Journal of Alloys and Compounds 583 (2014) 220–225

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Synthesis of barium ferrite ultrafine powders by a sol–gel combustion method using glycine gels

Y.Y. Meng [a], M.H. He [a], Q. Zeng [a], D.L. Jiao [a], S. Shukla [b], R.V. Ramanujan [b], Z.W. Liu [a,*]

[a] School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, PR China
[b] School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

ARTICLE INFO

Article history:
Received 1 August 2013
Accepted 24 August 2013
Available online 5 September 2013

Keywords:
Barium ferrite
Ultrafine powders
Sol–gel combustion technique
Glycine

ABSTRACT

The ultrafine powders of barium ferrite ($BaFe_{12}O_{19}$) were synthesized by a sol–gel combustion technique using glycine gels prepared from metal nitrates and glycine solutions. The effects of processing parameters such as initial Fe/Ba molar ratio, the dosage of glycine and calcination temperature on the crystalline phase formation, microstructure and magnetic properties were systematically investigated. The results showed that the formation of single-phase barium ferrite is significantly influenced by Fe/Ba molar ratio which is the optimum at 9/1. The XRD patterns revealed that high calcination temperature and large glycine dosage are beneficial for the formation of barium ferrite. The TEM and size distribution demonstrated that the $BaFe_{12}O_{19}$ powders have plate-like shape with crystallite size varied from 55 to 110 nm. The products with high coercive force of 5750 Oe and saturation magnetization of 67.7 emu/g were obtained when the glycine/nitrates molar ratio and calcination temperature are 12/9 and 900 °C, respectively.

1. Introduction

As one of the important classes of permanent magnetic materials, barium ferrites ($BaFe_{12}O_{19}$) have relatively large saturation magnetization (Ms), high coercive force (Hc) and high magnetic anisotropy field (H_A) as well as excellent chemical stability and corrosion resistivity [1]. Apart from traditional applications in permanent magnets, ultrafine barium ferrite powders with narrow particle size distribution are suitable for perpendicular high density recording media because they are desirable for increasing the capacity of information storage and reducing the medium noise [2,3].

As we know, the classical ceramic method for producing barium ferrites involves high temperature solid-state reactions between the constituent oxides and carbonates [4,5]. The disadvantages of this conventional method also include rather large and non-uniform particle size and introduction of the impurities, which restrict further improvement in the performance of the products [6]. In order to overcome these difficulties and to meet the requirements for new applications, various wet-chemical processes like sol–gel citrate [7–9], hydrothermal method [10,11], micro-emulsion process [12], co-precipitation technique [13,14], glass crystallization [15], and plasma spraying [16] have been considered for production of barium ferrite ultrafine powders with excellent magnetic properties. The use of sol–gel combustion process to synthesize homogeneous, ultrafine and reproducible barium ferrites with narrow size distribution at a relatively low calcination temperature appears to have attracted much attention in recent years [17–19]. For instance, Mali et al. [20] employed a sol–gel combustion route to synthesize nanosized barium ferrites using a nitrate-citrate gel. Shang et al. [21] also reported that barium ferrite nanoparticles with excellent magnetic properties have been prepared based on sol–gel combustion method using glucose as a fuel.

In our work, barium ferrites with excellent magnetic properties were prepared by a sol–gel combustion technique using a glycine gel. This technique has shown promising prospect due to its inexpensive precursors, easy operation, controllable conditions and ultrafine size of the obtained products. Also, use of glycine for fuel instead of conventional citric acid and urea can decrease the ignition temperature of combustion and save a quantity of external energy.

2. Experimental

As starting materials, appropriate amount of $Fe(NO_3)_3{\cdot}9H_2O$ and $Ba(NO_3)_2$ were dissolved in the 100 ml distilled water to form a clear aqueous solution. A proper amount of glycine was added into the solution to chelate Ba^{2+} and Fe^{3+}. All the materials which were purchased from Fuchen Company had an analytical purity and were used without further purification. The mixture solution was evaporated to dryness by heating on a hot plate with continuous magnetic stirring. As water evaporated, the solution became viscous and finally formed a very viscous brown dried gel. Subsequently, they were immediately transferred to a furnace with the temperature at 220 °C. The freshly obtained brown gels were auto-ignited after

---

* Corresponding author. Tel.: +86 2022236906.
E-mail address: zwliu@scut.edu.cn (Z.W. Liu).

