

# Effect of cationic CTAB surfactant on the microstructural and magnetic properties of barium hexaferrite

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## Abstract

M-type hexagonal ferrite samples with composition  $\text{BaFe}_{12}\text{O}_{19}$  have been prepared by two different chemical routes, namely co-precipitation and microemulsion, in presence of different amounts of cationic surfactant cetyltrimethyl ammonium bromide (CTAB). The microstructural and magnetic properties of the  $\text{BaFe}_{12}\text{O}_{19}$  hexaferrite particles have been investigated under the influence of cationic surfactant, CTAB using XRD, FTIR, SEM, TEM and Vibrating Sample Magnetometer (VSM) techniques. The X-ray diffraction patterns at room temperature show that the prepared samples have a single phase. FTIR results confirm the formation of pure barium hexaferrite. SEM analysis shows the effect of CTAB on reduction of particle size during synthesis using two different routes. TEM results reveal synthesis of barium hexaferrite nanoparticles after calcinations at 800° C temperature. VSM results reveal that the values of saturation magnetization ( $M_s$ ), intrinsic coercivity ( $H_c$ ) and remnant magnetization ( $M_r$ ) depend upon the method of preparation.  $\text{BaFe}_{12}\text{O}_{19}$  hexaferrite particles of single domain were produced by using a microemulsion technique.

**Keywords:** CTAB surfactant; Barium hexaferrite; Microemulsion; Co-precipitation; Microstructure; Magnetic properties

## 1. Introduction

M-type hexaferrites have prominent position in permanent magnet market due to their low cost, relatively high coercivity, excellent chemical stability and corrosion resistance [1,2]. Barium hexaferrites have been recently extensively studied for advanced recording applications such as disk drivers, video recorder, microwave absorbing materials [3,4]. M-type hexaferrites have a chemical composition of  $\text{AFe}_{12}\text{O}_{19}$  and a hexagonal crystal structure, where A represents divalent cation such as  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  or  $\text{Pb}^{2+}$ . A salient feature of M-type hexaferrite is the large uniaxial anisotropy inherent in hexagonal crystal structure. Several techniques have been suggested to prepare barium hexaferrite powder, in which wet chemical route has advantages such as excellent product homogeneity, better compositional control and low cost [5]. The synthesis method strongly determines homogeneity, particle size, shape and magnetic properties of final product [6,7].

We report synthesis, microstructural and magnetic properties of  $\text{BaFe}_{12}\text{O}_{19}$  hexaferrite particles in the presence of cationic CTAB

surfactant using co-precipitation and microemulsion routes. In the present work, co-precipitation method is adopted due to its mere simplicity while microemulsion synthesis is adopted mainly to control synthesis parameters and to produce tailor-made products. The basic purpose of our investigations is to study the effect of CTAB on morphology and characteristics of Ba-M hexaferrite and inter-comparison of two different synthesis routes.

The chemical co-precipitation is a low-cost technique suitable for mass production but undesired non-uniform particles are easily formed due to the agglomeration of particles. In order to block the agglomeration of particles, cationic surfactant CTAB is used. CTAB adsorbed on the surfaces of the formed hexaferrite precursors can suppress the mass transport, thus block/prevent the agglomeration of precursors. The microemulsion technique is considered as an efficient method for preparing nanoparticles and it is believed that microemulsion derived particles generally possess good chemical homogeneity and high purity but only limitation is production of less yields. The surfactant, which is composed of molecules with hydrophilic head and

hydrophobic tail, can improve microstructural and magnetic properties of the synthesized powder. In presence of surfactant, surface tension of solution is reduced and it facilitates nucleation and formation of new phases. The microstructural and magnetic properties of the  $\text{BaFe}_{12}\text{O}_{19}$  hexaferrite particles have been investigated under the influence of cationic surfactant, CTAB using XRD, FTIR, SEM, TEM and VSM techniques.

