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Effect of NaNO₃ foaming agent on barium ferrite hollow microspheres prepared by self-reactive quenching technology



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ABSTRACT

Al + Fe_2O_3 + BaO_2 and $NaNO_3$ as the reactive system and the foaming agent, respectively, are used to prepare barium ferrite hollow microspheres (BFHMs) by self-reactive quenching technology based on flame spraying technology, self-propagating high-temperature synthesis (SHS) technology and quick chilling technology. Effects of NaNO₃ on the particle size, morphology, phase structure and microwave absorption properties of BFHMs are investigated through SEM, XRD, particle size analyzer, high-speed camera and vector network analyzer. The results show that, after adding 10 wt.% NaNO₃, the average particle size of BFHMs decreases initially from 28 µm to 6 µm, as well as the particle distribution gets narrower. Micro-nano lamellar crystals appear on the surface of BFHMs, with the dimension ranging from 500 nm to 2 µm. BaFe₂O₄ and Fe₃O₄, which have spinel structures, can be seen in XRD, and they are beneficial for microwave absorption properties. The real part (ε'), imaginary part (ε'') of permittivity, and the imaginary part of permeability (μ'') increases in 0.5–18 GHz. The real part (μ') of permeability increases in 0.5-10.3 GHz, while decreases in 10.3-18 GHz. The microwave absorption properties are improved greatly, and the minimum reflectivity decreases from -3.1 dB to -9.8 dB. The reasons for improvement of microwave absorption properties after adding NaNO3 foaming agent may be the decreasing of the particle size of BFHMs, the appearance of ferrites (BaFe₂O₄ and Fe₃O₄) with spinel structure and special micro-nano tabular crystals. Magnetoplumbite-type barium ferrites ($BaFe_{12}O_{19}$) hollow microspheres are obtained after heat-treatment and the microwave absorption properties are further improved.

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1. Introduction

Magnetoplumbite-type barium ferrites (BaFe₁₂O₁₉) are widely used because they have multiple EM (electromagnetic) wave lossy mechanisms such as magnetic hysteresis loss, natural resonance, residual loss, and eddy current loss [1]. Additional attention is drawn due to their high stability, high-frequency response and narrow distribution of transmission field properties. BaFe₁₂O₁₉ materials have been prepared by various methods, including the chemical coprecipitation method [2,3], the glass crystallization [4], the sol–gel method [5,6] and the ceramic process [7]. In addition, many studies have also been concerned with cationic substitutions to improve the fundamental magnetic properties of BaFe₁₂O₁₉ [8–9]. For example, some experiments have used light

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rare-earth ions (LRE) such as La, Pr, and other metal cations in substitution for Ba and Fe, respectively, taking into account the ionic radius of the elements, and the magnetic properties are investigated [10].

These methods mentioned above have their own advantages. However, $BaFe_{12}O_{19}$ materials prepared by them are always with great density and poor high-temperature properties, which makes it difficult to meet the requirement of light absorbents [11]. If $BaFe_{12}O_{19}$ materials are fabricated into hollow structures, the weight can be significantly reduced without any reduction of microwave absorption properties. Hollow microspheres have special properties in physics and chemistry, namely, micro-particles, hollow structure and light weight [12,13]. Self-reactive quenching technology is a favorable method to prepare barium ferrite hollow microspheres (BFHMs), which combines flame spraying technology, self-propagating high-temperature synthesis (SHS) technology and quick chilling technology [14–16]. With a low input–output ratio, self-reactive quenching technology can also



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control the particle size, morphology, and phase structure of BFHMs. Meanwhile, the hollow structure effectively reduces the weight of BFHMs and forms special microwave absorption mechanisms, which has the development potential to meet the need of new-style absorbents "thin, light, wide and strong" [16].

Controlling the particle size of BFHMs by adjusting the technology parameters based on self-reactive quenching technology has being considered as a potential research since this technology was invented by our team. Considering previous investigation [17], it is indicated that polyethylene glycol (PEG) foaming agent can effectively improve the fluidity of agglomerate powders and increase the particle size of BFHMs. In addition, the microwave absorption properties are innovated. However, it has not been referred that how to decrease the particle size and obtain BFHMs with micron, micro-nano even nanometer particle size. Therefore, this study is established. Due to its high foaming quantity and excellent visbreaking properties, NaNO₃ has the potential to decreasing the particles of BFHMs.

