6.1 Introduction

Hexaferrites are classified into five types depending on chemical formulae and crystal structure. These include M-type (BaFe$_{12}$O$_{19}$), W-type (BaMe$_2$Fe$_{16}$O$_{27}$), X-type (Ba$_2$Me$_2$Fe$_{28}$O$_{46}$), Y-type (Ba$_2$Me$_2$Fe$_{12}$O$_{22}$), and Z-type (Ba$_3$Me$_2$Fe$_{24}$O$_{41}$) [1]. M type barium ferrite (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 [2]. Its symmetry is characterized by the space group P6$_3$/mmc. The magnetism of BaFe$_{12}$O$_{19}$ comes from the ferric iron, each carrying a magnetic moment of 5μB. These are aligned to give either parallel or anti parallel ferromagnetic interaction. 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 barium nanoferrites, according to the requirement for various applications. This modification can be done by different cation substitutions using different synthetic routes under varying conditions [3-7]. Sandaranarayanan et al. [3] studied the effect of annealing temperature on barium ferrites and reported that their crystallization begins around 550 °C and fully crystalline phase is obtained in the range of 700-900 °C. Mendoza-Suarez et al. [4] synthesized Zn-Sn doped Ba ferrites having composition BaFe$_{12-2x}$Zn$_x$Sn$_x$O$_{19}$ (0 ≤ x ≤ 1.0) using ball milling method and found that the coercivity decreased 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. [5] investigated the magnetic anisotropy change in BaFe$_{12-2x}$Ti$_x$Co$_x$O$_{19}$ (x =0.4, 0.8, 1.1) single crystals. The authors 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. [6] synthesized Co$^{2+}$ and Co$^{3+}$ substituted Ba ferrites via sol-gel method and found that Co$^{2+}$ doping decreased the value of coercivity and saturation magnetisation significantly.
However, Co\textsuperscript{3+} doping showed less change in magnetic properties. The authors also reported that the Co\textsuperscript{2+} doping decreased cell volume by 2.5 % where as 0.2 % increase was observed with increase in Co\textsuperscript{3+} substituted in barium ferrites. Ghasemi et al. [7] prepared Mn-Co-Zr substituted BaFe\textsubscript{12-x}(Mn\textsubscript{0.5}Co\textsubscript{0.5}Zr)\textsubscript{x/2}O\textsubscript{19} (0 to 3 in steps of 1) ferrite and concluded that Mn, Co and Zr substitution lead to rapid decrease in coercivity ($H_C$) from 258.7 A/m ($x = 0$) to 4.3 A/m ($x = 1$) at low level of substitution. Zhao et al. [8] prepared M-type barium ferrite (BaFe\textsubscript{12}O\textsubscript{19}) particles using precursor-directed method and reported that the coercivity and saturation magnetization were 5342 Oe and 68.3 emu g\textsuperscript{-1} respectively. The author also prepared Ba(CoTi)\textsubscript{x}Fe\textsubscript{12-2x}O\textsubscript{19} (0.25 ≤ x ≤ 1.0) through the same technique and concluded that the coercivity and saturation magnetization drastically decreased with increase in Co\textsuperscript{2+} and Ti\textsuperscript{4+} substitution. The effect of mechanical activation in synthesis of barium ferrite (BaFe\textsubscript{12}O\textsubscript{19}) powders was investigated by Liu et al. [9]. The sample was calcination at 700 and 800 °C. It was concluded that that mechanically active barium ferrite had crystalline size of 10 nm while as single phase platelets of size 50-100 nm were developed when sample was calcinated at 800 °C. The authors also reported that resultant material had corecivity 436.7kAm\textsuperscript{-1} and saturation magnetization 67.8 Am\textsuperscript{2} Kg\textsuperscript{-1}. Growth of minute single crystals of barium hexaferrite (BaFe\textsubscript{12-2x}Ti\textsubscript{x}Co\textsubscript{x}O\textsubscript{19}) with high-temperature solutions was carried out by Watanabe and Kawabe [10]. The authors reported that the crystallite size, lattice parameter and corecivity decreased with increase in TiO\textsubscript{2} and CaO dopants concentration. Sözeri et al. [11] investigated the magnetic, dielectric and microwave properties of M-Ti substituted barium hexaferrites BaFe\textsubscript{10}M\textsuperscript{2+}Ti\textsuperscript{4+}O\textsubscript{19} (M =Mn\textsuperscript{2+}, Co\textsuperscript{2+}, Cu\textsuperscript{2+}, Ni\textsuperscript{2+}, Zn\textsuperscript{2+}) by solid state reaction route. The saturation magnetization was observed in the range of ~50 emu/g with Co\textsuperscript{2+}, Cu\textsuperscript{2+} and Zn\textsuperscript{2+} substitution. The authors also reported that the electrical resistivity, dielectric constant and dielectric losses were enhanced by the substitution of Mn\textsuperscript{2+}, Co\textsuperscript{2+}, Cu\textsuperscript{2+} and Zn\textsuperscript{2+} divalent ions. Gurbuz et al. [12] produced Mn, Cu, Co, Sr and Ni-doped and undoped barium using sol-gel processing. The authors reported that the doping elements decreased the coercivity of these powders. The author also mentioned that the saturation magnetization was maximum in the case of MnCoNi-doped barium hexaferrite. Batlle et al. [13] studied the static magnetic properties of nanocrystalline Co-Ti doped barium ferrite BaFe\textsubscript{10.8}Co\textsubscript{0.8}Ti\textsubscript{0.8}O\textsubscript{19} and concluded that the saturation magnetization decreased with increase in temperature above 35 K. Koga and Tsutaoka [14] prepared Ti, Co-substituted M-type barium hexaferrite BaFe\textsubscript{12-x}(Ti\textsubscript{0.5}Co\textsubscript{0.5})\textsubscript{x}O\textsubscript{19} (x = 0, 1, 2, 3, 4 and 5) by citrate precursor