## 2. Experimental

$\text{BaFe}_{12}\text{O}_{19}$  hexaferrite particles were synthesized in presence of CTAB surfactant (1% and 2%) using co-precipitation and micro emulsion routes.

### 2.1. Co-precipitation (CP) technique

AR grade ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , > 98.0 purity, Merck), barium nitrate ( $\text{Ba}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , > 99.0 purity, Merck) and cetyltrimethyl ammonium bromide (CTAB 1% and then 2%, 99.0% purity, Sigma Aldrich) were used as starting materials without further purification. Appropriate amounts of iron nitrate and barium nitrate in a Fe/Ba ratio 12 were dissolved in a minimum amount of de-ionised water to form aqueous solution. The solution was stirred for 40 min and its pH was adjusted to 7, to make it neutral, using combination of  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{NH}_3\text{H}_2\text{O}$  (concentration 30 wt%) to make precipitates. The precipitates were washed with ethanol and de-ionised water by magnetic decantation several times, aged for 12 hrs and then dried at  $100^\circ\text{C}$  for 24 hrs. Finally, dark brown magnetic particles were calcinated in air atmosphere at  $800^\circ\text{C}$  for 6 hrs to obtain  $\text{BaFe}_{12}\text{O}_{19}$  hexaferrite samples (CP).

### 2.2. Microemulsion (ME) technique

In the first set of experiment, microemulsion I consisted of 2.4 gm CTAB, 8.8 ml iso-octane, 2 ml butanol, 0.12 M  $\text{Fe}(\text{NO}_3)_3$  and 0.011 M  $\text{Ba}(\text{NO}_3)_2$  according to Fe/Ba ratio 12 and ratio of aqueous phase to oil phase,  $R = V_{(\text{aqueous})} : V_{(\text{oil})} = 1:8$ . Keeping the same value of R, microemulsion II contained 1.2 gm CTAB, 4.4 ml iso-octane, 1 ml butanol, 0.1 M solution of ammonia,  $(\text{NH}_4)_2\text{CO}_3$  serving as a precipitating agent. Microemulsion II was added dropwise into microemulsion I and stirred vigorously for 4 hrs. After the solution was aged for 24 hrs, the precursor particles formed within the water pools of the reverse micelles were washed by centrifuging with dehydrous ethanol and de-ionised water several times in order to remove the surfactant and organic residuals. The

prepared nanoparticles were dried at  $100^\circ\text{C}$  in a vacuum dryer for 24 hrs followed by thorough grinding. The obtained dried particles were calcinated at  $800^\circ\text{C}$  for 6 hrs in air atmosphere followed by furnace cooling at room temperature to obtain  $\text{BaFe}_{12}\text{O}_{19}$  hexaferrite samples (ME). In the second set, the same experiment was repeated for 2% of CTAB in order to investigate the effect of CTAB on the formation of barium hexaferrite particles as well as microstructural and magnetic properties.

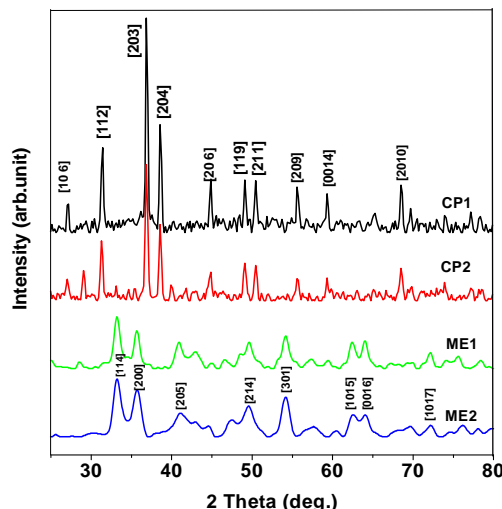
### 2.3. Characterization of prepared samples

