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One-step synthesis of barium hexaferrite nano-powders via microwave-assisted sol–gel auto-combustion

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Abstract

Single phase barium hexaferrite nano-powders have been innovatively one-step synthesized via a microwave-assisted sol–gel auto-combustion in a specially designed quartz vessel using citric acid and ethylene diamine tetraacetic acid as composite chelating agents and freeze-drying technique to remove sols' moisture. The auto-combustion product powder is characterized by fluffy particle aggregates with the crystallites ranging from 50 to 100 nm in diameter and containing single magnetic domains for each with a low apparent coercive field of 260 Oe and a high saturation magnetization of 64.1 emu/g. The direct formation of barium hexaferrite is believed to result from the effective improvement in the spatial distribution homogeneity of metal ions and oxidant in the gels. Moreover, the quartz vessel with barium hexaferrite ceramic pad on sample's support and film-strips on its interior wall can effectively build up a favorable temperature environment to promote the direct formation of barium hexaferrite with microwave assistance during the gel's uniform auto-combustion.

Keywords: Microwave processing; Sol–gel auto-combustion; X-ray methods; Magnetic properties; Ferrites

1. Introduction

Barium hexaferrite ($BaFe_{12}O_{19}$ or BaM phase) quasi-single crystals with their grains highly oriented are potentially a good gyromagnetic material in microwave or millimeter wave fields.[1,2] Obviously, the realization of such a well-organized microstructure will be based on the availability of high quality BaM powders, which should be composed of particles with precisely-controlled chemical compositions, single magnetic domain and narrow particle size distribution. Many methods such as reverse micro-emulsion, co-participation, hydrothermal process, sol–gel route, sol–gel auto-combustion, etc. have been developed and effectively used to synthesize BaM nano-powders. Most of these methods often comprise two steps: (1) wet-chemical process of starting materials for a homogeneous precursor; (2) heating treatment of the precursor at relatively high temperatures to promote the formation of BaM phase. Nevertheless, secondary high temperature heat-treatment is technologically detrimental and inevitably induces coalescence and coarsening of the nano-sized particles. In recent years, the sol–gel auto-combustion method seems to be exceptionally interesting for its proper utilization of the heat released from the in situ reactions of fuels (hydrocarbon species from chelating agents) and oxidants (nitrate radicles) leading to the rapid in situ formation of target nano-powders. As reported in literatures, various oxide nano-sized powders such as $La_{0.7}Ca_{0.3}MnO_3$,[3] $La_{9.33}Si_6O_{26}$,[4] $La_{9.33}Ge_6O_{26}$,[5] etc., have been directly synthesized via sol–gel auto-combustion. However, to our knowledge, it seems that no direct synthesis of single phase BaM nano-powders by this method has been ever reported. Since Huang et al.[6] first reported their work on the synthesis of ultrafine $BaFe_{12}O_{19}$ powders using citrate–nitrate sol–gel auto-combustion followed by a secondary heat-treatment, many investigations have been committed to the sol–gel auto-combustion synthesis of $BaFe_{12}O_{19}$, with efforts in probing the influences from the ratios of Fe^{3+} to Ba^{2+}, citric acid/metal ions and citric acid/nitrate as well as the pH values of the starting solutions.[6–11] Nevertheless, almost all the works showed that the intermediate phases including $BaFe_2O_4$, Fe_2O_3, etc. were usually formed during the auto-

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combustion process and BaM phase could be obtained only through a further heat-treatment at temperatures from 800 to 1000 °C.

