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# Preparation of M-Ba-ferrite fine powders by sugar-nitrates process

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In this paper, fine M-type barium hexaferrite (M-Ba-ferrite) particles were synthesized from sugar and nitrates by simple route, which revealed the feasibility of using sugar as chelating agent in forming solid precursors of $BaFe_{12}O_{19}$. The effects of factors, such as the molar ratio of Fe/Ba, calcination temperature and time, on the morphology, the phase component and the magnetic properties of M-type barium hexaferrite particles were studied by means of X-ray diffraction, infrared spectroscopy, transmission electron microscopy and physical property measurement system. The results showed that the molar ratio of $Ba^{2+}$ to $Fe^{3+}$ influenced significantly on the formation of the single phase barium ferrite. The hexagonal platelet barium ferrite particles with a specific saturation magnetization of 64.48 emu/g, remanence magnetization (Mr) of 33.84 emu/g, and coercive force (Hc) of 1848.85 Oe were obtained when the molar ratio of Fe/Ba was 11.5 and the calcination temperature was 1100 °C for 2 h.

## 1. Introduction

Barium ferrite is a well known permanent magnet. It is widely used as a magnetic recording media and an electromagnetic attenuation material [1–2]. In order to get pure crystalline particle of $BaFe_{12}O_{19}$, different synthesis techniques have been developed in recent decade, such as chemical co-precipitation [3], sol-gel technique [4], salt-melt technique [5], mechanochemically assisted process [6], low temperature combustion [7], and so on. Sol-gel processing is well accepted as a technology to prepare ferrite powders, where citric acid is used as a multidentate ligand and complexes with many multivalent ions to form chelates, and efforts are still continuing to prepare ferrite powders using citric acid [8, 9]. However, few groups paid attention to the feasibility of sugar as a source of chelating agent. It is known that sugar is a carbohydrate, which yields two monosaccharides upon hydrolysis, and the product can easily be further oxidized into carboxyl acid in the present of oxidizer. Carboxyl acid is a kind of ligands and complexes with many multivalent ions to form chelates. Therefore, we proposed using white granulated sugar as chelating agent. In the present study, a metal nitrates-white granulated sugar mixed solution was used to prepare the precursor of $BaFe_{12}O_{19}$, and then the precursors were thermally decomposed and transformed into fine powders of $BaFe_{12}O_{19}$. The effects of Fe/Ba molar ratio, decomposing temperature and time on the magnetic properties and other characteristics of the resultant barium ferrite were investigated. The prepared precursors and ferrites were characterized by XRD, FTIR, TGA and DSC. The microstructure was observed through TEM.

## 2. Experimental

The starting materials were: A.R. grade of $Fe(NO_3)_3 \cdot 9H_2O$ (99.9%), $Ba(NO_3)_2$ (99.5%) and white granulated sugar (Shanghai Sugar & Tobacco Industry Limited Company, China, GB317, sucrose $>$ 98%). The chemicals were weighed and mixed according to determined proportion. Ferric nitrate and sugar solutions were mixed and barium nitrate was added with continuous stirring for two hours. Then the mixed solution was evaporated slowly at 90 °C, during which the $Fe^{3+}$ and nitrate ion provided an in situ oxidizing environment for sugar being hydrolyzed and converted into carboxylic acids, and the nitrates themselves were decomposed to give out brown fumes of nitrogen dioxide. When the reaction completed, the obtained solution was cooled. In order to make carboxyl acid be ionized and carboxylic groups chelate $Fe^{2+}$ and $Ba^{2+}$, ammonia solution was slowly added to adjust the pH value of the solution to 6.5. The precursors

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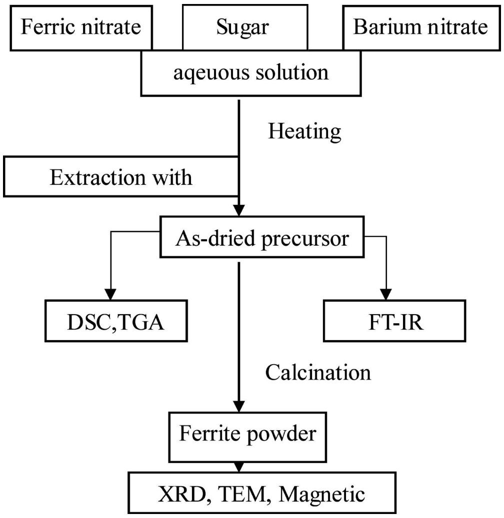

