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Influence of colloidal environment on the properties of Mg-Cu-Zn nanoferrites prepared by precursor method of self-combustion

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Mg-Cu-Zn nanoferrites prepared by precursor method of self-combustion are magnetic materials used at high frequency due to their high electrical resistance, thermal stability, low sintering temperature and reduced production cost. In the present paper two compositions, $Mg_{0.3}Cu_{0.2}Zn_{0.5}Fe_2O_4$ (A) and $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ (B), were prepared by precursor method of self-combustion in four colloidal environments with the ratio polyvinyl alcohol /metal (a/m) of 0.5, 1, 2, and 3. The a/m ratio determines the combustion temperature and rate, as well as its oxidizing or reducing character; the structure and composition of nanoparticles resulted from the combustion process are also affected by a/m ratio. The variation of the volume shrinkage and magnetic properties were investigated as a function of the a/m ratio and thermal treatment duration at 1000 ^oC. It was noticed that for higher concentrations of colloidal environment, the volume shrinkage increases during the sintering, the saturation magnetization decreases, magnetic permeability decreases, and the slope of the curve of permeability versus temperature is controllable (positive, negative or null) according to the duration of the heat treatment. These results are of great importance for electronic applications.

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1. Introduction

Mg-Cu-Zn ferrites prepared by precursor method of self-combustion [1,2] are magnetic materials used in high frequency due to their high electrical resistance, high Curie point, thermal stability, low sintering temperature and reduced production cost. This work presents the study of the influence of certain parameters of the preparation process on the structural and magnetic properties of some nanostructured Mg-Cu-Zn ferrites. The $Mg_{0.3}Cu_{0.2}Zn_{0.5}Fe_2O_4$ (A) and $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ (B) ferrites, prepared at several values of the ratio between the quantity of polyvinyl alcohol and metallic ions (a/m) and subjected to heat treatments at the same temperature (1000^{o}C) for several time intervals were studied.

The polyvinyl alcohol introduced in the precipitation solution plays a double role in the ferrite formation. The first role is to form a colloidal environment in which the homogeneous precipitation of the hydroxides with nanometer structure occurs [3-6]. The second role is to form, together with ammonium nitrate resulted from the precipitation reaction, a self combustion (pyrotechnical) mixture [7]. Since the amount of ammonium nitrate directly depends on the quantity of metallic nitrates entered in reaction, one can consider as the parameter of the A.P.V. concentration the ration between the polymer quantity and the metals quantity, or else, between the volume of the A.P.V. solution and the volume of nitrates solution. The experiments carried out on ferrite compositions with various a/m ratios led to the following conclusions [1,8-10]:

- The a/m ratio determines the combustion rate and temperature. At usual values of the a/m ratio, ranging between 0.3 and 2, the combustion rate varies between 2 and 0.5 cm/s respectively, and the temperature in the reaction front varies between 1200^{o}C and 800^{o}C respectively [1].

The same ratio determines the oxidizing or reducing character of the combustion. The excess of ammonium nitrate produces an amount of oxygen in the combustion gases, oxygen that can confer to some metallic ions a higher valence (Sn, Mn, etc). The excess of A.P.V. produces in the combustion gases carbon monoxide (CO) and free carbon, which can confer to certain ions a lower valence (Cu, Fe etc) or can even reduce some metallic oxides (PbO).

- The combustion temperature and rate, respectively the a/m ratio, determines the composition and structure of the particles resulted from combustion. At a reduced reaction temperature, below 900^{o}C, the ferrite generation reactions are incomplete. When the ratio a/m is small and the combustion temperature is high, beyond 1000^{o}C, the reaction between the metallic oxides is advanced [11].

When in the ferrite composition enters easily fusible metallic oxides (PbO, CuO, etc.), these are melted and produce an agglometation of nanoparticles at a higher temperature.