As regards whether the single phase of $BaFe_{12}O_{19}$ nano-powders can be formed via a sol–gel auto-combustion process alone, the answer is yes according to our recent researches on the synthesis of other functional oxides nano-crystals via sol–gel auto-combustion.[4,5] The study has enabled us to realize that the main problems for one-step formation of single phase $BaFe_{12}O_{19}$ nano-powders via the sol–gel auto-combustion arise primarily from the inhomogeneous distributions of metal ions and oxidants (nitrate radicles (NO_3^-)) in the gels for auto-combustion due to the unbalanced chelating of barium and iron ions by citrate and the possible presence of nitrate crystallites (of ammonium, for example), which could be greatly further enhanced by large ionic concentration ratio of iron to barium (Fe/Ba = 12) in comparison with those in the cases of $La_{9.33}Si_6O_{26}$, $La_{9.33}Ge_6O_{26}$, etc. In addition, non-uniform temperature field distribution in the gels and the unfavorable auto-combustion surroundings may cause heterogeneous ignition of hydrocarbon species from the thermal decomposition of fuel molecules like citric acid and then the fierce burst of burning pieces together with the turbulent flow of hot gas during the combustion, which may carry away the heat from combustion and make the combustion product particles' temperature drop rapidly so as to prevent the formation of BaM phase.

Therefore, it should be believed that one-step synthesis of barium hexaferrite nano-powders without additional heat-treatment can be well accomplished if all the inhomogeneities and adverse auto-combustion conditions concerned in the system are eliminated. In this paper, we report our recent work on the direct synthesis of single phase $BaFe_{12}O_{19}$ via a sol–gel auto-combustion.

2. Experimental

As starting materials, $Ba(NO_3)_2$ and $Fe(NO_3)_3{\cdot}9H_2O$ with A.R. grade were weighed in the stoichiometry of $BaFe_{12}O_{19}$ to prepare the aqueous solution of each with the concentrations of 0.1 and 0.6 M, respectively. To improve the chelating homogeneity, CA together with EDTA were used as composite of chelating agents with the amounts controlled by $EDTA/Ba^{2+} = 1.5$ and $CA/Fe^{3+} = 1.5$.[12,13] For the Fe^{3+}/CA solution, ethylene glycol (EG) was added by EG/CA = 1.5 to assist the formation of Fe^{3+}/CA complex network. The two solutions were adjusted to reach a pH value of 6.5 by using ammonia of 28% and ensure the free Ba^{2+} ions in the solution less than 10^{-4} M, which is actually much more difficult to be well chelated than Fe^{3+}, and continuously stirred for 2 h to ensure the complete chelation of metal ions at room temperature. Subsequently, they were mixed under steady stirring and a given amount of ammonium nitrate was added so as to obtain a homogeneous sol with an oxidizing degree Q of 1.25. In the meanwhile, ammonia solution of 28% was also incorporated by droplets to keep the sols at pH 6.5. As to the oxidizing degree, it is an index to indicate the richness of oxygen atoms available in the system with respect to the amount required for oxidizing all hydrocarbon species from chelating agents into CO_2, H_2O. As a great simplification, the oxidative and reductive reactions concerned in the auto-combustion of the system are supposed to happen by the following equations[14,15]:

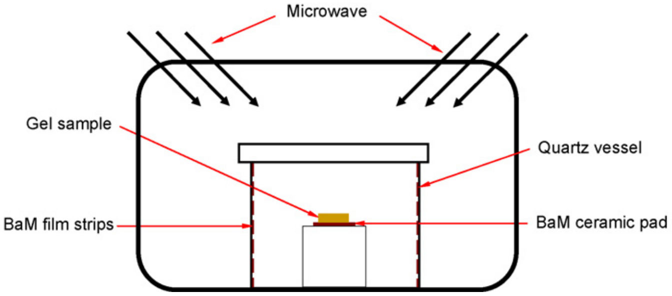

Fig. 1. The schematic illustration of microwave oven with a specially designed quartz glass vessel for fabricating barium hexaferrite nano-crystals.

