

## THE INFLUENCE OF CALCINATION TEMPERATURE IN Ni-Zn FERRITE DOPED WITH $Al^{3+}$

Polyana Tarciana Araújo dos Santos<sup>1a</sup>, [polyanaquimica@yahoo.com.br](mailto:polyanaquimica@yahoo.com.br)  
Patrícia Tatiana Araújo dos Santos<sup>1a</sup>, [patyquimica@hotmail.com](mailto:patyquimica@hotmail.com)  
Ana Cristina Figueiredo Melo Costa<sup>1a</sup>, [anacristina@dema.ufcg.edu.br](mailto:anacristina@dema.ufcg.edu.br)

<sup>1</sup>Department of Materials Engineering, Federal University of Campina Grande - Av. Aprígio Veloso, 882  
– Bodocongó – Campina Grande, PB- Brazil.

**Abstract:** Ferrites are thermally and chemically stable materials, which exhibit interesting magnetic properties, and therefore used in various applications. This study evaluates the influence of calcination temperature at 700°C/1h in type muffle oven in Ni-Zn ferrite doped with 0.3 mol de  $Al^{3+}$  synthesized by combustion reaction. The samples as synthesized, after calcination were characterized by X-ray diffraction, infrared spectroscopy, scanning electron microscopy, determination of carbon content and thermal analysis. The results show the formation of a major phase of Ni-Zn ferrite, and the calcination temperature favored an increase of crystallinity of 78% compared with the sample as synthesized. The infrared spectra showed characteristic vibrations of H-O and N-O possibly attributed to adsorbed water and nitrate residue. Morphologically, there was the formation of soft agglomerates with interparticles porosity for both samples. The samples studied had low carbon content, indicating that the urea used as a fuel was almost completely consumed in the reaction.

**Keywords:** Ni-Zn ferrite, doped, combustion reaction, nanoparticles

### 1. INTRODUCTION

The Ni-Zn ferrite present excellent properties such as high electrical resistivity ( $10^5$ - $10^{10}$   $\Omega$ .cm), relative magnetic permeability, 10-1000 (Goldman, 1991), low coercivity magnetic 3Oe (Sedláčik *et al.*, 2000), low hysteresis losses and eddy current ( $38 \times 10^{-4}$ ) in the frequency of 10kHz (Zahi *et al.*, 2007), mechanical hardness, chemical stability and high resistance to corrosion (Tsay *et al.*, 2000). These properties are dependent on the operating frequency, the method and conditions used as well as the intrinsic material composition, cations distribution in the spinel lattice, and the amount of dopant used.

The doping of materials is a useful technological tool to allow substantial changes in material properties through the incorporation of small amounts of dopant. In order to improve the electrical and magnetic properties of these materials has been tested several dopant in their compositions using different methods and different sintering conditions. Among some dopant can cite the cobalt (Tian *et al.*, 2009), chromium (Costa *et al.*, 2009), manganese (Bhise *et al.*, 1991), scandium (Rao *et al.*, 1997), samarium (Costa *et al.*, 2008), copper (Su *et al.* 2007; Msomi *et al.*, 2007; Jadhav *et al.*, 2009; Modak *et al.*, 2009; Kim and Ham, 2009, Lin *et al.*, 2009; Apesteguy *et al.*, 2009), aluminum (Sankpal *et al.*, 1998), among others.

Of the chemical methods used to obtain ferrites, the method by combustion reaction is a simple process that some materials with high purity and leads to obtaining powders with high chemical homogeneity have been an alternative and very promising method for the preparation of nanosized powders of Ni-Zn ferrite (Costa *et al.*, 2009). The conditions in which the synthesis by combustion reaction is performed, i.e., amount and fuel type, precursors type, purity, container type and an external source of heat, directly affects the parameters of time and temperature of the combustion flame, which are parameters that define the final characteristics of the powder obtained (Costa *et al.*, 2008).

Thus, the aim of this study is to assess the influence of calcination in Ni-Zn ferrite doped with  $Al^{3+}$  synthesized by combustion reaction using a crucible and source of external heating a base ceramic with resistance.