method. The results revealed that the saturation magnetization, corecivity and magnetic anisotropy decreased with increase in value of x. Chawla et al. [15] explored the structural and magnetic properties of M-type barium hexaferrites BaCo$_x$Zr$_{3-x}$Fe$_{12-2x}$O$_{19}$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0). The lattice constant and cell volume increased with increase in substitution of Co and Zr. The authors also concluded that the saturation magnetization varied from 63.63 to 56.94 emu/g while corecivity decreased from 5428 to 630 Oe with increase in doping of Co and Zr. Teh and Jefferson [16] synthesized cobalt (II)-doped magnetoplumbite (M-type) BaCo$_{1.0}$Fe$_{11}$O$_{19}$ via a sol–gel method using ethylene glycol as precursor. The authors concluded that the saturation magnetization and corecivity were reduced from 48 to 28 emu/g and 1080 G to 276 G respectively in the doped ferrite. Ulain et al. [17] manufactured Ti–Mn Co-doped Ba$_2$Co$_2$Fe$_{12-2x}$(Ti–Mn)$_x$O$_{22}$ (x = 0.2–1.0) Y type hexaferrites by sol gel method with crystalline size in the range of 30–54 nm. The DC resistivity increased with increase in Ti–Mn concentration. The catalytic activity for the decomposition of N$_2$O was enhanced by addition of Ti–Mn which was attributed to the collective electronic as well as surface anion vacancies. Qin et al. [18] carried out microwave absorbing properties of W-Type hexaferrite Ba(MnZn)$_{x}$Co$_{2(1-x)}$Fe$_{16}$O$_{27}$ (x = 0.1, 0.2, 0.3, 0.4 and 0.5). The authors reported that the wide band width and strong loss over the frequency range of 2 - 18 GHz. Choopani et al. [19] synthesized BaCo$_{0.5}$Mn$_{0.5}$Ti$_{1.0}$Fe$_{10}$O$_{19}$ hexaferrites using solid state reaction and concluded that the Mn–Co–Ti mixture was very effective in reducing H$_c$ at low level of substitution which made it good candidate for electromagnetic compatibility and other practical applications at high frequency. Du et al. [20] synthesized Co-Ti-doped barium-ferrite nanoparticles Ba(CoTi)$_x$Fe$_{12-2x}$O$_{19}$ (0.25 ≤ x ≤ 1.0) using solvothermal route. The authors concluded that the saturation magnetization and coercivity drastically decreased with increase in Co$^{2+}$ and Ti$^{4+}$ in the magnetoplumbite structure. Ata et al. [21] evaluated the electrical and dielectrical properties of BaCo$_{2x}$Zn$_x$Fe$_{12-2x}$O$_{19}$ (x = 0:4, 0.8, 1.2, 1.6 and 2). The authors concluded that the electrical conductivities and dielectric constants decreased Co and Zn ion substitution up to x =1.2 and thereafter enhanced with further substitution. This effect was attributed due to the tetrahedral site preference of newly added Zn ions and some Co ions which displaced Fe ions from A sites to B sites. Barium ferrite and its substituted derivatives BaFe$_{9.6}$Co$_{0.8}$Ti$_{0.8}$M$_{0.8}$O$_{19}$ (M =Cu, Zn, Cr, Al, Sn, Sb) were manufactured by Li et al. [22]. The results illustrated that the material can be used in high density magnetic recording media because of their promising magnetic properties. Kubo et al. [23] examined
the particle size effects on magnetic properties of $\text{BaFe}_{12-2x}\text{Ti}_x\text{Co}_x\text{O}_{19}$ ($x = 0, 0.5, \text{and } 0.85$) fine particles and displayed that the saturation magnetization declined with decrease in particle size. They also reported that the coercivity decreased with increase in Ti and Co substitution. Kuo et al. [24] discussed the magnetic properties of $\text{BaFe}_{12-2x}\text{Co}_x\text{Sn}_x\text{O}_{19}$ ($x = 0.0, 0.4, 0.6, 0.8, 1.0$ and $1.2$) prepared by co-precipitation method. The authors demonstrated that saturation magnetization decreased slowly while, the coercivity decreased rapidly with increasing $x$. Carey et al. [25] scrutinized the magnetic and magnetooptical properties of Co, Cr, Mn, and Ni substituted barium ferrite. The authors accounted that the magnetooptical properties of barium ferrite were increased with Co$^{2+}$ and Ti$^{4+}$ substitutions. Iqbal and Ain [26] analyzed the physical properties of Zr$^{4+}$–Co$^{2+}$ co-doped barium hexagonal ferrites $\text{Ba}_2\text{Cd}_2(\text{Zr,Co})_x\text{Fe}_{12-2x}\text{O}_{22}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) with crystallite size in the range of 46–59 nm. The authors reported that the activation energy and resistivity increased with increase in Zr–Co substitution.

