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

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The ultrafine powders of barium ferrite (BaFe12O19) 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 BaFe12O19 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.

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1. Introduction

As one of the important classes of permanent magnetic materials, barium ferrites (BaFe12O19) have relatively large saturation magnetization (Ms), high coercive force (Hc) and high magnetic anisotropy field (Ha) 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(NO3)3·9H2O and Ba(NO3)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 Ba2+ and Fe3+. 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
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 λ = 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 BaFe₁²O₁₉ 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 ($\text{BaFe}_{2}\text{O}_3$) phase can be obtained with the initial Fe/Ba molar ratio of 9. There is minor barium monoferrites ($\text{BaFe}_2\text{O}_4$) coexisting with barium ferrites phase when the initial Fe/Ba molar ratio is 8. Apart from $\text{BaFe}_2\text{O}_4$ phase, $\text{BaFe}_2\text{O}_5$ and $\alpha$-$\text{Fe}_2\text{O}_3$ peaks were also detected after increasing Fe/ Ba molar ratio to 10 and 11. The presence of $\text{BaFe}_2\text{O}_5$ phase in the obtained powders for Fe/Ba molar ratio of 8 can be explained that there are not enough $\text{Fe}^{3+}$ ions to form $\text{BaFe}_2\text{O}_5$ phase completely, which means $\text{Ba}^{2+}$ ions are excessive. The $\text{BaFe}_2\text{O}_5$ peaks gradually disappeared with increasing Fe/Ba molar ratio until the value of 9. However, continuously increasing Fe$^{3+}$ ions can reproduce $\text{BaFe}_2\text{O}_4$ as well as $\alpha$-$\text{Fe}_2\text{O}_3$ phase rather than form $\text{BaFe}_2\text{O}_5$ hexagonal structure. This phenomenon could be attributed to the fact that the appearance of $\alpha$-$\text{Fe}_2\text{O}_3$ with orthorhombic hexahedron structure prevent the formation of $\text{BaFe}_2\text{O}_5$ 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 $\text{BaFe}_2\text{O}_5$ due to the various solubility of the $\text{Fe}^{3+}$ and $\text{Ba}^{2+}$ 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].

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 ($M_s$) 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 $\alpha$-$\text{Fe}_2\text{O}_3$ and antiferromagnetic $\text{BaFe}_2\text{O}_4$ 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 ($\text{BaCO}_3$) and maghemite ($\gamma$-$\text{Fe}_2\text{O}_3$), 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, $\text{BaFe}_2\text{O}_5$ became the major phase with $\text{BaCO}_3$ and $\text{BaFe}_2\text{O}_4$ being minor phases. $\text{BaCO}_3$ disappeared at a calcination temperature of 800 °C. XRD also shows that single objective $\text{BaFe}_2\text{O}_5$ 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 $\text{BaFe}_2\text{O}_5$ 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 ~75.8%. 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).

\[
\text{C}_2\text{H}_3\text{N}_2\text{O}_2 + \text{Fe(NO}_3)_3 + \text{Ba(NO}_3)_2 = \text{BaCO}_3 + \gamma - \text{Fe}_2\text{O}_3
\]

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. 1. XRD patterns for the powders calcined at 900 °C for 2 h with glycine/nitrates molar ratio of 10/9 and various initial Fe/Ba molar ratios of 8, 9, 10, and 11.](image1)

![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.](image2)
3441 cm\(^{-1}\) and 3055 cm\(^{-1}\) are attributed to the O–H and N–H stretching of water and glycine, while characteristic band at 1632 cm\(^{-1}\) results from the anti-symmetrical and symmetrical stretching vibration bands of COO\(^{-}\) related to glycine. The bands located at 1351 cm\(^{-1}\) and 827 cm\(^{-1}\) are associated with the N–O stretching vibration and bending vibration of NO\(_3\)\(^{-}\). As for the burnt precursor (Fig. 5b), there are a series of new bands at 1443 cm\(^{-1}\), 858 cm\(^{-1}\), 694 cm\(^{-1}\) which come from barium carbonate, while the bands of NO\(_3\)\(^{-}\), –NH\(_2\) and COO\(^{-}\) are totally disappeared. Besides, other new absorption bands at 3420 cm\(^{-1}\), 1624 cm\(^{-1}\), 557 cm\(^{-1}\) are ascribed to maghemite. The disappearance of the absorption bands of NO\(_3\)\(^{-}\) ions, –NH\(_2\) and COO\(^{-}\) group in the FTIR spectra of the burnt precursor suggests that the NO\(_3\)\(^{-}\) ions, –NH\(_2\) and COO\(^{-}\) groups take part in the reaction during combustion. Therefore, the combustion can be described as a thermally induced anionic redox reaction of the glycine gel in which nitrate ions act as oxidant, as reported by other paper [28]. From the Fig. 5c and d, all new bands at 589 cm\(^{-1}\), 545 cm\(^{-1}\) and 440 cm\(^{-1}\) belong to the metal–oxygen stretching vibrations of BaFe\(_{12}\)O\(_{19}\) hexaferrite. No other band is observed, suggesting that single BaFe\(_{12}\)O\(_{19}\) hexaferrite powders be obtained when calcined between 900 and 1000°C, which can be identified by the XRD results as well.

The morphologies observed by SEM for the selected powders produced at various calcination temperatures of 900 and 1000°C are showed in Fig. 6. The particle size is ultrafine and distributed homogeneously for powders calcined at 900°C. Nevertheless, at 1000°C, the micrograph exhibits plate-like barium ferrite particles which have various grain sizes and agglomerate into large ones to some extent.

