NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2013, 4 (3), P. 363–369

STRUCTURAL PROPERTIES OF COBALT SUBSTITUTED BARIUM HEXAFERRITE NANOPARTICLES PREPARED BY A THERMAL TREATMENT METHOD

C. C. Chauhan[1], R. B. Jotania[2], K. R. Jotania[3]

[1]Department of Physics, Institute of Technology, Nirma University, Ahmedabad 382 481, Gujarat, India

[2]Department of Physics, University School of Sciences, Gujarat University, Navrangpura Ahmedabad 380 009, Gujarat, India

[3]Department of Physcis, Faculty of Science, The M. S. University of Baroda, Vadodara 390 002, Gujarat, India

chetumakwana@gmail.com, rbjotania@gmail.com, kanti.jotania@gmail.com

PACS 81.05.-t,81.05.Zx, 81.07.b, 81.07.Wx,81.40-z,61.46.-W, 68.37.Hk

A series of M-type hexagonal ferrites with $BaCo_xFe_{12-x}O_{19}$ (x = 2.0, 3.0) composition were synthesized using a simple heat treatment method. The aqueous solution, containing metal nitrates and polyvinyle pyrrolidone (PVP) as a capping agent was used to prepare M-type barium hexferrite nanoparticles. The prepared hexaferrite particles were calcined at microwave frequency (2.45 GHz, power 900W, 5 min) as well as at 650 ° C temperature. The structural properties of the samples were investigated using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). XRD pattern shows the pure M-phase. The particle size of the powder prepared by this method ranged from 20 nm to 27 nm. The thermal properties of the sample were investigated by thermogravimetric Analysis (TGA), which confirmed the thermal stability of the barium hexaferrite sample prepared by the heat treatment method.

Keywords: capping agent, hexaferrite particles, thermal treatment.

1. Introduction

Hexaferrites are classified into six fundamental types: M, W, Y, X, Z and U on the basis of their chemical composition and crystal structure [1, 2]. The crystal structures of these different types of hexaferrites are very complex and can be considered as a superposition of T, R and S blocks along the hexagonal *c*-axis [3]. M-type barium hexaferrite is a very useful material as an absorber of electromagnetic radiation in the microwave region [4]. The molecular structure of M-type ferrite is made up of one R and one S block with an overlap of hexagonally and cubically packed layers. The crystal structure of $BaFe_{12}O_{19}$ is described as SRS*R*, where R is a three layer block (O_4—BaO_3—O_4) with composition $BaFe_6O_{11}^{2-}$ and S is a spinel like two layer block (O_4—O_4) with composition $Fe_6O_8^{2+}$. Here the asterix (*) means the corresponding block has been turned 180 ° around the hexagonal *c*-axis. The O^{4-} and BaO^{3-} layers form a close packing. In this structure the smaller iron cations are distributed within five different kinds of sites (Three Octahedral — 12k, 2a, $4f_2$, one tetrahedral — 4f and one pseudo tetrahedral trigonal bi pyramidal — 2b). The ordering of magnetic moments of Fe^{+3}ions and the strong super exchange interaction explain the excellent magnetic behaviour of these materials [5].

Barium hexaferrite is currently of technical interest because of its permanent magnetic property, high uniaxial magneto-crystallilne anisotropy, saturation magnetization, excellent chemical stability and corrosion resistance [6, 7]. Recently, ceramic materials have been classified by their high resistivity and high permeability, resulting in their use in a number of applications, e.g. industry, technology, electronic devices, communication equipment, high density magnetic recording media, materials for permanent magnets and microwave devices[2, 8–12].

In the present work, barium hexaferrite nanoparticles were synthesized from an aqueous solution of metal nitrates, polyvinyl pyrrolidone and deionized water using a thermal treatment method. This method did not require the addition of other chemicals as surfactants, and had an advantage of simplicity, low cost, no byproducts and was environmentally benign. The structural and morphological characteristics of the prepared barium hexaferrite nanoparticles were studied to verify the particle size.

