Radiation-thermal synthesis of W-type hexaferrites

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Abstract. The results of investigations of the phase composition, structural parameters, static and dynamic magnetic properties of $BaCo_{0.7}Zn_{1.3}Fe_{16}O_{27}$ hexaferrites obtained by the method of self-propagation high-temperature synthesis in combination with mechanochemical activation and radiation-thermal post-sintering are presented. The prospects of the proposed energy-saving approach for the production of ferrite ceramics with a hexagonal structure is shown.

1. Introduction

Oxide ferromagnetic materials (ferrites) are widely used in various fields of modern technology and medicine. Industrial production of ferrites is based on the conventional multi-operational ceramic technology which involves a number of long-running operations. This technology has been used in the world practice for many decades, and its development is associated with optimization by varying the composition and processing method of the charge [1].

In the last decades, new methods of ferrite synthesis have been proposed based on self-propagating high-temperature synthesis (SHS) in the regime of filtration combustion of the mixture of powders comprising iron and oxide of some elements in the atmosphere of reacting gases: oxygen or air [2]. This method utilizes the internal chemical energy of the initial reagents, and is organized most favorably from the thermal viewpoint. In the process of obtaining ferrites, it substitutes the most important operation – ferritization – which in the conventional method of sintering is very long and proceeds at high temperatures.

The SHS method allows various cubic ferrites and hexagonal ferrites with M-phase composition to be synthesized [3]. However, the yield of the end product of synthesis of complex hexagonal barium and strontium ferrites with W-, Y-, and Z-compositions is low. In this regard, new resource-saving methods of synthesis of magnetic materials based on complex hexaferrites with W-composition are suggested with the SHS, mechanochemical pre- or post-activation, and final ferritization in electric furnaces [3, 4] that in comparison with the conventional methods allow the energy and material expenses for the production process to be reduced significantly. It is of interest to substitute the final ferritization operation in an electric furnace by radiation-thermal sintering (RTS) upon exposure to an electron beam. This process sharply accelerates ion diffusion due to joint thermal and radiation influence on the material and as a result, improves magnetic properties of the synthesized materials [5].

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[1] Work carried out in the framework of the increase of competitiveness of Tomsk State University

The present work is aimed at investigation of the influence of radiation-thermal sintering on the phase composition, structural parameters, and magnetic properties of the multiphase product based on barium hexaferrite with W-composition obtained by the method of self-propagating high-temperature synthesis.

2. Preparation of samples

To synthesize barium hexaferrite with W-composition, we used the chemical reaction

$$BaO_2 + 5Fe_2O_3 + 0.7CoO + 1.3ZnO + 6Fe + 4O_2 = BaCo_{0.7}Zn_{1.3}Fe_{16}O_{27} (Co_{0.7}Zn_{1.3}W).$$
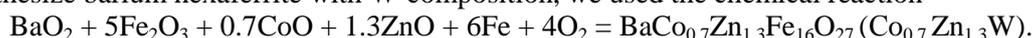
Barium hexaferrite with W-type composition was synthesized in following regimes:

- No 1: SHS,
- No 2: SHS with mechanical activation of the initial charge for 3 min and the grinding body mass to the powder mass in the ratio 20:1 that corresponded to a milling process power of 60g (MA3+SHS),
- No 3: SHS with mechanical post-activation of the product for 40 min for the grinding body mass to the powder mass in the ratio 10:1 that corresponded to a milling process power of 40g (SHS+MA40).

Radiation-thermal sintering of samples was carried out at the Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences (Novosibirsk) using an ILU-6 pulsed electron accelerator [6]. Sample preparation technique is described in detail in [7].

3. The results of x-ray researches

The x-ray analysis was performed using a SHIMADZU XRD-6000 polycrystalline diffractometer. For a qualitative analysis of the phase composition, the computer database of x-ray powder diffractometry or PDF4+ of the International Center of Diffraction Data (ICDD, Denver, USA) was used. The quantitative analysis of the phase composition and the refinement of the structural parameters of phases being detected were performed using the program Powder Cell 2.4 for full profile analysis. Results of x-ray structural analysis of ferrite ceramic samples after RTS are presented in table 1.

