

The paper presents the results of the synthesis of bismuth superconducting ceramics with compositions $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$) based on amorphous ceramics obtained by ultrafast melt quenching. In order to increase the rate of formation of superconducting compounds, effective devices have been developed for melting and hardening melts under the action of IR radiation. The sample holder was made of platinum. Melting and hardening were carried out in a continuous mode in an oxidizing environment in a flowing air atmosphere. The study of the elemental composition of the precursor samples established a slight deviation towards a decrease in the cationic composition of the precursors (Bi, Pb and Ca), relative to the stoichiometric composition. An increase in oxygen content by 12–15 % was also found. Synthesis of superconducting compounds was carried out in the temperature range of 843–850 °C, depending on the composition. The study found that in the sample $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_y$ (2245) the superconducting high-temperature phase 2223 crystallizes. It was found that the formation of the superconducting phase 2223 in the $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_y$ composition occurs in a lower and wider temperature range (843–848 °C) compared to the $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (2223) composition. The complete formation of the superconducting high-temperature phase 2223 in a sample with the nominal composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (2223) was carried out in a narrow temperature range of 849–850 °C, in a strict temperature regime with the participation of the liquid phase. An increase in the rate of formation of the superconducting compound 2223 in both studied compositions by 1.5–2.5 times was established, compared with the solid-phase method and other melt methods

Keywords: superconductivity, microstructure, elemental composition, ceramics, morphology, diffractogram, amorphous phase

SYNTHESIS OF HIGH-TEMPERATURE SUPERCONDUCTING CERAMICS IN THE Bi(Pb)-Sr-Ca-Cu-O SYSTEM BASED ON AMORPHOUS PRECURSORS

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1. Introduction

In the field of materials science, a separate niche is occupied by materials and products with special electrical properties: ferroelectrics, superionic conductors, semiconductors, and superconductors [1–4].

The compositions, properties and technology of their production are subject to special requirements due to the specifics of practical use.

In the above group, superconducting materials are of particular interest in connection with promising practical applications. They find application in such areas as energy, elec-

tronics, medicine, communications, etc. They are used in magnetic levitation trains [5], for the manufacture of cables [6], and in other applications where high current-carrying capacity is required [7]. They are used for creating electronic devices as well. Such devices include SQUID magnetometers [8], microwave oscillators [9], protective device for sensitive semiconductor elements [10]. They are also promising for the creation of quantum computers [11, 12], optical sensors [13], and high-speed electronics [14]. Bulk superconductors are considered for use in such products as magnetic bearings [15], electric motors and electric generators [16], etc.

After the discovery of superconductivity above the temperature of liquid nitrogen, several classes of high-temperature superconductors based on the copper-cuprate system (yttrium, bismuth, mercury, thallium and others) have been developed. Among these classes, bismuth-containing cuprates are of particular interest, because they have a high critical temperature, are stable, do not contain expensive and toxic components, and it is also possible to obtain an amorphous state from the melt. When using amorphous materials, it is possible to control the grain size, increase the texture. In the Bi-Sr-Ca-Cu-O bismuth system, three stable superconducting compounds of the homologous series $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=1, 2, 3$) with superconducting transition temperatures of 30–35 K, 80–90 K and 107–110 K, respectively. It has been established that with an increase in the number of Ca and Cu layers, the critical temperature also increases. According to model calculations, the next homologue with $n=4$ should have a temperature $T_c=142$ K [17], but obtaining a stable superconducting compound turned out to be a difficult task. Of the three compounds of the homologous series $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=1, 2, 3$), the most found practical application was found practical application for $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3$). Although these superconducting materials are already used in various fields, the problems of wider application are limited by the cost, the complexity of the technological implementation, and the values of critical parameters. Therefore, research aimed at developing effective methods for obtaining superconductors with high critical parameters is relevant.

2. Literature review and problem statement

A definite solution to the problem of creating HTS materials of a given composition with high critical parameters may be the development of melt methods and their further modification [18]. In particular, methods aimed at obtaining amorphous precursors, which have certain advantages over traditional solid-phase and some melt methods, have been developed. The method of synthesis from amorphous precursors makes it possible to obtain superconducting ceramics with the necessary phase composition, with a controlled grain size and high texture. In addition, due to the metastable state of amorphous precursors, the rate of formation of superconducting phases can increase. But, all this depends on the conditions and method of synthesis of amorphous precursors. On the one hand, the Bi(Pb)-Sr-Ca-Cu-O system contains elements that have variable valence. Depending on the conditions for obtaining precursors, they can be in different valence states, and in turn can affect the formation of the target compound and their properties. On the other hand, the methods of obtaining the melt: melting in a resistive furnace, induction melting, under the influence of laser radiation, concentrated optical radiation (solar), etc., i. e., the peculiarities of the influence of the

energy of exposure to the melt, as electromagnetic radiation. Among these methods, the traditional one is to obtain a melt in a crucible. For example, researchers [19] for the synthesis of the composition $(\text{Bi,Pb})_4\text{Sr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ ($m=0-0.06$) from an amorphous phase, melting was carried out in a platinum crucible and tempered by flaking between two massive plates. At the same time, the presence of low valence Fe^+ and Cu^+ cations was established, although Fe_2O_3 oxides were used, CuO and melting was carried out in an oxidizing medium. After the synthesis of superconducting ceramics at 840 °C for 40 hours, it was established that all samples consisted of 2212, 2223 and non-superconducting phases. Apparently, the annealing duration associated with the oxidation of epy cations to a highly valent state (especially Cu^{2+}) was insufficient for the complete synthesis of 2223.