The crystalline structure and phase purity of barium hexaferrite particles were determined using a Philips-PW 3050/60 diffractometer. XRD diffractograms were obtained in the  $2\theta$  range of  $25-80^\circ$ , with a step of  $0.02^\circ$ , using the  $\text{Cu K}\alpha$  radiation source of  $\lambda = 1.5406 \text{ \AA}$ . Scanning Electron Microscope (JEOL, Model JSM-6490) was used for recording the morphology of barium hexaferrite particles. Transmission Electron Microscope (Hitachi H-7500, resolution  $10 \text{ \AA}$ ) was used to study particle sizes and shapes. Fourier transform infrared (FT-IR) spectra were recorded using a FT-IR spectrometer analyzer (Bruker tensor 27) with KBr pellets in the wave number range of  $4000$  to  $400 \text{ cm}^{-1}$ . The magnetic properties (intrinsic coercivity, saturation and remanent magnetization) were measured with a vibrating sample magnetometer (VSM, EG&G Princeton 4500) under maximum applied field of 15 kOe.

## 3. Results and Discussion

### 3.1. XRD analysis of $\text{BaFe}_{12}\text{O}_{19}$

The X-ray diffraction pattern of  $\text{BaFe}_{12}\text{O}_{19}$ , synthesized using co-precipitation and microemulsion techniques in presence of CTAB (1% , 2%), was obtained at room temperature. Figure 1 shows X-ray diffraction pattern and confirms single M-type phase structure. All XRD reflection peaks are indexed by applying a hexagonal crystal system and space group  $\text{P6}_3/\text{mmc}$  (here planes [112], [203], [204], [206], [119], [211], [209], [0014] and [2010] used for CP samples; whereas planes [104], [200] and [301] used for ME samples), which confirms that the phase belongs to the magneto-plumbite crystal structure [8]. A comparison of XRD spectra of CP and ME samples reveals that ME samples have low crystallinity which is further confirmed by TEM measurements of particle size. Ultimately, this will have a predominant effect on the magnetic properties of ME samples.



**Figure 1.** XRD pattern of barium hexaferrite samples calcinated at 800° C for 6 hrs.

The values of lattice parameters and their ratio for all samples (CP1, CP2, ME1 and ME2) are listed in Table 1. It is clear from Table 1 that with increase of the concentration of CTAB, lattice parameters  $a$ ,  $c$  and cell volume  $V$  show slight decrease in values and  $c/a$  ratio shows slightly higher value for ME1 sample but remains constant for other (CP1, CP2, ME2) samples.

### 3.2. FTIR analysis

FTIR spectra of dried precursors as well as calcinated samples was taken at room temperature in order to monitor the structural changes during the synthesis process. Figure 2 (a, b) shows FTIR spectra of dried precursors (heated at 100° C for 24 hrs) and  $\text{BaFe}_{12}\text{O}_{19}$  hexaferrite particles calcinated at 800° C, respectively. The spectra of dried precursors (Figure 2a) indicates the characteristic bands in the range 3200-3600  $\text{cm}^{-1}$  assigned to O-H

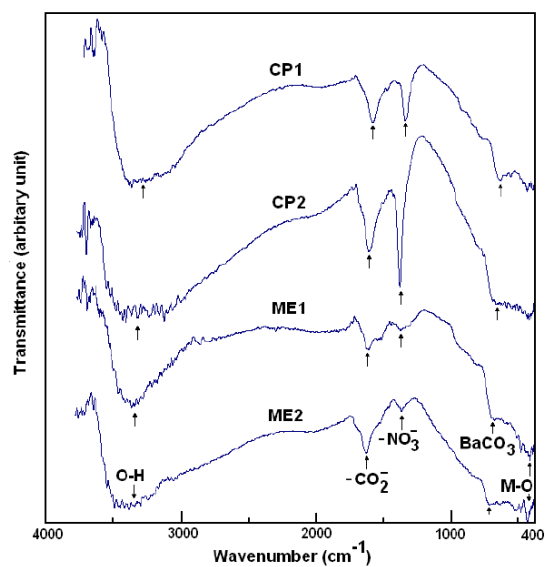
stretching vibration of water molecules, while the asymmetrical and symmetrical vibration bands of  $\text{CO}_3^{2-}$  are located around 1600  $\text{cm}^{-1}$ . The bands about 1380  $\text{cm}^{-1}$  are ascribed to the N-O stretching vibration of  $\text{NO}_3^-$ . The bands around 800  $\text{cm}^{-1}$  and 430  $\text{cm}^{-1}$  represent  $\text{BaCO}_3$  and M-O, respectively. FTIR results show that after calcination (Figure 2b), the absorption bands related to O-H,  $\text{CO}_3^{2-}$ , N-O and  $\text{BaCO}_3$  disappear. The bands appearing around 550  $\text{cm}^{-1}$  and 440  $\text{cm}^{-1}$  are attributed to M-O stretching vibration of Ba-M hexaferrite [9-11].