Hysteresis loops and magnetic properties of the powders calcined at different temperatures are shown in Fig. 7. It can be found that Ms. and Hc strongly depend on the calcination temperature. Fig. 7a shows that there is a slight step in the second quadrant hysteresis loop for the powders calcined at 700°C, which leads to relative low Ms. and Hc. Similarly, a gentle step exists in hysteresis loop of the sample calcined at 800°C, which can be explained by the co-existence of antiferromagnetic BaFe\(_{12}\)O\(_{4}\) with barium ferrites. Fig. 7b demonstrates that Ms. increases drastically with increasing calcination temperature, while Hc increases first, reaching a maximum value at 900°C, and then decreases for
temperature 1000 °C. The higher $M_s$ (66.7 emu/g) of sample calcined 900 °C could be a result of the well crystallized single hexaferrite phase. However, the relative low $H_C$ (4500 Oe) was obtained when the calcination temperature increased to 1000 °C. This could be attributed to the presence of a proportion of abnormal large particles caused by grain growth. The magnetic properties are well consistent with the results obtained from FTIR and XRD.

3.3. Effects of glycine dosage on the phase composition, morphology and magnetic properties

The results of XRD analysis of powders calcined at 900 °C with the different glycine/nitrates molar ratios and fixed optimum Fe/Ba molar ratio are shown in Fig. 8, which demonstrates the glycine dosage influences on the powders phase composition. Except BaFe$_{12}$O$_{19}$ hexagonal phase, the phases of $\alpha$-Fe$_2$O$_3$ and BaFe$_2$O$_4$ were also detected for the samples obtained with glycine/nitrates molar ratio of 5/9 and 6/9. When glycine/nitrates molar ratio was increased to 9/9, the peaks of BaFe$_2$O$_4$ gradually disappeared and there was only minor $\alpha$-Fe$_2$O$_3$ phase co-existed with BaFe$_{12}$O$_{19}$. As glycine/nitrates molar ratio increases to 10/9 and 12/9 with larger glycine dosage, the products were transformed to BaFe$_{12}$O$_{19}$ phase completely and no other impurity was examined. Moreover, the phase composition has no obvious change when more glycine was added. Therefore, it is important that glycine/nitrates molar ration must exceed 10/9 in order to get single barium ferrite phase.

The morphologies observed by SEM for the barium ferrite powders produced with different glycine/nitrates ratios of 10/9, 12/9 are shown in Fig. 9. It is found that the ultrafine powders with glycine/nitrates of 10/9 are more homogeneous than the other one. The latter has plenty of pores. We can suggest that the mass of pores result from drastic combustion between glycine and nitrates.

To clearly observe the morphology and confirm the phase structure of the products, selected samples with glycine/nitrates of 12/9 were examined by TEM and high resolution TEM (HRTEM), as shown in Fig. 10. TEM graphic demonstrates that the ultrafine powders are in plate-like shape with small thickness, which is in good agreement with other reports [29]. The inset HRTEM image clearly shows the crystal plane of (101) with d-space of 0.466 nm, which also indicates the ultrafine powders are well
crystallized into single crystal individually. No secondary phase was detected by HRTEM which is in agreement with XRD results.

The size distribution of the powders at calcination temperature 900 °C with Fe/Ba of 9/1 and glycine/nitrates of 12/9 characterized by laser particle size analyzer are shown in Fig. 11. The result suggests that the particle size is relative uniform and almost all of them are varied from 55 to 110 nm.

Magnetic properties of powders calcined at 900 °C with different glycine/nitrates molar ratios and fixed Fe/Ba molar ratio are shown in Fig. 12. There is considerable difference in the hysteresis loops of the samples calcined at different glycine/nitrates molar ratios, corresponding to the different phase structure discussed above. Both Hc and Ms. are relatively lower for the samples obtained at glycine/nitrates molar ratio of 5/9 and 6/9 than other samples, which can be attributed to the fact that the co-existence of antiferromagnetic BaFe2O4 and nonferromagnetic α-Fe2O3 phase restricts their hard magnetic properties significantly. With increasing glycine dosage, the magnetic properties improved dramatically until glycine/nitrates of 10/9 due to the single-phase of barium ferrites. However, there was a moderate increase in both Hc and Ms. of powders when further more glycine was added. Finally, the Hc and Ms. of the powders can achieve 5750 Oe and 67.7 emu/g, respectively, which is very close to the theoretically values of BaFe12O19 ferrite. Hence, the results indicate that the high glycine dosage is favorable to synthesize ultrafine barium ferrites with excellent magnetic properties.

4. Conclusion

The ultrafine barium ferrite powders have been synthesized using sol–gel combustion method with glycine as a fuel and metal nitrates as a reductant. In this work, glycine was used for a fuel instead of conventional citric acid and urea, which have decreased combustion temperature and simple experimental process. The processing parameters such as initial Fe/Ba molar ratio, glycine/nitrates molar ratio and calcination temperature have significant effects on the crystalline phase formation, microstructure and magnetic properties. The results show that the products calcined at 900 °C with Fe/Ba and glycine/nitrates molar ratio of 9/1 and 12/9 have high Hc of 5750 Oe and Ms. of 67.7 emu/g. This work provides a feasible approach and detailed processing parameters to prepare hard ferrite powders with fine particle size and good hard magnetic properties.

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References