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SYNTHESIS AND CHARACTERIZATION OF $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ AND $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ NANOPOWDERS AND THEIR APPLICATION AS RADAR ABSORBING MATERIALS

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ABSTRACT

There has been a growing and widespread interest in the development of radar absorbing materials (RAM) to reduce the radar signatures of navy platforms. Z-type barium hexaferrite is one of the most complex compounds in the family of hexagonal ferrites that due to its good magnetic properties, it is a promising candidate to be used as RAM.

In this work, the nanosized Z-type barium hexaferrite powders ($\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ and $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$) were synthesized at 950 °C by the citrate sol-gel process to be used as RAM in polychloroprene (CR) matrices. X-ray diffraction and X-ray fluorescence (XRD and XRF, respectively) were used to characterize these materials. Magnetic properties of the Z-type barium hexaferrites were also evaluated by using the vibrating sample magnetometer (VSM). The Cu^{2+} ions were incorporated into the structure of $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ and consequently, low temperature sintering and good magnetic properties were achieved. The microwave reflectivity levels (dB) of the Z-type barium hexaferrite:polychloroprene composites were determined for the frequency range 8.0 - 16.0 GHz. The permittivity (ϵ) and permeability (μ) values were measured by using the transmission/reflection (T/R) method in a waveguide medium. The nanocomposite 80:20 of $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$:CR. 3.0 mm thick, showed the best performance as RAM for the X-band, with a microwave absorption of 99.50 % (reflectivity of - 22.5 dB) in 9.5 GHz, which can be attributed to the increase in the magnetic properties due to the Cu addition.

INTRODUCTION

Radar absorbing materials (RAM) play an important role on the stealth technology, which corresponds to the invisibility of military platforms to the different systems of detection (radar, acoustic, infrared, etc), by suppressing microwaves reflected from metallic structures and so, reducing the radar signatures of the targets.

Recently, a great deal of attention is devoted to hexagonal ferrites as microwave materials for the 1-100 GHz band and a wide range of chemical methods have been used to obtain ultrafine particles. All of these methods require a low-temperature process in order to control the particles' size, as a first synthesis stage. In an attempt either to promote the formation of Z-type

ferrite and to improve the magnetic properties, we report the synthesis of these nanostructured materials by the sol-gel-citrate precursor method^{1, 2}. As magnetic materials, the barium hexaferrites are not generally replaced by any other magnetic material because they are relatively inexpensive, stable and have a wide range of technological applications. Barium hexaferrites have been classified according to their structures, into five main classes: $BaFe_{12}O_{19}$ (M-type), $BaMe_2Fe_{16}O_{27}$ (W-type), $Ba_2Me_2Fe_{28}O_{46}$ (X-type), $Ba_2Me_2Fe_{12}O_{22}$ (Y-type) and $Ba_3Me_2Fe_{24}O_{41}$ (Z-type), where Me represents a divalent ion from the first transition series.

Z-type barium hexaferrite is a promising material for applications as RAM in the frequency of GHz, which require high permeability, great resistivity and good chemical and thermal stabilities. $(Co-Cu)_2Z$ barium hexaferrite is a new type of soft magnetic compound, which presents these characteristics and a ferromagnetic resonance in the GHz frequency, being useful for inductor cores or in UHF communications, in the microwave region^{3, 4}.

In the conventional ceramic method, a high sintering temperature is necessary to obtain this Z-type hexaferrite due to the complex crystalline structure.

By using chemical methods, the calcination temperature can be reduced and the introduction of metallic ions makes possible the use of these ferrites as microwave absorbers in different frequency ranges, simply by varying the degree of substitution⁵. In this work, the citrate sol-gel process under inert atmosphere was used to obtain $Ba_3Co_2Fe_{24}O_{41}$ and $Ba_3Co_{0.9}Cu_{1.1}Fe_{24}O_{41}$ nanopowders. The introduction of Cu^{2+} ions in the structure of $Ba_3Co_2Fe_{24}O_{41}$ can also reduce the sintering temperature, because it can act as a flux, due to its low melting point (1084.62 °C)⁶.

Composites of $Ba_3Co_2Fe_{24}O_{41}$ and $Ba_3Co_{0.9}Cu_{1.1}Fe_{24}O_{41}$ with polychloroprene (CR) were obtained for the microwave absorption measurements, for the frequency range: 8.0 – 12 GHz (X-band) and 12 – 16 GHz (Ku-band). The magnetic properties of these materials are largely dependent of the sample microstructure.

