Методом низькотемпературної сумісно обпалюваної кераміки (LTCC – Low Temperature Co-fired Ceramics) отримані зразки ізотропних і анізотропних полікристалічних гексаферритов $BaFe_{12}O_{19}$ і $SrFe_{12}O_{19}$ для підкладок надмініатюрних мікросмужкових феритових розв'язуючих приладів короткохвильової частини міліметрового діапазонів довжин хвиль. Досягнуто ущільнення зразків при 900 °C в процесі спікання з додаванням невеликої кількості Bi_2O_3–B_2O_3–SiO_2–ZnO (BBSZ)

Ключові слова: гексагональний ферит, LTCC-технологія, мікроструктура, реакційні скла, густина

Методом низкотемпературной совместно обжигаемой керамики (LTCC – Low Temperature Co-fired Ceramics) получены образцы изотропных и анизотропных поликристаллических гексаферритов $BaFe_{12}O_{19}$ и $SrFe_{12}O_{19}$ для подложек сверхминиатюрных микрополосковых ферритовых развязывающих приборов коротковолновой части миллиметрового диапазонов длин волн. Достигнуто уплотнение образцов при 900 °C в процессе спекания с добавлением небольшого количества Bi_2O_3–B_2O_3–SiO_2–ZnO (BBSZ)

Ключевые слова: гексагональный феррит, LTCC-технология, микроструктура, реакционные стекла, плотность

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APPLYING THE LTCC-TECHNOLOGY TO OBTAIN HEXAFERRITES FOR BASE LAYERS OF MICROSTRIP SHF DEVICES

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1. Introduction

The promising low temperature co-fired ceramics (LTCC) – hexaferrites – is of much interest for high-frequency applications such as phase switches, circulators, antenna and wireless technologies for miniature electronic modules of the next generation. The rapid development of contemporary communication systems such as mobile communications and satellite connection requires miniaturization of SHF-components. To decrease the dimensions of SHF-devices, it is necessary to examine multilayer devices based on the low-temperature co-fired ceramics (LTCC), which consist of alternating ferrites and internal metal electrodes. As a rule, silver (Ag) is used as the internal metal electrode in multilayer devices because of its low losses and low electrical resistance at high frequencies [1, 2]. Since the melting point of Ag is 961 °C, it is necessary to design the LTCC materials that have sintering temperature about 900 °C, in order to avoid diffusion of Ag in ferrites.

Hexaferrites are usually obtained by the classic ceramic technology [3, 4] at high temperatures of sintering to 1350 °C, which are not suitable for the LTCC technology.

Development of the LTCC magnetic materials has a trend towards the use of a small quantity of additives and glass-ceramic systems, including softening glasses and magnetic ceramics with a high melting point. Typical additive for the low-temperature sintered hexaferrites, prepared by the low-cost method of mixing with the oxide, is Bi_2O_3. It is also possible to add lithium borosilicate glass or B_2O_3–Sb_2O_3. The basic problem of the low-temperature fired polycrystalline magnetic phases, such as $BaFe_{12}O_{19}$, is high porosity. Due to the high content of nonmagnetic phases (>10 % by volume), for example, glass or pores, the phase permeabilities are sharply reduced.

In the present work we developed a new method, which solves the problem of using hexaferrites of the M type as the LTCC base layers of the subminiature microstrip ferrite untying instruments of the short-wave part of the millimeter wavelength ranges. The LTCC technology makes it possible to simultaneously reach compression of the samples below 900 °C using the process of sintering hexaferrites with the addition of a small amount of reaction glasses that are based on Bi–B–Zn–Si–O (BBSZ).

2. Literature review and problem statement

Multilayer devices based on the low temperature co-fired ceramics (LTCC), prepared from the alternating layers of ceramics and internal electrode, were widely examined for the miniaturization of devices [5–7]. Silver (Ag), as a rule, is used as the internal metal electrode in the LTCC multilayer devices because of its low losses and low electric resistance at high frequencies. But the melting point of Ag is 961 °C only, which is, accordingly, low.