In this study, micron-sized BFHMs absorbent is prepared using $AI + Fe_2O_3 + BaO_2 + sucrose and NaNO_3$ as the reactive system and the foaming agent respectively based on self-reactive quenching technology. Effects of NaNO_3 foaming agent on particle size, morphology, phase structure and microwave absorption properties of BFHMs are investigated, and the mechanisms are studied. This thesis is carried out to master a controllable preparation method of BFHMs absorbent and lay the foundation on the future investigations.

2. Experiments

2.1. Materials and methods

Analytical reagent raw materials of Al powders, BaO_2 powders, Fe_2O_3 powders, sucrose (precursor of C, 50 g), epoxy resin (bonding agent, 50 ml) and NaNO₃ foaming agent were selected. Related information is showed in Table 1. Considering previous investigations, it is indicated that 10 wt.% (the mass percentage of reactive system including all the raw materials) is the best quantity of NaNO₃ foaming agent. Therefore, 10 wt.% NaNO₃ was selected. Eq. (1) shows the main reactive system. According to the stoichiometry ratio, two experiments were conducted: one was without NaNO₃, and the other was with 10 wt.% NaNO₃. Agglomerate powders were prepared as the following processes.

Firstly, the raw materials were put into LJM-5L ball mill, and anhydrous ethyl alcohol was taken as the medium sphere to be grinded for 6 h. After that, epoxy resin–alcoholic solution was added into the mill to be stirred for another 2 h. Epoxy resin was used to cooperate with sucrose to enlarge the contact area of the components in the agglomerate powders and to increase the bonding strength of reactive components. It can be transformed to CO, CO_2 and H_2O in SHS reaction due to the high temperature. Secondly, the mixtures were dried and carbonized at 200 °C in 101-2A horizontal drying cabinet until no smoke released, and then they were comminuted by the FW177 disintegrator. Thirdly, two kinds of agglomerate powders before and after adding NaNO₃ were selected for the experiment after the sieving process. Finally, BFHMs after adding NaNO₃ are heat-treated in Xiandai high-temperature resistance furnace at 1100 °C for 4 h with the heating rate of 3 °C/min.

Fig. 1 shows the preparation diagram of BFHMs. As shown in the figure, the agglomerate powders are sprayed into the flame field (about 3500 K) through a CP-D type high-energy flame-spraying gun, and the temperature of the materials increases gradually. When reaching the ignition temperature, the SHS reactions occur promptly, and the temperature of reactive system exceeds the melt point of products. So ceramic droplets are generated. Simultaneously, large volume of gases are produced, which results in the hollow structure of ceramic droplets.

Table 1	
Raw materials and their chemical composition used in the experiments.	

Material	Particle size (µm)	Chemical Purity (wt.%)
Al	≼40	$Al \ge 99$
BaO ₂	≼35	$BaO_2 \ge 97\%$
Fe ₂ O ₃	≼40	$Fe_2O_3 \ge 99.5$
Sucrose	≼5	$C_{12}H_{22}O_{11} \ge 99.9 H_2O < 0.1$
NaNO ₃	≼35	$NaNO_3 \ge 99.5\%$
Epoxy resin (6101)	Null	Epoxy resin ≥ 99

Then the ceramic droplets are quenched quickly into the cooling medium (the distilled water). As the gas cannot escape from the ceramic droplets, BFHMs are obtained immediately after the quenching products are dried and filtered. The reactive equation is showed in Eq. (1). In the experiment, the flame field is used to ignite the SHS reaction. And once the reactions occur, they can be self-sustaining based on the heat released by themselves and the flame field is not required.

In addition, the vibration of high-energy flame spraying gun parameters plays an important role in the products. According to the previous study, it is indicated that the atmosphere (such as O_2 , N_2 , and Ar) has great effect on the BFHMs, and it is found that oxygen provides an oxygen-enriched atmosphere, which benefits for the formation of hollow structures. In addition, the rate of O_2 and acetylene ($\beta = V_{O_2}/V_{C_2H_2}$) affects the temperature and oxidizability of flame, and in this experiment, the rate is set as 1.4. The quenching distance was set to 500 mm, which guarantee the high balling rates of BFHMs.

Moreover, different amounts of sucrose and epoxy resin will generate different amount of gases during the reaction, which will affect both the morphology and the properties of BFHMs. In this experiment, their amounts are 50 g and 50 ml, respectively.

