Tuning The Properties of Ba-M Hexaferrite $\text{BaFe}_{11.5}\text{Co}_{0.5}\text{O}_{19}$: A Road Towards Diverse Applications

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Abstract

The development of hexaferrite nanoparticles is scrutinized as potential sorbents for the removal of chromium (Cr) ions from aqueous chromium-containing solutions in a batch adsorption experiment. The transition metal Co doped $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite compounds (BHF) have been synthesized successfully via citrate auto combustion technique. Structural, morphological, and magnetic properties are testified. X-ray diffraction pattern ratifies the existence of hexagonal phase as a main phase for the prepared samples. The average crystallite sizes are found in the range of 47–49 nm. The high-resolution transmission electron microscopy (HRTEM), as well as the Fourier, transform infrared spectrophotometry results confirm an M-type hexagonal structure existing. The c-T indicates the temperature-dependent ferromagnetic behavior of BHF nanoparticles. The derivative shows a single transition temperature T_c at 698 °C, 710 for BHF and BHCF respectively. The prepared samples are utilized as an adsorbent for the removal of Cr (VI) from the aqueous solution. The maximum adsorption capacity (qm) of Cr (VI) on the nano hexaferrite is higher than that of various other adsorbents testified in the literature. The pseudo-second-order kinetic model gives a better fit to the experimental data

1. Introduction

One of the ferromagnetic materials which have unique magnetic properties is $\text{BaFe}_{12}\text{O}_{19}$ belonging to M-hexaferrite. It has a crystal structure of $P6_3/mmc$ space group, which consists of SRS^*R^* alternative layers of hexagonal (R) and spinel (S) layers. The S^* and R^* layers are the same as S and R but rotated at 180° along the c-axis. One unit cell of M-hexaferrite is containing 38 O^{2-} ions, two Ba^{2+} ions as well as 24 Fe^{3+} ions as shown in (Fig. 1) [1]. The large spontaneous polarization of hexaferrite is related to 5 polyhedral sites occupied by Fe^{3+} three of these octahedral sites (FeO_6) having spin up related to 2a, 2b, and 12 k and two spins down one of them $4f_1$ tetrahedral (FeO_4) and the other is $4f_2$ trigonal bipyramidal (FeO_5). Magnetic properties of Ba-hexaferrite can be tuned by doping of magnetic element in sit of Ba^{2+} enhanced coercivity, consequently adsorption of heavy metals [2].

The magneto plumbite unit cell ($\text{MFe}_{12}\text{O}_{19}$) of the hexaferrite system contains two formula units, consisting of 10 hexagonally close-packed oxygen layers stacked along the hexagonal basal plane (c-axis). The divalent ion, M^{2+} , is substituted for an oxygen atom in every fifth layer.

In the present research, we aimed to prepare ($\text{BaFe}_{12}\text{O}_{19}$) and $\text{BaFe}_{11.5}\text{Co}_{0.5}\text{O}_{19}$ hexaferrite nanoparticles using the citrate auto combustion technique. This method was successful to obtain single- phase ultrafine barium hexaferrite with nano size, and excellent homogeneity. On the other hand, the obtained magnetic properties, structural analyses, morphology are comparable with those previously reported.

2. Methodology

2.1. Material used

All chemicals $\text{Ba}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99%), $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (98%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and citric acid $[\text{C}_4\text{H}_8\text{O}_7]$, and ammonia solution (33%) were obtained from (LOBA, India).

2.2. Experimental technique

Nanoparticles of Barium and cobalt doped Barium hexaferrite were synthesized by the citrate auto-combustion method as mentioned in the previous work [3]. The proper amounts of the precursors corresponded to the stoichiometric ratios from nitrates were added. These precursors were mixed with citric acid by adding dropwise of distilled water under vigorous stirring. After that, the pH value was adjusted to 7, and the temperature was raised to 200 °C until all fumes were ended as illustrated in Fig. 2.

2.3. Characterizations and measurements

The phase formation was determined by X-ray diffraction (analytical-x' pertpro, Cu $K_{\alpha 1}$ radiation, $\lambda = 1.5404 \text{ \AA}$, 45 kV, 40 mA, Netherlands). Fourier transformed infrared (FT-IR) spectra were measured in the wavenumber range of $4000 - 400 \text{ cm}^{-1}$ by FT-IR spectrometer (Perkin-Elmer 2000). HRTEM (HRTEM, JEOL/JME 2100) (TEM, JEOL, JSM 7001F) microscope was used for morphology study. The magnetic susceptibility of the sample was determined by the Faraday technique. A very small amount of powdered sample was placed into a cylindrical glass tube at the point of a maximum gradient in different magnetic field intensities of 1340, 1660, and 1990 Oe.

