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Phase State of $\text{YBa}_2\text{Cu}_3\text{O}_d$ ($d = 6.7\text{--}7.4$) That Has Been Modified at Ambient Temperature

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Abstract

The capability of $\text{YBa}_2\text{Cu}_3\text{O}_d$ for an intensive exchange with oxygen of a gas phase even at ambient temperature (t_a) that has been detected previously has been studied with diversified physical methods. An X-ray photoelectron spectroscopy method has been applied to demonstrate that a degree of ionicity of cation-oxygen bonds increases during oxidation under the t_a conditions. Along with this phenomenon, oxygen appears in a state that is close to chemically unbonded. This correlates with evidence on spontaneous electric polarization that emerges in yttrium-baric cuprate under the test conditions. The obtained result has been explained in the context of $\text{YBa}_2\text{Cu}_3\text{O}_d$ model as of a virtual ferroelectric, the critical temperature of which in certain conditions can grow up to high positive values. In so doing, modification of chemical state of $[\text{BaO}_2]$ structural group occurs from formal peroxide to formal oxide with strengthening of a certain Ba–O bond and with weakening of another one.

INTRODUCTION

As of now, developments of so-called chemical containers are of great practical interest as safe and effective way to store a wide spectrum of gases. To take an example, certain intermetallic compounds can accumulate a significant amount of hydrogen, excretion of which occurs upon slight heating at ambient temperature. Intercalates around dicarbon fluoride accumulate hydrocarbons, freons, and other gases in large concentrations [1]. At the same time, molecules of oxygen are hardly susceptible of similar packing for their rather big size and for no polarity, which provided a motive for searching an appropriate intercalate among new, recently open compounds. In the previous work [2], we have demonstrated that dispersed yttrium-baric cuprate $\text{YBa}_2\text{Cu}_3\text{O}_d$ that has been treated with the expressly prepared gas mixture becomes modified and acquired the capacity to be intensive exchanged with oxygen of a gas phase even at ambient temperature (t_a). Accordingly, oxygen actively evolves during

the process of $\text{YBa}_2\text{Cu}_3\text{O}_d$ treatment with a mixture of 0–0.03 % O_2 , 0.04–0.12 % H_2O , and the balance of noble gas, and the d value becomes equal to approximately 6.0. An oxidation process that is analogous in its intensity occurs in an atmosphere with more than 3 % of oxygen (with the same level of absolute water content), and $d \approx 8.0$. Unusual manifestation of oxygen exchange has been attributed to a new phase that is formed in the mentioned conditions, namely, ϱ (according to its characteristic d parameters, we shall use later on the following designations: ϱ_{f} and ϱ_{b}). It is has been pointed out [2] that conversion to the ϱ -phase with the fixed regime parameters does not affect the whole volume of $\text{YBa}_2\text{Cu}_3\text{O}_d$. For example, only the sites that initially possess an *ortho*-I-structure [2] are subject to the modification at $p_{\text{H}_2\text{O}} \approx 110$ Pa (the specified humidity value is used for preparing samples in this work).

This work mounts an attempt to define the nature of the discovered phenomenon by means of diversified physical methods of research.

EXPERIMENTAL

Material for the research was prepared from CuO and Y_2O_3 oxides and from barium carbonate through calcination of an initial homogenized mix at 1213 K over the course of 100 h; $\approx 98\%$ of $YBa_2Cu_3O_d$ phase have been received. Oxidizing annealing of the compound was conducted in the air atmosphere at 773 K for 5 h with the result that its oxygen composition comprised, according to iodometric titration, $d = 6.72 \pm 0.02$ (hereinafter, the samples A). The subsequent treatment to yield "modified" samples was conducted according to the procedure [2] that consists in blowing-down of samples by a gas mixture with the controlled p_{O_2} and p_{H_2O} parameters and that involves careful adjusting of the magnitude of the second parameter. It should be emphasized that rather low p_{H_2O} values that are used within the suggested procedure (40–120 Pa) ensure chemical stability of yttrium-baric cuprate as regards its hydrating reaction [3, 4]. Moreover, according to the research [5], the surface of $YBa_2Cu_3O_d$ adsorbs less than a single H_2O layer at this humidity; water does not penetrate into the bulk of the oxide.

Figure 1 displays isochronous curves of oxidation of the A samples in coordinates "variation of mass (Δm) – p_{H_2O} " that were generated at $t_a = 298$ K. As it can be seen, a record increase of mass (by $\sim 2\%$) is evidenced at the regime parameters: $p_{O_2} = 21$ kPa, $p_{H_2O} = 110$ Pa (hereinafter, "the optimum composition"), which, according to [2], bears witness to the appropriate maximum quantity of additional oxygen that has penetrated in the material: $d_d = 2.43\Delta m$. (Hereinafter, by this is meant the variation in average oxygen content over a sample. Actually, only part of the material [2] undergoes certain modifications at t_a .) During further research, comparative analysis of the samples A and samples B that were processed with "the optimum composition" was conducted.

