

Synthesis and characterization of nanocrystalline $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ powder and its application in the reduction of radar cross-section

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There has been a growing and widespread interest in the development of radar absorbing materials (RAM). Z-type hexaferrite is one of the most complex compounds in the family of hexaferrites that may be used in many applications. In this work, the citrate sol-gel process under an inert atmosphere was used to obtain the nanocrystalline $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ powder to be used as RAM. 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. Composites of $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ with polychloroprene (CR) were obtained for microwave absorption measurements by the transmission/reflection method, using a waveguide medium for the S- band and X-Ku bands. The 80:20 nanocomposite of $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$:CR with 3.0 mm thickness exhibited the best performance as a RAM for the X-band, with 99.50% microwave absorption at 9.5 GHz.

Key words: *(Co-Cu)₂Z hexaferrite; hysteresis; inert atmosphere; citrate sol-gel process; nanocomposite; radar absorbing material; waveguide*

1. Introduction

Radar absorbing materials (RAM) play an important role in the stealth technology, which corresponds to the invisibility of military platforms to different systems of detection (radar, acoustic, infrared, etc), by suppressing microwaves reflected from metallic structures and reducing the radar cross section (RCS) of targets. Advanced ceramics (optical, electronic, structural, and magnetic ceramics) have been developed using a number of basic principles related to different structure levels, from the micro

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to macro level [1, 2]. Moreover, magnetic materials form the basis for numerous new devices, which rely on soft or hard (permanent) magnets [1].

As magnetic materials, 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: $\text{BaFe}_{12}\text{O}_{19}$ (M-type), $\text{BaMe}_2\text{Fe}_{16}\text{O}_{27}$ (W-type), $\text{Ba}_2\text{Me}_2\text{Fe}_{28}\text{O}_{46}$ (X-type), $\text{Ba}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$ (Y-type), and $\text{Ba}_3\text{Me}_2\text{Fe}_{24}\text{O}_{41}$ (Z-type), where Me represents a divalent ion from the first transition series.

Z-type barium hexaferrite is a promising material for applications such as RAM at GHz frequencies, which requires high permeability, great resistivity, and good chemical and thermal stability. These ferrites absorb microwaves due to various interactive loss mechanisms related to the magnetization and electric polarization of the material. The values of relative complex permeability ($\mu' - j\mu''$) and permittivity ($\epsilon' - j\epsilon''$) affect the reflectivity of such materials, and therefore their performance as RAM.

$(\text{Co-Cu})_2\text{Z}$ barium hexaferrite is a new type of soft magnetic compound which presents these characteristics and a ferromagnetic resonance at GHz frequencies, being useful for inductor cores or in UHF communications in the microwave region [3, 4]. In conventional ceramic methods, a high sintering temperature is necessary to obtain this Z-type hexaferrite due to the complex crystalline structure shown in Fig. 1.

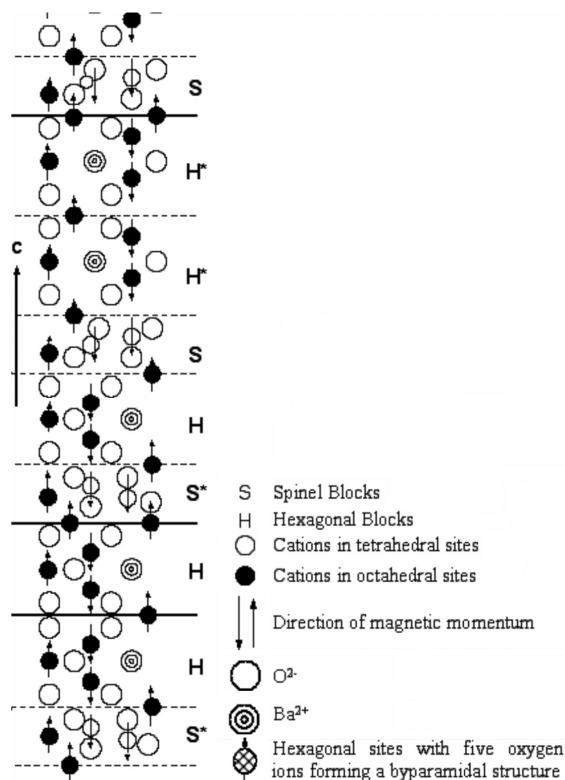


Fig. 1. Cross-section of one unit cell of the Z-type barium hexaferrite structure

By using chemical methods, this temperature can be reduced, which is necessary for modern cost-driven applications to produce electronic components, such as inductors, chips beads, beads arrays, LC filters, etc. [5].

