



Research Article

COMPARATIVE STUDY OF Ba-M HEXAFERRITE PARTICLES PREPARED USING MICROEMULSION PROCESSING AND CO-PRECIIPITATION TECHNIQUES

¹Virk H. S.*, ¹Poonam Sharma and ²Rajshree Jotania

Address for Correspondence

¹Nanotechnology Laboratory, DAV Institute of Engineering & Technology,
Kabir Nagar, Jalandhar-144008, India

²Material Science Research Laboratory, Department of Physics, University School of Sciences,
Gujarat University, Ahmedabad 380 009, India

Email: hardevsingh.virk@gmail.com; chem.sharma@gmail.com, rbjotania@gmail.com

ABSTRACT

BaFe₁₂O₁₉ hexaferrite precursors containing cetyltrimethyl ammonium bromide (CTAB) were synthesized using two different routes, namely, microemulsion processing and chemical co-precipitation techniques. The prepared barium hexaferrite precursors were calcinated at 950° C for 4 hours in a furnace, then slowly cooled to room temperature. The effect of synthesis techniques on structural and magnetic properties of BaFe₁₂O₁₉ hexaferrites has been studied. Decomposition behaviour is investigated by means of thermal analysis (TGA). Fourier Transform Infrared (FTIR) and X-ray diffraction (XRD) techniques have been used for characterization of barium hexaferrite particles. The X-ray diffractogram of the sample prepared by using a co-precipitation technique and microemulsion process show only single M-phase. Surface morphology of nonporous particles was examined using SEM and TEM. Magnetic measurements were carried out at room temperature using a Vibration Sample Magnetometer (VSM). The maximum coercivity and saturation magnetisation of prepared BaFe₁₂O₁₉ hexaferrite samples were determined by a VSM. The value of saturation magnetisation depends on the type of synthesis technique used. The sample prepared by a microemulsion route shows high saturation magnetisation (~71 emu/g), where as the sample prepared by a co-precipitation route exhibits low saturation magnetisation (~65 emu/g). Magnetic study reveals that prepared BaFe₁₂O₁₉ hexaferrite particles using both techniques possess single magnetic domain.

KEY WORDS: Barium hexaferrite, Microemulsion, Co-precipitation, Magnetic Properties, FTIR, XRD.

INTRODUCTION

Barium hexaferrite has been extensively studied for advanced recording applications like computer data storage, high density perpendicular magnetic and magneto-optic recording, disk driver and video recorder because of its high intrinsic coercivity, large saturation magnetisation, high Curie temperature, fairly large magneto-crystalline anisotropy constant, excellent chemical stability and corrosion resistivity [1-2]. M-type barium hexaferrite with hexagonal molecular structure BaFe₁₂O₁₉ is a high performance permanent magnetic material. The technological applications require barium hexaferrite particles with good

chemical homogeneity, and narrow particle size distribution. The magnetic properties of hexaferrite strongly depend upon particle size, method of preparation etc. In order to improve the properties of BaFe₁₂O₁₉ some measure can be taken such as improving its microstructure, controlling its chemical composition, size and morphology. Improvement of magnetic properties has been attempted extensively, which resulted in an important increase in coercivity, without a simultaneous drop in remanence. It is difficult to obtain monodispersed barium hexaferrite particles by using the conventional ceramic technique [3], which involves very high temperature (~1200° C).

Several low temperatures, non-conventional techniques are proposed in order to prepare ultrafine barium hexaferrite particles with high qualities. These techniques comprised co-precipitation [4, 5], hydrothermal [6], sol-gel [7], citrate precursor [8] and glass crystallization [9].

The chemical co-precipitation is a low cost technique suitable for mass production compared to other methods. 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. However, this method is widely used to prepare Spinel ferrites and other materials with good physical and chemical properties [10, 11], but is rarely used to synthesize hexaferrites. Recently, we have synthesized W and M type barium hexaferrite particles by using sol-gel and co-precipitation methods in presence of different surfactants and found that the method of preparation plays a crucial role in controlling the morphology and saturation magnetization of barium hexaferrite particles [12-14]. In the present paper, we report synthesis and characterisation of $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite precursors and particles prepared by using the microemulsion and the co-precipitation techniques in presence of cationic surfactant, CTAB.

Such a study is important to understand how to control the synthesis of single phase barium hexaferrite particles with homogeneous ultrafine size at low calcination temperatures.

MATERIALS AND METHODS

1. Synthesis of Barium Hexaferrite: A.R. Grade barium nitrate ($\text{Ba}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), cetyltrimethyl ammonium bromide (CTAB) were used as starting materials. Appropriate amounts of barium nitrate, CTAB (0.01 M surfactant in 100 ml de-ionized water) and ferric nitrate were dissolved, one by one, in 100 ml of de-ionized water. Ammonium hydroxide (NH_4OH) solution (w/v=30%) was added slowly in the mixture to adjust pH of 8. The mixed solution was stirred for two hours and was kept at room temperature 24 hours for aging. The barium hexaferrite precipitate was separated in a centrifuge machine at 2500 rpm for 20 min. The prepared precipitate was washed in 1:1 mixture of methanol and chloroform followed by 100% de-ionized water to remove residual surfactant impurities. The precipitate was dried at 100°C for 24 hours and calcinated at 950°C for 4 hours in order to obtain $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite particles. Barium hexaferrite particles were prepared by water in oil microemulsion technique involving cetyltrimethyl ammonium bromide (CTAB) as a surfactant, n-butanol as the co-surfactant, isooctane as the solvent (oil phase) and aqueous solution as water phase. The aqueous phase in microemulsion-I was a solution of 0.1 M barium hydroxide and 1.2 M ferric nitrate (5ml aqueous solution in 42.5ml microemulsion). The aqueous phase in microemulsion-II was a solution of ammonia (w/v=25%) as the precipitator agent (5 M aqueous solution of ammonia in 42.5 ml microemulsion). In order to obtain precipitation of barium