From the above literature it is clear that Co ion substitutions can be greatly helpful in tailoring the compounds for the desired electrical, magnetic, microwave and catalytic properties of barium ferrite. However, a systematic study on the cobalt substituted barium ferrites is not reported in the literature so far. Therefore, the aim of the present work is to systematically investigate the Co ion on structural, magnetic and electrical properties of barium ferrite.

### 6.2. SYNTHESIS OF COBALT SUBSTITUTED BARIUM FERRITE

Hexagonal M- type barium ferrite having composition $\text{BaCo}_x\text{Fe}_{12-x}\text{O}_{19}$ ($x=0.0, 0.2, 0.4, 0.6, 0.8 \& 1.0$) were synthesized using the sol-gel method [27,28]. In this method, the AR grade chemical of $\text{Ba(NO}_3)_2$, $\text{Fe(NO}_3)_3.9\text{H}_2\text{O}$, $\text{Co(NO}_3)_2.6\text{H}_2\text{O}$ were accurately weighed in stoichiometric proportion and dissolved separately in minimum amount of distilled water. The solutions were then heated at $80^\circ–90^\circ \text{C}$ and mixed with constant stirring. Citric acid (in the molar ratio 1:1 to metal cations) was then added followed by ethylene glycol to the nitrates solution. The solution was stirred until gel formation. Then these gels were self ignited until ferrite powder was obtained, which was annealed at $1000 \text{C}$ for $2h$ in a muffle furnace.
The elemental analytical data for all the ferrite compositions obtained by EPMA were consistent within ±2%. The synthesized samples were characterized using various techniques as discussed below:

6.2.1. FT-IR measurements

The FT-IR spectrum is of great importance as it is sensitive to the short range environment of the oxygen coordination around the cations in both tetrahedral and octahedral clusters of the ferrites. It gives information about the position of ions in the crystal lattices. Therefore, the FT-IR spectroscopy may be used to determine the local symmetry in the crystalline solids and ordering phenomenon in ferrites. It is predicted that two main bands below 1000 cm\(^{-1}\) are common feature of all the ferrites. Absorption in this region is also observed in metal oxides. These bands arise from the lattice vibrations of oxide ions against the cations. The tetrahedral stretching vibrations are observed at a higher wave number as compared to the octahedral stretching vibrations due to the fact that the M-O bond length in the tetrahedral site is shorter than that of the octahedral site [29,30]. In the present study, The FT-IR spectra of all the ferrite compositions have been recorded in the range of 800- 400 cm\(^{-1}\), using KBr plates as shown in Fig. 6.1.

![FT-IR spectra of BaCo\(_x\)Fe\(_{12-x}\)O\(_{19}\) samples annealed at 1000 °C for 2h.](image)

**Fig. 6.1:** FT-IR spectra of BaCo\(_x\)Fe\(_{12-x}\)O\(_{19}\) samples annealed at 1000 °C for 2h.
In the low frequency range, the spectra shows two main peaks corresponding to the vibrational modes of metal oxide bond of ferrites [31]. 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.