Similar results on the valence state of copper were obtained in [20]. They investigated the formation of superconducting phases of glass of the composition $\text{Pb}_{0.32}\text{Bi}_{1.68}\text{Sr}_{1.75}\text{Ca}_2\text{Cu}_3\text{O}_y$ at the early stages of heat treatment. Heat treatment was carried out at 440 °C (1.8 h), 499 °C (1 h), 598 °C (1 h). At low heat treatment temperatures, phases 2201, Ca_2PbO_4 and Cu_2O were manifested. And at a temperature of 598 °C, the lines of the Cu_2O phase did not appear on the diffractogram, but in addition to the phases 2201, Ca_2PbO_4 , traces of the superconducting phase 2212 were found. The lines of the superconducting phase 2223 did not appear. The absence of phase 2223 is associated with the separation into phases during the crystallization of glass and the low-valent state of copper.

In [21], superconducting ceramics of the composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ were synthesized by casting from a melt. As a result of prolonged annealing (150 hours), samples of the compositions of displaced superconducting phases 2212 and 2223 were obtained. The content of phase 2223 in this case was 60–65 %. Apparently, the slow rate of formation of phase 2223 is associated with the valence state of copper.

In studies on the synthesis of superconducting phases in the Bi(Pb)-Sr-Ca-Cu-O system from the glass phase, used a non-gel method for obtaining amorphous precursors [22]. Concentrated solar radiation was used as a heating source. In order to increase the critical temperature, samples of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{(n-1)}\text{Cu}_n\text{O}_y$ ($n=2-20$) compositions were synthesized. The power of concentrated solar radiation was 180–240 W/cm^2 . The synthesis of superconductor samples was carried out at a temperature of 840–853 °C up to 110 hours of heat treatment. In compositions $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{(n-1)}\text{Cu}_n\text{O}_y$ ($n=3-6$), the main phase was 2223 with $T_c=107$ K, traces of a phase with higher T_c were also found. And in the compositions of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{(n-1)}\text{Cu}_n\text{O}_y$ ($n=7-20$), in addition to phase 2223, phase 2212 and non-superconducting phases were present.

In [23], the synthesis of superconducting ceramics of the composition $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ was also carried out on the basis of amorphous precursors obtained under the influence of concentrated solar radiation. At a synthesis temperature of 845–850 °C, the content of the superconducting phase 2223 was 90 %, and the remaining 10 % was phase 2212. Such a high rate of formation of phase 2223 is apparently associated with the highly valent state of copper. When using concentrated solar radiation, the solubility of oxygen in the melt increases and the elements of variable valence acquire a higher degree of oxidation.

In [24], the effect of the crystal structure of the substrate (based on Al_2TiO_5 , cubic ZrO_2 and Al_2O_3) on the texture

of BSCCO (Bi-Sr-Ca-Cu-O) was studied by synthesizing composition 2223, also using precursors obtained under the action of solar radiation. The thickness of the superconductor samples was more than 300 microns. No noticeable change in phase composition and texture formation was observed in all samples. Perhaps, with a thick layer of samples deposited on the surface of the substrates in the form of powder, the effect of the substrate structure on the texture does not affect. The formation of the superconductor texture seems to be related to the properties inherent in the precursor during quenching.

In [25], superconducting ceramics of the compositions $\text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_2\text{CaCu}_2\text{O}_y$ (2212) and $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (2223) with a high crystallite texture in the crystallographic direction [001] (texture about 95 %) were synthesized on the basis of amorphous precursors. Amorphous precursors were obtained under the influence of concentrated optical radiation from two electric arc lamps with a total power of 20 kW. The formation of superconducting phases did not differ much from the cases in which concentrated solar radiation was used. Apparently, the spectral composition of radiation plays an important role in the production of amorphous precursors, since they are very similar in spectral characteristics. It should be noted that the technology of obtaining materials under the influence of concentrated solar radiation is unique, but energy-intensive.

