Particle morphology and magnetic properties of $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ powder calcined conventionally and by microwave heating

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ABSTRACT

Barium strontium hexaferrite ($Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$-BSF) has been prepared by sol–gel process involving use of D-Fructose as a fuel. The prepared precursor was calcined in two different calcinations techniques conventional and microwave furnace. X-ray powder diffraction studies confirmed the formation of single phase $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$. HR-SEM results show the morphology of the particles is hexagonal structures in platelet form. The average particle size of conventionally calcined BSF powder is 100–250 nm and that of microwave calcined powder is 30–100 nm. The broad hysteresis loop reveals that powder is well crystallized and exhibits hard magnetic properties.

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1. Introduction

M-type hexaferrites $MFe_{12}O_{19}$ (M = Ba, Sr or Pb) are important ferrimagnetic oxides. Because of their high intrinsic coercivity, large crystal anisotropy and low cost, they have been used in the production of electromechanical devices, electronic toys, door holders and also as components in microwave and high frequency devices [1,2]. The divalent ions (Ba, Sr and Pb) have approximately the same ionic radii as the case of divalent oxygen ions and these elements constitute the hexagonal M-type ferrites. In order to obtain single phase hexagonal ferrites, several techniques have been designed, such as citrate precursor [3], chemical co-precipitation [4], hydrothermal [5], micro-emulsion [6,7] and sol–gel [8]. The properties of hexaferrites are strongly dependent on the particle size, microstructure and morphology. Microwave processing of materials is fundamentally different from the conventional processing in its heating mechanism. In conventional heat treatment, heat is generated by external heating elements, which diffuse into the test sample via radiation, conduction and convection, producing temperature gradients and internal stresses. In microwave sintering, heat is generated internally within the test sample by rapid oscillation of dipoles at microwave frequencies instead of diffusion from external sources. Therefore, the internal and volumetric heating at high heating rate may lead to shorter processing times, im-

proved product yield and limited grain growth throughout the ceramic body [9,10]. The authors have prepared barium strontium hexaferrite pellet using microwave furnace. Magnetic properties of microwave sintered barium strontium hexaferrites has been reported elsewhere [11]. This paper reports the effect of conventional calcination and microwave furnace calcination on morphological and on the magnetic properties of $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ powder.

2. Experimental details

2.1. Preparation of $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$

The starting reagents are of analytical grade $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$ and D-Fructose. Metal nitrates and D-Fructose in the molar ratio of 1:1 were dissolved in distilled water to form aqueous solution. The solution was stirred for 2 h at room temperature to get a gel and followed by a heat treatment in hot air oven for two days to obtain the precursor. The gel was calcined using a conventional furnace and a microwave furnace at three different temperatures: 500, 750 and 900 °C, respectively, to study the variation in magnetic behavior of the intermediate and final crystalline powders.

2.2. Characterization

Thermo-gravimetric (TG) and differential thermal analysis (DTA) of the precursor was carried out on a NETZSCH STA 409 C/CD thermal analyzer, at a heating rate of 10 °C/min. The XRD (PANalytical X'pert pro) patterns were obtained by CuKα_1 radiation at 45 kV and 40 mA ($\lambda = 0.15406$ nm) in a wide range of 2θ ($20° < 2\theta < 80°$). The particle's morphology was analyzed using an FEI Quanta FEG 200-high resolution scanning electron microscope (HR-SEM). The magnetic properties were measured at room temperature with a vibrating sample magnetometer (Lakeshore 7304).

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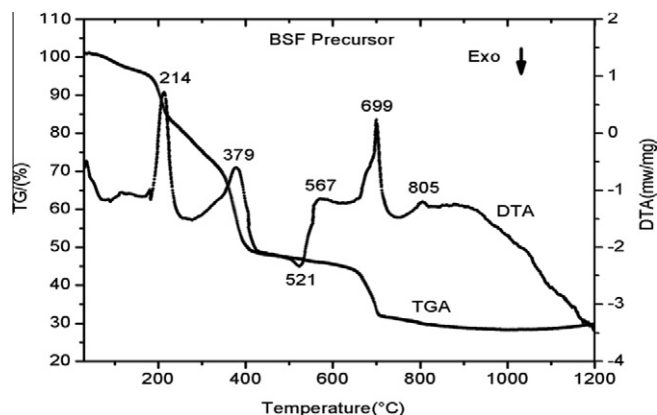 E-mail address: kanagu1980@gmail.com (S. Kanagesan).