2. Experimental

Ferrite samples having the chemical compositions: $Mg_{0.3}Cu_{0.2}Zn_{0.5}Fe_2O_4$ (A) and $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ (B), were prepared by precursor method of self-combustion method [1,2] followed by heat treatments, in four colloidal environments with the ratio polyvinyl alcohol /metal (a/m) of 0.5, 1, 2, and 3.

We used solutions of metal nitrates as starting materials (Fe(NO3)3·9H2O, Mg(NO3)2, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2$) . Polyvinyl alcohol 10% was added to make a colloidal solution. Ammonia solution (10% concentration) was added until the pH value was about 8 [12].

The resulting product is an intimate mixture of metal hydroxides, polyvinyl alcohol, ammonia nitrate and water. After a complete air-drying (in the dry kiln bellow 100°C) the material was enflamed. The heat generated by a quick combustion reaction converts the dried gel in a loose powder with nano-granular structure.

The material obtained as the result of the combustion was treated for 30 minutes at temperatures of 450 ÷ 500°C, then ground. From the resulted powder, annular samples with the mass of about 2 g, as well as cyllindrical samples with the mass of 1 g were pressed. The samples were pressed dry or wet with a force of 3000 daN.

The obtained samples were weighed, measured and then subjected to heat treatment in air at 1000°C, for time intervals ranging between 30 and 180 minutes. After every heat treatment, measurements were carried out to determine the volume shrinkage ($\Delta m/m$), saturation magnetization (σ_s) and temperature variation of the magnetic permeability.

The microstructures and morphology of the samples were examined by a high-resolution scanning electron microscope TESLA BS340. The grain size was determined by linear intercept method [13] from micrographs SEM on the fracture surfaces.

Spinel structure of the ferrite compound was confirmed by X-ray powder diffraction (XRD) peaks presence using DRON-2 diffractometer and FeK_α radiation.

In order to determine the saturation magnetization of the cyllindrical samples, a vibrating probe magnetometer was used, and for the measurement of the magnetic permeability 50 turns were wound on the annular samples, the coil inductance being measured with an automated RLC bridge. The temperature variation of the magnetic permeability was determined by simultaneous measurement of the temperature and coil inductance in an enclosure with adjustable temperature. For the analyzed compositions, the measurements were carried out within the temperature range 20°C - 200°C, in 20°C steps.

3. Results and discussion

X-ray diffraction (XRD), scanning electron microscopy (SEM) and density measurements were used to analyze the structure of samples.

Fig. 1 shows the XRD curves for A and B samples treated for 60 minutes at 1000°C. Both samples contain a single phase of the spinel structure. The lattice constant was evaluated to be 8.4080 ± 0.0012 Å.

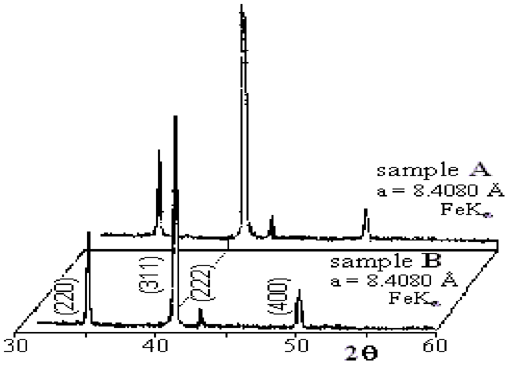
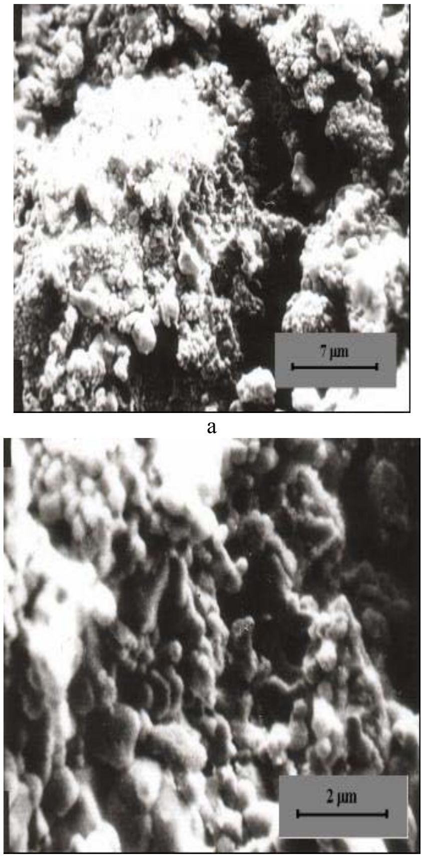