In this work, the citrate sol-gel process under an inert atmosphere was used to obtain $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$. The process permits the formation of the Z-type phase at lower sintering temperatures [6]. The introduction of Cu^{2+} ions in the structure of $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ can also reduce the sintering temperature, because it can act as a flux due to its low melting point (1084.62 °C). X-ray diffraction (XRD), X-ray fluorescence (XRF), thermal analysis (TGA/DTA), and atomic force microscopy (AFM) were used to characterize the synthesized material.

The relative complex permeability and permittivity parameters of ferrite-polymer composites may depend on the type, composition and concentration of ferrite, and the nature of the polymer besides the temperature and frequency of operation [6]. The way these magnetic and dielectric properties change with frequency is responsible for the performance of the RAM. In this way, composites of $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ and polychloroprene (CR) were obtained for microwave absorption measurements in the frequency ranges: 2.6–4.0 GHz (S-band), 8.0–12 GHz (X-band), and 12–16 GHz (Ku-band). The microwave measurements were based on the transmission/reflection method (T/R) using rectangular waveguides as the confining medium for the samples. The materials were analysed in the frequency ranges 2.6–4.0 GHz (S-band) and 8.0–16.0 GHz (X-Ku bands) [7]. The vibrating sample magnetometer (VSM) allowed the magnetic hysteresis loop to be determined.

2. Experimental

Each of several key-metal cations reacts with citric acid, under controlled pH conditions, to give the respective metal citrate, comprising a homogeneous joint metallic citrate precursor complex.

Nano-sized $(\text{Co-Cu})_2\text{Z}$ structured powders were synthesized by the citrate precursor method using reagent grade $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, monohydrate citric acid, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in stoichiometric molar ratios to obtain $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ hexaferrite. The solids were weighed and then placed into appropriate closed vessels subject to a super dry nitrogen atmosphere to obtain the precursor solutions [8]. Distilled water was added under agitation, until the total dissolution of the 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 the subsequent precipitation of the organometallic complex [8].

Pre-dried 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. While drying at 60 °C, leaving behind the desired solid phase, the remaining aqueous solution was eliminated. The ideal temperature for 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 on TA Instruments SDT-2960. The experiments were carried out in static air, using platinum crucibles between 20 and 1000 °C, with a heating rate of 10 °C/min.

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 hours at the sintering temperature. The material was then cooled to room temperature at the rate of 10 °C/min.

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 analysed in the form of a fused bead, using a 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 was employed with a dwell time of 1 deg/min in the θ -2 θ Bragg-Brentano geometry. Magnetic hysteresis loops were obtained using a vibrating sample magnetometer VSM 4,500 PAR. The morphological study was performed using a ZEISS DSM 940A scanning electron microscope and a Topometrix II® atomic force microscope.

In order to obtain composites for the measurements of microwave absorbing properties, the powders were mixed with polychloroprene (CR), resulting in a 80:20 composition (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). Vulcanised 8.0×4.0 cm² samples with variable thickness were obtained by compression moulding in a hydraulic press at 150 °C and 6.7 MPa. The vulcanisation 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.

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 in reflectivity (dB) versus frequency (GHz), using a HP 8510B network analyser system. The HP 8510B was employed to determine the values of ϵ' , ϵ'' , μ' , and μ'' at different frequencies, by measuring the reflected and transmitted scattering parameters, S_{11} and S_{21} . The materials were analysed in the frequency ranges 2.6–4.0 GHz (S band) and 8.0–16.0 GHz (X–Ku bands) [7, 9, 10].

3. Results and discussion

Results of the X-ray fluorescence analysis (Table 1) confirmed the elimination of the organic precursor and showed that the synthesized powders achieved the planned stoichiometry.

Table 1. Chemical composition of $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$

Compound	Content (wt. %)
BaO	18.17
CoO	2.66
CuO	3.46
Fe_2O_3	75.71

Figure 2 shows TGA and DTA curves of the precursor gel. No significant weight loss occurred above 400 °C, indicating that any remnant organic material had already been completely eliminated [9]. Based on this result, the gel was calcined at 410 °C.