### 2. METODOLOGY

To obtain the  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{1.97}\text{Al}_{0.3}\text{O}_4$  ferrite were used the following materials: nickel nitrate -  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , zinc nitrate -  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , iron nitrate -  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck), aluminium nitrate -  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck) as oxidants, and urea  $[\text{CO}(\text{NH}_2)_2]$  as reducing agents, all of them with purity above 98,5%. The proportion of each reagent was calculated based on the theory of propellants and explosives, in order to produce the stoichiometric ratio between oxidizer/reductor equal to 1 ( $\Phi_e = 1$ ), where  $\Phi_e$  is the elemental stoichiometric coefficient (Jain *et al.*, 1981). The reagents were mixed in a crucible and placed over a resistance used as heating source so that promote an ignition followed by combustion. The resulting products were crushed in an agate mortar and pestle and sifted through a 325 mesh sieve (45  $\mu\text{m}$ ), e em seguida foram submetidas para caracterização, sendo a outra parte submetida à calcinação em forno tipo mufla em 700°C/1h e que também logo após foram submetidas para caracterização.

During the synthesis were measured the parameters of combustion flame time and temperature, using a stopwatch (Vitese) and an infrared pyrometer (Raytek RAYR3I  $\pm 2^\circ\text{C}$ ), respectively. The samples were characterized by X-ray diffraction in a Shimadzu LAB 6000 diffractometer in a scan  $2\theta$  range of 15-85°, using  $\text{CuK}\alpha$  radiation ( $\lambda=1,5418\text{\AA}$ ). The average crystallite size was calculated from the broadening of the X-ray line (311) using Scherrer's equation, as in Eq. (1).

$$D = \frac{0,89\lambda}{\beta \cos \theta_B} \quad (1)$$

where  $D$  is the crystallite size;  $\lambda$  is the wavelength of the target used;  $\theta_B$  is half of the diffraction angle in radians; and  $\beta$  is full-width half maximum for this angle in radians.

Análise por espectroscopia de infravermelho realizada em um equipamento Perkin Elmer, modelo Spectrum 400 FT-IR/FT-NIR Spectrometer.

Thermal analysis were carried out on Shimadzu DTG-60H apparatus. Thermogravimetry (TG) curves of the samples were recorded over a temperature range up to 1000°C with a heating rate of 12.50°C/min in the atmosphere of nitrogen; sintered  $\alpha\text{-Al}_2\text{O}_3$  was the thermally inert reference material used for the TGA. Total organic carbon was measured by combustion with a CS-200 Leco analyzer on dried (105°C, 12h) and milled samples of approximately 1 g. The values of surface area, diameter and volume pore were obtained by nitrogen adsorption, using a Quantachrome NovaWin2 system (NOVA 3200). Surface area was determined using the BET model while to determine the radius and volume pore was used the BJH theory. The average particle size was calculated from BET data using the Eq. (2) (Reed, 1995).

$$D_{BET} = \frac{6}{D_t S_{BET}} \quad (2)$$

where  $D_{BET}$  represents the spherical diameter (nm);  $D_t$  is the theoretical density ( $\text{g}/\text{cm}^3$ );  $S_{BET}$  corresponds to the surface area ( $\text{m}^2/\text{g}$ ).

The analysis of the morphology of the ferrite samples resulting from the combustion reaction and after calcination was conducted by analysis of scanning electron microscopy using a scanning electron microscope (SEM), Philips, model XL30FEG.

### 3. RESULTS

The Figure (1) illustrates the results of reaction temperature as a function of reaction time measured 20 to 20 seconds for the Ni-Zn ferrite doped 0.3 mol of  $\text{Al}^{3+}$  obtained by combustion reaction.