As one of the important SHF magnetic materials, barium ferrite is widely used in the antennas and wireless connection owing to its high saturization magnetization, large magnetic crystalline anisotropy and corresponding width of the line of ferromagnetic resonance [6–8]. Unfortunately, the high temperature of sintering about 1000 °C is required frequently for barium hexaferrite, in order to form uniform crystal structure. For example, Mochsen obtained quality crystalline $BaFe_{12}O_{19}$ at the annealing temperature of 1200 °C [8]. Quasi-mono-crystalline barium hexaferrites were produced at 1280 °C by Lue and others [9]. Tomohisa and others synthesized barium ferrite by the SHF-induced hydrothermal method at 1000 °C. It is evident that the temperature of sintering of barium ferrites is too high; therefore they cannot be used in the LTCC technology. Accordingly, it is necessary to decrease their temperature of sintering. Large efforts, such as addition, at the low melting point of glass or oxides, chemical treatment and use of ultrathin raw materials were employed in order to decrease the sintering temperature [10–12]. Among these methods, additives with the low melting point of glass or oxides proved to be convenient and successful, for example, Bi_2O_3 [11], B_2O_3–SbO_3 [12] of glass were used for reduction in the temperature of sintering of ferrite approximately to 900 °C but the additives of glass frequently lead to the degradation of magnetic properties. Recently The additive $BaCu(B_2O_5)$ has been recently successfully used for reduction in the temperature of sintering of many microwave dielectric ceramics [13, 14].

However, despite the fact that there is a large amount of literature data in this area, there are no reports about using the glass Bi_2O_3–B_2O_3–SiO_2–ZnO (BBSZ) as auxiliary substance for reduction in the temperature of sintering of barium and strontium hexaferrites. This very method is proposed in this work.

3. Aim and tasks of the study

The purpose of this work was to obtain polycrystalline hexagonal ferrites of the M type for the base layers of the microstrip SHF-instruments of the millimeter wavelength range by the LTCC-technology.

To accomplish the set aim, it was necessary to solve the following problems:

– to develop the LTCC-technology of obtaining isotropic and anisotropic polycrystalline hexagonal barium and strontium ferrites based on the classic ceramic technology;

– to fabricate the samples of isotropic and anisotropic barium and strontium hexaferrites in the form of tablets and tapes, as well as to investigate their compatibility with the Ag-electrode.

4. Materials and methods of research

4. 1. Obtaining the objects of research

As the starting materials for hexaferrites of the M type $BaFe_{12}O_{19}$ we used $BaCO_3$, Fe_2O_3 of the HP type (high purity), for $SrFe_{12}O_{19}$ – $SrCO_3$, Fe_2O_3 of the HP type. As the additive for reduction in sintering temperature we used glass of bismuth borosilicate (BBSZ) on the base of Bi_2O_3–B_2O_3–SiO_2–ZnO (3, 5, 7 % by volume).

The glass BBSZ with the compositions $25Bi_2O_3$, $30B_2O_3$, $10SiO_2$ and 35ZnO was prepared by the process of melting. The original powders of the BBSZ glass were weighed and mixed in accordance with their ratio in the chemical formula, and then the mixed powders were melted at 1200 °C for 2 hours in the platinum crucible and were hardened in water with the formation of amorphous glass. Then the glass was dried and ground to the powder. To examine the temperature of vitrification and softening of glass, the part of the glass fusion was poured out into the mold in order to make a glass column. The measured temperatures of vitrification and softening were 585 and 650 °C, respectively.

The modified hexaferrites of the M type with the phase composition $BaFe_{12}O_{19}$ or $SrFe_{12}O_{19}$ were obtained in the following way. Reaction mixtures were prepared by using the following powders: Fe_2O_3, $BaCO_3$ or Fe_2O_3, $SrCO_3$, respectively. The powders were weighed on an analytical balance with the accuracy ±0,1 mg in the required proportions. Their joint grinding in the ball mill for 2 hours was performed after weighing the components. We carried out the synthesis of ferrite charge (ferritization) in the furnace to the temperature 1200 °C in the air. This temperature conditions were maintained for 5 hours. Then the cooling down to room temperature was conducted. To reduce the sintering temperature, the ground powder was mixed with the reaction glass of bismuth borosilicate on the base Bi_2O_3–B_2O_3–SiO_2–ZnO in the amount of 3, 5, 7 % by volume. We conducted splitting, crushing in the fine grinding mill with high energy «Pulverisette 6» by Fritsch (Germany) for 2 hours to the size of particles 0,8–1,8 μm for the compaction of the samples.

