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Study of formation mechanism of barium hexaferrite by sintering curve

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ABSTRACT

Barium hexaferrite ($BaFe_{12}O_{19}$) with hexagonal structure was fabricated by sintering the mixture of α-Fe_2O_3 and $BaCO_3$, ball milling of the mixture followed by heat treatment as well as glycin–nitrate method and subsequent heat treatment, respectively. The mechanism of formation of the $BaFe_{12}O_{19}$ in the three kinds of procedures was investigated by using sintering shrinkage curve and XRD measurements. It was found that the α-Fe_2O_3 reacted with $BaCO_3$ to form $BaFe_2O_4$ with orthorhombic structure as the mixture were sintered above 660 °C firstly and then the $BaFe_2O_4$ reacted with α-Fe_2O_3 to form $BaFe_{12}O_{19}$ in a sintering temperature ranging from 770 to 920 °C. However, the α-Fe_2O_3 reacted with $BaCO_3$ to form $Ba_xFe_{3-x}O_4$ with spinel structure when the mixture was milled for 80 h, while the $BaFe_{12}O_{19}$ was obtained by annealing the $Ba_xFe_{3-x}O_4$ at 700–1000 °C. In the glycin–nitrate procedure, the precursor powders containing α-Fe_2O_3, Fe_3O_4 and $BaFe_2O_4$ were fabricated by self-propagating reaction firstly, and then the single $BaFe_{12}O_{19}$ was produced by sintering the precursor powders at 1000 °C. The magnetic properties of the $BaFe_{12}O_{19}$ produced by the three kinds of procedures were reached. The saturation magnetization and the coercivity of the $BaFe_{12}O_{19}$ fabricated by ball milling followed by heat treatment were 47.24 emu/g and 5086.34 Oe, respectively, which were much larger than those of the $BaFe_{12}O_{19}$ produced by other procedures. The mechanism leading to that the $BaFe_{12}O_{19}$ produced by the different methods had different magnetic properties was discussed in the present work.

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1. Introduction

M-type barium hexaferrite with hexagonal molecular structure is of great importance for perpendicular magnetic materials, due to that the raw material for barium hexaferrite is abundant, the manufacturing cost is low, its properties are stable and the problem of oxidation of the product is avoided [1–2]. Furthermore, the barium hexaferrite makes it potentially important in high-density perpendicular recording media, electromagnetic interference, magnetic fluids, microwave devices, etc. [1,3–7]. Specially, the properties in demagnetizing behavior, moderate coercivity, very low switching field distribution (SFD) and so on make the barium hexaferrite suitable for recording media [8–10].

The magnetic properties of barium hexaferrite originate from the Fe^{3+} ions of the barium hexaferrite structure. So people are interested in cationic substitution of Fe^{3+} ions, which causes the significant change of saturation magnetization and coercivity. For example, high anisotropic field of barium hexaferrite can be reduced by substitution of some ions, such as Co^{2+}, Zr^{4+}, Ni^{2+}, Ti^{4+}, Sn^{2+} and so on [11–15], for Fe^{3+}. However, these substitutions can cause the intrinsic coercivity to decrease effectively but at the expense of decrease in saturation magnetization. Therefore, the cationic substitutions are not a suitable way to alter the magnetic properties of barium hexaferrite. And then, people pay more attention to purity, grain size and morphology of the precursor powder [1,16]. In addition, in order to obtain the $BaFe_{12}O_{19}$ with fine grain and morphology of the precursor powder, many methods are suggested to produce barium hexaferrite, such as, conventional sinter route [1], sol–gel auto-combustion [17], chemical co-precipitation [18], salt-melt [19], low temperature combustion [20], mechanochemical processing [21], mechanical alloying [22], etc. In these methods procedure, the formation of barium hexaferrite all undergoes the intermediate phase. Whereas the intermediate phase transformation is often overlooked in the formation of barium hexaferrite process. In fact, the different intermediate phase transformation will have a great impact on the magnetic properties of barium hexaferrite during the formation of barium hexaferrite.