X-ray diffraction (XRD), X-ray fluorescence (XRF), thermal analyses (TGA/DTA), and the vibrating sample magnetometer (VSM) were used to characterize the synthesized material.

The microwave measurements were based on the transmission/reflection method (T/R) using rectangular waveguides as the confining medium for the samples⁷.

EXPERIMENTAL

Nanosized $(Co-Cu)_2Z$ structured powders were synthesized by the citrate precursor method using reagent grade $Fe(NO_3)_3 \cdot 9H_2O$, $Ba(NO_3)_2$, monohydrate citric acid, $Co(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ in stoichiometric molar ratios to obtain $Ba_3Co_2Fe_{24}O_{41}$ and $Ba_3Co_{0.9}Cu_{1.1}Fe_{24}O_{41}$ hexaferrites. The solids were weighed and placed then into appropriate closed vessels subjected to a super dry nitrogen atmosphere to obtain the precursor solutions⁸. Distilled water was added under agitation, until total dissolution of solids.

The solutions were then transferred to a previously evacuated flask and mixed under super dry nitrogen operating as a reflux condenser, with intensive stirring. The resulting mixture was heated to 80 °C to complete the reaction under reflux, in order to keep the inert atmosphere and to allow subsequent additions of ammonium hydroxide (NH_4OH), added drop wise into the solution to render it neutral or slightly alkaline (pH 7.0 - 8.0), for subsequent precipitation of the organo metallic complex⁸.

Predried ethanol was previously added drop wise under vigorous stirring into the reaction mixture, to promote the precipitation of a complex citrate gel of barium, iron, copper and cobalt.

Drying at 60 °C, leaving behind the desired solid phase, the remaining aqueous solution was eliminated. The ideal temperature for the citrate gel decomposition was determined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Based on the results of the thermal analyses, the batch of dried solid was calcined inside a muffle furnace. TGA and DTA measurements were carried out in a TA Instruments SDT-2960. The experiments were carried out in static air, using platinum crucibles between 20 and 1,000 °C, with a heating rate of 10 °C min⁻¹.

The calcination was performed using the following heating schedule: 2 °C/min up to 410 °C, establishing a plateau for 1 hour, 10 °C/min up to the final sintering temperature with a residence time of 4 h at the sintering temperature. The material was then cooled to room temperature at a rate of 10 °C/min.

Then, X-ray fluorescence (XRF) measurements were carried out on a Philips model PW 2,400 sequential spectrometer. This quantitative method was used to determine the stoichiometry of the ferrite samples, which were analyzed in the form of a fused bead, using lithium tetraborate flux.

For the powder X-ray diffraction (XRD) analysis, the material was placed on a glass sample holder and spread out to form a thin layer. A Siemens AXS D5005 diffractometer with a dwell time of 1 °/min, in the θ -2 θ Bragg-Brentano geometry, was employed.

The magnetic hysteresis loops were obtained using the vibrating sample magnetometer VSM 4,500 PAR.

The Z-type barium hexaferrite structure is illustrated in Figure 1.

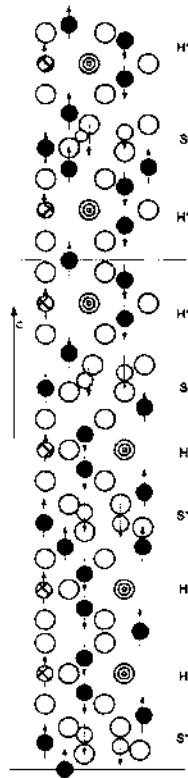


Figure 1: Z-type barium hexaferrite structure. where: S = spinel block, H - hexagonal block, \circ - cation in tetrahedral sites, \bullet = cation in octahedral sites, \uparrow = magnetic momentum direction, \bigcirc - O^{2-} , \odot - Ba^{2+} , \otimes - hexahedral sites.

In order to obtain the composites for the measurements of the microwave absorbing properties, the powders were mixed with polychloroprene (CR), resulting in the composition 80:20 (wt. %, ferrite:polychloroprene). The processing was carried out in a Berstorff two roll mill, at room temperature, with velocities of 22 and 25 rpm (back and forward). Vulcanized samples with 8.0×4.0 cm and 3.0 mm thick were obtained by compression moulding in a hydraulic press at 150 °C and 6.7 MPa. The vulcanization times were determined by the data obtained in the Monsanto Rheometer TM100 [7]. The dispersion of the magnetic particles in CR was evaluated by SEM, using a ZEISS DSM 940A microscope and the morphological study was performed by a Topometrix II® atomic force microscope.