Analysis of the obtained material was conducted by thermogravimetry method with the use of thermoanalyzer Du Pont Instruments 951 Thermogravimetric Analyser (USA), which is characterized by the following parameters: the sensitivity of 0.1 mg, precision of 0.2 %.

X-ray photoelectron spectroscopy (XRE) of samples was executed in a MULTIPROB

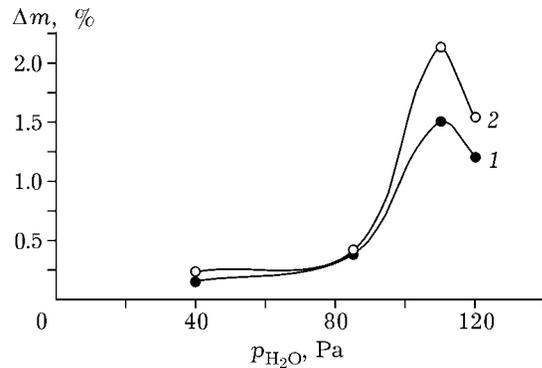


Fig. 1. Isochronous dependences of variation in the mass of the samples A on the humidity of the gas phase at $p_{O_2} = 21$ kPa. The duration of treatment with gas mixture, h: 50 (1), ≈ 150 (2).

spectrometer of Omicron Corporation (Germany). The energy scale of the device was corrected under calibrating standards, the maximums of $Au4f_{7/2}$, $Ag3d_{5/2}$ and $Cu2p_{3/2}$ peaks. To make allowance for "charging" of samples that arises during electronic emission, final adjusting of the peak positions was performed based on the position of a low-energy component of C1s spectrum (from organic impurities), the position being taken as 285.0 eV. There was no preliminary cleansing of the surfaces under investigation to rule out uncontrollable distortions of the results that are probable in these cases.

High-temperature photoelectric type dilatometer was applied to make an indirect estimation of the polarization magnitude (P) that is induced in an electrical field: the effect of change in the linear sizes was used (up to 20 %) for a bulk bed of a dispersible sample upon the emergence of dipole-dipole interaction between its particles. The mechanism of the dilatometer and the process of installation of a sample in its operation chamber are shown schematically in Fig. 2. Graduation of the device was performed at t_a with $LiNbO_3$ ferrosemiconductor, whose distribution of sizes is analogous to the composition of yttrium-baric cuprate, and for which the dependence of polarization on the intensity of external electrical field has been reported. The error of P magnitude that was determined in this way was as large as $\pm 30\%$.

Magnetic characteristics of $YBa_2Cu_3O_d$ were measured by method of magnetic induction in a gauge that was calibrated (the scale of

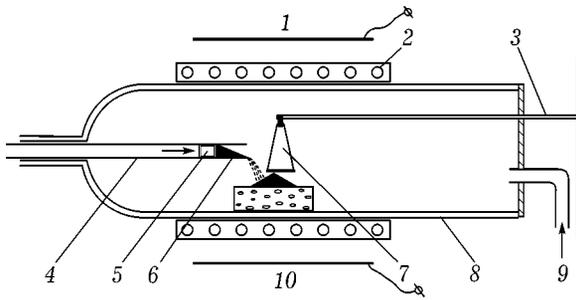


Fig. 2. Experimental scheme to determine temperature dependence of $\text{YBa}_2\text{Cu}_3\text{O}_d$ polarization: 1, 10 – the metal plates with the current leads that are intended to generate electrical field in the working space; 2 – heating elements; 3 – a rod that goes to a photoelectric transducer; 4 – a pipe (container) with $\text{YBa}_2\text{Cu}_3\text{O}_d$ material; 6; 5 – a piston; 7 – a gauge feeler; 8 – a test tube that limits the working space; 9 – a fitting pipe to inject the reaction gas mixture in the working space of the set-up.

magnetic susceptibility, negative values) at a temperature of 4.2 K with niobium and Al_2O_3 compositions. X-ray diffraction research was conducted in the DRON-2 diffractometer.

RESULTS AND DISCUSSION

Thermogravimetry

The sample B (to study its stability) was held in the low-oxygen medium in the atmosphere of humidified helium (the parameters: p_{O_2} @ 10^{-2} kPa, $p_{\text{H}_2\text{O}}$ @ 1 kPa, t_a). Sample drawing for TG analysis was made from one sample in certain time terms. Results of thermogravimetric experiments are presented in Fig. 3. The found dependences are of a standard form for $\text{YBa}_2\text{Cu}_3\text{O}_d$: a uniform decrease of mass (m) occurs, in an interval of 723–1193 K. At the same time, total relative change in the mass of the sample that has been taken immediately after the material B has been produced was higher than the standard value (1.15 % [6]) by 1.2 %, by the magnitude that was equal to an increase in mass during oxidizing treatment at t_a . For alternative samples, the magnitude Dm_{max} depended on the duration of the exposition that was conducted in helium atmosphere (see Fig. 3).