3. Results And Discussion

3.1 Structure Analyses:

3.1.1 XRD Diffraction

XRD patterns of BHF and BCHF hexaferrite are illustrated in (Fig. 3). All indexed peaks of the studied samples are similar to ICDD card number [00-043-0002] of $\text{BaFe}_{12}\text{O}_{19}$, indicating that the obtained samples are prepared successfully in a single-phase without any impurity. It is observed that Co^{2+} ions completely diffused into magneto plumbite structure for samples $\text{BaFe}_{12}\text{O}_{19}$.

The diffraction pattern for BCHF has eleven broad peaks at 30.4° , 32.3° , 34.2° , 37.2° , 40.4° , 42.6° , 55.2° , 56.6° and 63.2° , corresponding to (110), (107), (114), (203), (205), (206), (217), (2011) and (220) of pure BFO and BFCO phases. The crystallite sizes D for BHF and BCHF are calculated using the Scherrer equation [4] and tabulated in Table 1. The lattice parameters (a, c), and the volume (V) of the unit cell are calculated from the following equations [5] and presented in Table 1

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

$$V_{\text{cell}} = \frac{\sqrt{3}}{2} a^2 c \quad (2)$$

The changes in the lattice parameters can be attributed to the differences in ionic radii of Co^{2+} ($0.745\text{\AA}$), Fe^{3+} ($0.645\text{\AA}$) as well as the changes of the c-axis anisotropy with respect to the c-plane. [6]. In the present study, the c/a ratio equals 3.938, and 3.937 for pure and doped samples respectively. Additionally, the formation of oxygen vacancies is expected. The charge imbalance between trivalent ions (Fe^{3+}) is being replaced by divalent ions (Co^{2+}) altering the values of the lattice parameter as well as the unit cell volume [7].

Additionally, the theoretical density (d_x) is determined as mentioned earlier [8] and the obtained data are tabulated in the Table. As revealed in the Table, the presence of Co^{2+} increases the (d_x). This increase is due to the higher molar mass of Co^{2+} (58.933 amu) compare to that of Fe (55.845 amu) [9].

The number of dislocations in a unit volume can be measured by the dislocation density δ . The samples with fewer δ exhibit high mechanical strength. In addition, as the δ increases, the strength of the samples decreases. The dislocation density δ is calculated from the following relation [10] and the results are illustrated in the Table.

$$\delta = 1/D^2 \quad (3)$$

The obtained low δ values are indications of a good crystallinity in BHF and BCHF nanoparticles.

Table 1
Lattice parameters (a and c), volume, the crystallite size (D), Dislocation density (δ), and theoretical density (d_x) for BHF and BCHF.

Sample	Theoretical values			Calculated Values				
	a ($\text{\AA}$)	c ($\text{\AA}$)	V ($\text{\AA}^3$)	a ($\text{\AA}$)	c ($\text{\AA}$)	D (nm)	$\delta \cdot 10^{-4} \text{ (nm}^{-1}\text{)}$	d_x gm/cm ³
BHF	5.890	23.195	696.88	5.890	23.196	49.664	40	5.297
BCHF	5.889	23.187	696.55	5.889	23.187	47.825	43	5.306

3.1.2. FT-IR spectra

Figure 4. reveals FT-IR spectra of BHF and BCHF hexaferrite samples in wave numbers range of $400\text{--}4000\text{ cm}^{-1}$. Two significant absorption bands of M-type hexaferrite, ν_1 and ν_2 , are detected in the spectra. The intrinsic stretching vibrations of cation at site A–O bond are detected around 584. While the ν_2 is observed around 432 cm^{-1} , which is corresponding to metal ions at site B–O bond [11]. Because of the short bond length of the tetrahedral cluster consequently, tetrahedral vibration is greater than octahedral vibration [12, 13]. The presence of ν_1 and ν_2 bands ratify the successful preparation of hexaferrite [14].

While weak bands at 3430 and, 1434 cm^{-1} are due to stretching vibration of O-H [15]. and for the carboxylate group (C–O) respectively [16].

