Structure and conductivity of nanostructured YBCO ceramics

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Abstract. Superconducting nanostructured ceramics based on YBa2Cu3O7-δ were made of nanopowder obtained by burning nitrate-organic precursors. The structure, morphology, electrical resistivity, and density of ceramics were studied. Various porosity values of the ceramics were achieved by preliminary heat treatment of the nanopowder. The features of conductivity and the reason for increase of the of the superconducting transition temperature in these materials are discussed.

1. Introduction
The paper is devoted to the problem of establishing a connection between the structure of nanostructured ceramics based on YBa2Cu3O7-δ (YBCO) compounds and the effect of increasing the superconducting transition temperature. The structure and morphology of the obtained nanopowder and nanostructured ceramics of various densities were studied on X-ray diffractometer “PANalytical Empyrean series 2”, TEM “Titan 80-300”. Measurements of the electrical resistivity of high-temperature superconductors (HTSC) were carried out by the four-probe method.

2. Results and discussion
2.1. Structure and morphology of nanostructured ceramics YBa2Cu3O7-δ.
Nanostructured superconducting ceramic materials with different densities based on YBa2Cu3O7-δ were obtained from nanopowders. Nanopowders were produced [1] by burning nitrate-organic precursors obtained after evaporation of an aqueous solution of yttrium, barium and copper nitrates with the addition of various amounts of glycerin. Variation of the solution viscosities and the precursor burning speed allows one to obtain predetermined particle sizes as well as size distribution in the powders which contain also some amount of glycerin. Ceramics with different porosity were provided from these powders via appropriate preliminary heat treatment of the nanopowders. An optimal oxygen content in the ceramics was reach due to the high specific surface of nanopowders used for their sintering.

Figure 1 shows the results of diffraction analysis for four samples of HTSC ceramics containing ~ 95% phase of YBa2Cu3O7-δ. These samples were obtained from two batches of powders. The first batch differs from the second one by more glycerin amount used for the powder producing. The batches were thermally treated at 350 °C for 1 hour (Figures 1a and 1c) and at 910 °C for 20 hours (Figures 1b and 1d), respectively. Four briquettes were sintered at 920 °C for 1 hour after pressing the powders from both batches at a pressure of 100 MPa. Density of the ceramics obtained from the powders ther-
mally treated at 350 °C (Figures 1a and 1c) was equal to 2.5 and 3.0 g/cm³. Whereas the ceramics sintered from powders thermally treated at 910 °C (Figures 1b and 1d) have higher density of 6.0 and 5.7 g/cm³. Figure 1e also shows the reference diffraction pattern of YBa₂Cu₃O₇₋δ from the PAN-ICSD database. As 5% of the copper oxide crystalline phase is observed in the samples (Figures 1a and 1b) so they should also contain Y₂BaCuO₅ phase in the X-ray amorphous state. Indeed, this phase was observed (211) after its crystallization under prolonged heat treatment. The Y₂BaCuO₅ nanoparticles uniformly distributed in the YBa₂Cu₃O₇₋δ matrix produce pinning centers for the magnetic flux [2].

**Figure 1.** Diffraction patterns for ceramics made of two batches of thermally treated nanopowders. The first batch treated at 350 °C (a) and 910 °C (b). The second batch treated at 350 °C (c) and 910 °C (d). Reference YBa₂Cu₃O₇₋δ structure from the database PAN-ICSD (e).

As shown in [3], both highly porous (2.5 g/cm³) and dense (6.0 g/cm³) nanostructured ceramics made from the first batch of nanopowder consist of micron grains formed by the nanoparticles. According to the diffraction data, an average nanoparticle size was about 46 and 53 nm respectively. Slightly larger particle size of about 53 nm and 65 nm, respectively, was obtained for nanostructured ceramics made from the second batch of nanopowder which had the density of 3.0 g/cm³ and 5.7 g/cm³ [1].