In the context of the work [2], the obtained result may be interpreted as follows: after the transformation $ortho\text{-I} @ \mathfrak{g}_8$ has passed (under

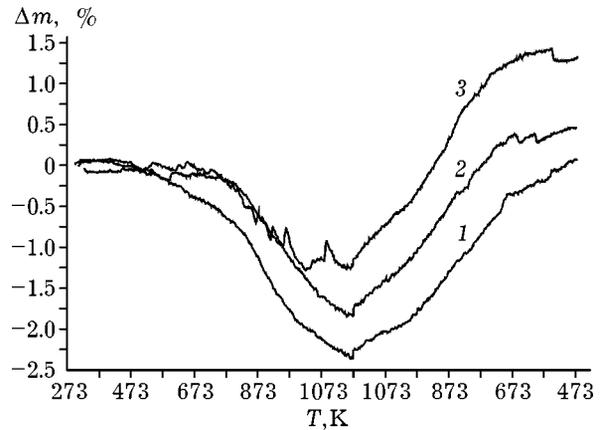


Fig. 3. TG dependences (heating-cooling) of $\text{YBa}_2\text{Cu}_3\text{O}_d$ samples that have been treated with gas mixture of “the optimum composition” and exposed in a helium atmosphere over the course of 0 (1), 2.5 (2), and 19 h (3).

conditions $p_{\text{H}_2\text{O}} = 110$ Pa, $p_{\text{O}_2} = 21$ kPa), the final phase that is unstable in helium atmosphere is transformed to the \mathfrak{g}_8 phase. The occurred changes in phase and oxygen composition have an influence on the magnitude of a descending branch of TG curves (Dm_d), which can be descriptively represented in terms of the equality

$$-\Delta m_d = \frac{k}{6.5} \{ [8\lambda + \delta^{298}(1 - \lambda)] - \delta^{1173} - 2\alpha\lambda \} \times 100 \%$$

where k , l are the respective mass concentrations of oxygen and of the $ortho\text{-I}$ -phase ($k = 0.158$) in the sample A; δ^{298} , δ^{1173} are the stoichiometrical parameters of $\text{YBa}_2\text{Cu}_3\text{O}_d$ in the initial and final points of heating respectively; α is an extent of realization of the transformation $\mathfrak{g}_8 @ \mathfrak{g}_8$. By the use of the known magnitudes Dm_d (see Fig. 3 and the data that were not included into it), it is easy to obtain the parameters that enter the equation (1): $l = 0.392$, whereas Fig. 4 presents the found values in the form of kinetic curve that reflects the instability of oxygen parameter of a new \mathfrak{g}_8 -phase in the atmosphere with a low p_{O_2} at t_a . Formal kinetic analysis of the received dependence demonstrates that the transformation $\mathfrak{g}_8 @ \mathfrak{g}_8$ by oxygen diffusion through the layer that is adsorbed on the $\text{YBa}_2\text{Cu}_3\text{O}_d$ surface represents the limiting stage. It is conceivable that the substance the bed consists of, according to [2], is the adsorbed moisture.

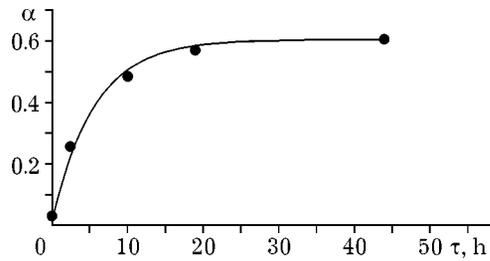


Fig. 4. Kinetic curve that corresponds to $\alpha_8 \rightarrow \alpha_6$ transformation that proceeds in an atmosphere of helium at $p_{\text{H}_2\text{O}} @ 1 \text{ kPa}$. The points are the experiment; the continuous line is the adjusting to comply with the equation $a = A - B \exp(-tC^{-1})$ with the factor $R^2 = 0.993$.

We shall examine the ascending branches of the curves in Fig. 3. The oxygen content in the final point of cooling is $d' = 7.3 \pm 0.1$ in all the experiments and it agrees with its initial value for the sample B. This is attributable, first, to the fact that the phase composition of $\text{YBa}_2\text{Cu}_3\text{O}_d$ is unaffected during the TG researches; and second, (in contrast to our earlier position [2]), to a high thermal stability of the α -phase.

