

Effect of mechanical activation and ferritization on the phase composition of W-type hexaferrites obtained by the method of self-propagating high-temperature synthesis

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Abstract. Hexagonal oxide W-type ferrimagnetic powders ($\text{BaCo}_{0.7}\text{Zn}_{1.3}\text{Fe}_{16}\text{O}_{27}$) are obtained by the method of self-propagating high-temperature synthesis (SHS) in combination with preliminary or further mechanochemical activation in a high-energy unit and ferritization. The data on the phase composition, structural parameters and fundamental magnetic properties of synthesized ferrimagnetic used to create effective absorbers of electromagnetic radiation in the range of natural ferrimagnetic resonance frequencies are presented. Dispersion of the SHS product is found to significantly affects the value of the effective constant of magnetic crystallographic anisotropy. To explain this fact, a model that considers the contribution to magnetic anisotropy from magnetoelastic interaction and a perturbed near-surface layer, which are additive, is used. SHS with further mechanical activation and fine grinding shows that the mechanical treatment of the SHS product in a high-energy unit (planetary mill) is a way of controlling the magnetic properties of oxide hexagonal ferrimagnetic and, in this sense, affects like chemical doping

1. Introduction

Oxide ferrimagnetic materials (ferrites) are widely used in radio engineering, radio electronics, computation engineering and other industries of developed countries. The area of their application is constantly expanding, and the production of products from ferrites is constantly growing. At the same time, the large-scale production of ferrites and ferrite products is based on classic furnace synthesis that is long and energy-consuming [1, 2].

In recent decades new methods have been developed for producing ferrites. These methods are based on self-propagating high-temperature synthesis (hereinafter, SHS) that is represented by the filtration combustion of a powder mixture of a metal and oxides of other elements in the atmosphere of reacting gases: oxygen or air [3, 4]. The SHS method uses the internal chemical energy of initial reagents and does not require significant consumption of energy in many cases. Manufacturing SHS processes fundamentally differ from traditional manufacturing processes with extreme conditions occurring in the combustion wave, where the reactive mixture converts into the desired final product with a maximum degree in a very short time at high temperatures.



The leading reaction in the synthesis of ferrites is the reactive combustion of iron in oxygen supplying through a porous medium that is one of the reagents. The main parameters that have an effect on filtration combustion, phase formation and the properties of final products are the ratio of components, porosity of the medium, dispersion of porous medium particles, and the gas pressure. These parameters, especially the amount of fuel in the exothermic mixture, determine the degree of conversion (phase formation), that is the chemical and phase composition, and structure and electrophysical properties of final products.

In addition to the mentioned above parameters, electric and magnetic fields, thermal effects and mechanical activation are used to control the process of self-propagating high-temperature synthesis. Electric and magnetic fields have non-thermal effects on combustion zones and post-processes and affect the kinetics of physical and chemical processes and, phase and structure formation during the synthesis and cooling of final products [5-10].

An effective way to control self-propagating high-temperature synthesis is to subject a powder mixture to mechanical activation (MA) which is usually used to stimulate solid phase reactions [11, 12]. MA is favorable for the initiation of SHS and significantly expands the number of systems capable of reacting in the combustion mode.

The main factors affecting chemical transformations in the reaction system during mechanical activation can be marked [12].

The kinetic conversion acceleration factor is related to the creation of a high defective structure with a large excess (absorbed) energy that reduces the activation barrier of chemical reactions and affects the rate of chemical transformations.

The structural conversion acceleration factor is related to the change in the structure of mixtures due to the dispersion of mixtures and the formation of mechanocomposites with a new interphase surface caused by the transport of material from one powder particle to another one. Further mechanical activation leads to the grinding of mechanocomposites, and the scale of heterogeneity which determines the characteristic mass transfer time of reagents to each other significantly reduces. Mechanocomposites are precursors of chemical reactions. They reduce temperature and increase the rate of chemical interactions.

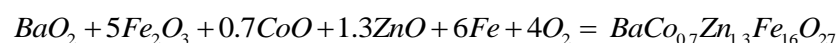
The temperature conversion acceleration factor is related to heat release of chemical reactions and dissipative heat release caused by the heating of grinding bodies, mill chamber walls and heterogeneous powder mixture due to their mechanical effect on each other.

Unfortunately, for ferrites that contains a high amount of oxygen and are doped with various elements necessary for the creation of new materials, the SHS method leads to the formation of a multi-phase product, the conversion of which into a single-phase product requires long thermal treatment.