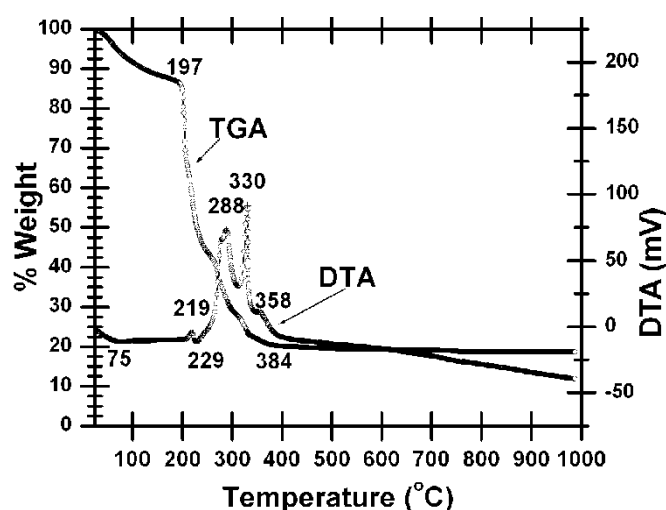


Fig. 2. TG-DTA curves for the Z-type precursor gel of $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ powder

XRD results presented in Fig. 3 indicate that at 950 °C the Z-type phase was clearly the majority phase, according to JCPDS 19-0097. According to Pullar et al., however, this material contains small undetectable amounts of the Y-type phase ($\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$), coexisting with the Z-type phase [11].

Atomic Force Microscopy (AFM) was used to characterize the Z-type ferrite powder and it is observed in Fig. 4 that the particles are sharply hexagonally plated with nanometric sizes ($230 \times 100 \text{ nm}^2$).

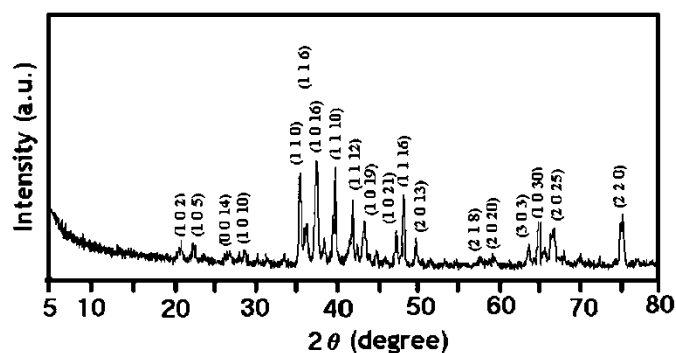


Fig. 3. X-Ray diffraction curve for the Z-type powder calcined at 950 °C

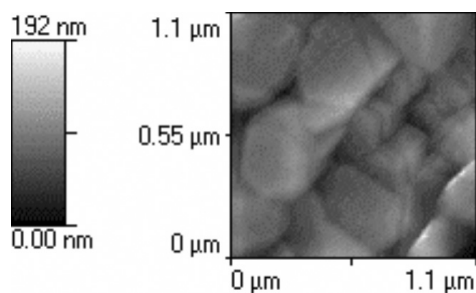


Fig. 4. AFM micrograph of $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ calcined at 950 °C (100 000 X, 200 kV)

The hysteresis curves for Z-type barium hexaferrites fired at 950 °C are shown in Fig. 5. The magnetization curves show typical features of magnetically soft ferrites. The saturation magnetization M_s was obtained by extrapolating $M(1/H)$ curves to $1/H = 0$, resulting in values of 57.8 emu/g for $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ and 52.3 emu/g for Co_2Z ($\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$).

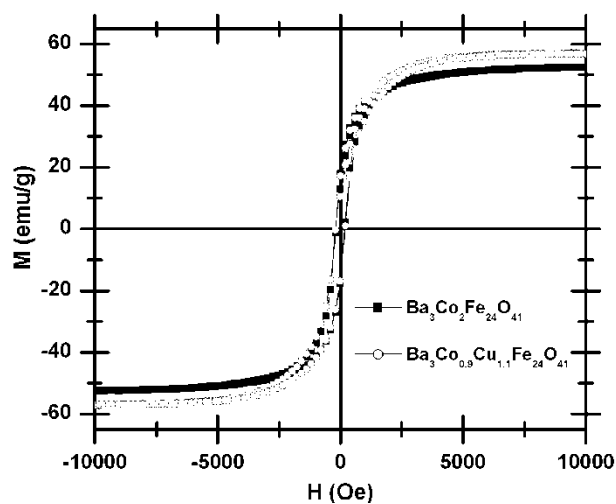


Fig. 5. Magnetic hysteresis curves of $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ and $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$ powders

The ionic radius of Cu^{2+} (0.085 nm) is very close to that of Co^{2+} (0.082 nm) and larger than that of Fe^{3+} (0.067 nm). The copper ions occupy the octahedral sites in the structure of Z-type hexaferrite and partially substitute cobalt ions. The Cu^{2+} ions distort the crystalline field due to their electronic configuration, and this behaviour results in an increase in M_s [5].