$$2Fe(NO_3)_3 \leftrightarrow Fe_2O_3 + 3N_2 + 15[O]; \tag{1}$$

$$Ba(NO_3)_2 \leftrightarrow BaO + N_2 + 5[O]; \tag{2}$$

$$NH_4NO_3 \leftrightarrow 2H_2O + N_2 + [O]; \tag{3}$$

$$C_{10}H_6N_2O_8 + 15[O] \leftrightarrow 10CO_2 + N_2 + 3H_2O; \quad \text{for EDTA} \tag{4}$$

$$C_6H_8O_7 + 9[O] \leftrightarrow 6CO_2 + 4H_2O; \quad \text{for CA} \tag{5}$$

$$C_2H_6O_2 + 5[O] \leftrightarrow 2CO_2 + 3H_2O; \quad \text{for EG} \tag{6}$$

The oxidizing degree Q defined as the molar ratio of the providing oxygen by nitrates to the required oxygen completely oxidizing the fuels to CO_2, H_2O and N_2 can be written as:

$$Q = \frac{5n_{Ba(NO_3)_2} + 7.5n_{Fe(NO_3)_3} + n_{NH_4NO_3}}{15n_{EDTA} + 9n_{CA} + 5n_{EG}} \tag{7}$$

where each n denotes the molar quantity of chemical reagent specified by its subscript.

To turn the sols to homogeneous gels, freeze-drying technique (CHRIST, Alpha 1-4LSC) with liquid nitrogen as the coolant was employed to remove the water contained in the sols. After 48 h of vacuum sublimation of moisture, the frozen sols were turned to yellowish dry powders. They were then pressed into flat pellets with diameter $D = 10$ mm and thickness $\delta = 4$–5 mm for auto-combustion, which was carried out in a household microwave oven with a specially designed quartz glass vessel to build up an environment favorable for the formation of BaM phase. As shown in Fig. 1, a small quartz glass beaker, serving to support the sample pellets for auto-combustion, is placed with bottom up in the center of a large quartz vessel with a removable cover. To compensate for the heat loss during the combustion, a piece of well sintered Ba-hexaferrite pad was put beneath the sample pellet by taking advantage of the fact that Ba-hexaferrite itself may greatly absorb microwave energy. Besides, in the same principle, the

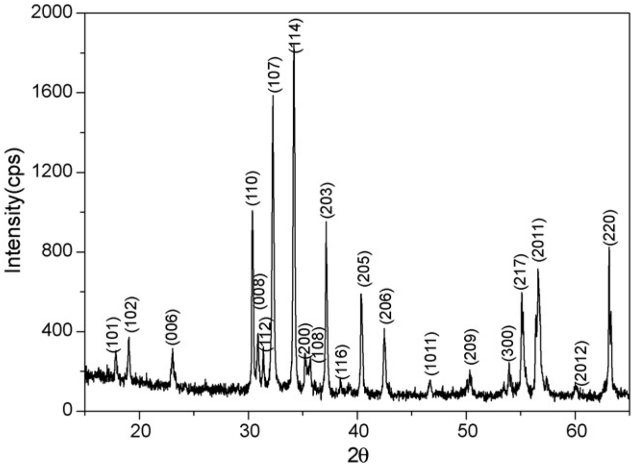

Fig. 2. XRD pattern of the auto-combustion product powder obtained via the present microwave-assisted sol–gel auto-combustion process.

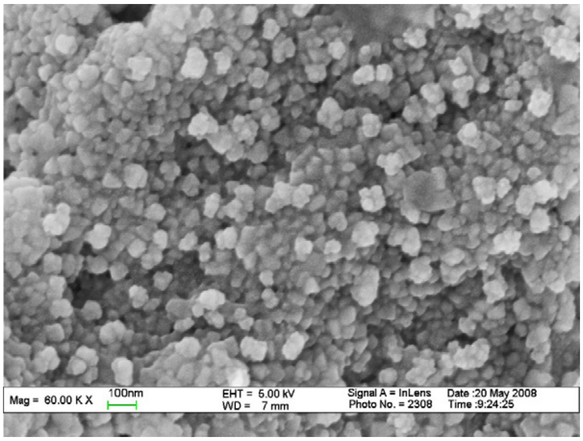

Fig. 3. FE-SEM image of BM phase powders one-step synthesized via microwave-assisted auto-combustion.

interior wall of large quartz vessel was coated with several film-strips of Ba-hexaferrite for heat protection so as to keep the wall warm enough not to absorb the heat from the fluffy particles erupted during the auto-combustion.

