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Co_2Z Hexaferrite obtained by the citrate precursor method in an inert atmosphere

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ABSTRACT

Nanoparticles of Co_2Z hexaferrite were synthesized by the citrate sol-gel process under an inert atmosphere, then thermally analyzed by Thermogravimetric and Differential Thermal Analysis and characterized by X-ray Diffraction, Scanning Electron Microscopy, Atomic Force Microscopy, X-ray Fluorescence and Vibration Sample Magnetometry. Z-type barium hexaferrite is a promising material for application in high frequency electronic devices involving up to 100 MHz, such as multi-layer chip inductors (MLCI), which require magnetic materials with high initial permeability, high resistivity, low magnetic and dielectric loss, and good thermal stability.

Keywords: Co_2Z hexaferrite, inert atmosphere, hysteresis, citrate, microstructure.

1 INTRODUCTION

Ultra high frequency (UHF) devices today are increasingly applied in miniaturized components, and the demand for even more diminutive products and components has led to the development of a component-track linking process using surface mounting devices (SMD). This process links terminals directly to tracks based on a technique similar to binding with glue, replacing the electric links with terminals that cross the perforations of an integrated circuit board (ICB) [1].

Component miniaturization has reduced the dimensions of copper tracks and their gaps and enhanced circuit integration, enabling integrated circuits to carry out an even growing number of functions, since greater numbers of components are mounted on the same surface area. The increasing complexity of interconnections has also given rise to another major change in process technology, beginning with the advent of double-faced boards with tracks on both sides of the ICB, followed by the introduction of multi-layer boards [1].

Multi-layer chip inductors (MLCI) are the most important passive SMDs of today's modern electronic industry [1-3], but the technology required for MCLIs is less advanced than that of multi-layer chip capacitors and resistors. Therefore, increasing interest is now focusing on the study of new materials for this application.

Hexagonal ferrites are part of a large family of ferromagnetic oxides with useful properties and there are many types of hexagonal ferrites (M, X, W, Y, Z and U). This paper discusses the Z-type barium hexaferrite ($Ba_3Co_2Fe_{24}O_{41}$ or Co_2Z), which is one of the materials used in the manufacture of MLCIs and which displays high performance at hyper-frequencies (100-1000 MHz). MLCIs are produced by tape-casting ferrite and screen printing internal electrode pastes alternately and then cofiring them.

Although Co_2Z hexaferrite is a promising material, NiZnCu is still the ferrite commercially used for this application. However, the disadvantage of NiZnCu ferrite is its low resonance frequency. Its spinel structure has a cut-off frequency below 300 MHz[2]. The Co_2Z hexaferrite can be considered the ideal material for MLCI applications in bands ranging from 300 to 1000 MHz, displaying high permeability, dielectric constants and ferromagnetic resonance from 1 to 3 GHz [4].

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Due to its complex crystalline structure, the temperature required to sinter the Z-type phase of Co_2Z must reach 1300°C when the conventional ceramic method is used. However, chemical synthesization methods require lower sintering temperatures. The citrate precursor method yields a more homogeneous nanomaterial at lower processing temperatures.

Due to the complex chemical composition of Co_2Z, any deviation from the stoichiometry or the appropriate oxidation states of the component elements can affect the magnetic properties of this material adversely [5]. One advantage resulting from the use of the citrate method is the homogeneity of the composition obtained.

Some aspects of the synthesis require special attention, such as the O_2 pressure. Based on a thermodynamic analysis [6], the authors concluded that both H_2O (g) and CO_2 (g) are less detrimental to the formation and stability of hexaferrite as the system's temperature rises.

The use of inert atmospheres or CO_2 (g) and H_2O (g) pressures of less than 10^{-13} allow the formation of barium hexaferrite at relatively low temperatures with a minimal formation of $BaCO_3$.

2 MATERIALS AND METHODS

The ultrafine Co_2Z powders were synthesized by the citrate precursor method, starting from $Fe(NO_3)_3.9H_2O$, $Ba(NO_3)_2$, monohydrate citric acid and $Co(NO_3)_2.6H_2O$ stoichiometric molar ratios to produce $Ba_3Co_2Fe_{24}O_{41}$ ferrite. The solutions were prepared by weighing the solids and placing then into appropriate closed vessels subjected to a superdry nitrogen atmosphere. Distilled water was added by injection (using a syringe) to each vessel, under agitation, until the solids were completely dissolved.