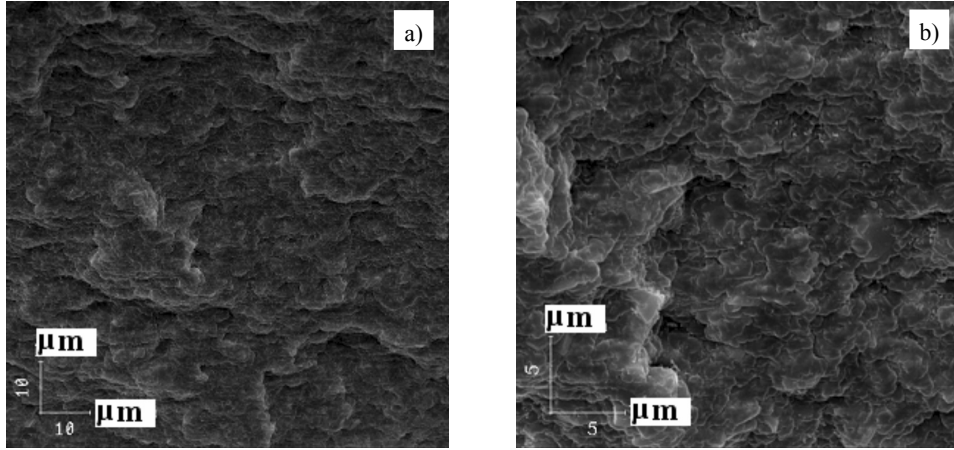


Fig. 6. SEM micrographs of $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}:\text{CR}$; magnification: a) 1000 \times , b) 3000 \times

Figures 6a and b show a good dispersion of Z-type hexaferrite magnetic particles in the polychloroprene matrix (80:20, wt. %). It can be seen from the SEM images (Fig. 6) that rubber mixing is a very good technique for the dispersion of Z-type hexaferrite particles, in spite of a high weight concentration used (80%) and the tendency of these particles to form magnetic agglomerates [7].

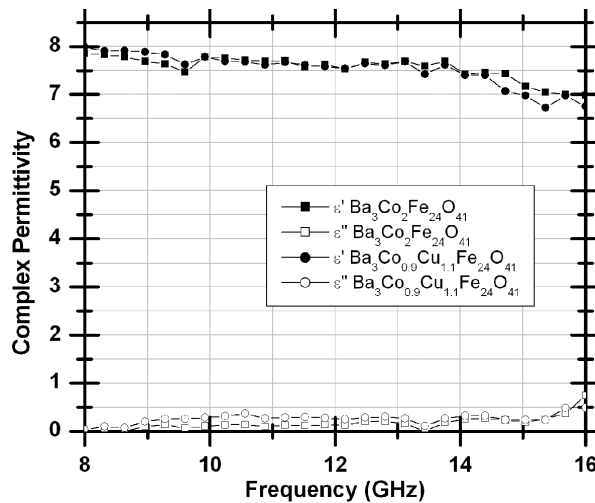


Fig. 7. Frequency dependences of the complex permittivity for the composites

Figure 7 indicates that the addition of Cu does not cause a significant variation in the permittivity measurements with frequency. Figure 8 shows the larger values of permeability for the $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$:CR nanocomposite, which can be attributed to the addition of Cu.

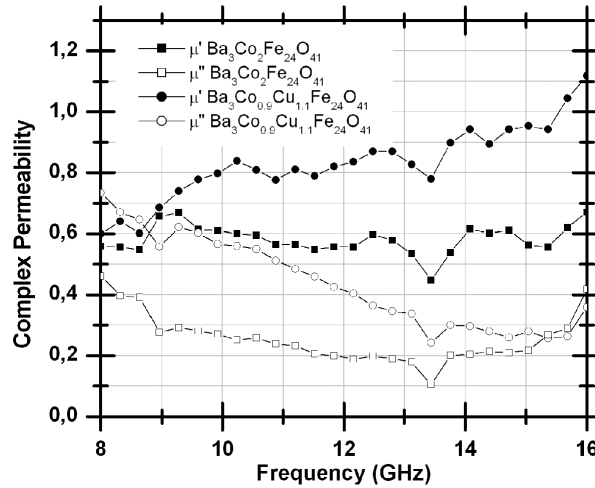


Fig. 8. Frequency dependences of the complex permeability for the composites

The microwave absorption spectra for the $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$:CR nanocomposites of various thicknesses are illustrated by the reflectivity curves in Fig. 9, for the frequency ranges: (a) 2.6–4.0 GHz (S-band), (b) 8.0–16 GHz (X-Ku bands) [12, 13].

