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RESEARCH ARTICLE

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SYNTHESIS AND CHARACTERIZATION OF $Cu_x Zn_{1-x} Fe_2O_4$ SOFT FERRITES USING MECHANOCHEMICAL ACTIVATION

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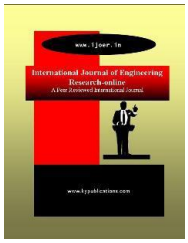

ABSTRACT

The synthesis of Cu-Zn spinel ferrites studied in three different compositions in the Cu_xZn_{1-x} Fe_2O_4 system, with x = 0.25; 0.55 and 0.65, from the $CuFe_2O_4$ and $ZnFe_2O_4$ ferrites. With these spinels, previously synthesized, intimate mixtures were prepared which were compacted in the form of cubical structures and subjected to heat treatment at 1000°C under N_2 atmosphere, during different time intervals. The materials thus obtained were characterized by x-ray diffraction (XRD), differential and gravimetric thermal analysis (DTA/TGA), vibrating sample magnetometer (VSM) and scanning electron microscopy (SEM). In addition, the densities of the sintered spinels were measured for the three compositions studied. The formation of the desired phases was observed for each case, with densities between 80 and 85% of the theoretical value and magnetic properties that exceed 90% of the values reported in the literature. These values are compared with those corresponding to these ferrites prepared by other methods. The effect of processing variables on the morphology and properties of synthesized materials is discussed.

Keywords: Cu-Zn spinel ferrites, magnetic properties, Characterization,

Introduction

Ferrites are widely applied ceramic materials such as memory devices, magnetic particles in recording tapes and transformer cores due to their combination of low electrical conductivity and high magnetization, which reduce energy losses from stray currents [1]. Soft ferrites have a high magnetization and low coercive field. Therefore, these ferrites are used in devices that require rapid magnetization and demagnetization. In addition, spinel ferrites have a wide range of magnetic properties in relation to the cationic distribution in the crystalline structure and the conditions employed in the preparative method [1, 2].

Cu-Zn ferrites are widely used in electronics for the manufacture of transformers, filters, recording heads, etc., due to their excellent properties such as high initial permeability, high saturation magnetization,

high resistivity and low losses. The magnetic properties of Cu-Zn ferrites are affected not only by the compositions, additives and sintering conditions, but also by the starting materials [3, 4].

At present, the preparation of these materials is carried out through a ceramic processing that is generally based on a solid state reaction, starting with oxides. This method involves the fine grinding of the oxides, followed by forming and final sintering at high temperature (T> 1300ºC) [5]. Other alternative methods are being developed such as: mechanochemical activation, sol-gel, salt decomposition and other wet methods [6-8].

Mechanochemical activation has been used in recent years as a material synthesis tool. This method is especially applied in cases where the reagents do not show sufficient reactivity, or when the formation of metastable phases is required [9]. Mechanochemical activation consists of the mechanical treatment of solids in high-energy mills. This processing provides mechanical energy to the solid state reactant systems, which can accumulate in plastic deformation of the crystals, production of crystalline defects and surface generation. Consequently, regions of special chemical reactivity are produced that facilitate the development of solid phase processes. Depending on the system and the activation conditions, solid phase reaction may occur during mechanical treatment at room temperature [10] and / or structural changes may be generated, reducing the necessary temperature of certain reactions [11].

In this work, soft ferrites of variable composition $Cu_xZn_{1-x}Fe_2O_4$ system, with x = 0.25 are prepared; 0.55 and 0.65 using mechanochemical activation for the preparation of Cu and Zn ferrites separately and subsequently mixed of these phases in appropriate proportions. The physicochemical and magnetic properties of the materials obtained are analysed.

2 MATERIALS AND METHODS

2.1 Obtaining Zn Fe_2O_4 and Cu Fe_2O_4 ferrites: $ZnFe_2O_4$: The preparation of the Zn ferrite was carried out by mechanochemical activation and subsequent heat treatment in air at 700 ° C of a mixture of Zn: Fe_2O_3, in 3: 2 molar ratio. This method is described in detail in previous work [12].

$CuFe_2O_4$: For the preparation of Cu ferrite, Fe_2O_3 (Mallinckrodt, 98%) and CuO (Aldrich, 99.9%) were used. With these reagents, a 1: 1 molar ratio mixture was prepared, and subjected to a one hour mechanical treatment.

According to the results obtained in the DTA / TGA analyzes of the activated CuO-Fe_2O_3 samples, the conditions of the heat treatment required to obtain the Cu ferrite were established. Thus, approximately 10 g of the activated CuO- Fe_2O_3 mixture was calcined, at 1200 ° C under N_2 atmosphere for 1h, using a heating rate of 10 ° C / min.