Fig. 1. TG–DTA curves for the dried precursor.
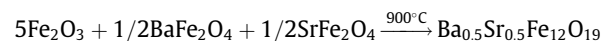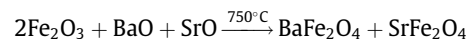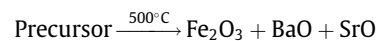
3. Results and discussion

3.1. Thermal study

In order to investigate the synthesis process for BSF, a TG/DTA analysis is performed for the precursor and the results are shown in Fig. 1. From the curve, the first step represents two major endothermic peaks and weight loss between 200 and 400 °C, due to the decomposition of D-Fructose. In the TGA of D-Fructose, a major weight loss between 200 and 400 °C [12], supports our results. This was reported in our previous research. Within the same range (200–400 °C), the nitrates are decomposed and gaseous products are also librated from the sample. Two distinct endothermic peaks between 200 and 400 °C are due to the decomposition of D-Fructose and the one exothermic peak around 521 °C may be the decomposition of the residual amorphous carbon. From the result it is clear that dry fructose burns drastically after absorbing some energy and gives out a great quantity of heat. Therefore D-Fructose produces self-heat to promote the reaction and to reduce the crystallization temperature of the hexaferrite. In the second step, endothermic and exothermic peaks and weight loss at the temperatures between 400 and 750 °C can be assigned to the starting formation of monoferrite and hexaferrite. The next moderate peak corresponding to the weight loss at 804 °C is assigned to the formation of crystalline phase. No, significant weight loss is observed at the

temperature range of above 890 °C, which confirmed the formation of stable barium strontium hexaferrite and the minimum crystalline temperature at 900 °C to get BSF powders using the sol–gel method.

3.2. Structural studies

Fig. 2(A) shows the XRD pattern of the powders which were conventionally calcined at 500, 750 and 900 °C for 3 h. The peaks corresponding to Fe_2O_3, BaO and SrO were obtained for the precursor calcined at 500 °C. $BaFe_2O_4$, $SrFe_2O_4$ and hexagonal $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ planes can be detected for samples calcined at 750 °C. No clear hexagonal crystalline phase was seen in this pattern. Clear diffraction peak of $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ was obtained for powder calcined at 900 °C. Fig. 2(B) shows the phase development of microwave calcined powder at temperatures 500, 750 and 900 °C each for 10 min. It shows diffraction peaks corresponding to the standard diffraction pattern of BaO, Fe_2O_3, $BaFe_2O_4$ and $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$. Singh et al. [13], have reported synthesis of $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ by the conventional ceramic method. In their experiment, the crystallization occurred when the precursor was calcined at 1250 °C.

This analysis illustrates that the optimum calcination temperature for BSF is around 900 °C. The sequences of reaction taking place are shown in the following steps,

$$Precursor \xrightarrow{500°C} Fe_2O_3 + BaO + SrO$$

$$2Fe_2O_3 + BaO + SrO \xrightarrow{750°C} BaFe_2O_4 + SrFe_2O_4$$

$$5Fe_2O_3 + 1/2BaFe_2O_4 + 1/2SrFe_2O_4 \xrightarrow{900°C} Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$$

