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Fabrication of nano-sized $Ba_xMg_{1-x}Fe_2O_4$ ferrite powders by using self-propagating high temperature synthesis reaction and mechanical milling

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ABSTRACT

Nano-sized $Ba_xMg_{1-x}Fe_2O_4$ ferrite particles less than about 150 nm were prepared by using self-propagating high temperature synthesis (SHS) and mechanical ball milling. As the ratio of BaO_2 to MgO in the initial powder composition varied from 0.25 to 4.0, coercive force (iHc) decreased about 102%, whereas, maximum magnetization (Ms) and residual magnetization (Mr) increased about 324% and 221%, respectively. Oxygen pressure changes from 0.25 to 1.0 MPa during SHS reaction resulted in decreasing iHc about 46%, whereas, increasing Ms and Mr about 59% and 4%, respectively. An empirical equation to describe the SHS reaction with oxygen pressure was obtained.

1. Introduction

Barium ferrites are especially useful for microwave and millimeter devices. The ferrites are conventionally prepared by various techniques of solid state chemistry of co-precipitation, precursor methods, freezing–drying and self-propagating temperature synthesis (SHS) to make various forms like polycrystalline, aggregates, thin and thick films and single crystal [1–5]. Ideal ferrite powders are small equiaxed particles with narrow size distribution of high purity and homogeneous composition [6]. A common problem in all these methods is the agglomeration of particles during precipitation or removal of the solvent [7]. One of the interesting characteristics of the SHS reaction is that the SHS products, especially which includes gas–solid reaction, are so porous as to be well pulverized by mechanical milling. Accordingly, in this study, the SHS reaction for the formation of Ba–Mg ferrites is selected as the chemical reaction expressed as $x\mathrm{BaO_2} + (1-x)\mathrm{MgO} + y\mathrm{Fe} + z\mathrm{Fe_2O_3} + w\mathrm{PO_2} = \mathrm{Ba}_x\mathrm{Mg}_{1-x}\mathrm{Fe_2O_4}$ which is known as a gas–solid reaction in which iron is oxidized and releases a weak heat of formation. Since the chemical reaction includes oxidation of iron and reduction of oxide phases, the oxygen partial pressure and the initial composition ratio are important to produce barium–magnesium ferrites. Although there have been many attempts to obtain various ferrites, little information about ferrites formed by using SHS is available, especially about nano-sized ferrites [8–10]. Hence, the objectives of this study were to fabricate nano-sized barium–magnesium ferrite particles by using SHS followed by mechanical milling and to characterize the materials. Emphases are on the effects of initial composition of the SHS reactant and oxygen pressure during the SHS reaction on the magnetic properties of the nano-sized barium–magnesium ferrite particles formed by using SHS reaction and mechanical milling.

2. Experimental method

Reagent grade iron powders with about 6 μm of average particle size and various size of barium peroxide (BaO_2, <150 μm), magnesium oxide (MgO, <120 μm) and iron oxide (Fe_2O_3, <1 μm) powders were used as starting materials. Each powder mixture with a suitable molar composition was mechanically blended by using a ball-mill (SPEX 8000) for 5 min with two steel balls. The powder process was carried out in a glove box to minimize exposure. The reactant powders were ignited with various oxygen pressures of 0.25–1.0 MPa in an autoclave type SHS chamber [11]. The combustion temperature and the propagating rate were determined by using a two-thermocouple method. The phase of the SHS product was analyzed by using X-ray diffractometry (MXP3A-HF2000) with copper target ($\lambda = 0.15405$ nm). Mechanical milling of the SHS products was carried out with a ball-mill (SPEX 8000). The morphology of the SHS product was observed by using field emission scanning electron microscopy (FESEM, JSM Joel 6400). The magnetic properties were determined with a vibrating sample magnetometer (Toei VSH-5).

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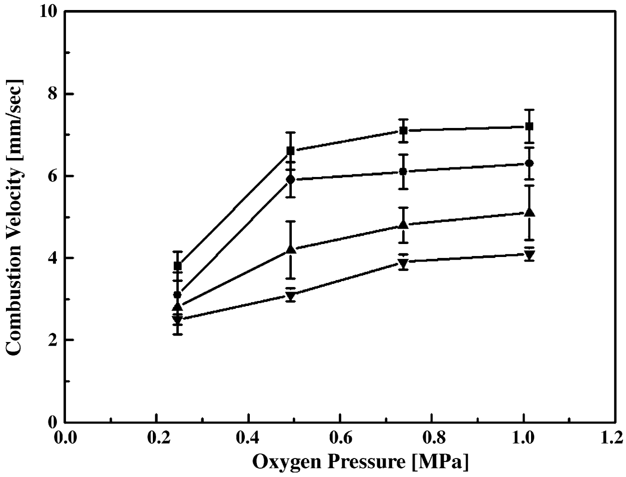

Fig. 1. Effect of the oxygen partial pressure on the average combustion velocity of the SHS reactants with different BaO_2/MgO molar ratios: (■) 0.25, (⧫) 0.75, (▲) 1.0, and (▼) 4.0.

