Properties of Bismuth-Based Superconductors Precursors obtained under the influence of the Radiant Flux

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Abstract. The results of the study on the synthesis of high-temperature superconductors in the system Bi-Pb-Sr-Ca-Cu-O based on amorphous precursors were considered in this article, and were obtained under the influence of the radiant flux. A study of the elemental composition of amorphous precursors has showed the presence of 20 at.% superstoich iometric oxygen. The increase in the rate of formation of the superconducting phase and the high texture of the particles in the ceramic samples along the plane [001] were established. The synthesized samples were composed of superconducting phase Bi₁₋₋₇Pb₀₋₋₃Sr₂Ca₂Cu₃O₉. Research has established a presence in samples of HTSC phase with Tc up to 181K.

1. Introduction

HTSC are based on the system of Bi-Sr-Ca-Cu-O and recognized as one of the most promising, as are characterized by high critical parameters (Tc, Jc), a significantly lower degradation and constant composition. It was established that the HTS compounds are based on this system of homologous series with general formula Bi₂Sr₂Caₙ₋₁CuₙOₙ (n = 1, 2, 3...) [1, 2]. The critical temperature of the superconducting transition (Tc) increases with the number "n" and makes 35K, 90K, 110K, respectively. Also the interest is the possible existence in the system of superconducting phase (Bi₂Sr₂Caₙ₋₁CuₙOₙ (n = 4, 5, 6 ...)), on the model calculations, far above the critical temperature of the phase Bi₂Sr₂Ca₂Cu₃O₉ (110 K) [3]. From the above HTS practical application are found the compounds having the highest Tc - Bi₂Sr₂Ca₂Cu₂O₇ and Bi₂Sr₂Ca₂Cu₃O₉.

For practical application, in addition to the critical temperature, very important are the critical current (Jc) and critical magnetic field (Hc). If the thin-film high-temperature superconductors have been reached high values of Jc, then the massive high-temperature superconductors (ceramic) to achieve high values of Jc remains as difficult task. Creating ot technology of superconducting ceramics with high and reproducible critical parameters, largely constrained by the lack of reliability of the developed synthesis process, as initial precursors, and, to a lesser extent, the process of getting the target ceramics. The problem is the need of accounting simultaneously influence of factors that lead to the flow of competing reactions, separation of the individual phases, local melting, a breach of the composition due to selective evaporation of components, formation of dendritic structures, and others.
A very common method of solid-phase reaction does not provide a high critical current density due to the formation of the granular structure, which is the main cause of weak Josephson bonds at the grain boundaries.

Melt technology (QMG, MQMG, MC, et al.) can provide texture, eliminating this deficiency. Glass-crystalline technologies, aimed to getting of amorphous precursors are positive addition to the melt methods. The advantage of this method is: the ability to control the grain size, achieving a high texture, high homogeneity, reduced segregation, lightweight molded and getting of high density products of desired shape.

With respect to the glass-crystal technology the using of concentrated light flux as a heating source can bring a number of positive factors [4, 5]. This type of heating eliminates the introduction of impurities from the crucible and technological equipment, can process a given amount of starting material in a high-gradient conditions with high speed to change the conditions for getting the melt and cooling. In addition, the concentrated light output includes UF.

UV, visible and infrared regions of the spectrum that can affect the formation of the fine structure and the critical parameters of the target HTSC ceramics.

The aim is to study of the impact of characteristics of radiant energy on the formation of the superconducting phase, morphology, and the critical temperature (\(T_c\)) superconducting ceramic based system Bi-Pb-Sr-Ca-Cu-O.

2. Methods of Experiment

For the synthesis of the original samples of nominal composition mixture Bi_{1.7}Pb_{0.3}Sr_{2}Ca_{n-1}Cu_{n}O_{\delta} (n = 2-12) are made from pre-annealed at 873 °K powders of Bi_{2}O_{3}, PbO, SrCO_{3}, CaO, CuO, and compressed into rods with size 5x10x150 mm. Synthesis of the melt and subsequent rapid quenching was carried out using as a heating source of concentrated radiant flux (LPC) - solar furnace 3 kW and optical URAN type furnace equipped with a xenon arc lamp power of 10 kW. The hardening of the melt was carried out at a rate of up to 10^{6} deg/sec by spraying.

The phase composition was monitored by X-ray diffraction on a DRON-4-M, CuK\(_\alpha\)-radiation and Diffractometer Model Rigaku Co, Ltd., Tokyo, Japan. The microstructure was examined on the microscope Neophot and TEM, Model JEM-1200EX11, JEOL Co., Ltd., Tokyo, Japan). The critical temperature was determined by measuring the temperature dependence of the resistivity by a four and the temperature dependence of the magnetic susceptibility of a one-induction method.