hexaferrite particles, microemulsion-II was added drop wise in microemulsion-I under vigorous stirring for 2 hours; then the solution was aged for 12 hours. The precursor particles within the water pool of micelles were washed by centrifuging with anhydrous methanol and water to remove the remaining surfactant and organic residual. The precipitate was dried at 100° C for 24 hours in an oven and then calcinated at 950° C for 4 hours followed by furnace cooling to room temperature.

2. Characterization: The Fourier transformed (FT-IR) spectra of $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite samples were recorded on a FTIR spectrometric analyser (Bruker Tensor 27 Model). TGA curve of dried material was recorded using a thermo gravimetric analyzer model no.TGA 50 in the region of 50° C to 800° C with a rate of 10° C/min. Phase and quantitative analysis were performed by X-ray diffraction using a $\text{Cu-K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$, 45.0 kV, 50.0 mA) on a Philips diffractometer (PW 3050/60) with a step scan 0.02° C/min. The 2θ angles were scanned over a range of 20°-

80°. In order to study the particle morphology Scanning electron microscope (Make-Leo/Lica model Stereo scan 440) and TEM (Hitachi H-7500 Model) were used. The magnetic measurements were recorded at room temperature using a vibrating sample magnetometer, EG & G Princeton Applied Research Model 4500 under maximum applied field of 15 kOe.

RESULTS AND DISCUSSION

1. FTIR Spectra: To investigate ferrite phase formation, the prepared $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite particles were characterized via Fourier transformed Infrared spectra (FTIR) analysis. The room temperature infrared spectra of calcinated samples were recorded in mid IR range, 4000 cm^{-1} to 400 cm^{-1} . A few milligrams of $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite particles were mixed with anhydrous KBr powder and made in the form of pallet for the measurements. Fig. 1 shows FTIR spectra of $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite particles calcinated at 950° C for 4 hrs. The absorption bands between 580 cm^{-1} to 440 cm^{-1} can be attributed to the formation of hexaferrite [15, 16].

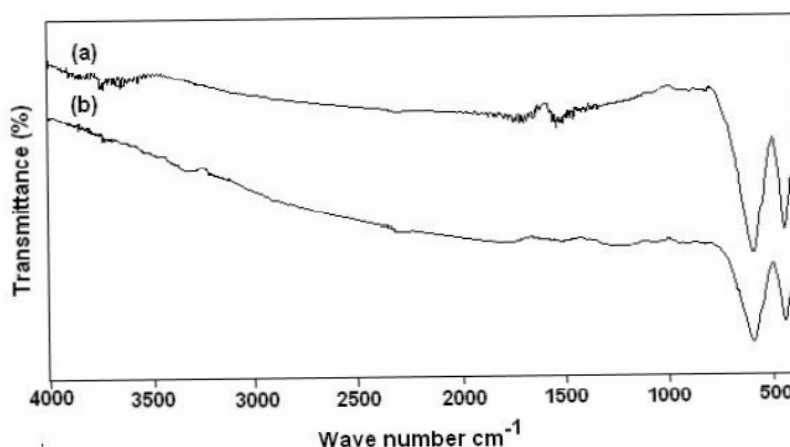


Fig. 1 FTIR spectra of $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite particles prepared using (a) co- precipitation and (b) microemulsion techniques (calcinated at 950° C for 4 hrs.).

2. Thermal Studies: TGA curves of dried gel were recorded using a thermogravimetric analyser in the region of 50° C to 800° C with a heating rate of 10° /min in static air.

To have a better understanding of $\text{BaFe}_{12}\text{O}_{19}$ forming mechanism from gel to the solid precursor obtained by using co precipitation and microemulsion techniques, the gel was thermally analyzed and resultant TG curves are shown in figure 2. During the heat treatment of gel, several processes such as dehydration, oxidation of the residual organic groups, decomposition and sintering take place. TG curves show three distinct steps of weight loss. The first step weight loss between 50° C to 300° C (~7 wt.% in microemulsion sample and ~9% in the sample prepared by using a co- precipitation technique) due to desorption of adsorbed

water molecules. In the second step, a sharp weight loss between 300° C to 480° C (~14 wt. % in both cases) occurs. In the third step, the weight loss is different in different samples, it is about 5 wt. % in the sample prepared by using a microemulsion process, observed in temperature range between 480° C and 510° C. The weight loss observed in the sample prepared by using co-precipitation technique is about 15% between temperature ranges of 480° C to 680° C. These weight losses may be due to combustion of organic substances [15, 17]. It can be seen from figure that there is no weight loss after 510° C in the sample prepared by using microemulsion technique, which confirms the high thermal stability of the sample synthesized by using a microemulsion process.

