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Structural and Magnetic Properties of SHS-Produced Multiphase W-Type Hexaferrites: Influence of Radiation-Thermal Treatment

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Abstract—Characterized were phase composition, structural parameters, magnetic parameters, and microwave absorption properties of $BaCo_{0.7}Zn_{1.3}Fe_{16}O_{27}$ hexaferrites produced by a method combining SHS, mechanical activation, and radiation-thermal treatment. The suggested process takes advantage of its lower time and energy consumption.

Keywords: SHS, mechanochemical activation, radiation-thermal treatment, hexaferrites, ferromagnetic resonance, magnetic permeability spectra, radar absorbing properties

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INTRODUCTION

Over the past decades, several methods for synthesis of ferrites have been suggested, including SHS method [1]. In order to improve the yield of hexagonal complex ferrites with a W-type structure, new resource-saving methods combining SHS with mechanical activation and heat treatment in a furnace have been suggested for synthesis of such materials [2]. It seemed interesting to replace the final thermal treatment in a furnace by radiation-thermal treatment (RTT) with an electron beam. Moreover, RTT could also be expected to improve the magnetic properties of synthesized materials [3].

In this work, we investigated the influence of RTT on phase composition, structural parameters, and magnetic properties of SHS-produced barium hexaferrites with a W-type structure.

EXPERIMENTAL

W-type barium hexaferrites were synthesized by the following scheme:

$$BaO_2 + 5Fe_2O_3 + 0.7CoO + 1.3ZnO + 6Fe + 4O_2 \rightarrow BaCo_{0.7}Zn_{1.3}Fe_{16}O_{27}\ (Co_{0.7}Zn_{1.3}W).$$

The commercial powders of BaO_2, Fe_2O_3, CoO, ZnO, and Fe were used as raw materials. The oxide powders were dried in a vacuum oven at 60–70°C for 2–3 h. The weighed amounts of the reagents were mixed by grinding in a porcelain mortar, placed into a horizontal quartz tube (tightly closed from both ends by metal caps with holes for input and output of gas reactant), and ignited with an electrically heated coil in a flow of oxygen gas maintained at some preset pressure. In our experiments, the oxygen flow rate was 0.6–0.8 m^3/h at pressures of 10.7–12.7 kPa.

Mechanical activation (MA) of powders was carried out in a planetary ball mill with water cooling in atmospheric air.

W-type barium hexaferrites in question were synthesized in the following three processing modes:

Process **I**: SHS in non-activated mixtures

Process **II**: SHS in mixtures activated for 3 min (ball/mill ratio 20 : 1, $a = 60\ g$)

Process **III**: SHS in mixtures activated for 40 min (ball/mill ratio 10 : 1, $a = 40\ g$)

Radiation-thermal treatment (RTT) of SHS-produced ferrites was carried out as described in [4]. Synthesized materials were characterized by XRD (Shimadzu XRD-6000 diffractometer, ICDD database, Powder Cell 2.4 software) and SEM (Philips 515 microscope).

RESULTS AND DISCUSSION

Table 1 illustrates the influence of RTT on phase composition and structural parameters of synthesized $Co_{0.7}Zn_{1.3}W$ hexaferrites. With increasing RTT temperature (from 1100 to 1250°C) the W-phase content of product is seen to grow for the samples prepared in processes **I** and **III** and to decrease in case of process **II** (accompanied by formation of Fe_3O_4 and Fe_2O_3).

Table 1. Influence of RTT on phase composition and structural parameters of $Co_{0.7}Zn_{1.3}W$ hexaferrite

Process	Phase composition, vol %				L, nm	$(\Delta d/d) \times 10^3$
	W-phase	Fe_3O_4	Fe_2O_3	M-phase		
I	9	58	12	21	40	1.8
I + RTT at 1100°C	54	40	6		46	1.3
I + RTT at 1200°C	93	7	–		170	1.9
I + RTT at 1250°C	98	1	<1		>500	0.2
II	5	64	4	27	31	2.3
II + RTT at 1100°C	53	46	1		140	0.7
II + RTT at 1200°C	89	11	–		>300	0.2
II + RTT at 1250°C	54	40	6		400	0.2
III	1	85	2	12	10	11.0
III + RTT at 1100°C	53	41	6		135	0.7
III + RTT at 1200°C	88	12	0		140	0.4
III + RTT at 1250°C	93	7	–		>300	0.2

Moreover, high internal elastic strains (proportional to $\Delta d/d$) remained practically intact for all samples. The mean size (L) of W crystallites is seen to grow with increasing RTT temperature.