The range of absorption bands obtained is in agreement with that reported by Mahadevan et al.[17]. The values of transmittance bands ν_1 and ν_2 shift to a lower wave number due to numerous reasons. The first one is the average atomic weight of Co^{2+} ions which is smaller compared to Fe^{3+} ions [18]. Secondly, for all the samples, the transmission band at about 1635 cm^{-1} exhibits the stretch and bending of the surface hydroxyl group (-OH) of M-type hexaferrite. [15].

3.1.3. EDAX and mapping analyses

EDAX analyses for $\text{BaFe}_{12}\text{O}_{19}$ and $\text{BaCo}_{0.5}\text{Fe}_{11.5}\text{O}_{19}$ are shown in (Fig. 5a-b). The typical peaks in the spectrum include Ba, Fe, Co, and O. The atomic percentage (at%) and weight percentage (wt%) of component elements are obtained theoretically using the formulas $\text{BaFe}_{12}\text{O}_{19}$ and $\text{BaCo}_{0.5}\text{Fe}_{11.5}\text{O}_{19}$. The data acquired from EDAX elemental analysis is depicted in the figure as an inset.

The distribution of the elements is approved by EDAX mapping images for synthesizing samples. The results indicate that Ba, Fe, Co, and O are uniformly distributed in the hexaferrite structure. Thus, the samples have highly homogeneous structures, as shown in (Fig. 6).

3.1.4. Microstructural features

Fig. 7. shows the HRTEM of hexaferrite samples. HRTEM images of the testified samples display hexagonal structures. The particles of various sizes and shapes are observed. The particles have mostly hexagonal with rectangular shapes which are compatible with the hexaferrite structure. The doped samples have spherical together with hexagonal shaped particles. Similar morphology was observed for Barium hexaferrite by Jun Young et al [19]. The doping with a small amount of Co^{2+} has no effect on the morphology of particle size as detected from the figure. The magnetic nature of the cobalt causes small agglomerations of nano particles as shown in the images.

The selected area electron diffraction (SAED) indicates the well-defined crystalline nature and single phase nano BHF and BCHF hexaferrites (Fig. 7:c,g). The data are fitted to the Gaussian distribution and the average particle size of samples are in the range of 95 nm for BHF and BCHF respectively. The obtained data from HRTEM result is in agreement with XRD results.

3.1.5. Surface topography

Fig. (8:a-b) show the AFM height images of BHF and BCHF nanoparticles. The height images reveal that the physical dimensions and thickness of the nano samples can be easily obtained from the height profiles.

The roughness on the surface is indicative of the high degree of crystallographic defects, which tend to possess higher free energy and a higher surface activity [20]. Fig. 8. illustrates powder's grain boundaries with comparable grain sizes for BHF and BCHF. From the images, one can detect that the grain roughness

for the BHF sample is smoother than the grain roughness for the BCHF sample. The maximum peaks height of the roughness are obtained as 4.64, 6.17 nm For BHF and BCHF respectively. The difference in roughness between substituted BHF and BCHF ferrites is due to the larger particle size of the former. The roughness profile section height difference (R_{dc}) values for BHF and BCHF are 4.38 nm and 4.92 nm, respectively. The skewness of the roughness profile (R_{sk}) of $BaFe_{12}O_{19}$ and $BaCo_{0.5}Fe_{11.5}O_{19}$ are -2.26 and -1.41 respectively.

Better values of magnetic properties as will be discussed later exhibit by samples with cobalt. This is related to a more regular grain shape and a narrow grain size distribution. We can observe in AFM images that BCHF shows a regular grain shape and a larger grain roughness compared with the parent sample .

3.2 Magnetic Susceptibility

The thermo-magnetic plots (χ) of the BHF and BCHF samples at the different applied fields are shown in (Fig. 9), together with their derivative with respect to temperature. It is clear that the χ_m decreases until reaching zero point (T_c) with increasing temperature due to thermal energy which causes disordering of the dipoles in field direction and the material begins to act as paramagnetic material. From the figure, the increase in the field intensity reduces the values of χ_m . This is due to the alignment of spin magnetic moments in field direction until all of them reach saturation (the magnetization nearly become constant) resulting in the decrease of χ_m . A prominent increase of nearly 2% in the Curie temperature (T_c) has been detected in BCHF samples. The derivative shows a single T_c at 698°C, 710 for BFO and BFCO respectively. This indicates that the studied samples consist of a single Ba M phase. Higher T_c will enable this material to be used in high-temperature magnetic devices.

The increase in the T_c may be associated with partial substitution of Co^{2+} ions at the octahedral site of the BFCO lattice. This behavior can be attributed to the improvement in the strength of the super-exchange interactions between spin-up and spin-down sublattices.