Fig. 1 X-ray diffractograms for $Mg_{0.3}Cu_{0.2}Zn_{0.5}Fe_2O_4$ (A) and $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ (B) samples treated for 60 minutes at 1000°C

Fig. 2 (a) and (b) presents the SEM micrographs for the **A** sample, after a heat treatment of 90 minutes for different magnifications. One can notice a porous structure with big agglomerates of particles and with big pores between those. The particles of ferrite sample have sub-micron sizes and tend to a spherical shape.



a

b

Fig. 2. SEM micrograph for two different magnifications for the $Mg_{0.3}Cu_{0.2}Zn_{0.5}Fe_2O_4$ (A) sample, after a heat treatment of 90 minutes at 1000 °C

The shrinkage was studied during the thermal treatment for the samples A and B prepared with the a/m ratio of 0.5, 1, 2 şi 3. The evolution of the shrinkage Δv/v with the heat treatment duration is presented in Fig. 3. With the increase of the a/m ratio, after combustion, powders are obtained with finer microstructure and smaller apparent density. As the result of the heat treatment, the samples with large a/m ratio suffer a larger shrinkage and reach a bigger density. The shrinkage is faster during the first 30 minutes of treatment and then the

The shrinkage values are higher for the B samples than for the A samples with less copper, and they increase with the increasing a/m ratio; after a treatment lasting more than 60 minutes, all the samples become hard, resistant and are coloured in black. The smaller the shrinkage of the samples, the more porous they result.

At the samples with a small a/m ratio, the ferrite formation occurs mainly during the combustion, such that only an increase of crystals size takes place. After a long treatment, all the samples become hard, resistant and black.

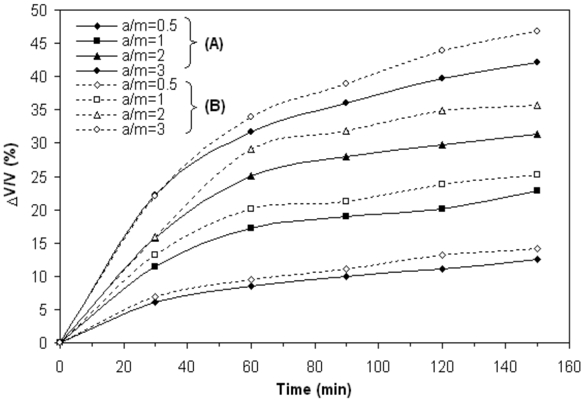


Fig.3 Variation of the volume shrinkage with the heat treatment duration for the studied samples $Mg_{0.3}Cu_{0.2}Zn_{0.5}Fe_2O_4$ *(A) and* $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ *(B) prepared with different a/m ratios.*

Prior to the heat treatments, the both samples are magnetic. The saturation magnetization of the samples behaves during the treatments like in Fig. 4. One can notice that, generally, the saturation magnetization increases with the treatment duration due to the reduction of the non-magnetic fraction. In the case of the samples prepared with the ratio a/m = 3, the magnetization decreases during the first 30 minutes of treatment. The phenomenon can be explained by the dissapearance of some magnetic phases (γFe_2O_3, Fe_3O_4) generated during combustion. The highest value of the magnetization belongs to the samples prepared with the ratio a/m = 0.5, in which the ferrite is practically formed during the combustion.