In [26], a superconductor of the composition $\text{Bi}_{1.65}\text{Pb}_{0.35}\text{Sr}_{1.9}\text{CaCu}_2\text{O}_y$ doped with Ag with a high crystallite texture was synthesized by the melt method under conditions of a strong magnetic field (1 Tesla). After a long annealing process (more than 160 hours) in an O_2+Ar atmosphere, the texturing effect shifted from Bi(Pb)2212 to Bi(Pb)2223. It is possible that such a long texturing process is associated with the structural features of superconductors, which have a strong anisotropy of the structure and a large parameter "c" along the axis [001].

All these studies suggest that in some cases a high texture with the necessary phase compositions and critical parameters is achieved, but in technical execution it is quite long and energy-intensive. And in other cases, superconducting ceramics are multiphase and do not have the necessary critical parameters. Therefore, it is advisable to conduct a study devoted to the development of effective methods for the production and synthesis of high-temperature superconducting ceramics in the Bi(Pb)-Sr-Ca-Cu-O system with high critical parameters.

3. The aim and objectives of the study

The aim of the work is to develop an effective technology for obtaining superconducting ceramics in the Bi(Pb)-Sr-Ca-Cu-O system based on amorphous precursors synthesized under the influence of infrared radiation.

To achieve this aim, the following objectives are accomplished:

- to develop a device and to obtain amorphous precursors of compounds $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$);
- to investigate the phase and elemental compositions of precursors of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ compositions ($n=2, 3, 5$);
- to synthesize superconducting ceramic samples of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$) compositions based on amorphous precursors;
- to investigate the microstructure and critical temperature of superconducting ceramics of compositions $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$).

4. Materials and methods of research

For the synthesis of HTSC ceramics with the compositions $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$), the following chemical reagents were used: Bi_2O_3 , $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, PbO , PbO_2 , SrCO_3 , CaO , CuO . The phase composition of amorphous precursors and HTSC ceramics was controlled by X-ray diffraction on diffractometers Bruker D8ADVANCE-CEECO, XPertPRO (Netherlands) and Dron-6, $\text{CuK}\alpha$ radiation. Microstructural and elemental analyzes of the samples were carried out on JEOL-6490LA scanning electron microscopes (Japan) with an energy-dispersive analyzer system "OXFORD Instruments Analytical Limited" (Great Britain) and JSM-6390LV (Japan) with a built-in energy-dispersive X-ray analyzer (EDS).

The critical parameters of the obtained samples were determined using a four-probe method using a closed cryochamber "CryoIndustry REF-1808-ACS" cooled with helium gas and a temperature meter "LakeShoreModel 340" and a microvoltmeter.

5. Experimental results on the synthesis of superconducting ceramic compositions $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$)

5.1. Development of a device and production of amorphous precursors of nominal compositions $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$)

In the synthesis of high-temperature superconducting materials by the melt method based on amorphous precursors, the method and conditions for obtaining precursors and their properties are of great importance, since they can affect the kinetics of the formation of superconducting phases, and the critical parameters of superconducting materials. In this work, to obtain amorphous precursors, a device was developed using IR radiation. Initial samples for melting were prepared in the following way: chemical reagents of stoichiometric composition were thoroughly mixed and pressed into rods $60 \times 10 \times 12$ mm in size and annealed at a temperature of $820-830^\circ\text{C}$ for 2 hours. The process of melting the initial samples and obtaining amorphous precursors was carried out by ultrafast quenching of the melt under the influence of IR radiation. The substrate for melting the initial samples was made of platinum. Ultrafast hardening was carried out by spraying the melt onto the surface of a water-cooled wall with a rotating stainless steel disk. The disk rotation speed was 3000 rpm. The process of obtaining precursors was carried out in an oxidizing atmosphere created by flowing air. Precursors are shown in Fig. 1.

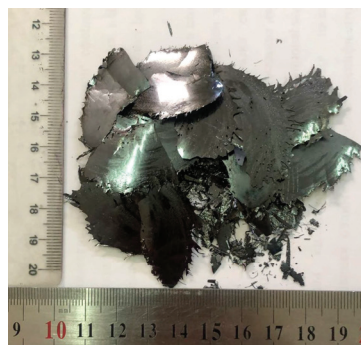


Fig. 1. Initial precursors obtained by ultrafast melt quenching

The initial precursors mainly consisted of plates 160–180 μm thick (about 90 %). Precursors were also in the form of needles and small spheres.

5.2. Investigation of the Phase and Elemental Composition of Initial Precursors

The phase composition of the initial precursors of plates with a nominal composition of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$) were studied by X-ray diffraction method. Studies have shown that with an increase in the content of calcium and copper, the ability to crystallize in the series of

$\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$) increases. Since the precursors of the plates of compositions 2212 and 2223 were completely amorphous, and traces of crystalline phases were present in the precursors of composition 2245. As for the elemental composition of the samples of amorphous precursors, the measurements were carried out from local points on the surface of the plates. The results of the elemental composition of the amorphous precursors of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ plates ($n=2, 3, 5$) obtained by the electron microscopy method with an energy-dispersed attachment are shown in Fig. 2–4.