The endotherms with their maxima at 567, 699 and 805 °C are due to the further by product decomposition and the starting formation of hexaferrite. The continuous exothermic process happens above 870 °C, which corresponding to the formation and transition of crystalline phases of BSF. Song et al. [14] have reported synthesis of $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ by gel-precursor transformation process, where the crystallization temperature was observed as 1000 °C. In the present investigation, the crystallization has been observed at a low calcination temperature of about 900 °C.
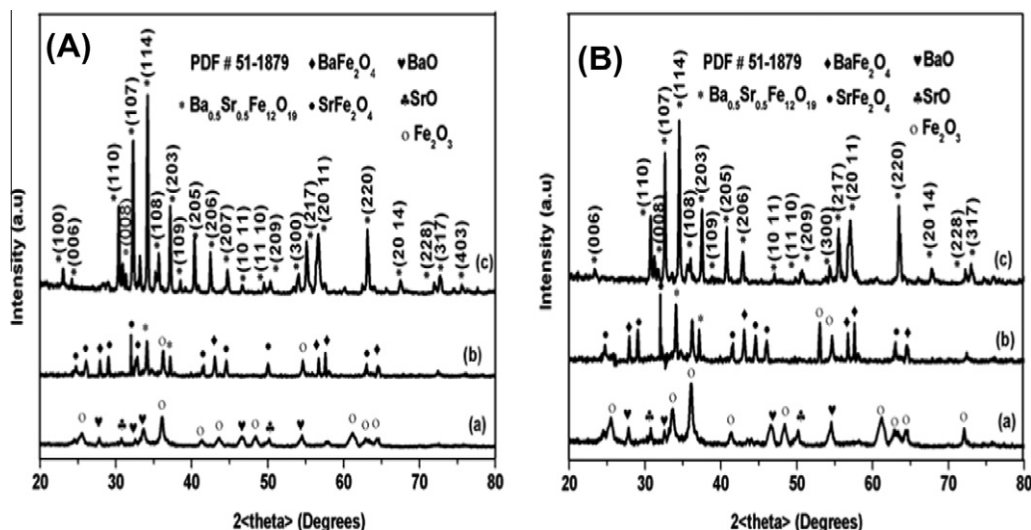

Fig. 2. XRD Pattern of the powder (A) conventionally calcined at (a) 500 °C (b) 750 °C and (c) 900 °C for 3 h, (B) microwave calcined at (a) 500 °C (b) 750 °C and (c) 900 °C for 10 min.
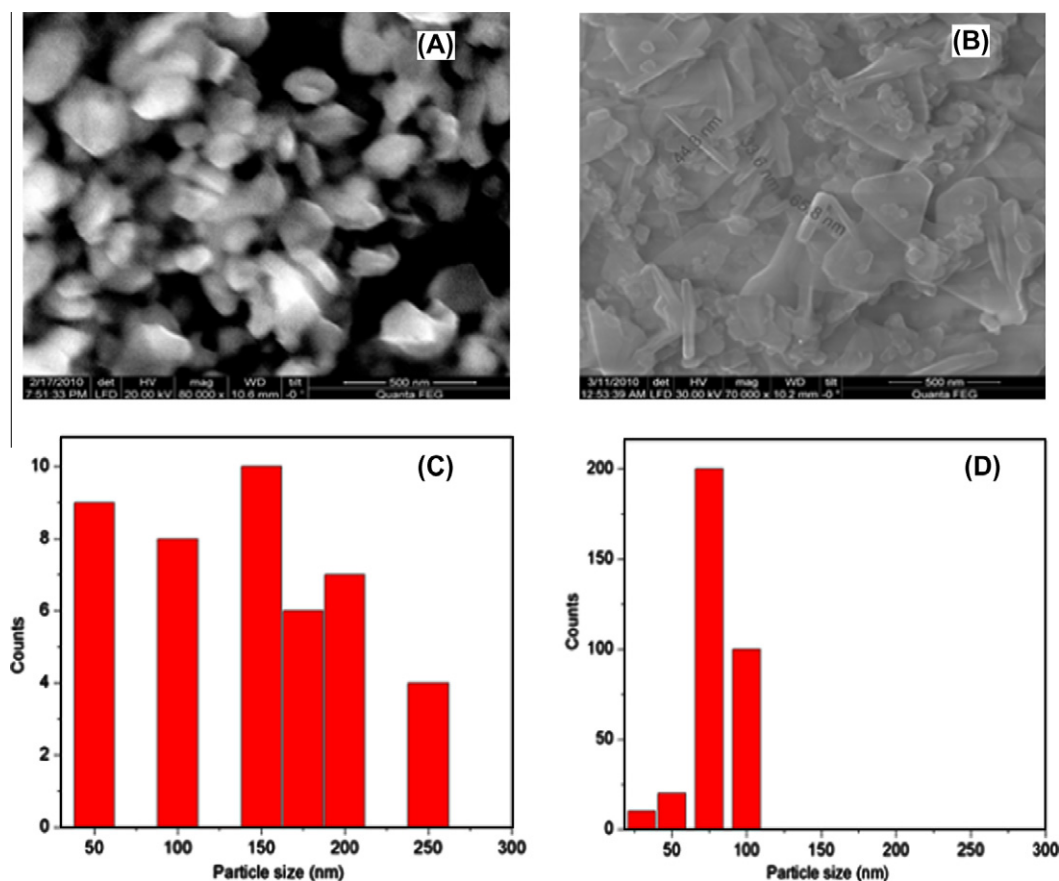
Fig. 3. (A) Morphology of conventionally calcined powder at 900 °C for 3 h, (B) morphology of microwave calcined powder at 900 °C for 10 min, (C) histograms of HR-SEM images of conventionally calcined powder, and (D) microwave calcined powder.