### 3.3. SEM Analysis

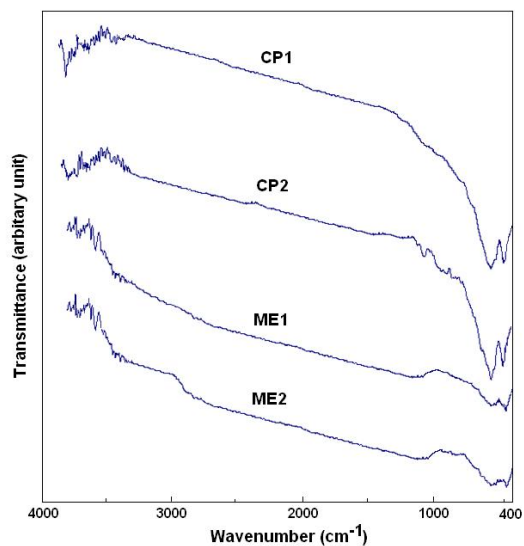
SEM images of all raw samples dried at 100° C for 24 hrs are shown in Figure 3 (a, b, c, d). A comparison of platelets of Ba-hexaferrite samples confirms the predominant influence of CTAB addition, resulting in reduction of particle size. CP1 and ME1 sample powders show very

**Table 1.** Structure parameters  $a$ ,  $c$ , cell volume  $V$  and crystallite size for Barium hexaferrite samples (calcinated at 800° C for 6 hrs) prepared using two different techniques.

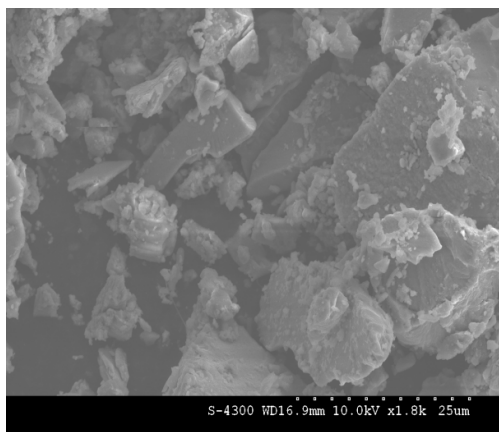
Sample Code	Preparation routes	CTAB (%)	$a$ (Å)	$c$ (Å)	$c/a$	$V$ (Å <sup>3</sup> )
CP1	Co-precipitation	1	5.9228	23.2147	3.9195	705.2637
CP2	Co-precipitation	2	5.8893	23.1083	3.9237	694.1059
ME1	Microemulsion	1	5.8905	23.2621	3.9490	699.0100
ME2	Microemulsion	2	5.8830	23.0648	3.9206	691.3182