The solutions were then transferred to a balloon and mixed; this balloon was previously evacuated and then filled with superdry nitrogen operating as a reflux condenser under intensive stirring. The resulting mixture was heated to 80ºC to complete the reaction under reflux in order to keep the atmosphere inside the reaction vessel inert and to allow for subsequent additions of NH_4OH. Ammonium hydroxide was added dropwise into the solution to render it neutral or slightly alkaline. In the latter case, the pH was about 8.0, a condition suitable for subsequent precipitation of organometallic complexes.

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.

Predried ethanol was then added dropwise under vigorous stirring into the reaction mixture to promote the precipitation of a complex citrate gel of barium, iron and cobalt (see Figure 1).

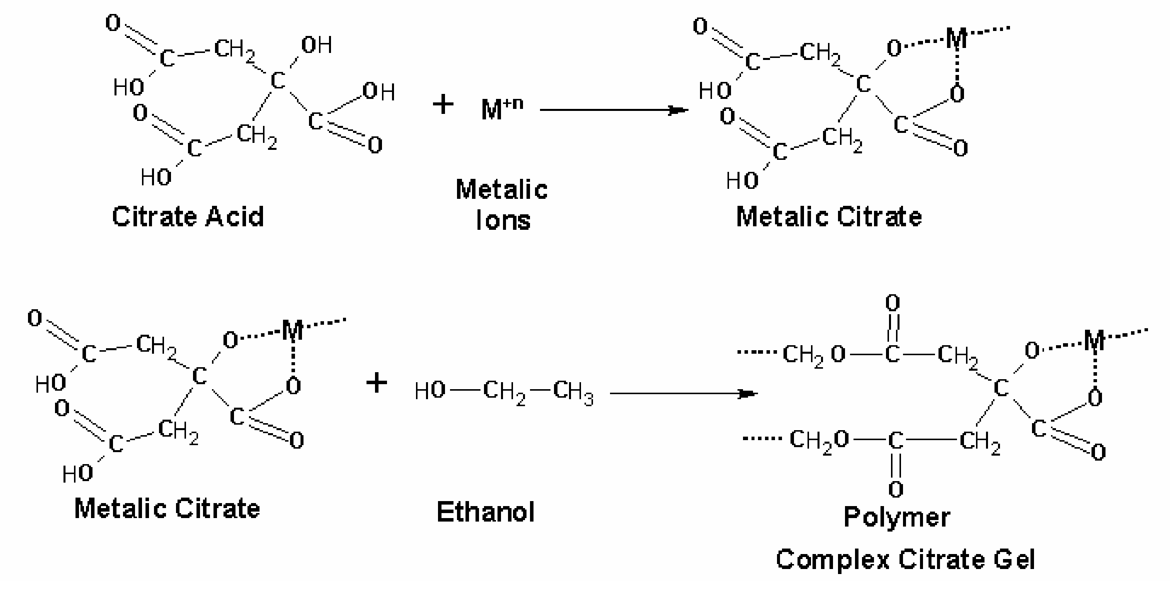


Figure 1: Reactions in the citrate precursor method

Following the above procedure, the remaining aqueous solution was eliminated by drying at 70°C, leaving behind the desired solid phase. The entire synthesization process was carried out in a superdry nitrogen atmosphere to prevent contact of the solutions with contaminants, particularly carbon dioxide [6].

The ideal temperature for the citrate gel decomposition and the behavior of the complex under heating were determined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

Based on the results of these thermal analyses, the batch of dried solid was calcined inside a muffle furnace within a temperature range of 600 to 1200ºC.

The calcination was performed using the following heating schedule: 2°C/min up to 400°C, a 400°C plateau for 1 hour, 10°C/min up to the final sintering temperature with a 4-hour residence time at the sintering temperature. The material was then cooled to room temperature at a rate of 10°C/min.

The calcined product was subjected to X-ray diffraction in order to ensure the formation of the crystalline and magnetic phase of barium hexaferrite. X-ray fluorescence was also carried out to check the product's stoichiometry. The microstructure was evaluated by Atomic Force Microscopy and Scanning Electron Microscopy, and the magnetic hysteresis loop was determined by vibrating sample magnetometry.