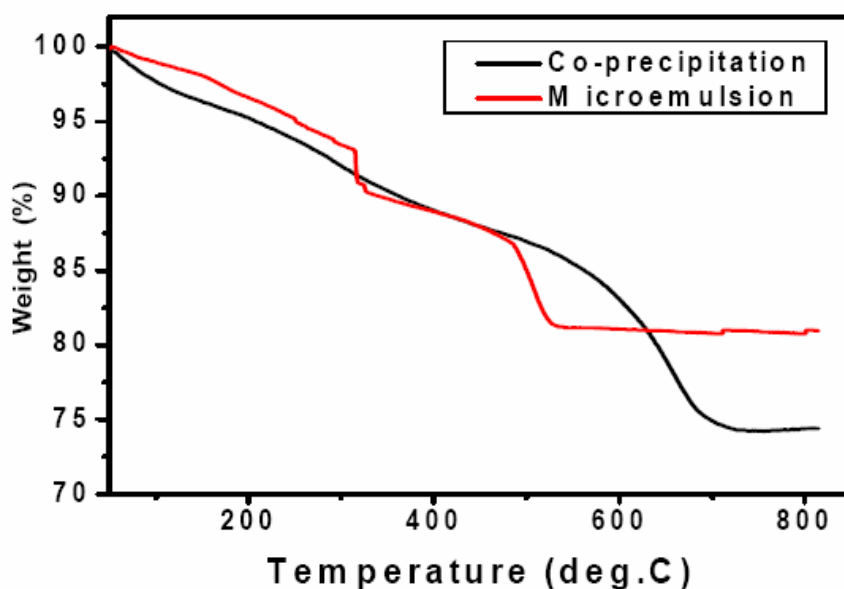


Fig. 2 TGA curves of dried gel prepared by co-precipitation and microemulsion techniques.

3. Structural Investigation and Phase Analysis:

Fig. 3(a, b) shows the X-ray diffractograms of $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite particles prepared using microemulsion and co-precipitation techniques, respectively.

The diffraction peaks appearing in the XRD pattern were indexed with the standard pattern for M-type hexagonal $\text{BaFe}_{12}\text{O}_{19}$ crystals (JCPDS 72-0738 for microemulsion sample and JCPDS 84-0757 for co-precipitation sample).

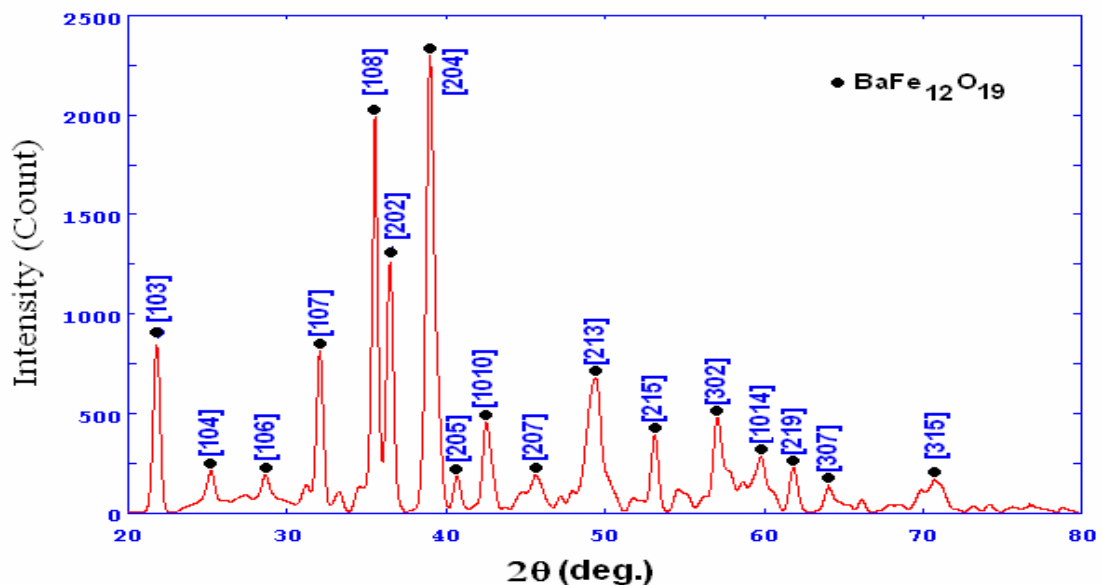
A high purity barium ferrite phase was obtained using microemulsion and co-precipitation techniques, with no other phases detected in the prepared particles by XRD phase analysis. Well defined sharp Bragg peaks indicate good crystalline quality of prepared samples. Lattice constants a and c of $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite samples were calculated using eq.

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

Where h , k and l are Miller indices, d is inter-planer distance. With the values of a and c , the lattice volume, V , of hexagonal crystal sample can be obtained using eq. (2)

$$V = \frac{\sqrt{3}}{2} a^2 c \quad (2)$$

The values of lattice constants and lattice volume are listed in Table 1. As shown in Table 1, sample prepared by a microemulsion route leads to a slightly higher values of a and c , which results in a slight increase in lattice volume. The shrinkage of lattice is observed in $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite sample prepared using co-precipitation route may be due to partial solubility of Fe^{3+} ions in the Spinel block of M-type hexagonal structure.