0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2013.08.156

several minutes in the furnace and automatically burnt out within 1 min with lots of smelling gas out. Finally, the auto-combustion powders were calcined in air at different temperatures of 700–1000 °C to obtain the desired product.

The phase structures for all samples were determined by X-ray diffraction (XRD, Philips X Pert) with Cu Kα radiation (wavelength $\lambda = 0.15405$ nm) at room temperature. The surface morphology of the powders was examined by scanning electron microscope (SEM) (Nova NanoSEM 430), transmission electron microscope (TEM) (Philips F20) and high resolution TEM (HRTEM, Joel 3100). The size of the products was characterized by laser particle size analyzer. The thermal behavior of the gel and the burnt precursor was studied by thermo gravimetric analysis (TG) and differential scanning calorimeter (DSC) with the heating rate of 10 °C/min on the NETZSCH STA449 C instrument. The absorption vibrations of the samples were performed by a Fourier transformed infrared (FTIR) spectrometer (Vector 33) from 4000 to 400 cm^{-1} by the KBr pellet method. All the magnetic properties of the particles were measured at room temperature by physical properties measurement system (PPMS) equipped with a high accuracy vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. Effect of Fe/Ba molar ratio on the phase composition and magnetic properties

The process for preparing $BaFe_{12}O_{19}$ ultrafine powders was systematically studied. Fig. 1 shows the XRD patterns for powders calcined at 900 °C for 2 h with fixed glycine/nitrates molar ratio of 10/9 and the varied initial Fe/Ba molar ratio of 8, 9, 10, and 11. The results reveal that single barium ferrite ($BaFe_{12}O_{19}$) phase can be obtained with the initial Fe/Ba molar ratio of 9. There is minor barium monoferrites ($BaFe_2O_4$) coexisting with barium ferrites phase when the initial Fe/Ba molar ratio is 8. Apart from $BaFe_{12}O_{19}$ phase, $BaFe_2O_4$ and α-Fe_2O_3 peaks were also detected after increasing Fe/Ba molar ratio to 10 and 11. The presence of $BaFe_2O_4$ phase in the obtained powders for Fe/Ba molar ratio of 8 can be explained that there are not enough Fe^{3+} ions to form $BaFe_{12}O_{19}$ phase completely, which means Ba^{2+} ions are excessive. The $BaFe_2O_4$ peaks gradually disappeared with increasing Fe/Ba molar ratio until the value of 9. However, continuously increasing Fe^{3+} ions can reproduce $BaFe_2O_4$ as well as α-Fe_2O_3 phase rather than form $BaFe_{12}O_{19}$ hexagonal structure. This phenomenon could be attributed to the fact that the appearance of α-Fe_2O_3 with orthorhombic hexahedron structure prevent the formation of $BaFe_{12}O_{19}$ hexagonal structure at a low temperature [6]. Several papers have reported that an iron deficient non-stoichiometric mixture with moderate excess of barium is needed to form the single-phase $BaFe_{12}O_{19}$ due to the various solubility of the Fe^{3+} and Ba^{2+} in aqueous media [1,22]. In our work, Fe/Ba molar ratio of 9 is desirable to prepare single barium ferrite crystalline which is in disagreement with other reports [23,24].

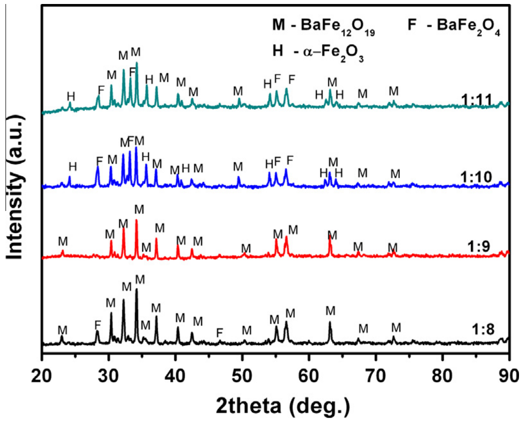

Fig. 1. XRD patterns for the powders calcined at 900 °C for 2 h with glycine nitrates molar ratio of 10/9 and various initial FeBa molar ratios of 8, 9, 10, and 11.

