Magnetic Properties of Nanoscale BaFe₁₂O₁₉ Particles

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Nanoscale BaFe₁₂O₁₉ particles have been synthesized by citrate precursor technique. X-ray diffraction studies showed the formation of pure, fine grained, monophasic BaFe₁₂O₁₉ particles and decrease in lattice parameters with the particle size. Magnetic clusters were observed by SEM and BET surface area measurements. Mössbauer results and the field dependence magnetic studies reveal the superparamagnetic and ferrimagnetic nature of nano-size particles and the change of hyperfine parameters. The observed reduction of σ_s values compared to bulk is due to the presence of superparamagnetic fraction, size and surface effects for nano-size particles. Interestingly, a maximum H_{ic} of 484.6 kAm⁻¹ and 448.8 kAm⁻¹ are achieved for nano-size BaFe₁₂O₁₉ particles for Fe/Ba ratio of 10.8 and 12.0 respectively. These are the highest values reported for isotropic BaFe₁₂O₁₉, which are close to the theoretical limit and explained based on coherent rotational model for an assembly of single domain particles oriented at random. The temperature dependence magnetization behaviour of nanosize BaFe₁₂O₁₉ particles shows an enhancement of T_C from 743 to 880 K when the particle size is reduced from 18.5 to 5.4 nm respectively and is explained using finite size scaling with correlation length $\nu = 0.67 \pm 0.06$.

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I. Introduction

Nanoscale clusters and particles make the bridge between atoms and molecules on the one extreme and the bulk systems on the other. Materials in the above two extremes have been extensively investigated whereas the study of nanoscale systems have begun receiving the well deserved attention only in recent years^{(1)–(6)}. One of the major difficulties associated with the study of nanometer systems is their preparation. The conventional ceramic methods employed in the preparation of materials invariably yield larger particles in the micrometer range owing to the high temperature, usually more than 1273 K, required for diffusion controlled solid state reactions. The advent of low temperature synthetic methods, e.g. chemical methods, in recent years has made the preparation and investigation of submicroscopic ultrafine particles a reality. Nevertheless, for the preparation of particles in the lowest size range-nanoscale systems (particle size 1–100 nm) a very few methods exist. The citrate precursor method has been proved to be a very versatile method for the synthesis of nanoscale particles in the case of garnets and ferrites^{(7)–(10)}. In the precursor method, an intimate blending of compositional ions in the atomic state is achieved leading to the formation of a homogeneous metal citrate precursor. The precursor is decomposed at lower temperatures to obtain stoichiometric, pure and single phase fine particles of these materials.

M-type barium hexaferrite, BaFe₁₂O₁₉, has a variety of applications as a permanent magnet material and in microwave devices. Recently the particles in the nano-

meter size range are of special interest for the research and high density perpendicular magnetic recording media^{(11)–(17)}. Inter-particle interactions of the nanosize particles can affect their magnetic behaviour⁽¹⁸⁾⁽¹⁹⁾. Thus, in the present study we have synthesized nanoscale particles of BaFe₁₂O₁₉ and investigated these particles for their interesting magnetic properties, including high coercivity.

II. Experimental Procedure

In the citrate precursor technique, first the barium citrate solution is formed from stoichiometric amounts of barium nitrate and citric acid in the molar ratio 1:1. This was further mixed with stoichiometric amount of ferric citrate solution. Ba: Ferric citrate: citric acid is mixed in the ratio 1:12:1. The resultant homogeneous solution with pH=2.6 was refluxed at 373 K for 12 h and further dehydrated from ethanol (1:10 ratio) to obtain citrate precursor, BaFe₁₂O₆(C₆H₆O₇)₁₃. By following the solid state reactivity studies⁽⁹⁾, the dehydrated precursor was thermally decomposed at 823 K to form the nanosize crystalline BaFe₁₂O₁₉ materials which was further heat treated to appropriate higher temperatures to obtain, the controlled fine particles of the BaFe₁₂O₁₉ phase. These details are described elsewhere⁽⁹⁾. The composition of the citrate precursor and thermally decomposed end products were analyzed by atomic absorption spectroscopy and chemical analyses methods^{(20)–(22)}. Citrate content in the precursor was estimated using Karpov's method in which 2 cm³ of citrate precursor solution was mixed with 25 cm³ of 0.1 kmol·m⁻³ K₂Cr₂O₇ and 5 cm³ Con.H₂SO₄. The solution was heated gently and the excess of dichromate was titrated against 0.1 kmol·m⁻³ solution of Mohr's salt using 3 to 4 drops of 0.1% phenyl