The conventional sinter method, mechanical alloy method and glycin–nitrate method are three common methods of preparing barium hexaferrite. In this work, the three methods are used to synthesize barium hexaferrite. The purpose is to reveal that the intermediate phase transformation of three kinds of procedures are different in the formation of barium hexaferrite process and the dif-

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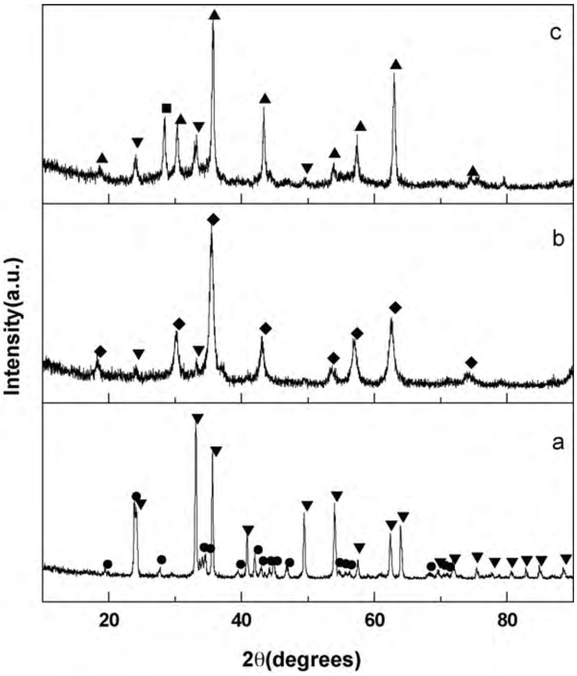

Fig. 1. XRD patterns for conventional route (a), 80 h high-energy ball-milled $BaCO_3 + 6F_2O_3$ (b) and glycin–nitrate method (c) powders: (▼) α-Fe_2O_3; (●) $BaCO_3$; (♦) $Ba_xFe_{3-x}O_4$; (■) $BaFe_2O_4$; (▲) Fe_3O_4.

ferent phase transformation have a great influence on the magnetic properties of barium hexaferrite in the aspects of physics method and chemical method, equilibrium condition and non-equilibrium condition.

2. Experimental procedures

A mixture of 99% pure nonmagnetic α-Fe_2O_3 and $BaCO_3$ powders were used as starting materials for production of $BaFe_{12}O_{19}$ by conventional sinter method and mechanochemical reaction in a high-energy ball milling. The molar ratio of α-Fe_2O_3 to $BaCO_3$ was 6:1 in the mixture. In the conventional sinter process, the mixture was sintered from room temperature to 1000 °C. In the mechanochemical reaction process, the mixture was milled in a mill firstly and annealed under ambient pressure in a temperature ranging from room temperature to 1000 °C. A stainless vial filled with stainless balls having diameter of 5–15 mm was used as the milling medium. The mass of the mixture was 7 g and the balls-to-powder mass ratio was 15:1. The mixture was milled under air ambient without any additives (dry milling). In the glycin–nitrate process, the starting materials used were 99% pure iron nitrate($Fe(NO_3)_3{\cdot}9H_2O$), barium nitrate($Ba(NO_3)_2$), glycin and distilled water. Appropriate amount of $Fe(NO_3)_3{\cdot}9H_2O$ and $Ba(NO_3)_2$, in a Fe/Ba molar ratio of 12 were dissolved in the required amount of distilled water. The molar ratio of glycin to total moles of nitrate ions was adjusted at 1.5:1. The precursor powders were annealed under ordinary pressure ambient in a temperature ranging from room temperature to 1000 °C. These samples were pressed into disk (under pressure of 0.2 GPa) and sintered for 2 h in air atmosphere in a temperature ranging from 700 to 1000 °C.

The structure of the samples was characterized by using a Rigaku-D-Max X-ray diffractometer (XRD) with CuKα radiation ($\lambda = 1.5418$ Å). The sintering shrinkage curve was measured using a Netzsch DIL 402C dilatometer, which was operated from room temperature to 1000 °C with an air purge flow rate of 60 ml/min. The thermal behaviors of the samples were examined by thermogravimetric and differential scanning calorimeter (TG/DTA, STA 449C, Netzsch) in a temperature ranging from room temperature up to 1000 °C with a heating rate of 10 °C/min. Raman spectra of the samples were recorded at room temperature, using a Renishaw inVia Raman spectrometer with a charge coupled device detector. An argon-ion laser (514.5 nm wavelength) was used as the excimer. The laser power operated on the sample was 20 mW. Measurement of magnetic properties were performed in a vibrating sample magnetometer (VSM) at room temperature with a maximum applied field of 1100 kA/m (Lake Shore 7410 vibrating sample magnetometer).