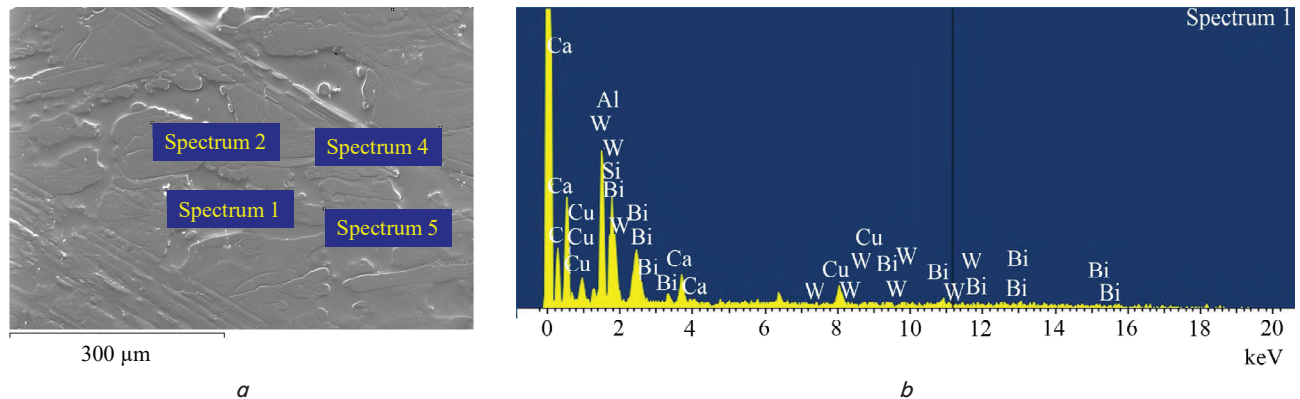


Fig. 2. Results of elemental analysis of a sample of the initial plate of composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{CaCu}_2\text{O}_y$ obtained by ultrafast melt quenching: *a* – the microstructure of the plate surface; *b* – energy dispersive spectrum

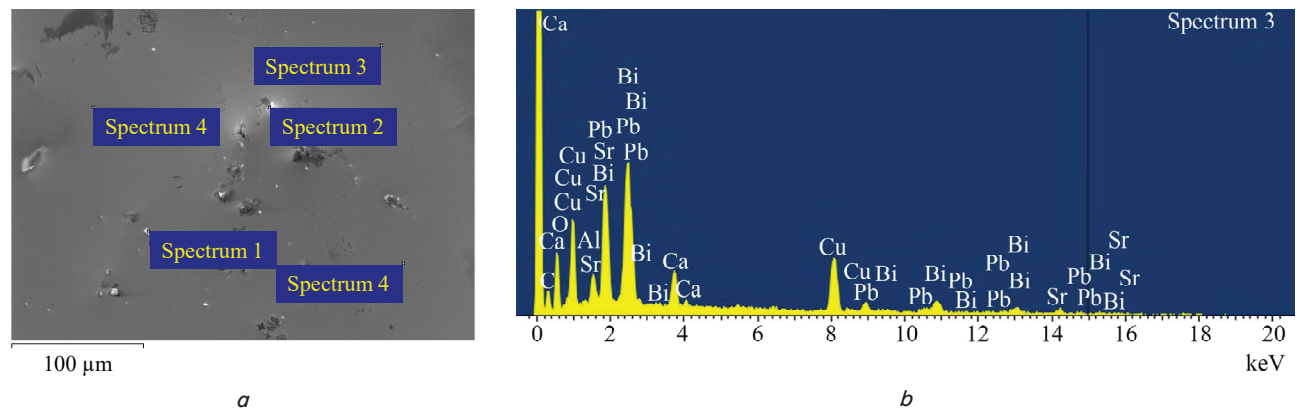


Fig. 3. Results of elemental analysis of a sample of the initial plate of composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ obtained by ultrafast melt quenching: *a* – the microstructure of the plate surface; *b* – energy dispersive spectrum