Figure 5 displays analogous TG dependences, during generating of which the humidity in the working space of the thermoanalyser was under control. It is evident that as the $p_{\text{H}_2\text{O}}$ is varied, oxygen that has implanted in the compound at t_a evolves in various temperature intervals during heating. (It is supposed that the release of the mentioned oxygen is accounted for in the curves 1 and 2 by the observed intermittent changes of m that are equal in the absolute value to a relative increase in the mass of the sample upon the special treatment with gas mixture). Further behaviour of the TG

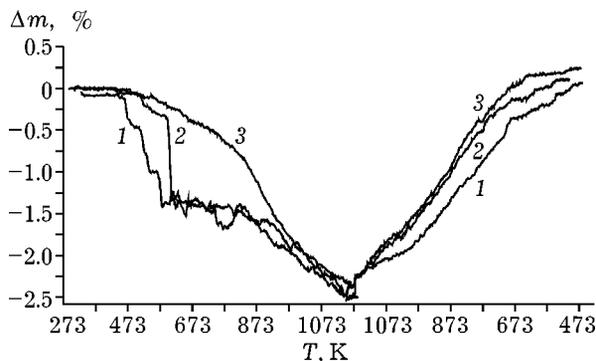


Fig. 5. Thermogravimetric dependences (heating-cooling) for $\text{YBa}_2\text{Cu}_3\text{O}_d$ samples that were treated with gas mixture of "the optimum composition". $p_{\text{H}_2\text{O}}$ values, kPa: 0.7 (1), 0.8 (2), 1.0 (3).

curves shows no any other features, with the exception that oxygen composition of all the samples during cooling is characterized by the value $d' @ 7.3 \pm 0.1$ that is the same as in the experiments depicted in Fig. 3. Considering the results that were acquired at the given stage of the research, we have found that the temperature of initial intensive evolving of O_2 correlates with thermal desorption peaks of proton-bearing groups that are reported for the same $p_{\text{H}_2\text{O}}$ values in [4, 7]. In compliance with these facts (and along with the data that have been received previously), a final conclusion has been made that the adsorbed moisture serves as a diffusion barrier for oxygen that evolves from the α_8 -phase.

Hence, we can ascertain that desorption of oxygen that has implanted at t_a may occur either by way of athermic jump mode at rather low temperatures (less than 623 K), or over an extended temperature interval: 773–1173 K. In the context of thermodynamics, this implies that between the above intervals, substantial strengthening of oxygen binding to the lattice occurs.

X-ray diffraction

Table 1 lists the results of X-ray crystal analysis of samples A and B that has been performed at t_a . The results are also represented in the form of points in Fig. 6. It is evident that an unusual stability of the lattice parameter c constitutes a feature of the samples under study. It differs radically from the dependence $c = f(d)$ with the characteristic steepness that has been determined in studies [8–10] (see the dashed curves in Fig. 6), when variation of d occurred during the high-temperature annealing. However, the works [11, 12] described the structural feature that is similar to the one that has been also observed by us. The authors of these publications examined regularities of variation in the oxygen index at low temperatures (reduction of $\text{YBa}_2\text{Cu}_3\text{O}_d$ by hydrogen at 443–473 K [11], as well as the process of O_2 evacuation under high vacuum at 430–550 K [12]), and they have found that the parameter c is unaffected during the process.

In the context of works [11, 12], the behaviour we observed for the lattice parameter c turns out to be rather ordinary: it is

TABLE 1

Crystallographic parameters of an initial sample A and sample B that has been treated with a gas mixture of "the optimum composition"

Treatment duration (t), h	Lattice parameters, nm			h	Dd
	a	b	c		
	<i>Sample A</i>				
	0.38305±0.00003	0.38727±0.00004	1.16776±0.00006	0.01103	–
	<i>Sample B</i>				
15	0.38231±0.00005	0.38868±0.00005	1.16840±0.00018	0.01664	+0.333
25	0.38193±0.00009	0.38812±0.00008	1.16699±0.00022	0.01621	+0.400
50	0.38031±0.00032	0.38793±0.00011	1.16740±0.00035	0.02002	+0.610
150	0.38228±0.00019	0.38684±0.00015	1.16647±0.00036	0.01193	+0.855

independent of the procedure to change the oxygen content of the samples (our procedure was not an exception) and it is formed only in connection with the low (seemingly, lower than ~550 K) temperature of conducting the given process.

The behaviour of parameter h ($h = (b - a)/a$) is worthy to be mentioned as well. A growth and a decrease of this parameter in the intervals $0 \leq Dd \leq 0.61$ and $0.61 \leq Dd \leq 0.86$ occur for the most part because of oscillations of the lattice size along an axis a (see Table 1). In this part of the plot, the points we received show a dome-shaped dependence that is close to the calculated one [13]. Consequently, the variations in mass that have been observed in these experiments are a consequence of the changing oxygen parameter d of the material under investigation.