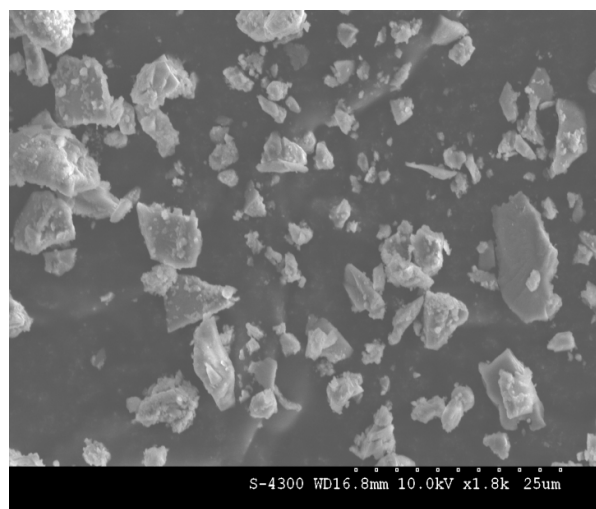
**Figure 2a.** FTIR spectra of barium hexaferrite precursors dried at 100° C for 24 hrs.



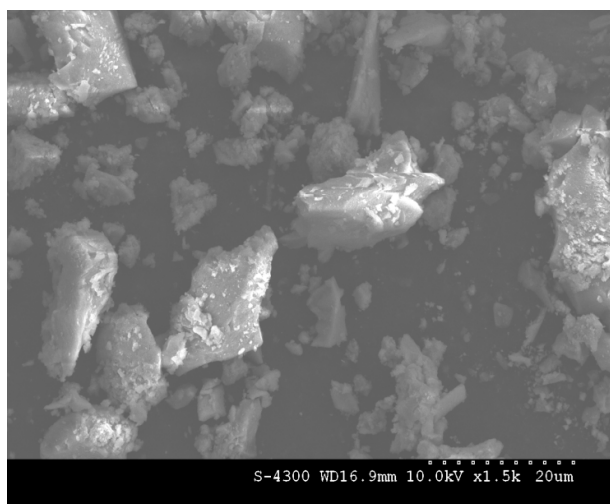
**Figure 2b.** FTIR spectra of barium hexaferrite samples calcinated at 800° C for 6 hrs.



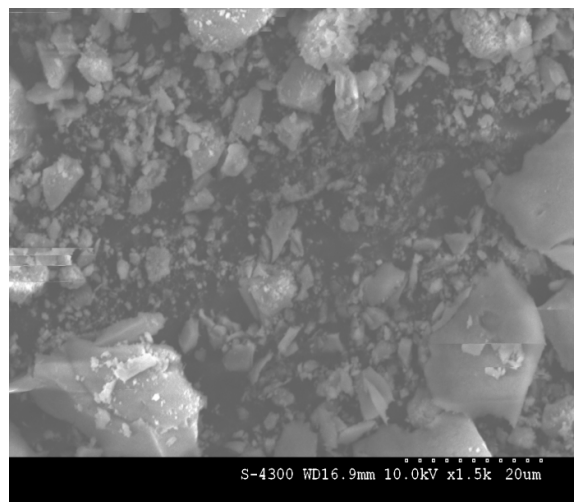
**Figure 3a.** SEM image of CP1 precursors dried at 100° C for 24 hrs.



**Figure 3b.** SEM image of CP2 precursors dried at 100° C for 24 hrs.



**Figure 3c.** SEM image of ME1 precursors dried at 100° C for 24 hrs.



**Figure 3d.** SEM image of ME2 precursors dried at 100° C for 24 hrs.



large, irregular agglomerated clusters of particles; whereas CP2 sample shows separated and relatively small particles. The particle size of Ba-hexaferrite particles decreases considerably, on the average more than half its original size for CP samples, when CTAB concentration is increased from 1% to 2%, is our most important observation. The results for ME samples are not so clearly marked but it is certain that particle size reduction is apparent on addition of higher concentrations of CTAB. It means CTAB is a favorable surfactant for reducing the particle size of  $\text{BaFe}_{12}\text{O}_{19}$  in co-precipitation and micro emulsion techniques, as it prevents the agglomeration of particles. Similar results have been observed for  $\text{BaFe}_{12}\text{O}_{19}$  hexaferrite powder obtained from solvent-free synthesis recently [12].