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anthranilic acid as an indicator. The end point is the change of red violet to green colour⁽²⁰⁾. Barium was estimated gravimetrically by using hot excess H₂SO₄ and weighed as barium sulphate⁽²¹⁾. Iron gas estimated volumetrically after reducing Fe³⁺ to Fe²⁺ by SnCl₂. The addition of HgCl₂ results in curdy white precipitate. To this properly reduced solution 30% of phosphoric acid solution and few drops of sodium diphenylamine sulphate indicator were added and titrated with K₂Cr₂O₇ solution to change the colour of the solution from green to grey green⁽²²⁾. The stoichiometry of the end product was found to be close to BaFe₁₂O₁₉.

The powder X-ray diffraction (XRD) patterns of BaFe₁₂O₁₉ particles were recorded with CuK α radiation and Ni filter in the 2 θ range of 20°–80° using a Rich Seifert Isodebyflex X-ray unit model 2002. The crystallite size was calculated from d (114) and d (107) XRD line broadening using the Scherrer relationship, $D = K\lambda / B \cos \theta$, where d is the diameter in nm, K is the constant (shape factor ~ 0.9), B is the half-maximum linewidth, and λ is the wavelength⁽²³⁾. The half-maximum linewidth is calculated with respect to the standard (silica), $B^2 = B_M^2 - B_0^2$, where B_M and B_0 is the measured breadth of the diffraction line of the sample and standard respectively. A scanning electron microscope (SEM), JEOL JSM-840A was used to investigate the particle size distribution and morphology of BaFe₁₂O₁₉ powder samples. Surface area measurements were carried out to investigate particle size using the single point Branauer-Emmett-Teller (BET) method with a Micrometrics Pulser Chemisorb 2700 using N₂ gas as the absorber. Degassing is done by heating the samples at 473 K and flushing He gas. Magnetization measurements were carried out using a vibrating sample magnetometer, PAR-Model 150A, in conjugation with a varian electromagnet assembly model (V7200), that provides a magnetic field up to 875.3 kAm⁻¹. The temperature variations of the magnetization were studied using a furnace assembly model 151 associated with the magnetometer and which can provide a temperature of up to 1000 K. Mössbauer spectra of the BaFe₁₂O₁₉ particles were recorded at room temperature (298 K) using a ⁵⁷Co source deposited on a Rh matrix. The experimental spectrum was analyzed using the Mössbauer analysis software PC-MOS supplied by

CMTE elektronik, Germany.

III. Results and Discussions

1. X-ray diffraction studies

Figure 1 shows the X-ray powder diffraction patterns of nanosize BaFe₁₂O₁₉ particles heat treated at various temperatures. These XRD patterns fit well with the BaFe₁₂O₁₉ pattern reported in the literature⁽¹⁴⁾⁽²⁴⁾ and showed absence of other extraphases like, α Fe₂O₃, BaFe₂O₄. Samples heat treated below 823 K exhibit broad hump indicating its amorphous nature. The crystallization of amorphous phase occurred at 823 K and indicated the incipient formation of a BaFe₁₂O₁₉ phase. The growth of XRD crystallites occurred with heat treatment temperature, which is given in Table 1. This crystallite size/particle size has been referred in the text during the discussion of Mössbauer parameters and magnetic properties of nanocrystalline BaFe₁₂O₁₉ particles. The corresponding lattice parameters calculated for

Fig. 1 X-ray diffraction patterns of nanosize BaFe₁₂O₁₉ particles heat treated at various temperatures.

