Superconducting YBCO ceramics after exposure to a plasma flow to a mixture of argon and oxygen

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Abstract. The structure and properties of superconducting nanostructured ceramics YBa$_2$Cu$_3$O$_{y}$ (YBCO) before and after exposure to a plasma flow consisting of a mixture of argon and oxygen (at ~ 600 °C for ~ 1 min) are investigated. Plasma surface treatment, in addition to compaction of grains, leads to a change in the oxygen stoichiometry index and average crystallite size, as well as to a decrease in the proportion of the superconducting phase in the ceramic. After plasma treatment of ceramics, the character of the temperature dependence of the electrical resistance $\rho = f(T)$ changes from metallic to semiconductor, and the temperature $T_{c, \text{onset}}$ remains constant.

1. Introduction
Interest in ceramic materials based on YBCO as classical superconductors does not diminish not only in fundamental but also in practical terms [1, 2]. On the basis of these superconductors, they create: short-circuit current limiters [3], electrodes in piezoelectric resonators [4], magnetic bearings [5], coils [6], various transport systems [7], etc. Ceramics for creating permanent magnets, mainly, are made in the form of rings [8].

In recent years, technologies have been developed for producing coarse-grained bulk superconductors by growing textured grains from a melt [9] to improve and improve the properties of ceramics. Depending on the area of application, both dense [10] and porous [11] samples of superconducting ceramics are manufactured. Particular attention is paid to highly porous superconductors obtained by nanostructuring [12], including by 3D printing [13]; in the form of foam [14], fabric of nanowires [15,16], etc. A detailed review of the properties of superconductors with porosities above 50% is presented in [17]. Not only chemical methods [12], but also methods based on plasma treatment [18, 19] of ceramics are promising for the preparation of samples with a gradient porosity.

This paper presents the results of studying the structure and properties of a nanostructured ceramic superconductor YBCO exposed to a plasma flow from a mixture of argon and oxygen.

2. Methods
Nanostructured ceramics YBCO with a density of ~ 3.1 g/cm$^3$ was made from nanopowder in one sintering stage [12, 18]. Nanopowder was obtained from an aqueous solution of nitrates: Y
(NO$_3$)$_2$·6H$_2$O (99.99% purity), Ba(NO$_3$)$_2$ (99.99%) and Cu(NO$_3$)$_2$·3H$_2$O (99.99%), adding glycerin (~0.7% of solution) and concentrated nitric acid. Preliminary heat treatment of the formed precipitate was carried out for 1 hour at a temperature of 350 °C with a rise rate of ~10 °C/min. (initial powder - P1). Further, this initial nanopowder was heated to 915 °C at a rate of ~4.9 °C/min (~2 hours) and kept at this temperature for 20 hours, then in 2 hours the temperature was dropped to 450 °C at a rate of ~3.8 °C/min, the powder was kept at 450 °C for 5 hours (powder - P2). Cooling to room temperature was carried out at a rate of ~1.5 °C/min.

After heat treatment, the powder P2 was pressed under a pressure of no more than 40 MPa. The ceramic sintering mode - C1 was chosen as follows: heating at a rate of ~0.75 °C/min to 920 °C, holding for 1 hour, then in 2 hours a decrease to 450 °C at a rate of ~3.9 °C/min, holding at this temperature for 5 hours and cooling to room temperature at a rate of ~1.5 °C/min. The process of oxygenation of the ceramic sample was carried out at 450 °C. It was found in [12] that the samples of nanostructured ceramics prepared by the above method exhibit nanoscale structural inhomogeneities at the atomic level. The processing of a ceramic sample with a plasma flow (sample after plasma treatment – C2) was carried out with the following characteristics: medium – a mixture of argon and oxygen; gas flow rate ~1 g/sec; current ~300 A; voltage up to 27 V; temperature ~600 °C and duration ~1 min.

Diffraction analysis of the composition of the nanostructured ceramic samples was carried out on a PANalytical Empyrean series 2 diffractometer (X-ray wavelength $\lambda_{CuK\alpha} = 1.5406$ Å, HighScore Plus software). The crystallite size was determined by the Scherrer method from the peak widths. The electrical resistance of the samples was investigated by the 4-probe method.

3. Results and discussion Methods

Figure 1 shows diffraction patterns for powders P1 and P2, as well as nanostructured ceramics C1 and C2. As can be seen, powder P1 mainly consists of oxides of copper, yttrium, and barium; however, up to ~21% of the phase with stoichiometry YBa$_2$Cu$_3$O$_9$ is present.

