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# Structural and Magnetic Properties of $BaCo_xFe_{12-x}O_{19}$ ($x$ = 0.2, 0.4, 0.6, &1.0) Nanoferrites Synthesized Via Citrate Sol-Gel Method

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## ABSTRACT

*Cobalt substituted barium ferrites*, $BaCo_xFe_{12-x}O_{19}$ ($x$ = 0.2, 0.4, 0.6 & 1.0) *have been synthesized via citrate sol-gel method. All the samples have been annealed at* 1000℃ *and characterized using Fourier Transform Infra Red spectroscopy*, *X-Ray Diffractography and Vibrating Sample Magnetometry. The FT-IR spectra of the samples exhibit two frequency bands in the range of* 580 $cm^{-1}$ *and* 460 $cm^{-1}$, *corresponding to the formation of metal oxides. The XRD studies reveal a crystallite size of* ~55 *nm. The saturation magnetization decreases from* 96.3 *emu/g to* 47.8 *emu/g with increasing concentration of cobalt due to the lower magnetic moment of* $Co^{2+}$ (3 $\mu B$) *as compared to* $Fe^{3+}$ (5 $\mu B$). *The coercivity values also show a decreasing behaviour from* 3800 *Oe to* 1750 *Oe with increasing cobalt concentration due to reduced magnetocrystalline anisotropy.*

**Keywords:** *Barium Ferrite*, *Magnetic Moment*, *Coercivity*, *XRD*

## 1. Introduction

M-type Barium hexaferrites are magnetically hard materials that possess versatile properties like high saturation magnetization, high coercivity, large uniaxial anisotropy and excellent chemical and magnetic stability. These properties make them well suited materials for numerous applications. They have been extensively used in permanent magnets, high density recording media and magneto optical recording technologies [1-4]. In addition, they are suitable microwave absorbing materials due to a significant permeability value (>1) [5].

$BaFe_{12}O_{19}$ has a magnetoplumbite structure and its unit cell is a combination of two structural blocks aligned in the direction of hexagonal c-axis: $RSR^*S^*$. In R block, the lattice is made of $O^{2-}$ ions, forming a hexagonal closed packed structure, with iron ions occupying the tetrahedral, octahedral and bipyramidal sites. However, in S block, $O^{2-}$ ions form a cubic closed packed lattice and iron ions occupy the tetrahedral and octahedral sites [6]. It is well known that their structural and magnetic properties are closely connected to the distribution of Fe ions among various interstitial sites, and it has been found that these properties can be changed by doping of $Fe^{3+}$ and $Ba^{2+}$ with different types of cations and cation combinations. Due to this, researchers have a lot of interest in modifying structural, magnetic and electrical properties of nanoferrites, according to the requirement for various practical applications by different cation substitutions and by using different synthetic routes under varying conditions [7-11]. Sandaranarayanan *et al*. [7] studied the effect of annealing temperature on Barium ferrites and reported that their crystallization begins around 550℃ and fully crystalline phase is obtained in the range of 700℃ - 900℃. Mendoza-Suarez *et al*. [8] synthesized Zn-Sn doped Ba ferrites, $BaFe_{12-2x}Zn_xSn_xO_{19}$, using ball milling method and found that the coercivity decreases due to reduction of the magnetocrystalline anisotropy. The saturation magnetization has also been reported to decrease with increase in Zn-Sn concentration. Kresisel *et al*. [9] reported that with increasing concentration of Co-Ti dopants in barium ferrites, axial anisotropy reduced and further changed to nearly planar magnetic anisotropy. Teh *et al*. [10] synthesized $Co^{2+}$ and $Co^{3+}$ substituted Ba ferrites via sol-gel method and found that $Co^{2+}$ doping decreases the value of coercivity and saturation magnetisation significantly. However, $Co^{3+}$ doping shows less change in magnetic properties. Ghasemi *et al*. [11] prepared Mn-Co-Zr substituted Ba ferrites and studied that substitution of these cations is very effective in reduction of coercivity at low level of substitution.

 

The present work deals with the formation of nanoferrites of cobalt substituted M-type barium ferrites via citrate sol-gel method. Their characterisation has been done by Fourrier Transform Infrared (FT-IR) spectroscopy, powder X- Ray Diffraction (XRD) studies and Vibrating Sample Magnetometry (VSM). The effect of increasing $Co^{2+}$ concentration on the magnetic properties has also been studied.

