Journal of Alloys and Compounds 583 (2014) 145–150

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Barium hexaferrite nanoparticles with high magnetic properties by salt-assisted ultrasonic spray pyrolysis

Guk-Hwan An [a], Tae-Yeon Hwang [a], Jongryoul Kim [b], JinBae Kim [c], Namseok Kang [c], Seil Kim [a], Yo-Min Choi [a], Yong-Ho Choa [a,*]

[a] Department of Fine/Fusion Chemical Engineering, Hanyang University, Ansan 426-791, South Korea
[b] Department of Metallurgy and Materials Engineering, Hanyang University, Ansan 426-791, South Korea
[c] Advanced Research Institute, LG Electronics Inc., Seoul 137-724, South Korea

ARTICLE INFO

Article history:
Received 24 July 2013
Received in revised form 14 August 2013
Accepted 14 August 2013
Available online 3 September 2013

Keywords:
Barium hexaferrite
High coercivity
Non-agglomerate
Ultrasonic spray pyrolysis
Molten salt

ABSTRACT

Herein, we synthesized non-agglomerated barium hexaferrite nanoparticles by salt-assisted ultrasonic spray pyrolysis at different reaction temperatures. NaCl was used as an added salt, melted at 850, 900, and 950 °C to act as a solvent in the reaction processes. It was found that at 950 °C, the salt melted sufficiently and therefore accelerated the subsequent nucleation and growth of barium hexaferrite nanoparticles. The barium hexaferrite nanoparticles synthesized by the salt-assisted ultrasonic spray pyrolysis method were exquisitely compared with the barium hexaferrite synthesized by conventional ultrasonic spray pyrolysis method. The particles were characterized by XRD, SEM, and TEM analyses. The salt-free barium hexaferrite obtained at 950 °C revealed the presence of hematite, whereas the salt-added barium hexaferrite nanoparticles synthesized at 950 °C showed the existence of only barium hexaferrite phase. The salt-added barium hexaferrite nanoparticles synthesized at 950 °C showed a hexagonal plate shape, 72 nm in size and with good crystallinity. The magnetic properties were investigated by vibrating sample magnetometer (VSM) at room temperature. The magnetic properties of the salt added barium hexaferrite at 950 °C showed the coercivity of 5735 Oe and saturation magnetization of 63.2 emu/g.

1. Introduction

Since hexagonal ferrites were discovered in the 1950s, there has been a great demand and interests due to their suitable applications such as permanent magnet, magnetic recording, data storage devices, and components in the electrical industry [1]. Among of hexagonal ferrites, the M-type barium hexaferrite (BaM, $BaFe_{12}O_{19}$) has been widely investigated because of its excellent properties such as high Curie temperature, good chemical stability, corrosion resistance, and large coercivity [2]. For instance, BaM to be used as permanent magnet requires improved magnetic properties (large saturation magnetization and coercivity) to enhance their industrial performance.

In order to achieve these appreciable properties, the size and the crystallography have been investigated [3]. Various synthetic methods such as solid state calcination [4–6], reverse micro emulsion method [7], citrate process [8], sol–gel combustion [9], spray pyrolysis [10–12], and molten salt synthesis [4,13] have been used to control the properties of these magnetic materials. It is well known that the coercivity increases when size of the magnetic particles decreases to a nanoscale [1]. However, the conventional solid state calcination cannot easily synthesize the nanoscale magnetic particles. The solution based method such as reverse micro emulsion, citrate process, and sol–gel combustion can be used to obtain nanoscale magnetic particles. However complicated steps must be accomplished and unfortunate grain growth and necking of particle can usually occur during the calcination step. The molten salt synthesis that involves introduction of metal salt such as NaCl, KCl, LiCl, Na_2SO_4, and K_2SO_4 , in the calcination step has been adopted [1,4,13]. This method can obtain hexagonal plate shape and submicron sized single domain particle but it also has complex steps because it is established by conventional methods. In case of spray pyrolysis, a nanoscale particle can be yielded and it is considerably a simple but produces hard agglomerated particles necked with each other.