Table 1 Particle size, surface area and lattice parameters of BaFe₁₂O₁₉ particles when heat treated at various temperatures for 4 h.

Heat treatment temperature (K)	Particle size, D (nm)			Surface area, S 10 ³ (m ² /kg)	Lattice parameters		
	XRD	SEM	BET		a (nm)	c (nm)	Unit cell volume (nm ³)
773	5.4	34.0	33.1	34.3	0.585	2.282	0.781
803	8.0	40.5	45.2	25.1	0.585	2.282	0.781
823	9.3	46.0	53.0	21.4	0.586	2.288	0.785
853	13.5	52.5	64.0	17.8	0.587	2.295	0.791
873	14.4	58.0	73.5	15.46	0.588	2.302	0.791
973	16.2	65.0	112.5	10.10	0.589	2.309	0.801
1073	18.5	78.0	154.0	7.4	0.589	2.309	0.801

these crystallites are comparable with the literature values of $a=0.588$ nm and $c=2.303$ nm⁽²⁵⁾. The decrease in the lattice parameter occurred with decreasing particle size, which may be due to the lattice strain causing lattice contraction.

2. BET surface area measurements

Table 1 shows the reduction in BET surface area from 34.3×10^3 to 7.4×10^3 m²/kg for nanosize BaFe₁₂O₁₉ particles, when the heat treatment temperature is varied from 773 to 1073 K. The reduction in surface area occurred because of the growth of particles and the calculated mean diameter is in the range of 33.1 to 154.0 nm for these particles. Table 1 shows the growth of mean particle size of BaFe₁₂O₁₉ with heat treatment temperature representing the monotonous increase in growth of particles. The dimension of the particles calculated from the BET surface area is found to be relatively larger than the XRD crystallite size. This would indicate the formation of magnetic cluster/aggregate of several crystallites due to their highly energetic surfaces.

3. Electron microscopy

Figure 2 shows the SEM micrographs of nanosize BaFe₁₂O₁₉ particles when heat treated at various temperatures. The average particle size calculated from SEM micrographs increases from 34.0 to 78.0 nm, when heat treated from 773 to 1073 K and is given in Table 1. The smaller particles are found to form larger size cluster/aggregates (Fig. 2(a)). The cluster size decreases with the increase in heat temperature (Figs. 2(b) and (c)). However, the samples heat treated at higher temperature are relatively well separated (Fig. 2(d)). The micro-

graph showed that the particles are nearly uniform in size and exhibit a narrow particle size distribution. The hexagonal platelet-like morphology is exhibited by larger particles obtained at higher heat treatment temperature. The histogram studies from SEM micrographs of BaFe₁₂O₁₉ samples point out the peak of the frequencies formed around $D=60$ –70 nm and the number of particles whose D values are in the range of 30–80 nm account for about 90% of the total particles observed.

4. Mössbauer spectroscopy

The room temperature ⁵⁷Fe Mössbauer spectra of nanosize BaFe₁₂O₁₉ particles along with its fitted sub-spectra is shown in Fig. 3. The particles having size 5.4 nm (*i.e.* heat treated around 773 K) show superparamagnetic doublet, isomershift $\delta=0.33$ mm/s with reference to metallic Fe, quadrupole splitting, $\Delta E_q=0.84$ mm/s and line width, $\Delta H=0.64$ mm/s indicating superparamagnetic nature. However, these particles show amorphous XRD pattern. The samples having particle sizes in the range 8.0 to 13.5 nm (*i.e.* heat treated in the temperature range 793–853 K) exhibit a mixed pattern indicating the coexistence of ferrimagnetic and superparamagnetic particles. The spectra were deconvoluted and attributed to five sextets and a superparamagnetic central doublet. However, for the particles having size above 13.5 nm (*i.e.* heat treated above 853 K), the superparamagnetic particles were not detected and a typical hyperfined Mössbauer profile of ferrimagnetic BaFe₁₂O₁₉ particles were observed. These spectra were resolved into five sextets corresponding to 12k, 4f₁, 4f₂, 2a and 2b sites. Mössbauer line shapes varies with the particle size for 5.4 to 18.5 nm particles (*i.e.* heat treatment temper-

Fig. 2 SEM photographs of BaFe₁₂O₁₉ particles heat treated at (a) 773 K, (b) 823 K, (c) 973 K and (d) 1073 K.

