Nonmonotonic Structural Changes in HTSC Bi-2201 Ceramics
Depending on Oxygen Nonstoichiometry

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Abstract—Effect of the oxygen content in ceramic high-temperature superconductors Bi$_2$Sr$_2$CuO$_{6+\delta}$ on their phase composition, crystal structure, and charge state of cations has been studied. As the oxygen content changes, the lattice parameters were shown to exhibit nonmonotonic variation; no changes in the phase composition and charge state of cations take place. According to neutron diffraction data, the overstoichiometric oxygen atoms are introduced only into the BiO$_{1+\delta}$ layers. The nonmonotonic variations observed are explained assuming that, at a certain oxygen content, the hole charge carriers induced by introduced oxygen are localized in the BiO$_{1+\delta}$ layers rather than “flow down” into superconducting CuO$_2$ layers.

Keywords: HTSC cuprates, crystal structure, overstoichiometric oxygen

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INTRODUCTION

It was shown earlier for HTSC Bi-based Bi$_2$Sr$_2$CaCu$_2$O$_{6+\delta}$ (2212) [1–3] and Bi$_2$Sr$_2$CuO$_{6+\delta}$ (2201) [4–5] materials that the dependence of the lattice parameters on the charge carrier concentration (oxygen content in a sample [1–4] or the concentration of lanthanum, which substitutes heterovalently for strontium [5]) is nonmonotonic. This fact remains unexplained up to date. In this connection, we studied samples of the Bi$_2$Sr$_2$CuO$_{6+\delta}$ system, which is the simplest member of the Bi$_2$Sr$_2$Ca$_{y-1}$Cu$_y$O$_{2n+4}$ homological series with a single CuO$_2$ plane per unit cell. We are planning to check three possible causes for the nonmonotonic variations of the lattice parameter, namely, (1) changes in the charge state of cations; (2) the occupation of different types of positions by overstoichiometric oxygen; and (3) a non-single-phase state of the samples. The changes in the charge state of cations have been studied by X-ray absorption near-edge spectroscopy (XANES); the positions of overstoichiometric oxygen were refined by neutron diffraction analysis.

EXPERIMENTAL

The ceramic Bi-2201 samples were prepared by solid-state synthesis. The starting materials Bi$_2$O$_3$, SrCO$_3$, and CuO were taken in amounts corresponding to the stoichiometric composition, mixed carefully, compacted, and annealed at 750°C; the intermediate grinding and compacting continued until the intensities of the X-ray diffraction reflections stop changing. The materials prepared were characterized by structural modulations described, in particular, in [4, 6].

To obtain compositions differing in the oxygen content, the synthesized powder was annealed at 700°C at low oxygen pressures (log $P$(O$_2$)/atm = –1.7, –1.3, and –1 for samples 1, 2, and 3, respectively), in air (log $P$(O$_2$)/atm = –0.7 for sample 4), and in pure oxygen atmosphere (log $P$(O$_2$)/atm) = 0 for sample 5) using a vacuum circulation setup [7].

X-ray diffraction analysis was performed using a Shimadzu XRD-7000 diffractometer, Cu Kα radiation, and a graphite monochromator. The lattice parameters were calculated using 13 reflections and least-squares method for the tetragonal setting. Neutron diffraction analysis of samples 1, 4, and 5 was performed in the Kurchatov Institute Russian Research Center using an IR-8 reactor, DISK station (wavelength 1.668 Å), and double monochromator [8]. The extended X-ray absorption fine structure (EXAFS) spectroscopy and the XANES spectroscopy for Bi L$_3$ and L$_1$ and Cu K edges were performed in the Structural Materials Station, Kurchatov Institute Russian Research Center, in transmission geometry using a single-block channel-cut Si(111) monochromator and two ionizing chambers (filled with nitrogen–argon mixtures) as detectors [9]. The analysis was performed using Bi, Bi$_2$O$_3$, and NaBiO$_3$ spectra as the standards for the Bi$^{2+}$, Bi$^{3+}$, and Bi$^{5+}$ states, respectively. The magnetic measurements were performed during cooling using a CFS-9T-CVTI vibrating-sam-
ple magnetometer (Cryogenic Ltd.) in the constant-field ($B = 0.1 \, T$) regime; the transition temperature was determined by the two-tangent method. The crystal structure of the samples was analyzed using X-ray diffraction data and a GSAS program package [10]. As the initial structure, the model was used obtained by analyzing a single crystal in [11]: space group $Cccm$ (orthorhombic structure) with the atomic coordinates

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\begin{align*}
\text{Bi} & : (0.2682, 0.0634, 0) \\
\text{Sr} & : (0.2473, 0.1776, 0.5) \\
\text{Cu} & : (0.75, 0.25, 0.5) \\
\text{O}_1 & : (0.5, 0.2512, 0.75) \\
\text{O}_2 & : (0.227, 0.144, 0) \\
\text{O}_3 & : (0.347, 0.07, 0.394)
\end{align*}
\]

The occupation number for $\text{O}_3$ atoms was taken to be 0.25 in X-ray diffraction calculations; when fitting neutron diffraction data, this parameter was varied. The reliability factors for X-ray and neutron diffraction are $R_p \approx 6\%$, $\omega R_p \approx 4-5\%$, and $R_p \approx 3.5\%$, $\omega R_p \approx 4.6\%$, respectively. The EXAFS data were processed using an IFEFFit program complex [12]. As the initial structure model, a structure was taken characterized by the space group $Amaa$ with the atomic coordinates $\text{Bi} : (0, 0.271, 0.0658)$, $\text{Sr} : (0, 0.755, 0.1802)$, $\text{Cu} : (0, 0.25, 0.25)$, $\text{O}_1 : (0.25, 0.0245)$, $\text{O}_2 : (0.25, 0.156)$, $\text{O}_3 : (0.25, 0.055)$, $\text{O}_4 : (0.25, 0.5, 0.055)$ [13]. This more complex model was used in order to take into account the fact that the stoichiometric and overstoichiometric oxygen ions can be located at different distances from a bismuth ion. In the case under consideration, the $\text{O}_3$ and $\text{O}_4$ positions were assumed to be stoichiometric and overstoichiometric, respectively. The reliability factor reached was $2.7-7.4\%$.

**RESULTS AND DISCUSSION**

Figure 1 shows X-ray diffraction data for samples 1–5. Their phase compositions are identical; X-ray diffraction patterns exhibit weak additional lines (almost identical for all samples 1–5), which correspond to superlattice modulations [4, 6, 14]. In Fig. 1, the Miller indices for a simplified tetragonal cell with the lattice parameters $a = b = 5.38$ and $c = 24.5 \, \text{Å}$ (ignoring modulations) are given.

Figure 2 displays the oxygen concentration determined from the dependence of the overstoichiometric oxygen content on the oxygen partial pressure [4]. We failed to directly determine the oxygen content in samples by the reduction to simple oxides because of the high volatility of bismuth oxide.

The lattice parameters were determined using 13 lines whose indices are shown in Fig. 1; the root-mean-square deviations of the calculated angular (20) positions from the experimental ones are less than 0.02°; the maximum deviation did not exceed ±0.035°. Figure 3 shows a nonmonotonic dependence of the lattice parameter on the oxygen content.

![Fig. 1. X-ray diffraction patterns for Bi-2201 samples annealed in various atmospheres. The Miller indices for a simplified tetragonal lattice (ignoring modulations) are shown above the diffraction maxima. The order numbers of the samples (1–5) are given near each line.](image-url)