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Structural and Magnetic properties of $BaMg_2Fe_{10}O_{19}$ hexaferrite particles

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Abstract: $BaMg_2Fe_{10}O_{19}$ hexaferrite particles were synthesized by using a Stearic acid gel method. The prepared Ba-Mg hexaferrite particles were calcinated at Microwave frequency (2.45 GHz, power 900W, 5 min.) as well as at 650°C, 750°C, 850°C and 950°C. Decomposition behavior and the phase associated therein are investigated by means of thermal analysis (DTA, TGA, DSC) and XRD, respectively. The X-ray diffractograms of prepared samples calcinated at 650°C, 750°C, 850°C and 950°C show the presence of M and α- Fe_2O_3 Phases, whereas the sample heated in a microwave oven shows only single M-phase. Surface morphology of nonporous particles has been examined by using SEM. The samples prepared by conventional heat treatment produces agglomerated clusters of various size particles whereas, the sample heated in a microwave oven shows separate particles with size ranging from 80-240nm. There is significant change in crystallite size of the resultant Ba-Mg hexaferrite particles prepared at microwave frequency. It was observed that heat treatment condition plays a very crucial role in controlling morphology of prepared Ba-Mg hexaferrite particles. Room temperature magnetic measurements were carried out using VSM. Magnetic study reveals that prepared $BaMg_2Fe_{10}O_{19}$ particles possess single magnetic domains.

Introduction

Barium hexaferrites are excellent ferromagnetic materials very suitable for permanent magnet, high density recording media, and microwave applications because of their high coercivities, moderate saturation magnetization, chemical stability and corrosion resistivity [1-5]. Hexaferrite can be classified in to six categories: M-type ($BaFe_{12}O_{19}$), W-type ($BaMe_2Fe_{16}O_{27}$), Y-type ($BaMe_2Fe_{12}O_{22}$), X-type ($Ba_2Me_2Fe_{28}O_{46}$), U-type ($Ba_4Me_2Fe_{36}O_{60}$) and Z-type ($Ba_2Me_2Fe_{24}O_{41}$), where Me represents, divalent cations of the first transition metal group like Ni, Co, Zn, Mg. The crystal structure of $BaFe_{12}O_{19}$ (space group $P6_3/mmc$) is described as SRS*R*, where R is a three layer block ($O_4 - BaO_3 - O_4$) with composition $BaFe_6O_{11}^{2-}$ and S is a spinel like two layer block ($O_4 - O_4$) with composition $Fe_6O_8^{2+}$. Here the asterix (*) means the corresponding block has been turned 180° around the hexagonal c-axis. The O^{4-} and BaO^{3-} layers form a close packing. In this structure the smaller iron cations are distributed within five different kinds of sites (Three Octahedral – 12k, 2a, $4f_2$, one tetrahedral – 4f and one pseudo tetrahedral trigonal bi pyramidal – 2b). The ordering of magnetic moments of Fe^{3+} ions and the strong super exchange interaction explain the excellent magnetic behavior of these materials [6]. The application of hexaferrite in high density magnetic recording media require materials with high control of homogeneity, morphology and magnetic properties resulting from their methods of preparation and heat treatments [7,8].Many methods have been proposed in order to prepare barium hexaferrite particles with the desired particle size, morphology and homogeneity. A versatile method for preparing sub micron particles at low temperature is the sol-gel technique [9]. We have adopted a Stearic acid gel method in order to prepare homogeneous ultra fine hexaferrite. Use of microwave energy for synthesis and processing

of materials is new field with enormous potential for synthesizing new materials with novel microstructure [10, 11]. The growing interest in recent times is mainly due to the reduction in manufacturing cost, shorter processing time and improved product uniformity & yields. In present work, we have tried conventional as well as microwave induced synthesis process in order to produce barium magnesium hexaferrite particles. Microwave processing of materials is fundamentally different from conventional processing due to its heating mechanism. In a microwave oven, heat is generated within a sample itself by the interaction of microwaves within the material. In conventional heating, the heat is generated by heating element and is then transferred to the sample surface [12].In the present paper, we report the synthesis and characterization of $BaMg_2Fe_{10}O_{19}$ hexaferrite particles prepared by using a Stearic acid gel method. The effect of heat treatment conditions on the morphology and phase purity of Ba-Mg hexaferrite has been studied.

