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Influence of stoichiometry on phase constitution, thermal behavior and magnetic properties of Ba-hexaferrite particles prepared via SHS route

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Abstract

Barium hexaferrite magnetic particles were synthesized via self-propagating high temperature synthesis (SHS) route by thermal initiation of compact mixed powders of iron, iron oxide and barium nitrate using various $Fe_{(total)}$/Ba molar ratios of 9–12. As-SHS treated and post synthesis specimens were characterized by X-ray powder diffraction, VSM, DTA/TGA and SEM. DTA/TGA studies revealed that the formation temperature of barium hexaferrite decreased by increasing of Fe/Ba molar ratio. VSM measurement also indicated that saturation magnetization (M_s) and coercivity (H_c) of the annealed specimens increased by increasing of Fe/Ba molar ratio. XRD results confirmed by those obtained from DTA/TGA and VSM, indicated that the Fe/Ba molar ratio of 12 is favorable for the formation of single-phase barium hexaferrite.

Keywords: Barium hexaferrite; Stoichiometry; Self-propagating high temperature synthesis (SHS); X-ray diffraction

1. Introduction

Barium and strontium hexaferrites have been intensively investigated due to their high uniaxial magnetic anisotropy and chemical stability. They can compete technically and economically with metallic permanent magnets [1]. Conventional mixed oxide ceramic method [2], mechanical alloying [3] and some chemical techniques, e.g. sol–gel combustion [4] hydrothermal [5], co-precipitation [6], glass crystallization [7] have been also used to produce hexaferrites. Self-propagating high temperature synthesis (SHS) which driven by an exothermic chemical reaction between reactant elements leading to provide sufficient energy for synthesis [8,9], is strongly employed for low-cost production of functional materials such as advanced ceramics, catalysts and intermetallics compounds [10,11]. Using of SHS method in synthesis of barium hexaferrite has been reported by few researchers by using iron, iron oxide and barium peroxide precursors [12,13]. In most synthesis methods, usually, without a certain barium surplus it is impossible to crystallize the hexaferrite without intermediate phases [14,15]. This certain excess barium is represented by stiochiometry factor or Fe/Ba molar ratio which is influenced significantly by preparation technique and also starting materials [16]. In the present paper, the influence of Fe/Ba molar ratio on phase constitution, magnetic properties and thermal behavior of barium hexaferrite magnetic particles synthesized by SHS technique from iron, iron oxide and barium nitrate precursors has been studied.

2. Experimental procedure

Fe (Merck, 99.5%), Fe_2O_3 (Merck, 99%) and $Ba(NO_3)_2$ (BDH, 99%) powders used as chemical precursors where ground and mixed in pestle and mortar at room temperature. The total Fe (comes from Fe_2O_3 and Fe) to Ba molar ratio was adjusted to 9–12. Fe/Fe_2O_3 molar ratio was fixed at 2 regarding the previous investigations [13,17]. SHS reactions were conducted by placing a hot wire on top of the 18 mm diameter and 15 mm height disks in air. As-SHS specimens were ground and annealed at 1050 and 1150 °C for 2 h in a resistant heating furnace with a heating rate of 10 °C/min in air. Phase composition of the specimens was studied by Philips PW3170 XRD using Cu Kα radiation. Differential thermal analysis and theromogravimetry analysis were employed to study thermal behavior of as-SHS specimens by Linseis L81 DTA/TGA with heating rate of 10 °C/min in air; pure alumina powder was used as the reference specimen. Magnetic properties of specimens were measured by vibrating sample magnetometer (VSM) at room temperature in the

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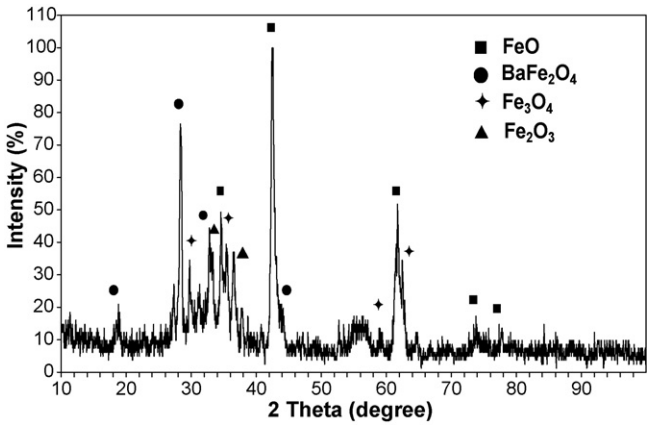

Fig. 1. XRD pattern of synthesized specimen with a Fe/Ba molar ratio of 11.

nobreak maximum magnetic field of 14 kOe. Philips XL 30 scanning electron microscopy was used to characterize the particles morphology.