### 3.4. TEM analysis

TEM study of  $\text{BaFe}_{12}\text{O}_{19}$  hexaferrite particles was carried out on calcinated ( $800^\circ\text{C}$  for 6 hrs) samples by ultrasonically dispersing the barium hexaferrite powders prepared by two different routes in ethanol prior to loading on TEM carbon coated copper grids under ultra-high vacuum. High temperature calcination is desirable to remove cationic CTAB surfactant from the precursors to improve morphology and magnetic properties. Figure 4 (a,b) shows formation of spherical nanoparticles of Ba-hexaferrite in both CP and ME samples. However, there are dramatic changes in particle sizes when barium hexaferrite particles prepared using two different routes are compared. The average particle size of samples prepared using co-precipitation and microemulsion routes are

observed to be 41.2 nm and 6.2 nm, respectively. The values of particle sizes obtained by TEM in the present study for CP samples are comparable with those reported earlier (30–60 nm) for M-type hexaferrites [13]. However, the average particle size for ME samples is much lower than the size (38 nm) reported elsewhere [8]. We may conclude from TEM study that the average particle size of calcinated Ba-hexaferrite decreases by an order of 7 using microemulsion route of synthesis.

### 3.5. VSM analysis

Figures 5(a) and 5(b) show initial saturation magnetization and magnetic hysteresis curves of  $\text{BaFe}_{12}\text{O}_{19}$  samples calcinated at  $800^\circ\text{C}$  for 6 hrs, respectively. Magnetic parameters are listed in Table 2. It is evident from magnetization results that ME samples exhibit relatively high values of saturation and remanent magnetization as compared to CP samples. However, the coercivity values of ME samples show an opposite trend with much lower values as compared to CP samples. Since all samples were synthesized by using two different chemical routes under same conditions (chemical composition, calcination temperature and time etc.), the VSM analysis implies that on addition of 2% CTAB, the saturation and remnant magnetization of CP2 sample is enhanced slightly, whereas coercivity values tend to decrease. We may conclude that improvement in saturation magnetization of CP samples can be attributed to more complete crystallization of the  $\text{BaFe}_{12}\text{O}_{19}$  phase [14]. A comparison of hysteresis loops of CP and ME samples (Figure 5b) reveals the influence of particle size and

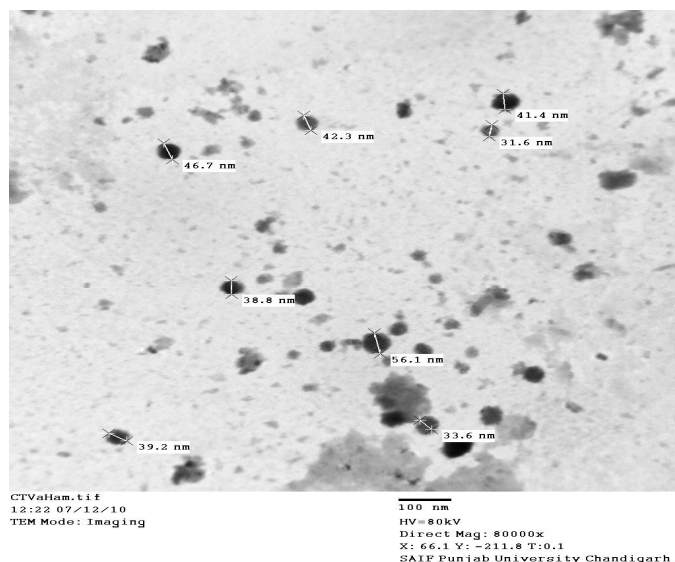


Figure 4a. TEM image of CP samples calcinated at  $800^\circ\text{C}$  for 6 hrs.