(a)

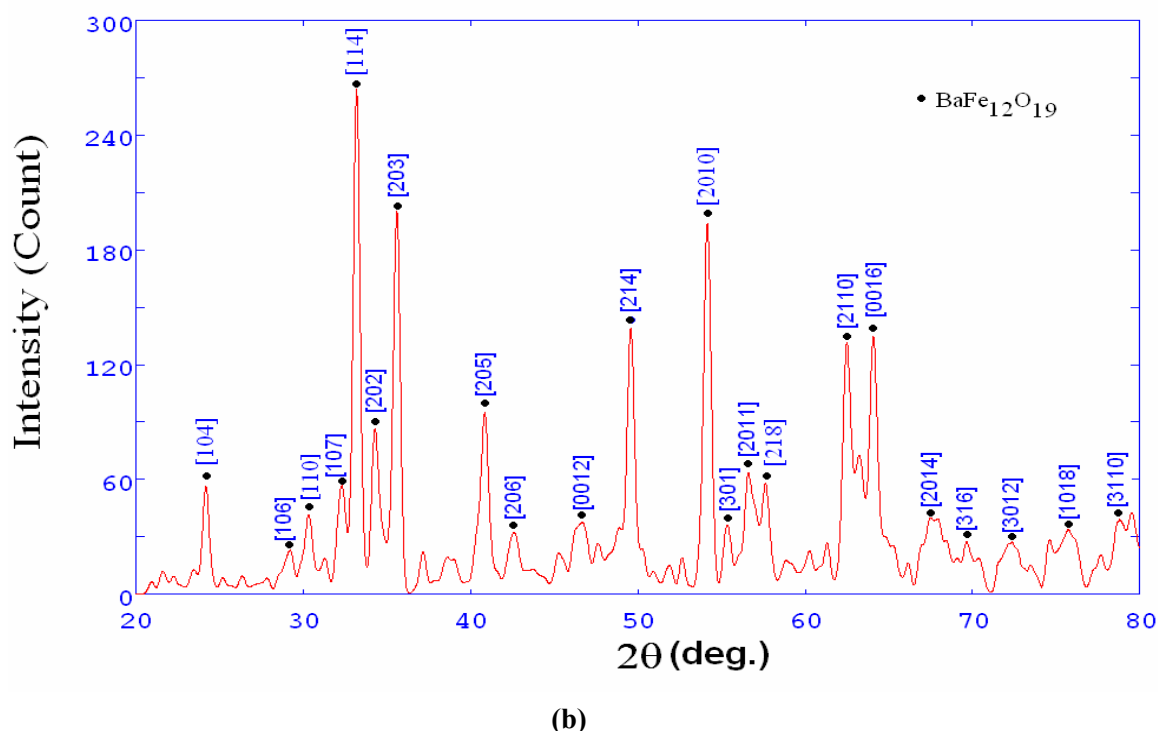


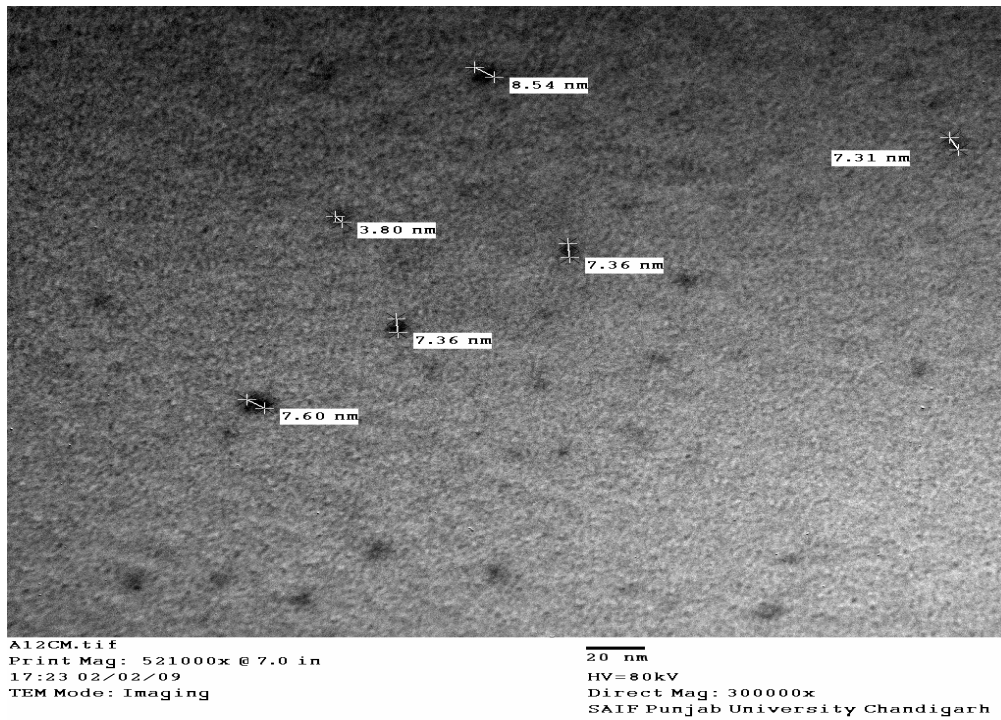
Fig. 3(a, b) XRD pattern of $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite particles (calcinated at 950°C for 4hrs.) prepared using (a) co- precipitation, and (b) microemulsion techniques

Table 1: Structure parameters a, c and cell volume V for Barium hexaferrite samples (calcined at 950°C for 4 hrs) prepared using different techniques

