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# Nanoparticles of $Ni_{1-x}$ $Zn_x$ $Fe_2$ $O_4$ used as Microwave Absorbers in the X-band

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Ferrites nanoparticles of $Ni_{1-x}Zn_xFe_2O_4$ ferrites with x varying between 0 and 1, in steps of 0.2, were obtained by solution combustion synthesis (SCS) and dispersed in oil paint at the concentrations of 10, 20, 30 and 40% by ferrite weight of ferrite, with the aim of producing electromagnetic wave absorbing composites, in the X band (8-12 GHz). The ferrite powders obtained were characterized by X-ray diffraction (XRD), and to determine to mean crystallite size, crystallographic phases, as well as lattice parameters, was used the Rietveld method. The XRD results revealed the majority presence of the spinel cubic ferrite phase for all stoichiometries with crystallite size between 44 and 81 nm. The composites were characterized by the rectangular waveguide transmission line method to measure the absorption of the electromagnetic wave in the X band. The nanocomposites with 40% of $NiFe_2O_4$ and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ presented the highest electromagnetic wave absorption performance.

**Keywords:** *Ni-Zn ferrite nanoparticles, electromagnetic radiation absorbent materials (RAM), solution combustion synthesis (SCS).*

## 1. Introduction

Ferrites find applications in several areas of technological interest. These materials, when in nanometric form, have its properties enhanced owing to its large surface area. In these dimensions, the nanoferrites present high chemical reactivity, thermal stability, and different magnetic and electrical properties[1]. Furthermore, another advantage in the use of ferrite nanoparticles is the possibility of enhancing its properties by the addition of small amounts of transition metals[2-3].

The crystalline structure of the Ni-Zn mixed ferrite is partially inverted spinel type, in which the ion distribution is represented in equation 1, where the divalent Ni and Zn ions are distributed in the tetrahedral and octahedral sites[2-5].

$$[M^{2+}{}_{1-X}Fe^{3+}x](M^{2+}xFe^{3+}{}_{2-x})O_4 \qquad (1)$$

Nanometric ferrites can be employed in a considerable number of applications. As electromagnetic radiation absorbing materials (RAM), these materials have the ability to absorb or attenuate electromagnetic waves in a process that transforms incident energy into thermal energy through wave/matter interaction[6].

The use of RAM was increased after World War II, being adopted by the military sectors as a technological tool for defense and public safety. RAM are employed in the electromagnetic shielding of aircraft, ships and military vehicles, making them imperceptible to radars[7]. In Brazil, RAM are on the list of advanced materials for national defense and public safety elaborated through a study conducted by the Center for Management and Strategic Studies (CGEE) in conjunction with scientists linked to the Ministry of Science and Technology[8].

RAM are also used in the civil sector owing to its capacity to absorb undesirable radiation from electronic devices radio reception and transmission, interference control of TV signals, aircraft internal security systems, internal coating of microwaves ovens, electromagnetic shielding of pacemakers, among other applications[7,9].

For microwave absorbing, the material must have some requirements. Such good absorbance over a broad frequency range, lightweight, small thickness and, facile synthesis. Moreover, electromagnetic wave absorbers should have conductive and magnetic characteristics. Among conventional materials, metallics are very heavy, and can suffer corrosion, whereas, polymers are of low density, though, they are insulation and less stable, being necessary the addition of conductive particles and magnetic[10].

Among electromagnetic radiation absorbers materials, carbon allotropes such as graphene, carbon nanotubes, and fullerenes, are the most investigated materials. For instance, Shu et al. fabricated Multi-walled carbon nanotubes/zinc ferrite (MWCNTs/ZnFe2O4) hybrid composites by one-step solvothermal method. Their results showed minimum return loss $RL_{min}$ of −55.5 dB at 13.4 GHz and effective absorption bandwidth (EAB, $RL \leq -10$ dB) of 3.6 GHz with a thickness of only 1.5

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mm[11]. In another work[12], they synthesized the nitrogen-doped Co-C/MWCNTs nanocomposites obtained from bimetallic metal-organic frameworks (MOFs). The $RL_{min}$ achieved −50.0 dB and EAB, $RL \leq -10$ dB of 4.3 GHz for a thin thickness of 1.8 mm and low filler loading ratio of 25 wt%. However, the synthesis of these materials on a large scale is still a challenge for the industry.