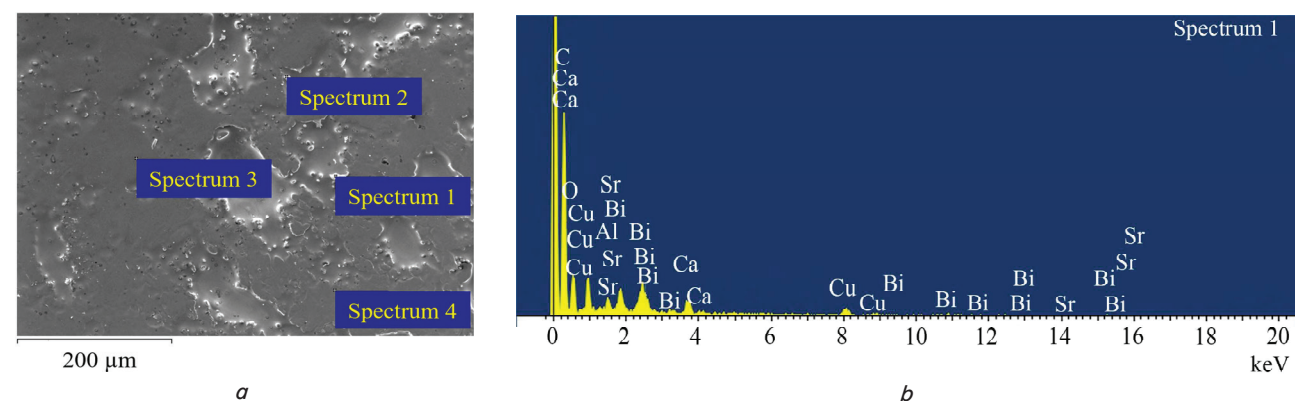


Fig. 4. Results of elemental analysis of a sample of the initial plate of composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_y$ obtained by ultrafast melt quenching: *a* – the microstructure of the plate surface; *b* – energy dispersive spectrum

The results of the elemental analysis of plates with compositions $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$) show that the cationic composition shows slight deviations from the stoichiometric content of Bi, Pb, Ca, i. e. there is a decrease. As for oxygen, their content increased in relation to the stoichiometric composition by 12–15 %.

5.3. Synthesis of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$) Superconducting Ceramics Based on Amorphous Precursors and Investigation of Properties

For the synthesis of superconducting samples based on amorphous precursors, the material was ground with an agate mortar to a fineness of 2–3 μm and pressed into pellets 15 mm in diameter and 2.0 mm thick. Synthesis of HTSC samples was carried out by heat treatment in isothermal mode in a muffle furnace at a temperature of 845–850 °C for 96 hours with intermediate grinding every 24 hours. Initially, heat treatment of all the studied samples was carried out in the same mode, at a temperature of 845 °C. After 24 hours of heat treatment, the samples of the nominal composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=3$, and 5) consisted of superconducting phases 2212 and 2223. With an increase in the heat treatment time, the amount of the high-temperature phase 2223 increased. After 72 hours, the $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}$ samples consisted of the high-temperature phase 2223 (Fig. 5). And in the samples of composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, in addition to the high-temperature phase 2223, about 15 % of the low-temperature phase 2212 was present (Fig. 6). A further increase in the synthesis time to 96 hours did not lead to a noticeable change in the phase composition in the 2245 samples, and in the $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ sample, a slight decrease in the amount of the 2212 phase was observed. Synthesis at 845 °C did not lead to single-phase samples. Single-phase samples of the nominal composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ were obtained at a higher annealing temperature (849–850 °C) and a duration of 72 hours. Based on the results obtained, it can be said that during the synthesis, the rate and temperature regime of the formation of HTSC ceramics of the 2223 phase based on amorphous precursors changes, depending on the content of Ca and Cu. The results of studying the phase composition of superconducting ceramics $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$) by the X-ray diffraction method are shown in Fig. 5–7.

An analysis of the results of an X-ray study of a sample with a nomi-

nal composition $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{CaCu}_2\text{O}_y$ shows (Fig. 7) that the diffraction pattern mainly showed X-ray reflections of the low-temperature superconducting phase 2212. It is also important to note that in addition to the 2212 phase, the samples contain reflections of the superconducting high-temperature 2223 phase (about 10 %).

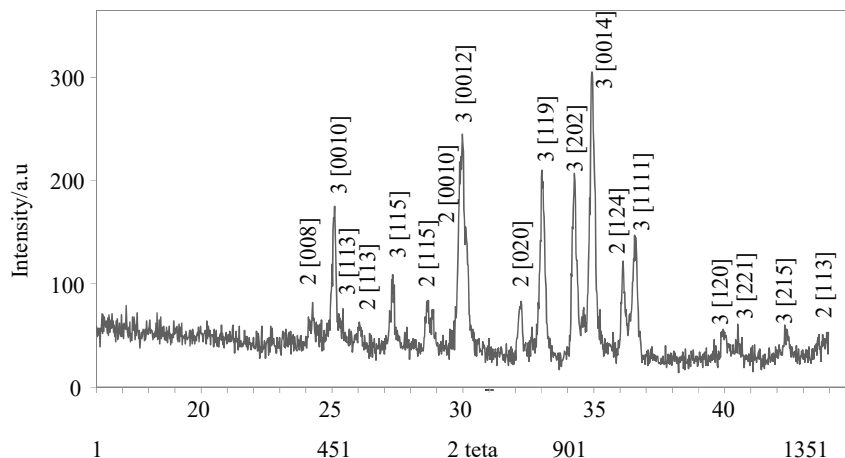


Fig. 5. X-ray diffraction pattern of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_y$ superconducting ceramic synthesized on the basis of amorphous precursors at 845 °C, 96 hours

