zn_{0.5}Fe_2O_4$ *ferrites sintered at 1050* ^{0}*C.*

During sintering experiments, a strong volume shrinkage of specimens was noticed (Fig. 4), which can lead to the development of significant stresses that can affect the ferrite quality by the microcrack formation. The highest shrinkage (48%) was obtained for x = 0.3, by sintering at 1050 ^{o}C. From obtained results it was established an empirical relation between sintered density and volume shrinkage to evaluate the density at an intermediary sintering temperature,

$$d = \frac{d_{1100}(1-\frac{\Delta V}{V_0})_{1100}}{(1-\frac{\Delta V}{V_0})_{T_S}},$$

where d is the sintered density at a certain sintering temperature T_s and $\Delta V/V_0$ is the relative shrinkage.

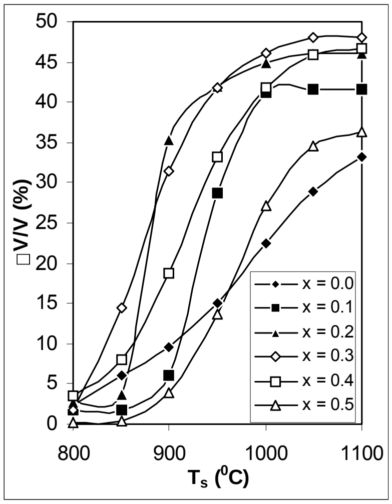

Fig. 4. Relative shrinkage versus sintering temperature and Mg content $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ ferrites.

Fig. 5 shows the variation of the d.c. resistivity ρ and microhardness H_V versus MgO content for samples sintered at 1050 ^{o}C. For x > 0.1 the d.c. resistivity increases with increasing Mg content. The resistivity for x = 0.4 is higher by four orders of magnitude than for x = 0.1, indicating that the Mg ions decrease the electrical conductivity. It is known [14] that the copper and magnesium ions prefer to occupy octahedral sublattice (B-sites) in the spinel lattice of MgCuZn ferrite. Mg ions have fixed valence, of +2, whereas Fe and Cu ions have variable valence, +3/+2 for Fe ions and +1/+2 for Cu ions. In ferrites, the dominant conduction mechanism is the electron hopping between Fe^{2+} and Fe^{3+} ions on octahedral sites. The replacement of Cu ions by stable Mg ions is expected to decrease the Fe^{2+}/Fe^{3+} ratio on octahedral sites leading to an increase of the resistivity as can see in Fig. 5. Another explanation for the increase in resistivity can be attributed to the decrease in average grain size, accompanied by an increase of the grain boundary surface which normally accounts for high electrical resistance of a polycrystalline material [15, 16].

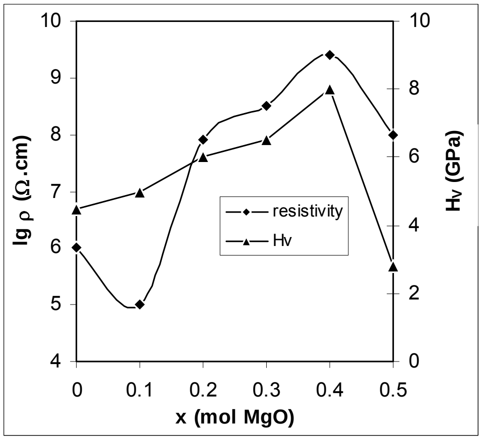

Fig. 5. Variation of the resistivity ρ and microhardness H_V with MgO content for $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ ferrites sintered at 1050^0C.

In addition, it is known [17] that the oxidation advances faster in smaller grains due to larger surface to volume ratio. Therefore, in smaller grains re-conversion of Fe^{2+} formed during the sintering process, back to Fe^{3+} may take place and the conduction due to hopping of electrons decreases. The Vickers hardness varied with MgO content similar to the resistivity. One can remark an increase in H_V from 4.5 GPa to about 9 GPa when x increases up to x = 0.4. The low values of H_V for MgZn ferrite without copper (x = 0.5) can be ascribed to its high porosity.