In the literature, there are a lot of research of nanoparticles ferrites as absorbers of electromagnetic radiation obtained by different methods of synthesis and dispersed in different matrices for production of composites[13,14,15]. For instance, Nassim et al. evaluated the absorption capacity of polyaniline / $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (PANI / NiZn ferrite) composites obtained by sucrose method[16]. It was showed that different concentrations of ferrite by weight can absorb different fractions of the radiation. Mandal et. Al produced $NiFe_2O_4$ nano-hollow spheres by solvothermal process and found an optimal RL of −59.2 dB at 11.7 GHz[17]. Ali el al. fabricated $Mn_{0.1}Ni_{0.45}Zn_{0.45}Fe_2O_4$ (PANI/MnNiZn ferrite) nanocomposites by sol gel technique and the best result presented was at 11.3 GHz with $RL_{min}$ of −31.32 dB with a thickness of 3 mm[18].

This study aims to evaluated the absorbing of Ni-Zn ferrites dispersed in the oil paint in four ferrite weight concentrations. The SCS method was used to obtain nanoparticles of $Ni_{1-x}Zn_xFe_3O_4$, with x between 0 and 1, with step of 0.2. To produce the composite nanoparticles were dispersed in the paint matrix oil in the weight proportions of ferrite/paint 10, 20, 30 and 40%. The ferrites were characterized by X-ray diffraction and the magnetic composites were tested by transmission line method with a rectangular waveguide in the X-band (8 - 12 GHz).

## 2. Experimental Procedure

The powder of ferrite nanoparticles was obtained by solution combustion synthesis (SCS) technique[19-20].

The following reagents were used in the synthesis: $Ni(NO_3)_2.H_2O$ (CRQ - 98% of purity), $Zn(NO_3)_2.6H_2O$ (Aldrich - 98% of purity), $Fe(NO_3)_3.9H_2O$ (Aldrich - 98% of purity) e $C_5H_5NO_2$ (Aldrich - 98.5% of purity). The solid reactants were solubilized in deionized water and heated to a temperature of 100°C with magnetic stirring at 300 rpm[21], until spontaneous, exothermic and self-sustaining combustion occurred.

The ferrites synthesized were characterized by X-ray diffraction using the angular detector diffraction and X'PERT PRO PANalytical copper (λ = 1.54056Å) (XCELERATOR), with tube voltage adjustment at 40 kV and current at 40 mA, step size 0.05°, count per second (cps) of 160, scan range 10 θ - 110 θ. The resulting diffraction patterns were refined by the Rietveld method, which uses fundamental parameters through TOPAS-Academic software, version 4.1, and index cards that were extracted from the database Inorganic Crystal Structure Database (ICSD).

The samples used for the electromagnetic characterization were made by mixing the powders of the Ni-Zn ferrites as manufactured with oil paint to obtain composites in the concentrations of 10, 20, 30 and 40% by weight of ferrite. The procedure for obtaining the nanometric composites is described in an earlier work carried out by research group[21].

The morphology of the composites was observed on a scanning electron microscope (SEM) Field Emission Gun FEI QUANTA FEG 250 (FEI Corporate, Hills-boro, OR, USA) at an accelerating voltage of 1.6 kV, and work distance of 4.5 mm.

For the characterization and analysis of the absorption of electromagnetic radiation, the waveguide transmission line method X band was used.

The waveguide used in the electromagnetic measurements has rectangular geometry with standard size WR-90 (0.900 x 0.400 inches), manufacturer by Silver-Lab-Philips, model pn7366x, including the HP brand adapters (model X281A) and a short waveguide. The vector network analyzer is from the Anritsu family (40 MHz - 20 GHz), model 37247D, with Anritsu coaxial cable model 3670nn50-2. For the calibration, the TRM (Thru, Reflect, Match) method was used, using short, thru and load as standards.

The absorption curves were obtained from the conversion of S parameters to absorption coefficients, from equation 2, and plotted as percentage absorption as a function of the operating frequency band X[22].

$$A_1 = 1 - 10^{\frac{S_{11}[dB]}{10}} - 10^{\frac{S_{21}[dB]}{10}} \quad (2)$$

where $A_1$ is the radiation absorbed by the sample, $S_{11}$ represents the energy reflected at port 1, and $S_{21}$ is the energy transmitted from port 1 to port 2.