Experimental procedure

The A.R grade of ($Ba(OH)_2$), ($Mg(NO_3)_2.6H_2O$) and ($Fe(NO_3)_2.9H_2O$) [Sigma Aldrich, 99.99%] were mixed in a proper amount of Stearic acid. The mixture was heated at 80-100°C for 2 hours under vigorous stirring and slowly cooled to room temperature to obtain the gel. The gel was dried at 100ºC for 24 hours and then calcinated at 650, 750, 850 and 950ºC for 4 hours in a furnace. In another set of experiments, Ba-Mg hexaferrite material was prepared by using a microwave sintering process. This involves preparation of $BaMg_2Fe_{10}O_{19}$ using a microwave oven. The obtained gel was washed with water and acetone, and then heated in commercially available microwave oven (Power 900W) for 5 min.

Results and discussion

1. FTIR analysis

The room temperature infrared spectra of gel and calcinated samples were recorded in mid IR range ($4000cm^{-1}$ to $400cm^{-1}$)using FTIR Spectrophotometer (Bruker Tensor 27 Model). A few milligrams of the samples were mixed with anhydrous KBr powder and made in the form of pallet for the measurements. Fig.1, shows FTIR spectra of $BaMg_2Fe_{10}O_{19}$ hexaferrite particles calcinated at various temperature. The absorption band at 3400 cm^{-1} in gel (Fig. 1 (a)) is due to OH^- vibrations. The intensity of these bands decreases in the samples calcinated at higher temperature, which may be due to the decrease in the quantity of water molecules in the sintered samples. The band at 1384 cm^{-1} corresponds to NO_3^- ions, which disappears at higher temperature. The absorption band between 580 and 440 cm^{-1} increases when the heat treatment is increased, confirming the formation of hexaferrite [13].

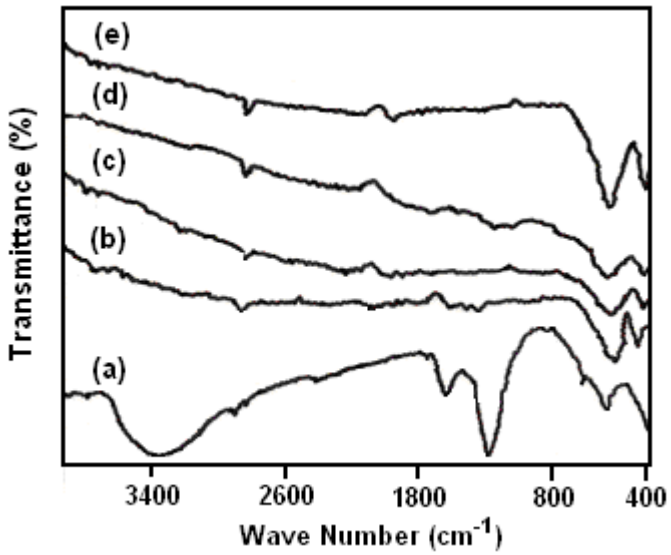

Fig. 1. FTIR spectra of $BaMg_2Fe_{10}O_{19}$ hexaferrite particles prepared by a Stearic acid gel route: (a) gel, (b) 650°C, (c) 750°C, (d) 850 °C and (e) 950°C.

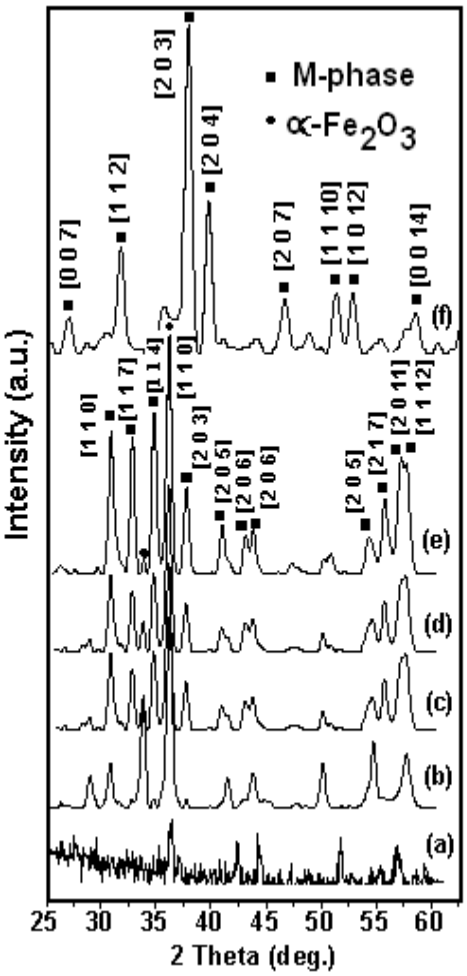

Fig.2: XRD pattern of $BaMg_2Fe_{10}O_{19}$ hexaferrite particles (a) gel and the sample calcinated at (b) 650° C (c) 750° C (d) 850° C (e) 950°C (f) Microwave sintered (Power 900W, 2.45GHz, 5min)