## 2. Experimental

### 2.1. Synthesis

$BaCo_xFe_{12-x}O_{19}$ ($x$ = 0.2, 0.4, 0.6, 0.8 & 1.0) were synthesized using the citrate sol-gel method [12,13]. AR grade $Ba(NO_3)_2$, Fe $(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$ and citric acid were weighed in appropriate stoichiometric proportions and dissolved in minimum amount of distilled water at 80℃. Ethylene glycol was added as gelling agent. Then, all the dissolved solutions were mixed with continued stirring and a homogenous mixture was obtained. The resulting solution was then heated at 10℃ and stirred using a hot plate magnetic stirrer that resulted in gel formation. Thermal decomposition was carried out and the ferrite powder was obtained, which was annealed at 1000℃ for 2 hours in muffle furnace.

### 2.2. Physical measurements

Fourier Transform infra red (FT-IR) spectra have been recorded using Perkin Elmer RX-1 FT-IR spectrophotometer with KBr pellets in the range 4000 – 400 $cm^{-1}$. Powder X-ray diffraction (XRD) studies have been carried out using a Bruker AXS, D8 Advance spectrophotometer with Cu-Kα radiation Hitachi (H-7500). The magnetic properties have been measured at room temperature by a Vibrating Sample Magnetometer (VSM) (155, PAR) up to a magnetic field of ±10 kOe.

## 3. Results and Discussion

### 3.1. FT-IR Measurements

The FT-IR spectra of all the ferrite compositions have been recorded in the range of 4000 - 400 $cm^{-1}$, using KBr plates. In the low frequency range, the spectra show two main peaks corresponding to the vibrational modes of metal oxide of ferrites that are interpreted in the light of literature study of absorption region of ferrite [14]. The peak observed in the range of 580 $cm^{-1}$ is attributed to the stretching vibration of tetrahedral group. However, the peak in the range of 460 $cm^{-1}$ is due to stretching vibration of octahedral group.

### 3.2. X-Ray Diffraction Studies

The powder X-Ray diffractographs for all the as obtained as well as annealed samples have been recorded and are shown in **Figure 1**. The XRD patterns of the ferrite samples show characteristic diffraction peaks corresponding to the M-type barium ferrite structure, having point group $P6_3/mmc$, indicating that the crystal structure does not transform and remains hexagonal magnetoplumbite after substitution with cobalt ions. The average crystallite size for each composition has been calculated from the line broadening of the most intense peak corresponding to (1,1,4) plane of magnetoplumbite structure according to Scherrer equation [15] given below

$$D = k\lambda/\beta\cos\theta$$

where $D$ is the average size of the crystallites, $k$ is the scherrer constant, $\lambda$ is the wavelength of radiation (1.5405 Å), $\beta$ is the peak width at half height or full width half maximum. The values of crystallite size are listed in **Table 1** and the average crystallite size is found to be ~55 nm.

The lattice parameters, $a$ and $c$, have been calculated using Powley as well as Le-Bail refinement methods (built in TOPAS V2.1 of BRUKER AXS), and are listed in Table 1. It is observed that the lattice parameters remain constant on increasing $Co^{2+}$ concentration.

### 3.3. Magnetic Properties

The room temperature magnetic hysteresis loops for all the as obtained as well as annealed samples have been recorded. Typical loops for all the annealed ferrite samples are shown in **Figure 2**. From these plots, saturation magnetization ($M_s$), coercivity ($H_c$) and squareness ratio ($S_q$) have been calculated and are given in **Table 1**. From **Table 1**, it is seen that the saturation magnetization decreases as the $Co^{2+}$ concentration is increased. This is