3 RESULTS AND DISCUSSION

The X-ray fluorescence analysis (Table 1) confirmed that the synthesized powders of the present study reached the intended stoichiometry.

Table 1: Chemical compositions of $Ba_3Co_2Fe_{24}O_{41}$ powders obtained by X-ray Fluorescence.

Z-Type Hexaferrite	**Compounds (weight %)**			
	BaO	**CoO**	**ZnO**	**Fe_2O_3**
$Ba_3Co_2Fe_{24}O_{41}$	18.21	5.93	—	75.89

Figure 2 shows the TGA and DTA curves of the gel. No significant weight loss occurred above 400°C, indicating that any remanent organic material had already been completely eliminated [6, 7]. Based on this information, it was decided to calcine the gel above 400°C; the crystalline nature of the powders was confirmed by X-ray Diffraction.

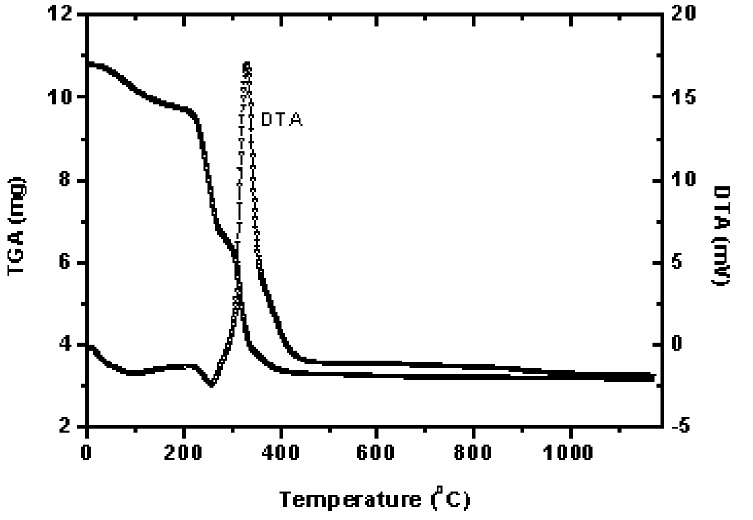


Figure 2: DTA and TGA curves for the metal citrate precursor behavior during heating, in air with heating rate of 10°C/min.

Unlike the preparation of pure $BaFe_{12}O_{19}$ by the citrate precursor method, the Z-type phase powder is not so easily produced due to the complexity of its structure, which imposes progressive transformations through intermediate ferrites before reaching the final desired structure.

The experimental results revealed the following transformations: (a) at 600°C, the material consisted of a mixture of hematite, $BaFe_2O_4$, $CoFe_2O_4$, $BaFe_{12}O_{19}$ (Ba M-type) and $Ba_2Co_2Fe_{12}O_{22}$ (Ba Y-type) [3]; (b) at 800°C, M-type and spinel phases were found; (c) at 850°C, the product consisted of Y and Z phases; (d) at 900°C, Co_2Z had already become the predominant phase; and (e) at 950°C, this Z-type phase had clearly become the major phase.

X-ray Diffraction analysis (Figure 3) indicates that at 950 °C, the Z-type hexaferrite phase was clearly the majority phase.

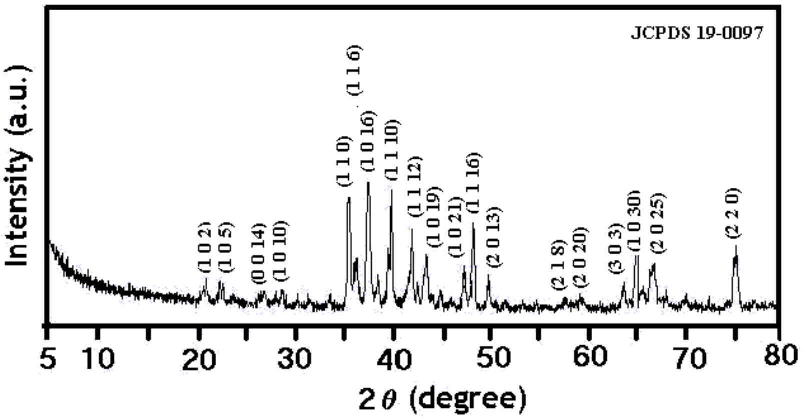


Figure 3: X-ray Diffraction pattern to the synthesized Z-type hexaferrite at 950°C.

