

# Magnetic properties of cobalt substituted M-type barium hexaferrite prepared by co-precipitation

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## Abstract

The co-precipitation and solid state methods were used in the synthesis of barium hexaferrite (BaM). Phase pure BaM was obtained with 1, 2, 3, 5, 10, 15, 20 and 30 wt% cobalt oxide ( $\text{Co}_3\text{O}_4$ ). The addition of  $\text{Co}^{2+/3+}$  ions to the BaM increased the permeability and magnetic loss tangent to a value of 3.5 at 5% and reduced to 1 at 30% doping. With increased Co doping,  $M_s$  was reduced from 87–58 emu/g,  $M_r$  increased from 11 to 40 emu/g with 3–5 wt% Co and 9 emu/g for 30% doping.  $H_c$  sharply increased from 540 to 2200 Oe with a reduction to 280 Oe at 10 K with increasing temperature to 300 K.  $T_c$  increased from 740 to 750 K for 30% Co doping. DTA–TGA studies of green body showed decarboxilation to occur at around 825 °C and the transformation of residual  $\text{Co}_3\text{O}_4$  to  $\text{Co}_2\text{O}_3$  at around 577 °C. The XRD data confirmed the Co ions substituting into Fe sites until a 10–15% doping level where the structure altered to W-type hexaferrite. The densities of the compounds varied with doping to a maximum of 4.45 g/cm<sup>3</sup>.

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## 1. Introduction

The permanent magnet and high density magnetic recording media [1–3] are just two of the many applications that exist for M-type hexagonal barium hexaferrite with its stoichiometric chemical formula  $\text{BaFe}_{12}\text{O}_{19}$ , often denoted as BaM. It is also known to possess high mechanical strength as well as superior stoichiometric stability. Ferrites and garnets are ferromagnetic oxides with dielectric and magnetic properties that are useful for RF and microwave applications. The parent oxide,  $\text{BaFe}_{12}\text{O}_{19}$ , is a hard ferrite with a hexagonal structure belonging to the space group of P63/mmc [4]. Due to high commercial interest in the suitability of this compound as a material for magnetic recording, much effort has been made to the production of cation substituted BaM to further improve its magnetic attributes. A variety of different cation substitutions are possible in  $\text{BaFe}_{12}\text{O}_{19}$ . Divalent transition metals such as

$\text{Ni}^{2+/3+}$  and  $\text{Co}^{2+/3+}$  for  $\text{Fe}^{2+/3+}$  are frequently used due to their similarity in ionic radii and electronic configurations. However, both the electrical and magnetic properties of substituted BaM ferrites are strongly dependent on the synthesis conditions as disproportionate charge distributions generally occur for multivalent cationic doping. There is also a concomitant structural implication when doping with  $\text{Co}^{2+/3+}$  ions influencing the magneto-dielectric properties of this compound. Thus, cobalt doping in particular has been the subject of many such investigations [5–7]. This paper examines the influence of thermogravimetric, crystal structural evolution from M-type to W-type hexaferrite, complex relative permeability and density in hexaferrites substituted by  $\text{Co}^{2+/3+}$  ions. Hexaferrites are classified into five main types depending upon chemical formula and crystal structure; these are M, W, X, Y and Z-type. The aim of introducing divalent cations such as cobalt into M-type stoichiometry was to reduce the loss at high frequencies whilst enhancing the permeability values. The preparation techniques as well as the structural doping of Co and/or Ti ions influence the magneto-dielectric properties of this compound. For example, Mosallaies [8]

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used barium hexaferrite mixed with cobalt oxide ( $\text{Co}_3\text{O}_4$ ) and barium carbonate ( $\text{BaCO}_3$ ), developed at Trans-Tech Inc., and obtained a material with relative permittivity, ( $\epsilon_r'$ ) and relative permeability, ( $\mu_r'$ ) both approximately 16, a loss tangent of 0.001 dielectric and 0.03 magnetic at a frequency of 500 MHz. These authors used the material in electronic band-gap (EBG) structures and microstrip patch antenna applications. However, they provided little experimental information as to the material preparation or synthesis method. It is also unclear about the actual stoichiometric composition of their material that has been characterised. Similarly, there are many other conflicting reports of the dielectric and magnetic properties of BaM with little or scarce information on the ceramic or sol-gel preparative method [9,10]. Therefore, the work presented within this paper is hoped to show the magnetic properties of BaM when doped with increasing quantities of cobalt. The synthesis of samples was performed by both the ceramic and co-precipitation methods. However, the results of measurements are for the co-precipitation prepared samples and the ceramic samples were done as a comparison, results of which are not presented within the paper. Dielectric property measurements of the compound are still in progress and will be reported at a later date.