*Figure 1* Schematic diagram for the preparation of ferrite powders.

were precipitated and separated from the reaction medium by adding ethanol. The shallow green product was then filtered, and dried at 80 °C for 24 h, and turned into a dried precursor. Finally, powders of the dried precursor were annealed at different temperatures for 2 h with a heating rate of 8 °C per minute to obtain barium hexaferrite powders. A schematic diagram of the synthesis process is shown in Fig. 1.

Thermal Analysis (TGA) was carried out on TA Instruments TGA2050 Thermo-gravimetric Analyzer with a heating rate of 20 °C per minute. The thermal decomposition behavior of the as-dried powders was examined by NETZSCH thermische analyse DSC404 instruments with a heating rate of 20 °C per minute. X-ray powder diffraction patterns of the samples were recorded by X-ray diffractometer (D8 ADVANCE, BRUKER-AXS) using the wavelength of 1.54051 Å of CuK$_\alpha$ radiation. FT-IR spectra of species in the IR range of 400–4000 cm$^{-1}$ were measured by FT-IR spectrometer (Equinox 55, Bruker Analytische Messtechnik GmbH). Transmission electron microscopy (PHILIPS CM200) was used at 200 kV to observe the particle size and morphology of the sample. The specific saturation magnetization and coercivity of the $BaFe_{12}O_{19}$ particles were measured by means of physical property measurement system (PPMS-9, America) at a maximum applied field of 50 kOe at room temperature.

## 3. Results and discussion

As already known, white granulated sugar is a kind of carbohydrate and can be hydrolyzed into fructose and glucose under acid conditions, and glucose is further easily to be oxidized to carboxyl acid or a poly hydroxyl acid in the present of oxidizer ($Fe^{3+}$ and $NO_3{}^-$). The reaction is shown as follows:

$$C_{12}H_{22}O_{11}\ \text{(sugar)} + H_2O \rightarrow C_6H_{12}O_6\ \text{(glucose)} + C_6H_{12}O_6\ \text{(fructose)}$$

$$C_6H_{12}O_6\ \text{(glucose)} \rightarrow C_6H_{12}O_7\ \text{(gluconic acid)}$$

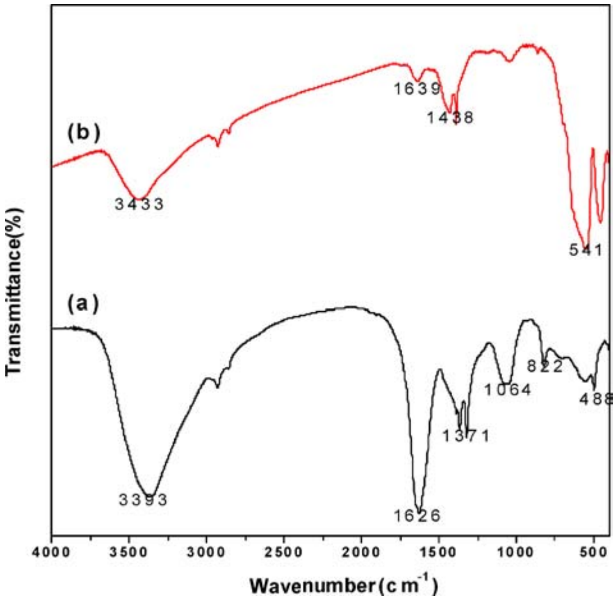

*Figure 2* FT-IR spectra of (a) the dried precursor and (b) precursor calcined at 400 °C for 2 h.