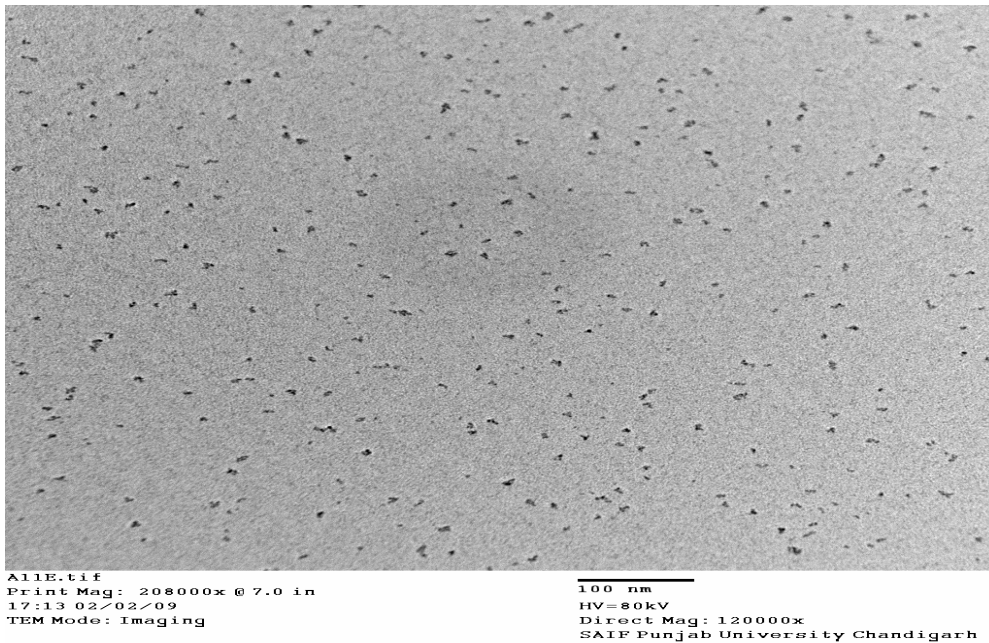
Preparation techniques	a (Å)	c (Å)	V (Å ³)
Microemulsion	5.8905	23.2621	699.01
Co-precipitation	5.8000	23.1800	675.31

4. Micro-structural Analysis: TEM images of barium hexaferrite precursors, dried at 100°C for 24 hours, prepared by using the co- precipitation and microemulsion techniques are shown in Figs. 4(a) and 4(b), respectively. TEM images of dried precursors were taken by ultrasonically dispersing of barium ferrite precursors in ethanol prior to decomposition into TEM copper grid. The observation shows the nano-structured particles of spherical shape and narrow size distribution. The precursors

prepared by using a co-precipitation technique shows the average particle size is about 7.0 nm, where as the precursors prepared by using a microemulsion process shows the average particle size about 4.0 nm. One concludes from TEM study that both processes are favourable to obtain nanoprecursors with small dimensions. There are dramatic changes in both morphology and particle size when precursors are heated at 950°C for 4 hrs.



(a)

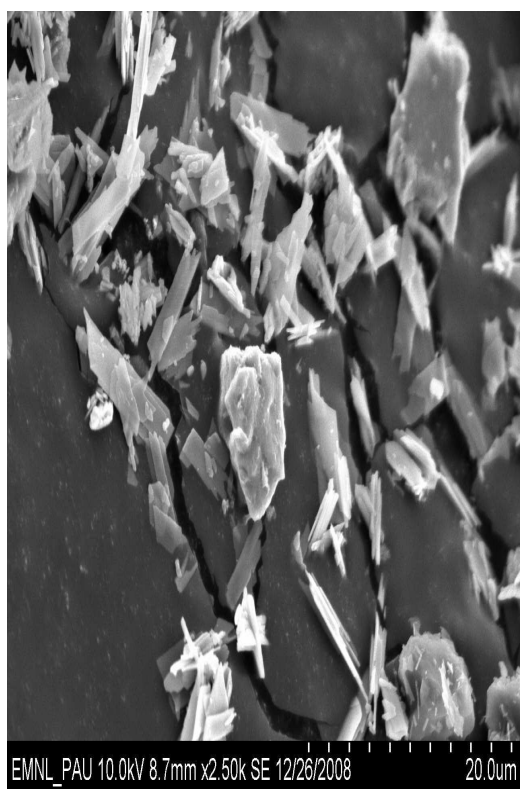


(b)

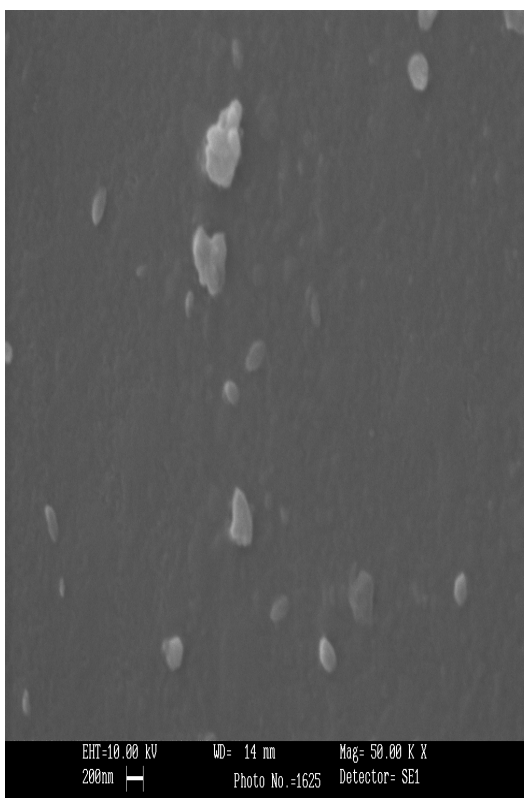
Fig. 4(a,b) TEM images of $\text{BaFe}_{12}\text{O}_{19}$ hexferrite precursors (dried at 100°C for 24 hrs) prepared using (a) co-precipitation technique, and (b) microemulsion process.