The morphology inside the grains of nanostructured ceramics of 3.0 and 5.7 g/cm³ density are respectively shown in Figures 2a and 2b. The TEM have revealed presence of nanoscale defects in the nanocrystalline structure of YBCO grains, which are formed as a result of a “topological” transition from the nanoparticle agglomerate in the original powder to the crystalline grains consisting of nanosized domains and containing defects. Nano-domains in micro-sized grains are oriented chaotically. Defects are distortions of the crystal lattice at the atomic level. As seen in Figures 2a and 2b, the structure defectiveness of the grains at the atomic level is higher for ceramics with lower density. Similar results were obtained for the ceramics made from both batches of the nanopowder.
Reducing the size of particles and increasing the role of surface tension forces obviously should lead not only to the structure distortion at the atomic level, but also affect other properties of the ceramics.

![Figure 2. Morphology inside grains of the nanostructured YBa$_2$Cu$_3$O$_{7-δ}$ ceramics: (a) porous, (b) dense. The insets show electron diffraction patterns for corresponding grains](image)

2.2. Electrical resistivity of nanostructured YBa$_2$Cu$_3$O$_{7-δ}$ ceramics having various porosity.

According to data given in [1,3], transition to the superconducting state begins at temperature $T_c$ of about 96 K in samples from batches of dense and porous ceramics. Values of electrical resistivity $\rho$ of ceramics with greater porosity are an order of magnitude higher. The temperature coefficient of resistivity $\partial\rho/\partial T$ is lower and the transition is stretched for these ceramics. That apparently is associated with a smaller contact area between the grains. As shown in [1,3] samples from both batches of dense and porous ceramics have the same size of the grains. Higher values of electrical resistivity for porous ceramics are caused not only by a smaller contact area between the grains, but also by a higher defectiveness at the atomic level of the grains themselves (Figure 2a). Size of agglomerates and nanoparticles in the nanopowders from both batches, as well as size of grains in porous and dense ceramics are approximately the same. Therefore we can expect also the same values for transition temperatures $T_c$.

In this case, the $T_c$ increase up to ~ 96 K in the nanostructured ceramics appears to be caused by decrease of the crystalline-domain size by about twenty times in comparison with that for ordinary ceramics having micro-sized grains and $T_c = 92$ K. The decrease of the nanoparticles size leads to a corresponding increase in the interatomic interaction forces. As known [4], YBCO is characterized by loose packing and negative thermal expansion. Therefore, an increase of the interatomic interaction forces averaged over the lattice can compensate growth of the interatomic distances due to the thermal expansion and lead to the ordering of the oxygen ions in the $b$ direction of the unit cell in a wider (up to ~ 96 K) temperature range.

Figures 3 and 4 show the experimental data on temperature dependences of the electrical resistivity and their temperature coefficient for both batches of dense and porous ceramics. As seen, the onset of the superconducting transition occurs at a temperature of about 96 K.

According to the location of the most intense peak, the average transition temperature $T_c$ for the batch with a larger particle size (from 65 to 53 nm) is about 95.5 K (see Figure 4), while for the batch (Fig. 3) with a smaller particle size (from 53 nm to 46 nm) it varies from 92.6 to 94.3 K. At the same time, as seen in Figures 3 and 4, there is a tendency to reduction of average $T_c$ values when size of the nanoparticles decreases from 65 to 46 nm.

Several peaks in the $\partial\rho/\partial T$ dependencies indicate presence of phases with different values of oxygen index. As known [5], presence of superconducting phases with different $T_c$ is associated with pre-
cipitates of extrinsic nanostructured phases of different stoichiometry [6-8] and a violation of the cationic composition of YBCO.

**Figure 3.** Temperature dependences of the electrical resistivity and the temperature coefficient of electrical resistivity for porous (a) and dense (b) ceramics made of nanopowder from the first batch. Resistivity of dense sample (b) is multiplied by ten.

**Figure 4.** Temperature dependences of the electrical resistivity and the temperature coefficient of electrical resistivity for porous (a) and dense (b) ceramics made of nanopowder from the second batch.
3. Conclusion
Developed chemical technology of production and heat treatment of nanopowders allow us to produce nanostructured YBa$_2$Cu$_3$O$_{7-x}$ ceramics with predetermined density and optimal oxygen content in one step process. Increase of the transition temperature up to ~ 96 K in these ceramics is apparently caused by decrease of particle size and a corresponding increase of the interatomic interaction forces. At the same time, when the dimensions of the nanoparticles decrease below ~ 50 nm, there is a tendency to reduction of average $T_c$ values.

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