3. Results and discussion

SHS reactions were thermally initiated produced a fast propagation wave resulting in a black product. Iron acts as a fuel and the exothermicity of its reaction with oxygen drives the synthesis in self-propagating mode. Iron oxide as another source of iron for formation of barium hexaferrite acts as a moderator [18]. Fig. 1 shows the X-ray powder diffraction pattern of synthesized specimen with a Fe/Ba molar ratio of 11. XRD patterns of synthesized specimens with various Fe/Ba molar ratios exhibit the same phase composition which indicates the co-existence of FeO, $BaFe_2O_4$, Fe_3O_4 and small amount of Fe_2O_3. This implies the fully decomposition of barium nitrate and completely formation of barium monoferrite during the synthesis process [19].

The existence of different iron oxides in as-SHS specimen has also been reported in synthesis of barium hexaferrite via SHS method by using of barium peroxide precursor [20]. The presence of barium monoferrite phase in as-SHS specimen is in conformity with literature, i.e. the formation of barium hexaferrite occurs usually by two step reactions in which barium monoferrite formation starts at temperature around 800 °C as an intermediate phase at first step [21], although some researchers reported the crystallization of barium hexaferrite without formation of barium monoferrite [22]. As shown in Fig. 2 there are some exothermic peaks above 800 °C in DTA/TGA traces of synthesized specimens.

The exothermic peak with slight weight change in DTA/TGA traces is correlated to gradual formation of barium hexaferrite which has been reported by other researchers [23]. It could be observed that the exothermic peak has shifted to lower temperatures with increasing the $Fe_{(total)}$/Ba molar ratio from 9 to 12. In other word, formation temperature of barium hexaferrite decreased from 828 °C in specimen with $Fe_{(total)}$/Ba molar ratio of 9 to 814 °C in specimen with $Fe_{(total)}$/Ba molar ratio of 12 which could be due to the faster rate of formation reaction of barium hexaferrite in higher $Fe_{(total)}$/Ba molar ratio. It may be explained by the reaction kinetics of barium hexaferrite formation. Barium hexaferrite formation is based on a diffusion process by a solid-state reaction [1], for this reason the smaller particle size can increase surface energy and also activity of particles which accelerates the diffusion rate and favors

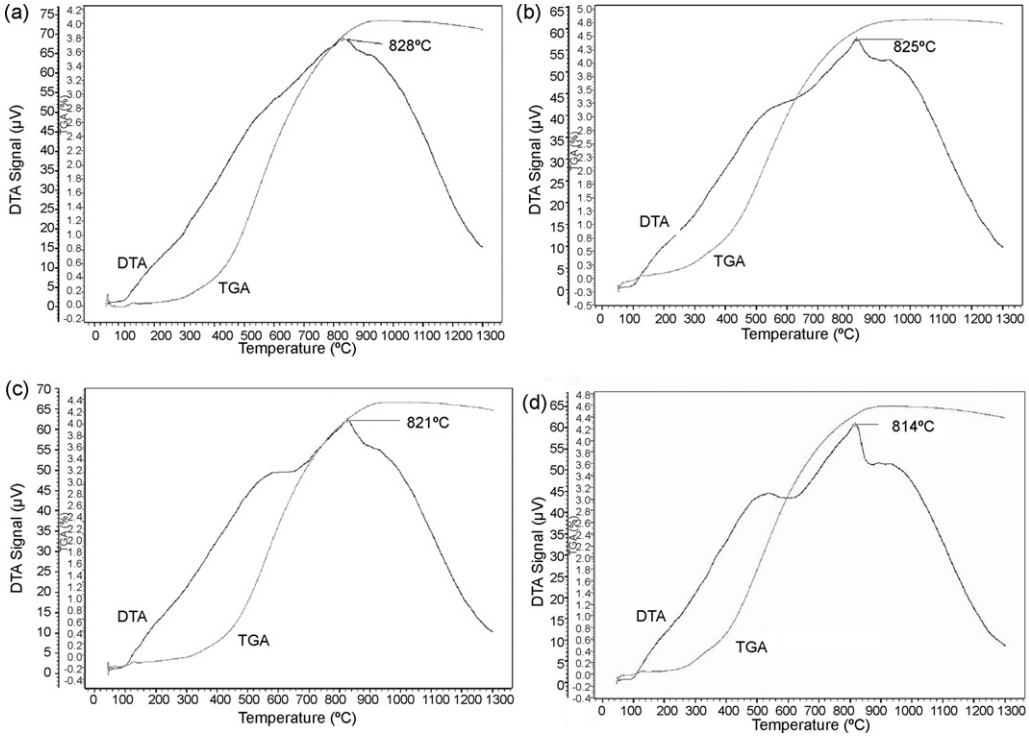

Fig. 2. DTA/TGA traces of synthesized specimens with different Fe/Ba molar ratios of (a) 9, (b) 10, (c) 11, and (d) 12.