2. XRD analysis

Room temperature XRD patterns of gel, calcinated samples and microwave sintered sample were recorded on Philips diffractometer (PW 1830) using CuKα radiation (λ=1.5405 Å) with a step scan 0.02ºC/min. Fig.2 shows the XRD patterns of normal Barium-Magnesium hexaferrite particles calcinated under different conditions. It was found that the calcinated condition plays a critically important role in the formation of barium magnesium ferrite phase. A high purity Ba-Mg ferrite phase was obtained when the precursor was sintered in a microwave oven at 2.45 GHz for 5 min (Fig. 2f). The diffraction peaks appearing in the XRD pattern were indexed with the standard pattern for M-type hexagonal crystals (JCPDS). The normal samples calcinated at 650, 750, 850 and 950ºC [Fig.2 (b-e)] show two different phases: M and α- Fe_2O_3, which implies that conventional heat treatment is not beneficial in the formation of high purity $BaMg_2Fe_{10}O_{19}$ hexaferrite particles. The gel sample almost exhibits flat diffractogram, indicating that no oxide segregation or crystallization occurred during solidification of the liquid solution. It can be seen from Fig. 2 that, as the temperature increases, the diffraction intensities of all peaks increases, whereas the half height width of peak decreases. This significant increase of diffraction intensity can be attributed to the crystal growth and improvement of crystal perfection of $BaMg_2Fe_{10}O_{19}$ hexaferrite. Zhang et. al. [14] suggested that the unit cell of BaM hexaferrite gradually shrinks as the temperature increases, which may lead to different microstructures in the present samples. Lattice constants a and c of hexagonal barium magnesium hexaferrite were calculated from eq. 1, where h, k and l are Miller indices, while d is interplanar distance. Lattice volume V of hexagonal crystal is obtained from eq. 2.

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

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

Lattice constants and volumes are listed in Table 1.

Preparation route	Temperature conditions	a (Å)	c (Å)	V (Å)
Stearic acid gel	conventional	5.872	23.180	689.79
	Microwave sintering	5.939	23.250	710.19

Table 1: Structure Parameters a and c and cell volume V of normal samples (calcinated at 950° C for 4hrs, sintered in a Microwave oven for 5 min.)

3. Scanning electron microscopy study

Scanning electron micrographs of prepared Ba-Mg hexaferrite samples are obtained using a Make-Leo/Lica model Stereo scan 440 scanning electron microscope. Fig. 3a, b show SEM micrographs of normal and microwave sintered samples. From Fig. 3a, it is seen that, normal Ba-Mg hexaferrite particles are well agglomerated to form the clusters of different sizes and shapes. The particles are found to be nonporous in nature. Fig.3b shows micrograph of Ba-Mg sample sintered in microwave oven for 5 min. It is clear from Fig. (3a, b) that the sample heated in microwave oven gives separate particle in nano form with particle size ranging from 80-240 nm.