The morphological features of SHS-produced hexagonal hexaferriters and then subjected to RTT are depicted in Fig. 1. The quasi-spherical grains typical of cubic ferrospinels are seen to co-exist with hexagonal platelets with the aspect ratio $a/c \approx 10$ typical of hexagonal ferrites. An increase in RTT temperature led to significant changes in the morphology of hexagonal ferrite ceramics: the quasi-spherical particles disappeared and the aspect ratio of hexaferrite crystallites markedly increased (to around 20).

Ferromagnetic resonance (FMR) spectra in the frequency range 26–37 GHz were taken by using standard waveguide transmission technique [5] and then processed as described in [6]. Thus determined values of gyromagnetic ratio $\gamma = ge/2mc$, field anisotropy H_{a1}, and saturation magnetization M_s are presented in Table 2. The negative sign at H_{a1} is indicative of the easy-plane anisotropy of these materials. The measured fields are close to those of materials synthesized by conventional ceramic technology [6]. In case of **I** + RTT at 1200°C processing, MA is seen (Table 2) to increase the values of $\gamma/2\pi$ and H_{a1}. In case of **II** + RTT at 1200°C processing, MA had little or no influence on the measured $\gamma/2\pi$ and H_{a1} values.

Comparison of Tables 1 and 2 shows that the values of $\gamma/2\pi$, H_{a1}, and M_s are affected by the amount of hexagonal W-type and spinel Fe_3O_4 phases only slightly, apparently because of small difference between the magnetic parameters of these phases [7]. In our opinion, the observed differences in the magnetic parameters are due to different size of the W-type and spinel particles.

We also measured the complex permittivity ($\varepsilon = \varepsilon' - i\varepsilon''$), permeability ($\mu = \mu' - i\mu''$), and radar absorbing properties of the composites prepared through the **III** + RTT at 1250°C process. Thus prepared materials were ground in a ball mill to a particle size of below 100 μm and embedded into a matrix of urethane alkyd varnish UNICA SUPER in an amount of 50 (H-50 samples) or 79.5 wt % (H-79.5 samples).

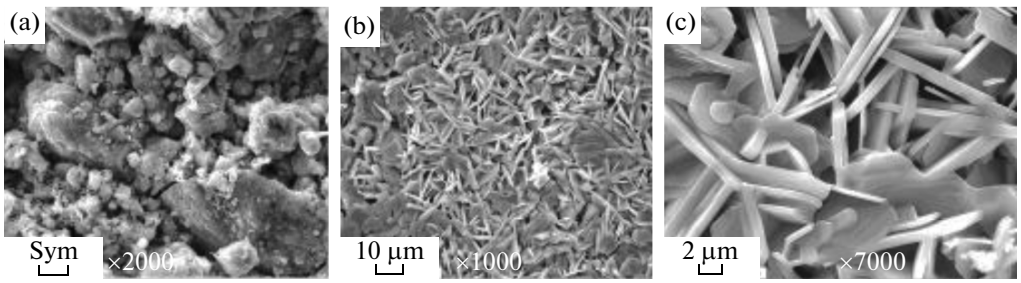

Fig. 1. SEM images of the ferrites produced in processes **I** + RTT at 1100°C (a) and **I** + RTT at 1250°C (b), (c).

Table 2. Magnetic parameters of synthesized materials

Process	$\gamma/2\pi$, GHz/kOe	H_{a1}, kOe	M_s, Gs
I + RTT at 1200°C	2.56	−0.8	440
II + RTT at 1200°C	2.62	−1.5	520
III + RTT at 1200°C	2.62	−1.5	525
I + RTT at 1250°C	2.58	−1.0	490
II + RTT at 1250°C	2.58	−1.0	480
III + RTT at 1250°C	2.58	−1.0	450

The magnetic permeability spectra (Fig. 2) were obtained by using a method suggested by us previously [8]. This technique requires knowledge of the initial magnetic permeability μ_0. The measured values of μ_0 (Agilent E4980A LCR meter) are also presented in Table 3. A maximum of μ'' around $f = 1$ GHz can be associated with oscillations of the domain boundaries. Subsequent increase in losses with increasing f is due to natural ferromagnetic resonance (NFMR) in the presence of a domain structure. Similar behavior of the permeability spectrum was observed [9] for polycrystalline hexaferrites $Co_{2-x}Zn_xW$ with x close to 1.3. The essential difference between the $\mu''(f)$ spectra for powder composites and polycrystalline material is a larger width of the NFMR region. With increasing x, the magnetic losses in the NFMR region markedly grew.