2.2 Mechanical Mixing of Ferrites: Three mixtures of $ZnFe_2O_4$ and Cu Fe_2O_4, designated B5, B6 and B8, of different composition were prepared according to what is indicated in Table 1.

Table 1: Name and composition of the three samples studied.

Mixture Code	Molecular Formula of obtained Ferrite	Molar composition of the starting mixture
B5	$Cu_{0.25}Zn_{0.75}Fe_2O_4$	25% $CuFe_2O_4$ + 70% $ZnFe_2O_4$
B6	$Cu_{0.55}Zn_{0.45}Fe_2O_4$	55% $CuFe_2O_4$ + 45% $ZnFe_2O_4$
B8	$Cu_{0.65}Zn_{0.35}Fe_2O_4$	65% $CuFe_2O_4$ + 35% $ZnFe_2O_4$

Each of these mixtures was ground in the planetary mill, using Si3N4 containers and balls in a mass ratio of grinding media to powder equal to 4; the rotation speed of the grinding vessels was 1000 rpm. The grinding was carried out dry for 2 minutes and then wet (by adding isopropyl alcohol) for another 10 minutes. The mixtures were then dried in an oven at 80 ° C.

The grinding conditions used were chosen with the intention of producing intimate mixing of the components, but without causing structural damage. With the first 2 minutes of dry treatment it is intended to

homogenize the particle sizes of both ferrites, while with the wet treatment it is intended to achieve efficient mixing of the phases. Mixtures B5, B6 and B8 were characterized by XRD and VSM.

2.3 Heat Treatments: The powders of each of the mixtures were compacted by uniaxial pressing at 200 Kg / cm2 in 6 mm diameter and 1-2 mm high pads. These tablets were calcined at 1000 ° C under N2 atmosphere for times of 1 and 4 h. The materials obtained were analyzed by XRD, VSM and SEM.

2.4 Characterization Techniques: XRD analyzes were performed using a Philips PW1830 diffractometer with CoKa radiation. For thermal analysis, a Shimadzu device with a TA50-WSI analyzer was used, using a heating rate of 10ºC / min. The VSM analyzes were performed on a LakeShore 7300 magnetometer. The SEM observations were made in a Philips 505 device, on the fracture surfaces of the metallic pads with Au previously. Finally, the densities of the tablets were determined by immersion in water, using the Archimedes method.

3 RESULTS AND DISCUSSION

Figure 1 shows the DTA / TGA analyzes of the CuO-Fe_2O_3 mixture, performed up to 1000 ° C in an air atmosphere. A broad exothermic band between 200 ° C and 700 ° C is observed by DTA that corresponds to the increase in mass observed by TGA. Around 1050°C an endothermic peak can be seen in DTA as well as a decrease in mass in TGA. The exothermic band could be attributed to the partial oxidation of CuO to Cu_2O_3 while the endothermic peak would correspond to the decomposition of this oxide. The hypothesis of oxidation of Cu^{1+} to Cu^{2+} was confirmed after performing an X-ray diffractogram to a sample treated under similar conditions, but only up to 800 ° C, in which the presence of Cu_2O_3 and Fe_2O_3 was observed.

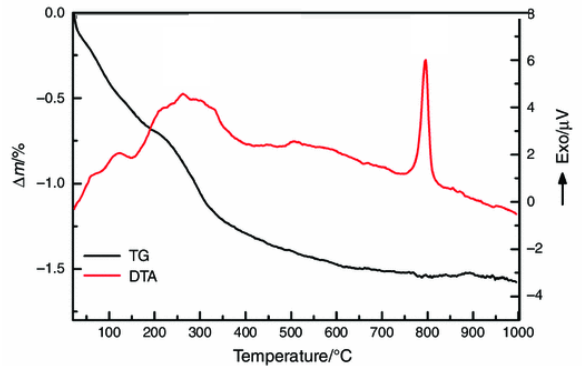

Figure 1: DTA / TGA curves in air of the CuO-Fe2O3 mixture activated 1h.

After performing DTA analysis of the same mixture under N_2 atmosphere, it was observed by XRD that the resulting sample was composed solely of Cu ferrite (Figure 2). It was concluded that the way to obtain this phase from the activated CuO- Fe_2O_3 mixture is by heat treatment at 1200 ° C under an N2 atmosphere, to avoid oxidation of CuO.