Therefore, the use of an inert atmosphere effectively reduces the temperature required to form Z-type hexaferrite, a behavior remarkably unlike that which the same starting mixture undergoes when synthesized in air (instead of inert atmosphere), in which case the calcined product consisted of: (a) a mixture of Y and M-types at 1000°C; (b) Z-type phase peaks were evident only at 1150°C [8].

However, according to Pullar *et al.* [9, 10], the material synthesized in an inert atmosphere contains small undetectable amounts of Y-type phase ($Ba_2Co_2Fe_{12}O_{22}$) coexisting with the Z-type phase.

Atomic Force Microscopy was used to characterize powders obtained at 950°C (Figure 4). As can be seen, the particles are more or less uniform in size, in the shape of sharply hexagonal nanometric sized plates with 200 x 145 nm.

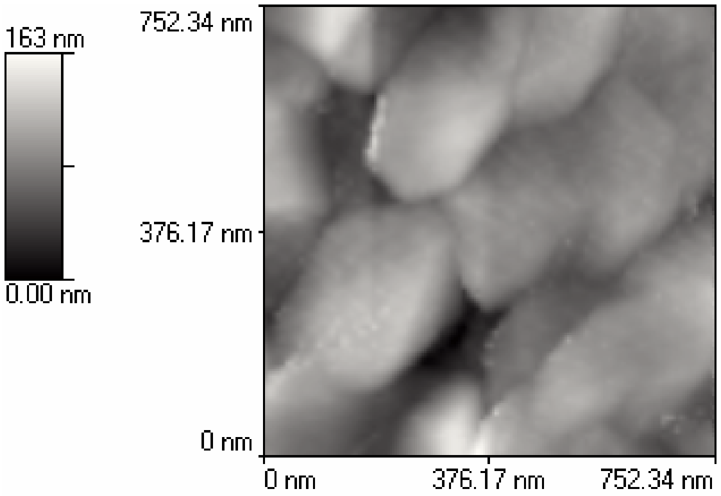


Figure 4: Atomic Force Micrograph of powder calcined at 950°C in inert atmosphere (X 50000).

To evaluate the microstructure of the compact material, disc-shaped compacts (1.5 cm diameter and 0.5 cm height), obtained by dry pressing the powder, were analyzed by scanning electron microscopy (the samples were mounted on aluminum supports and coated with a film of gold).

Large particles generally sinter more slowly and require higher sintering temperatures or longer sintering times to attain an equivalent degree of densification. Surface diffusion and grain boundary diffusion are usually predominant with smaller particles sizes.

As shown in Figure 5, the fracture surface micrograph of a sample sintered at 950°C/4h reveals a well densified material presenting grains of a hexagonal plate-like shape.