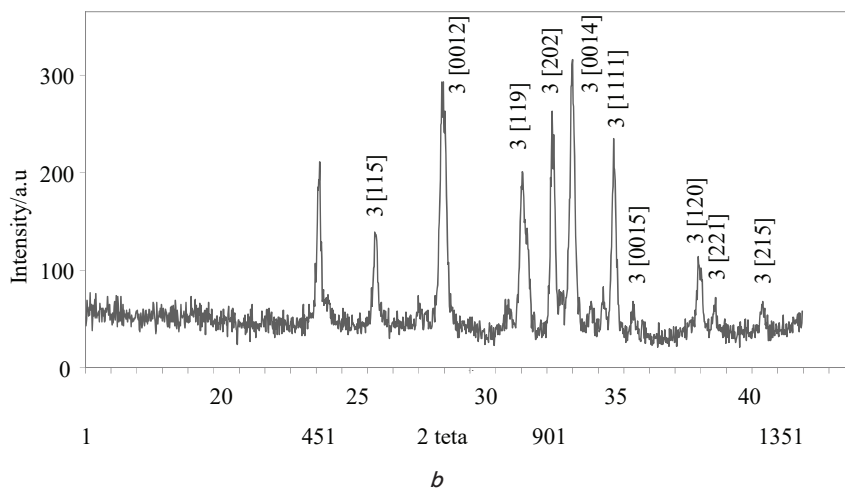
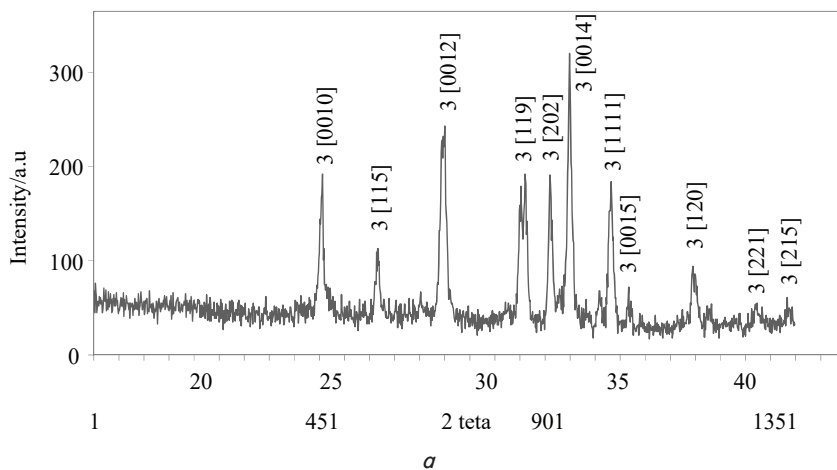


Fig. 6. X-ray diffraction pattern of superconducting ceramics of composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ obtained on the basis of amorphous precursors: *a* – synthesis at 845 °C, 96 hours; *b* – synthesis at 850 °C, 72 hours

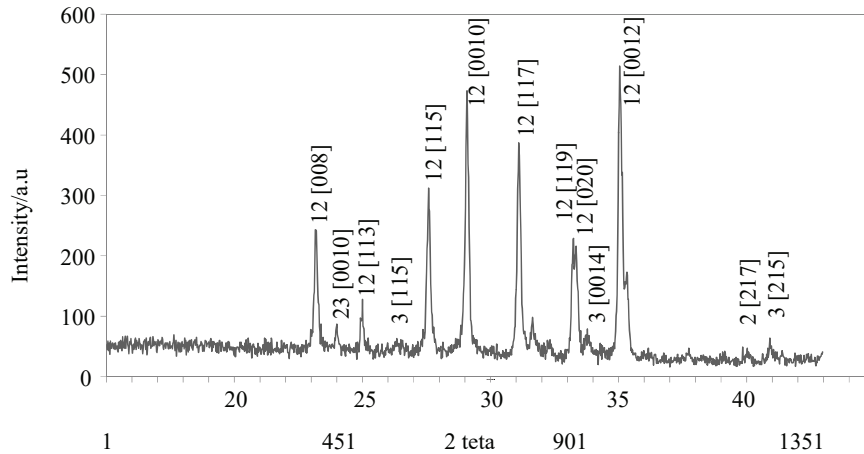


Fig. 7. X-ray diffraction pattern of superconducting ceramics of composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{CaCu}_2\text{O}_y$ obtained on the basis of amorphous precursors at 845 °C, 96 hours

5. 4. Studies of the microstructure and critical temperature of superconducting ceramics of composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$)

The study of the microstructure of ceramics shows that the samples consist of lamellar crystallites. The crystallite size ranges from 1 micron to 4–5 microns, and the thicknesses vary from 120–130 nm to 300–350 nm (Fig. 8).

The results of the study of the temperature dependence of the resistance (critical temperatures) of samples of super-

conducting ceramics compositions $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=3, 5$) are shown in Fig. 9.