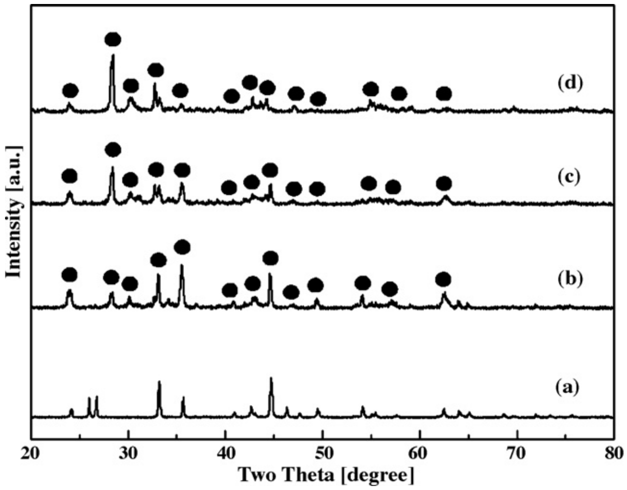

Fig. 3. Typical X-ray spectra of $Ba_xMg_{1-x}Fe_2O_4$ prepared by SHS with different BaO_2/MgO molar ratio: (a) reactant, (b) 0.25, (c) 1.0, (d) 4.0, and (●) $Ba_xMg_{1-x}Fe_2O_4$ peaks.

3. Results and discussion

The SHS reaction for each powder mixture occurred well with oxygen pressures of 0.25–1.0 MPa. Figs. 1 and 2 are the combustion temperature and the average combustion velocity with oxygen pressure. As Figs. 1 and 2 show, the combustion temperatures and the combustion velocity are in the ranges of 605–1148 K and 3.8–6.3 mm/s, respectively. Both of them tend to be increased with increasing molar ratio of magnesium oxide to barium peroxide in the reactant powder mixtures, and oxygen partial pressure during the SHS reaction. This means that the SHS reaction is competitive reaction between oxidation and reduction reactions. The dependence of combustion velocity on combustion temperature (T_c) of the porous samples with oxygen partial pressure (PO_2) is given as: rate = $A\exp(\theta/(1+\beta\theta))\xi(P)$ where ($\beta = RT/E$, $\theta = (T_c - T)E/RT^2$, $\xi(P) = PO_2/P$, E = activation energy, T = temperature and R = gas constant) [12]. The model assumes a steady state adiabatic heat transfer condition in a one-dimensional homogeneous media, diffusion kinetics to describe the reaction kinetics, and independence of thermodynamical parameters on temperature. The dependence of the combustion rate and temperature on oxygen pressure can be described with a similar empirical equation. Combining a polynomial equation to describe the relation between oxygen pressure and combustion temperature in Fig. 1 and the exponential equation to describe the relation between oxygen pressure and combustion rate in Fig. 2, we can obtain an empirical rate equation to describe the Ba–Mg ferrite powder formation during the combustion reaction below an adiabatic temperature as follows: $\nu = A\exp(T_c/B - 1)$, where the pre-exponential term (A), constant (B) and the power of the oxygen pressure (n) were determined as average values from the best fit results. A, B and n were 6.3, 1347 and 0.3, respectively. Although the empirical equation cannot clearly describe composition dependence separately, the empirical equation indicates that the combustion velocity is dependent simultaneously upon the combustion temperature and oxygen pressure.

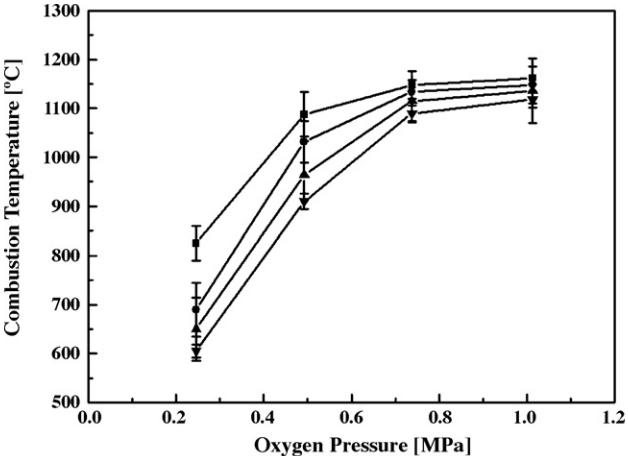

Fig. 2. Effect of the oxygen partial pressure on the combustion temperature of the SHS reactants with different BaO_2/MgO molar ratio: (■) 0.25, (⧫) 0.75, (▲) 1.0, and (▼) 4.0.