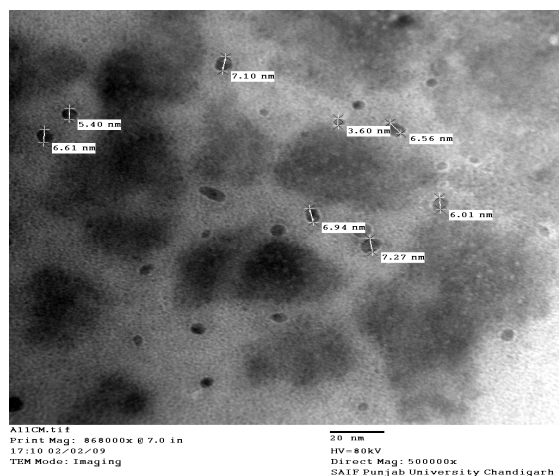


Figure 4b. TEM image of ME samples calcinated at 800°C for 6 hrs.

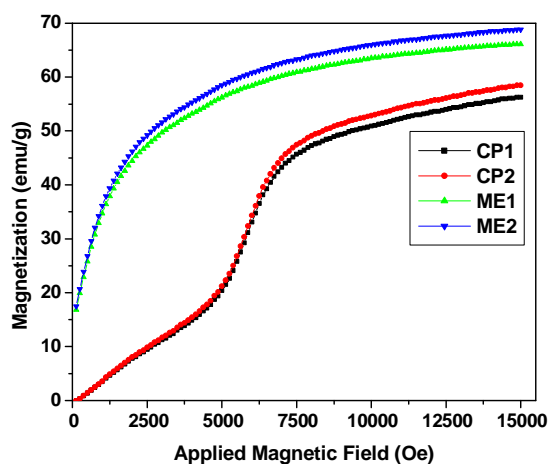


Figure 5a. Magnetization curves of  $\text{BaFe}_{12}\text{O}_{19}$  nanoparticles calcinated at 800° C for 6 hrs in air.

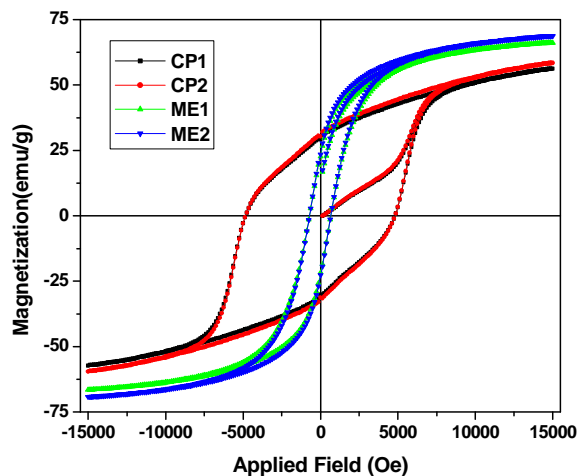
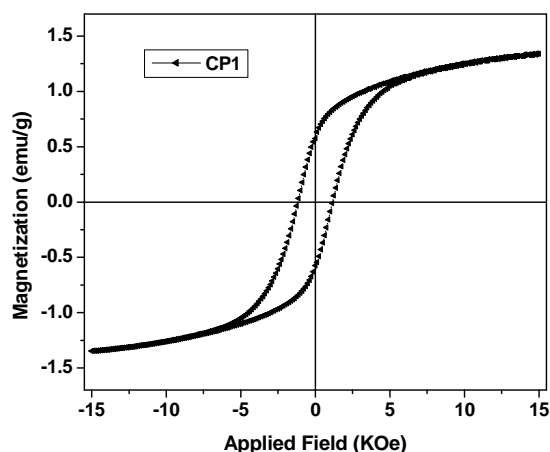


Figure 5b. The hysteresis loops of  $\text{BaFe}_{12}\text{O}_{19}$  nanoparticles calcinated at 800° C for 6 hrs in air.



**Figure 5c.** The hysteresis loop of  $\text{BaFe}_{12}\text{O}_{19}$  precursor dried at  $100^\circ\text{C}$  for 24 hrs in air.

crystallinity on the magnetic properties and performance of  $\text{BaFe}_{12}\text{O}_{19}$  hexaferrite materials. Hysteresis loss of ME samples is almost half of that of CP samples.