3. Results and Discussion

Amorphous precursors were the plates and needles. The plates have a thickness of less than 0.3 mm and needles of up to 10mm and a diameter less than 0.4 mm. Depending on the content of Ca and Cu phase composition of needles and plates changed. If compositions Bi_{1.7}Pb_{0.3}Sr_{2}Ca_{n-1}Cu_{n}O_{\delta} (n=2-5) and the needle plate is an amorphous phase, the compositions for Bi_{1.7}Pb_{0.3}Sr_{2}Ca_{n-1}Cu_{n}O_{\delta} (n = 6-12) with increasing Ca content and Cu tendency of precursors to crystallization was increasing.

The microstructure analysis showed the increase of crystalline inclusions in the samples with increasing content of Ca and Cu. For example, figure 1 shows the microstructure of the samples was Bi_{1.7}Pb_{0.3}Sr_{2}Ca_{n-1}Cu_{n}O_{\delta} (n = 5, 9).

![Figure 1. The microstructure of the original plate precursor compositions Bi_{1.7}Pb_{0.3}Sr_{2}Ca_{n}Cu_{n}O_{\delta} (a) and Bi_{1.7}Pb_{0.3}Sr_{2}Ca_{n}Cu_{n}O_{\delta} (b), produced by quenching of the melt with using a concentrated radiant flux.](image-url)
It is particularly important to note the presence in the amorphous precursors to 15-20% excess oxygen. Presumably, it is due to the passage of the melting process in strongly oxidising atmosphere - atmospheric ozone. Under the influence of concentrated radiant flux is ionized oxygen to form ozone. Ozone has increased solubility in the melt than oxygen molecules. This leads to oxidation of polyvalent cations to high valent condition. In research [6] it indicates that in the smelting process is a reduction of oxygen content in the melt and stabilize Cu$^+$, where the monovalent copper is $R(Cu^+) = Cu^+/2(Cu^++Cu^{2+}) = 0.7-0.8$. Perhaps a strong deficiency of oxygen in the dense amorphous precursors reduces the speed of the formation of the superconducting structure that is connected slow diffusion of oxygen into the sample during heat treatment. The oxygen content in the starting precursors that determine the valence conditions of the cations, can affect to the mechanism of superconducting compounds, the rate of their formation, defective of crystal structure and the critical parameters of the target material.

Synthesis of superconducting phase was carried out by heat treatment in the range from 973K to 1138K, with a holding time of 5 hours to 150 hours. For all compositions superconducting phase $Bi_{1.7}Pb_{0.3}Sr_{2}CaCu_{2}O_{δ}$ (2212) began to take the shape at 973-1023K. For the composition $Bi_{1.7}Pb_{0.3}Sr_{2}CaCu_{2}O_{δ}$ temperature of maximum rate of formation of the 2212 phase was lying under 1123-1133K. In this temperature range the single-phase samples were formed 5-10 hours of heat treatment that is 6-7 times greater than the rate of formation of HTSC phase in comparision with solid phase method. Increasing the annealing temperature to partial melting (1133-1138K) and surface treatment with a concentrated radiant flux led to the sealing of the sample and the formation of high-texture of the particles along the plane [001] (figure 1).

![Figure 2. XRD pattern of textured HTSC ceramic samples of nominal composition $Bi_{1.7}Pb_{0.3}Sr_{2}CaCu_{2}O_{δ}$ 1133-1138K synthesized at the surface and processed concentrated radiant flux.](image)

Samples of the compositions $Bi_{1.7}Pb_{0.3}Sr_{2}Ca_{n-1}Cu_{n}O_{δ}$ ($n = 3-12$) were synthesized in the range 1115-1125K with a holding time of 60-120 hours. X-ray diffraction study revealed that in the diffractograms of nominal compositions $Bi_{1.7}Pb_{0.3}Sr_{2}Ca_{n-1}Cu_{n}O_{δ}$ ($n = 3-5$) were present only reflected ray reflexes related to the superconducting phase in 2223 (figure 3).
The duration of a complete formation of 2223 phase was 60-80 hours. The increase in heat treatment time up to 150 hours led to the partial collapse of the superconducting 2223 phase with the formation of the 2212 phase, which may be due to tensions at the junction of the crystallites by increasing their size. In samples with a high content of Ca and Cu temperature of formation of the superconducting 2223 phase decreased. If the nominal composition Bi$_{1.7}$Pb$_{0.3}$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{\delta}$ optimal synthesis temperature ranged 1123-1125K, then ended Bi$_{1.7}$Pb$_{0.3}$Sr$_2$Ca$_{11}$Cu$_{12}$O$_{\delta}$ it was lying in the range 1115-1117K.