## 3. Results and Discussion

### *3.1 X-ray diffraction (XRD) and SEM analysis*

The diffractograms obtained in the characterization by X-ray diffraction indicated the presence of the characteristic peaks of the diffracted planes of the ferrite, as can be observed in Figure 1. The majority formation of the ferrite phase and the cubic crystalline structure were confirmed by the refinement performed by the Rietveld method. The ferrites $Ni_{0.2}Zn_{0.8}Fe_2O_4$ and $ZnFe_2O_4$ presented traces of zinc oxide, while the ferrites $NiFe_2O_4$, $Ni_{0.8}Zn_{0.2}Fe_2O_4$ and $Ni_{0.6}Zn_{0.4}Fe_2O_4$ presented traces of the tainite and nickel oxide phases. By this method, the lattice parameters and the mean crystallite size of the ferrites were obtained, where the goodness of fit parameter (GOF) was used to evaluate the refinement quality, as verified in Table 1. The crystallite sizes found are on the nanometer scale between 44 and 81 nm. It was observed a decreased crystallite size and increased lattice parameter by the addition of zinc, as verified in previous studies[23-24].

However, the $Ni_{0.4}Zn_{0.6}Fe_2O_4$ ferrite showed a slight deviation from this linear behavior. Fluctuations in the synthesis temperature may have caused this variation as shown in Table 1.

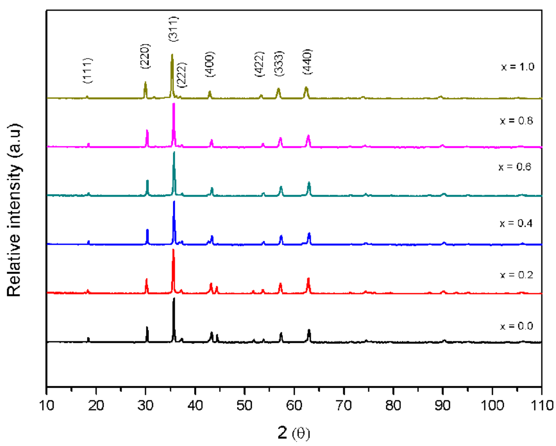


**Figure 1.** X-ray diffractograms of ferrites.

**Table 1.** Crystallite size (Tc), lattice parameter (a) and goodness of fit (GOF) obtained by Rietveld refinement.

| Ferrites | % Ferrite phase | Tc (nm) | a (Å) | GOF |
|---|---|---|---|---|
| $NiFe_2O_4$ | 75.40 | 81 | 8.35 | 1.47 |
| $Ni_{0·8}Zn_{0·2}Fe_2O_4$ | 77.49 | 63 | 8.35 | 1.77 |
| $Ni_{0·6}Zn0._4Fe_2O_4$ | 82.63 | 57 | 8.38 | 2.16 |
| $Ni_{0·4}Zn_{0·6}Fe_2O_4$ | 92.24 | 52 | 8.36 | 1.83 |
| $Ni_{0·2}Zn_{0·8}Fe_2O_4$ | 98.52 | 50 | 8.39 | 2.02 |
| $ZnFe_2O_4$ | 98.22 | 44 | 8.40 | 1.91 |

XRD pattern (Figure 1) of the sample of x = 1 stoichiometry indicates that the crystallographic planes diffracted with greater intensity and are characteristic of the spinel cubic ferrite[14-15]. Less intense diffraction peaks observed by X-ray, corresponding to the other phases that were formed during the synthesis.

SEM micrographs of $Ni_{1-x}Zn_xFe_2O_4$ nanocomposites for all stoichiometries with 40% by weight of ferrite are shown in Figure 2. In this figure, one can see a similar morphology for all composites. Ni-Zn ferrites were agglomerated in the oil paint matrix with a diameter between 115- 600 nm. This increase in diameter is due to the oil paint coating.

### *3.2 Electromagnetic absorption*

The black curves of Figures 3 and 4 are related to air as reference, in which there is total transmission of the electromagnetic radiation. These figures also presented measurements of the absorption of oil paint matrix with 0% ferrite, as highlighted by the red curves which present a maximum absorption of 3.3% to 8.2 GHz.

Electromagnetic measurements for composites with a concentration of less than 40% by weight of ferrite provided insignificant values of electromagnetic absorption. Otherwise, composites with a concentration of 40% by weight of ferrite showed better results, as one can see in Figure 3. Concentrations by weight of ferrite above 40% were tested, but did not produce a good interaction between the particles and matrix of composites. Weight dependence of ferrite in the composites on microwave absorption was observed. Such behavior also has been mentioned in the previous works.[16,25,26].