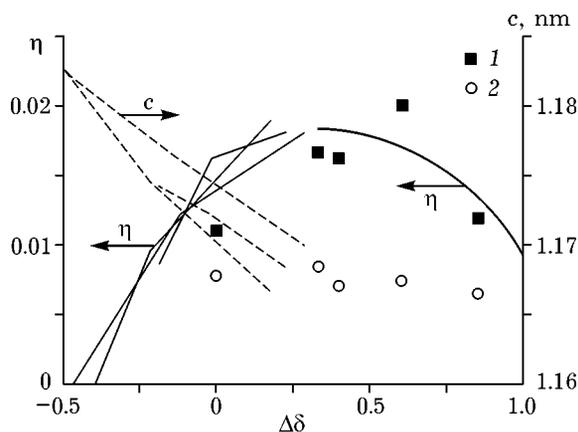


Fig. 6. Dependences of the extent of trimetric distortion h (1) and parameter c (2) on variation of oxygen stoichiometry during $\text{YBa}_2\text{Cu}_3\text{O}_{6.72}$ treatment with a gas mixture of the optimum composition. The dashed curves are the data of [8–19]; the full curve is the computation [11].

X-ray photoelectron spectroscopy

The quantitative XRE-analysis of a superficial layer of the sample B, during the course of which a total fraction of oxygen as the surface constituent was determined, has demonstrated that the obtained elemental ratio corresponds to the value $d \gg 7.4$ and agrees with gravimetry data. Hence, it follows a conclusion that a uniform variation in the $\text{YBa}_2\text{Cu}_3\text{O}_d$ composition in the course of treatment with the gas mixture occurred throughout the bulk of the material.

$\text{O}1s$ spectra of A and B samples that are given in Fig. 7 do not contain the background part of the signal (it has been isolated previously with the Shirley method). We shall consider a spectrum that corresponds to the sample A. It is made up of four components with binding energy maxima E_b in 529.6, 531.8, 533.1, and 535.1 eV. According to the conventional opinion [14–20], the low-energy peak of 529.6 eV should be associated with the oxygen that is embedded into the lattice of $\text{YBa}_2\text{Cu}_3\text{O}_d$. The value of binding energy that we received is close in its magnitude to the one presented in the work [17], where the calibration of spectrometer was also performed according to standard samples.

Meanwhile, opinions as to the second-largest peak as regards the binding energies (at 531.8 eV) disagree essentially. Certain works do not divide it from the third peak (533.1 eV) and they correlate it solely to the impurities or with ectogenic non-superconducting phases of the surface [18–20]. However, the work [17] presents evidence on asymmetry and significant

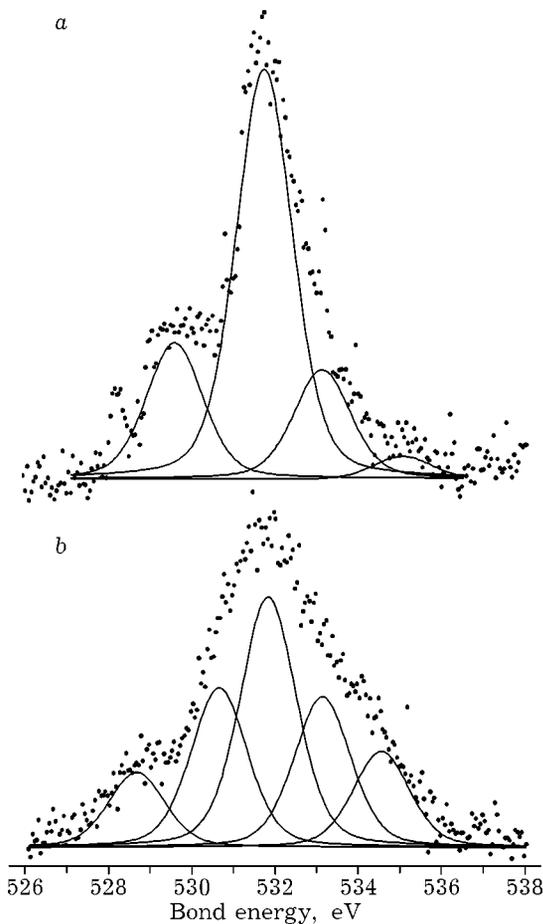


Fig. 7. Results of XRE study of samples A (a) and B (b).

width of the spectral envelope at 531–534 eV. For this and several alternative reasons, a more popular is the belief that superposition of two peaks occurs in the given interval of energies, the low-energy peak being associated with CO_3^{2-} groups, whereas the high-energy peak, with oxygen of $\text{YBa}_2\text{Cu}_3\text{O}_d$. To take an example, the work [21] demonstrated that a signal at 531–532 eV significantly decreases, if the alkaline earth element that is the constituent of cuprate compound is being replaced by lanthanum that is a less reactive as regards atmospheric impurities.

