Changes in the surface structure of nanostructured ceramics YBa$_2$Cu$_3$O$_{7-y}$ after exposure to a plasma stream

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Abstract. The paper presents the results of a study of the surface structure of nanostructured superconducting ceramics YBa$_2$Cu$_3$O$_{7-y}$ (YBCO) before and after short-term exposure to a plasma stream. Exposure to the plasma stream changes the structure of the ceramic surface and the oxygen content in it, and also slightly increases the average crystallite size.

1. Introduction

With nanostructuring of YBCO superconducting ceramics, the sizes of crystalline grains and the strength of intergranular bonds decrease. In addition, nanoscale structural defects are formed that promote [1-3] vortex pinning.

It is known [4, 5] that vacuum-arc synthesis methods are effectively used to create pinning centers. To increase the surface strength of microcrystalline HTSC ceramics by amorphizing it and reducing the fraction of defects at grain boundaries, plasma treatment is usually used [6]. It was also established [7, 8] that with plasma exposure to the surface, superconducting characteristics in the bulk of the sample do not decrease. Therefore, it is of interest to analyze the mechanisms of the formation of the necessary structure and surface composition of nanostructured ceramics, as well as the optimization of the corresponding processes as a result of plasma exposure to ceramics.

Nanostructured ceramics of YBCO composition was made from nanopowder obtained by chemical technology [7-10]. The diffraction analysis of the composition of this ceramic was carried out on a PANalytical Empyrean series 2 diffractometer (X-ray wavelength $\lambda_{CuK\alpha} = 1.5406$ Å). Data processing was performed using HighScore Plus software. The crystallite size was determined from the width of the peaks by the Scherrer method. The oxygen content ($y = 7-\delta$) in the samples was determined by X-ray diffraction analysis and Raman spectroscopy from the ratio of the intensities of the Raman shift lines 500 cm$^{-1}$ and 340 cm$^{-1}$ obtained with the Ntegra Spectra setup (Raman mode). The plasma flow from a mixture of argon and oxygen on the surface of an optimally doped sample of superconducting nanostructured YBCO ceramics was carried out by a plasmatron [11].

2. Results and discussion

YBCO nanopowder synthesized by burning nitrate – organic precursors was previously heat treated at 915°C for 20 hours. Nanopowder briquettes pressed at $\sim 100$ MPa were sintered at a temperature of
920°C for 1 hour. After saturation with oxygen at 450°C for 5 hours, the ceramic samples contained 100% of the superconducting phase.

Figure 1 shows the diffraction patterns of the superconducting nanostructured YBCO ceramic before and after short-term (~ 60 s) exposure to its surface by a plasma stream. The initial sample had a superconducting orthorhombic structure YBa$_2$Cu$_3$O$_{6.91}$. After exposure to the plasma stream, a slight decrease (up to 84%) in the proportion of the superconducting phase and the appearance of side phases — Y$_2$BaCuO$_5$ and CuO. As can be seen in Figure 1, such an effect, along with an increase in the resolution of the [013] reflex, leads to displacements of the [013] and [103] peaks in the region of lower angles. Similar displacements are observed for reflections [006], [020] and [200], which are responsible for the oxygen content. The mixing of the peaks and their broadening indicate insignificant changes in the oxygen stoichiometry index (from 6.91 to 6.82) and the average crystallite size (from ~ 52 to ~ 56 nm), respectively, in the surface layer of the sample subjected to plasma exposure.

![Figure 1. Fragments of diffraction patterns of nanostructured YBCO ceramics before (1) and after (2) exposure to a plasma stream](image)

Fragments of Raman spectra of nanostructured YBCO ceramics before and after exposure to a plasma stream containing centrosymmetric modes: (O$_2^+$ /O$_3^-$) at ~ 340 cm$^{-1}$ (superconducting phase) and (O$_2^+$ /O$_3^+$) at ~ 450 cm$^{-1}$ (tetragonal phase), as well as the mode corresponding to ~ 500 cm$^{-1}$, are shown in Figure 2. Centrosymmetric modes characterize the vibrations of oxygen atoms in the CuO$_2$ plane of the conduction block. A peak at ~ 500 cm$^{-1}$ characterizes the vibrations of apical oxygen atoms (O4). With an increase in the oxygen content in the samples, the line intensity at ~ 500 cm$^{-1}$ usually increases. In this case, before and after plasma exposure, the intensity ratio I$_{500}$/I$_{340}$, indicating a high degree of doping, decreases slightly, despite the fact that the value of I$_{500}$ increases.