Fig. 3 is the typical X-ray spectra of $Ba_xMg_{1-x}Fe_2O_4$ prepared at the oxygen pressure of 0.25. Barium–magnesium ferrites phase was clearly observed in the X-ray diffraction spectra of the SHS products. The variations of the combustion temperature and the combustion velocity with the reactant composition and oxygen pressures are related to the on-going combustion reaction mechanisms. Since the

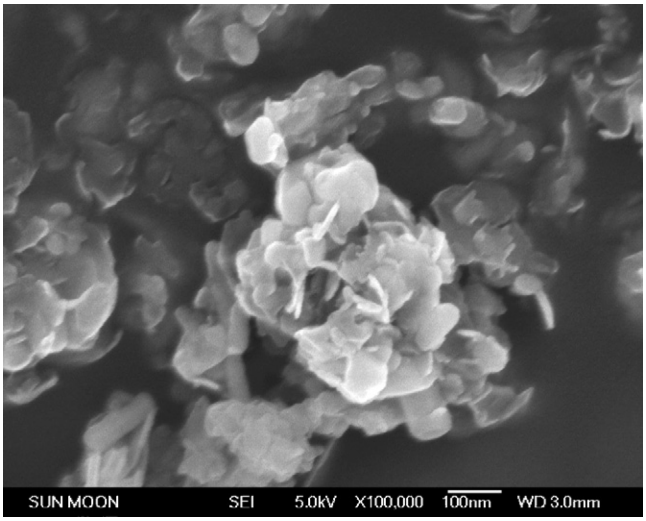

Fig. 4. Typical morphology of nano-sized $Ba_xMg_{1-x}Fe_2O_4$ ferrite particles observed by using FESEM.

Table 1
Magnetic properties of barium–magnesium ferrites with the initial composition ratio of barium peroxide to magnesium oxide and oxygen partial pressure during SHS reaction.

Sample #	BaO_2/MgO	PO_2 (MPa)	Maximum magnetization, Ms ($A\,m^2/kg$)	Residual magnetization, Mr ($A\,m^2/kg$)	Coercive force, iHc (kA/m)
BM-1-1	4	1.0	31.17	5.37	12.87
BM-1-2	1	1.0	23.09	5.20	25.50
BM-1-3	1	0.25	14.48	5.02	37.16
BM-1-4	0.25	1.0	7.34	1.67	25.99

ferrite formation reaction involves the oxidation of iron and the reduction of oxides, such as barium peroxide, magnesium oxide and iron oxide, retardation of the combustion reaction at a low molar ratio of barium peroxide to magnesium oxide accounts for the heat-loss during the reduction reaction at the combustion front. It means that the heat-loss is larger at barium peroxide than at magnesium oxide. These observations also support the combustion reaction is a self-propagating process with the aid of exothermic heat released during the oxidation of iron [13].

Fig. 4 is the typical morphology of a product observed by using field emission scanning electron microscopy. The powder sample was prepared by a ball-milling of the SHS products for 5 min. As Fig. 4 shows, the SHS products were agglomerated-powders in which nano-sized particles were present. The particle size of the pulverized-powders obtained was approximately less than about 150 nm.

Figs. 5 and 6 present typical magnetization curve of nano-sized Ba–Mg ferrites for the same initial molar ratio of barium peroxide and magnesium oxide of 1.0 with different oxygen pressure during the SHS reaction and the initial composition, respectively. As Figs. 5 and 6 show, the maximum magnetization (Ms), the residual magnetization (Mr) and the coercive force (iHc) of the nano-sized barium–magnesium ferrite particles formed by using SHS significantly depended on the oxygen partial pressure during SHS reaction and initial molar ratio of barium peroxide and magnesium oxide in the SHS reactant powder mixtures. Soft magnetic properties were improved by increasing oxygen pressure during the SHS reaction. The maximum magnetization tended to be increased as increasing barium peroxide content.