6.2.2. X-Ray diffraction studies

The phase evolutions of the synthesized ferrites were studied using the powder X-ray diffraction technique. The powder X-Ray diffractographs for all the samples annealed at 1000 °C is shown in Fig. 6.2. The XRD patterns of the ferrite samples show characteristic diffraction peaks corresponding to the M-type barium ferrite structure. All the diffraction peaks could be indexed to the (110), (107), (114), (103), (203), (205), (206), (217), (2011), (220) and (317) planes of on the basis of JCPDS card no 00-007-0276. They have point group P6\(_{3}/mmm\), indicating that the dopants replace Fe without significant change of structure. The small peak shifts displayed that the cell parameters changed with the doping amount (Table 6.1). This signifies that the dopants successfully entered the lattice of barium ferrite and altered the relative peak intensity in XRD but not the type of lattice.

Fig. 6.2: X-Ray diffractographs of BaCo\(_x\)Fe\(_{12-x}\)O\(_{19}\) samples annealed at 1000 °C.
The average crystallite size for each composition was calculated from the line broadening of the most intense peak corresponding to (1 1 4) plane of magnetoplumbite structure according to Scherrer equation [32] given below:

\[ D = \frac{k\lambda}{\beta\cos\theta} \]  

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 6.1. 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 6.1. It was observed that the lattice parameters remained constant on increasing Co ion concentration.

Table 6.1: Crystallite size, D (nm); Lattice parameter (Å); Saturation magnetization \( (M_s) \), Coercivity \( (H_c) \) and squareness Ratio \( (S_q) \) of the ferrites annealed at 1000 °C.

<table>
<thead>
<tr>
<th>Ferrite composition</th>
<th>Lattice parameter (Å)</th>
<th>Crystalline size (D nm)</th>
<th>Saturation magnetization ( M_s ) (emu/g)</th>
<th>Coercivity ( H_c ) (Oe)</th>
<th>Squareness ratio ( S_q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaFe(<em>{12})O(</em>{19})</td>
<td>( a= 5.8423 ) ( c=22.9945 )</td>
<td>40</td>
<td>50.8</td>
<td>5200</td>
<td>0.60</td>
</tr>
<tr>
<td>BaCo(<em>{0.2})Fe(</em>{11.8})O(_{19})</td>
<td>( a=5.8846 ) ( c=23.1640 )</td>
<td>45</td>
<td>96.2</td>
<td>3800</td>
<td>0.59</td>
</tr>
<tr>
<td>BaCo(<em>{0.4})Fe(</em>{11.6})O(_{19})</td>
<td>( a=5.8920 ) ( c=23.1943 )</td>
<td>62</td>
<td>55.7</td>
<td>3500</td>
<td>0.58</td>
</tr>
<tr>
<td>BaCo(<em>{0.6})Fe(</em>{11.4})O(_{19})</td>
<td>( a=5.8835 ) ( c=23.1742 )</td>
<td>64</td>
<td>53.5</td>
<td>2800</td>
<td>0.55</td>
</tr>
<tr>
<td>BaCo(<em>{1.0})Fe(</em>{11.8})O(_{19})</td>
<td>( a=5.8801 ) ( c=23.1772 )</td>
<td>52</td>
<td>47.8</td>
<td>1750</td>
<td>0.49</td>
</tr>
</tbody>
</table>
6.2.3. Magnetic properties

The information of magnetic properties like saturation magnetization ($M_s$), coercivity ($H_c$), retentivity ($M_r$), squareness ratio ($S_q$) is deduced from hysteresis loop. Therefore, the room temperature hysteresis loops of the entire ferrite compositions, annealed at 1000 °C temperatures, were recorded using a Vibrating Sample Magnetometer (VSM). The results are shown in Fig. 6.3 and calculated data is given in Table 6.1. From Table 6.1, it is seen that the saturation magnetization decreases as the Co concentration increased. This was attributed to the lesser magnetic moment of Co ions (3µB) as compared to Fe$^{3+}$ ions (5µB) and their substitution in 12k and 2a sites of the lattice, in preference to the 4f$_2$ sites. The coercivity value decreased from 5200 to 1750 Oe with increasing cobalt concentration (x=0.0 to 1.0) due to reduction in magnetocrystalline anisotropy [33,34].

![Hysteresis loops](image)

**Fig. 6.3:** Hysteresis loops of BaCo$_x$Fe$_{12-x}$O$_{19}$ (x=0.0, 0.2, 0.4, 0.6, 1.0) annealed at 1000 °C.

The value of squareness ratio was calculated by formula:

$$S_q = \frac{M_r}{M_s}$$

(2)
where \( M_r \) is the remenance and \( M_s \) is the saturation magnetization. It was observed that the squareness ratio decreases with increase in cobalt ion concentration (Table 6.1).