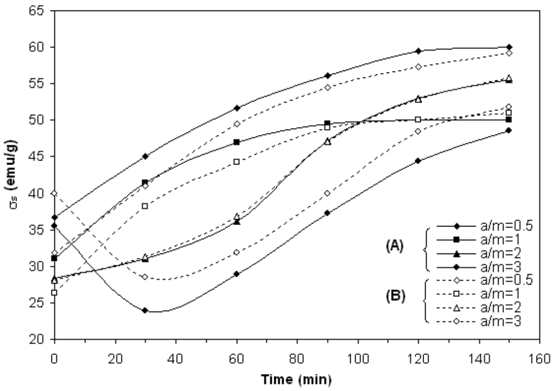


Fig.4: Variation of the saturation magnetization with the duration of the heat treatment for the studied samples $Mg_{0.3}Cu_{0.2}Zn_{0.5}Fe_2O_4$ *(A) and* $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ *(B) prepared with various a/m.*

Fig. 5 presents the characteristics magnetic permeability vs. temperature for a ferrite A prepared with the ratio a/m = 1 with four heat treatments between 30 min and 180 min. All the characteristics present an increase of permeability with temperature up to a maximum around 115°C and a fast decrease at higher temperature, with a Curie point of about 132°C. The reduction of permeability beyond the Curie point is complete, which indicates the absence of other magnetic phases. Figure 5 also presents the permeability vs. temperature characteristic for a ferrite prepared with the ratio a/m = 3 treated for 180 minutes. One can notice that, as compared to the samples analyzed above, the permeability is twice as large, the Curie point is 5°C higher, and the permeability diminution occurs within a narrower temperature interval. The characteristic is typical for a single phase well formed ferrite.

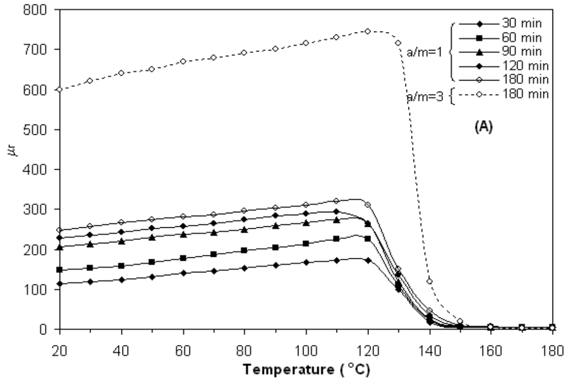


Fig.5 Variation of magnetic permeability with temperature for the sample $Mg_{0.3}Cu_{0.2}Zn_{0.5}Fe_2O_4$ *(A) prepared with the ratio a/m=1.3 and with different duration of the heat treatment.*

The magnetic permeability of the B samples thermally treated in air at a temperature of 1000°C increases with the treatment duration, according to Fig. 6.

This figure presents the characteristics of magnetic permeability vs. temperature for a B ferrite prepared with the ratio a/m = 0.5 subjected to four thermal treatments between 60 minutes and 150 minutes. One can notice that the sample treated for 60 minutes shows a diminution of permeability with temperature, the one treated for 90 minutes keeps its permeability almost constant, and for those with a longer treatment the permeability increases with temperature. The Curie point is about 145°C, higher than at the samples with copper substitution. The permeability values are relatively small.

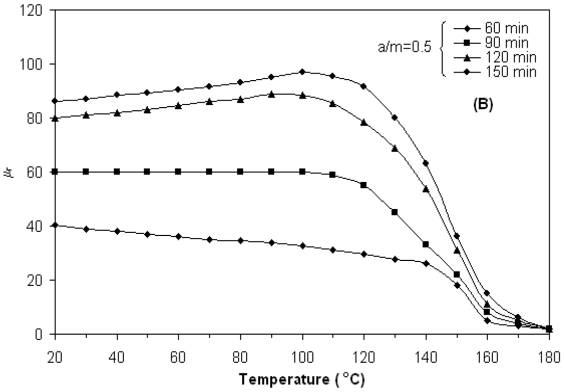


Fig.6. Magnetic permeability variation with temperature for the sample $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ (B) prepared with the ratio a/m=0.5 and different durations of the heat treatment

At the samples prepared with the ratio a/m = 1 and four heat treatments between 30 minutes and 120 minutes, the values of permeability are some times higher, as one can notice in Fig. 7. The sample treated for 30 minutes shows a diminution of permeability with temperature, the one treated for 60 minutes keeps its permeability constant, while for those treated longer the permeability increases with temperature. The permeability values are much higher than for the previous sample. The Curie point is about 148°C.