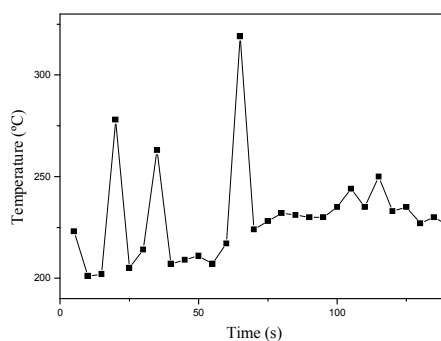


Figure 1. Temperature and reaction time for the Ni-Zn ferrite doped 0.30 mol of  $\text{Al}^{3+}$ .

It is observed that the temperature variation as a function of reaction time is not regular, i.e., the graph shows that the reaction occurs with great variations in temperature until it reaches the maximum combustion temperature of 319°C for 65 seconds followed by a decline in the temperature to 224°C, staying low oscillations in the range of 71 to be 140 seconds of reaction, when the flame ceases. The low temperature was observed possibly due to a large release of gas during the reaction, which led to high energy dissipation for the neighbors, leading to lower combustion temperatures.

The Figure (2) illustrates the X-ray diffractogram for Ni-Zn ferrite doped with 0.30 mol of Al<sup>3+</sup>, as synthesized (Fig. 2a) and after calcination (Fig. 2b).

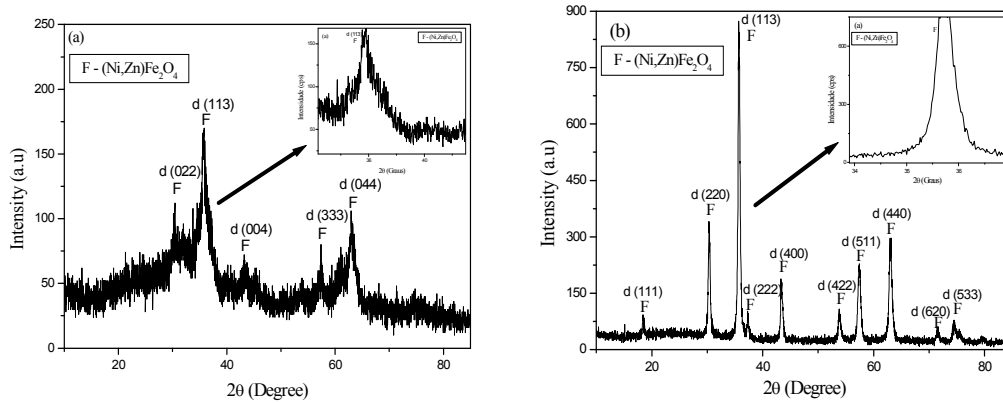


Figure 2. X-ray diffraction patterns for Ni-Zn ferrite doped with 0.3 mol of Al<sup>3+</sup>, (a) as synthesized, (b) calcined.

Through the spectra of X-ray diffraction for Ni-Zn ferrite doped with and without calcination, can observe the formation of major phase inverse cubic spinel according to the statement JCPDF (52-0278) for both samples. For the sample as synthesized (Fig. 2a) can be observed that the diffraction spectrum shows lines of basal reflections quite wide, with a high noise. This indicates that there were no complete phase crystallization, or possibly not all material reacted in the reaction combustion, which makes the poorly crystalline material. Because the crystallinity is less than 30% could not be determined by its percentage program used. Also observed that the calcination (Fig. 2b) led to the emergence of new peaks, but also increased the intensity of the peaks and reduced the basal width, which consequently led to an increase in crystallinity, resulting in values of 78%.

Table 1 and 2 are shown the intensities, the planes (hkl), their angles of diffraction, crystallite size and micro-deformations calculated from the data of X-ray diffraction corresponding sample of Ni-Zn ferrite doped with 0.3 mol of Al<sup>3+</sup> as synthesized, after calcination.

Table 1 - Structural data obtained from the XRD results for the sample as synthesized.

Intensity	hkl	2θ	Cristallite Size	
			(nm)	Microdeformation
38	022	30.28	11	0.012901
100	311	35.78	8	0.015139
26	004	43.35	12	0.008452
33	333	57.33	14	0.005587
41	044	63.00	9	0.007405

Table 2 - Structural data obtained from the XRD results for calcined sample.