The temperature at which the transition to the superconducting state begins for the compositions $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=3, 5$) is 110 K. The transition temperature to the superconducting state is about 100 K. As for the ceramic sample of the composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{CaCu}_2\text{O}_y$, the temperature of the onset of the transition to the superconducting state is 80 K.

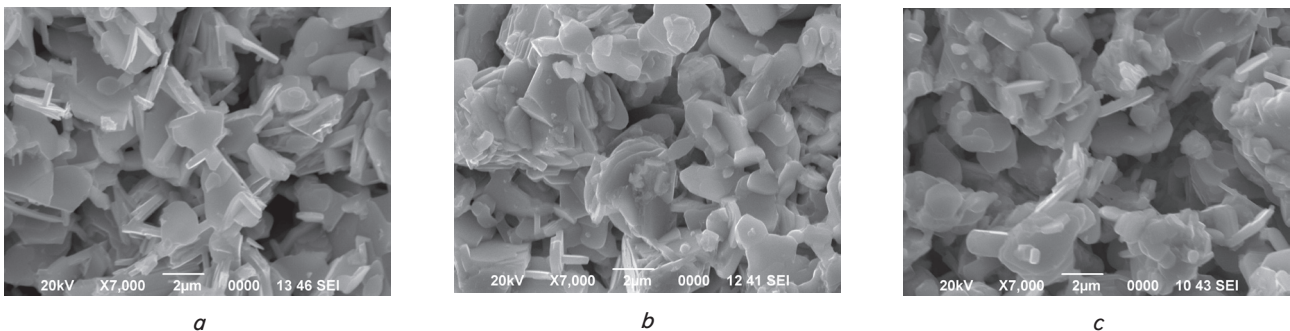


Fig. 8. Microstructure of superconducting ceramics with compositions $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$) synthesized on the basis of amorphous precursors: *a* – 2212; *b* – 2223; *c* – 2245

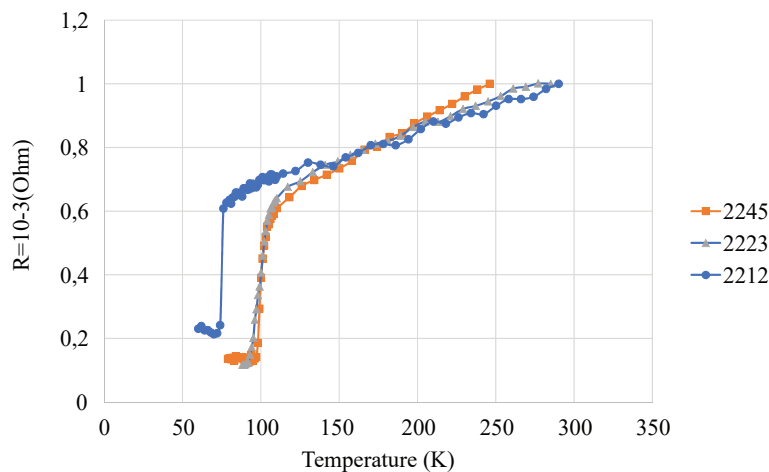


Fig. 9. Temperature dependence of the resistance of superconducting ceramics of composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$) synthesized on the basis of amorphous precursors 10^3 Ohm

6. Discussion of the results of a study on the synthesis of superconducting ceramics of composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$)

In the synthesis of bismuth-containing superconducting materials from amorphous precursors, the properties of the precursors, which depend on the preparation conditions, are of great importance. The production conditions (methods of melting, quenching rate, atmosphere, etc.), in turn, affect the phase and elemental compositions, and structural features of the precursors. The results of the study of the initial precursors by the X-ray diffraction method showed that the precursors of the compositions $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3$) represent an amorphous phase. And in the precursors of the composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=5$) there were traces of crystalline phases, so that the tendency to crystallization increased with an increase in the content of calcium and copper. The study of the elemental composition of the precursors by electron microscopic analysis established that the oxygen content is 12–15 % higher than the stoichiometric composition of all the samples under study [27]. As well as a slight decrease in the cationic composition (Bi, Pb, Ca), which are more volatile. But their violation does not greatly affect the properties of the superconductor, since in the bismuth system, cations can easily replace the positions of other atoms. As for oxygen, with its excess, cations of variable valence Bi, Pb, Cu pass into an increased valence state (especially Cu). This, in turn, leads to an increase in the rate of formation of superconducting phases. Traditionally, in the synthesis of bismuth superconductors from an amorphous phase, the samples are melted in corundum or platinum crucibles. According to the data [28], during the melting of the initial samples in the crucible, a strong decrease in the oxygen content occurs, so that the ratio of $\text{Cu}^+ / (\text{Cu}^+ + \text{Cu}^{2+})$ cations can reach a value of 0.7–0.8. In turn, oxygen deficiency can adversely affect the rate of formation of superconducting phases and the properties of the superconducting material.