With such an auto-combustion setting, the dried gel sample has been found to be ignited in about 15 s under the microwave irradiation when the output of microwave was set around 450 W and, once on ignition, the combustion took place fiercely ad last about 10 s. From the bottom and wall of the quartz glass vessel, the fluffy combustion product particles were collected and their phase identification and microstructural characterization were performed with X-ray diffractometer (ARL XTRA) with Cu Kα radiation and FE-SEM (LEO-1530VP). Their magnetic properties were measure by a vibrating sample magnetometer (VSM HH-15).

3. Results and discussion

The typical XRD pattern of the as-obtained auto-combustion product powder is illustrated in Fig. 2. It is very interesting to find that all the XRD peaks can well be ascribed to the reflections by the hexagonal $BaFe_{12}O_{19}$ phase rather than any others. This result evidently indicates that a single phase barium hexaferrite has been one-step synthesized via the present microwave-assisted sol–gel auto-combustion process. It strongly supports our above-mentioned analysis and manifests that it is the improved homogeneities in gel's chemical composition and in auto-combustion process aided with heat protection and compensation that make the possibilities for the direct formation of single BaM phase through a short-lived sol–gel auto-combustion.

Fig. 3 gives the FE-SEM image of as-synthesized barium hexaferrite nano-powders. It can be clearly noted that the powder particles are composed of many tiny crystallites, which appear to possess the particle size ranging from 50 to 100 nm and have spherical or ellipsoidal shape in contrast to the ordinary hexagonal flake shape. Probably, this isotropic characteristic in the shape of the product particles is due to the rapid simultaneous homogenous nucleation in the uniform temperature field and the limited secondary crystal growth with respect to the very short-lived auto-combustion process.[16]

The magnetization measurements were carried out at room temperature with the obtained powders pre-dispersed in alcohol. As shown in Fig. 4, the as-synthesized BaM nano-powders show a magnetization loop characterized by rapidly reaching saturation at an external magnetic field of as low as 1000 Oe and a saturation magnetization of about 64.1 emu/g, which is still much lower than the theoretical value of BaM single crystal about 72 emu/g, but a little higher than or similar to the reported results in literatures.[6–9,16] Several theories, including surface effects, spin-canting phenomenon, purity and particle size effects, have been proposed to account for the relatively low magnetization of nano-particles.[17] Since barium hexaferrite demonstrates a high uniaxial anisotropic field of 3.3×10^5 J/m^3, the critical volume of the nano-particles could be as small as approximately 300 nm^3, much smaller than for the soft magnetic spinel magnetite ($K = 1.4 \times 10^4$ J/m^3),[18] which is approximately 7200 nm^3. From this point of view, the particles size of the as-synthesized powder must in the size range of ferromagnetic single domain and such a low coercive field of 260 Oe must

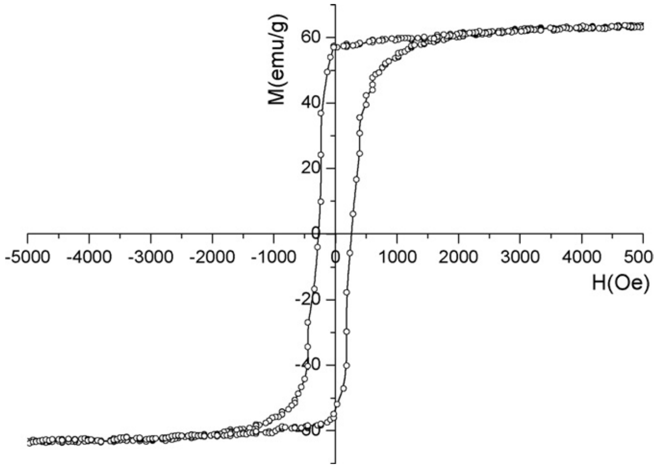

Fig. 4. The magnetization hysteresis loop of BM powders one-step synthesized via microwave-assisted auto-combustion.