Research of the microstructure composition of the HTSC samples showed that the crystals have a lamellar structure. The samples are also set an excessive content of oxygen, as in the amorphous precursors. For example, figure 4 shows the microstructure of samples of HTSC compounds Bi$_{1.7}$Pb$_{0.3}$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{\delta}$ (n = 3, 5).

For practical application in high technology the main parameter HTS is the critical current, which depends, in particular, from the texture and density of the particles. In order to obtain high texture,
sample previously synthesized pattern HTS of composition Bi$^{1.7}$Pb$^{0.3}$Sr$^{2}$Ca$^{n-1}$Cu$^{n}$O$_{\delta}$ milled to grain fraction 2-3 mkm layers and compressed into tablets with a diameter of 15 mm and a thickness of 1.5 - 2 mm. After the heat treatment at the temperature 1123-1125K, 24 hours in the diffraction pattern appears only intensive reflections of the 2223 phase [0010] [0012] [0014] that can be said to be a high-texture of the particles in the ceramic along the plane [00I] (figure. 5).

![Figure 5. The XRD pattern of textured HTSC samples of nominal composition Bi$^{1.7}$Pb$^{0.3}$Sr$^{2}$Ca$^{n}$Cu$^{n}$O$_{\delta}$ (2223) obtained with stratified compression.](image)

Studying of critical parameters showed that the samples consisted of 2223 superconducting phase with $T_c = 107$K. It is important to note that the samples except 2223 phase were presented the system of superconducting phases exceeding 107K (2223). For example, in a sample of nominal composition Bi$^{1.7}$Pb$^{0.3}$Sr$^{2}$Ca$^{4}$Cu$^{5}$O$_{\delta}$ besides the main 2223 phase, the superconducting phase system is detected with $T_c$ up to 181K (figure 6).

Formation of superconducting phases in samples of HTSC with $T_c$ in the 107-181K can be explained as follows: firstly, in the process of melting the raw material non-equilibrium condition due to melting of the anisotropic effects of concentrated radiant flux creates a strong gradient conditions in the melt, which can form a region with microscopic structure; secondly, the concentrated radiant flux including a wavelengths of ultraviolet, visible and infrared regions of the spectrum can affect the resonant atoms and change their energy state; thirdly, the excessive dissolution of ozone into the melt under the influence of the concentrated light flux can change the valence condition of cations. Together, these factors in rapid quenching of the melt can stabilize the amorphous condition, which includes a certain number of microregions have: a certain energy condition; appropriated on the composition; and prestructure (amorphous or semi-amorphous) of superconducting phases Bi$^{1.7}$Pb$^{0.3}$Sr$^{2}$Ca$^{n}$Cu$^{n}$O$_{\delta}$ ($n = 4, 5, 6$). When heat treatment, these microregions can transfer to the superconducting phase with lattice parameters corresponding to compositions Bi$^{1.7}$Pb$^{0.3}$Sr$^{2}$Ca$^{n}$Cu$^{n}$O$_{\delta}$ ($n = 4, 5, 6$) having elevated $T_c$ in the range 107-181K.
Figure 6. Dependence of the logarithmic decrement ($\delta$) and the oscillation period ($t$) from the temperature of HTSC samples of nominal composition $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{2}\text{Ca}_{2}\text{Cu}_{3}\text{O}_{y}$ (a) and $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{2}\text{Ca}_{2}\text{Cu}_{3}\text{O}_{y}$ (b).

4. Conclusion

On the basis of amorphous and crystalline glass precursors obtained by quenching the melt under the influence of concentrated radiant flux were synthesized HTSC ceramic nominal composition $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{2}\text{Ca}_{n-1}\text{Cu}_{n}\text{O}_{\delta}$ ($n = 2-12$). For all samples of $n = 3 - 12$, the main phase was the superconducting 2223 phase. The increase of the rate of formation of HTSC phases was established, which may be associated with the stabilization of highvalent variable valence condition of cations and metastable condition of amorphous precursors. In the samples, except for the main superconducting 2223 phase (110K) were found the systems of HTSC phase having a higher $T_c$, up to 181K. The high texture of the particles along the plane [001] is established in the samples.

References

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