From the above discussion, it is clear that the saturation magnetization increases with the introduction of \( \text{Co}^{2+} \) ion into the barium ferrite lattice thereafter it decreased with increase in \( \text{Co}^{2+} \) ion substitution in the barium ferrite. Therefore, in the subsequent research work, the concentration of \( \text{Co}^{2+} \) ion was fixed at \( \text{BaCo}_{0.2}\text{Fe}_{11.8}\text{O}_{19} \) and \( \text{Cd}^{2+} \) ion was doped into the barium ferrite to improve its magnetic properties. The ferrites were also used in catalytic activity for the degradation of dye.

6.3. Synthesis and characterization of \( \text{BaCo}_{0.2}\text{Cd}_x\text{Fe}_{11.8-x}\text{O}_{19} \) (\( x = 0.2, 0.4, 0.6, 0.8 \) and 1.0) using sol-gel method.

6.3.1. Synthesis of \( \text{BaCo}_{0.2}\text{Cd}_x\text{Fe}_{11.8-x}\text{O}_{19} \) (\( x = 0.2, 0.4, 0.6, 0.8 \) and 1.0) ferrite

\( \text{BaCo}_{0.2}\text{Cd}_x\text{Fe}_{11.8-x}\text{O}_{19} \) nanoferrites were prepared using sol-gel process as reported earlier. In this method, the desired proportion of \( \text{Ba(NO}_3\text{)} \), \( \text{Co(NO}_3\text{)}_2.6\text{H}_2\text{O} \), \( \text{Cd(NO}_3\text{)}_2.3\text{H}_2\text{O} \), \( \text{Fe(NO}_3\text{)}_3.9\text{H}_2\text{O} \) and citric acid were separately dissolved in minimum amount of distilled water according to the stoichiometric formula. All the metal nitrates solution was mixed followed by the addition of citric acid. The stirring and heating of the solution was continued and 10 mL of ethylene glycol was added. The obtained solution was heated to between 80–90 \( ^\circ \text{C} \) for 2 h and gels were formed. The obtained gels were further ignited in the self-propagation manner to obtain ferrite powders. Then these gels were further heated which converted into nano ferrites which then annealed in furnace at 1000 \( ^\circ \text{C} \) for 2 h.

6.3.2. Photo-catalytic activity measurements

Photo-catalytic activity of all the magnetic nano-particles was evaluated by measuring the degradation of methyl orange (MO) in the aqueous solution under visible light irradiation as shown in Fig. 6.4. A 400 W visible Hg lamp was employed as light source. For each experiment, 0.1g of photo-catalyst was dispersed in 100 ml of 30mg/L of the MO aqueous solution. Prior to the irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure the adsorption-desorption equilibrium of MO aqueous solution with the photocatalyst. The solution was exposed to visible light under stirring after addition of 0.1 ml of 30% \( \text{H}_2\text{O}_2 \). At given time intervals, 3 mL of aliquots were withdrawn and centrifuged to
remove ferrite particles. The concentration of MO in aqueous solution was determined with the help of UV-Visible spectrophotometer.

Fig. 6.4: Schematic representation of the photochemical reaction testing system.

6.4. RESULTS AND DISCUSSION

6.4.1. FT-IR measurements

The FT-IR transmission spectra give information about the presence of M-O bonds which confirms the formation of nano ferrite. FT-IR spectra for entire ferrites were recorded in the range from 400 to 4000 cm⁻¹. FT-IR spectra of all the compositions BaCo₀.₂CdₓFe₁₁.₈₋ₓO₁₉ (x = 0.2, 0.4, 0.6, 0.8 and 1.0) are shown as in Fig. 6.5. The spectra of these samples generally contains the bands in the range of 400 to 600 cm⁻¹ which is assigned to vibration of bond between the oxygen atom and metal ion (M-O) confirming the formation of the hexagonal barium ferrite. The band at higher frequency corresponds to M-O stretching vibrations in the tetrahedral site and the band at lower frequency corresponds to M-O stretching vibrations at the octahedral sites [35]. The peak above 720 cm⁻¹ corresponds to nujol [36].
Fig. 6.5: FT-IR spectra observed for BaCo$_{0.2}$Cd$_x$Fe$_{11.8-x}$O$_{19}$ annealed at 1000 °C.
6.4.2. Powder X-ray Diffraction Analysis

The structures of the nano ferrites were determined by wide angle XRD. The powder XRD patterns of the entire ferrite compositions annealed at 1000 °C for 2h were recorded at room temperature and are shown in Fig. 6.6. All the observed diffraction peaks of ferrite samples, annealed at 1000°C, was matched well with JCPDS card No. 00-007-0276. All the samples are found have $P6_3/mmc$ space group. The absence of any additional peaks indicates that the synthesized samples had hexagonal magnetoplumbite structure. The average crystallite size has been calculated from the line broadening of most intense peak (114) using the classical Scherrer relationship [32]. $D_{hkl} = \frac{0.9\lambda}{B\cos\theta}$, where $D_{hkl}$ is the particle diameter, B is the half maximum line width, $\lambda$ is wavelength of the radiation used and $\theta$ is the angle of diffraction. The average crystallite size is found to be varies from ~ 50 nm and its values are listed in Table 6.2.