This indicates the occupation of positions in the direction a by the atoms of excess oxygen obtained by the sample from the plasma stream. The almost complete population of the positions of the crystal lattice in the b direction is confirmed by the preservation of a high degree of doping of ceramics before and after plasma exposure. This follows from the data of diffraction analysis and Raman scattering. The oxygen index y, determined from the ratio of the intensities of the Raman shift line 500 cm$^{-1}$ and 340 cm$^{-1}$, after exposure was ~ 6.70, whereas before exposure it was ~ 6.73. Low y values, in comparison with the data obtained from diffraction analysis, are associated with the fact that the accuracy of determination of oxygen stoichiometry by the Raman method is lower. However, the
Raman method makes it possible to establish an excess or deficiency of oxygen content during optimal doping of the sample, providing it with high values of the temperature of transition to the superconducting state.

![Figure 2. Raman spectra of nanostructured ceramics YBCO, before - 1) and after - 2) plasma exposure.](image)

The results of studying the electrical resistance before and after exposure to plasma are shown in Figure 3. As can be seen, exposure to plasma does not lead to significant changes in the temperature of the transition to the superconducting state - \( T_c \), it remains at its optimum value - 92K. The temperature of the onset of the transition to the superconducting state (\( T_{c_{onset}} \)) before and after exposure also does not change significantly (to ~ 93.9 K, and after ~ 93.6 K). However, the temperature of the end of the transition to the superconducting state (\( T_{c_{offset}} \)) after exposure to the plasma stream increases by about 15K and amounts to ~ 70K (extrapolated value). Before treatment with a plasma stream (Figure 3, curve 1), the dependence of the electrical resistance on temperature is metallic; the average value of the temperature coefficient of resistance (TCR) in the range 300-110K is \( 1.6 \cdot 10^{-3} \) K\(^{-1}\). After exposure to a plasma flow (Figure 3, curve 2), it changed significantly — a semiconductor character of conductivity with a TCR of \( 1.02 \cdot 10^{-3} \) K\(^{-1}\) in the same temperature range is observed. In this case, for the amorphized surface layer after exposure to a plasma stream, the semiconductor character of the \( \rho = f(T) \) dependence (Figure 3, curve 3) is also observed without transition to the superconducting state. The TCR of this dependence is 3 times higher than for the entire sample, and is \( -3.1 \cdot 10^{-3} \) K\(^{-1}\) in the range of 300-110K. The value of resistance at 300K (\( \rho_{300K} \)) in the sample after exposure increases by 1.7 times, and for the surface layer it is 5 times higher.

3. Conclusion

Short-term plasma treatment (~ 60 s) of the surface of a YBCO nanostructured ceramic sample with a mixture of argon and oxygen leads to changes: the oxygen stoichiometry index (from 6.91 to 6.82) and the average crystallite size (from ~ 52 to ~ 56 nm), a decrease fraction of the superconducting phase (from ~ 100% to ~ 84%). The ratio of the intensities I500/I340 of the Raman spectra after plasma exposure decreases slightly.

The temperature \( T_c \) beginning before and after exposure does not change significantly (from ~ 93.9 K to ~ 93.6 K), but \( T_{c_{set}} \) of set increases by about 15K. After exposure to plasma, the character \( \rho = f(T) \) of the sample changes from metallic to semiconductor. The average value of TCR varies from 1.6 \cdot 10^{-3} \) K\(^{-1}\) to -1.02 \cdot 10^{-3} \) K\(^{-1}\) in the same temperature range. Amorphized surface layer after exposure is not
superconducting, TCR is \(-3.1 \cdot 10^{-3} \text{K}^{-1}\). The value of \(\rho_{300K}\) after exposure in a bulk sample increases by 1.7 times, and in a surface sample by 5 times.

![Temperature dependence graph](image)

**Figure 3.** Temperature dependences \(\rho/\rho_{300K}\) for YBCO ceramics: before exposure - 1); after exposure to the sample and its surface layer - 2) and 3), respectively. Notation: the approximated function \(y = f(x)\) and the correlation coefficient \((r)\) are.

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