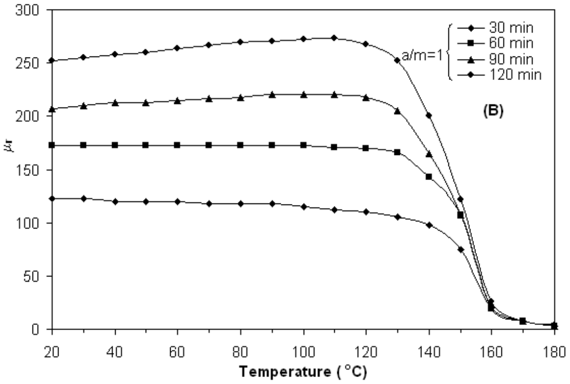


Fig. 7. Temperature variation of magnetic permeability for the sample $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ (B) prepared with the ratio l a/m = 1 and different heat treatment durations.

At the samples prepared with the ratio a/m = 2 the values obtained for the magnetic permeability are even higher. Figure 8 presents the characteristics permeability vs. temperature for four thermal treatments lasting between 30 and 120 minutes. Besides the high permeability values, an increasing characteristic of permeability with temperature is noticed for all the thermal treatments carried out.

When the treatment duration increases, an increase of permeability and of maximum permeability temperature is noticed, as well as the diminution of the time interval within which the permeability decreases. The Curie point is about 141°C.

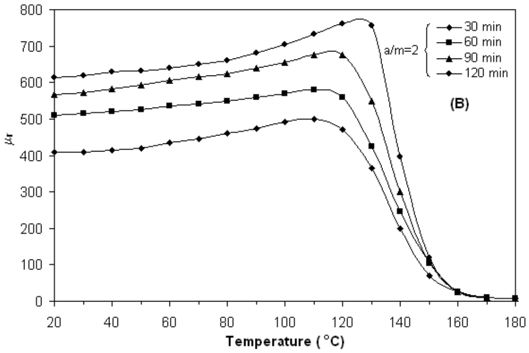


Fig. 8. Magnetic permeability variation with temperature for the sample $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ (B) prepared with the ratio a/m = 2 and with different heat treatment durations.

4. Conclusions

- The colloidal environment where the precipitation of ferrite precursors occurs acording to self-combustion method, highly influences both the structural and magnetic properties of the ferrites.
- Besides the initial components and the conditions of the heat treatment, the ratio a/m offers an additional parameter with respect to the production of a certain final ferrite compozition.
- The ferrites prepared with a small amount of polyvinyl alcohol (small ratio a/m) are mainly formed during the combustion, have a small shrinkage and reduced permeability. Those prepared with a big quantity of polyvinyl alcohol a are mainly formed during the heat treatment, are compact and have a high permeability.
- With the increase of the heat treatment duration, an increase of the ferrite density, magnetization and permeability occurs, besides the increase of the crystals size.
- The temperature variation of the magnetic permeability (heat constant) is relatively constant up to 100°C and it can be positive, negative or null, depending on the parameters of the preparation process.
- Starting from a certain ionic composition, ferrites can be obtained with a large range of properties, by modifying the ratio a/m and the duration of the heat

treatment, a very important quality from a practical standpoint.

● As compared with the Mg-Cu-Zn ferrites prepared through the classical method, the studied ferrites have a small density, close magnetization and a magnetic permeability realizable within large limits, and with various heat constants [12,14-16].

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