The preparation of a molding powder was then conducted. The synthesized charge was added with the binder (the 10 % solution of polyvinyl alcohol in the amount of 15 % of charge by weight) and SAS. The prepared powder was pressed into tablets or poured out in the form of a tape. The press-samples were made by cold one–sided pressing at pressure 200 MPa. The obtained articles were sinterred in tunnel kilns in the air medium at T=900–950 °C. The duration of sintering was 5 hours. The furnace was disconnected after the period of sintering and natural cooling of the samples was conducted in the open air.

4. 2. Techniques of the experimental studies

The roentgen phase and X-ray diffraction analysis of the examined objects was carried out in the X-ray diffractometer DRON-3M (Russia) (Fig. 1).

When running the roentgen phase analysis, we used the CuKα-emission, as well as the tube with the iron anode (operating current – 25 mA, voltage – 25 kW). Wavelength of emission is 0,193728 nm. When taking photographs of the samples, we used the filter from Mn. Focusing was performed according to the Bragg-Brentano method with two Soller slits. The measurements were carried out at room temperature.

Fig. 1. Roentgen diffractometer DRON-3M

Identification of intensive peaks in the diffractogram was conducted with the help of the software PDWin 4.0 (NPO «Burevestnik» Russia). The roentgen phase analysis of the samples came down to determining a series of interplanar distances and their comparison with reference data of the powder diffraction database, which is based on the PDF2 card index.

A study of microstructure and quantitative analysis of the samples were carried out on the scanning electron microscope «Carl Zeiss» (Germany) of the SEM LEO-420 trade mark with the microprobe attachment INKA ENERGY-400.

In order to investigate the compatibility of hexaferrites and Ag-electrode, ferrite sheet with the Ag electrode was prepared by tape casting and co-firing at 900 °C.

5. Results of research and discussion

Full technological process of obtaining polycrystalline hexagonal ferrites $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ is represented in Fig. 2.

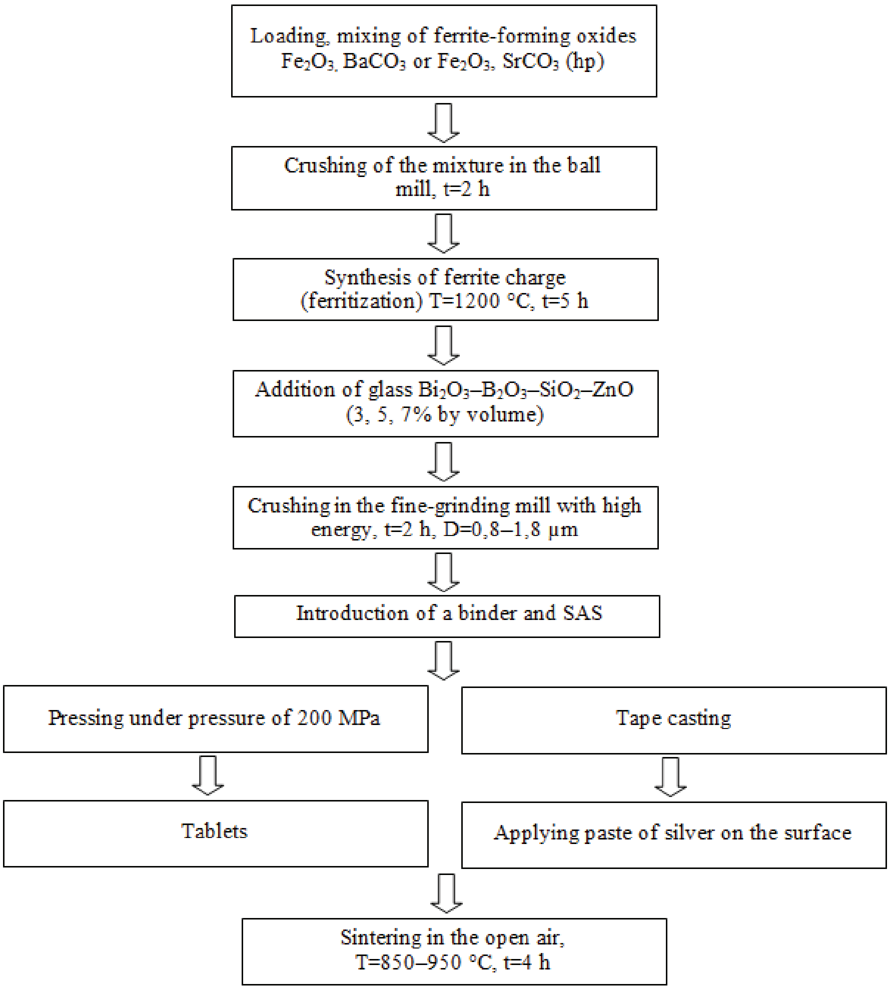

Fig. 2. Technological scheme of obtaining hexaferrites $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$