Table 1. Influence of RTS regimes of the SHS product on the phase composition and structural parameters of barium hexaferrite.

Sample	Phase composition of the product, vol. %			Mean W-phase crystallite size, nm	$\Delta d/d \cdot 10^3$
	W-phase	Fe_3O_4	Fe_2O_3		
No 1 + RTS at 1050°C	45	50	5	67	0.6
No 1 + RTS at 1100°C	54	40	6	46	1.3
No 1 + RTS at 1200°C	93	7	–	170	1.9
No 1 + RTS at 1250°C	98.4	1.4	0.2	>500	0.2
No 2 + RTS at 1050°C	39	54	6	100	0.9
No 2 + RTS at 1100°C	53	46	1	140	0.7
No 2 + RTS at 1200°C	89	11	–	>300	0.2
No 2 + RTS at 1250°C	54	40	6	400	0.2
No 3 + RTS at 1050°C	64	28	8	110	0.3
No 3 + RTS at 1100°C	53	41	6	135	0.7
No 3 + RTS at 1200°C	88	12	0	140	0.4
No 3 + RTS at 1250°C	93	7	–	>300	0.2

From table 1 it follows that the yield of the target (W) phase at RTS temperatures of 1200–1250°C is about 90–98 vol.%. Moreover, sufficiently high internal elastic microstresses proportional to the relative change in interplanar distances $\Delta d/d$ remain for all compositions. The mean microcrystallite size estimated on the size of coherent scattering regions (CSR) increases with RTS temperature.

4. The results of scanning electron microscopy

The morphological characteristics of hexagonal ferrimagnetic materials synthesized by a combination of SHS and RTS methods were analyzed using a Phylips 515 electron microscope with different magnifications. Results of the scanning microscopy for some samples are shown in figure 1.
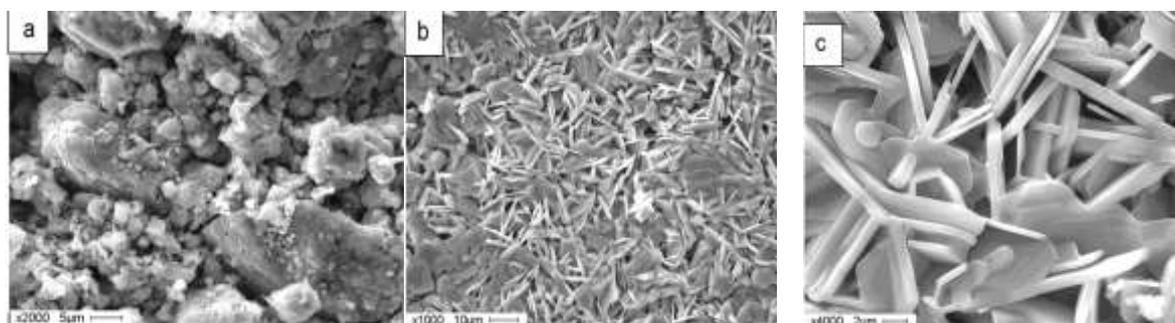

Figure 1. Scanning microscopy: *a*) No 1 + RTS at 1100°C; *b*) and *c*) No 1 + RTS at 1250°C with indicated magnifications.

The morphology of samples obtained at RTS temperatures of 1100–1200°C was characterized by the presence of grains having quasi-spherical shapes characteristic for cubic ferrospinels along with particles shaped as hexagonal plates whose linear size and thickness were in the aspect ratio $a/c \approx 10$ typical for ferrites with hexagonal composition. An increase in the RTS temperature to 1250°C caused a significant change of the morphology of ferrite ceramics with hexagonal structure. Quasi-spherical particles practically disappeared, and the aspect ratio a/c of hexaferrite crystallites considerably increased (to ≈ 20).