To overcome these problems, we adopt salt-assisted ultrasonic spray pyrolysis (SA-USP). It is based on the spray pyrolysis using ultrasonic atomizer and addition of a salt in the precursor solution. This method has been adopted to make ceramic nanoparticles with various advantages such as non-agglomeration, single crystalline, high crystallinity and short reaction time [14,15]. Furthermore, to the best of our knowledge, this is the first time to apply this technique in the synthesis of the hexagonal ferrites. In this study, we

* Corresponding author. Tel.: +82 31 400 5650; fax: +82 31 418 6490.
E-mail address: choa15@hanyang.ac.kr (Y.-H. Choa).

0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2013.08.105

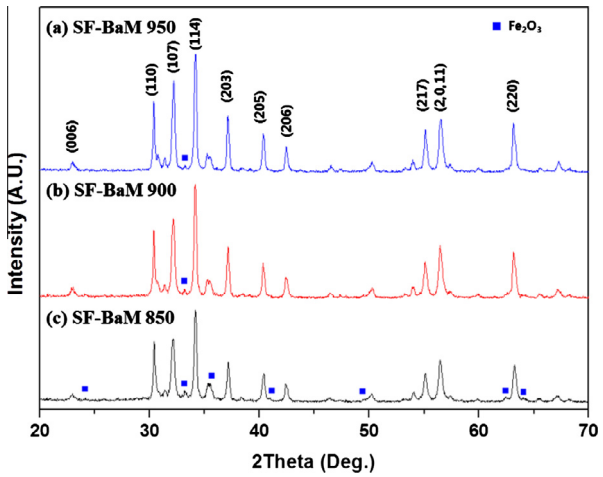

Fig. 1. XRD patterns of barium hexaferrite without salts synthesized by USP method at different temperature: (a) SF-BaM 950, (b) SF-BaM 900, and (c) SF-BaM 850.

Table 1
Crystallite size and weight ratio of barium hexaferrites from analyzing XRD patterns.

	Crystallite size (nm), calculated with (200)	Weight ratio (%)	
		BaM	Fe_2O_3
SF-BaM 950	42.2	98.3	1.7
SF-BaM 900	39.6	96.4	3.6
SF-BaM 850	29.0	92.2	7.8
SA-BaM 950	44.2	100	0
SA-BaM 900	43.4	97.8	2.2
SA-BaM 850	35.5	88.7	11.3

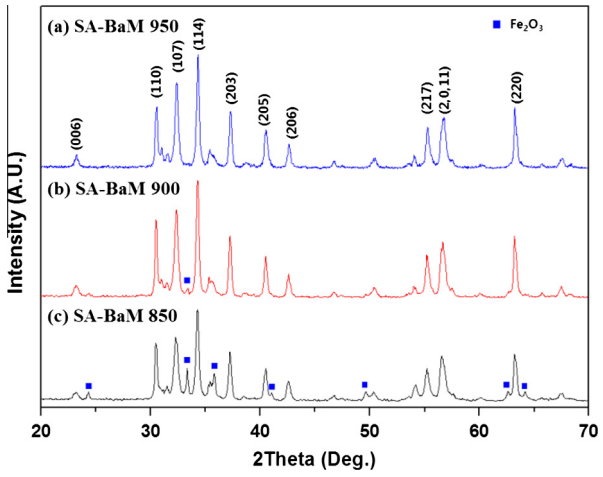

Fig. 2. XRD patterns of barium hexaferrite synthesized by salt assisted USP method at different temperature: (a) SA-BaM 950, (b) SA-BaM 900, and (c) SA-BaM 850.

discussed the characters of both particles synthesized at the USP and SA-USP processes, and the effect of salt addition on the growth of hexaferrite particles. Finally, the magnetic properties were also investigated and discussed in terms of size and crystallinity of the produced nanoparticle.

