Journal of Alloys and Compounds 500 (2010) 125–128

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Barium hexaferrite synthesis by oxalate precursor route

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ARTICLE INFO

Article history:
Received 1 December 2009
Received in revised form 25 March 2010
Accepted 31 March 2010
Available online 8 April 2010

Keywords:
Barium hexaferrite
Annealing temperature
Magnetic properties
Oxalate precursor

ABSTRACT

Magnetic materials are important electronic materials that have a wide range of industrial and commercial applications. Barium hexaferrite ($BaFe_{12}O_{19}$), is of great importance as permanent magnets, particularly for magnetic recording as well as in microwave devices. An aim of this study was to synthesize stoichiometric and single phase barium hexaferrite by a technique of oxalate precursor. Effect of different annealing temperature on the particle size, microstructure and magnetic properties of the resulting barium hexaferrite powders has been studied, and reported in the presented paper. The Fe^{3+}/Ba^{2+} mole ratio was controlled at 12, while the annealing temperature was controlled from 800 to 1200 °C. The resultant powders were investigated by differential thermal analyzer (DTA), X-ray diffractometer (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM). Single well crystalline $BaFe_{12}O_{19}$ phase was obtained at annealing temperature 1200 °C. The SEM results showed that the grains were regular hexagonal platelets. In addition, maximum saturation magnetization (66.36 emu/g) was observed at annealing temperature 1100 °C. However, it was found that the coercivity of the synthesized $BaFe_{12}O_{19}$ samples was lower than the theoretical values.

1. Introduction

Magnetic materials can be regarded now as being indispensable in modern technology. They are components of many electromechanical and electronic devices. Permanent magnet materials are essential in devices for storing energy in a static magnetic field. As a result of its specific magnetic properties barium hexaferrite and its derivatives can be used for permanent magnets, magnetic recording media and microwave applications [1]. $BaFe_{12}O_{19}$ (M-type hexagonal ferrites) is currently magnetic material with great scientific and technological interest, because of its relatively high Curie temperature, high coercive force and high magnetic anisotropy field as well as an excellent chemical stability and corrosion resistivity [2]. Barium hexaferrite ($BaFe_{12}O_{19}$) has a complex hexagonal unit cell and belongs to the magnetoplumbite structures [3]. Magnetoplumbite are of the type $A^{2+}O1{\cdot}6B_2{}^{3+}O_3$. The arrangement of the 12 Fe^{3+} ions in the unit cell is as follows: two ions in the tetrahedral sites (four nearest O^{2-} neighbors), nine ions in the dodechedral sites (six nearest O^{2-} neighbors) and one ion in the hexagonal site (five nearest O^{2-} neighbors). Materials of this type have a strong uniaxial magnetic direction, making as permanent magnets. This type of ferrites is termed as hard ferrite due to their high coercive force, high saturation magnetization, high Curie temperature and chemically inert. The reported theoretical calculated coercive force, saturation magnetization and Curie temperature values for pure and single domain barium hexaferrite was 6700 Oe, 72 emu/g and 450 °C, respectively [4,5]. It is difficult to obtain ultrafine and monodispersed particles by the commercial ceramic method (solid state reaction) which involves the firing of stoichiometric mixture of barium carbonate and α-iron oxide at high temperatures (about 1200 °C) [6]. In this respect, several low-temperatures chemical methods were investigated for the formation of ultrafine $BaFe_{12}O_{19}$ particles. These methods comprised co-precipitation [7–10], hydrothermal [11–13], sol–gel [14–16] microemulsion [17], citrate precursor [18], glass crystallization [19], sonochemical [20] and mechano-chemical activation [21]. It has been reported that synthesis of barium ferrite by a hydrothermal reaction is preferable as it can be carried out at lower temperatures and fewer unwanted intermediates and/or impurities are obtained [22]. It is recognized that the magnetic properties of barium ferrite, $BaFe_{12}O_{19}$ (BaM) can be optimized for particular purposes through doping. Solid state reaction method is used for the fabrication of barium based hexaferrites. The sites occupied by Fe ions can be replaced with Al, Co, Zr, Mn, Zn, Sm and Sn, or rare earth elements such as Ho^{3+}, Nd^{3+} [22–25]. In this study, the oxalate precursor technique was used to synthesize nanocrystalline barium ferrite with high saturation magnetization and narrow size distribution. Effect of the annealing temperature on the synthesis of ferrite powders was investigated. The annealing temperature was controlled from 900 to 1200 °C at Fe^{3+}/Ba^{2+} mole ratios 12.