2.2. Characterization of the samples

The morphology of the quenching products was detected by scanning electron microscope (SEM, QUANTA FEG-250). The phase composition of the quenching products was studied by X-ray diffraction (XRD, BRUKER D2 PHASER). Particle size distribution was measured by using Laser Particle Size Analyzer (Beckman Coulter LS 13 320, testing from 0.04 μ m to 2000 μ m). The density of BFHMs was determined by Archimedes Method. High-speed camera (Fastcam-Ultima512) was selected to observe the flight combustion behavior of agglomerate powders in the flame field. The resolution factor of sensor was 512 × 512 picture dots, and the mutograph speed was 500 fps. Xiandai F112 High-temperature Resistance Furnace was used to heat-treat BFHMs.

2.3. Measurement of microwave-absorbing behavior for BFHMs-paraffin composite

The absorbing composite were prepared by molding and curing the mixture of BFHMs and paraffin. Paraffin was used as a polymer matrix due to its good flexibility and wave-transparent property. And it has little effect on investigating the microwave absorption properties of BFHMs-paraffin composite. The mix ratio of BFHMs-to-paraffin was 3:2 by weight. The testing specimens have a toroidal shape with the thickness at 3 mm, and the outer and inner diameters are respectively 7.0 mm and 3.0 mm. The ε' , ε'' , μ' and μ'' versus frequency were measured by coaxial reflection/transmission method using Vector Network Analyzer (Agilent-N5242A) in 0.5–18 GHz range.

The absorbing characteristics can be represented as the reflection loss (R.L.), as shown in Eqs. (2) and (3).

Where Z_{in} is the normalized input impedance related to the impedance in free space, $\varepsilon_r = \varepsilon' - j\varepsilon''$, $\mu_r = \mu' - j\mu''$ is the complex relative permeability and permittivity of the material, *d* is the thickness of the absorber, and *C* and *f* are the velocity of light and the frequency of microwave in free space, respectively.

To represent the perfect absorbing properties, the impedance matching condition is given by $Z_{in} = 1$. The impedance matching condition is determined by the combination of six parameters ε' , ε'' , μ' , μ'' , f and d. Also, knowing ε_r and μ_r , the R.L. value versus frequency can be evaluated by using metlab 8.0 at a specified thickness.

3. Results and discussion

3.1. Effect of NaNO₃ on the morphology, particle size and phase structure of BFHMs

Fig. 2(A) illustrates the SEM images of the quenching products under the Al + Fe₂O₃ + BaO₂ + sucrose + epoxy resin reactive system without NaNO₃. The adiabatic combustion temperature (T_{ad}) is 2526 K, and the heat of reaction (ΔH_{f}°) is -820.6 kJ/mol. Fig. 3(B) shows the SEM images of Al + Fe₂O₃ + BaO₂ + sucrose + epoxy resin + NaNO₃ reactive system (T_{ad} = 2620 K, ΔH_{f}° = -836.5 kJ/mol). Because $T_{ad} \ge 1800$ K, two SHS reactions could occur. Images A1-A3 are magnified 200, 5000 and 10,000 times respectively, while Images B1-B3 are enlarged 1000, 5000, and 20,000 times. According to the SEM images, the particle size is getting smaller and the particle distribution is more uniform after adding NaNO₃. In addition, the morphology of BFHMs changes drastically. As shown in Image A3 and B3, the surfaces are relatively smooth without NaNO₃, on which there are a small number of fine spherical and irregular particles. After adding NaNO₃, the spheres are



Fig. 1. Principle diagram for preparation of BFHMs absorbent by self-reactive quenching technology.



Fig. 2. SEM photographs of the BFHMs without (A1-A3) and with NaNO₃ (B1-B3).

composed of micro-nano lamellar crystals, ranging from 500 nm to 2 $\mu\text{m}.$

The energy spectrums of hollow microspheres before and after adding NaNO₃ are analyzed in Fig. 3. Fig. 3(a) and (b) shows the EDS patterns of Spot 1 (marked in Fig. 2A2) and Spot 2 (marked in Fig. 2B3), respectively. The results show that the quenching products both consist of Ba, Fe, Al, and O elements, whether NaNO₃ is added or not. However, C element disappears and the content of Al element declines after adding NaNO₃. This may be ascribed to the follows reasons. Properties of the agglomerate powders are improved so drastically that each reaction unit is mixed more uniformly and reacts more sufficiently. As a result, all sucrose are burned and released in forms of gas. In addition, the further sufficient aluminothermic reactions result in the decreasing quantity of Al element. The exact reasons will be clarified in the following passage.