The purpose of this work is to study the effect of preliminary (before SHS) and further (after SHS) mechanical activation, followed by ferritization on the phase composition of W-type hexaferrite $\text{BaCo}_{0.7}\text{Zn}_{1.3}\text{Fe}_{16}\text{O}_{27}$. This compound is characterized by a high magnitude of magnetic crystallographic anisotropy fields and can be used in devices based on the resonance of internal fields in the microwave range, as well as for the creation of radio absorbing coatings as a filler.

2. Experimental procedure

Synthesis of hexaferrite $\text{BaCo}_{0.7}\text{Zn}_{1.3}\text{Fe}_{16}\text{O}_{27}$ was conducted using a chemical reaction:



In this case, the oxidizing agent is oxygen which is contained in barium peroxide and supplied to the reaction mixture, as well as it is supplied by filtering the active gas from the external environment. As a result, filtration combustion takes place in oxygen that oxidizes free iron added to the mixture components. Thus, the mechanism of interaction of reagents combines the features of gasless and filtration combustion [13, 14]. Barium peroxide contains much more labile oxygen than oxides and

carbonates used in traditional production methods, so its use in ferrite formation reactions is more beneficial and prevents the presence of impurities, in particular carbon.

Barium peroxide BaO_2 , cobalt (II) oxide CoO , iron (III) oxide Fe_2O_3 , zinc (II) oxide ZnO and iron powder were used as initial materials for synthesis.

The powders of oxides and barium peroxide were dried in a vacuum oven at a temperature of 120°C for 4 hours, and then were weighted using a batch weighing scales and mixed by milling in a porcelain jar.

The preliminary and further mechanical activation (MA) of the powder mixture was conducted in air in a water-cooled planetary ball mill (60g). The volume of steel drums was 1000 cm^3 , and hardened steel balls with a diameter of $\sim 4\text{--}5\text{ mm}$ were used as grinding bodies. The ball-to-powder weight ratio was 20:1. The time of preliminary MA of the mixture was equal to 3 minutes, and the time of further MA was 10, 20, 40 minutes.

After MA, the mixture of components was placed into the reactor represented by a horizontal quartz tube, the both ends of which were sealed with metal lids with openings for supply and removal of reacting gas, as well as for introducing a thermocouple and an electrical coil to ignite the mixture. After placing the mixture of the initial porosity of 60–70% into the reactor, oxygen was passed through it, maintaining the specified pressure. The oxygen flow rate was measured using a rotameter, and the pressure was determined using a water manometer. For the selected synthesis conditions, the oxygen flow rate and the pressure of the reactor were $(0.6\text{--}0.8)\text{ m}^3/\text{h}$ and $(10.7\text{--}12.7)\text{ kPa}$, respectively. Ferritization was conducted in a muffle furnace in air at a temperature of 1250°C for 2 hours.

The X-ray diffraction and structure analysis of the samples obtained were carried out using a Shimadzu XRD 6000 powder diffractometer (CuK_α radiation). The phase composition and structural parameters of the phases revealed are determined using the Powder Cell 2.4 program. The size of the coherent-scattering regions (CSR) is calculated by the Sherrer's equation. The CSR are usually used for rough estimation of particle sizes.

Magnetic measurements included the study of magnetization curves in pulsed fields up to 7 kOe. The values of saturation magnetization M_s and field of magnetic crystallographic anisotropy H_a were calculated. The singular point method was used to determine anisotropy fields [15].

3. Results and discussion

Mechanical treatment of the mixture in the planetary mill for 1-3 min leads to the formation of agglomerates, while the specific surface area decreases from $3.9\text{ m}^2/\text{g}$ to $2.8\text{ m}^2/\text{g}$. With a further increase in the mechanical treatment time up to 15 minutes, the specific surface area remains almost unchanged.

The X-ray diffraction shows that the products synthesized in the combustion modes 1 and 2 consist of three phases: W-phase, M-phase and Fe_3O_4 , while the average size of coherent scattering regions is approximately 90 nm for the W-phase (Table 1).

Ferritization of the SHS product subjected to preliminary mechanical activation held at 1250°C for 2 h (mode 3) increases of the W-phase content to 96 vol.%, and the coherent scattering region increases to 450 nm. The lattice constants of the W-phase in the basal plane - a and along the hexagonal axis - c approximately correspond to the literature data.

The static magnetic properties of the CoZn-W phase obtained by the SHS method with preliminary mechanical activation at $T = 293\text{ K}$ and the Curie temperature are as follows: saturation magnetization is 360 Gs, effective anisotropy field is 2.35 kOe, and the Curie temperature is 625 K.