Carboxyl acid is a kind of ligands to be able to complex with many multivalent cations to form chelates. Gluconic acid which is composed of a carboxylic acid group in one end and five linear hydroxyl groups, easily forms the metal ion complex [10 ]. It forms a complex with metal cations by coordinating through hydroxyl groups in small micelles. Fig. 2 shows FT-IR spectra of the as-dried precursor (a) and precursor annealed at 400 °C for 2 h (b). The spectrum of dried precursor indicates the characteristic bands of O-H stretching vibration of water at 3393 cm$^{-1}$, anti-symmetrical and symmetrical stretching vibrations of $COO^-$ at 1626 cm$^{-1}$ and 1371 cm$^{-1}$. This $COO^-$ comes from the hydrolyzing and redoxing products of the white granulated sugar. It was also observed that C-O stretching vibration of C-OH at 1064 cm$^{-1}$ is seen for the as-dried precursor as given in Fig. 2(a). After heating of the precursor, bands of carboxylate can still be found at 1639 cm$^{-1}$ and 1438 cm$^{-1}$, however, it became very weak. Obviously, the functional groups of $COO^-$ have been decomposed during the heating process to the dried precursor. The new bands at 541 cm$^{-1}$ and 488 cm$^{-1}$ should be ascribed to metal-oxygen stretching vibration of heated powders [11], the formation of metal oxide can also be proved by XRD measurement.

The TGA pattern and DSC pattern of the dried precursor are shown respectively in Figs 3 and 4. As we can see that three distinct weight-loss steps occur at 160–190 °C, 371–409 °C and 648–667 °C successively in the TG curve. The first weight loss step over the temperature ranging from room temperature to about 190 °C is due to the evaporation of residual water in the precursor. The second and third weight loss steps from about 371 °C to 667 °C are presumably due to the decomposition of the precursor. The DSC curve shows five distinguished endothermic peaks respectively at 112 °C, 235 °C, 413 °C,

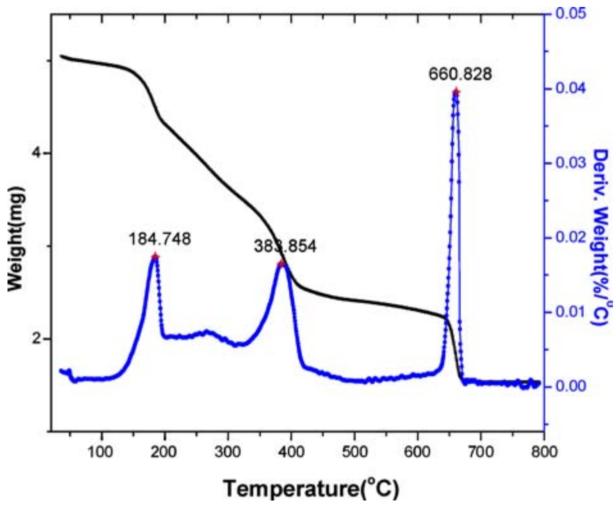

*Figure 3* TG-TGA curves for the dried precursor.

682 °C and 1150 °C occurred at the temperatures between 50 °C and 1200 °C. The endothermic temperature in the DSC pattern is consistent with the weight loss temperature in the TGA pattern. We think that the endothermic peaks at 112 °C, 235 °C could be attributed to the evaporation of the water of free or crystal in the precursor during heating. The endothermic peaks at 413 °C, 682 °C are due to the decomposition reaction of the precursor. The endothermic peak at 1150 °C is due to the solid-phase reaction because there is no significant weight loss within this temperatures range. The likelihood decomposition mechanism was proposed after discussing the result of X-ray pattern in the later text.

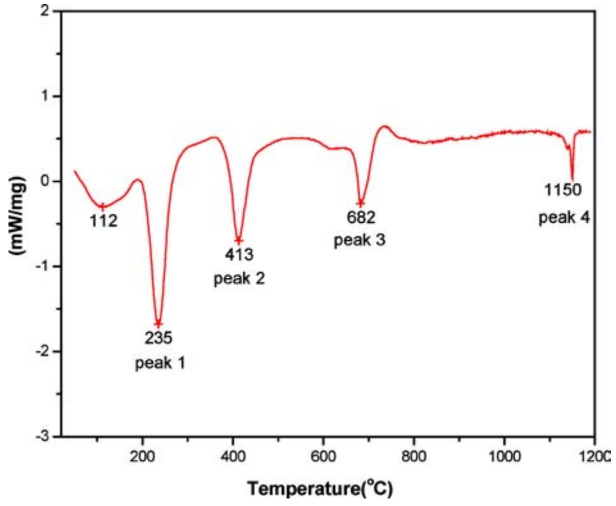

*Figure 4* DSC curve for the dried precursor.