The particle size distributions of BFHMs sample is shown in Fig. 4. The particle size has an average value of 28 μ m with 92% between 5 and 65 μ m without NaNO₃. After adding NaNO₃, the average particle size decreases to 6 μ m with 68% between 1 and 10 μ m. It is indicated that the particle size is getting smaller and the distribution is getting narrower after adding NaNO₃.

XRD patterns of BFHMs before and after adding NaNO₃ foaming agent are showed in Fig. 5. From XRD, it can be concluded that changes of phase components have taken place. Without NaNO₃, BFHMs are constituted of BaFeO_{3-x}, Fe₂O₃ and Al₂O₃. While the



Fig. 3. EDS patterns of the microspheres marked in Fig. 2.



Fig. 4. Particle size distribution of BFHMs samples without (a) and with NaNO₃ (b).

phase components are BaFe₂O₄, Fe₃O₄, Fe₂O₃ and Al₂O₃ after adding NaNO₃. The results show that, BaFe₂O₄ is obtained and some of Fe₂O₃ transforms to Fe₃O₄. Integrating the results of Fig. 3(b), it is concluded that micro-nano lamellar crystals may consist of Fe₃O₄, Fe₂O₃, BaFe₂O₄ and Al₂O₃. Among these phases, BaFe₂O₄ is an important precursor to form BaFe₁₂O₁₉. Moreover, BaFe₂O₄ and Fe₃O₄ have spinel structures, which greatly influence the microwave absorption properties. As is known in Fig. 1, self-reactive quenching technology has great subcooled temperature when the droplets are quenched into the distilled water. Droplets are solidified so fast that sufficient crystallization cannot occur. As a result, BaFe₁₂O₁₉ have not been present, which needs a heat-treatment experiment to obtain.

3.2. Effect mechanism analysis of $NaNO_3$ foaming agent on the preparation of BFHMs

When flying into oxyacetylene flame field provided by the flame-spraying gun, agglomerate powders produce series of physical and chemical reactions and undergo three progresses including energy storage progress, SHS reaction progress, and post-combustion progress [12]. During energy storage progress, agglomerate powders are preheated gradually from surface to inside. Particles with low melting point including Al (933 K) and BaO₂ (723 K) are first melted and spread on the surface of Fe₂O₃ (1838 K) by

capillary osmosis. During SHS reaction progress, the temperature of agglomerate powders increases drastically and reaches to the SHS ignition temperature immediately, then $Al + Fe_2O_3$ $(T_{ad} = 3000 \text{ K})$ reaction happens promptly and releases much heat, as is shown in Eq. (4). The releasing heat guarantees the continuing reaction of Fe + BaO₂ + Fe₂O₃ (T_{ad} = 2170 K), as is shown in Eq. (5). In Eq. (5), Fe is produced by the reaction of $Al + Fe_2O_3$. The heat released by Eqs. (4) and (5), together with the high temperature of oxygen-acetylene flame, guarantee the products keeping in a melting status. Meanwhile, the combustion of epoxy resin and sucrose releases much CO₂ and the gas stores inside the droplets. So hollow droplets are generated. During post-combustion progress, convection and radiation of the flame field make the surface temperature of droplets reach to about 1000 K. With the flying distance increasing, the temperature decreases gradually. However, there are still many complexed chemical reactions inside the droplets. When sprayed into the cooling medium, droplets are solidified rapidly in a great subcooled temperature, and gases keep inside the droplets instead of escaping. Therefore, microspheres with hollow structure are obtained.

Effects of NaNO₃ foaming agent on the particle size of BFHMs could be closely ascribed to its special foaming mechanism. Characteristics of high foaming quantity and stable foaming processes, NaNO₃ decomposes gradually and releases a large amount of gas under high temperature. It decomposes into NaNO₂ and O₂



Fig. 5. XRD patterns of the BFHMs before and after adding NaNO₃.

when it is 653 K, and releases N_2 and O_2 between 673 and 873 K. NO sets free in 973 K and NO_2 as well as N_2O release between 1048 and 1138 K. The decomposition processes are showed from

Eqs. 6-9 [16]. As NaNO₃ and Na₂O have no microwave absorption properties themselves, NaNO₃ is only used as the foaming agent. Moreover, though Na₂O exists in the sample, it is not marked in XRD patterns.