2. Sample Preparation

Barium hexaferrite particles were synthesized using metal nitrate precursors with polyvinyl pyrrolidone (PVP) as a capping agent and deionized water as the solvent. The aqueous solution of PVP was prepared by dissolving 3 g of PVP in 100 ml of deionized water. The mixture was heated at 70 ° C for 2 hours then after 1.2 mmol iron nitrate and 0.1 mmol barium nitrate added in the solution (pH of solution was 1–2). The obtained solution was kept under constant magnetic stirring for 2 hours until a colourless transparent solution was obtained and then solution was heated at 80 ° C for one hour to evaporate the water. The resulting orange solid dried powder was crushed for 15 min and heated at 650 ° C for 3 hours in order to pyrrolyze the organic compounds and crystallize the nanoparticles. The prepared barium hexaferrite particles were also calcined via microwave irradiation (2.45 GHz, 900 W, 5 min).

3. Experimental Techniques

Prepared barium hexaferrite samples were characterized using various experimental techniques to study structural properties and particle size. The structure and phase purity of $BaCo_xFe_{12-x}O_{19}$ (x = 2.0, 3.0) samples were investigated on a Philips X-ray diffractometer (PW 1830) using CuKα radiation (λ=1.5405 Å) with a scan rate of 0.02 degree/min. The room temperature infrared (IR) spectrum of $BaCo_2Fe_{10}O_{19}$ hexaferrite sample heated at 650 ° C was recorded in the mid IR range (4000cm^{-1} to 400cm^{-1}) using a FTIR spectrophotometer (Bruker Tensor 27 Model). Scanning electron micrographs of prepared barium hexaferrite samples were obtained using a Make-Leo/Lica model Stereo scan 440 scanning electron microscope.

3.1. XRD Analysis

Fig. 1 shows the XRD patterns of $BaCo_xFe_{12-x}O_{19}$ (x = 2.0, 3.0) hexaferrite samples calcined at 650 ° C for 3 hours and heated with microwave irradiation. The XRD pattern of all samples showed pure M-phase. All samples exhibited quite similar XRD patterns. The average particle size of the M-type hexaferrite was calculated from the full width at the half maximum (FWHM) of the XRD patterns, using the well known Scherer formula:

$$d = 0.90\frac{\lambda}{\beta cos\theta}, \tag{1}$$

where d is the crystallite size (nm), β is the full width of the diffraction line at half of the maximum intensity measured in radians, λ is the X-ray wavelength of Cu Kα = 0.154 nm and θ is the Bragg angle.

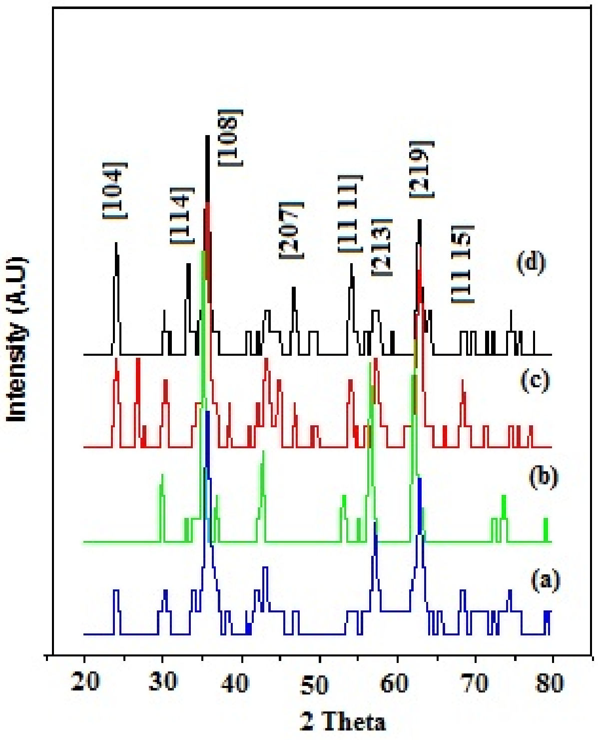

Fig. 1. X-ray diffraction pattern of (a) $BaCo_2Fe_{10}O_{19}$ calcinated at 650 ° C (b) $BaCo_2Fe_{10}O_{19}$ heated with microwave irradiation (c) $BaCo_3Fe_9O_{19}$ calcinated at 650 ° C and (d) $BaCo_3Fe_9O_{19}$ heated with microwave irradiation