The microwave measurements conducted in this work were based on the Transmission/Reflection method (T/R) using rectangular waveguides as the confining medium for the samples. The microwave absorption of the sheet composites was illustrated by variations of reflectivity (dB) versus frequency (GHz), using the HP 8510 network analyzer system. The materials were analyzed for the frequency range from 8.0 to 16.0 GHz (X-Ku bands)^{7,9-13}.

RESULTS AND DISCUSSION

Figure 2 illustrates TGA and DTA curves of the precursor gel. From the DTA curve analysis, no significant weight loss occurred above 400 °C, indicating that any remanent organic material had already been completely eliminated⁹. Based on this result, the gel was calcined at 410 °C.

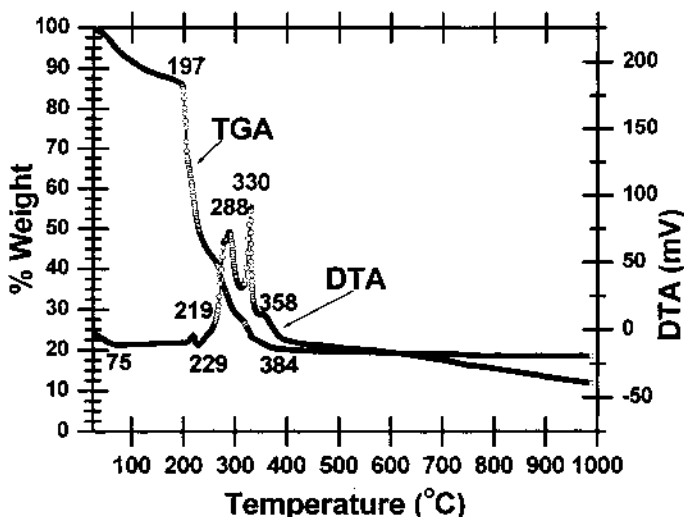


Figure 2: TG-DTA curves for the Z-type precursor gel of $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ powder.

The thermal behavior of the organic precursor showed that the weight losses from 25 to 197 °C and from 197 to 384 °C were respectively illustrated by an endothermic and four exothermic changes in the DTA curve. The evaporation of water was observed for temperatures below 75°C.

The decomposition of the unreacted citric acid should occur between 150°C - 229°C. The organic complex citrate decomposition occurred between 229°C - 384°C. In total, it resulted in about 82 % loss in weight from the initial temperature up to 400°C.

XRD results in Figure 3 indicate that at 950 °C, the Z-type phase was clearly the majority phase, according to JCPDS 19-0097. However, according to Pullar et al¹¹, this material contains small undetectable amounts of Y-type phase ($\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$), coexisting with the Z-type phase.

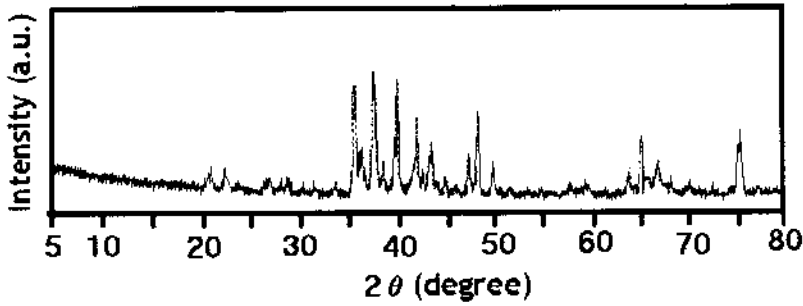


Figure 3: X-Ray diffraction curve for the Z-type powders calcined at 950 °C.

Results from X-ray fluorescence analysis curve for the Z-type powders calcined at 950 °C are shown at Table 1. The theoretic and experimental values are very similar, which indicate the absence of carbon (complete organic precursor elimination) and that the synthesized powders achieved the planned stoichiometry.

Table 1: Chemical compositions of $Ba_3Co_2Fe_{24}O_{41}$ and $Ba_3Co_{0.9}Cu_{1.1}Fe_{24}O_{41}$.

Z-type barium hexaferrite	Chemical Compound							
	BaO		CoO		Fe ₂ O ₃		CuO	
	Theoretic	Experimental	Theoretic	Experimental	Theoretic	Experimental	Theoretic	Experimental
$Ba_3Co_2Fe_{24}O_{41}$	18.2094	18.21	5.9326	5.93	75.8580	75.89	—	—
$Ba_3Co_{0.9}Cu_{1.1}Fe_{24}O_{41}$	18.1729	18.17	2.6643	2.66	75.7059	75.71	3.4569	3.46

The hysteresis curves for Z-type barium hexaferrites fired at 950 °C are illustrated in Figure 4. The magnetization curves show typical feature of magnetically soft ferrites. The saturation magnetization M_s was obtained by extrapolating $M(1/H)$ -curves to $1/H = 0$, resulting in the value of 57.8 emu/g for $Ba_3Co_{0.9}Cu_{1.1}Fe_{24}O_{41}$ and 52.3 emu/g for $Ba_3Co_2Fe_{24}O_{41}$.