SHS with further mechanical activation and grinding (modes 4-6) forms a multiphase product, but increasing the time of mechanical activation, the content of the W-phase increases to 50 vol.%, and further ferritization is used to obtain a product with the phase content of up to 96% vol.% (modes 7-9).

The increased content of the CoZn-W phase with increasing the duration of mechanical activation and grinding of samples after the SHS stage is primarily due to the formation of nanomechanocomposites. It is known that mechanochemical transformation of phase diagrams of hexagonal ferrimagnetics occurs under such conditions [16, 17].

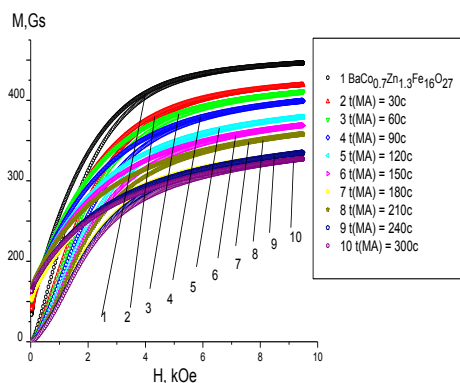
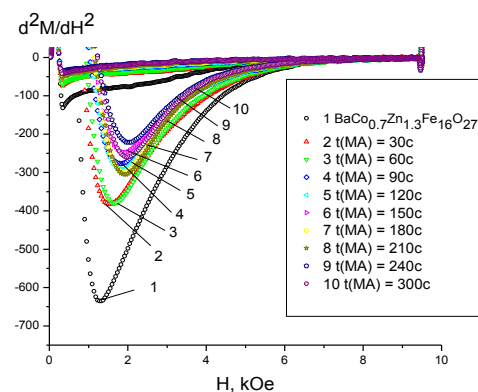
Table 1. X-ray diffraction analysis of SHS products synthesized in different modes of preliminary and further mechanical activation, followed by ferritization.

No	Processing mode of a reaction mixture	Content of phases in final product, (vol.%)		
		W-phase	M-phase	Fe ₃ O ₄
1	SHS	3	54	43
2	3 min MA + SHS	10	50	40
3	3 min MA + SHS + Ferritization	96	-	4
4	SHS + 10 min MA	27	1	72
5	SHS + 20 min MA	33	-	67
6	SHS + 40 min MA	50	25	25
7	SHS + 10 min MA + Ferritization	90	-	10
8	SHS + 20 min MA + Ferritization	90	-	10
9	SHS + 40 min MA + Ferritization	96	<1	3

In contrast to traditional ferrimagnetic synthesis methods, which involve high temperature sintering at the last stage, the final product, the CoZn-W phase, is formed not by synthesizing low-temperature phases and their subsequent decomposition, but mainly from the nanosized state [16, 17], while the synthesis temperature of a required phase noticeably reduces.

Thus, intensive mechanical activation and fine grinding in high-energy units leads to a significant increase in the kinetic and structural factors for accelerating a chemical reaction, and with further heating and ferritization, to a change in phase diagrams, synthesis temperature of a final product and its magnetic properties.

Figure 1 shows the saturation magnetization as a function of the magnitude of the field for the W-type hexaferrite BaCo_{0.7}Zn_{1.3}Fe₁₆O₂₇ obtained by the SHS method, followed by mechanical activation at different MA times.

**Figure 1** Saturation magnetization M_s as a function of the magnitude of the field of W-type hexaferrite BaCo_{0.7}Zn_{1.3}Fe₁₆O₂₇ obtained by the SHS method, followed by mechanical activation and ferritization**Figure 2** Second derivative (d^2M_s/dH^2) as a function of the magnitude of the field of SHS hexaferrite BaCo_{0.7}Zn_{1.3}Fe₁₆O₂₇ subjected to mechanical activation and ferritization

This plot shows that an increase in the time of mechanical activation leads to gradual increasing the residual magnetization and narrowing the hysteresis loop, which indicates an increase in the magnitudes of anisotropy field and coercive force. In this case, the saturation magnetization ($M_s = M_{H \rightarrow 0}$) decreases with increasing the duration of mechanical activation and grinding.

Figure 2 demonstrates the second derivative of the magnetization as a function of the value field for W-type SHS hexaferrite $\text{BaCo}_{0.7}\text{Zn}_{1.3}\text{Fe}_{16}\text{O}_{27}$ subjected to mechanical activation. It can be seen that increasing the time of mechanical activation, the minimum of the curve shifts towards the increase in the anisotropy field.