Without adding NaNO₃, gases mainly release from the combustion of epoxy resin and sucrose. The quantity of gases is limited. The melting phases of the droplets including Al₂O₃ have the capacity to restrain the gas from escaping the droplets [18]. By adding NaNO₃, the restraining capacity and the viscosity of the droplets are significantly reduced. In addition, massive gases are generated due to decomposition of NaNO₃. And the droplets are filled with thousands and hundreds of bubbles immediately, then grow gradually when their internal air pressure increases continuously.



Fig. 7. TEM photograph of BFHMs after adding NaNO₃.





When the resultant force of all bubbles exceeds the surface tension of droplets, the droplets break into several drips with small particle size. The reaction progresses can be proved by high-speed photography experiment [19]. Fig. 6 illustrates the flying progress of Droplet A in the flame field (0.002 s/frame). According to the figure, it can be concluded that significant decrepitation phenomenon of the droplet appears when t = 0.006 s. And the broken droplets transform to BFHMs with small particle size after being quenched into the coolant.

Fig. 7 shows the TEM image of microspheres after adding NaNO₃, which demonstrates that hollow structures exist. By using the Archimedes Method it is found that the densities of microspheres are 1.79 g/cm^3 and 2.05 g/cm^3 before and after adding NaNO₃, respectively. While the destiny of hexagonal BaFe₁₂O₁₉ solid powder is 5.364 g/cm^3 , which further indicates that the microspheres are of hollow structures prepared by self-reactive quenching technology before and after adding NaNO₃. According to the data mentioned above, it can be concluded that although large amount of gas are released in the decrepitation progress, part of gas are still stored in the small droplets. As a result, microspheres with hollow structure are obtained after adding NaNO₃ foaming agent.

The particle size distribution of BFHMs gets narrower after adding NaNO₃. It is mainly ascribed to the following two causes. On one hand, droplets break into small drips with uniform particle size. On the other hand, NaNO₃ (580 K) reduces the melting point of agglomerate powder [18]. The liquid phases including NaNO₃, Al and BaO_2 rapidly enter the agglomerate powders by capillary osmosis and spread on the surface of Fe_2O_3 . This mechanism sufficiently accelerates SHS reactions. As the melting point of agglomerate powder is reduced, the preheated time decreases obviously. As a result, the reaction units of agglomerate powder have sufficient time to react in the flame field. The droplets are formed earlier and transform to BFHMs with a uniform distribution.

Adding NaNO₃ makes much influence on the morphology of BFHMs, which may be attributed to its effect on the particle size of droplets. After the droplets break, the particle size decreases obviously, and the radiating becomes faster in coagulation. So the crystallization is relatively fast. In contrast, droplets are of big particle size and slow radiating without adding NaNO₃, so its coagulation and crystallization are slow. The growth of crystals is restrained. Therefore, the surface of BFHMs is smooth without NaNO₃, while special micro-nano lamellar crystals appear on the surface after adding NaNO₃. In addition, some irregularity particles are present after adding NaNO₃. It is possibly because the broken droplets easily fly to the edge of the flame field where the temperature is lower, and the droplets solidify in the cooling medium without sufficient reaction.

By adding NaNO₃, some Fe₂O₃ transforms to Fe₃O₄ phases, so some Fe²⁺ turns to Fe³⁺. In addition, BaFe₂O₄ with spinel structure is generated after adding NaNO₃. As demonstrated, BaFe₂O₄ is an important precursor to form BaFe₁₂O₁₉, which might influence the microwave absorption properties. The exact mechanism will be shown in the following section.



Fig. 8. Permittivity and permeability of BFHMs before and after adding NaNO3.



Fig. 9. Reflection-frequency curves of the BFHMs before and after adding NaNO₃.



Fig. 10. XRD patterns of the BFHMs after heat-treatment.