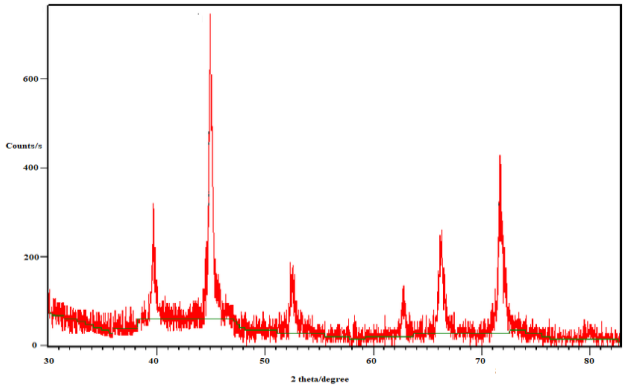

Figure 2: XRD diagram of synthesized Cu ferrite.

Figure 3 shows the diffractograms of samples B5, B6 and B8, prepared by mechanical mixing of Zn Fe_2O_4 and $CuFe_2O_4$. For the three compositions diffraction patterns are observed that reveal a good crystallinity of both ferrites. This indicates that the mechanical treatment during mixing did not produce significant changes on the structures of these ferrites.

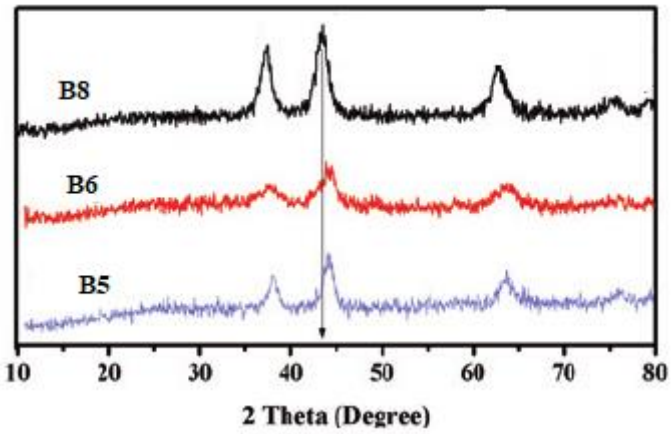

Figure 3: XRD diagrams of samples B5, B6 and B8 without calcining.

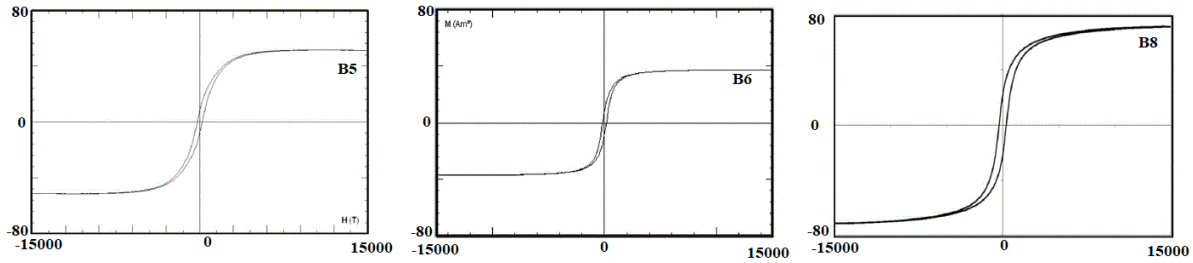

Figure 4: Hysteresis cycles of samples B5, B6 and B8.

In hysteresis cycles (fig. 4) the increase in saturation magnetization, Ms, is observed, depending on the content of Cu, as expected according to the magnetic properties of both ferrites.

Taking into account the mass percentages of Cu $Fe_2O_4$of each of the samples, the value of Ms per gram of Cu Fe_2O_4can be calculated. This gives between 78 and 79 emu / g for the three compositions, very close to the theoretical value reported at room temperature (78.5 emu / g), which confirms that the crystalline structure of this phase has not been altered by grinding.

Figure 5 shows the XRD diagrams for samples B5, B6 and B8 calcined at 1000°C for 1 and 4h. For one hour of treatment, the presence of a single phase is already observed for the three compositions, which reveals the formation of the corresponding mixed ferrite. That is to say, that the thermal treatment of the Zn $Fe_2O_4$and Cu Fe_2O_4 mixtures produces the chemical reaction generating the mixed ferrite corresponding to the composition of the reactive mixture.