The SEM micrographs of $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite particles calcined at 950°C for 4 hrs., prepared by using co-precipitation and microemulsion techniques are shown in Figs. 5(a) and 5(b), respectively. It can be observed from Fig. 5 (a) that barium hexaferrite particles are arranged in some laminate-like structures which include different size particles of micrometer range with large non- uniform distribution. We think that an attractive force existing between the molecules of barium and ferric ions may lead to a surface inhomogeneity in

the sample prepared using co-precipitation technique. It can be also seen from Fig. 5(b) that $\text{BaFe}_{12}\text{O}_{19}$ particles prepared by a microemulsion route produce partially uniform, separate crystallites which include very small particles, order of 80 nm to large grains of more than 200 nm. One may conclude that microemulsion route leads to the formation of nano size, separated particles having single phase barium hexaferrite (also confirmed by XRD analysis).



(a)



(b)

Fig. 5(a, b) SEM images of $\text{BaFe}_{12}\text{O}_{19}$ hexferrite particles (calcined at 950°C for 4 hrs.) prepared using (a) chemical co-precipitation, and (b) microemulsion techniques

Table 2: Magnetic parameters of BaFe₁₂O₁₉ hexaferrite particles prepared by using microemulsion and co-precipitation techniques, calcinated at 950°C for 4 hrs

Preparation techniques	Coercivity (H _c) Oe	Saturation Magnetisation (M _s) emu/g	Remanent Magnetisation (M _r) emu/g	M _r /M _s	K(HA ² /kg.)
Microemulsion	4702	70.69	35.94	0.508	2.626×10^{-3}
Co-precipitation	4825	64.66	32.99	0.512	2.464×10^{-3}

Coercivity-H_c, saturation magnetisation-M_s and remanent magnetisation-M_r, magnetocrystalline anisotropy constant-K were measured at room temperature under H_{max} = 15 kOe.

5. Magnetic Properties: The field dependent magnetization of different powders of barium hexaferrites were measured at room temperature on a vibrating sample magnetometer with a maximum applied field of 15 kOe. The initial magnetization curves and hysteresis loops of the barium hexaferrite samples calcined at 950° C for 4 hrs. are shown in Figs. 6 and 7, respectively. The results of magnetic parameters are summarized in Table 2.

It is clear from Table 2, saturation magnetisation of the sample prepared by a microemulsion route is higher than that of the sample prepared by a co-precipitation route, but the value of M_r/M_s is about 0.5 (both cases), which indicates that BaFe₁₂O₁₉ hexaferrite particles of single domains were produced. In general, as commonly observed in the case of ultrafine particles, the saturation magnetisation values are lower than the theoretical saturation magnetisation for single crystal of barium hexaferrite (M_s = 72 emu/g.) as reported by Shirk and Buessem [18]. In present case the saturation magnetisation value is observed very near to the theoretical value of the sample prepared using microemulsion route, where as there is a deviation of this value in the sample

prepared using a co-precipitation technique. Also, the value of intrinsic coercivity obtained for our samples are lower than theoretical calculation (H_c= 6700 Oe) using the Stoner - Wohlfarth model of single domain magnetic particles [19]. Various theories, including surface area, spin canting and sample inhomogeneity have been proposed to account for the relatively low magnetisation in fine particles [20]. It may also be due to presence of super paramagnetic fraction of very fine particles in formed ferrite particles. The variation in coercivity is reasonable (Table 2) because of the variation of particle size. The low value of M_r is observed in the sample prepared using a co-precipitation technique may be due to reduction of number of surface atoms with respect to volume atom and decrease in intra-granular porosities.

The magneto-crystalline anisotropy constant K can be determined using eq. (3)

$$H_C = 2K/\mu_0 M_S \quad (3)$$

Where μ_0 is the universal constant of permeability in free space, $4\pi \times 10^{-7}$ H/m. As shown in Table 2, sample prepared by using a microemulsion technique shows the high value of magneto-crystalline anisotropy

constant. The energy barrier (E_A) for rotation of magnetisation orientation in single domain particle is given by eq. (4) [19]

$$E_A = KV \sin^2 \theta \quad (4)$$

Where V is the volume of particle and θ is the angle between an applied field and easy axis of the particle. It is clear from eq. (4) that the energy barrier (E_A) is directly proportional to the product of KV (under the same magnetisation direction). There is change in the values of coercivity as well as

volume and hence one can estimate the order of energy barrier by substituting value of V from Table 1 and it should be E_A (microemulsion) $> E_A$ (co-precipitation), [E_A (microemulsion) = $1.838 \sin^2 \theta$, E_A (co-precipitation) = $1.668 \sin^2 \theta$]. Lower the anisotropy of the particles, lower will be the activation energy barrier and hence lower field is required to spin reversal (hence lower coercivity) for the barium hexaferrite sample prepared using a microemulsion route.