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doi:10.1016/j.jallcom.2010.03.230

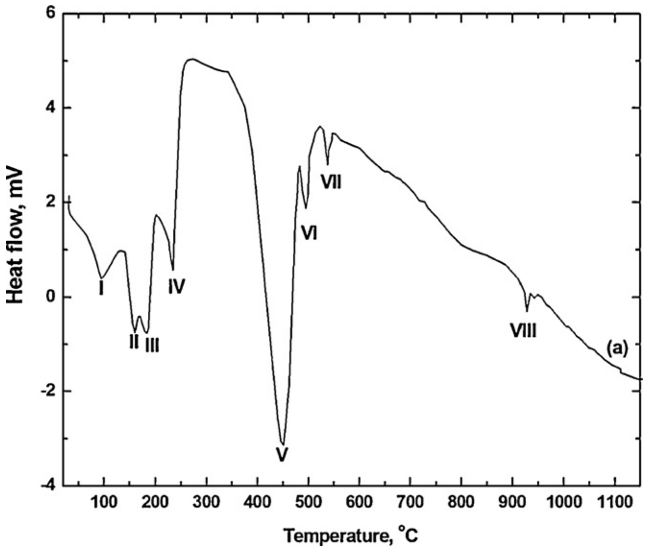

Fig. 1. Thermal profiles (DTA) of mixtures of barium–iron oxalate precursors at Fe^{3+}/Ba^{2+} mole ratios 12.

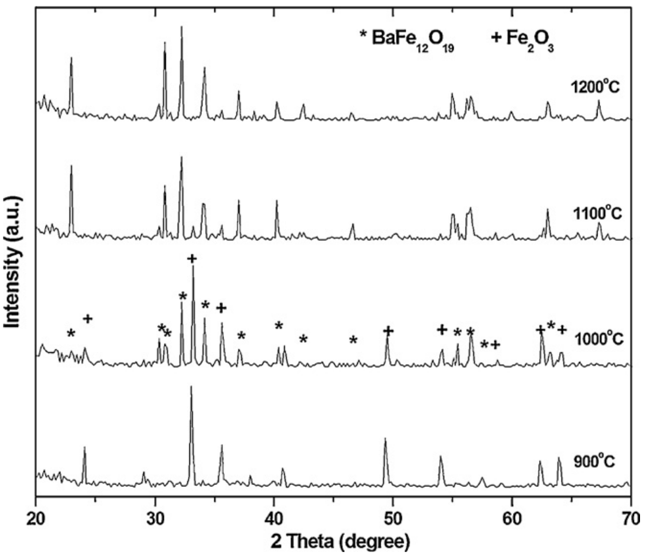

Fig. 2. XRD patterns of $BaFe_{12}O_{19}$ from barium–iron oxalate precursor with Fe^{3+}/Ba^{2+} mole ratio 12 thermally treated at different temperatures (900–1200 °C) for 2 h.

2. Experimental

The oxalate precursor method was applied for the preparation of barium hexaferrite ($BaFe_{12}O_{19}$). Chemically grade ferric chloride ($FeCl_3$–$6H_2O$), barium chloride ($BaCl_2{\cdot}H_2O$) and oxalic acid as source of organic were used as starting materials. A ferric chloride and barium chloride solution with Fe^{3+}/Ba^{2+} molar ratio of 12, and containing equivalent amount of oxalic acid were prepared. A mixture of barium chloride and ferric chloride solutions were prepared and then stirred for 15 min on a hot-plate magnetic stirrer, followed by addition of an aqueous solution, which was heated to 80 °C with constant stirring until dry and then dried in a dryer at 100 °C overnight. The dried powders obtained as barium ferrite precursors. Differential thermal analyzer (DTA) analysis of various un-annealed precursors was carried out. The rate of heating was kept at 10 °C/min between room temperature and 1000 °C. The measurements were carried out in a current of argon atmosphere.

For the formation of the barium ferrite phase, the dry precursors were annealed at the rate of 10 °C/min in static air atmosphere up to different temperatures (900–1200 °C) and maintained at the temperature for annealing time (2 h). The crystalline phases presented at differently annealed samples were identified by XRD on a Brucker axis D8 diffractometer using Cu–kOe (λ = 1.5406) radiation and secondary monochromator in the range 2Ø from 10 to 80°. The ferrites particles morphologies were observed by scanning electron microscope (SEM, JSM-5400).

