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Review

Formation and properties of $Ba_xFe_{3-x}O_4$ with spinel structure by mechanochemical reaction of α-Fe_2O_3 and $BaCO_3$

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ABSTRACT

Magnetic $Ba_xFe_{3-x}O_4$ ($x \sim 0.23$) with spinel structure was fabricated by ball milling of mixture of $BaCO_3$ and nonmagnetic α-Fe_2O_3 powders, and the molar ratio of $BaCO_3$ and α-Fe_2O_3 is 1:6. In the milling process, a mechanochemical reaction took place between $BaCO_3$ and α-Fe_2O_3, and Ba cation incorporated into α-Fe_2O_3 with rhombohedral structure to form a α-$(Fe,Ba)_2O_3$ solid solution. The Ba content in the α-$(Fe,Ba)_2O_3$ increased with increasing milling time, when the Ba content exceeded a limited solubility, the α-$(Fe,Ba)_2O_3$ transformed into a phase of $Ba_xFe_{3-x}O_4$ with spinel structure, where the Ba cation occupied an octahedral site or tetrahedral site. The product obtained in the balling process was different from that prepared in the annealing process at atmospheric pressure, which was $BaFe_2O_4$ with orthorhombic structure. Accompanying the crystal structure transition from α-$(Fe,Ba)_2O_3$ to $Ba_xFe_{3-x}O_4$, the magnetic properties also changed from nonmagnetism into ferromagnetism. The saturation magnetization was 53.3 emu/g and coercivity was 113.7 Oe. The mechanism of transitions of the crystal structure was discussed in the present work.

Contents

1. Introduction

The development of ferrite materials, such as, α-Fe_2O_3 (hematite), γ-Fe_2O_3 (maghemite) and Fe_3O_4 (magnetite), has attracted much attention of researchers for a long time, due to their important application in electrical and magnetic devices. Especially, Fe_3O_4 with spinel structure belongs to a kind of soft magnetic materials, and is widely used in radio frequency (RF) and microwave (MW), etc. devices. In the recent years, many attempts have been done to incorporate an element into ferrite to obtain a new kind of tri-element ferrites or improve properties of ferrites. For example, the spinel type $M_xFe_{3-x}O_4$ is of great value in the view of ferrofluid, magnetic drug delivery, magnetic recording media, etc. [1–3].

In order to improve physical and chemical properties of ferrite and fabricate of new ferrite, cation substitution in spinels may be at one or both cation sites, with magnetic or nonmagnetic ions with different valence [4]. Cations incorporated in spinel lattice change magnetic interactions and magnetic anisotropy, influencing the saturation magnetization and coercivity values of parent compounds [5] such as, Ni, Zn [6,7], Ho [8], Li [9], Mg [10,11] and so on. Ba element is recently considered as a good candidate for changing magnetic properties of ferrite recently, for example, it makes the soft magnetic or nonmagnetic ferrite change into hard magnetic barium ferrite.

It is well known that physical and chemical properties of a material depend on its crystal structure, which is usually influenced by

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the preparation methods and conditions. High-energy ball milling technique has attracted much attention in the materials science field. It has been used in the preparation of alloy, amorphous alloy, nanostructured materials and other new matters, and is considered as an effective technique to fabricate new kind of materials, especially those materials which cannot be produced in thermodynamic equilibrium state, such as non-miscible materials [12,13]. Recently, mechanochemical processing activated by high-energy ball milling has been successfully used to prepare high quality ferrite nanoparticles [14,15].

In the present work, the ball milling technique is used to prepare new kind of ferrite containing Ba, and a particular $Ba_xFe_{3-x}O_4$ with spinel structure is synthesized by using mechanochemical reaction of α-Fe_2O_3 and $BaCO_3$. Its formation mechanism and properties are discussed.

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 $Ba_xFe_{3-x}O_4$ by mechanochemical reaction in a high-energy ball mill. The molar ratio of α-Fe_2O_3 to $BaCO_3$ was 6:1 in the mixture. A stainless vial filled with stainless balls having diameter of 5–15 mm was used as the milling medium. The mass of the powder was 7 g and the balls-to-powder mass ratio was 15:1. The mixture was milled under air ambient without any additive (dry milling). In order to investigate the forming process of the $Ba_xFe_{3-x}O_4$, the mechanical milling was interrupted every 5 h to take a small amount of samples from the vial for various analyses. The mixture was also pressed into disk and sintered for 2 h in air atmosphere in a temperature ranging from 300 to 1000 °C to compare the reaction between α-Fe_2O_3 and $BaCO_3$ in the sintering process with that of in the ball milling process.

The structure of the samples were characterized by using a Rigaku-D-Max X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 Å). Composition of the sample was detected by energy dispersive X-ray spectroscopy (EDS) microanalysis equipped in a scanning electron microscopy (SEM) (JEOL JXA-8200) and X-ray photoelectron spectrometry (XPS) (Thermo ECSAlAB250) with Al Kα X-ray source. The binding energy scale was calibrated by C1s peak of 284.55 eV. Magnetic measurement was 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)–(d) shows XRD patterns of the mixture of the α-Fe_2O_3 (hematite) and $BaCO_3$ milled for 0, 10, 40 and 80 h, respectively. Fig. 1(a) indicates that the starting mixture consists of α-Fe_2O_3 and $BaCO_3$. Upon milling of 10 h, the diffraction peaks intensity of the $BaCO_3$ decrease greatly and the diffraction peak positions of α-Fe_2O_3 shift towards low diffraction angle, as shown in Fig. 1(b). Since atomic radius of Ba is larger than that of Fe, the decrease in diffraction angle is due to the fact that some Ba cations have substituted for Fe cations in the α-Fe_2O_3 to form α-$(Fe,Ba)_2O_3$ solid solution.