To preparing anisotropic hexaferrite billets, the pressing occurs in the magnetic field, applied along the direction of pressing. A special press is used for it, equipped with two coils (electromagnet), which create magnetic field. The upper coil accepts the press's plunger with the cap fixed to it; its form contributes to the concentration of magnetic field. In the lower coil, there is the base for the mold with the opening for water discharge, which ends with a coupling for fastening the hose, connected through the trap to the mechanical vacuum pump. The source that feeds the electromagnet provides for obtaining direct current to 10 A with voltage of up to 20 V.

X-ray studies confirmed that, as a result of the applied technology, we obtained polycrystals of both isotropic and anisotropic hexagonal ferrites $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$. Characteristic X-ray diffractograms are represented in Fig. 3, 4.

Dilatometric studies of the thermal treatment of the samples with different amount of the BBSZ glass were carried out in order to establish the influence of shrinkage on the density of the obtained samples. Results are displayed in Fig. 5. Shrinkage grows with the increase in the amount of the BBSZ glass. Porosity, evaluated with the aid of the Archimedes method, decreases with the increase in the amount of the BBSZ glass.

Fig. 6–9 demonstrate microstructure of the surface of hexaferrite $BaFe_{12}O_{19}$ with different content of the BBSZ additives.

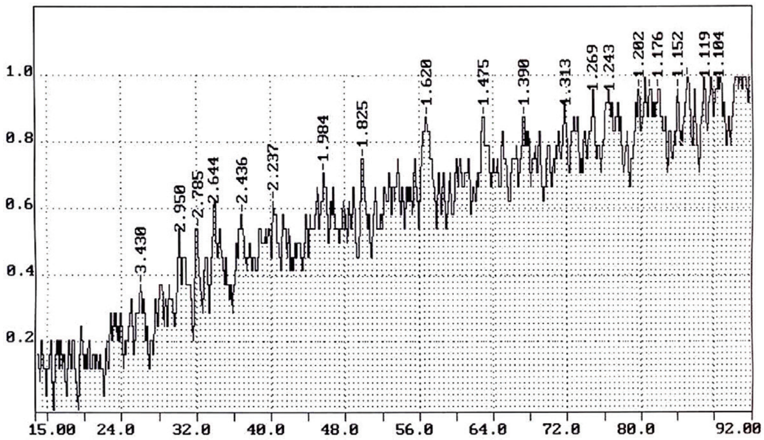

Fig. 3. Characteristic X-ray diffractogram of the sample of polycrystalline isotropic hexaferrite $BaFe_{12}O_{19}$

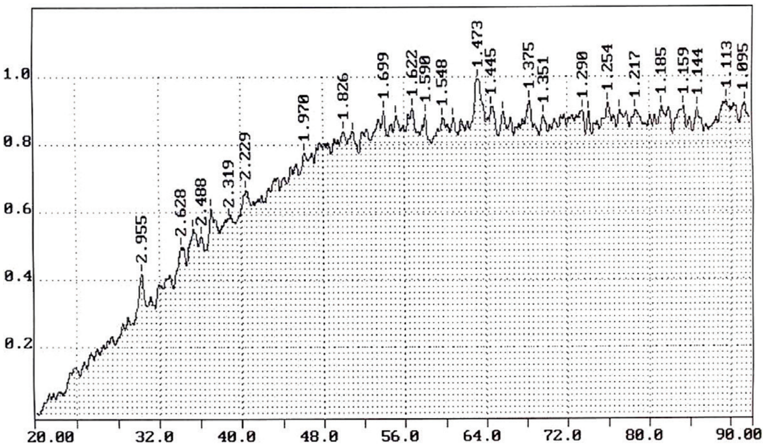

Fig. 4. Characteristic X-ray diffractogram of the sample of polycrystalline isotropic hexaferrite $SrFe_{12}O_{19}$