Subsequent heat treatment at ~915 °C for 20 hours led to the formation (in powder P2) of a superconducting YBCO phase (up to ~91%) with an oxygen index of ~6.96 and a non-superconducting Y$_2$BaCuO$_5$ phase (up to ~9%). In this case, ceramic C1 after sintering at 920 °C consists almost 100% of the YBa$_2$Cu$_3$O$_{6.9}$ phase. Additional reflections on X-ray patterns for C1 are

![Figure 1. Diffraction patterns for: powders P1 – a), P2 – b); ceramics C1 – c) and C2 – d)
not observed. After treatment with a plasma flow at ~ 600 °C for ~ 1 min, the C2 ceramics by ~ 84% consists of the YBa2Cu3O6.8 phase and the copper oxide phase by ~ 16%. The X-ray diffraction pattern (Fig. 1d) shows insignificant peaks that are difficult to identify. The action of a plasma flow on the C2 ceramics (Figs. 1c and 1d), along with an increase in the resolution of the (013) reflection, leads to displacements, by about 0.1 °, of the peaks (013) and (103) to the region of smaller angles. In ceramics C2 (see Fig. 1 c and d), the positions of reflections (006), (020), and (200), which are responsible for the oxygen content, are shifted by the same amount. The average crystallite size for ceramics C1 and C2, calculated from the values of the half-width of the reflections, is ~ 52 and ~ 56 nm, respectively.

The results of studying the morphology of powders P1 and P2 and ceramics C1 and C2 are shown in Figure 2. As can be seen (Figs. 2a, b), after heat treatment at ~ 915 °C, not only YBCO phase was formed, but also the recrystallization of the initial amorphous precipitate occurred.

![Figure 2. Morphologies for powders P1 – a), P2 – b); ceramics C1 – c) and C2 – d)](image)

Despite the fact that the heat treatment was carried out at sufficiently high temperatures, nanosized grains remain in the ceramics (Fig. 2). For the sample C2, in contrast to C1, on the surface (Fig. 2c and 2d) areas of insignificant compaction of grains are observed. In this case, the density of ceramics after exposure to plasma increased from 3.1 g/cm³ to 3.5 g/cm³, mainly due to the surface layer.

Elemental analysis of the powder showed that after heat treatment at 915 °C, the Y content decreased by ~ 1.5 times, the Ba content increased by ~ 3.6 times, and Cu and O decreased by about 1.2 times. For P2 powder, the content of elements, on average, is: Y - 8.3%; Cu - 12.7%; Ba - 29.5%; O - 49.6%. The results of studying the elemental analysis of ceramic samples (Fig. 3) before and after exposure to plasma (C1 and C2) showed the following content of elements: Y - 8.8%, Cu - 12.1%, Ba - 26.9%, O - 51.1% and Y - 8.2%, Cu - 12.7%, Ba - 32.0%, O - 47.1%, respectively, and the carbon content is less than ~ 1%.
Figure 3. Results of elemental analysis of ceramics C1 - a) and C2 - b).

The temperature dependences of electrical resistivity in the region of superconducting transition for ceramics C1 and C2 are shown in Fig. 4. As can be seen, as a result of exposure to the plasma flow, the type of the $\rho = f(T)$ dependence changed from metallic to semiconducting. In this case, the average value of the temperature coefficient of resistance (TCR) in the range 300-110K for ceramics C1 is $\sim 1.6 \cdot 10^{-3}$ K$^{-1}$, and for C2 it is approximately $1.02 \cdot 10^{-3}$ K$^{-1}$.

Figure 4. Dependences $\rho = f(T)$ for ceramics C1 - a) and C2 - b).
Exposure to the plasma flow did not lead to significant changes in the temperature of the onset of the transition to the superconducting state ($T_{c,\text{onset}}$), which for ceramics C1 and C2 is ~ 93.9 K and ~ 93.6 K, respectively. However, the temperature of the end of the transition to the superconducting state ($T_{c,\text{offset}}$) after plasma exposure increases by about 15K, for ceramics C2 it is ~ 70K (extrapolated value).

4. Conclusion
Short-term plasma treatment of the surface of nanostructured YBCO ceramics at a temperature of ~ 600 °C for ~ 1 min, in addition to the positive effect associated with grain compaction, leads to changes in the oxygen stoichiometry index and average crystallite size, and to a decrease in the value of the fraction of the superconducting phase. After exposure to the plasma flow, the character of the $\rho = f (T)$ dependence changed from metallic to semiconducting. The average TCR value in the range of 300-110K for ceramics C1 is ~ $1.6 \cdot 10^3$ K$^{-1}$, and for C2 it is approximately $-1.02 \cdot 10^3$ K$^{-1}$. The treatment of ceramics with a plasma flow did not lead to significant changes in the temperature $T_{c,\text{onset}}$ at the same time, the temperature $T_{c,\text{offset}}$ increases by about 15K.

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