When extending milling time to 40 h, as Fig. 1(c) shows, two additional weak diffraction peaks, located at 29.98° and 42.82°, respectively, were observed besides diffraction peaks of α-$(Fe,Ba)_2O_3$ solid solution. The *d* values of the peaks at 29.98° and 42.82° are close to the *d* values of (2 2 0) and (4 0 0) plane of Fe_3O_4 with spinel structure, respectively. So, we deduced that some α-$(Fe,Ba)_2O_3$ transform into Ba-containing Fe_3O_4 solid solution.

Fig. 1(d) shows XRD pattern of the mixture milled for 80 h, indicating that the diffraction peaks of the α-$(Fe,Ba)_2O_3$ almost disappear, instead some strong diffraction peaks, located at 18.31°, 30.16°, 35.49°, 43.10°, 53.46°, 57.00°, 62.59° and 74.24°, respectively, appear. The *d* values of these peaks are close to that of Fe_3O_4 with spinel structure, and the ratio of square of reciprocal of the *d* values is 3:4:8:11:..., which is a characteristic of face-centered cubic structure, indicating that the phase related to these diffraction peaks is of spinel structure. Based on the discussion mentioned above, it is concluded that the most of α-$(Fe,Ba)_2O_3$ transform into of Ba–Fe–O phase with spinel structure (denoted as $Ba_xFe_{3-x}O_4$ in the following) upon milling of 80 h. Only a little of α-$(Fe,Ba)_2O_3$ remained.

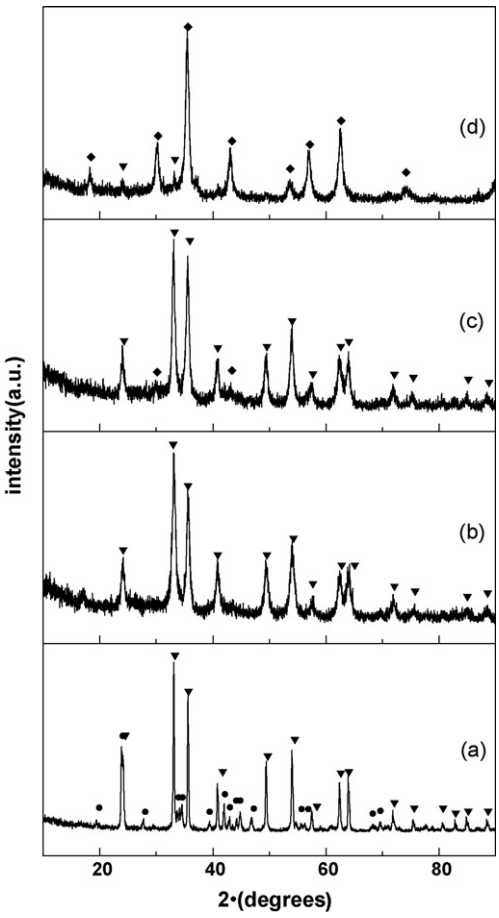

Fig. 1. XRD pattern of the mixture of α-Fe_2O_3 and $BaCO_3$ powder milled for 0 h (a), 10 h (b), 40 h (c), 80 h (d): (▼) α-Fe_2O_3; (●) $BaCO_3$; (♦) $Ba_xFe_{3-x}O_4$.

By using XRD results of Fig. 1, lattice constants of α-Fe_2O_3 as well as α-$(Fe,Ba)_2O_3$ and $Ba_xFe_{3-x}O_4$ prepared at various milling time are calculated, as shown in Fig. 2. It can be seen from Fig. 2 that the lattice constant of α-Fe_2O_3 in *a*-axis is *a* = 0.5038 nm and

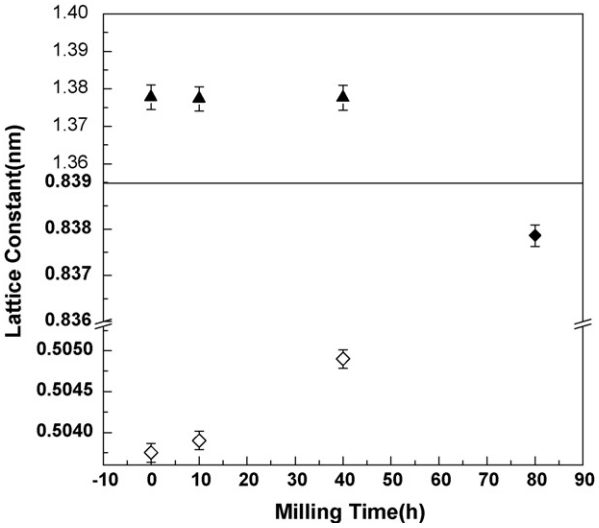

Fig. 2. Plot of lattice constant *a* (a) and *c* (b) of α-Fe_2O_3 milled for 0, 10 and 40 h and $Ba_xFe_{3-x}O_4$ (◊) lattice constant *a* of α-Fe_2O_3; (♦) lattice constant *a* of $Ba_xFe_{3-x}O_4$; (▲) lattice constant *c* of α-Fe_2O_3.