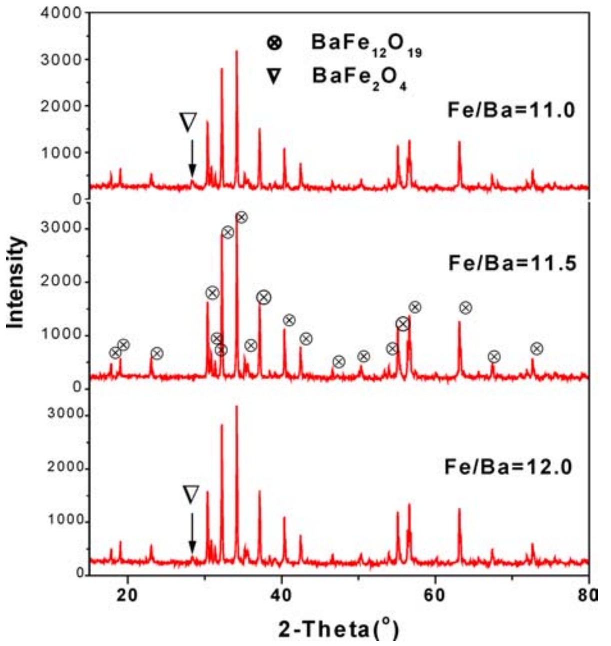

*Figure 5* XRD patterns of powders calcined at 1100 °C for 2 h at different Fe/Ba ratios.

Fig. 5 showed XRD patterns of the specimens obtained at different Fe/Ba ratios. The calcination temperature and time were fixed at 1100 °C and 2 h respectively. As we expected, the Fe/Ba ratio plays an important role in the formation of single phase $BaFe_{12}O_{19}$, and the single phase $BaFe_{12}O_{19}$ powders can be obtained at a Fe/Ba ratio of 11.5. In contrast, small amount of $BaFe_2O_4$ impurity phase appears at the Fe/Ba ratios of 11 and 12. The appropriate molar ratio of Fe/Ba may vary with the production method used and the starting materials, with claims varying from a Fe/Ba molar ratio of 8–12. The single phase barium ferrite can be made from a stoichiometric mixture of Fe/Ba = 12 via a sol-gel route [12–13]. An investigation of the synthesis of barium ferrite by co-precipitation method showed that the M-type phase only forms as a pure product in a non-stoichiometric mixture with a Fe/Ba = 11 [14]. It has also been found that the pure hexaferrite was obtained at Fe/Ba = 10.5 in the work of Carp et al. [15]. Usually an irondeficient nonstoichiometric mixture with excess barium is needed to form the single-phase product. They suggested that the small amount of barium volatilized during the calcinations process was responsible for the "off stichiometry" [16]. The result is also shown in our experiment.

Fig. 6 shows the X-ray powder diffraction patterns of $BaFe_{12}O_{19}$ with the molar ratio of Fe/Ba = 11.5 annealed at different temperatures for 2 h. According to Fig. 6, the powder that was annealed at 400 °C shows mainly a mixture of phase $\alpha$-$Fe_2O_3$, $\gamma$-$Fe_2O_3$, $BaCO_3$. As the temperature reached 650 °C, the intensity of $\gamma$-$Fe_2O_3$ deceased markedly, and $BaCO_3$ phase disappeared, the $BaFe_{12}O_{19}$ and intermediate phase identified as barium iron oxides were formed. In the range of temperature from 850 °C to 1000 °C, $BaFe_{12}O_{19}$ was the major phase with a small amount of residual $\alpha$-$Fe_2O_3$. Finally, single hexagonal $BaFe_{12}O_{19}$ phase was formed completely at 1100 °C. It is disaccord with the prior research, where the single phase barium ferrite can be easily made directly from $\alpha$-$Fe_2O_3$ in sol-gel systems, where no $BaCO_3$ is involved, and without formation of the intermediate phase [12]. In this study, $\alpha$- and $\gamma$-$Fe_2O_3$ co-exist in the intermediate phase in