![XRD patterns for all the samples BaCo_{0.2}Cd_{x}Fe_{11.8-x}O_{19} annealed at 1000 °C.](image)

**Fig. 6.6:** XRD patterns for all the samples BaCo_{0.2}Cd_{x}Fe_{11.8-x}O_{19} annealed at 1000 °C.
Table 6.2: Crystallite size, D (nm); Lattice parameter (a); and volume of the ferrites annealed at 1000 °C.

<table>
<thead>
<tr>
<th>Ferrite composition</th>
<th>Lattice parameter (Å)</th>
<th>Volume (Å³)</th>
<th>Crystalline size D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCo_{0.2}Cd_{0.2}Fe_{11.6}O_{19}</td>
<td>a=5.802 c=22.185</td>
<td>646.8</td>
<td>56</td>
</tr>
<tr>
<td>BaCo_{0.2}Cd_{0.4}Fe_{11.4}O_{19}</td>
<td>a=5.884 c=23.174</td>
<td>694.9</td>
<td>48</td>
</tr>
<tr>
<td>BaCo_{0.2}Cd_{0.6}Fe_{11.2}O_{19}</td>
<td>a=5.892 c=23.174</td>
<td>696.7</td>
<td>48</td>
</tr>
<tr>
<td>BaCo_{0.2}Cd_{0.8}Fe_{11.0}O_{19}</td>
<td>a=5.894 c=23.175</td>
<td>697.1</td>
<td>46</td>
</tr>
<tr>
<td>BaCo_{0.2}Cd_{1.0}Fe_{10.8}O_{19}</td>
<td>a=5.895 c=23.176</td>
<td>697.5</td>
<td>50</td>
</tr>
</tbody>
</table>

The lattice parameters (both a and c) are found to be concentration dependent [37]. The lattice parameter increased with increase in value of x. The parameter a & c increases from 5.802 to 5.895 and 22.185 to 23.176 Å respectively. The cell volume increased monotonically with increase in x which might be due to the substitution of large ionic radius of Cd^{2+} as compared that of Fe^{2+}. Structural parameters derived from the XRD data analysis are given in Table 6.2.

6.4.3. Magnetic properties

Magnetic parameters like saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c) depend upon number of factors viz. density, anisotropy, grain growth and A–B exchange interactions. The magnetic properties of ferrites arise from the super exchange couplings between magnetic ions via the mediating oxygen O^{2-} anions. The predominant super exchange interactions occur between A-B sites. These super exchange interactions between the magnetic ions, favor anti-parallel alignments of the spins at A
and B sites resulting in parallel alignment among the spins at A sites and among those at B sites [38]. Magnetic properties were studied by using vibration sample magnetometer for the samples with composition $\text{BaCo}_{0.2}\text{Cd}_x\text{Fe}_{12-x}\text{O}_{19}$ at room temperature, as depicted in the following hysteresis loop with maximum applied field of 20kOe. The typical hysteresis loops for all the compositions annealed at 1000 °C is shown in Fig. 6.7. The value of saturation magnetization decreased as the concentration of the substituted cadmium was increased from 0.2 to 1.0. It can be seen from Fig. 6.7 that all the samples under investigation exhibited a clear hysteresis behavior under applied magnetic field at room temperature. When Cd contents are added to the $(\text{BaCo}_{0.2}\text{Cd}_x\text{Fe}_{12-x}\text{O}_{19}, x = 0.2, 0.4, 0.6, 0.8$ and $1.0)$, these may change the configuration and distribution of electrons in the ferrite system. This will ultimately change the magnetization of the material. The decrease in saturation magnetization in the present case may also be due to the replacement of paramagnetic material (Fe$^{2+}$) by a diamagnetic metal (Cd$^{2+}$). So, the introduction of Cd$^{2+}$ ions in barium ferrite results in the dilution of the magnetization at the A and B-site which will reduce the saturation magnetization.