3. Results and discussion

Fig. 1(a) shows the XRD pattern of the mixture of α-Fe_2O_3 and $BaCO_3$ powders with molar ratio of 6:1, indicating that the mixture consists of α-Fe_2O_3 and $BaCO_3$ with rhombohedra and orthorhombic structure, respectively. Using the mixture as starting material, we try to fabricate barium hexaferrite ($BaFe_{12}O_{19}$) by conventional sinter method. In order to understand the mechanism of formation of the $BaFe_{12}O_{19}$, a sintering shrinkage curve for the cylinder of the mixture is measured in a temperature ranging from room temperature to 1000 °C, as shown in solid line in Fig. 2(a). In order to better understand the sintering reaction process of the mixture by the sintering shrinkage curve, the curve is differentiated, and the differential result is also shown by dot line in Fig. 2(a). As AB segment of the curve in Fig. 2(a) shows, the length variation fraction of the mixture ΔL ($\Delta L = (L - L_0)/L_0$, here L and L_0 are lengths of the cylinder of the mixture at a temperature (T) and room temperature (T_0), respectively) which increases linearly with increasing temperature in a temperature ranging from room temperature to 660 °C, because of the thermal expansion of the mixture. When the temperature exceeds 660 °C, the ΔL begins to decrease non-linearly till the temperature up to about 920 °C, as shown in BCD segment of the curve, implying that a chemical reaction may occur. This reaction is confirmed by thermal gravity measurement, as shown in Fig. 3(a). It can be seen from Fig. 3(a) that the mass of the mixture decreases slowly with increasing temperature between room temperature and 660 °C, but greatly in a temperature ranging from 660 to 920 °C. The former is due to the release of gas and vapor absorbed on the surface of the mixture, and the latter implies the release of some gas produced by some chemical reaction. Some literatures reported previously [23] that α-Fe_2O_3 reacts with $BaCO_3$ to form $BaFe_2O_4$ with orthorhombic structure as they are sintered above 600 °C in air ambient, accompanied by release of CO_2. The reaction can be expressed as follow:

$$BaCO_3 + Fe_2O_3 \rightarrow BaFe_2O_4 + CO_2\uparrow \tag{1}$$

Therefore, we deduce that the α-Fe_2O_3 reacts with $BaCO_3$ to form $BaFe_2O_4$ with orthorhombic structure as they are sintered above 660 °C.

In order to demonstrate this reaction, the mixture is sintered for 2 h at 700 °C in air ambient. Fig. 4(a) shows the XRD pattern of the sintered mixture. It is found that the intensity of diffraction peaks of $BaCO_3$ decreases greatly, meanwhile, some additional diffraction peaks are observed in the XRD profile besides the diffraction peaks of α-Fe_2O_3. These additional peaks are demonstrated to be the diffractions of $BaFe_2O_4$ with orthorhombic structure. This implies that the α-Fe_2O_3 reacts with $BaCO_3$ to form $BaFe_2O_4$ with orthorhombic structure as they are sintered at 700 °C in air ambient.

The dot line in Fig. 2(a) indicates the that variation rate of length variation fraction with temperature changing in BC segment is much smaller than that in CD segment, which implies that some additional chemical reaction may occur in CD segment besides the reaction between α-Fe_2O_3 and $BaCO_3$. In order to understand the additional reaction, the mixture is sintered for 2 h at 1000 °C, and measured by XRD, as shown in Fig. 5(a). In comparison with Fig. 4(a), the intensity of diffraction peak of the α-Fe_2O_3 decreases greatly and the diffraction peak of the $BaFe_2O_4$ is not almost observed in Fig. 5(a), meanwhile, the diffraction peaks of barium hexaferrite ($BaFe_{12}O_{19}$) are observed and become dominant, while the diffraction peaks of the α-Fe_2O_3 become very weak. The results of Fig. 4(a) and Fig. 5(a) indicate that the mixture sintered at 1000 °C mainly consists of $BaFe_{12}O_{19}$ and a small amount of α-Fe_2O_3. The $BaFe_{12}O_{19}$ is formed by following reaction process:

$$BaFe_2O_4 + 5Fe_2O_3 \rightarrow BaFe_{12}O_{19} \tag{2}$$

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