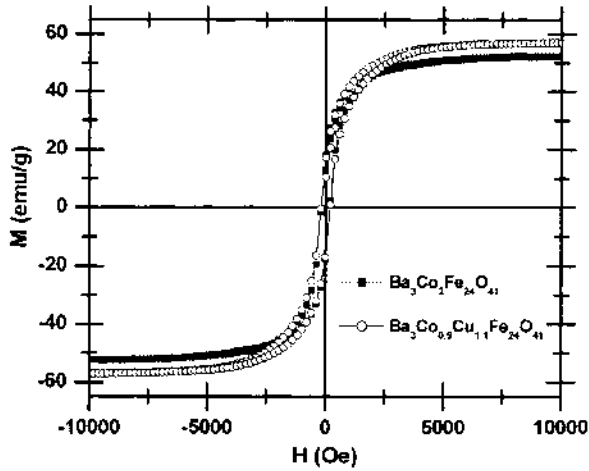


Figure 4: Magnetic hysteresis curves of $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ and $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ powders.

In the Z-type barium hexaferrites, the metallic ions such as Fe^{3+} , Co^{2+} and Cu^{2+} are located in different sites such as octahedral and tetrahedral ones. Co^{2+} ions show strong magnetocrystalline anisotropy and its substitution by Cu^{2+} ions may result in the improvement of the magnetic properties.

The ionic radius of Cu^{2+} (0.085 nm) is very near to that of Co^{2+} (0.082 nm) and larger than Fe^{3+} (0.067 nm), as show in Table 2.

Table 2: Ionic radius, coordination, magnetic momentum/ion and alignment in Z-type hexaferrite.

Ion	Ionic radius (nm)	Coordination	Magnetic Momentum/ion	Magnetic Momentum alignment
$\text{Fe}^{3+}/\text{Fe}^{2+}$	0.067 (0.090)	Tetrahedral/ decahedral	5/4	$\uparrow\uparrow$
Co^{2+}	0.082	Octahedral	3	$\uparrow\uparrow$
Cu^{2+}	0.085	Octahedral/ decahedral	1	$\uparrow\downarrow$
Ba^{2+}	0.143	Oxygen site	-	-
O^{2-}	0.132	Oxygen site	-	-

The copper ions shall occupy the octahedral sites in the structure of Z-type hexaferrite and substitute partially cobalt ions. The Cu^{2+} ions distort the crystalline field due to their electronic configuration, and this behavior results in an increase of the M_s ⁵.

The introduction of Cu^{2+} ions promotes the partial substitution of the Fe-Fe strong magnetic interactions by the weak ones of Co-Fe, as a result it can be observed a decrease of the initial permeability value.

The introduction of Cu^{2+} ions also promotes the reduction of the calcination temperature of the Z-type barium hexaferrite and the probability of the reactions (1), (2) e (3) to occur:



Figure 5 shows the AFM micrograph of $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ magnetic hexagonal particles with nanometric size (230 x 100 nm), while Fig. 6 illustrates the good dispersion of these nanoparticles in polychloroprene matrix (80:20, wt. %).