5. Results of the study of the magnetization curves

The static magnetic characteristics of ferrite ceramic samples, including the specific saturation magnetization and effective magnetic anisotropy field, were investigated using an automated complex intended for investigation of the magnetic characteristics in pulsed magnetic fields. The measurement procedure was described in detail in [8]. The main magnetic characteristics: the saturation magnetization M_S and the effective anisotropy fields $H_{a\,eff}$ for samples with maximum content of the $Co_{0.7}Zn_{1.3}W$ target phase are presented in table 2.

Table 2. Results of static measurements of the magnetic parameters of samples.

Sample	M_S, Gs	$H_{a\,eff}$, kOe
No 1 + RTS at 1200°C	493	2.03
No 2 + RTS at 1200°C	487	2.23
No 3 + RTS at 1200°C	482	2.41
No 1 + RTS at 1250°C	484	2.22
No 2 + RTS at 1250°C	487	2.43
No 3 + RTS at 1250°C	447	1.89

6. The study of the ferromagnetic resonance spectra

The ferromagnetic resonance (FMR) spectra were measured by the standard waveguide transmission technique in the frequency range 26–37 GHz using an automated radio spectroscope built on the base of a R2-65 analog scalar circuit analyzer. To investigate the FMR, hexaferrite powders were charged into quartz tubes with inner diameter of 0.7 mm and length of 10 mm. The density of powder samples was identical and equal to ≈ 2.9 g/cm^3. The spectra were processed using the procedure described in [9, 10].

Investigations of the ferromagnetic resonance spectra of powder and polycrystalline oxide ferrimagnetic materials with hexagonal crystal structure allowed a number of magnetic parameters of

these materials important for practical applications to be determined [9]. Such as: magnitude and sign of magnetocrystalline anisotropy fields (H_{ai}); saturation magnetization (M_S); value of the gyromagnetic ratio $\gamma = ge/2mc$, where g is the effective g-factor of the examined material, e is the electron charge, m is the electron mass, and c is the velocity of light.

Table 3 presents the gyromagnetic ratios, anisotropy fields, and saturation magnetizations of the synthesized materials. The parameters $\gamma/2\pi$ and H_{a1} were estimated from a comparison of the positions of maxima for theoretical and experimental curves of ferromagnetic resonance at different frequencies.

Table 3. Magnetic parameters of materials measured by the FMR method

Sample	$\gamma/2\pi$, GHz/kOe	H_{a1}, kOe	M_S, Gs
No 1 + RTS at 1200°C	2.56	–0.8	440
No 2 + RTS at 1200°C	2.62	–1.5	520
No 3 + RTS at 1200°C	2.62	–1.5	525
No 1 + RTS at 1250°C	2.58	–1.0	490
No 2 + RTS at 1250°C	2.58	–1.0	480
No 3 + RTS at 1250°C	2.58	–1.0	450

Values of the saturation magnetization M_S given in table 3 are close to M_S values estimated from the measured magnetization curves (see table 2). The difference between M_S values measured by different methods did not exceed 10%. We note that the negative sign of the anisotropy field H_{a1} demonstrates that the anisotropy of easy magnetization type is observed for these materials. The measured fields are close to those obtained from analysis of magnetization curves in pulsed fields and to the literature data for these materials synthesized by the conventional ceramic technology [10].

In the first series of samples (RTS at a temperature of 1200°C), the mechanical activation leads to an increase $\gamma/2\pi$ and H_{a1} values estimated from the FMR experiment. Processing of the data of experiments for samples of the second series demonstrated that $\gamma/2\pi$ and H_{a1} values for these materials coincide within the limits of the experimental errors.

7. Spectra of permittivity and permeability of composites based on a sample No 3 + RTS at 1250°C

This section presents the results of measurements of the complex permittivity ($\varepsilon = \varepsilon' - i\varepsilon''$), permeability ($\mu = \mu' - i\mu''$) spectra of composites made on the basis of the sample No 3 + RTS at 1250°C. Investigations were carried out on the equipment Center of collective use "Center of radio physical measurements, diagnostics and research parameters of natural and artificial materials» [11].