The radar absorbing properties were measured for composite H-79.5 with a different thickness (d) of radar-absorbing layer. The results are presented in Fig. 3. As follows from Fig. 3a, for the coating with $d = 1.5$ mm reflectance $|R|^2$ is below −3 dB for $f > 7.3$ GHz and below −10 dB for $f > 11.2$ GHz. In case of $d = 2.5$ mm (Fig. 3b), the reflection minimum is seen to shift toward lower frequencies. Here the reflectance below −3 dB is observed at $f = 5$ GHz and below −10 dB, for

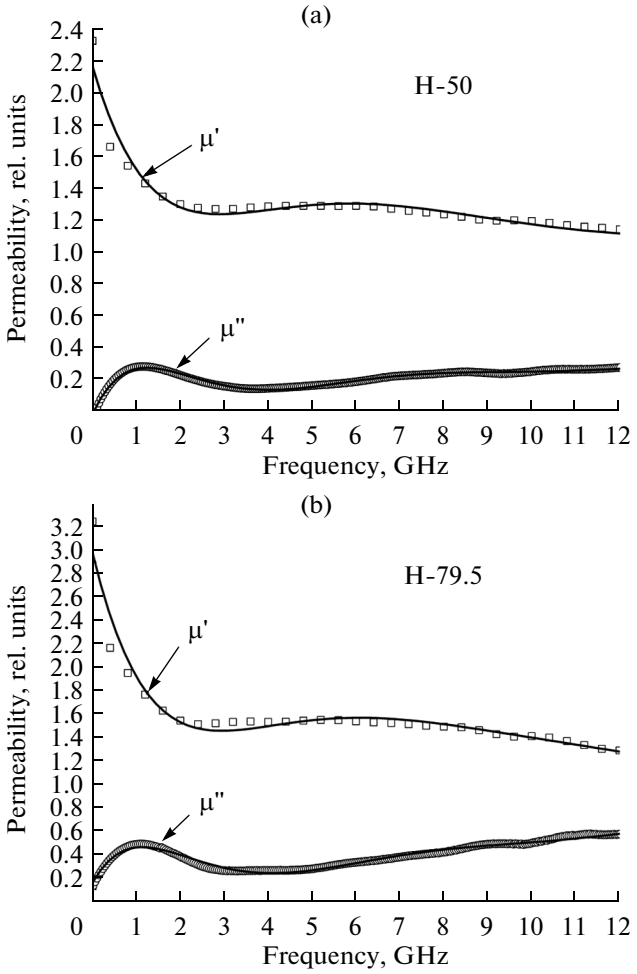

Fig. 2. Magnetic permeability spectra of composites H-50 (a) and H-79.5 (b): data points, measured; solid lines, calculated.