Fig. 3 Room temperature ⁵⁷Fe Mössbauer spectra of nanosize BaFe₁₂O₁₉ particles with various sizes.

ature range 773 to 1073 K). Figure 3 clearly indicated the growth of particles from superparamagnetic to ferromagnetic particle size, which corresponds to the doublet and sextet patterns. In comparison with spectra of standard BaFe₁₂O₁₉, the sextets correspond to the same sublattice sites. Mössbauer parameters; isomer shift, δ , quadrupole splitting, ΔE_q , and magnetic hyperfine field, H_n for BaFe₁₂O₁₉ particles in the size range 14.4 to 18.5 nm are given in Table 2 and these parameters are compared with the reported data for bulk BaFe₁₂O₁₉ materials⁽²⁶⁾.

The Mössbauer parameters for nanosize BaFe₁₂O₁₉ show a number of features with the decrease in particle size. All the five sublattice sites show the smaller hyperfine field, H_n values for nanosize particles compared to bulk values and it increases with increase of particle size to approach the bulk value. Fine particles of a variety of magnetic materials have been reported to show a relatively lower hyperfine field when compared to the bulk materials and various theories encompassing surface effects and intrinsic size effects, have been proposed to account for such reduction^{(27)–(31)}. The Fe³⁺ sites of smaller particles of BaFe₁₂O₁₉ show smaller quadrupole splitting compared to the bulk (Table 2) and it increases with increasing particle size. The lattice contribution of the quadrupole splitting depends on the electric field gradient around the Fe nucleus resulting from the deviation of the Fe–O polyhedra from cubic symmetry where the core and valence contributions are

Table 2 Room temperature Mössbauer parameters for various nanosize BaFe₁₂O₁₉ particles along with bulk data⁽²⁶⁾.

$D_{\text{XRD}} = 14.4 \text{ nm}$					
Iron site & spin orientation	Structural subunit	$H_n 10^3$ (kAm ⁻¹)	δ (mm/s)	ΔE_q (mm/s)	RA (%)
12k↑	R-S	32.58	0.38	0.62	50.3
4f ₁ ↓	S	37.64	0.35	0.32	22.3
4f ₂ ↓	R	40.50	0.48	0.36	13.0
2a↑	S	39.98	0.36	0.06	10.6
2b↑	R	31.19	0.16	1.92	3.8
$D_{\text{XRD}} = 16.3 \text{ nm}$					
Iron site & spin orientation	Structural subunit	$H_n 10^3$ (kAm ⁻¹)	δ (mm/s)	ΔE_q (mm/s)	RA (%)
12k↑	R-S	32.74	0.37	0.68	49.2
4f ₁ ↓	S	38.88	0.33	0.35	21.0
4f ₂ ↓	R	40.84	0.46	0.38	14.7
2a↑	S	40.43	0.39	0.13	9.0
2b↑	R	31.85	0.19	2.05	6.1
$D_{\text{XRD}} = 18.5 \text{ nm}$					
Iron site & spin orientation	Structural subunit	$H_n 10^3$ (kAm ⁻¹)	δ (mm/s)	ΔE_q (mm/s)	RA (%)
12k↑	R-S	32.87	0.35	0.74	48.6
4f ₁ ↓	S	39.00	0.33	0.38	19.9
4f ₂ ↓	R	41.07	0.45	0.38	16.6
2a↑	S	40.54	0.42	0.18	8.2
2b↑	R	32.09	0.21	2.24	6.7
Bulk Sample					
Iron site & spin orientation	Structural subunit	$H_n 10^3$ (kAm ⁻¹)	δ (mm/s)	ΔE_q (mm/s)	RA (%)
12k↑	R-S	32.94	0.35	0.76	50.0
4f ₁ ↓	S	39.15	0.31	0.40	16.6
4f ₂ ↓	R	41.14	0.44	0.40	16.6
2a↑	S	40.66	0.45	0.20	8.3
2b↑	R	32.31	0.20	2.30	8.3