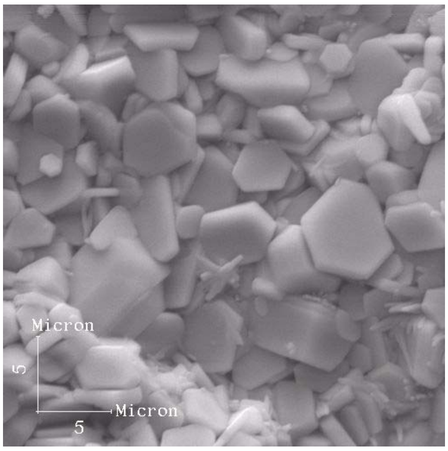
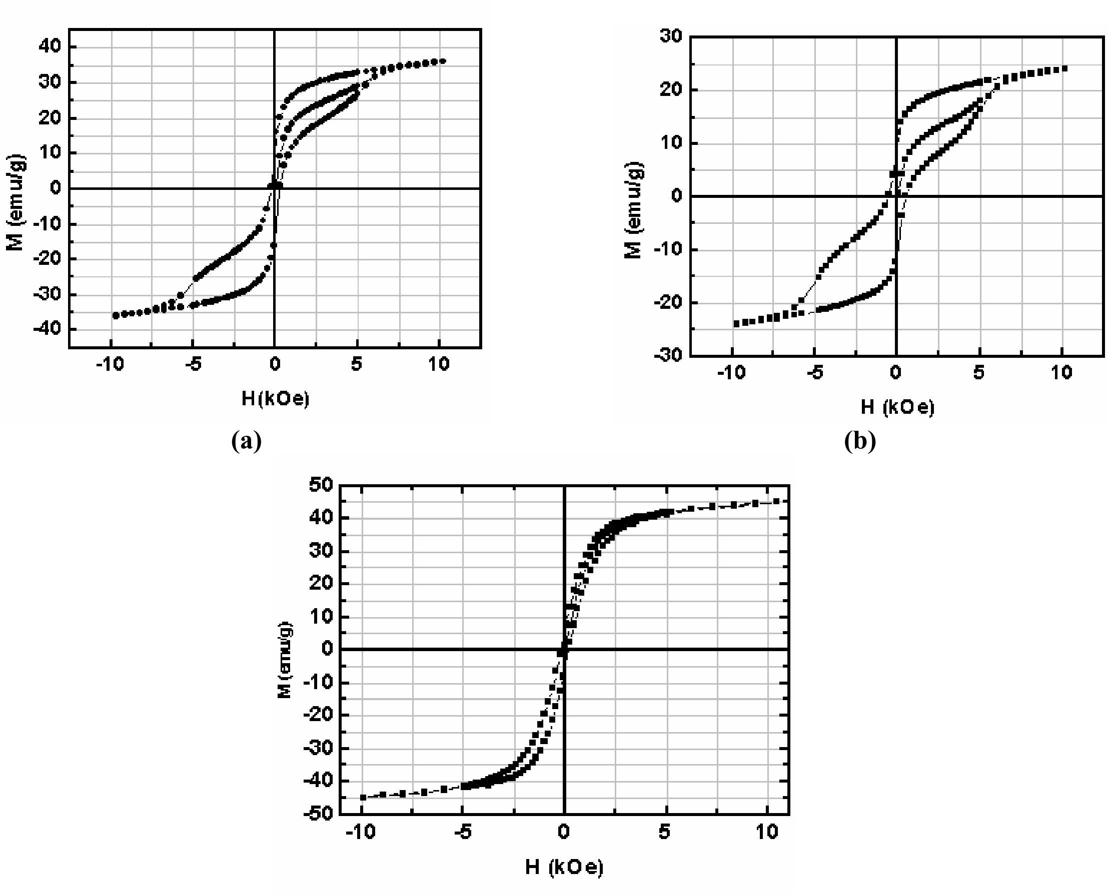


Figure 5: Scanning Electron microphotograph of Co_2Z powder synthesized at 950°C.

Magnetization of samples calcined at various temperatures was measured using a vibrating-sample magnetometer at both room temperature and high temperature. Figure 6 shows the magnetic hysteresis curves at room temperature for samples calcined at different temperatures.



(a)

(b)

(c)

Figure 6: The magnetization curves at room temperature of the samples: (a) calcinated at 600°C; (b) calcinated at 800°C and (c) calcinated at 950 °C.

The uncalcined powder presented magnetic properties, but it was a mixture of phases and the temperature had to be increased to obtain the Co_2Z ferrite phase.

The sample composed of M-type and spinel ferrites did not reach magnetic saturation because M-type ferrite has a very high anisotropic field. Obviously, the powder is a mixture of magnetically hard M-type phase and soft spinel phase.

The magnetization curves of the product synthesized in this work showed typical features of magnetically soft materials and a decreasing coercive force (H_c) and the remanent magnetization (B_r) were observed when the calcination temperature was increased, a behavior consistent with the disappearance of the M-type phase and increasing Z-type phase [6, 7].

The powder calcined at 900°C also showed no magnetic saturation, which was only achieved in the product calcined at 950°C for 4 hours (magnetization of 45.1 emu/g and a coercive force of 110 Oe).

4 CONCLUSIONS

The use of an inert temperature allowed us to obtain ultrafine Co2Z powders with hexagonal plate-like particles by the citrate precursor method at a calcination temperature below 950oC.

In addition to reducing the calcination temperature required for the formation of the Z-type phase, the method developed here allowed for the production of Z-type barium hexaferrite with excellent magnetic properties.

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