Lattice constants a and c of hexagonal barium cobalt hexaferrites were calculated using Eq.(2):

$$\frac{1}{d} = \frac{4}{3}\frac{h^2 + k^2 + l^2}{a^2} + \frac{l^2}{c^2}, \tag{2}$$

where h, k and l are Miller indices, d is inter planer distance. Lattice volume of all the samples can be obtained using Eq.(3):

$$V = \frac{\sqrt{3}}{2}a^2c \tag{3}$$

The cell volume was observed to increase with higher cobalt content (Table 1). The microwave heated samples showed small cell volume relative to conventionally-heated samples. It is seen from the table 1 that lattice parameters a and c were slightly decreased with increased cobalt content. The calculated values for lattice parameters a and c are in agreement with previous literature [13]. The cell volume changed little with varying cobalt content, as the ionic radius of both the ions are almost same (Co^{+2} = 0.65 Å and Fe^{+3}= 0.645 Å).

Table 1. Structure Parameters a and c and cell volume V for hexaferrite samples

$BaCo_xFe_{12-x}O_{19}$ (x = 2.0, 3.0)	Heat treatment	a (nm)	c (nm)	c/a	Cell volume V $(nm)^3$
$BaCo_2Fe_{10}O_{19}$	650 °C	0.550	2.3456	4.2647	1.291
$BaCo_2Fe_{10}O_{19}$	Microwave	0.545	2.3780	4.3633	1.284
$BaCo_3Fe_9O_{19}$	650 °C	0.548	2.3423	4.2742	1.36
$BaCo_3Fe_9O_{19}$	Microwave	0.5445	2.3772	4.3658	1.294

Table 2. Crystalline Size from Debye Scherrer Formula

$BaCo_xFe_{12-x}O_{19}$ (x = 2.0, 3.0)	θ (degree)	Cos θ	β FWHM (rad)	Crystalline size d (nm)
$BaCo_2Fe_{10}O_{19}$ (650 °C)	17.314	0.9546	0.0052	27.87
$BaCo_2Fe_{10}O_{19}$ (microwave)	17.32	0.9546	0.0062	23.22
$BaCo_3Fe_9O_{19}$ (650 °C)	17.171	0.9559	0.0061	23.89
$BaCo_3Fe_9O_{19}$ (microwave)	17.22	0.9551	0.0068	20.89

3.2. FTIR Analysis

Figure 2 shows FTIR spectrum of $BaCo_2Fe_{10}O_{19}$ hexaferrite heated at 650 °C recorded in the mid IR range (4000 cm^{-1} to 400 cm^{-1}). A few milligrams of $BaCo_2Fe_{10}O_{19}$ powder mixed with anhydrous KBr powder and made in the form of a pellet for measurement. The absorption bands at 2923.88 cm^{-1} and 2151.35 cm^{-1} were due to OH vibrations. The other bands are at 1445, 1427, 1415.5, and 858.26 cm^{-1}, corresponding to the stretching and bending vibrations of C=O, H-C-H, C-H and C-C respectively. The absorption bands between 544 and 468.57 cm^{-1} assigned to the vibration of the bond between the oxygen atom and the metal ions (M–O), confirming the formation of hexaferrite [14]. The TGA curve of the dried precursor of $BaCo_3Fe_9O_{19}$ was recorded using a SII Differential Thermal analyzer Model No. SSC 5100 from 50 °C to 700 °C with a rate of 10 °C/min.