To understand the origin of magnetic properties of barium hexaferrite particles further, VSM measurement on CP1 precursors dried at  $100^\circ\text{C}$  for 24 hrs, has been carried out as shown in Figure 5c. VSM results (Table 2) reveal that the values of saturation magnetization and coercive force are much higher than those of bulk materials [15]. However, it should be noted that dried precursors of CP1 sample were repeatedly washed by de-ionised water and ethanol to remove surfactant and other organic impurities, but still some organic impurities are detected (confirmed by FTIR, Figure 2a) in CP1 dried powder. These organic impurities may be responsible for the low values of magnetic parameters, which are ultimately removed by calcination in all samples to enhance magnetic properties.

Our magnetic measurements show that calcination process helps us improve magnetic properties of prepared barium hexaferrite nanoparticles. This improvement of magnetic properties in all prepared samples (in presence of CTAB) may be due to decrease in the concentration of oxygen vacancies during calcination process in air. These oxygen vacancies can change the number of near neighbour oxygen ions with Fe and this effect makes contribution to super-exchange interaction of Fe-O-Fe and enhanced magnetic properties. From further investigation of magnetic properties, we can observe that with increase of CTAB (from 1% to 2%), there is hardly any change in the values of Mr/Ms in CP as well as ME samples. Further, the calculated values of Mr/Ms are found to be close to 0.5 for ME samples, which indicate that single domain particles of  $\text{BaFe}_{12}\text{O}_{19}$  are produced by the microemulsion route [16].

**Table 2.** Magnetic parameters of  $\text{BaFe}_{12}\text{O}_{19}$  powder.

S. No	Sample code	Calcination temperature and time	<sup>a</sup> Hc (Oe)	<sup>b</sup> Ms (emu/g)	<sup>c</sup> Mr (emu/g)	Mr/Ms
1	CP1		4812	52.14	29.38	0.563
2	CP2	800°C,	4750	54.16	30.36	0.561
3	ME1	6hrs	697	63.50	33.39	0.525
4	ME2		650	66.00	34.61	0.524
5	CP1,dried precursor	100°C, 24 hrs	1148	1.257	0.61	0.485

<sup>a</sup>coercivity,

<sup>b</sup>saturation magnetization and

<sup>c</sup>remnant magnetization measured at room temperature under  $H_{\text{max}} = 15\text{ kOe}$



#### 4. Conclusions

M-type barium hexaferrite ( $\text{BaFe}_{12}\text{O}_{19}$ ) mono phase and well crystallized particles have been successfully synthesized by using the microemulsion and chemical co-precipitation techniques in presence of cationic surfactant, CTAB (1%, 2%). The results obtained from our investigations using FTIR, XRD, TEM, SEM and VSM, are summarized as follows:

(i) XRD analysis of barium hexaferrite particles prepared by the microemulsion and co-precipitation techniques confirmed the formation of single phase compound. Increase of CTAB concentration results in slight decrease in the lattice parameters and cell volume.

(ii) FTIR results confirm the formation of pure barium hexaferrite and structural changes produced after calcination at high temperatures.

(iii) SEM analysis clearly shows the effect of CTAB on reduction of particle size during synthesis using two different routes. TEM results reveal the synthesis of barium hexaferrite nanoparticles after calcination at high temperatures.

(iv) Magnetization results reveal the effect of preparation routes. Saturation magnetization increased but hysteresis loss decreased in Ba-hexaferrite particles prepared using microemulsion route. CTAB effect appears in magnetization curves only at high applied magnetic fields.

(v) The values of saturation magnetisation, intrinsic coercivity and remnant magnetisation depend upon the method of preparation.  $\text{BaFe}_{12}\text{O}_{19}$  hexaferrite particles of single domain were produced by using microemulsion technique.

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