The obtained data obeys the well known Curie–Weiss law. The values of the Curie constant (C), T_c , Curie-Weiss constant (θ), and the effective magnetic moment (μ_{eff}) are calculated from the reciprocal of χ_m with temperature (not illustrated here)[21]. The calculated data are tabulated in Table 2.

Table 2
Magnetic parameters of Curie temperature (T_c), Curie constant (C), Curie-Weiss constant (θ) and effective magnetic moment (μ_{eff})

	T_c (K)	C (emu.mole.K/g)	θ (K)	μ_{eff} (B.M)
$BaFe_{12}O_{19}$	698	5.128	625	6.40
$BaCo_{0.5}Fe_{11.5}O_{19}$	710	11.24	630	9.49

3.3 Heavy metal removal (HMR)

3.3.1. Effect of Cr⁶⁺ ion concentration

The BaFe₁₂O₁₉ and BaFe_{11.5}Co_{0.5}O₁₉ nano particles are examined at numerous experimental parameters as heavy metal concentration HMC, as well as pH to determine the optimum conditions for HMR. The adsorption of Cr⁶⁺ is increased on sample surfaces by increasing the HMC till it achieved the maximum adsorption of 9%, 21% for BaFe₁₂O₁₉ and BaFe_{11.5}Co_{0.5}O₁₉ respectively as exposed in (Fig. 10:a-b).

There is no further increase in the adsorption of HM after the optimum concentration (40 ppm). This behavior can be clarified due to the available active sites on the sample surface which leads to adsorption of HM at a lower concentration. By increasing the HMC, these active sites are occupied by Cr⁶⁺ ions more and more till the optimum concentration is achieved. At this concentration, all active sites are fully occupied and consequently, increasing the HMC above its optimum value, causing no change in adsorption of Cr⁶⁺ ion.

3.3.2 Effect of pH on Cr⁶⁺ removal

The effect of the pH solution on adsorption performance is illustrated in (Fig. 10:b). The BaFe₁₂O₁₉, as well as BaFe_{11.5}Co_{0.5}O₁₉, have the same trend in which the increase of pH is accompanied by increasing the adsorption of heavy ions. The small value of the adsorption of Cr (VI) at low pH can be attributed to a large amount of H⁺ which competes with Cr⁶⁺ on the available active sites [22]. The increase of pH value to 7, causes a decrease in the number of H⁺. Consequently, more active sites become available for Cr (VI) adsorption [23]. However, the ability of HM ions to form precipitates has occurred at the basic medium (pH = 8). Therefore, the removal of Cr (VI) ions is due to precipitation as well as adsorption. Finally, it can be detected that the adsorption efficiency of BaFe_{11.5}Co_{0.5}O₁₉ is higher compared to BaFe₁₂O₁₉. The small crystallite size of BaFe_{11.5}Co_{0.5}O₁₉, as well as the high surface area, are the main causes for the observed behavior.

The Langmuir and Freundlich isotherms models are used to clarify the adsorption process. Langmuir and Freundlich isotherms are expressed by equation (4) and (5) respectively [24].

$$\frac{C_e}{q_e} = \frac{1}{K_f q_m} + \frac{C_e}{q_m} \quad (4) \quad \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

where q_e and q_m (mg g⁻¹) are the adsorption capacity at equilibrium and maximum adsorption respectively, and K_f (L mg⁻¹) is the affinity binding constant. while K_f and n are physical constants signifying the adsorption capacity and intensity of adsorption, respectively.

The monolayer and heterogeneous surfaces are related to the Langmuir and Freundlich isotherms respectively [25]. The investigated samples are fitting well with the Langmuir neither Freundlich isotherm models. Consequently, Cr⁶⁺ adsorption on the surface of prepared samples occurs through monolayer adsorption as detected in Fig. (11:a-d).

Kinetics of HM adsorption is principally studied through pseudo-first-order (P.F.O.) or pseudo-second-order (P.S.O) kinetics. P.F.O.M. kinetic explains the physisorption. Physisorption is weak and occurs using Van der Waals forces without any chemical bonding. As a result, this process is reversible. Though, P.S.O.M. kinetic is related to chemisorption adsorption which is happened by two reactions. The first reaction extends equilibrium quickly. While the second one leaks slowly and reaches equilibrium after a long time [26]. In chemisorption, bond formation exists between adsorbents and adsorbates via electron sharing. Subsequently, it is tougher than physisorption. Another kinetic model is testified by Weber and Morris I.D.M. They found that the intra particle diffusion model (IDM) is the single rate –determining the stage and the removal of adsorbate is done thought-out a rapid procedure.