Intensity	Crystallite Size			Microdeformation
	hkl	2θ	(nm)	
14	111	18.54	25	0,009139
45	220	30.38	23	0.006109
100	311	35.78	22	0.005364
06	222	37.32	29	0.003836
25	400	43.40	21	0.004614
10	422	53.96	19	0.004118
25	511	57.48	17	0.004453
35	440	63.01	16	0.004227
02	620	71.59	19	0.003335
08	533	74.50	20	0.002978

It can be observed that for Ni-Zn ferrite doped with 0.3 mol of Al<sup>3+</sup> no ash was identified only single spinel phase reverse, as indicated by five characteristic peaks of the spinel phase, whose main peak (d311) was observed by reflection baseline to 2 θ = 35.78 °, with crystallite size of about 8 nm and microdeformation of 0.015139. For the sample after calcination was also observed only a single phase of inverse spinel ferrite Ni-Zn indicated by the 10 major peaks. The main peak (d311) was observed by reflection basal θ 2 = 35.78, with crystallite size of about 22 nm and microdeformation of 0.005364.

The Figure (3) illustrates the vibration spectrum in the infrared region of the Ni-Zn ferrite doped with 0.3 mol of Al<sup>3+</sup> in the range 4000-400 cm<sup>-1</sup> as synthesized (Fig. 3a) and calcined (Fig. 3b). According to the spectra of Fig (3) are observed for both samples a broad band in the range of 3600 cm<sup>-1</sup> characteristic of H-O-H bonds, referring to the presence of water in the samples is confirmed at about 1630 cm<sup>-1</sup>. Another band observed at approximately 1400 cm<sup>-1</sup> attributed to the vibration of the N-O bond due to nitrate, this group, present in the reaction product of combustion.

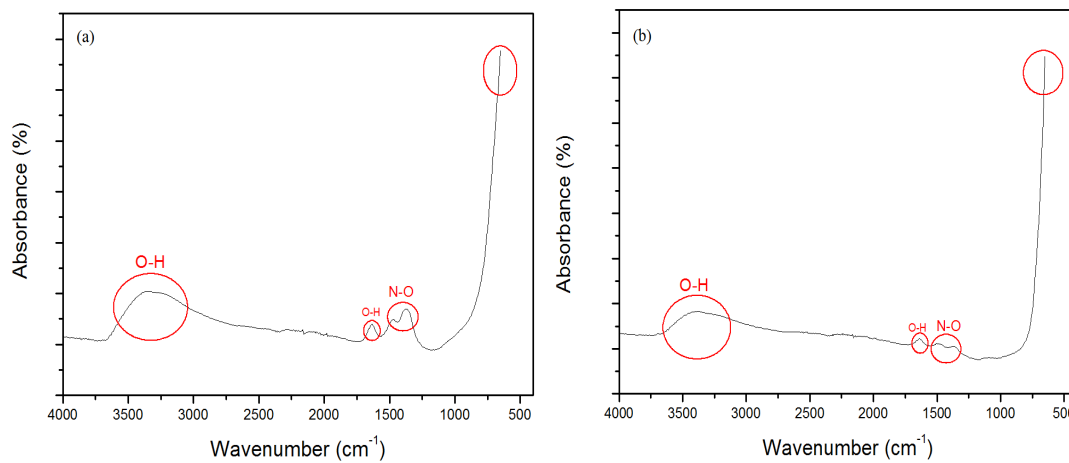


Figure 3. Spectrum in infrared region for samples of Ni-Zn ferrite doped with 0.3 mol of Al<sup>3+</sup>, (a) as synthesized, (b) calcined.