According to a position of many researchers (see, for example, [15, 17]), the peak at 533 eV corresponds to copper-oxygen bonds of a basic plane (of CuO chains). The state of oxygen of this plane is defined in [15] as that of peroxide nature, O_2^{2-} . This opinion is supported by the results of works [16, 22] that analysed O1s spectra for various states of oxygen and made

an inference about most probable qualification of the signal at 533 eV either to peroxide, or to superoxide compound – O_2^- .

Analysis that was similar in the procedure that has been given in [16, 22] was conducted in the work [14]: positions of O1s maxima for $\text{YBa}_2\text{Cu}_3\text{O}_d$ and for BaO, CuO, and Y_2O_3 simple oxides were compared. The authors have made a conclusion that the low-energy peak at ~529.5 eV accounts exclusively for Ba–O bonds of cuprate. Meanwhile, a signal from oxygen of the adjacent CuO_2 plane, this oxygen being involved in Cu–O and Y–O bonds, enters as a component of the spectral envelope at ~531.5 eV. Let us note that this refinement yields a good quantitative coincidence of the O1s spectrum with the ratio of oxygen positions in the unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_d$.

It appears that the peak of a small intensity that we recorded at 535.1 eV has no direct relation to cuprate structure. According to [22], it is of an extrinsic (H_2O) origin.

The B sample that was oxidized at t_a shows a shift of low-energy peak by ~1 eV towards smaller E_b values (compare with the sample A). Of interest is to compare this result with the dependence $E_b(d)$ for the given peak that has been recorded in the work [19], where it has been demonstrated that E_b behaves antipately to the oxygen content of $\text{YBa}_2\text{Cu}_3\text{O}_d$: $dE/d d = -1.25$ eV/atomic units of O. Having applied this formula, we shall receive that our sample must have changed oxygen composition by $\Delta d = +0.8$ atomic units of O during the oxidation. This coincides with the result of direct mass measurements. It is also necessary to note the changes that took place in the intensity of other peaks (see Fig. 7): the increase of signals at ~533 and ~535 eV and a decay at 531.8 eV. In addition, a new peak emerges at 530.7 eV, and its emergence together with a decrease of peak at 531.8 eV that is equal in the area can be interpreted in the context of [14] as a shift of the signal from CuO_2 plane towards lower E_b values.

At the same time, the registered evolution of the O1s spectrum that relates to a substantial growth of oxygen content d has practically no effect on the position of peak at 533.1 eV, which points to the stability of the state of labile oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_d$. Significant growth of a

peak at 534.5 eV that accounts for planar water is related probably to a new signal overlapping over it from anions that are even less connected to the lattice than is the labile oxygen that has been mentioned previously. This state can be characterized as close to chemically unbound one.

A decrease of E_b for core electrons of oxygen in the majority of structural positions of $\text{YBa}_2\text{Cu}_3\text{O}_\delta$ is attributable to weakening of hybridisation between d - and p - (and also s - and p -) states that causes the lengths of the associated chemical bonds to reduce [23]. Using $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ferroelectric as an example, the authors [23] have demonstrated that the lowering of the hybridisation degree for d - and p -electron orbitals may occur as polarization appears in a compound during its transformation from *para*-phase into ferroelectric phase.

Dilatometry that is applied to study polarization of $\text{YBa}_2\text{Cu}_3\text{O}_\delta$

Experiments into study of dipole electric moment were conducted in connection with the data that have been obtained in XRE research into characteristic displacement of $\text{O}1s$ peaks of the sample B. First of all, polarizing properties available in the material have been fundamentally proved in simple, but reliable experiments that involved a direct action of an electrified dielectric rod on the sample B. To obtain quantitative characteristics of the polarization, the sample A was introduced into a testing chamber of a dilatometric set-up (see Fig. 2) that was blown through by the reaction mixture of the optimum composition; the electric field strength in the working area was as large as $E = 10^4$ V/m. Hence, the formation of a polarization in the sample was detected directly in the process of low-temperature oxidation during the formation of the sample B (and during the process of the subsequent high-temperature mass transfer as well). Figure 8 displays temperature dependences of the polarization of the compound at various humidity of the atmosphere in the working chamber. It is evident that when heating in "optimum" conditions, the polarization monotonically increases, reaching a point $P = 23\text{--}28$ $\mu\text{C}/\text{cm}^2$ at the reached maximal temperature of 1193 K. It comes natural to associate such behaviour