The magnetic properties of the ferrites were measured at room temperature using a vibrating sample magnetometer (VSM; 9600-1 LDJ, USA) in a maximum applied field of 10 kOe. From the obtained hysteresis loops, the saturation magnetization (M_s), remnant magnetization (M_r) and coercivity (H_c) were determined.

3. Results and discussion

Differential thermal analysis (DTA) plot of the synthesized mixture of barium–iron oxalates precursors is shown in Fig. 1. It can be seen in peaks I–IV that an endothermic reaction occurred at around (95.11, 158.52, 182.45 and 232.15 °C) which corresponds to the dehydration of iron and barium oxalates. This is consistent with earlier findings suggesting that, two different crystals hydrate types namely $MeC_2O_4{\cdot}2H_2O$ and $MeC_2O_4{\cdot}3H_2O$ (Me: metal ion) [26]. Thereafter, peaks V–VII (448.02, 493.88 and 586.56 °C) were significantly related to the anhydrous oxalate mixture decomposition into both metal oxide and gases (CO_2 and CO).

Peak VIII in the plot at (956.90 °C), showed the initial step to form $BaFe_{12}O_{19}$, which is consistent with XRD diffraction patterns in (Fig. 2). The XRD patterns are of the calcined powder of $BaFe_{12}O_{19}$, obtained from barium–iron oxalate precursor solutions, with Fe^{3+}/Ba^{2+} mole ratio 12 thermally treated at different temperatures (900–1200 °C) for 2 h. On the start of the annealing process at (900 °C), a complete absence of M-type barium ferrite phase. Instead, the hematite Fe_2O_3 phase appears as a major phase. But at (1000 °C) concentration of the hematite phase decreases, and barium ferrite phase was detected. Increasing the annealing temperature to 1100 °C, enhanced the formation of barium hexaferrite phase, and diminished the hematite Fe_2O_3 phase. At the calcination temperature (1200 °C), single phase of barium hexaferrite ($BaFe_{12}O_{19}$) evidently was formed.

Effect of calcination temperatures on the synthesized $BaFe_{12}O_{19}$ powders was observed on the crystalline size, as shown in Fig. 3. The particle size estimated from the Scherrer formula. It can be seen that, the minimum particle size appeared at 1000 °C (≈145 nm), and the maximum size was found at 1200 °C (≈168 nm), which most likely explained by the formation of the single phase of barium hexaferrite ($BaFe_{12}O_{19}$). However, this observed crystalline size for the single phase barium hexaferrite produced via oxalate precursor route is much higher than that produced by other wet chemical methods. This finding was also observed by other authors [26,27].

Further investigation was carried out by SEM, to show the morphology of the particles as synthesized, as well as the development of grain structure. Fig. 4(a) shows very fine particles of

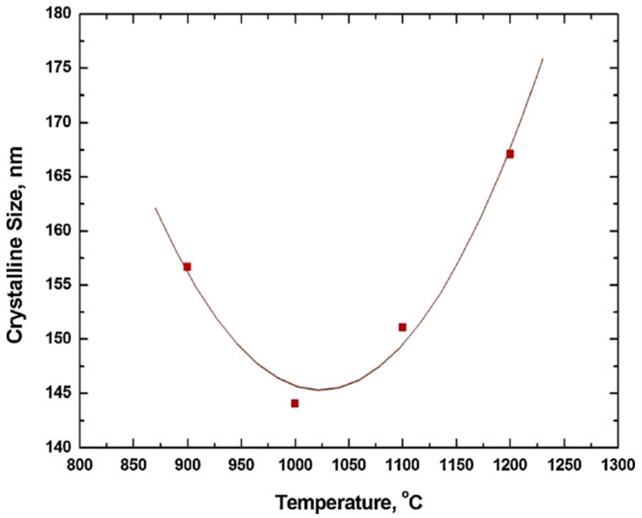

Fig. 3. Effect of calcination temperatures on the crystalline size of synthesized $BaFe_{12}O_{19}$ powders obtained from oxalate precursors with Fe^{3+}/Ba^{2+} mole ratios of 12 and calcined for 2 h.