In the range of  $1000\text{--}400\text{ cm}^{-1}$ , the infrared bands of solids are generally characterized by vibrations of ions in the crystal lattice. The main bands in the range are around  $600$  and  $400\text{ cm}^{-1}$  corresponding to the stretches  $\nu_1$  and  $\nu_2$  of tetrahedral and octahedral sites of the crystal structure. It is observed in both samples at  $1000\text{ cm}^{-1}$  to give the beginning of a band that reaches about  $650\text{ cm}^{-1}$ . Thus, the main bands of spinel and inverse  $\nu_1$  and  $\nu_2$  were not observed in the spectrum under study, due to the limitation of the test equipment because the equipment is used to track the detection limit at  $650\text{ cm}^{-1}$ .

We also observe that for the calcined sample (Fig. 3b) the bands appear as weak absorptions, ie, less intense compared to the sample as synthesized (Fig. 3b). Thus, calcination promoted the formation of more crystalline phase and greater crystal size, therefore, the material becomes less reactive as a consequence of the lower surface energy (surface tension), which leads to a lower moisture adsorption.

The Figure (4) illustrates the morphological characteristics obtained by scanning electron microscopy (SEM), samples of Ni-Zn ferrite doped with  $0.30\text{ mol}$  of  $\text{Al}^{3+}$  prepared by combustion synthesis, as synthesized (Fig. 4a) and after calcination (Fig. 4b).

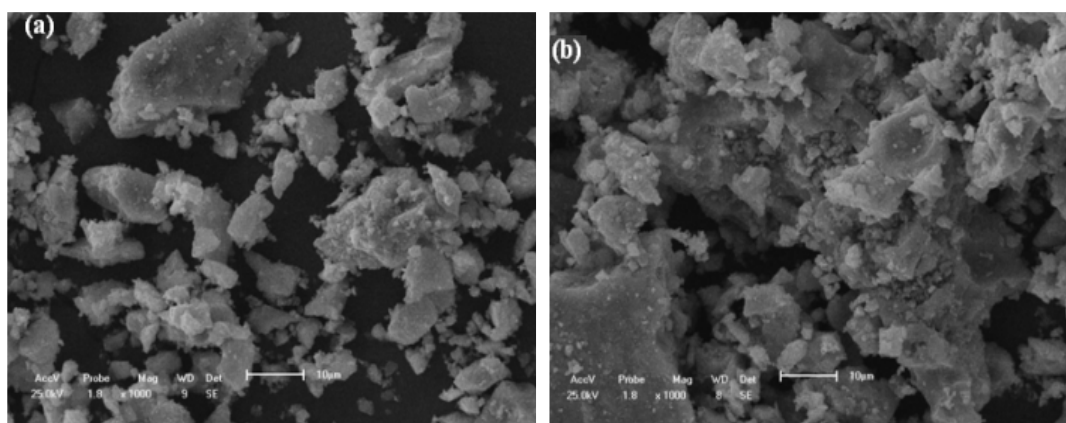


Figure 4. Micrograph obtained by SEM for samples of Ni-Zn ferrite doped with  $0.3\text{ mol}$  of  $\text{Al}^{3+}$ , (a) as synthesized, (b) calcined.

It can be observed by micrograph Fig (4) for both samples, the ferrite particles as synthesized by combustion, present small size, formation of soft agglomerates (formed by weak forces of Van der Waals) format and irregular distribution. Comparing the micrographs of samples without calcination (Fig. 4a) and calcination (Fig. 4b) showed that the temperature increase caused an increase in the size and uniformity of clusters, resulting in a closer and more regular distribution. Table 3 shows the results of the determination of carbon in the sample of Ni-Zn ferrite doped with  $\text{Al}^{3+}$  as synthesized and calcined.

Table 3 - Results for determination of carbon samples of Ni-Zn ferrite doped with  $\text{Al}^{3+}$  as synthesized and calcined.

Samples	Mass (g)	C (%)
As synthesized	0.4295	0.1875
Calcined	0.3680	0.0197

From the results, it was found that the sample synthesized by combustion reaction showed a low carbon content around  $0.2\%$ , indicating that the urea used as a fuel was almost completely consumed in the reaction. The calcination temperature of  $700\text{ }^{\circ}\text{C}/1\text{h}$  provided a reduction of  $88.5\%$ , indicating that the calcination temperature was effective in the release of carbon.