To prepare composite materials samples of No 3 + RTS at 1250°C were ground in a ball mill to a particle size less than 100 microns. As the matrix in the manufacture of composite samples used urethane alkyd varnish UNICA SUPER. Mass fraction of ferrite in the composites was 50 % (sample H-50) and 79.5% (sample H-79.5).

Since all methods of measurement of spectra complex permittivity and permeability are not free of systematic and random error of measurement the verification of the experimental spectra $\mu = \mu' - i\mu''$ using the Cramers-Kronig dispersion relations was carried out. The method was developed by us in [12]. During the verification of the spectra is necessary to know the magnitude of the initial magnetic permeability μ_0. It was determined with using a precision LCR meter Agilent E4980A on the same toroidal samples, which are used in the waveguide method measurements of complex permittivity and permeability. The measured values of μ_0 samples are shown in table 4.

Table 4. The initial magnetic permeability μ_0 and the permittivity of composites

Sample	μ_0, rel. units	ε', rel. units	ε'', rel. units
H-50	2.3 ± 0.1	7.3 ± 0.1	0.9 ± 0.1
H-79.5	3.2 ± 0.1	9.1 ± 0.1	2.5 ± 0.1

Measurements permittivity spectra of these materials in the frequency range $0.01 \div 12$ GHz shown that an appreciable frequency dependence of the $\varepsilon = \varepsilon' - i\varepsilon''$ in this range is absent. Table 4 shows the

average value over the frequency range of the real and imaginary parts of the permittivity of the composite materials. According to table 4, the increase in concentration of the magnetic fraction in the composite from 50 to 79.5 wt. % most significantly affected on the value of ε''. It has been increased by 64 %, whereas μ_0 at 28 % and ε' at 20 %.

The spectra of the permeability of composite materials investigated are presented in figure 2.
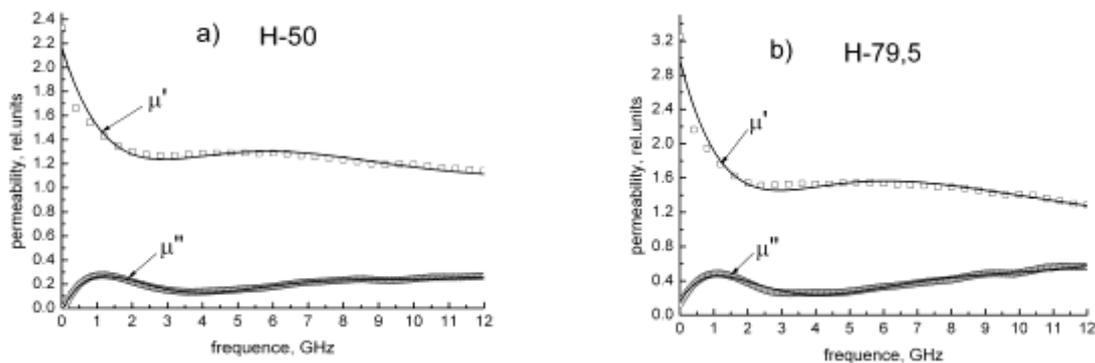

Figure 2. Spectra of permeability composites: *a*) sample H-50, *b*) sample H-79.5. Points - experiment, the line - the results of processing of the spectra by the method of [12].

It is seen that the spectra of the imaginary part of permeability of both materials present a maximum near the frequency of 1 GHz, due to oscillations of the domain boundaries. With further increase of frequency we observed growth of losses due to natural ferromagnetic resonance (NFMR) in the presence of a domain structure. Similar behavior of the permeability spectrum was observed in [13] for polycrystalline hexaferrites $Co_{2-x} Zn_xW$ system with close to $x = 1.3$ composition. The essential differences spectrum of $\mu''(f)$ powder composite materials from polycrystalline is higher bandwidth of NFMR region. With increasing concentration the magnetic losses in NFMR region significantly increased.