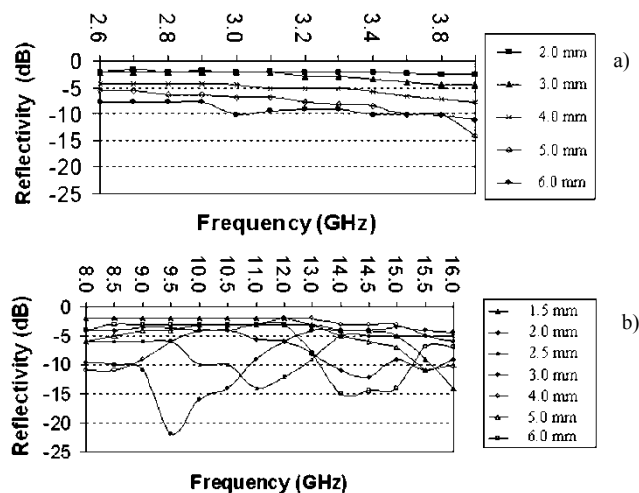


Fig. 9. Reflectivity curves for 80:20 (wt. %) $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$:CR composites: (a) S-band and (b) X-Ku bands

As seen in Fig. 9b, the $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$:CR nanocomposites (80:20) showed better performance as RAMs for the X-Ku bands (8–16 GHz), with smaller thickness. A microwave absorption of 90.00 % (a reflectivity of -10 dB) was observed in the frequency range 10.0–13.0 GHz for the thickness of 2.5 mm, with a maximum absorption of approximately 96.90 % (-15 dB) at 11.0 GHz. The effect of adding Cu on reflectivity measurements can be seen in Fig. 10.

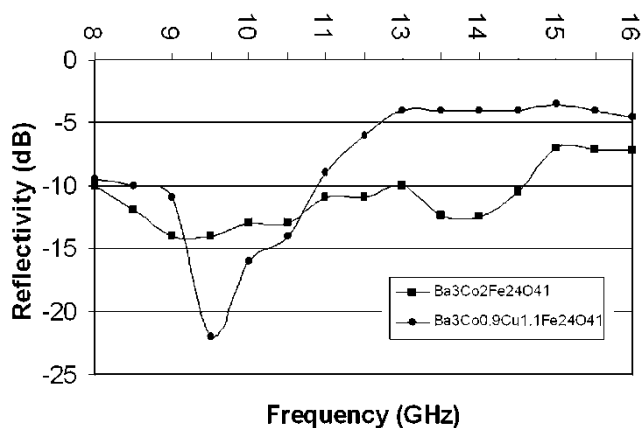


Fig. 10. The effect of adding Cu on the reflectivity measurements for 80:20 composites of $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$: CR and $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$:CR, with thicknesses of 3.0 mm

The highest microwave absorption for the $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$:CR nanocomposite (99.50% at 9.5 GHz) with the thickness of 3.0 mm can be attributed to the addition of Cu, resulting in an increase of the magnetic properties.

4. Conclusions

The citrate method promoted the formation of nanocrystalline Z-type hexaferrite at a lower temperature (950 °C) than that employed by the conventional methods (1200–1300 °C). The introduction of Cu^{2+} ions improved the magnetic properties of this ceramic, as illustrated by an increase of 5.5 emu/g in M_s and permeability. As a result, the 80:20 nanocomposite of $\text{Ba}_3\text{Co}_{0.9}\text{Cu}_{1.1}\text{Fe}_{24}\text{O}_{41}$:CR with the thickness of 3.0 mm showed the best performance as a RAM for the X-band, with a microwave absorption of 99.50% (-22.5 dB) at 9.5 GHz. This result allows its application by covering some strategic metallic parts of Brazilian Frigate superstructures, reducing the radar cross section of these targets.

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