Electromagnetic measurements for all stoichiometries at 40% ferrite weight concentration are shown in Figure 4. A similar absorptive behavior is found for most stoichiometries.

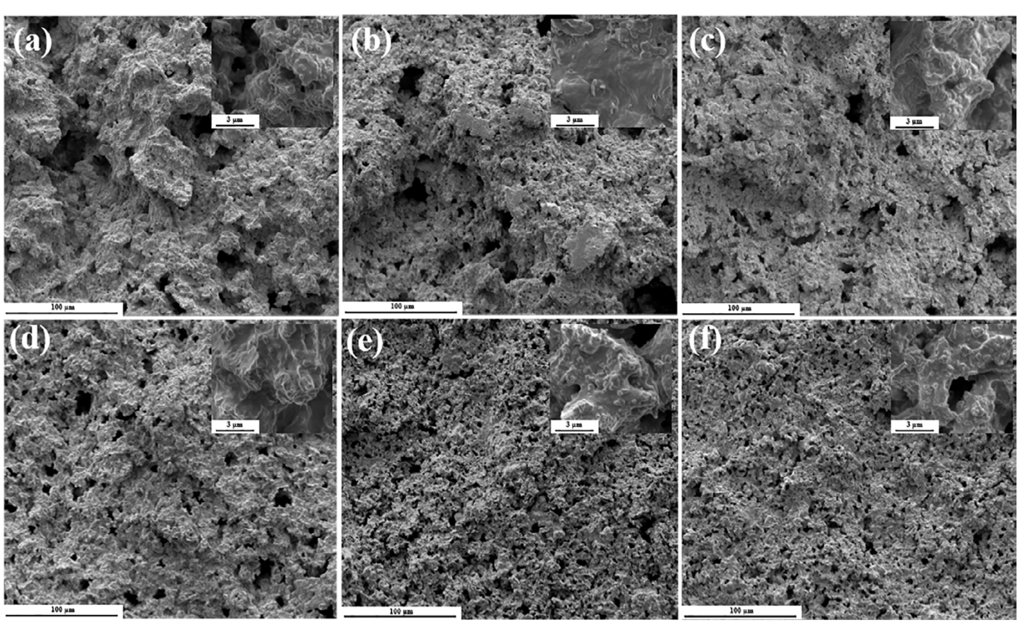


**Figure 2.** Composites morphologies with 40% by ferrite weight. (a) $NiFe_2O_4$, (b) $Ni_{0,8}Zn_{0,2}Fe_2O_4$, (c) $Ni_{0,6}Zn_{0,4}Fe_2O_4$, (d) $Ni_{0,4}Zn_{0,6}Fe_2O_4$, (e) $Ni_{0,2}Zn_{0,8}Fe_2O_4$ and (f) $ZnFe_2O_4$.