These results are confirmed by the values of Ms extracted from the magnetometries (Table II). It is generally observed that calcination time does not produce an increase in Ms.'s values

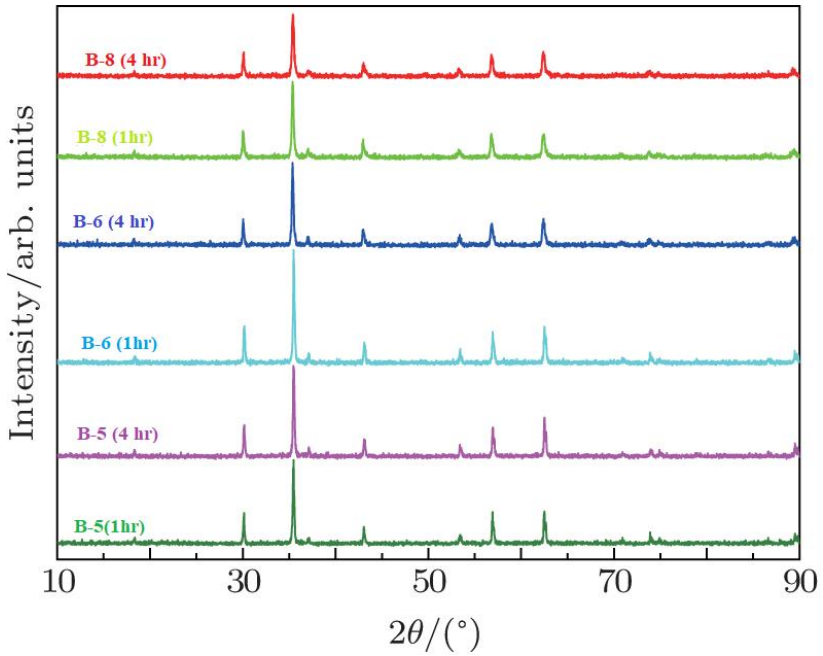

Figure 5: XRD diagrams of samples B5 (a), B6 (b) and B8 (c) calcined at 1000 ° C for 1 and 4h.

Table II: Saturation magnetization measured for samples calcined for different times.

Sample	***Ms* [emu/g]**	**% *Ms* theoretical**
B5 1000 1h	53.5	89.2
B5 1000 4h	53.3	88.8
B6 1000 1h	74.4	96.6
B61000 4h	73.7	95.7
B81000 1h	84.6	98.4
B81000 4h	83.1	96.6

Figure 6 shows the micrographs obtained by SEM of samples B5, B6 and B8 calcined at 1000°C for 4h. A homogeneous microstructure with an average grain size of 5 mm is observed. In addition, a greater degree of sintering can be noted as the content of Cu of the material increases. This could indicate a dependency between the sintering of these materials with the Cu / Zn ratio.

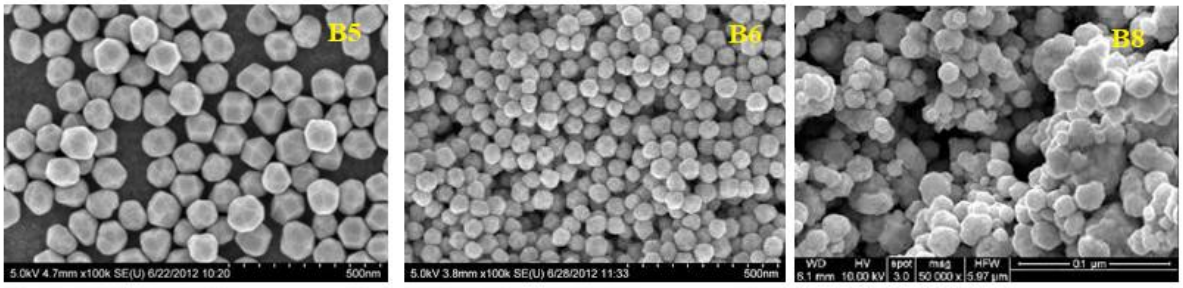

Figure 6: SEM photographs of samples B calcined at 1000 ° C for 4 hours

Density measurements for these tablets gave values between 80 and 85% with respect to theoretical densities.

The analysis by electron microscope of the profiles of the sintered pads revealed a constant Zn content in the entire volume of the material, indicating that there is no loss of this metal by evaporation. This is important because it would allow sintering at higher temperatures, which could result in higher densities.

4 CONCLUSIONS

The conditions of preparation of the Cu Fe_2O_4ferrite consisting of the mechanochemical activation of a CuO- Fe_2O_3 mixture and subsequent heat treatment at 1200 ° C in an inert atmosphere have been determined. A synthesis methodology for soft ferrites of the Cu_xZn_{1-x} Fe_2O_4 system has been established, with 0.1 <x <1, from the mechanical mixing of the pure Zn and Cu ferrites and their subsequent reaction at 1000 ° C under N_2 atmosphere.

The materials obtained by this method have good magnetic properties for soft ferrites. Sintering for 4h at 1000° C resulted in densities not very high; however, in this treatment no loss of Zn is observed, which would allow the sintering temperature to be raised by improving the density values and the magnetic properties of the materials obtained.

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