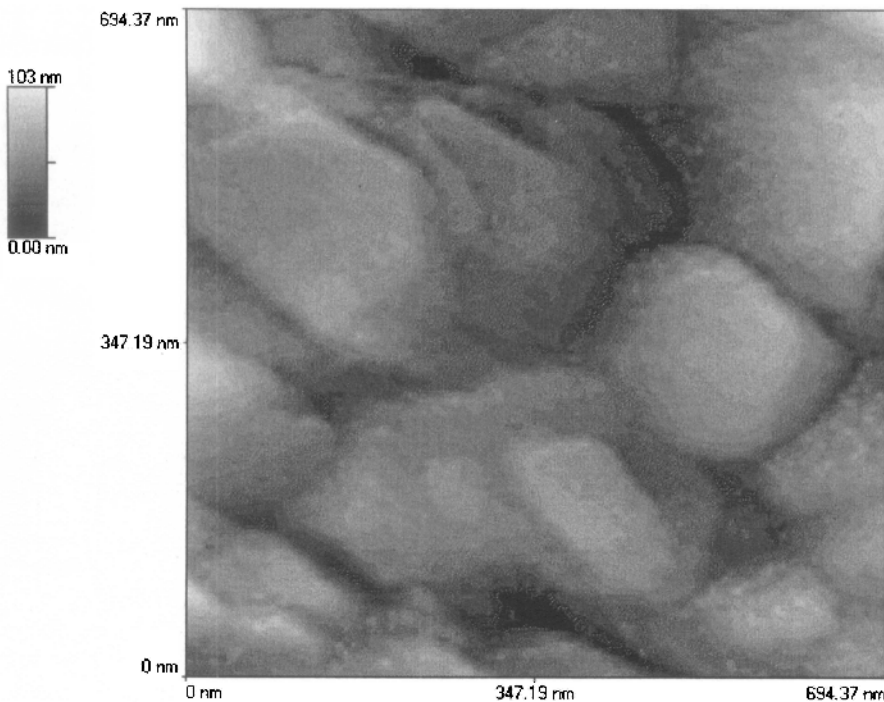


Figure 5: AFM micrograph of $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ calcined at 950°C (100,000 X; 200 kV).

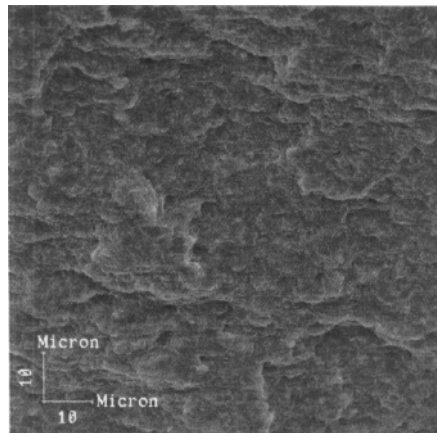


Figure 6: SEM micrograph of $Ba_3Co_{0.9}Cu_{1.1}Fe_{24}O_{41}$:CR, magnification of 1,000.

From the SEM image, it can be seen that rubber mixing is a very good technique for the dispersion of the Z-type hexaferrites particles, in spite of the high weight concentration used (80 %) and the tendency of these particles to form magnetic agglomerates⁷.

The effect of Cu addition on the reflectivity measurements can be seen in Fig. 7.

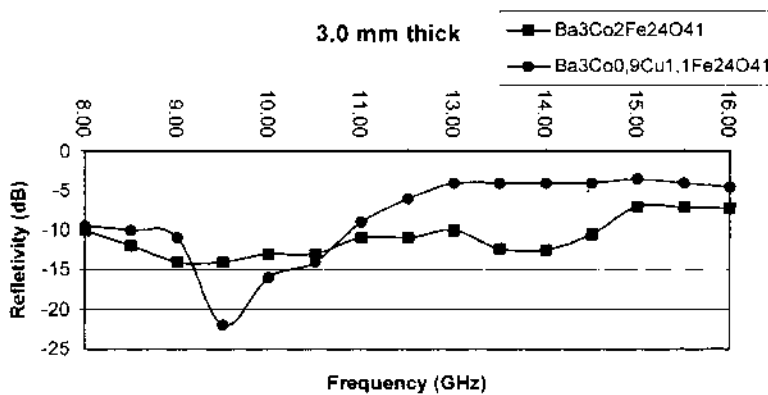


Figure 7: Effect of Cu addition on the reflectivity measurements for the composites 80:20 of $Ba_3Co_2Fe_{24}O_{41}$:CR and $Ba_3Co_{0.9}Cu_{1.1}Fe_{24}O_{41}$:CR, 3.0 mm thick.

The greatest microwave absorption of 99.50 % in 9.5 GHz for the $Ba_3Co_{0.9}Cu_{1.1}Fe_{24}O_{41}$:CR 3.0 mm thick nanocomposite, can be attributed to the addition of Cu, resulting in an increase of the magnetic properties.

CONCLUSION

The citrate sol-gel method promoted the formation of nanocrystalline Z-type hexaferrite at a lower temperature (950 °C) than that employed by the conventional one (1,200 - 1,300 °C). The introduction of Cu^{2+} ions improved the magnetic properties of this ceramic illustrated by the increase of 5.5 emu/g in the Ms. As a result, the nanocomposite 80:20 of $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$:CR 3.0 mm thick, showed the best performance as RAM for the X-band, with a microwave absorption of 99.50 % (reflectivity of - 22.5 dB) in 9.5 GHz.

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