3.3. Morphological analysis

Fig. 3(A) shows a FE-SEM image of BSF powder conventionally calcined at 900 °C for 3 h. Even though the particles are not uniform in size, the shape of the particles are plate like hexagonal. The diagonal lengths of the hexagonal particles are varying from 100 to 250 nm. The major portion of the microwave calcined particles is in the range about 30–100 nm, showing hexagonal grains. The size of the microwave calcined particles (Fig. 3(B)) is smaller than the conventionally calcined particles. Researchers [15,16] have reported that microwave sintering of oxide ceramics lead to a reduction of particle size. However, the particle size reduction was limited to some extent. Patterson et al. [17] reported on microwave and conventionally sintered ceramic samples. The mean grain size was 3.19 and 4.38 μm in microwave and conventional processing, respectively. Hard magnetic materials with hexagonal structure are mainly due to the microwave energy coupled through polarization, electronic and ionic conductivity loss. Therefore the smaller particle size resulted from the enhanced diffusion and accelerated densification [16]. The histograms of HR-SEM images shown in Fig. 3A and B are presented in Fig. 3C and D, respectively. From the histograms, it is confirmed that the ranges of particle sizes are getting reduced when the sample was calcined using microwave furnace.

3.4. Magnetic measurements

Fig. 4A and B show the hysteresis loops of the samples calcined conventionally at 750 °C for 3 h and calcined using the microwave furnace at 750 °C for 10 min, respectively. Saturation

magnetization (M_s) values of conventionally calcined and microwave calcined samples are 27, and 30 Am^2/kg, respectively. Coercivity values of conventionally calcined and microwave calcined samples are 135 and 179 G, respectively. These samples exhibit ferromagnetic behavior at room temperature.

When the samples temperature is increased to 900 °C, the saturation magnetization values are 61 Am^2/kg for conventionally, and 49 Am^2/kg for microwave, treated powder, respectively (Fig. 4C and D). The hysteresis loops are smooth confirming the formation of pure BSF. Though the microwave treatment decreases the saturation magnetization, it increases coercivity value from 4565 to 5591 G. Saturation magnetization (M_s) for conventionally calcined sample is 61 Am^2/kg slightly more than that of obtained without using a fuel by sol–gel method [18]. The coercivity (H_c) of the conventionally calcined sample is 4565 G. The H_c is lower compared to the value from the sol–gel method (5994 G) [18] but higher compared to the value from the two-route standard ceramic method (2263 G) [13]. The low coercivity value was obtained for the particles which are not uniformly distributed; the particle size and morphology are the main reasons for the low coercivity as reported by Tang et al. [19]. The microwave calcined $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ at 900 °C also shows hysteresis behavior with the coercivity (H_c) of 5591 G, and a lower specific magnetization of 49 Am^2/kg. This is less than that from the two-route standard ceramic method (63 Am^2/Kg) [13].