assumed to be negligible for Fe³⁺. Therefore, the lower quadrupole splitting in fine particles could be due to an increased symmetry around the Fe³⁺ sites. However, it is still surprising that fine particles have less distorted polyhedra. It may be possible that due to fine particle nature, lattice strain may alter the Fe–O bond distances in such away that the symmetry of Fe–O polyhedra is increased^{(32)–(36)}. Therefore the changes in isomer shift values occur due to distortion in polyhedra since the change of Fe–O bond distances. Larger isomer shift corresponds to lower s-electron density at the Fe-nucleus and hence may indicate larger Fe–O bond distance. The 12k, 4f₂ and 2a (octahedral sites) show relatively larger isomer shifts for smaller particles compared to 4f₁ tetrahedral site) and 2b (trigonal bipyramidal site). However, the isomer shift for fine particles and bulk cannot be directly correlated for hexaferrites unlike garnets⁽³²⁾.

Fig. 4 Specific Magnetization (σ) vs. field (H) plots for nanosize $\text{BaFe}_{12}\text{O}_{19}$ having different particle size.

Fig. 6 Coercive force, (H_{ic}), saturation magnetization, (σ_s) and remanent magnetization (σ_r) of $\text{BaFe}_{12}\text{O}_{19}$ particles for the maximum field of 1671 kA m^{-1} as a function of particle size.

Fig. 5 Specific Magnetization (σ) vs. field (H) plots for nanosize $\text{BaFe}_{12}\text{O}_{19}$ having different particle sizes (a) 9.3 nm, (b) 13.5 nm, (c) 16.3 nm and (d) 18.5 nm.

5. Magnetic studies

Figures 4 and 5 show the room temperature field dependence magnetization curves for nanosize $\text{BaFe}_{12}\text{O}_{19}$ particles. The magnetization curves for $\text{BaFe}_{12}\text{O}_{19}$ particles in the size range 5.4 to 8.0 nm do not saturate even in the high applied field of 1671 kA m^{-1} and do not exhibit any hysteresis (Fig. 4). These characteristics indicate the superparamagnetic behaviour of smaller particles which

has been already confirmed in the Mössbauer studies (Fig. 3(a) showing quadrupole doublet). Nanosize $\text{BaFe}_{12}\text{O}_{19}$ particles in the size range 9.3 to 18.5 nm show the formation of hysteresis loops indicating ferrimagnetic behaviour of particles. The hysteresis loops broadens with the increase in particle size (Fig. 5). The variation of intrinsic magnetic properties H_{ic} , σ_s and σ_r with the change in particle size for $\text{BaFe}_{12}\text{O}_{19}$ are shown in Fig. 6. The measurements are carried out at a maximum applied field of 1671 kA m^{-1} . The H_{ic} value gradually increases with the increase in particle size and reaches a maximum of 448.8 kA m^{-1} when the particle size is 16.2 nm and further decreases at higher particle size. This is because of interparticle interactions and an occurrence of grain growth of unstable superparamagnetic small particles to magnetically stable particle size in the single domain range. This has been also confirmed from the SEM studies (Fig. 2). However, the σ_s and σ_r values show the monotonic increase to plateau region with the increase in particle size.