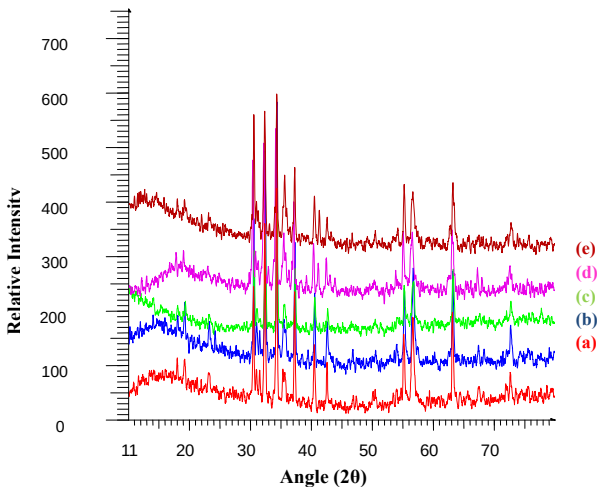


**Figure 1. X-Ray diffractographs of (a) $BaCo_{0.2}Fe_{11.8}O_{19}$; (b) $BaCo_{0.4}Fe_{11.6}O_{19}$; (c) $BaCo_{0.6}Fe_{11.4}O_{19}$; (d) $BaCo_{0.8}Fe_{11.2}O_{19}$; (e) $BaCo_{1.0}Fe_{11}O_{19}$ annealed at 1000℃.**

 

**Table 1. Crystallite size, *D* (nm); Lattice parameter (*a*); Saturation Magnetisation ($M_s$), Coercivity ($H_c$) and Squareness Ratio ($S_q$) of the ferrites annealed at 1000℃.**

| Ferrite composition | Lattice parameter (Å) | Crystallite size D (nm) | Saturation Magnetization $M_s$ (emu/g) | Coercivity $H_c$ (Oe) | Squareness Ratio ($S_q$) |
|---|---|---|---|---|---|
| $BaCo_{0.2}Fe_{11.8}O_{19}$ | $a$ = 5.8846<br>$c$ = 23.1640 | 45.43 | 96.27 | 3800 | 0.5920 |
| $BaCo_{0.4}Fe_{11.6}O_{19}$ | $a$ = 5.8920<br>$c$ = 23.1943 | 62.99 | 55.77 | 3500 | 0.5826 |
| $BaCo_{0.6}Fe_{11.4}O_{19}$ | $a$ = 5.8835<br>$c$ = 23.1742 | 64.46 | 53.59 | 2800 | 0.5597 |
| $BaCoFe_{11}O_{19}$ | $a$ = 5.8801<br>$c$ = 23.1772 | 52.29 | 47.81 | 1750 | 0.4914 |

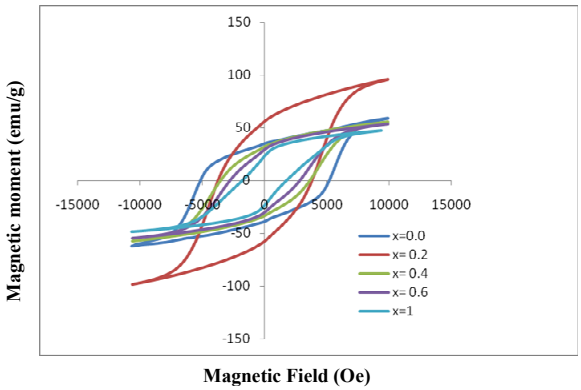


**Figure 2. Hysteresis loops of $BaCo_xFe_{12-x}O_{19}$ ($x$ = 0.0, 0.2, 0.4, 0.6, 1.0) annealed at 1000℃.**

attributed to the lesser magnetic moment of $Co^{2+}$ ions (3 μB) as compared to $Fe^{3+}$ ions(5 μB) and their substitution in 12k and 2a sites of the lattice, in preference to the $4f_2$ sites. The coercivity value decreases from 5200 to 1750 Oe with increasing cobalt concentration ($x$ = 0.0 to 1.0) due to reduction in magnetocrystalline anisotropy [16,17].

The value of squareness ratio has been calculated by formula

$S_q=M_r/M_s$

where $M_r$ is the remnance and $M_s$ is the saturation magnetisation. From **Table 1**, it is observed that the squareness ratio increases with increase in cobalt ion concentration.

## 4. Conclusions

Cobalt substituted barium ferrites $BaCo_xFe_{12-x}O_{19}$ (0.2, 0.4, 0.6 & 1.0) were synthesized using citrate sol-gel method. The formation of M-type ferrites has been confirmed by FT-IR and XRD characterization. The crystallite size is found to be ~55 nm. The values of saturation magnetization and coercivity decrease with increasing cobalt substitution due to less magnetic moment of $Co^{2+}$ ions as compare to $Fe^{3+}$ ions and reduced magnetocrystalline anisotropy respectively.

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