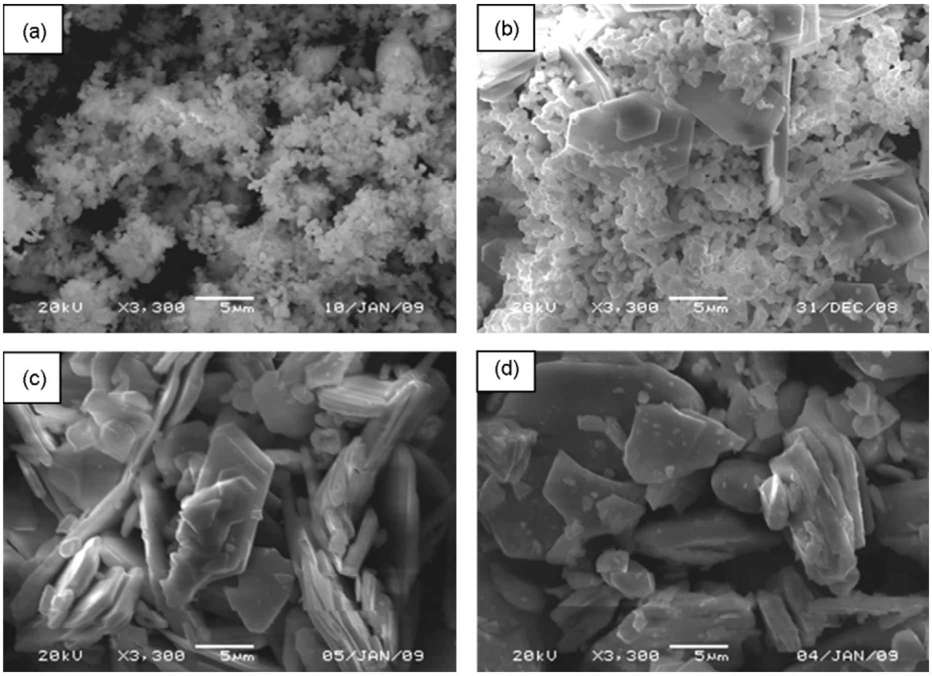

Fig. 4. Effect of calcination temperatures on the microstructure of synthesized $BaFe_{12}O_{19}$ powders obtained from oxalate precursors with Fe^{3+}/Ba^{2+} mole ratios of 12 and calcined for 2 h. (a and b) 900 °C, (c and d) 1000 °C, (e and f) 1100 °C and (g and h) 1200 °C.

hematite powder started to agglomerate at 900 °C. No clear crystalline microstructure can be seen in this stage, which provides evidence that, the calcination temperature at 900 °C is insufficient for complete crystalline structure. However, this stage most likely is the nucleation of particles followed by the growth of the larger particles.

Fig. 4(b) shows the SEM micrographs of the samples calcined at 1000 °C. At 1000 °C, the micrograph provides evidence that the sample consists of both hexagonal platelet crystals of barium hexaferrite and hematite. As annealing temperature increases to 1100 °C Fig. 4(c), a single phase of hexagonal platelet crystals of barium hexaferrite was observed. With an increase of annealing temperature up to 1200 °C, grains have coalesced to form larger grains, which can be explained by assuming this temperature of calcinations is the highest temperature to obtain an optimum composition of synthesized $BaFe_{12}O_{19}$ powder from oxalate precursors with Fe^{3+}/Ba^{2+} mole ratios of 12.

Figs. 5 and 6 present the most important findings of the magnetic properties of the synthesized barium ferrite powders, which were obtained at room temperature under an applied field of 10 kOe. Fig. 5 displays the effect of annealing temperature on the hysteresis loop of $BaFe_{12}O_{19}$ powders. The results showed that, the saturation magnetization of the produced powders increased by increasing the annealing temperature. It exhibited a maximum value of (66.36 emu/g) at annealing temperature 1100 °C for 2 h. This is likely due to the presence of single domain of $BaFe_{12}O_{19}$ particles. Such high saturation magnetization for barium ferrite at 1200 °C can be attributed to the high-phase purity and well-defined crystallinity of $BaFe_{12}O_{19}$. This is consistent with earlier findings of the XRD and SEM. Moreover, the shape of the curve of the hysteresis loop confirmed that, the barium ferrite is a hard magnet.