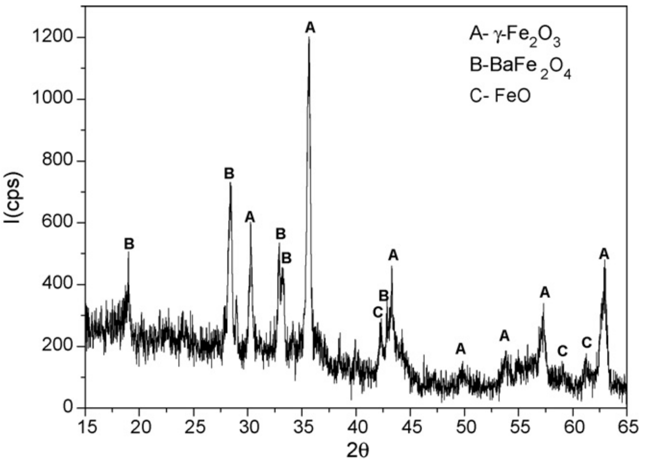

Fig. 5. XRD pattern of the auto-combustion products obtained with conventional citrate-gel's sample and microwave ignition.

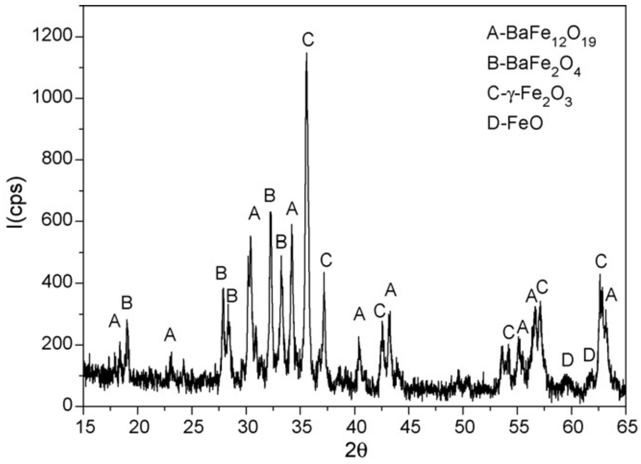

Fig. 6. XRD pattern of the auto-combustion products obtained with heat compensation from $BaFe_{12}O_{19}$ pad beneath the citrate-gel's sample irradiated by microwave.

be just an apparent value rather than the intrinsic value of the obtained powders, which indicates that the obtained nanocrystallites can be easily aligned under the external applied magnetic field for constructing high oriented BaM quasi-single crystals.[19]

In order to better understand the influences from the various inhomogeneities on the formation of BaM phase, the typical XRD diagrams for three cases with different inhomogeneities are presented below for comparison:

(1) The gels were obtained by using CA alone as chelating agent and no freeze-drying technique was used. In this case, three phases including Fe_2O_3, $BaFe_2O_4$ and FeO, but no BaM phase were found as the result of sol–gel auto-combustion ignited simply by microwave irradiation, as shown in Fig. 5. Obviously, this result, very similar to those mostly reported in literature, should be caused primarily by severe inhomogeneity in gel's chemical composition notwithstanding the unfavorable conditions for auto-combustion. The severe non-stoichiometric distribution of Ba^{2+} and Fe^{3+} ions in the gels inevitably leads to the in situ formation of rich- and poor-barium phases like $BaFe_2O_4$ and Fe_2O_3. This attribution can be further supported by the results of the following cases. As to the phase of FeO, it may result from the reduction of Fe^{3+} by highly reductive C–H species from the pyrolysis of organic fuels when an adequate amount of oxygen atoms is not available somewhere in the system from the thermal decomposition of nitrates under the microwave irradiation.

(2) The same gels were used as above but, to compensate for the heat loss during the combustion, a piece of Ba-hexaferrite ceramic pad was put beneath the gel's pellet. In this case, as shown in Fig. 6, a minor quantity of $BaFe_{12}O_{19}$ phase has been identified among other intermediate phases like Fe_2O_3, $BaFe_2O_4$ and FeO. The emergence of $BaFe_{12}O_{19}$ phase in the auto-combustion products significantly manifests that the thermodynamic conditions for the formation of $BaFe_{12}O_{19}$ phase during the auto-combustion should be entirely satisfied when the heat loss during the auto-combustion is properly supplemented by the heat released from the Ba-hexaferrite ceramic pad beneath the gel's sample.

