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Intermediate milling energy optimization to enhance the characteristics of barium hexaferrite magnetic nanoparticles

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ABSTRACT

Nano-sized barium hexaferrite particles were synthesized by mechanical activation of $BaCO_3$ and Fe_2O_3 powders mixture as starting materials. The effects of mechanical milling energy on the phase composition, morphology, thermal behavior and magnetic properties of the samples were systematically investigated by employing X-ray diffractometer, field emission scanning electron microscopy, differential thermal/thermo gravimetry analysis and vibrating sample magnetometer, respectively. The milling energy was calculated at five different levels using collision model. It was found that there is an optimum milling energy value for obtaining barium hexaferrite phase. The results revealed that applying a minimum total milling energy of 93.7 kJ/g was necessary for formation of almost single barium hexaferrite at a relatively low calcination temperature of 800 °C. FESEM micrograph of the above sample exhibited nano-size particles with a mean particle size of 80 nm. Further increase in milling energy leads to dramatic decrease in phase purity as well as magnetic characteristics of the samples. By increasing the milling energy from 93.7 to 671.9 kJ/g, saturation magnetization (M_s) decreased from 22.5 to 0.39 emu/g, and also coercivity (H_c) decreased from 4.28 to 1.46 kOe.

1. Introduction

Barium hexaferrite ($BaFe_{12}O_{19}$) belongs to a hexagonal M-type magnetoplumbite $AFe_{12}O_{19}$ where A = Ba, Sr, Ca and Pb with easy magnetization along *c*-axis [1]. Moreover, it is a magnetic ceramic material which is widely used due to its superior properties such as low production cost, high Curie temperature, high coercivity, chemical stability and corrosion resistance [2]. $BaFe_{12}O_{19}$ has many applications in magnetic recording media, ferrofluids, sensors and microwave absorbing materials [2–4]. Ultra-fine particles of barium hexaferrite cannot be produced easily by the conventional mixed oxide ceramic method, which involves the calcination of a mixture of $BaCO_3$ and α-Fe_2O_3 at 1200 °C [5]. Many methods, including co-precipitation [6–8], sol–gel [9,10], hydrothermal [11], mechano-combustion [12] and mechanical milling [13,14] have been developed to produce ultra-fine particles of $BaFe_{12}O_{19}$. Among these methods, mechanical milling is a simple technique and economical one, since the starting materials are usually commercially available and inexpensive [15].

Mechanical milling has been known to activate the solid–solid and even solid–liquid chemical reactions during milling [16]. Additionally, the mechanical milling process can produce particulate powders with nanometer size [17,18]. Particle size reduction which increases the contact surface among particles is the direct consequence of milling. In addition, it increases the energy of the system resulting in a decrease in $BaFe_{12}O_{19}$ formation temperature. The most significant characteristic of this technique is that the reaction is activated by mechanical energy instead of heating energy that is required during the conventional solid-state reaction process [19].

The milling energy was calculated using collision model. According to Magini and Iasonna [20], collision is the predominant energy transfer phenomenon in a planetary ball mill. The way by which energy is transferred to the milled powder and consequently the nature of final products are significantly affected by the milling conditions [21,22]. In addition to the structural characteristics of a ball mill, milling speed, milling time, ball to powder mass ratio and calcination temperature highly influence the formation of $BaFe_{12}O_{19}$ nanoparticles.

In the present work, the effect of milling energy driven from mechanical milling, on $BaFe_{12}O_{19}$ formation temperature has been investigated. Also, the effects of milling energy on the phase composition, morphology and magnetic properties of the prepared powders are discussed. We found that there is an optimum amount of milling energy for obtaining barium hexaferrite nanoparticles with appropriate characteristics.

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2. Experimental

The starting materials of Fe_2O_3 (⩾99%, Merck) and $BaCO_3$ (⩾99%, Merck) powders were mixed in a Fe/Ba molar ratio of 11. It is noted that the stoichiometric molar ratio of Fe/Ba in barium hexaferrite ($BaFe_{12}O_{19}$) is 12, however using excess barium ions has been recommended in the previous works [4,23]. Mechanical activation was carried out at five different milling energy levels in a high-energy planetary ball mill with hardened steel vial and balls under air atmosphere. The processed samples were then calcined in air at 750, 800, 900 and 1000 °C for 1 h with a heating rate of 10 °C/min. The details of milling conditions are summarized in Table 1.

It has already been reported that overfilling of vial badly influences the milling process and also attributes to balls reciprocal hindering [22,24,25], thus the charging volume in this study was limited to 2/3rd of the volume of each vial. Phase composition of the samples were characterized by X-ray diffraction (XRD) on a Philips PW-1730 X-ray diffractometer using Cu Kα radiation (λ = 1.5405 Å) in the range of $20° \leqslant 2\theta \leqslant 70°$ and step size of 0.02°. The mean crystallite size of the samples was measured by X-ray line-broadening technique using Williamson–Hall formula [26]. The morphology of powders was examined by field emission scanning electron microscope (FESEM, TESCAN MIRA3). Thermal behavior of the samples were investigated by differential thermal analysis/thermo gravimetry analysis (DTA/TGA LINSEIS L70/2171) in air with the heating rate of 10 °C/min. Magnetic properties were measured by a vibrating sample magnetometer (VSM) under a maximum applied field of 10 kOe at ambient temperature.