Microwave calcined samples shows high coercivity compared to conventionally calcined samples: this it may be due to the smaller particle size in the microwave process. It is well known that the coercivity of BSF depends on many factors, such as chemical composition, particle size, degree of crystallinity, shape, magnetic
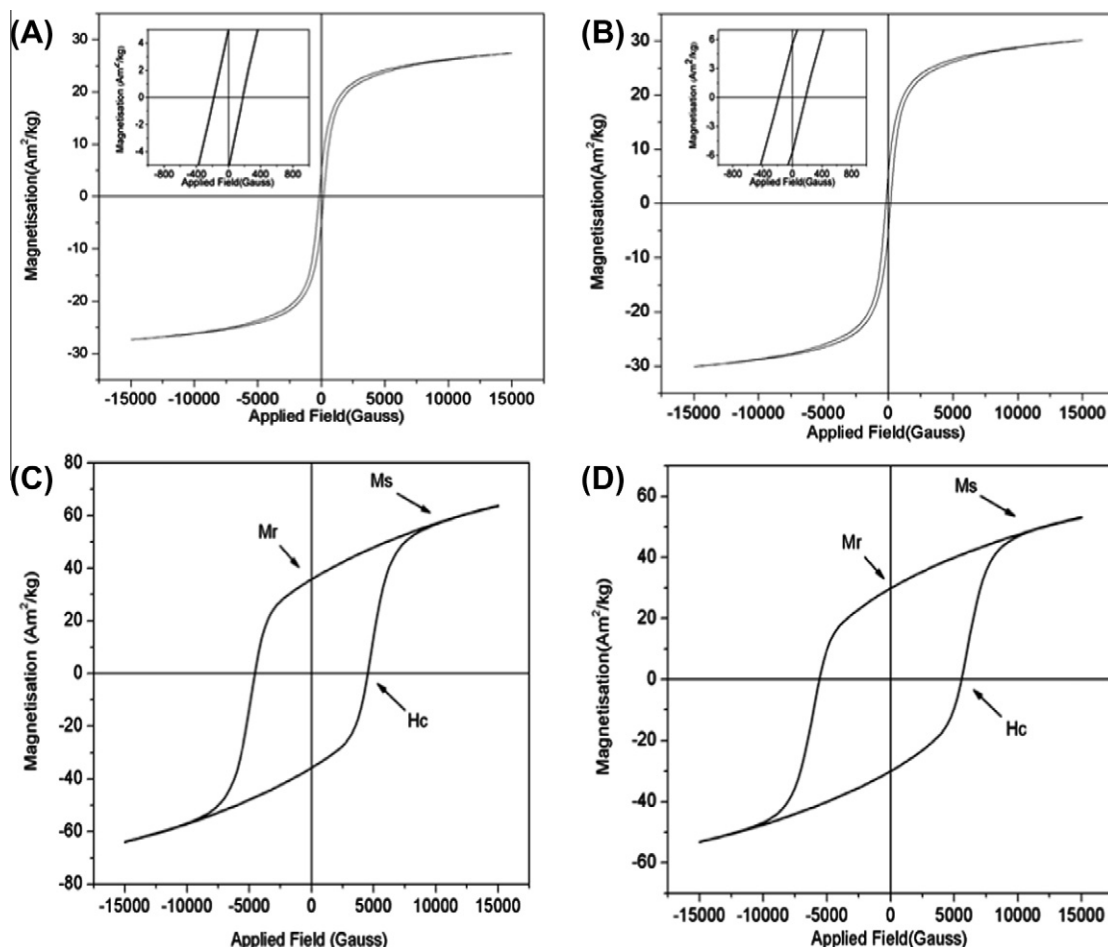
Fig. 4. Hysteresis curves of $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ (A) powder conventionally calcined at 750 °C for 3 h, (B) powder microwave calcined at 750 °C for 10 min, (C) powder conventionally calcined at 900 °C for 3 h, and (D) powder microwave calcined at 900 °C for 10 min.

anisotropy, etc. However, recent studies indicate that coercivity is strongly influenced by the particle size, particle shape and temperature [12,20–22], whose variation can also induce the obvious change in saturation magnetization.

4. Conclusion

Syntheses of $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ powders were reported by sol–gel technique using D-Fructose as a fuel. Single phase barium strontium hexaferrite was formed at relatively low temperature (900 °C) for both microwave and conventional treated powders. The crystals are hexagonal in shape, and the diagonal length of the particles ranges from 100 to 250 nm for conventional and 30–100 nm for microwave calcinations, respectively. The specific saturation magnetization (M_s) and coercivity (H_c) of the samples are comparable with the previous reports. The result indicates that the hard magnetic property of barium strontium hexaferrite is higher for microwave treated powder than that of conventionally calcined powder. The effects of the application of microwave energy and its benefits to process of ferrite materials as shown above are noticeable in the field of materials science.

Acknowledgement

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