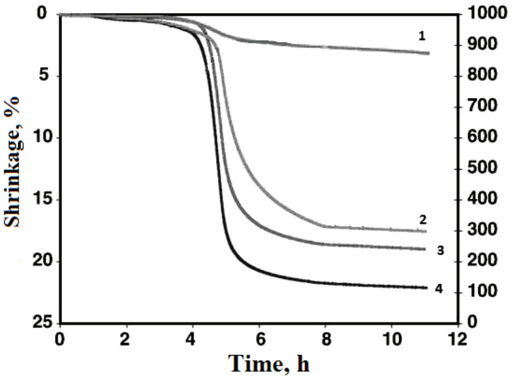

Fig. 5. Influence of the content of the BBSZ glass on the linear shrinkage of $BaFe_{12}O_{19}$: 1 – 0 % of BBSZ by volume; 2 – 3 % of BBSZ by volume; 3 – 5 % of BBSZ by volume; 4 – 7 % of BBSZ by volume

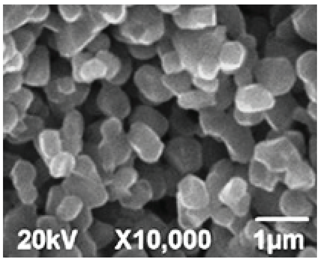

Fig. 6. Microstructure of hexaferrite $BaFe_{12}O_{19}$, sintered at 900 °C without BBSZ

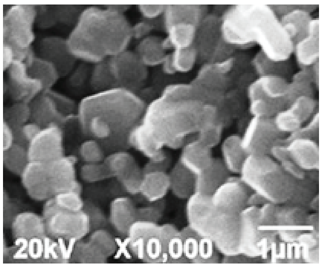

Fig. 7. Microstructure of hexaferrite $BaFe_{12}O_{19}$, sintered at 900 °C with 3 % of BBSZ by volume

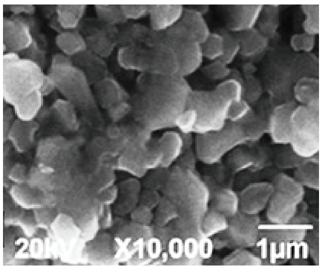

Fig. 8. Microstructure of hexaferrite $BaFe_{12}O_{19}$, sintered at 900 °C with 5 % of BBSZ by volume

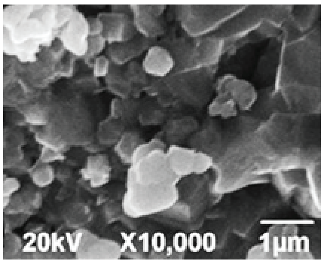

Fig. 9. Microstructure of hexaferrite $BaFe_{12}O_{19}$, sintered at 900 °C with 7 % of BBSZ by volume

When adding 3 % of BBSZ by volume, it is possible to observe the porous microstructure (Fig. 7). This indicates that the amount of liquid phase is still insufficient for the compaction of hexaferrite. Papers [13, 14] reported that with an increase in the content of glass in the dielectric ceramics, the microstructure becomes denser. In the given article it was also established that with an increase in the content of the BBSZ additive, hexaferrite's microstructure is compressed. With the content of 5 % of BBSZ by volume, it is possible to observe a uniform microstructure. Size of the grain is 0,2–0,5 μm (Fig. 8). This can be explained by the fact that the BBSZ – additive contributed to the compaction of ferrite, while at the same time the growth of grains was inhibited by high energy of the surface [14].

6. Conclusions

In the work we obtained polycrystalline hexagonal ferrites for the base layers of the subminiature microstrip ferrite untying instruments of the short-wave part of the centimeter and millimeter wavelength ranges by the LTCC-technology.

The developed methods make it possible to achieve compaction of the samples at 900 °C in the process of sintering hexaferrites with the addition of a small amount of reaction glasses with the composition Bi_2O_3–B_2O_3–SiO_2–ZnO (BBSZ).

The use in the LTCC-technology of the operation of pressing the samples (tablets) in the magnetic field makes it possible to obtain anisotropic hexaferrites, pressing without magnetic field – isotropic hexaferrites.

Application in the LTCC-technology of the method of casting a tape makes it possible to obtain entirely isotropic samples.

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