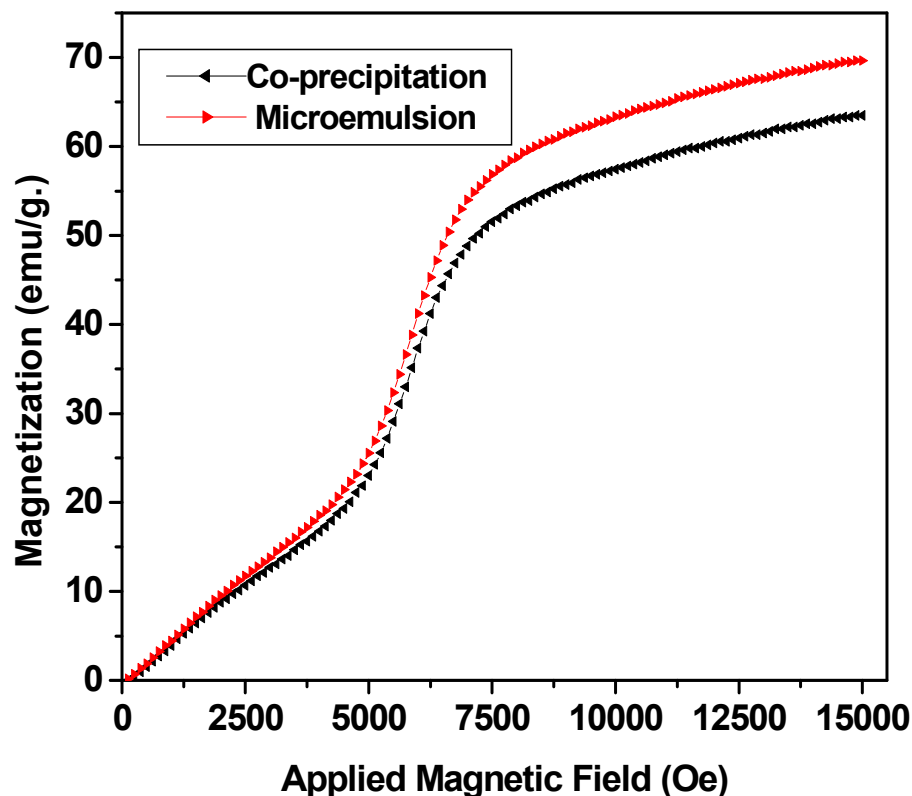


Fig. 6 The initial magnetisation curves of $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite particles prepared using co-precipitation and microemulsion technique, calcinated at 950°C for 4 hrs.

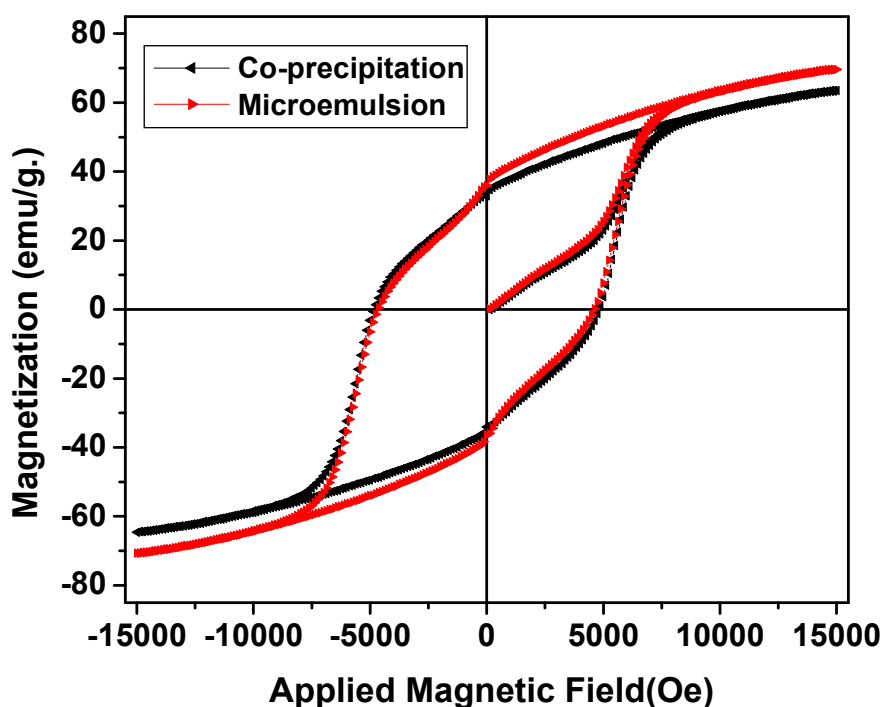


Fig. 7 The hysteresis loops of $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite particles prepared by using co-precipitation and microemulsion techniques, calcinated at 950°C for 4 hrs.

CONCLUSION

M-type barium hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$) mono phase, well crystallized particles have been successfully synthesized by using the microemulsion and chemical co-precipitation techniques in presence of cetyltrimethyl ammonium bromide (CTAB) with ammonium hydroxide as a precipitator. It has been observed that use of microemulsion route prevents the agglomeration of prepared barium hexaferrite particles. Results of our observations from the XRD, TEM/SEM micrographs, thermal and magnetic studies 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.

(ii) Barium hexaferrite precursors with nano dimensions were obtained using both the microemulsion and chemical co-precipitation processes.

(iii) Thermal stability of the sample synthesized by using a microemulsion process is higher compared to the sample prepared by using a co-precipitation technique.

(iv) Magnetisation results reveal the existence of ferromagnetic behaviour of $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite particles prepared by using microemulsion as well as chemical co-precipitation processes.

(v) $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite particles of single domain were produced.

- (vi) The values of saturation magnetisation, intrinsic coercivity and remanent magnetisation depend upon the method of preparation.
- (vii) The sample prepared by microemulsion technique exhibits larger magnetocrystalline anisotropy constant and the activation energy barrier.