3. Theory and calculation

To evaluate milling energy, the linear velocity of balls was calculated according to the procedure given by Burgio et al. [27]. Evaluating the effect of milling parameters on the $BaFe_{12}O_{19}$ formation, the total energy transferred during ball milling was calculated using collision model (see Table 2). All the milling parameters are accounted for determining two main energy parameters, i.e. the impact energy of each individual ball (E_b) and the total energy transferred (E_t) to the powders in a certain milling time [28]. The calculation of impact energy produced by each individual ball during the milling process was conducted earlier by Murty et al. [21]:

$$E_b = \frac{1}{2}(m_b V_b^2) \tag{1}$$

where m_b is the mass of one ball and V_b is the linear velocity of the ball. V_b can be calculated as below [28]:

$$V_b = \frac{2\pi}{60}\left[R_p^2\Omega^2 + (R_v - r_b)^2\omega^2\right]^{1/2} \tag{2}$$

where R_p, R_v and r_b are the radii of the plate, vial and ball, respectively. Besides, ω and Ω are the angular velocities of the vial and plate, respectively. In the situation where more than one ball is present in the vial, the energy of each ball can be gained from the equation below:

$$E_b' = \varphi_b E_b \tag{3}$$

where φ_b is the correlation factor for different degrees of filling of the vial [21,27]. E_t for a given time can be expressed as:

$$E_t = \frac{f E_b' n_b t}{w_p} \tag{4}$$

where t is the milling time in second, n_b is the number of balls and w_p is the weight of powders in each vial. The frequency of impact (f) according to Burgio et al. [27] is calculated through:

Table 1
Milling conditions of the samples.

Energy level	Milling time (h)	Milling speed (rpm)	BPR	Ball diameter (mm)
AR	Mixture of the as received materials			
L	10	200	8:1	10
M	30	300	20:1	10
H	50	400	35:1	10
UH	80	400	35:1	10

Table 2
Calculated impact energy of each ball (E_b) and the total energy transferred (E_t) in various energy levels.

Energy level	E_b (mJ/hit)	E_t (kJ/g)
L	18	6.1
M	40.4	93.7
H	72	419.9
UH	72	671.9

$$f = \frac{k(w_p - w_v)}{2\pi} \tag{5}$$

where k is the proportionality constant and approximately equal to 1, w_p is the angular velocity of the plate and w_v is the angular velocity of the vial.

The impact energy of each ball (E_b) and the total energy transferred (E_t) to the powder for all the milled samples are provided in Table 2.

4. Results and discussion

Fig. 1 shows the DTA/TGA traces for AR, M and UH samples. As indicated in Fig. 1a and b for AR and M samples, the endothermic peaks with weight loss of 1% appears at about 188 °C and 180 °C, respectively, which could be due to the loss of water from samples. The exothermic peak with a weight loss of 2.5% was observed in AR sample at about 908 °C which stands for the formation of $BaFe_{12}O_{19}$ phase, whilst this anomaly was seen at 788 °C with a weight loss of 1.5% in M sample. The exothermic peaks in both AR and M samples at temperatures below barium hexaferrite formation attribute to the formation of barium monoferrite ($BaFe_2O_4$) phase. The last exothermic peak in M sample at around 843 °C could be corresponded to the decomposition of barium hexaferrite according to the following reaction as noted by Kojima [29]:

$$BaFe_{12}O_{19} + BaFe_2O_4 \rightarrow 4Fe_2O_3 + Ba_2Fe_6O_{11} \tag{6}$$

The DTA/TGA analysis of UH sample shown in Fig. 1c indicates that the endothermic peak regarding the loss of water from sample is formed at around 184 °C with a ~2% weight loss. The peak in accordance with $BaFe_2O_4$ phase was not detected. Such phenomenon was reported earlier [30,31]. $BaFe_{12}O_{19}$ and $BaFe_2O_4$ are neighboring phases with a eutectic (1315 °C) in between [32]. During normal sintering processes, the intermediate phase of $BaFe_2O_4$ is formed due to the tendency to run in the direction of such eutectic. However when mechanical activation replaces such high temperature, the segregation of these two phases is reduced and $BaFe_{12}O_{19}$ phase can be obtained directly. Thus, the exothermic peak with a small weight loss of 1% at about 887 °C can be assigned for the formation of $BaFe_{12}O_{19}$. In comparison to the DTA/TGA trace for the AR sample, the formation temperature of $BaFe_{12}O_{19}$ was significantly decreased in M sample. Reduction of crystallite size and introduction of clean surfaces on particles could be responsible for decreasing barium hexaferrite formation temperature [8].

However, the higher formation temperature of $BaFe_{12}O_{19}$ in UH sample highly emphasizes that milling energy more than a critical value hinders barium hexaferrite formation. This can be due to (1) the introduction of impurities like iron and (2) elimination of some barium ions that both of them could alter the appropriate molar ratio of Fe/Ba affecting the formation kinetics of barium hexaferrite.

Fig. 2 depicts XRD patterns of the samples milled under five milling energy levels. The results showed the coexistence of $BaCO_3$ and α-Fe_2O_3 in the AR sample. However, one can see that