(3) To further improve the conditions for auto-combustion, the interior wall of large quartz beaker was coated by strip-film of $BaFe_{12}O_{19}$ for heat protection in addition to the above-mentioned heat compensation. In this case, as illustrated in Fig. 7, BaM phase was interestingly found to be the major component along with the minor phases of Fe_2O_3, $BaFe_2O_4$ as the auto-combustion products. It is believed that when the quartz vessel's interior wall was coated with $BaFe_{12}O_{19}$ film-strips, the wall can be heated to a relatively high temperature under microwave irradiation and makes the auto-combustion product particle aggregates' temperature drop greatly reduced so as to allow the formation of $BaFe_{12}O_{19}$ to proceed for a longer time than in the case without the heat protection film-strips. In comparison with the cases 2 and 1, the disappearance of FeO phase seems

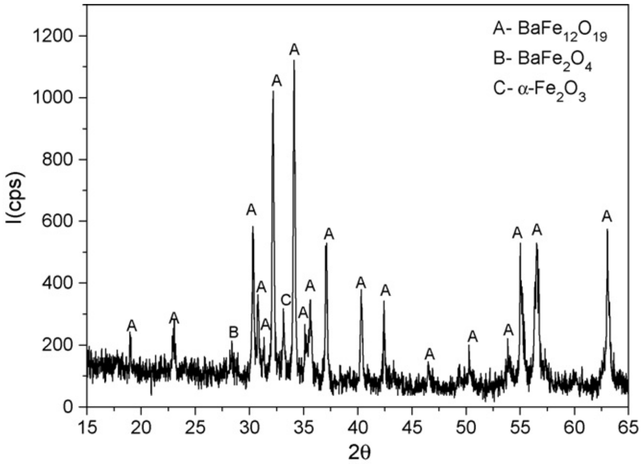

Fig. 7. XRD pattern of the auto-combustion products obtained with heat protection from $BaFe_{12}O_{19}$ strip-films on the interior wall of quartz vessel in addition to the heat compensation.

to show that with the heat protection, the decomposition of organic fuels and the oxidation of their pyrolytic species may happen in a more synergetic manner to avoid the reduction of the ferric ions.

It should be pointed out that although both heat compensation and heat protection have been taken in this case, the auto-combustion product is still composed of multiple phases despite the presence of $BaFe_{12}O_{19}$ as a major phase. It is believed that the favorable auto-combustion conditions may greatly enhance the in situ reactions between Ba–O and Fe–O species. But non-stoichiometric distribution of metal ions and oxidants prevents the direct formation of a single phase $BaFe_{12}O_{19}$ through such reactions. Therefore, to eliminate the inhomogeneity of chemical composition within the gels is of vital significance, which makes it possible for any in situ reactions between Ba–O and Fe–O species to directly from the single BaM phase.

4. Conclusion

The single phase $BaFe_{12}O_{19}$ nano-powders have been successfully one-step synthesized via a microwave-assisted sol–gel auto-combustion. The obtained powders are characterized by fluffy particle aggregates with the crystallites ranging from 50 to 100 nm in diameter and containing single magnetic domains for each with a low apparent coercive field of 260 Oe from the inter-particle resistance to aligning movement. Using both citric acid and EDTA as composite chelating agents and freeze-drying technique for removal of sol's moisture can effectively improve the spatial distribution homogeneity of metal ions and oxidant in the gels and, therefore, eliminate the formation of rich- and poor-barium intermediate phases. Moreover, the specially designed quartz vessel with $BaFe_{12}O_{19}$ ceramic plate as supporting pad and film-strips on the vessel's interior wall can effectively build up a temperature environment with the assistance of microwave irradiation to favorably promote the direct formation of single phase $BaFe_{12}O_{19}$ during the gel's uniform auto-combustion ignited by microwave.

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