An analysis of the results of an X-ray diffraction study of the phase composition on the formation of superconducting compounds in the compositions $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=3, 5$) shows that the superconducting high-temperature phase 2223 crystallizes in both samples. In early studies, during the synthesis of the composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_y$ (2245) complete formation of the superconducting phase 2223 was not observed. At the same time, the optimal temperature for the formation of the 2223 phase in the $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_y$ (2245) composition is 5–6 degrees lower than in the $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ (2223) composition. And the temperature interval for the formation of the 2223 phase is wider (843–848 °C). When both, the 2223 phase in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (2223) is formed in a narrow temperature range (849–850 °C), in a strict temperature regime with the participation of the liquid phase. The rate of formation of the superconducting phase 2223 in both compositions is 2–2.5 times higher than in the solid-phase method and in other melt methods. This is possibly related to the following:

- a metastable state of amorphous precursors, but due to non-equilibrium conditions of melting of the initial samples and hardening, which can affect interfacial reactions;
- highly oxygenated amorphous precursors. With oxygen deficiency, the formation of superconducting phases is

hampered by the diffusion of oxygen during synthesis into the dense crystalline structure of the superconductor;

- features of the influence of the IR region of the spectrum as electromagnetic radiation, affecting the energy states of the system.

An analysis of the results of an X-ray diffraction study of the formation of a superconducting compound in the composition of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{CaCu}_2\text{O}_y$ (2212) shows that the presence of a superconducting high-temperature phase 2223 in an amount of 10–12 % was established on the sample. We have not previously observed such a result in the synthesis of HTSC ceramics based on amorphous precursors obtained by other methods, as well as by solid-phase synthesis.

During the synthesis of samples of HTSC ceramics with the nominal composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{CaCu}_2\text{O}_y$, in addition to the base phase 2212, the superconducting high-temperature phase 2223 was also present in an amount of about 10 %. We have not previously observed such a result in the synthesis of HTSC ceramics based on amorphous precursors obtained by other methods, as well as by traditional solid-phase synthesis. It is possible that the tendency to crystallization of high-temperature superconducting phases (even compositions with a high content of calcium and copper) and an increase in the rate of formation of the superconducting high-temperature phase 2223 during synthesis based on amorphous precursors obtained under the influence of IR radiation are associated with the metastable initial state of precursors with a structure close to structure 2223.

A study of the dependence of resistance on temperature established a superconducting transition at a temperature of 80 K with a narrower width of the transition to the superconducting state, which is possibly related to the ordering of the structure.

When obtaining superconducting ceramics with compositions $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2, 3, 5$), the use of technology from amorphous precursors under the influence of IR radiation is a more technological and efficient option compared to solid-phase synthesis and other methods. Compared to the technology of obtaining superconducting ceramics under the influence of concentrated solar radiation, this technique is much less energy-intensive.

These studies can find practical application for obtaining oxide superconducting materials with glass-forming properties. The use of the results of the study can also be applied to increase the current-carrying characteristics of ceramics. When using amorphous precursors, it is possible to control the size of crystallites by technological modes of heat treatment, to increase the density and texture, which mainly determine the critical current of superconducting ceramics.

7. Conclusions

1. The melting device was a thermal insulation chamber with an IR radiation source. The initial sample was placed inside the chamber on a platinum substrate and, under the influence of IR radiation, gradually melted and flowed to the quenching device. Ultrafast quenching of the melt was carried out by spraying a rotating at a speed of 3000 rpm with a stainless steel disc on the water-cooled wall of the device.

The quenching rate was about 10^4 – 10^5 degrees/sec. At lower speeds of rotation of the disk (at a lower quenching speed) amorphous-crystalline precursors in the form of spherulites have stabilized.

2. It was found that with an increase in the content of Ca and Cu in the series $n=2, 3, 5$, the tendency to crystallization increases. An increase in the solubility of atmospheric oxygen in the melt was revealed, since an increase in the oxygen content in the precursors relative to the stoichiometric composition by 12–15 % was found.

3. It is established that the superconducting phase 2223 is stabilized in the compositions $\text{Bi}_{1.5}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=3, 5$). It was revealed that the formation of the superconducting phase 2223 in the composition of $n=5$ at a lower temperature and in a wide temperature range (843–848 °C). Whereas in the composition of $n=3$, phase 2223 is formed at 850 °C in a strict temperature regime. The optimal synthesis mode of phase 2212 is at 843–850 °C. In all compositions, the rate of formation of superconducting phases is 1.5–2.5 times higher than in solid-phase synthesis and other melt methods, which may be due to the metastable state of amorphous precursors and excess oxygen.

4. It was found that the compositions 2223 and 2245 have the onset of the transition to the superconducting state at 110 K. In the $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=5$) composition, the 2245 phase was not detected by the four-contact measurement method. For the composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n=2$), the onset of the transition temperature corresponds to 80 K.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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