3.3. Effect of NaNO $_3$ foaming agent on the microwave absorption properties of BFHMs

Complex permittivity and permeability represent the dielectric and dynamic magnetic properties of materials [20]. The real parts (ε' and μ') of complex permittivity and permeability symbolize the storage and transform capability of electromagnetic energy. The imaginary parts (ε'' and μ'') represent the loss of electromagnetic energy. The frequency dependence of complex permittivity and permeability for BFHMs is shown in Fig. 8. It is indicated that, by adding NaNO₃, the real part of permittivity (ε') increases and maintains at about 6.5. It is possible that surfaces of micro-nano tabular crystals on BFHMs have different polarity and conductivity. In the action of electrical field, charges accumulate rapidly in grain boundaries and space-charge polarization is generated. In addition, BaFe₂O₄ and Fe₃O₄ which have spinel structure are formed after adding NaNO₃. Compared with intermediate phases (such as BaFeO_{3-x}), BaFe₂O₄ and Fe₃O₄ are of cubic crystal with a high symmetry, and they have high real part of permittivity [21]. The imaginary part of permittivity (ε'') stays relatively stable in 0.5-8 GHz. However, ε'' has a noticeable enhancement in 8–18 GHz. The ε'' value refers to the dielectric loss ability of electromagnetic wave. From that it can be concluded that dielectric loss increases apparently in 8–18 GHz by adding NaNO₃.

From Fig. 8(c) and (d), it can be indicated that the real part of permeability (μ') increases apparently in 0.5–10 GHz and the initial permeability is high by adding NaNO₃. The amplification of permeability (μ') decreases gradually with the increasing of the frequency. However, the μ' value is less than that without NaNO₃ in 10–18 GHz. The imaginary part of permeability (μ'') has an obvious enhancement in 0.5–18 GHz, and the span is between 0.08 and 0.35.

Fig. 9 shows the calculated reflectivity curve of BFHMs before and after adding NaNO₃. From the picture, it is concluded that the minimum reflectivity is -3 dB at 10 GHz without NaNO₃. After adding NaNO₃, the minimum reflectivity is -9.8 dB at 9.5 GHz, and there is an obvious absorption of electromagnetic waves in 6–14 GHz. Consequently, the microwave absorption properties are greatly improved after adding NaNO₃ which mainly decided by the following aspects:

Firstly, micro-nano tabular crystals are generated on the surface of BFHMs after adding NaNO₃. On one hand, the surface of BFHMs is smooth before adding NaNO₃, and the main contacting method



Fig. 11. Reflection-frequency curves of the BFHMs after heat-treatment.

among BFHMs is point-contact. By adding NaNO₃, multiple contacting methods including point-contact, line-contact and surface-contact appear. And conducting networks easily generate among BFHMs. As a result, the action of electron transition in microscopic structures of BFHMs is enhanced, which increases the dielectric loss. On the other hand, micro-nano tabular crystals have large flakiness ratio and high magnetocrystalline anisotropy. When impressed alternating magnetic field exists, more magnetic domain structures on the surface of crystalline grains will absorb energy. Natural resonance effect will appear when the frequency of impressed alternating magnetic field equals the natural frequency of magnetic moment precession inside the micro-nano tabular crystals. In the action of natural resonance, BFHMs will absorb the energy of alternating magnetic field drastically. In addition, more grain boundaries form due to the appearance of micro-nano tabular crystals, which restrains the relative motions of magnetic domain walls. Consequently, the magnetic loss increases.

Secondly, with the decreasing particle size of BFHMs, the specific area increases. Accordingly, the proportion of atoms on the surface increases and become more active. In addition, the dangling bonds and defects increase, which make it easy to form surface polarization. Moreover, stronger rayleigh scattering are generated when incidence waves go to the surface of BFHMs. As a result, dielectric loss of BFHMs increases obviously. Therefore, it is clear that surface polarization and multiple scattering increase the microwave absorption properties of BFHMs.

Thirdly, $BaFe_2O_4$ and Fe_3O_4 are formed. They are of spinel structure and have a high electrical resistivity. The electron vacancies inside them transform from an equilibrium position to another in the electric field, which need to remove the energy barriers and consequently drop behind the electromagnetic field. As a result, electromagnetic waves are absorbed by strong polarization relaxation.