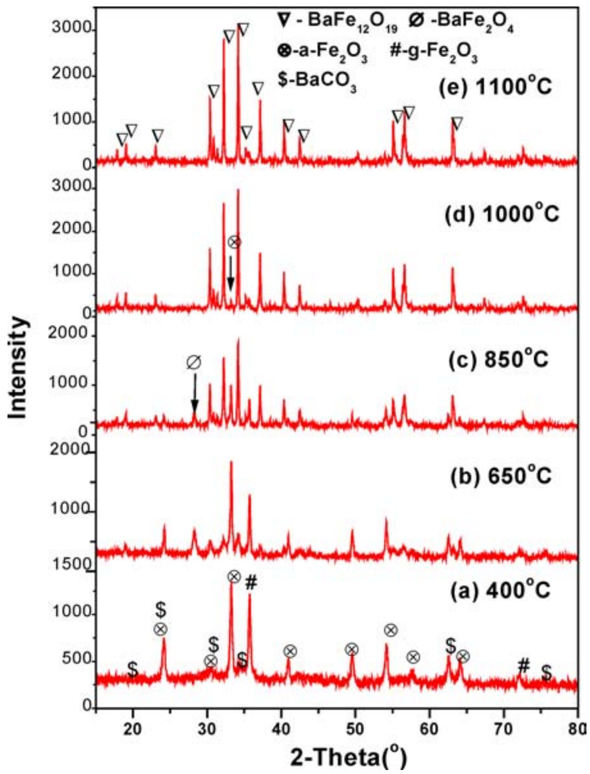

*Figure 6* XRD patterns of powders with a Fe/Ba ratio of 11.5 calcined at different temperatures for 2 h.

pattern (a). The $\gamma$-$Fe_2O_3$ is cubic spinel, chemical formula of which is $Fe[Fe_{5/3}\square_{1/3}]O_4$, where $\square$ stands for the hole of cation [17]. Its structure is similar to that of S block in barium ferrite, so $\gamma$-$Fe_2O_3$ can react with $BaCO_3$ easily to form $BaFe_{12}O_{19}$ phase at a low temperature. However, $\alpha$-$Fe_2O_3$ is $FeTiO_3$-type structure which belongs to the trigonal crystal system. Its crystal cell is orthorhombic hexahedron which is difficult to transform into $BaFe_{12}O_{19}$ phase, a complete conversion of the mixture into single $BaFe_{12}O_{19}$ phase requires high temperature.

According to the above TGA, DSC and the X-ray analysis results of the dried precursor in the course of heated process, the following decomposition mechanism can be assumed for the solid precursors in our experiment:

$[Fe_{12}Ba(\text{gluconic acid})_{19}] \cdot yH_2O$—$[Fe_{12}Ba(\text{gluconic acid})_{19}]+yH_2O$ (where y stands for the number of crystal water) (the peak 1 in Fig. 4)

$$[Fe_{12}Ba(\text{gluconic})_{19}]\text{—}(\alpha-, \gamma - Fe_2O_3) + BaCO_3 + CO_2 + H_2O \text{ (the peak 2 in Fig. 4)}$$

$$6(\gamma - Fe_2O_3) + BaCO_3\text{—}BaFe_{12}O_{19} + CO_2 \text{ (the peak 3 in Fig. 4)}$$

$$6(\alpha - Fe_2O_3) + BaO\text{—}BaFe_{12}O_{19} \text{ (the peak 4 in Fig. 4)}$$

Fig. 7 shows M-H hysteresis loops of the specimens at 1100 °C for 1 h and 2 h, respectively. The specimen annealed at 1100 °C for 1 h exhibited magnetization (measured at 50 kOe; M(50 kOe)) of 42.34 emu/g, remanence magnetization (Mr) of 20.6 emu/g, and coercive force (Hc) of 1624.9 Oe. At 1100 °C for 2 h, M (50 kOe), Mr, and Hc became 64.48 emu/g, 33.84 emu/g, and 1848.9 Oe, respectively. The calcination time has a significant effect on the specific magnetic saturation, as shown in Fig. 7. The specific magnetic saturation increases with the calcination time, which is attributed to the improved purity and crystallinity of the $BaFe_{12}O_{19}$. Mr/M (50 kOe) value is 0.487 at 1100 °C for 1 h and 0.52 for 2 h, which indicates the formation of single magnetic domain sizes $BaFe_{12}O_{19}$ [18 ]. The values of specific magnetic saturation are lower than the theoretical one, 72 emu/g, and the coercivity values for the products were much lower than those reported one (over 5000 Oe) [19]. Such a low coercivity should not be the result of a small amount of amorphous impurities undetectable by XRD and the diameters of the particles. It is know that