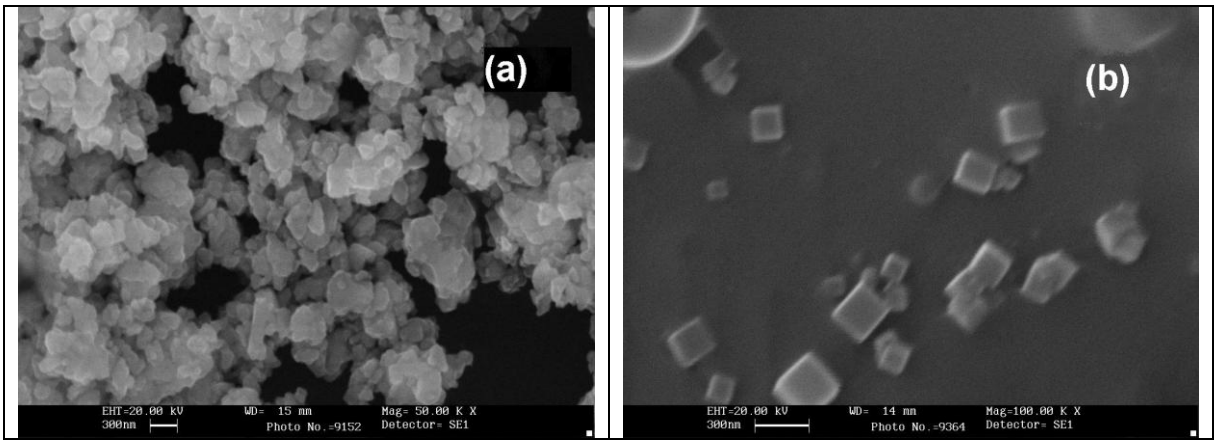

Fig.3: SEM Micrographs of $BaMg_2Fe_{10}O_{19}$ hexaferrite particles prepared by using a Stearic acid gel route (a) Normal sample calcinated at 950° C for 4 hrs (b) Microwave sintered (Power 900W, 2.45GHz, 5min)

4. Thermal analysis

TGA curves of dried materials were recorded using a SII Differential Thermal analyzer Model No. SSC 5100 in the region of 40ºC to 700ºC with a rate of 10ºC/min and is shown in Fig.4A.Thermo gravimetric analysis shows three distinct steps of weight loss. The first step weight loss is between 40ºC to 100ºC, with 9.5 % wt. loss due to desorption of absorbed water molecules. In the second step, 30% wt. weight loss is observed between 100ºC to 200ºC, whereas in third step, the weight loss is about 7%, in the temperature range between 200ºC to 500ºC. These weight losses may be due to combustion of organic substances. It can be seen from Fig.4A, that above 500ºC there is very less weight loss which confirms the thermal stability of the prepared sample synthesized by the Stearic acid gel technique. DSC and TGA curves of dried gel are shown in Fig. 4B. The DSC curve of a normal sample shows first broad endothermic peak at 110ºC, which may be due to evaporation of water molecules. The sample experiences strong exothermic changes between 150ºC to 400ºC (~ 30% wt. loss in TGA, four endothermic peaks in DTA), mainly attributed to the decomposition and oxidation of organic substances[15-18].