The data obtained can be explained as follows. Powders subjected to mechanical activation in high-energy mills contain energy that accumulates mainly in the surface layer of material in the form of lattice distortions and redistribution of cations. An increase in the magnitudes of anisotropy fields may be related to the change in the components of the effective magnetic anisotropy constant, each of which varies significantly with increasing the time of grinding and MA. There is a known anisotropy field changing model, according to which the effective constant of magnetic crystallographic anisotropy of ultrafine particles is presented in the form

$$K_{\text{eff}} = \left(1 - \frac{V_s}{V_v}\right) K_v + \left(\frac{V_s}{V_v}\right) K_s + K_\sigma + K_m, \quad (1)$$

Where K_v is the constant of magnetic crystallographic anisotropy of the unperturbed sample volume; K_s is the constant of magnetic anisotropy of the perturbed near-surface particle layer; K_σ is contribution to the constant of anisotropy of magnetoelastic interactions; K_m is contribution due to anisotropy of the shape of particles; V_s is the volume of the perturbed near-surface layer; V_v is the volume of the unperturbed part of the sample [17].

In addition, it should be noted that the role of magneto-elastic contribution to the magnitude of the effective anisotropy field increases for the materials with spin-orientation phase transitions.

Using $\text{BaCo}_{0.7}\text{Zn}_{1.3}\text{Fe}_{16}\text{O}_{27}$ hexaferrite, the process flow diagram was developed for the obtaining of oxide hexagonal ferrimagnets by the SHS method in combination with mechanical activation and further ferritization. The final product was a powder for radio absorbing coatings.

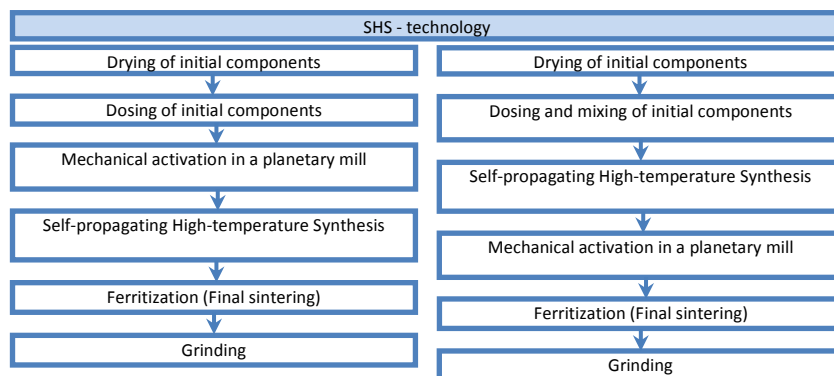


Figure 3 Process flow diagram for the obtaining of hexagonal oxide W-type ferrimagnets by the method SHS in combination with mechanical activation and ferritization.

The proposed new technological methods for the production of complex barium hexaferrites based on self-propagating high-temperature synthesis in combination with preliminary or subsequent mechanical activation and ferritization allow:

- reduce the number of technological operations (four);
- reduce energy and material costs of production by reducing the temperature and the final sintering time.

4. Conclusion

SHS in combination with preliminary or further mechanical activation and ferritization can be used to obtain barium hexaferrite powder with a high content of W-phase, enhanced magnetic resonant properties, as well as the main uniform magnetic properties.

The magnetic characteristics of W-type barium hexaferrite obtained by the method of self-propagating high-temperature synthesis with preliminary or further mechanical activation and final ferritization, were found to be close to the properties of analogues obtained by the traditional ceramic method. The temperature dependences of magnetic permeability and the Curie temperature are close, and the change in the magnetic crystallographic anisotropy field are probably caused by internal concentration inhomogeneities, in particular, by the difference in the distribution of magnetoactive ions Fe^{3+} and Co^{2+} in nonequivalent crystallographic lattice positions.

The new resource-saving methods were proposed for the obtaining of magnetic materials based on hexaferrites with a yield of 94-99%, using self-propagating high-temperature synthesis in combination with preliminary or further mechanochemical activation and ferritization. These new methods decrease the number of manufacturing operations and significantly reduce the energy consumption and production costs as compared with the ceramic method.

Notification

SHS - self-propagating high-temperature synthesis

MA - mechanical activation,

Powder Cell 2.4 program – a free powder pattern calculation program for single crystal data and refinement of experimental curves,

CSR - coherent-scattering regions

W-phase – $\text{BaCo}_{0.7}\text{Zn}_{1.3}\text{Fe}_{16}\text{O}_{27}$ hexaferrite,

M-phase - $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite,

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