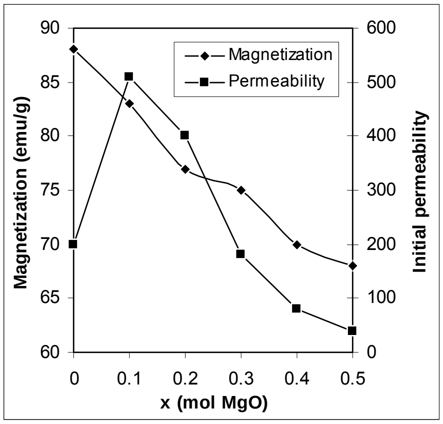

Fig. 6. The influence of Mg content on the specific magnetization and the initial permeability.

The influence of Mg ion content on the specific magnetization σ_s and initial permeability μ_i is depicted in Fig. 6. The magnetization decreases nearly linear with increasing Mg content. By substituting Cu^{2+} ions ((which has a magnetic moment of 1 μ_B) with nonmagnetic Mg^{2+} ions on the octahedral sites (B-sites) [14], a magnetic dilution of B sublattice is obtained leading to the decrease of the magnetization of ferrite. Taking into account that some Mg^{2+} ions move to the tetrahedral sites (A sublattice) [14] the magnetization uniformly decreases at each step of substituent. It may also mentioned that the decrease of the grain size influence the decrease of the magnetization [18, 19].

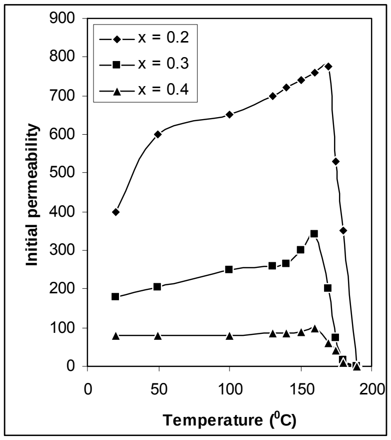

Fig. 7. Temperature dependence of the initial permeability of $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ ferrites (x = 0.2 – 0.4) sintered at 1050 ^{0}C.

Concerning initial permeability (Fig.6), a significant increase is obtained, from 200 for x = 0 to 400 – 500 for x = 0.1 – 0.2. This effect can be correlated with the Mg ion influence on the crystallite size (Fig.3). This correlation suggests that for D ≤ 5 μm the domain structure is absent and the low initial permeability must be predominantly rotational in origin. For D > 5 μm, the initial permeability is dominated by domain wall movement and increases with increasing crystallite size according to Globus model [20]. Of course, one can not neglecte the other factors as grain boundary, internal stress, secondary phases, distribution of pores, chemical inhomogeneity which can affect both initial permeability value and its thermal stability.

In Fig. 7 is plotted the temperature dependence of the initial permeability for some samples. With increasing Mg^{2+} content, the μ_i – T curve becomes flatter.

4. Conclusions

Important conclusions can be drawn.

The magnesium substitution for copper in $Mg_{-x}Cu_{0.5-x}Zn_{0.5}Fe_2O_4$ ferrite improves the densification when magnesium concentration does not exceed x=0.2.

Up to x=0.4 magnesia improves the mechanical properties of the ferrites.

The d.c. resistivity exhibits a marked increase for x ≥ 0.2.

The magnetic and electrical properties presented indicate that the controlled substitution of Mg for Cu in $Cu_{0.5}Zn_{0.5}Fe_2O_4$ ferrite can be an important way to obtain a MgCuZn ferrite with greatly improved properties in comparison with the terminal members of series $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$: $Cu_{0.5}Zn_{0.5}Fe_2O_4$ or $Mg_{0.5}Zn_{0.5}Fe_2O_4$.

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