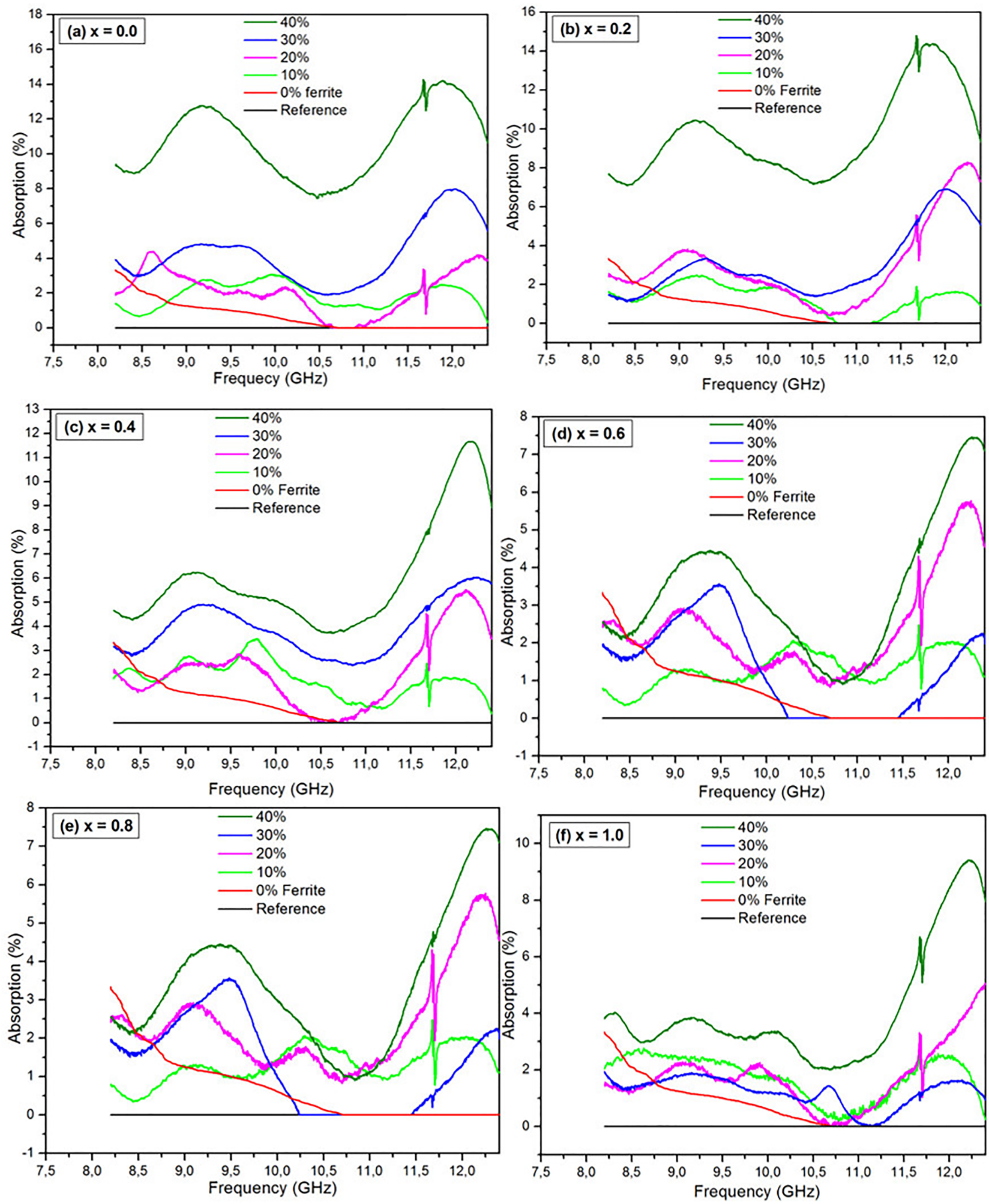


**Figure 3.** Comparison of ferrites with the same stoichiometry and different mass concentrations. (a) x= 0. (b) x= 0.2. (c) x= 0.4. (d) x= 0.6. (e) x= 0.8. (f) x= 1.

There are regions where maxima and minima of radiation absorption are observed, with a dependence of the frequency at which the radiation is absorbed. There is a better performance for the stoichiometries $NiFe_2O_4$ and $Ni_{0.8}Zn_{0.2}Fe_2O_4$. The crystallite sizes for these nanoparticles are 81 and 63 nm, respectively, indicating a higher absorption for larger particles. Other researchers have also observed a similar effect with respect to the influence of particles size on microwave absorbing capacity [27,28,29].

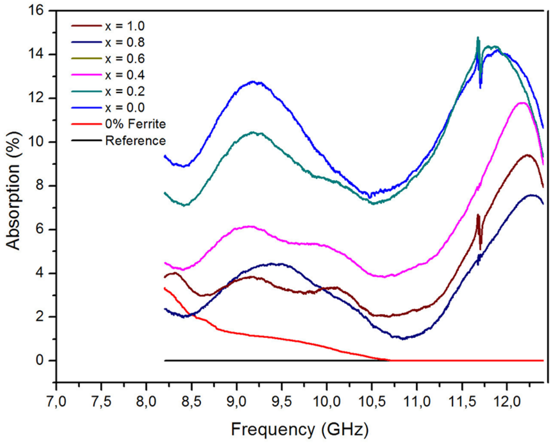


**Figure 4.** Electromagnetic absorption for all stoichiometries in 40% by weight of ferrite.

## 4. Conclusions

The measurements in the X-ray diffraction demonstrated that the method of synthesis by combustion in solution is a good alternative to obtain nanoparticles of ferrite with high degree of purity in nanometric sizes. The zinc addition increased the lattice parameter and decreased the crystallite size. The electromagnetic characterization showed that nanoparticles with larger crystallite sizes have better absorbing performance in the X band. Furthermore, the results indicated that the effect of the ferrite content is related to the amount of radiation absorbed. The $NiFe_2O_4$ and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ stoichiometries had the best results in terms of percentage of absorption of the incident radiation.

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