![Hysteresis loops of BaCo$_{0.2}$Cd$_x$Fe$_{12-x}$O$_{19}$ annealed at 1000 °C.](image)

**Fig. 6.7: Hysteresis loops of BaCo$_{0.2}$Cd$_x$Fe$_{11.8-x}$O$_{19}$ annealed at 1000 °C.**
The coercivity, $H_c$, decreased with increase in Cd$^{2+}$ concentration. A decrease in coercivity with increase in cadmium concentration may be attributed to the decrease in anisotropy field, which in turn decreased the domain wall energy \[39, 40\]. From the values of coercivity, $H_c$ and the saturation magnetization, $M_s$ the value of anisotropy constant ($K$) can be calculated using the relation \[41\]: $H_c = 0.98 K/M_s$. The anisotropy constant decreased with increasing Cd$^{2+}$ concentration, due to decrease in the coercivity with increase in Cd$^{2+}$ substitution. The squareness ratio, $S_q$ for all the samples annealed at 1000 °C was calculated by using relation $S_q=M_r/M_s$, where $M_r$ is remanance and $M_s$ is the saturation magnetization and its values increased from 0.54 to 0.87.

The observed magnetic moment ($n_B$) per formula unit in the Bohr magneton ($\mu_B$) was calculated using the relation \[42\]:

$$n_B = \frac{M_s \times M_W}{5585} \tag{3}$$

where $M_W$ is the molecular weight and $M_s$ is the saturation magnetization of the sample.

All the calculated parameters are given in Table 6.3.

### Table 6.3: Coercivity($H_c$), Saturation magnetization($M_s$), remanant magnetization($M_r$), squareness ratio($S_q$), magnetic moment ($n_B$)and anisotropy constant ($K$) samples annealed at 1000 °C.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$H_c$</th>
<th>$M_s$</th>
<th>$M_r$</th>
<th>$S_q$</th>
<th>$n_B$</th>
<th>Anisotropy constant (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BaCo}<em>{0.2}\text{Cd}</em>{0.2}\text{Fe}<em>{11.6}\text{O}</em>{19}$</td>
<td>3800</td>
<td>69.9</td>
<td>38</td>
<td>0.54</td>
<td>11</td>
<td>276727</td>
</tr>
<tr>
<td>$\text{BaCo}<em>{0.2}\text{Cd}</em>{0.4}\text{Fe}<em>{11.4}\text{O}</em>{19}$</td>
<td>3500</td>
<td>52.9</td>
<td>29</td>
<td>0.55</td>
<td>8</td>
<td>192901</td>
</tr>
<tr>
<td>$\text{BaCo}<em>{0.2}\text{Cd}</em>{0.6}\text{Fe}<em>{11.2}\text{O}</em>{19}$</td>
<td>3250</td>
<td>46.1</td>
<td>25</td>
<td>0.54</td>
<td>7</td>
<td>156236</td>
</tr>
<tr>
<td>$\text{BaCo}<em>{0.2}\text{Cd}</em>{0.8}\text{Fe}<em>{11}\text{O}</em>{19}$</td>
<td>3250</td>
<td>36.3</td>
<td>24</td>
<td>0.66</td>
<td>6</td>
<td>122994</td>
</tr>
<tr>
<td>$\text{BaCo}<em>{0.2}\text{Cd}</em>{1.0}\text{Fe}<em>{10.8}\text{O}</em>{19}$</td>
<td>2500</td>
<td>27.3</td>
<td>24</td>
<td>0.87</td>
<td>4</td>
<td>71119</td>
</tr>
</tbody>
</table>


6.4.5. Electrical Properties

Ferrites have emerged as useful materials for applications in electronics. This is because they behave as semi-conductor materials, having high resistivity, low dielectric losses and high Curie temperature. Their electrical conductivity (or resistivity) gives useful information about the conduction mechanism. The conductivity in ferrites may be explained on the basis of Verwey’s hopping mechanism [43]. According to this mechanism, the electronic conduction in ferrites arises due to the hopping of electrons between ions of same element, present in more than one valence state, distributed randomly over equivalent crystallographic sites.

The D.C. resistivity of the materials has been calculated by two probe method in the temperature range 323-413 K (50-140°C). The sintered ferrite sample was molded into a pellet using hydraulic press by applying pressure of 3 tones. The silver paint was applied on both sides of the pellet for good ohmic contact. A constant voltage (40V) was applied across the series combination of sample holder containing sample and a standard resistance whose value was always less than the sample resistance. The measurements were recorded in the steps of 10K and the error in the resistivity was approximately 3%. The voltage developed across the standard resistance was measured with the help of a digital pico-ammeter model: DPM-111 from which the current in the in circuit could be readily known. Knowing the current flowing through the circuit and voltage across the sample, resistivity of the sample could be calculated by using the following equation [44]:

\[ \rho = \frac{RA}{l} \ \Omega \text{cm} \]  \hspace{1cm} (4)

where R is the resistance of the sample, A = \( \pi r^2 \) is the surface area, r is radius of the sample, l is the thickness of the pellet and \( \rho \) is the resistivity of the sample. The effect of temperature on resistivity of the material is shown in Fig. 6.8. The DC electrical resistivity decreased with increase in temperature, indicating semiconducting nature of the ferrite samples.
Semiconductor nature of the compounds is very useful tool for the photo-catalytic applications [45]. It is reported in literature that the semiconductors are used in the degradation of the organic compounds [46]. The semiconductors have band gap which is suitable for the photo-catalytic activity.