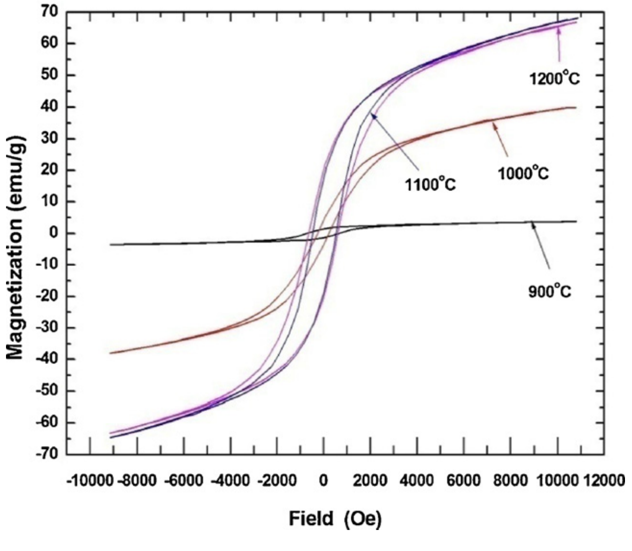

Fig. 5. Effect of annealing temperature on the M–H hysteresis loop of synthesized $BaFe_{12}O_{19}$ powders obtained from oxalate precursors.

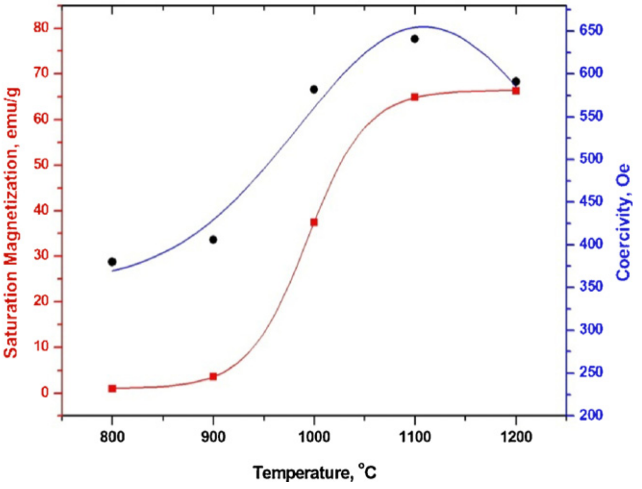

Fig. 6. The saturation magnetization and the coercivity as a function of annealing temperature of $BaFe_{12}O_{19}$ synthesized from barium–iron oxalate precursor annealed for 2 h.

The coercivity denoted here as H_c, also call the coercive force, of the ferromagnetic samples. The values in Fig. 6 refer to the intensity of the magnetic field required to reduce the magnetization of the samples to zero, after the magnetization of the sample has reached saturation. The results obtained in this work of H_c, are in substantial disagreement with the published literature [3,4]. The reported theoretical calculated coercive force value for pure and single domain barium hexaferrite was 6700 Oe, which is much lower than the reported values in Fig. 6. These findings can be explained by assuming that oxalate precursor route seems to produce ferrite with lower coercivity than the other preparation routes. In addition, the barium ferrite powder exhibited particles coarsening (plate-like hexagonal structure) and grain growth at high annealing temperature.

4. Conclusions

This paper presented synthesis of barium ferrite ($BaFe_{12}O_{19}$) powder by the route of oxalate precursor. The results can be summarized as follows:

(i) At the calcinations temperature (1200 °C), single phase of barium hexaferrite ($BaFe_{12}O_{19}$) evidently was formed.

(ii) Regarding the particles size, it can be seen that, the minimum particle size appeared at (1000 °C), and the maximum size was found at (1200 °C), which most likely explained by the formation of the single phase of barium hexaferrite ($BaFe_{12}O_{19}$).

(iii) The morphology of the particles at 1000 and 1100 °C were hexagonal platelet crystal. While, at 1200 °C grains have coalesced to form larger grains.

(iv) The oxalate precursor route has proven to produce pure barium ferrite powders with good magnetic properties with maximum saturation magnetization value of (66.36 emu/g), and coercivity force value of (6400 Oe).

(v) Annealing temperature has great effect on the magnetic properties of barium hexaferrite, and most likely the temperature of 1200 °C is the ideal temperature for annealing the powders with Fe^{3+}/Ba^{2+} mole ratios of 12.

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