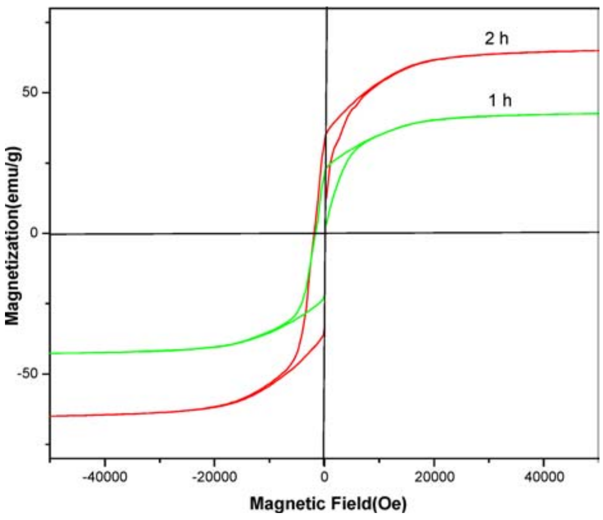

*Figure 7* M–H hysteresis loops at 300 K for samples calcined at 1100 °C for 1 h, 2 h, respectively.

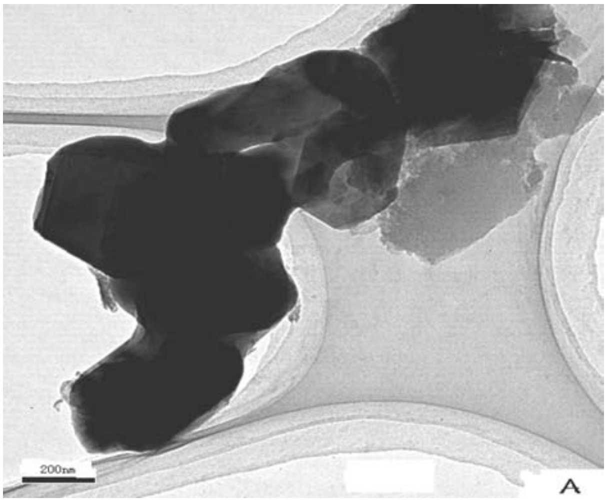

*Figure 8* TEM micrograph of barium ferrite powders calcined at 1100 °C for 2 h.

the magnetic properties are sensitive to many factors, in addition to the particle size and the particle size distribution, the morphology and microstructure of particles, the synthesis method, and so on. From the transmission electron micrograph (Fig. 8), it is observed that the particle shape is not an ideal hexagonal and platelike, moreover, evident agglomeration exists. We think that the morphology and microstructure of particles should be the main reason for the low coercivity. In addition, the synthesis method might be another reason for the low coercivity.

Fig. 8 presents the morphology of the specimens with Fe/Ba ratio of 11.5 annealed at 1100 °C for 2 h. The particles are hexagonal platelet crystals. They stack on the top of each other due to their magnetic attraction and exhibit a partially sintered microstructure. The diameter of particles is about 300–400 nm, which is lower than the critical size, 1 um. The powder is single magnetic domain particles, which is consistent with this result of the magnetic measurement.

## 4. Conclusion

The precursors for barium hexaferrite production were prepared using sugar as a source of chelating agent. Barium hexaferrite powders were successfully synthesized by using sugar-nitrates process. According to the thermal analysis by DSC/TGA and the phase analysis by XRD, the decomposition mechanism was suggested. The effect of annealed time on magnetic properties of barium ferrite powders was studied. The hexagonal platelet barium ferrite particles with a specific saturation magnetization of 64.48 emu/g, remanence magnetization (Mr) of 33.84 emu/g, and coercive force (Hc) of 1848.85 Oe were obtained when the molar ratio of Fe/Ba was 11.5 and the calcination temperature was 1100 °C for 2 h.

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