3.3. SEM Analysis

Fig. 3 (a–d) shows the SEM images of barium cobalt hexaferrite samples heated at 650 °C and microwave irradiation. The morphology and grain size are found to be porous, non-uniform and agglomerated in all samples, these agglomerations may be due to small particle size and the magnetic nature of the hexaferrite particles.

3.4. Thermogravimetric Analysis (TGA)

Figure 4 shows TGA curve of $BaCo_3Fe_9O_{19}$ precursor. TG curve shows three steps of weight loss. The first weight loss between 50 °C to 150 °C ($\sim$5 wt%) is due to the desorption of absorbed water molecules. In the second step, a sharp weight loss is observed between temperature of 150 °C to 200 °C ($\sim$57 wt%). In the third step, the weight loss is very less ($\sim$1.2 wt%) in the temperature range between 200 and 350 °C. These weight losses may be due to combustion of organic substances [14, 15]. There is no weight loss

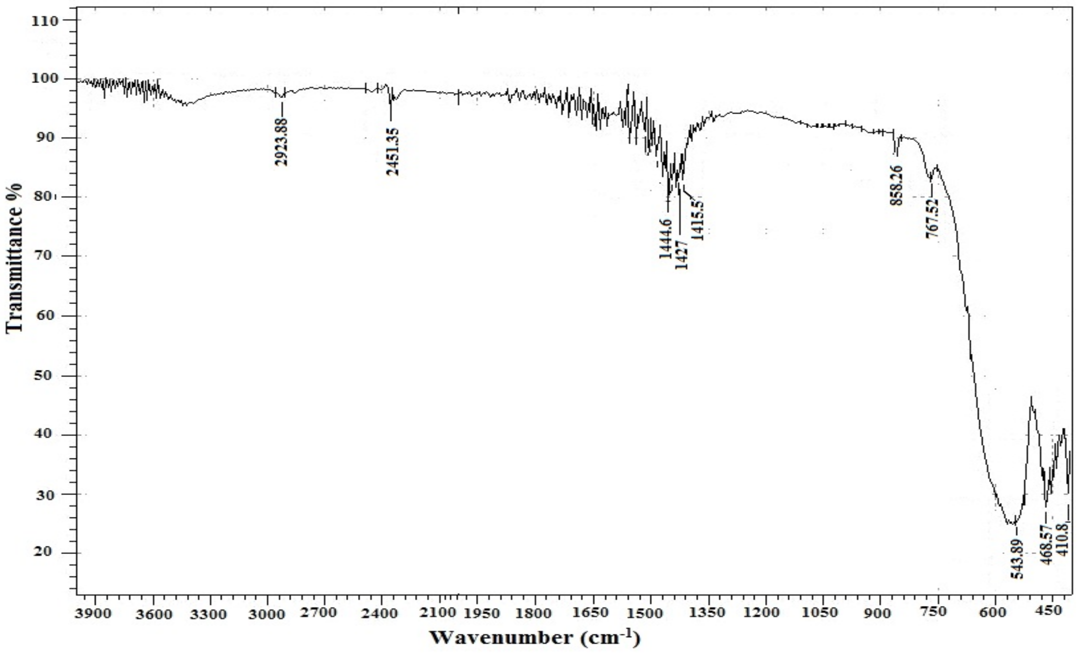

Fig. 2. FTIR spectra of $BaCo_2Fe_{10}O_{19}$ hexaferrite heated at 650 ° C

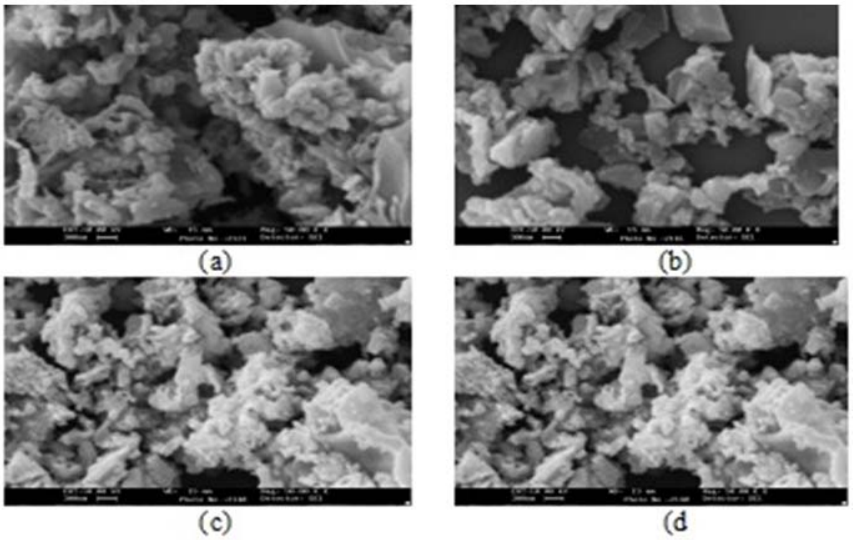

Fig. 3. SEM images of $BaCo_2Fe_{10}O_{19}$ (a) calcinated at 650 ° C (b) heated at microwave frequency, $BaCo_3Fe_9O_{19}$ (c) calcined at 650 ° C and (d) heated at microwave frequency

above 305 ° C, which confirms the high thermal stability of the sample synthesized by a thermal treatment method.

4. Conclusion

M-type hexagonal ferrites $BaCo_xFe_{12-x}O_{19}$ (x = 2.0, 3.0) were synthesized using a simple thermal treatment method. The samples were heated using a muffle furnace and a microwave oven. The observations from the XRD, SEM and TGA studies are summarized as follows:

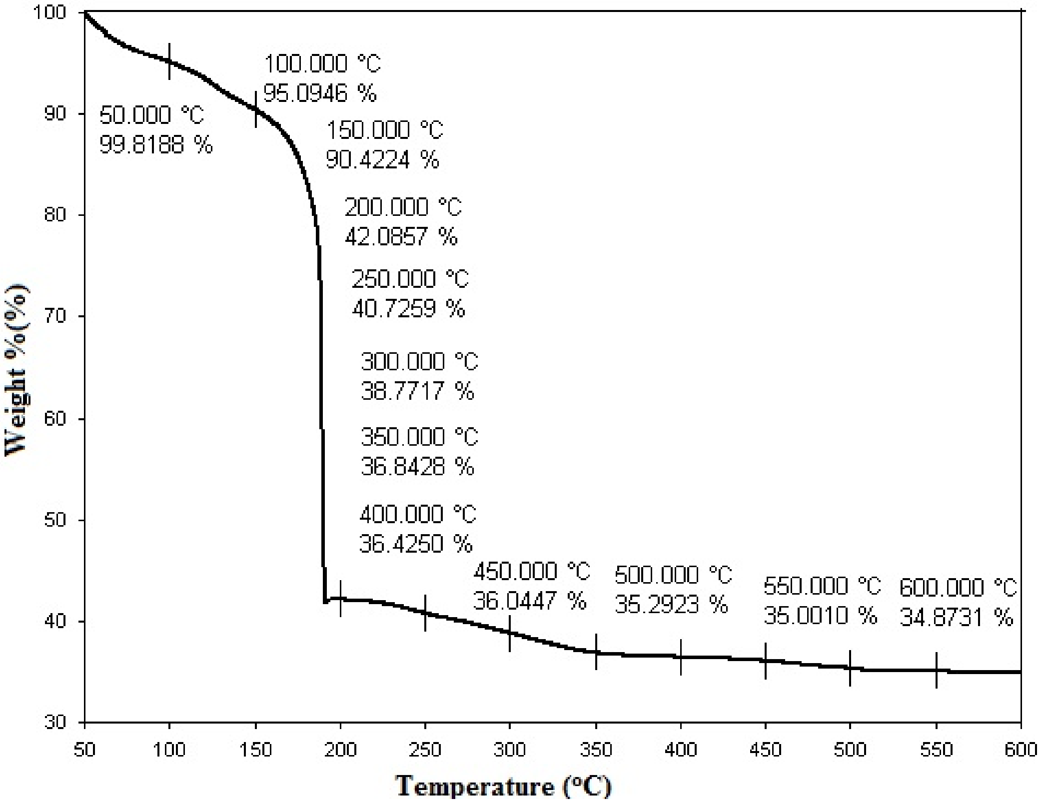

Fig. 4. TGA curve of $BaCo_3Fe_9O_{19}$ precursor

I. XRD results confirm the formation of mono phase.
II. SEM images confirm formation of agglomerated grains.
III. Thermal stability of prepared barium-cobalt hexaferrite sample is high.

Acknowledgment

This work was carried out under DRS-SAP programme of UGC, Physics Department, Gujarat University, Navrangpura, Ahmedabad, India.

References

[1] Salunkhe M.Y., Kulkarni, D.K. Structural, magnetic and microstructural study of $Sr_2Ni_2Fe_{12}O_{22}$. *J. Magn. Magn. Mater.*, **279**, P. 64–68 (2004).
[2] Smit J., Wijn H.P.J., in: Ferrites, Philip's Tech. Library, New York (1959).
[3] Zhang Haijun, Yao Xi, Zhang Liangying, The Preparation and microwave properties of $BaZn_{2-x}Co_2Fe_{16}O_{27}$ ferrite obtained by a sol-gel process, *Ceram. Int.*, **28**(1), p. 171–175 (2002).
[4] Eugene P., et al., *Chem. Sustain. Dev.* **10**, P. 161 (2002).
[5] Carp O., Barjega R., Segal E., Brezeanu M., *Thermo-chem. Acta*, P. 57–62 (1998).
[6] Pullar R. C., Bhattacharya A. K., Crystallisation of hexagonal M-ferrite from a stochiometric sol-gel precursor without formation of α – Fe_2O_4 intermediate phase, *Mater. Lett.* **537**, P. 537–542 (2002).