The Figure 5 illustrates the overlapping curves TGA and DTA of the samples under study. In Figure 5a shows the curves for samples as synthesized and in Figure 5b for the samples calcined. Before the results of the TGA curve for the ferrite samples as synthesized (Figure 5a), we observed that the first mass loss occurred at about  $100\text{ }^{\circ}\text{C}$  with  $3.62\%$  mass loss, was attributed to evaporation of residual water material. By DTA curve was also observed two exothermic events at  $485^{\circ}\text{C}$  and  $600^{\circ}\text{C}$ , which possibly corresponds to the evaporation of residual nitrates and crystallization of the spinel phase, respectively. The total mass loss for the sample doped with  $\text{Al}^{3+}$  was synthesized as  $9.84\%$ . For the calcined sample (Figure 5b) revealed the occurrence of a small weight loss at about  $100^{\circ}\text{C}$ , and was attributed to water evaporation of residual material.

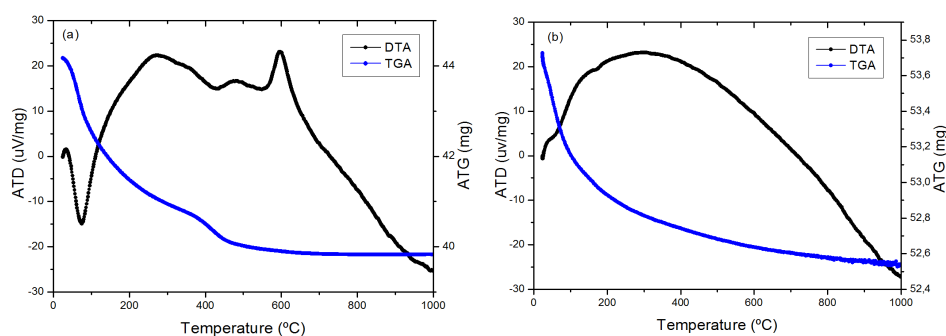


Figure 5 - TGA and DTA curves for Ni-Zn ferrite doped with 0.3 mol of  $\text{Al}^{3+}$ : (a) as synthesized and (b) calcined.

This result is in agreement with the results of which were observed in the FTIR weak absorption bands of O-H groups, which also favored the firing complete crystallization of the spinel phase. The loss of total mass of the calcined sample was very small, approximately 2.20%. Fu *et al.*, (2004) when they studied the preparation and magnetic properties of ferrites  $\text{Ni}_{0.25}\text{Cu}_{0.25}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  microwave-induced combustion observed this same events of mass loss before 100°C attributed to the evaporation of residual water, and peak exothermic around 550°C related to the residual nitrate and organic matter, and another peak at 620°C corresponding to crystallization of the spinel phase.

#### 4. CONCLUSION

The maximum temperature and combustion time achieved during synthesis Ni-Zn ferrite doped with 0.30 mol of  $\text{Al}^{3+}$  was 32°C and 09 seconds respectively. The synthesis by combustion reaction was efficient sample preparation and nano-phase inverse spinel, with crystallite size of 8 nm. The firing has favored the complete formation of the crystalline phase of doped ferrite crystallite size of 22 nm. Characteristic bands of H-O and N-O links from possibly adsorbed water and nitrate residue were identified. The samples showed morphology of soft agglomerates with interparticles porosity. After calcination have an increase in the size and uniformity of clusters resulting in a closer and more regular distribution. The sample as synthesized had low carbon content around 0.2% and calcination led to the almost total elimination, indicating that the calcination temperature was effective in the release of carbon. The mass loss was low being 9.84 and 2.20% for as synthesized and calcined samples, respectively. The calcination temperature was effective because of 700°C/1h promote the complete formation of the spinel phase, reducing the residual carbon in the synthesis, but maintaining the characteristics of nanoparticles, with morphology consisting of soft agglomerates in size and more uniform distribution.

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