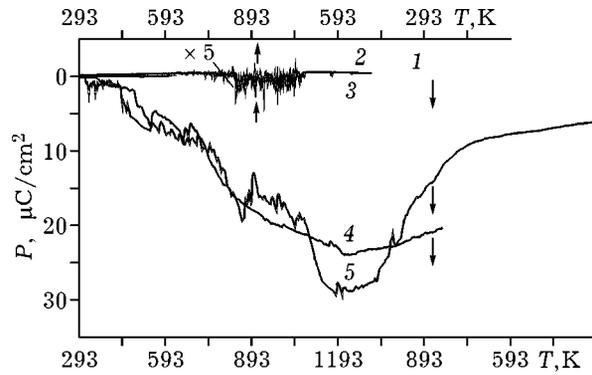


Fig. 8. Temperature dependence of the polarization of samples during a "heating-cooling" cycle at a rate of 10 K/min. Regime parameters of the experiment for the gas atmosphere: $p_{\text{O}_2} = 21$ kPa; $p_{\text{H}_2\text{O}}$, Pa: 40 (1), 80 (2), 120 (3), 110 (4, 5); the curve 5 is received at an increased rate of the temperature change over 1070 K, namely, 20 K/min.

with ferroelectric phase that is accumulated in the initial sample. Magnetic transformation temperature in that consideration is located outside the being investigated temperature band. At the same time, the observed almost symmetric run of all curves as regards a temperature maximum serves as an indicator of the effect of electromagnetic radiation from the heater on the sample (see pos. 2 in Fig. 2). This is also suggested by a sharp increase of a speed dP/dT at the increased intensity of heating-cooling (see the curve 5 in Fig. 8). Thus, in our estimate of electrical dipole moment of $\text{YBa}_2\text{Cu}_3\text{O}_\delta$, we took into consideration the value P that corresponds to an asymptotics of the curve 5 from cooling side (a regime of "cooling with the furnace" took place at this stage). The maximum polarization magnitude thus comprises (7.0 ± 2.1) $\mu\text{C}/\text{cm}^2$, which is typical of ferrosemiconductor ceramics. An increase in the intensity of the external permanent field E does not result in a variation of the parameter to be recorded, which is indicative of a steady regime of saturation of the dipole moment; a small magnitude of the sating field ($\sim 10^4$ V/m) bears witness to a weak coercive field of the material under investigation. Our attention is engaged by oscillations in the curves that arise in points 703, 783 and 868 K, etc. Standing out of them is a peak that locates in the region of polymorphic transformation of $\text{YBa}_2\text{Cu}_3\text{O}_\delta$ from trimetric to tetragonal phase (the air atmosphere, 883 K [24]) and that is present on the majority of the curves. It appears that phase

changes that are characteristic to the polar modification of $\text{YBa}_2\text{Cu}_3\text{O}_d$ are realized in the points of the observed oscillations. An increase in the mobility of structural defects that occurs at these moments [25] causes the coercive field of the polar phase to reduce and thus causes the influence of the external electromagnetic field on the phase to strengthen.

Magnetic measurements

Temperature dependence of magnetic susceptibility χ of the samples A and B was examined in a range of 293–77 K. At the temperatures higher than 85 K, both of the samples shaped a signal that matched $\chi = 0$. A sharp drop in the susceptibility of the material A at $T < 85$ K is suggestive of diamagnetic properties that emerge in it (superconductivity), which is typical of yttrium-baric cuprate that has been oxidized in the air at 773 K [26]. At the same time, the analysis of the curve $\chi(T)$ for the material that has been oxidized at t_a has not revealed any evidence of diamagnetism throughout the studied interval of temperatures. The effect is attributable to a decreased degree of $2p$ – $3d$ hybridization in CuO_2 planes of yttrium-baric cuprate (in the samples B) (see “X-ray photoelectron spectroscopy” section) that is of considerable importance in the phenomenon of high-temperature superconductivity [27].

According to numerous investigations [12, 28–32], properties of ordinary $\text{YBa}_2\text{Cu}_3\text{O}_d$ also undergo significant modifications when the temperature is lowered below ~ 600 K. Accordingly, reorganization in the oxygen sublattice that is accompanied by changes of h [28–31] has been observed in various temperature ranges. Studies of $\text{YBa}_2\text{Cu}_3\text{O}_d$ ($d = 6.4$) [32] by differential scanning calorimetry have demonstrated that there are two modes of the oxidation process that are characterized by different enthalpy, with the boundary that is between 583 and 663 K. The weakening of oxygen interaction with $\text{YBa}_2\text{Cu}_3\text{O}_d$ lattice at low temperatures is also evidenced by an established fact of emission of significant amount O_2 in high vacuum at 430–550 K [12]. In addition, it has been recorded [33] that trimetric deformations in $\text{YBa}_2\text{Cu}_3\text{O}_d$ at $d \gg 6.55$ show the features of structural ferroelectric reorganization.

Hence, it is necessary to treat the effects we observed as a manifestation that is typical, but extreme in its character for the processes that are generally occur in $\text{YBa}_2\text{Cu}_3\text{O}_d$. In so doing, an assumption can be made that the low-temperature instability that is typical for ordinary $\text{YBa}_2\text{Cu}_3\text{O}_d$ phases is nothing more nor less than the capability of a paraelectric system to transform to a metastable ferroelectric state under certain conditions. To make an estimate of instability of $\text{YBa}_2\text{Cu}_3\text{O}_d$, we shall introduce a parameter that defines its state as that close to a ferroelectric state: a virtual Curie temperature T_C ($T_C < 0$) (by analogy with SrTiO_3 compound that is called «a virtual ferroelectric» in this relation [34]), and we shall consider a phase change *ortho* \leftrightarrow *g* in parallel with the transformation paraelectric \leftrightarrow ferroelectric that takes place upon an increase of a concentration parameter x in $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ solid solution.