Heat-treatment experiment of BFHMs with NaNO₃ is conducted to further improve microwave absorption properties, according to Literature [22]. The heat-treatment temperature is 1100 °C and the heating rate is 3 °C/min. After the temperature reaching to 1100 °C. the samples are held at that temperature for 4 h. Fig. 10 shows XRD patterns of BFHMs with NaNO3 after heat-treatment. And it is found that magnetoplumbite-type ferrite BaFe₁₂O₁₉ is obtained, as well as Fe₃O₄, Fe₂O₃, and Al₂O₃. Fig. 11 shows reflectivity of BFHMs with NaNO3 after heat-treatment. The minimum reflectivity is -14.7 dB at 9.5 GHz, and the frequency band lower than -10 dB is 7.8-11.2 GHz, with a bandwidth of 3.4 GHz. Compared with BaFe₂O₄, BaFe₁₂O₁₉ has a higher effective field of magnetocrystalline anisotropy. which results in a higher natural resonance frequency. When alternating magnetic field frequency of incident wave equals the frequency of effective field of magnetocrystalline anisotropy, natural resonance with great amplitude happens and massive electromagnetic waves are absorbed. This may be the reason for improvement of microwave absorption properties after heat-treatment.

4. Conclusions

BFHMs containing micro-nano tabular crystals have been prepared by self-reactive quenching technology with NaNO₃ foaming agent. Effect of NaNO₃ on the particle size, morphology, phase structure and microwave absorption properties is investigated.

(1) The average particle size of BFHMs is 28 μm, and the surface is relatively smooth without obvious crystals before adding NaNO₃. By adding NaNO₃, the average of particle size is 6 μm and micro-nano tabular crystals appear on the surface. BaFe₂O₄ and Fe₃O₄ with spinel structure are obtained in the phase component.

- (2) NaNO₃ foaming agent releases high quantity of gas and makes the droplets break into small liquid drops in the flame field. This is the main reason for decreasing of BFHMs' particle size. After adding NaNO₃, the melting point of agglomerate powders decreases, and the reactive mechanisms are improved. As a result, BFHMs with a uniform particle distribution are obtained. The decreasing particle size of droplets promotes the rate of heat dissipation, which is beneficial for the coagulation and crystallization. Therefore, micro-nano tabular crystals with a favorite grain growth appear on the surface of BFHMs.
- (3) The real part (ε') and imaginary part (ε'') of complex permittivity increase obviously after adding NaNO₃. The real part of complex permeability (μ') increases in 0.5–10.2 GHz, while decreases in 10.2-18 GHz. The imaginary part of complex permeability (μ'') increases in 0.5–18 GHz. In addition, the microwave absorption properties of BFHMs are improved in the whole frequency band. The minimum reflectivity decreases from -3 dB to -9.8 dB. Appearance of micro-nano tabular crystals, decreasing particle size of BFHMs and the formation of BaFe₂O₄ and Fe₃O₄ are main reasons for the improvement of microwave absorption properties. After BFHMs with NaNO₃ being heat-treated at 1100 °C for 4 h, magnetoplumbite-type ferrite BaFe₁₂O₁₉ is obtained and the microwave absorption properties are further improved. The minimum reflectivity is -14.7 dB at 9.5 GHz, and the frequency range lower than -10 dB is 7.8-11.2 GHz, with a bandwidth of 3.4 GHz.

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Appendix A

Equations

$$2\text{Al} + \text{BaO}_2 + 6\text{Fe}_2\text{O}_3 + \text{C} + 2\text{O}_2 \rightarrow \text{Al}_2\text{O}_3 + \text{BaFe}_{12}\text{O}_{19} + \text{CO}_2 \qquad (1)$$

$$R.L.(dB) = 20log_{10} \left| \frac{(Z_{in} - 1)}{(Z_{in} + 1)} \right|$$
(2)

$$Z_{\rm in} = \left(\frac{\mu_r}{\varepsilon_r}\right)^{1/2} \tanh\left[j\left(\frac{2\pi fd}{C}\right)\left(\frac{\mu_r}{\varepsilon_r}\right)^{1/2}\right]$$
(3)

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3 \tag{4}$$

$$2Fe + 3BaO_2 + 17Fe_2O_3 \rightarrow 3BaFe_{12}O_{19} \tag{5}$$

$$2\text{NaNO}_3 \rightarrow 2\text{NaNO}_2 + \text{O}_2 \uparrow (653 \text{ K}) \tag{6}$$

$$4NaNO_3 \rightarrow 2Na_2O + 2N_2\uparrow + 5O_2\uparrow (673 - 873 \text{ K}) \tag{7}$$

$$4NaNO_3 \rightarrow 2Na_2O + 4NO \uparrow + 3O_2 \uparrow (973 \text{ K}) \tag{8}$$

$$8NaNO_3 \to 4Na_2O + 4NO_2 \uparrow + 2N_2O + 5O_2 \uparrow (1048 - 1138 \text{ K})$$
 (9)

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