However, some measurements were carried out for $\text{BaFe}_{12}\text{O}_{19}$ with Fe/Ba = 10.8 which show the BET particle size of 98 nm (XRD crystallite size of 15.4 nm). Interestingly, a maximum coercive force, H_{ic} of 484.6 kA m^{-1} is achieved for these particles, which is higher than the reported literature value of 477.4 kA m^{-1} (14)(37)–(39). The σ_{max} and σ_r value for these particles are $7.89 \times 10^{-8} \text{ Hm}^2/\text{kg}$ and $4.15 \times 10^{-8} \text{ Hm}^2/\text{kg}$ respectively. The critical diameter of $\text{BaFe}_{12}\text{O}_{19}$ particles for single domain formation is calculated and is found to be in the range of 0.81 to $0.92 \mu\text{m}$ and agrees with the reported value of $0.9 \mu\text{m}$ (25). The nanosize $\text{BaFe}_{12}\text{O}_{19}$ particles with Fe/Ba ratio of 12.0 and 10.8 having BET particle sizes 113 and 98 nm respectively show the highest H_{ic} values of 448.8 kA m^{-1} and 484.6 kA m^{-1} . These par-

Fig. 7 Magnetic hysteresis curve (σ - H) at $H_{\max}=1671 \text{ kAm}^{-1}$ for randomly oriented BaFe₁₂O₁₉ particles with Fe/Ba ratio of (a) 12.0 and (b) 10.8. Stoner-Wohlfarth theoretical curve (dotted) is shown.

ticles are in the range of single domain size where the magnetization proceeds by reversible rotation at high applied fields and thus the S-W calculations are applied here⁽⁴⁰⁾.

Figure 7 shows the magnetic hysteresis of nanosize BaFe₁₂O₁₉ particles for Fe/Ba ratios 12.0 and 10.8 respectively. Taking the effective anisotropy field,

$$H_k = 2K_1/M_s - NM_s = 1217.4 \text{ kAm}^{-1} \quad (1)$$

(for anisotropy constant $K_1 = 3.25 \times 10^5 \text{ J/m}^3$, $M_s = 380 \text{ G}$ and $N = 4.85$ for nearly spherical particles) we have $H_{\max}/H_k = 1.37$ which gives $\sigma_{\max}/\sigma_s = 0.96$. Consequently σ_s values were calculated which are $8.09 \times 10^{-8} \text{ Hm}^2/\text{kg}$ and $8.22 \times 10^{-8} \text{ Hm}^2/\text{kg}$ for Fe/Ba ratios of 12.0 and 10.8 respectively. These values are nearly in good agreement with the literature values⁽¹⁴⁾⁽³⁸⁾⁽³⁹⁾. Using the values of H_k and σ_s derived above, S-W magnetization and demagnetization curves are plotted in Fig. 7. These BaFe₁₂O₁₉ particles almost display the S-W behaviour, although the experimental values of H_{ic} for these particles are lower than the theoretical values of 588.8

Fig. 8 Characteristic plot of specific magnetization (σ) vs. temperature at a field of 477.4 kAm^{-1} for various particle sizes of BaFe₁₂O₁₉. Vertical arrows designate T_C .

and 635.0 kAm^{-1} for the Fe/Ba ratios of 12.0 and 10.8 respectively. In the present system, the nanosize BaFe₁₂O₁₉ particles are prepared by the control of solid state reactivity leading to fine grained monophasic particles which are in the single domain size range where the magnetization proceeds by reversible rotations at high applied fields.

Figure 8 show the characteristic plots of specific magnetization, σ against temperature for nanosize BaFe₁₂O₁₉ particles obtained at heat treatment temperature in the range 773 to 1073 K for 4 h. For bigger particles, $D > 16.2 \text{ nm}$, (D =diameter) the demagnetization effect appears at a temperature T_C around 742 K. This effect disappears for smaller size particles $D < 16.2 \text{ nm}$ where, T_C is increased due to the decrease in particle size and no sharp features were observed in the region of T_C . The change in T_C is due to decrease in particle size. The smaller particles show lower σ values because of spin canting preferentially at the surface of the particles. Such results are also reported in the literature⁽³⁾⁽⁴⁾⁽⁷⁾⁽¹⁰⁾⁽³⁹⁾⁽⁴¹⁾.