The variation of magnetic properties for all powders under various initial Fe/Ba molar ratio of 8, 9, 10, and 11 were showed in Fig. 2. The powders obtained under Fe/Ba ratio of 9 have a coercive force (*Hc*) of 5650 Oe and a saturation magnetization (*Ms*) of 66.7 emu/g, both of which are higher than those of other samples. The poor magnetic properties for others can be contributed to the presence of nonferromagnetic α-Fe_2O_3 and antiferromagnetic $BaFe_2O_4$ which lead to lower saturation magnetization and coercivity.

3.2. Effect of calcination temperature on the phase composition, microstructure and magnetic properties

In order to study the influences of calcination temperature on the phase composition, morphology and magnetic properties of obtained powders, the combustion precursor was calcined for 2 h at 700 °C, 800 °C, 900 °C, 1000 °C with the fixed optimum glycine/nitrates and Fe/Ba molar ratio. Fig. 3 illustrates the XRD patterns of the combustion precursor and the calcined powders at different temperatures. All peaks of combustion precursor match well with barium carbonate ($BaCO_3$) and maghemite (γ-Fe_2O_3), which suggests that, unlike other spinel ferrites [25,26], single phase barium ferrites could not be prepared directly by sol–gel combustion technique. For the sample calcined at 700 °C, $BaFe_{12}O_{19}$ became the major phase with $BaCO_3$ and $BaFe_2O_4$ being minor phases. $BaCO_3$ was disappeared at a calcination temperature of 800 °C. XRD also shows that single objective $BaFe_{12}O_{19}$ hexagonal structure was detected without any other impurities for powders calcined at 900 °C and 1000 °C for 2 h, which means all intermediate phases were transformed into $BaFe_{12}O_{19}$ phase when the calcination temperature is above 900 °C. It can be easily found that with increasing calcination temperature the peaks width becomes narrower, indicating that the mean crystalline size of synthesized ferrites gradually increased.

The DSC/TG curves for the glycine–nitrates dried gel prepared with a Fe/Ba molar ratio of 9/1 and glycine/nitrates molar ratio of 10/9 are shown in Fig. 4. There is only one sharp exothermic peak at about 158.6 °C in DSC curve with a large weight loss of ~75.9%. It could be concluded that the combustion temperature for glycine and nitrates system is 158.6 °C, which is below the conventional citric/nitrates combustion system [27]. Combined with the XRD results, the combustion reaction between glycine and nitrates can be deduced in Eq. (1).

$$C_2H_5NO_2 + Fe(NO_3)_3 + Ba(NO_3)_2 = BaCO_3 + \gamma - Fe_2O_3 \qquad (1)$$

Fig. 5 shows FTIR spectra for the dried gel, burnt precursor, and the powders calcined at 900 °C and 1000 °C. The dried gel spectrum (Fig. 5a) illustrates that the main absorption bands at

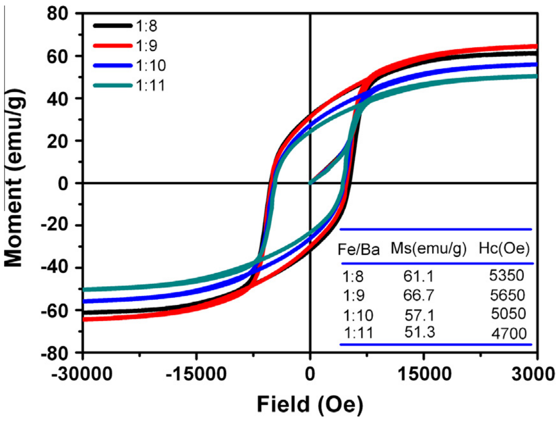

Fig. 2. Magnetic properties for powders calcined at 900 °C for 2 h with glycine/nitrate molar ratio of 10/9 and varied initial Fe/Ba molar ratio of 8, 9, 10, and 11.