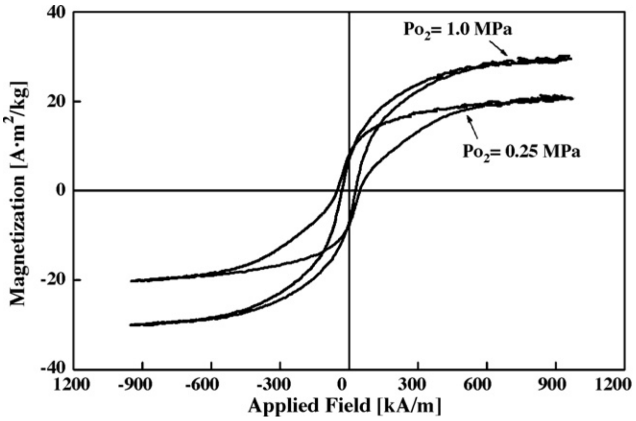

Fig. 5. Typical magnetization curves of $Ba_xMg_{1-x}Fe_2O_4$ ferrite prepared by using SHS reaction at various oxygen pressures.

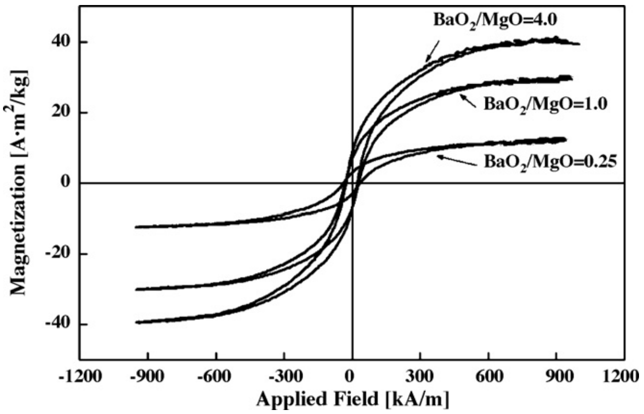

Fig. 6. Typical magnetization curves of $Ba_xMg_{1-x}Fe_2O_4$ ferrite prepared by using SHS reaction with different barium peroxide and magnesium oxide ratio.

Table 1 summarizes the magnetic properties for the samples, as determined with a vibrating sample magnetometer. As Table 1 shows, Ms, Mr and iHc of the quasi-nano-sized barium–magnesium ferrite particles formed by using SHS significantly depended on the initial composition and oxygen partial pressure during SHS reaction. The Ms, Mr and iHc of the quasi-nano-sized barium–magnesium ferrite particles formed by SHS at 1.0 MPa of oxygen partial pressure are 31.17 $A\,m^2/kg$, 5.37 $A\,m^2/kg$ and 12.87 kA/m for 4.0 of the initial molar ratio of barium peroxide to magnesium oxide, 23.09 $A\,m^2/kg$, 5.20 $A\,m^2/kg$ and 25.50 kA/m for 1.0 of the initial molar ratio of barium peroxide to magnesium oxide, and 7.34 $A\,m^2/kg$, 1.67 $A\,m^2/kg$ and 25.99 kA/m for 0.25 of the initial molar ratio of barium peroxide to magnesium oxide, respectively. As oxygen pressure during the SHS reaction decreased from 1.0 to 0.25 MPa, the values changed from 23.09 to 14.48 $A\,m^2/kg$, 5.20–5.02 $A\,m^2/kg$ and 25.5–37.16 kA/m, respectively. Although the magnetic properties of the ferrite powders depended on the microstructure and the measured parameters such as the particle size, the porosity, and the magnetizing frequency, the magnetic properties of the nano-sized barium–magnesium ferrite particles prepared by using SHS shows slightly higher values than the sintered magnesium ferrite and lower values than sintered barium ferrite powders [10,14]. The iHc of the nano-sized barium–magnesium ferrite particles shows lower value for the ferrite prepared by co-precipitation method and thin film process [15,16]. The value can be further improved by reducing pore, cracks, local grain boundary and improving the *c*-axis orientation of grains in polycrystalline ferrite. Hence, the barium–magnesium ferrite prepared by using SHS reaction followed by a mechanical milling is cost effective in mass-production of future microwave devices.

4. Conclusions

Nano-sized barium–magnesium ferrite powders were prepared by self-propagating high temperature reaction with various oxygen pressures and mechanical milling and the following conclusions were drawn:

(1) The combustion temperature and the combustion velocity are in the ranges of 605–1148 K and 3.6–6.3 mm/s, respectively, which tend to be increased with increasing initial molar ratio of magnesium oxide to barium peroxide and oxygen partial pressure during the SHS reaction.
(2) The SHS products are mainly barium–magnesium ferrites. They are agglomerated-powders in which nano-sized particles with less than 150 nm exist.

(3) As the molar ratio of barium peroxide to magnesium oxide decreases and the oxygen pressure during SHS reaction increases, the maximum magnetization, the residual magnetization increase and the coercive force decreases, respectively.
(4) In the view of the improved magnetic properties and productivity, the fabrication of the Ba–Mg ferrites by using self-propagating high temperature synthesis at a high oxygen pressure followed by mechanical milling is one of useful methods for mass-production.

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