The three adsorption kinetics models can be clarified as follows

$$\text{P.F.O.M. } \ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t \quad (6)$$

$$\text{P.S.O.M. } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

$$\text{I.D.M. } q_t = k_3 t^{1/2} + C \quad (8)$$

Where k_1 , k_2 , and k_3 are the P.F.O, P.S.O, and ID rate constants in (min^{-1}) and ($\text{g mg}^{-1} \text{ min}^{-1}$), respectively.

It can be concluded that the furthestmost of HM ions adsorption on the surface of prepared samples has well-fitting with the P.S.O kinetic model, refereeing to the (Fig. 12). Consequently, the adsorption of Cr (VI) by using $\text{BaFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{11.5}\text{Co}_{0.5}\text{O}_{19}$ is done through Langmuir isotherm and the adsorption mechanism kinetics is P.S.O.M

Conclusion

The diffraction patterns showed characteristic diffraction peaks related to the M-type Ba-ferrite structure. This showed that the crystal structure did not change and remained hexagonal magneto plumbite even after substitution with cobalt.

It is also clear that with cobalt doping the grain size decreased and agglomeration increased.

HRTEM data reveal that the samples have mostly hexagonal and the particle sizes are in the nano range.

The particle surface roughness can affect the magnetization of ferromagnetic particles. It facilitates their magnetization and enhanced the transition temperature.

The investigated samples are fitting well with the Langmuir neither Freundlich isotherm models. Additionally, the furthestmost of heavy metal ions adsorption on the surface of prepared samples has well-fitting with the pseudo-second-order kinetic model.

Declarations

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Conflict of interest

The authors declare that they have no conflict of interest.

Availability of data and material

Not applicable

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Figures

Figure 1

(a) Schematic hexagonal nanoparticles and crystal structure of the M-type BaFe₁₂O₁₉. The polyhedral with different color depict the different Fe³⁺ sites with their surrounding O²⁻ ions. The yellow spheres depict the Ba²⁺ ions.

Figure 2

Schematic of preparation of BHF nanoparticle.

Figure 3

XRD Diffraction pattern of $\text{BaFe}_{12}\text{O}_{19}$ and $\text{BaCo}_{0.5}\text{Fe}_{11.5}\text{O}_{19}$

Figure 4

FTIR of $\text{BaFe}_{12}\text{O}_{19}$ and $\text{BaCo}_{0.5}\text{Fe}_{11.5}\text{O}_{19}$ hexaferrite samples

Figure 5

EDAX for (a) $\text{BaFe}_{12}\text{O}_{19}$ and (b) $\text{BaCo}_{0.5}\text{Fe}_{11.5}\text{O}_{19}$. The inset table provides quantitative estimates of elements determined directly from the spectrum via weight and atomic percentages.

Figure 6

EDAX elemental mapping images of a) $\text{BaFe}_{12}\text{O}_{19}$ and b) $\text{BaCo}_{0.5}\text{Fe}_{11.5}\text{O}_{19}$ hexaferrites.

Figure 7

HRTEM micrographs of $\text{BaCo}_{0.5}\text{Fe}_{11.5}\text{O}_{19}$ hexaferrite samples.

Figure 8

AFM images for grain boundaries with comparable grain sizes for two samples of (a) $\text{BaFe}_{12}\text{O}_{19}$ and (b) $\text{BaCo}_{0.5}\text{Fe}_{11.5}\text{O}_{19}$ hexaferrites.

Figure 9

Magnetic susceptibility as a function of temperature for $\text{BaFe}_{12}\text{O}_{19}$ and $\text{BaCo}_{0.5}\text{Fe}_{11.5}\text{O}_{19}$ at different field intensities.

Figure 10

a) Effect of heavy metal concentration (Cr^{6+}), and b) Effect of pH on the removal efficiency of $\text{BaFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{11.5}\text{Co}_{0.5}\text{O}_{19}$

Figure 11

(a-d). The Langmuir and Freundlich isotherms for $\text{BaFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{11.5}\text{Co}_{0.5}\text{O}_{19}$ respectively.

Figure 12

(a-b) Pseudo-first-order model, (c-d) Pseudo-second-order model and (e-f) Intra particle models for the adsorption of Cr^{6+} at $\text{BaFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{11.5}\text{Co}_{0.5}\text{O}_{19}$ surfaces