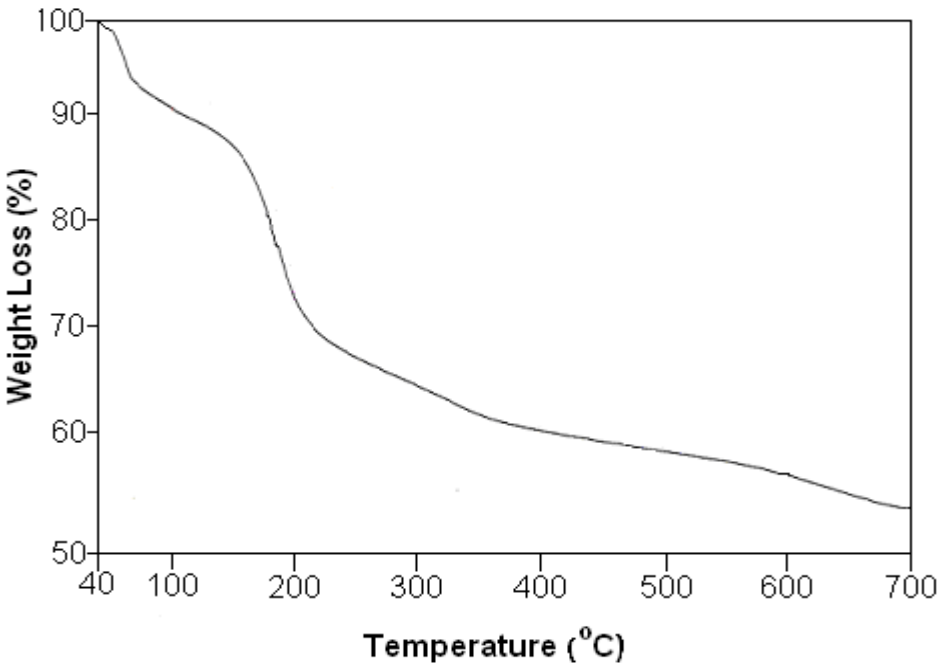

Fig.4A. TGA curve of dried gel

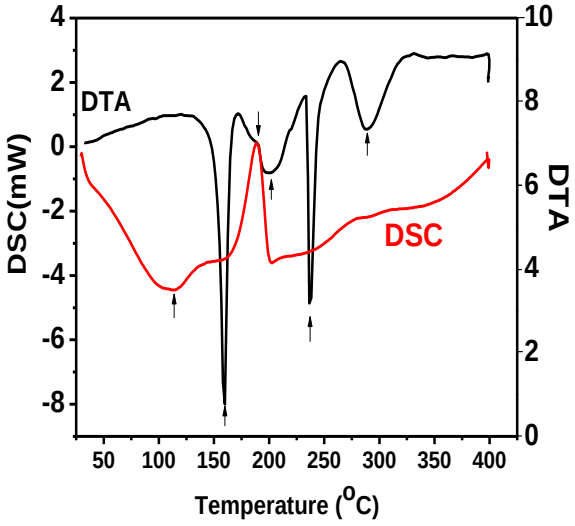

Fig.4B: DTA and DSC curves of dried gel

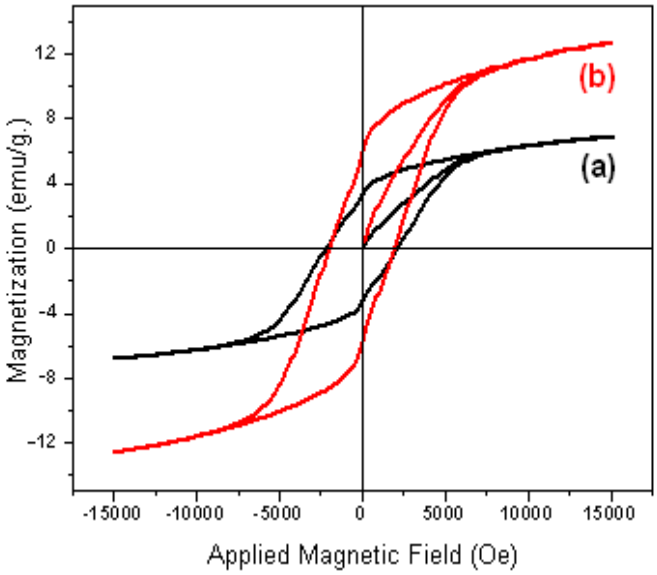

Fig.5: Hysteresis loops of Ba-Mg hexaferrite
(a) Normal, calcinated at 950° C for 4 hrs
(b) Microwave sintered (Power 900W, 2.45GHz, 5min)

5. Magnetic Properties

The magnetization measurement of Ba-Mg hexaferrite particles was recorded at room temperature using VSM, EG & G Princeton Applied Research instrument Model 4500 under the applied field of 15 KOe. Low saturation magnetization is observed in normal sample calcinated at 950° C for 4 hrs and high saturation magnetization is obtained in the sample prepared in a microwave oven. This can be explained using XRD results, It is clear that microwave sintered sample shows highly pure single M-phase and hence high saturation magnetization. The hysteresis loops of the normal (calcinated at 950ºC for 4 hrs) and microwave sintered samples are shown in Fig. 5(a, b). The magnetic parameters are listed in Table 2. The value of Mr/Ms is about 0.5 (actually 0.4876 for normal sample and 0.4690 for microwave sintered sample) indicating that $BaMg_2Fe_{10}O_{19}$ powder of single domain was produced [19].

Preparation route	Temperature conditions	Heating time	Hc (Oe)	Ms (emu/g.)	Mr (emu/g.)	Mr/Ms
Stearic acid gel	Conventional 950ºC	4 hrs.	2250	6.85	3.34	0.4876
	Microwave sintered	5 min.	1880	12.91	5.91	0.4690

(Coercivity Hc, saturation Magnetization-Ms, remanant magnetization-Mr at 15 KOe)
Table 2: Magnetic parameters of $BaMg_2Fe_{10}O_{19}$ particles prepared by a Stearic acid gel route

Conclusions

$BaMg_2Fe_{10}O_{19}$ hexaferrite particles were successfully synthesized by using a Stearic acid gel route. It has been observed that heat treatment conditions play a very crucial role in controlling morphology and the formation of high purity Ba-Mg hexaferrite particles.
The observation from XRD, SEM and VSM studies can be summarized as follows.
(a) XRD results show that the conventional heat treatment on Ba-Mg hexaferrite particles produces α- Fe_2O_3 and M-type phases; whereas microwave sintered treated sample produces highly pure single M-phase.
(b)$BaMg_2Fe_{10}O_{19}$ hexaferrite particles prepared by using microwave sintering process show nano dimension separate particles. However the normal $BaMg_2Fe_{10}O_{19}$ sample calcinated at 950°C shows agglomerated clusters of different sizes and shapes.
(c) Magnetization result revels that $BaMg_2Fe_{10}O_{19}$ hexaferrite particles of single domains were produced.

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