8. The study of radar absorbing properties of the composite H-79.5

Theoretical analysis and experimental study of radar absorbing properties of materials are usually carried out for the simplest case of normal incidence of a plane electromagnetic wave (EMW) on a magnetodielectrics (MD) layer. Permeability (μ) and permittivity (ε) of the layer are considered as complex scalar quantities. For reduction of radar signature a model of MD layer disposed on the metal surface is used. Expression for the reflection coefficient (R) for located on the metal plate layer of MD has the form [14]:

$$R = [\rho - \exp(-2i\gamma d)] / [1 - \rho \exp(-2i\gamma d)]$$

(1)

Here: $\rho = (Z-1)/(Z+1)$ − reflection coefficient from the front edge of MD. $Z = \sqrt{\mu/\varepsilon}$ − wave impedance. $\gamma = k_0\sqrt{\varepsilon\mu}$ − EMW propagation constant in MD. $k_0 = \omega/c$ − the wave number of free space. $\omega = 2\pi f$ − circular frequency of the EMW. c − speed of light. d − thickness of the layer. $i = \sqrt{-1}$.

The study of radar absorbing properties have been conducted on the composite H-79.5 with different thicknesses of MD layer. The results of experimental studies and calculations of the reflection coefficient $|R|^2$ from the measured permeability and permittivity spectra are shown in figure 3. Points – experimental date, solid lines - calculation by formula (1).
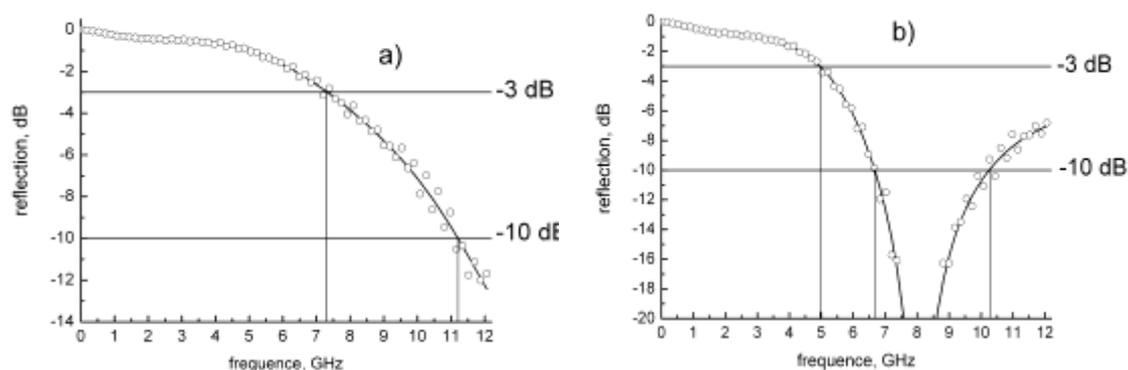
Figure 3. The frequency dependence of the reflection coefficients of of the absorber layers: *a*) – composite H-79.5, *d* = 1.5 mm thick, *b*) – composite H-79.5, *d* = 2.5 mm thick. Points – experiment, line – calculation.

From the figure 3a it is seen that for a coating thickness of *d* = 1.5 mm reflectance smaller –3 dB is observed at frequencies above 7.3 GHz and lower then –10 dB at frequencies more than 11.2 GHz. The increase in coating thickness up to *d* = 2.5 mm (figure 3b) leads to a shift in the reflection minimum to lower frequency region. Reflectance less than –3 dB, begins with a frequency of 5 GHz and $|R|^2 < -10$ dB in the frequency band 6.7 ÷ 10.3 GHz. Results in figure 3 show that there is good agreement between measured and calculated from the spectra of μ and ε reflection coefficients.

9. Conclusion

Thus, the technology combining SHS, mechanical activation, and radiation-thermal sintering allows complex multicomponent ferromagnetic materials with hexagonal crystal structure to be synthesized and magnetic characteristics no worse than and in some cases even exceeding the corresponding characteristics of samples synthesized by the conventional ceramic technology. An advantage of the suggested technology is a significant decrease of the time of synthesis and energy consumption.

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