## 2. Experimental

### 2.1. Synthesis

A chemically reliable co-precipitation route as well as the classic solid state synthesis method from relevant oxides was used in the preparation of a stoichiometric composition of BaM.

The solution route involved a slow and drop wise addition of excess ammonium hydroxide ( $\text{pH} = 12$ ) to the aqueous solution consisting stoichiometric amounts of nitrates of Ba and Fe (99.99% purity, Aldrich) that resulted in the co-precipitation of a gel like cake. The cake was thoroughly washed with deionised water and purified ethanol, dried at  $105^\circ\text{C}$  and was subsequently heated to various temperatures.

The ceramic method involved firstly the formation of stoichiometric monoferrite,  $\text{BaFe}_2\text{O}_4$  using  $\text{BaCO}_3$

(99.999% purity, Aldrich) and  $\text{Fe}_2\text{O}_3$  (99.98% purity, Aldrich) as raw constituents, followed by further reaction with excess  $\text{Fe}_2\text{O}_3$  to obtain barium hexaferrite. Following intermittent heating at  $800^\circ\text{C}$  for 3 h and grinding (in an agate mortar and pestle) various samples were formed and different percentages of  $\text{Co}_3\text{O}_4$  by weight were added to the phase pure  $\text{BaFe}_{12}\text{O}_{19}$ . Following further intermittent heating at  $800^\circ\text{C}$  for 3 h and grinding the final material samples were pelletised using a Specac uniaxial press to 6000 psi producing disk samples of 16 mm in diameter. Sintering of these pellets was carried out at temperatures ranging from  $900$  to  $1200^\circ\text{C}$ , the latter being the final sintering temperature. The barium cobalt ferrite composition produced by both methods was subjected to identical temperature regimes and time intervals.

### 2.2. Density measurements

The density of the samples from the green to a sintered state was measured using the well known liquid displacement Archimedes' technique. The measurements were carried out to record the change in density following various sintering treatment protocol.

### 2.3. X-ray diffraction measurements

Chemical composition analysis was carried out by powder X-ray diffraction (XRD). XRD patterns for samples of 0%, 3%, 15% and 30%  $\text{Co}_3\text{O}_4$  doping by weight treated at various temperatures and times were recorded in the region of  $2\theta = 10\text{--}80^\circ$  with a step scan of  $0.02^\circ/\text{min}$  on a Philips diffractometer (Model PW1710) using  $\text{CuK}_\alpha$  radiation. Automated powder diffraction software package that included both standard International Centre for Diffraction Data (ICDD) and calculated ICSD diffraction files was used to match the evolving phases. Cell parameters were calculated and further refined using linear regression procedures (Philips APD 1700 software) applied to the measured peak positions of all major reflections up to  $2\theta = 90^\circ$ .

The well-known Scherrer formula [11] was used to determine the crystallite size from the line broadening of diffraction profile of the strongest peak. The formula,

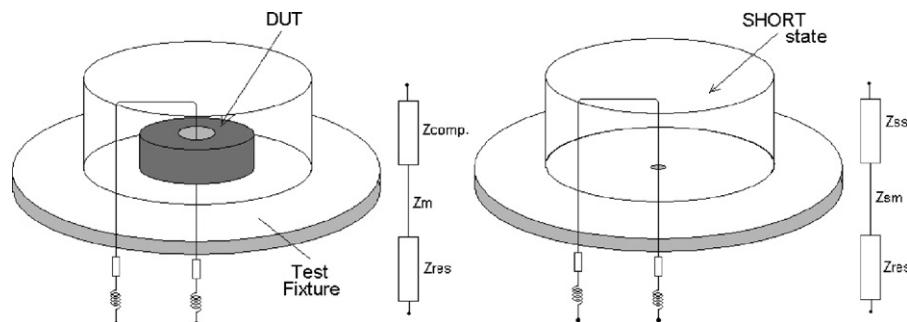


Fig. 1. (a) Parallel plate test fixture measurement method. (b) Equivalent circuit model.

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