[7] Dho J., Lee E. K., Park J. Y., Hur N. H., Effects of the grain boundary on the coercivity of barium ferrite $BaFe_{12}O_{19}$, *J. Magn. Magn. Mater.*, **285**, P. 164–168 (2005).
[8] Vishwanathan B., Murthy V. R. K., *Ferrite Materials; Science and Technology*. Narosa publishing house, New Delhi, U. P. (1990).
[9] Snelling E .C., *Soft Ferrites/Properties and Appllication*, second ed. Butter Worths, London (1988).

[10] Morisako A., Matsumoto M., Naoe M., The effect of oxygen gas pressure on Ba-ferrite sputtered films for perpendicular magnetic recording media, *IEEE Trans. Magn.*, **24**(6), P. 3024–3026 (1988).

[11] Hylton T. L., Parker M. A., Ullah M., Coffey K. R., Umphress R., Haward J. K., Ba ferrite thin film media for high density logitudinal recording media, *J. Appl. Phys.*, **75**(10), P. 5960–5965 (1994).

[12] Niesen T. P., M., de Guire, Deposition of ceramic thin films at low temperatures from aqueous solutions, *J. Electroceram.*, **6**, P. 169–207 (2001).

[13] He H. Y., preheating effects on the particle size and anisotropy of M-type $BaAl_2Fe_{10}O_{19}$ powders prepared via sol gel method, *Advances in Natural and Applied Sciences*, **3**(1), P. 211–215 (2009).

[14] Temuujin J. J., Aooyama M., Senna M., Masuko T., Ando C., Kishi, H. *J. Solid State Chem.*, **177**, P. 221 (2004).