2. Experimental procedure

The barium-hexaferrites (BaM, $BaFe_{12}O_{19}$) were prepared using the ultrasonic spray pyrolysis method as follows. Precursor solutions were prepared for two-types of solution that were classified with presence or absence of sodium chloride. The

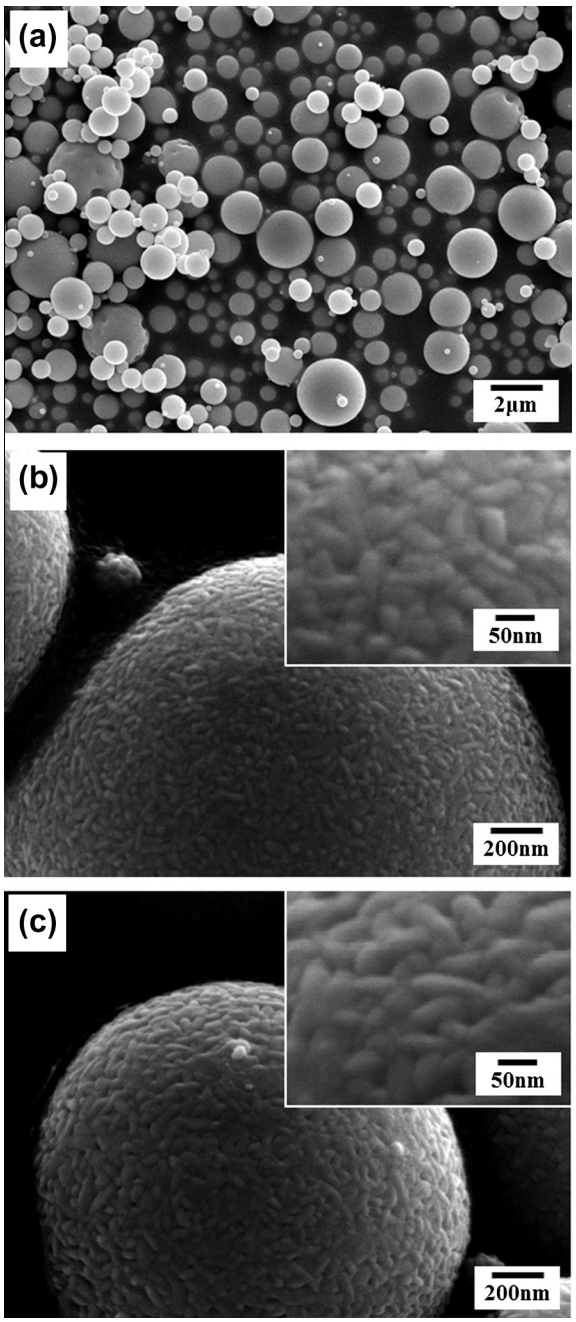

Fig. 3. SEM images of barium hexaferrites synthesized by USP method at different temperature: (a) SF-BaM 850 with low magnification, (b) SF-BaM 850 with high magnification, and (c) SF-BaM 950 with high magnification.

precursor was prepared by dissolving 60 mmol of iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, 99.9%, Kojundo, Saitama, Japan), 5 mmol of barium nitrate ($Ba(NO_3)_2$, 99%up, Kojundo) and 190 mmol of sodium chloride (NaCl, 99%, Samchun, Pyeongtaek, South Korea) in 200 mL of distilled water. Another experiment was performed using the same precursors excluding NaCl to obtain a salt-free BaM. The precursor solution was atomized at a frequency of 1.7 MHz using an ultrasonic atomizer. The atomized droplets were transferred to a tubular furnace by O_2 as a carrier gas. A flow rate of carrier gas was 1 L/min and the tube in the furnace was 30 mm in diameter and 500 mm long. The heating stage was performed in both the inlet side and outlet side. The droplet induced in the tube furnace was dried at the inlet side and pyrolyzed at the outlet side. Each stage was controlled independently. The temperatures of the outlet stage were controlled at 850, 900, and 950 °C while the inlet stage was maintained at 300 °C. The reaction time (passing the droplet through the heating stage) was only about 20 s. The product moved out from the furnace was immediately trapped in a filter paper using a vacuum pump. The salt-assisted barium-hexaferrite (SA-BaM) was dispersed through sonication, washed with distilled water several times and dried at a temperature of 80 °C for 24 h. The salt-free barium-hexaferrite (SF-BaM) was characterized at once without a washing process. The