The Curie point is measured in the most direct and unambiguous manner possible by the spontaneous change in magnetization as the temperature varies through T_C with the sample in the presence of applied field. T_C was determined from the intersection of extrapolation of the greatest slope possible and flat region above T_C . There is only one transition observed for 5.4, 8.0, 9.3, 13.5, 14.4 and 18.5 nm particles and T_C tends to increase from 742 to 880 K with declining particle size. The particles below 13.5 nm exhibit the mixed ferrimagnetic/superparamagnetic behaviour because of particle size distribution and better superparamagnetic fraction crystallizes with decreasing particle size. Therefore, the

Fig. 9 Shift of reduced Curie temperature vs. particle diameter, D . Solid line is fitted by eq. (2) with $\lambda = 1.49$ and $D_0 = 1.63$ nm.

superparamagnetic fraction known from Mössbauer studies to exist for an average size $D \leq 9.3$ nm and do not affect our determination of T_C for these samples. Therefore, the increase in T_C is due to the decrease in particle size. However, some rounding off the expected jump at T_C is observed due to (for the most part) the finite size distribution. Thus, the enhanced T_C is not due to the fluctuation broadening and will still increase with decreasing D .

The behaviour of T_C can be explained by using the finite size scaling⁽³⁾. In order to predict the shift in T_C from that of the bulk, we should depend on the dimension of the system in the following manner⁽⁴²⁾:

$$[T_C(D) - T_C(\infty)][T_C(\infty)]^{-1} = \pm (D/D_0)^{-\lambda}. \quad (2)$$

Figure 9 describes the log-log plot of $[T_C(D) - T_C(\infty)][T_C(\infty)]^{-1}$ versus D assuming $T_C(\infty) = 740$ K. The plot is linear and supports the above equation with correlation length $\nu = 0.67 \pm 0.06$ where $\nu = 1/\lambda$ and $\lambda = 1.49 \pm 0.14$. This value of ν is well in the range of 0.65–0.73 values predicted for the isotropic three dimensional Heisenberg model⁽⁴³⁾. The value of intrinsic diameter D_0 we find is 1.63 nm. Assuming a spherical size, from the diameter D_0 , the volume of the particle is calculated to be 2.26 nm³. This is roughly thrice the unit cell volume of BaFe₁₂O₁₉ lattice (Table 1) which is reasonably comparable. Thus we conclude that finite size scaling describes the shift in T_C very well.

IV. Conclusions

Nanoscale particles of BaFe₁₂O₁₉ were synthesized by citrate precursor technique at a relatively lower temperature around 823 K. XRD studies shows the formation of monophasic BaFe₁₂O₁₉ and effective line broadening with the reduction in particle size. Decrease in the lattice parameters occurred with the decrease in particle size, which may be due to the lattice strain causing lattice contraction. The dimension of the particle is calculated from BET measurement, which is relatively found to be larger than that of XRD and SEM measurements due to

the formation of magnetic clusters. Mössbauer studies show the ferrimagnetic and superparamagnetic nature of these particles with respect to their dimension. The decrease in hyperfine field, H_h , for smaller particles is due to the effect of fine particle size.

The room temperature field dependence magnetization curves for nanosize BaFe₁₂O₁₉ particles in the size range 5.4 to 8.0 nm do not saturate even in the applied field of 1671 kAm⁻¹ and do not exhibit any hysteresis indicating superparamagnetic behaviour of smaller particles. The temperature dependence magnetization behaviour of nanosize BaFe₁₂O₁₉ particles showed a considerable enhancement in T_C from 742 to 880 K with declining particle size from 18.5 to 5.4 nm measured by XRD when all the dimensions of ferrimagnetic BaFe₁₂O₁₉ system were reduced to the nanoscale without changing composition and their crystal structure. The shift in T_C from the bulk value is explained using finite-size scaling with correlation length $\nu = 0.67 \pm 0.06$ which is in the range of Heisenberg three dimensional model. The value of D_0 we find is 1.63 nm. Interestingly, maximum H_{ic} of 484.6 kAm⁻¹ and 448.8 kAm⁻¹ are achieved by BaFe₁₂O₁₉ particles for Fe/Ba ratios of 10.8 and 12.0 respectively which are found to be higher than the reported values. These particles are in the range of single domain size where the magnetization proceeds by reversible rotation at high applied fields and thus display S-W behaviour.

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