ACKNOWLEDGMENTS

Authors wish to express their gratitude to the Principal and Regional Director, DAV Institute of Engineering and Technology, Jalandhar, India for providing research facilities in nanotechnology. They are thankful to National Chemical Laboratory (NCL), Pune for providing VSM facility to carry out magnetic measurements.

REFERENCES

- 1 K.B.M. Paul, Magnetic and structural properties of Ba M-type ferrite-composite powders, *Physica B: Condensed Matter*. 388 (1- 2) (2007) 337-342.
- 2 H.F. Yu, P.C. Liu, Effects of pH and calcination temperatures on the formation of citrate-derived hexagonal barium ferrite particles, *J Alloys Compounds*. 416 (1-2) (2006) 222-227.
- 3 M.V. Cabañas, J.M. González-Calbet, M. Vallet-Regí, Influence of the synthetic route on the BaFe₁₂O₁₉ properties, *Solid State Ionics* 63-65 (1993) 207-212.
- 4 O. Carp, R. Barjega, E. Segal, M. Brezeanu, Nonconventional methods for obtaining hexaferrites - II. Barium hexaferrite, *Thermochim. Acta* 318 (1) (1998) 57-62.
- 5 T. Ogasawara, M.A.S. Oliveira, Microstructure and hysteresis curves of the barium hexaferrite from co-precipitation by organic agent, *J. Magn. Magn. Mater.* 217 (1-3) (2000) 147-154.
- 6 D. Mishra, S. Anand, R. K. Panda, R.P. Das, Studies on characterization, micro structures and magnetic properties of nano-size barium hexa-ferrite prepared through a hydrothermal precipitation-calcination route, *Mater. Chem. Phys.* 86 (1) (2004) 132-136.
- 7 R. Martinez Garcia, E. Reguera Ruiz, E. Estevez Rams, R. Martinez Sanchez, Effect of precursor milling on magnetic and structural properties of BaFe₁₂O₁₉ M-ferrite, *J. Magn. Magn. Mater.* 223 (2) (2001)
- 8 V.K. Sankaranarayanan, D.C. Khan, Mechanism of the formation of nanoscale M-type barium hexaferrite in the citrate precursor method, *J. Magn. Magn. Mater.* 153 (3) (1996) 337-346.
- 9 M. El-Hilo, H. Pfeiffer, K. O'Grady, W. Schüppel, E. Sinn, P. Gönert, M. Rösler, D.P.E. Dickson, R.W. Chantrell, Magnetic properties of barium hexaferrite powders. *J. Magn. Magn. Mater.* 129 (2-3) (1994) 339-347.
- 10 S -C. Ng, L -M. Gan, X. Liu, J. Wang, J. Ding, An ultrafine barium ferrite powder of high coercivity from water-in-oil microemulsion, *J. Magn. Magn. Mater.* 184 (3) (1998) 344-354.
- 11 V. Pillai, P. Kumar, D.O. Shah, Magnetic properties of barium ferrite synthesized using a microemulsion mediated process, *J. Magn. Magn. Mater.* 116 (3) (1992) L299-L304.
- 12 R.B. Jotania, R.B. Khomane, C.C. Chauhan, S.K. Menon and B.D. Kulkarni, Synthesis and magnetic properties of barium-calcium hexaferrites prepared by a microemulsion and sol-gel route in presence of surfactants, *J. Magn. Magn. Mater.* 320 (2008) 1095-1101.
- 13 R.B. Jotania, R.B. Khomane, A.S. Deshpande, C.C. Chauhan and B.D. Kulkarni, Physical and magnetic properties of barium-calcium hexaferrite nanoparticles synthesized by water-in-oil reverse micelle and co-precipitation techniques, *J. Sci. Res.* 1 (2009) 1-13.
- 14 R.B. Jotania, C.C. Chauhan, S.K. Menon, Kanti Jotania, Structural and magnetic properties of BaMg₂Fe₁₀O₁₉ hexaferrite particles, *Adv. Mater. Res.* 67 (2009) 137-142.
- 15 J. Temuujin, M. Aoyama, M. Senna, T. Masuko, C. Ando, H. Kishi, Synthesis of Y-type hexaferrites via a soft mechanochemical route, *J. Solid State Chem.* 177 (2004) 3903-3908.
- 16 R.C. Pullar, M.D. Taylor, A.K. Bhattacharya, Novel aqueous sol-gel preparation and characterization of barium M ferrite, BaFe₁₂O₁₉ fibers, *J. Mater. Sci.* 32 (2) (1997) 349-352.

- 17 X. He, Q. Zhang, Z. Ling, Kinetics and magnetic properties of sol-gel derived NiZn ferrite-SiO₂ composites, *Materials Letters* 57 (20) (2003) 3031-3036.
- 18 B.T. Shirk, W.R. Buessem, Magnetic properties of barium ferrite formed by crystallization of a glass, *J. Am. Ceram. Soc.* 53 (4) (1970) 192-196.
- 19 E.C. Stoner, E. P. Wohlfarth, A. Philos, Mechanism of magnetic hysteresis in heterogeneous alloys, *Trans. R. Soc. London A* 240 (1948) 599-642.
- 20 P.A. Mariño-Castellanos, J.C. Somarriba-Jarque, J. Anglada-Rivera, Magnetic and microstructural properties of the BaFe_{(12-(4/3)x)}Sn_xO₁₉ ceramic system, *Physica B: Condensed Matter* 362(1-4) (2005) 95-102.