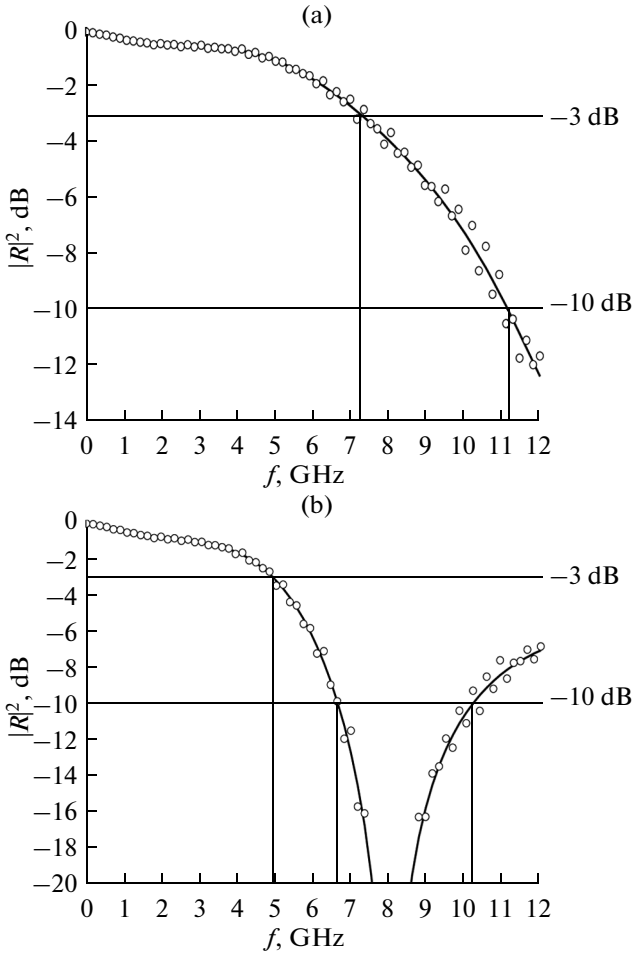

Fig. 3. Microwave reflectance $|R|^2$ as a function of f for H-79.5 layers with thickness $d = 1.5$ (a) and 2.5 mm (b): data points, measured; solid lines, calculated using the measured values of μ and ε.

Table 3. The permittivity of composites H-50 and H-79.5

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

f = 6.7–10.3 GHz. The results presented in Fig. 3 also demonstrate good agreement between the directly measured $|R|^2$ values and those calculated from the measured values of μ and ε.

CONCLUSIONS

The process combining SHS, mechanical activation, and radiation-thermal treatment can be readily used to fabricate complex multicomponent ferromagnetic materials whose magnetic properties are not deteriorating those of conventionally produced ceramics. The suggested process takes advantage of its lower time and energy consumption.

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REFERENCES

1. Komarov, A.V., Nersesyan, M.D., Avakian, P.B., and Merzhanov, A.G., Self-propagating high-temperature synthesis of ferrites, *Int. J. Self-Propag. High-Temp. Synth.*, 1993, vol. 2, no. 3, pp. 239–246.
2. Itin, V.I., Kirdyashkin, A.I., Minin, R.V., Gabbasov, R.M., and Naiden, E.P., Self-propagating high-temperature synthesis of hexagonal ferrimagnetic oxide with a W-type structure, *Izv. Vyssh. Uchebn. Zaved., Tsvet. Metall.*, 2006, no. 5, pp. 83–88.
3. Vereshchagin, V.I., Pletnev, P.M., Surzhikov, A.P., Fedorov, V.E., and Rogov, I.I., *Funktsional'naya keramika* (Functional Ceramics), Novosibirsk: Izd. Inst. Inorg. Chem. Sib. Otd. RAN, 2004.
4. Naiden, E.P., Zhuravlev, V.A., Minin, R.V., and Itin, V.I., Influence of radiation-thermal treatment on phase composition and structural parameters of the SHS product based on W-type hexaferrite, *Russ. Phys. J.*, 2013, vol. 56, no. 6, pp, 674–680.
5. Naiden, E.P., Zhuravlev, V.A., Itin, V.I., Minin, R.V., Suslyaev, V.I., and Dotsenko, O.A., Structural and static and dynamic magnetic properties of $Sr(Co_xTi_x)Fe_{12-2x}O_{19}$ hexaferrites produced by self-propagating high-temperature synthesis, *Russ. Phys. J.*, 2013, vol. 55, no. 8, pp. 869–876.
6. Zhuravlev, V.A., Ferromagnetic resonance in the polycrystalline hexagonal ferrites $Co_{2-x}Zn_xW$, *Phys. Solid State*, 1999, vol. 41, no. 6, pp. 956–959.
7. Smith, J. and Wijn, H.P.J., *Ferrites*, New York: Wiley, 1959.
8. Zhuravlev, V.A. and Suslyaev, V.I., Analysis and correction of the magnetic permeability spectra of $Ba_3Co_2Fe_{24}O_{41}$ hexaferrite by using Kramers–Kronig relations, *Russ. Phys. J*, 2006, vol. 49, no. 8, pp. 840–846.
9. Zhuravlev, V.A. and Suslyaev, V.I., Analysis of microwave magnetic permeability spectra of ferrites with hexagonal structure, *Russ. Phys. J.*, 2006, vol. 49, no. 9, pp. 1032–1037.

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