Further, the resistivity decreased with increase in cadmium ion concentration. This might be attributed to the increase n-type conduction due to $\text{Fe}^{2+}$-$\text{Fe}^{3+}$ hopping and the p-type conduction due to $\text{Co}^{2+}$-$\text{Co}^{3+}$ hopping. However, the n-type conduction dominates the p-type conduction. This may be due to the fact that cadmium ions strongly prefer tetrahedral sites, thus the substitution of iron by the cadmium ion at tetrahedral sites, caused the migration of $\text{Fe}^{3+}$ ions to the octahedral B- sites [47]. The increase of $\text{Fe}^{3+}$ ions in the B-sites increased the hopping rate between $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ on B sites, which lead to an increase in the conductivity of the ferrites. Hence the resistivity of the ferrites decreased with increase in cadmium concentration. The d.c. electrical resistivity values for all the samples are given in Table 6.4.

![Graph: Variation of DC resistivity with temperature of BaCo$_{0.2}$Cd$_x$Fe$_{12-x}$O$_{19}$ (0.2 $\leq x \leq 1.0$) annealed at 1000 °C]
Resistivity and temperature are related as [48]:

$$\rho = \rho_0 e^{\Delta E/kT}$$  \hspace{1cm} (5)

where $\rho_0$ is the resistivity extrapolated to infinite temperature, $T$ is the absolute temperature, $k$ is Boltzmann constant, $\Delta E$ is activation energy. The activation energy of all the samples has been calculated by the slope of $(\log \rho)$ versus $(1000/T)$ (Fig. 6.9). It is observed that the activation energy increased with increase in the value of $x$ as tabulated in Table 6.4.

![Graph](image.png)

**Fig. 6.9:** Log $\rho$ vs 1000/T graphs for BaCo$_{0.2}$Cd$_x$Fe$_{12-x}$O$_{19}$ annealed at 1000 °C.

**Table 6.4:** D.C. resistivity and Activation energy measured at 323 K for all the ferrite compositions annealed at 1000 °C.

<table>
<thead>
<tr>
<th>Ferrites composition</th>
<th>Resistivity ($10^{10} \Omega$cm)</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCo$<em>{0.2}$Cd$</em>{0.2}$Fe$<em>{11.6}$O$</em>{19}$</td>
<td>2.87</td>
<td>1.35</td>
</tr>
<tr>
<td>BaCo$<em>{0.2}$Cd$</em>{0.4}$Fe$<em>{11.4}$O$</em>{19'}$</td>
<td>2.03</td>
<td>1.13</td>
</tr>
<tr>
<td>BaCo$<em>{0.2}$Cd$</em>{0.6}$Fe$<em>{11.2}$O$</em>{19}$</td>
<td>1.54</td>
<td>1.10</td>
</tr>
<tr>
<td>BaCo$<em>{0.2}$Cd$</em>{0.8}$Fe$<em>{11}$O$</em>{19}$</td>
<td>1.14</td>
<td>1.05</td>
</tr>
<tr>
<td>BaCo$<em>{0.2}$Cd$</em>{1.0}$Fe$<em>{10.8}$O$</em>{19}$</td>
<td>0.87</td>
<td>1.00</td>
</tr>
</tbody>
</table>
6.4.6. Catalytic performance on methyl orange dye:

The degradation of methyl orange (MO) was studied by BaCo$_{0.2}$Cd$_x$Fe$_{11.8-x}$O$_{19}$ (x = 0.2, 0.4, 0.6, 0.8 and 1.0) nanoparticles under identical reaction conditions in the presence of H$_2$O$_2$ at room temperature. The absorption spectra of BaCo$_{0.2}$Cd$_x$Fe$_{11.8-x}$O$_{19}$ (x = 0.2, 0.4, 0.6, 0.8 and 1.0) annealed at 1000°C, obtained using the UV-Vis spectrophotometer, are illustrated in Fig. 6.10.

**Fig. 6.10:** Change in absorption with time of methyl orange solution in the presence of BaCo$_{0.2}$Cd$_x$Fe$_{11.8-x}$O$_{19}$ annealed at 1000 °C.