Thus, a decrease in electronegativity of a strong cation (and thus an increase in the degree of ionicity of the metal-oxygen bonds) upon the isomorphous replacement of strontium by barium appears to be a crucial factor of the sharp jump of T_K in the field of positive values. Let us suppose that two alternative states of Ba cations (that describe the polarizing properties of the phases, specifically, *ortho* and *g*) may exist in $\text{YBa}_2\text{Cu}_3\text{O}_d$. One of them (in the *g*-phase) possesses a lowered electronegativity in relation to the environment that represents a multilayered motive $\text{Y-CuO}_2\text{-O}_{\text{ap}}$ (O_{ap} is an apical oxygen that links copper ions from the planes and the chains); accordingly, the alternative state possesses an increased electronegativity. The reality of these two states follows from the fact that $\text{O}1s$ peaks (at 528.7 and 530.7 eV) of the B sample are biased with respect to analogous peaks of the sample A that has been pointed out in XRE research (see the section “X-ray photoelectron spectroscopy”). From chemical point of view, barium ions can exist in a normally oxidized and peroxide states (for example, in BaO and BaO_2), the boundary between which for the oxides in $T - p_{\text{O}_2}$ coordinate plane almost coincides with $d = 6.5$ isocomposition line of the $\text{YBa}_2\text{Cu}_3\text{O}_d$ compound. If we assume together with the authors of the work [35] that in the ordinary $\text{YBa}_2\text{Cu}_3\text{O}_d$, barium ions form a weak chemical bond (along

with bonds in alternative planes) with an oxygen of the basic plane, and hence they exist in a peroxide state, then as this bond is “switched off” upon the transformation into α -phase, this will lead to a new state of Ba – with a decreased electronegativity. In addition, the same result will be also achieved upon “switching-off” of an alternative baric bond, with the strengthening of the considered one (ferroelectrics are described at least by two states with the polarization vectors that are different in their direction). In so doing, new states emerge for the oxygen that is arranged in the basic plane of $\text{YBa}_2\text{Cu}_3\text{O}_d$. Conceivably, it is these states that manifest themselves in so unordinary manner in the thermogravimetry experiments (see Figs. 3, 5). For example, if there was no binding between an oxygen from the basic plane and barium at the initial moment of the sample heating (the α -phase has been produced under conditions of helium atmosphere at t_a), then a switching of ferroelectric phase into the alternative state might occur at elevated values of temperature and p_{O_2} , this state being characterized by the enhanced binding between the mentioned components (the transformation into β -phase). (However, it is necessary to recognize that XRE study does not show the enhanced binding of oxygen of the basic plane with the lattice of the sample B.)

Meanwhile, it is known that low concentration of free charge carriers n_e and a significant width of energy gap $D E_g$ provide the necessary conditions to reach high values of T_C . For example, the critical temperature $T_C = 408$ K for BaTiO_3 , for which $D E_g = 3.2$ eV and which is typified by a low concentration $n_e (10^{17} - 10^{18} \text{ cm}^{-3})$ [34]; after it is doped by rare earths, which leads to the extrinsic hole conductivity, the mentioned ferroelectric properties die out completely. The parameter $n_e \approx 2 \times 10^{21} \text{ cm}^{-3}$ and the conductivity is of a metallic type in yttrium-baric cuprate that is doped by superstoichiometrical oxygen ($d > 6.5$) [26]. In such an event, the values that are observable in this work, $T_C > 1183$ K, allow a suggestion that deep electron-hole recombination with the established semi-conductor state occurred in the material during $\text{YBa}_2\text{Cu}_3\text{O}_d$ treatment with special gas mixture. The additional XRE investiga-

tions we performed for the valence band of the samples A and B enabled us to determine $D E_g$ values that, as might be expected, were equal to 0 eV for the sample A, and approximately 2 eV for the sample B. The occurrence of a semiconductor state in $\text{YBa}_2\text{Cu}_3\text{O}_d$, obviously, is related to delocalised electron holes that overflow from CuO_2 structural layers into the basic plane.

CONCLUSION

It has been demonstrated that a degree of ionicity of cation-oxygen bonds increases upon $\text{YBa}_2\text{Cu}_3\text{O}_d$ oxidation under the conditions of t_a . In addition, another part of oxygen emerges that exists in a state that is close to chemically unbounded. This correlates with spontaneous electric polarization that appears within yttrium-baric cuprate under the test conditions. The received experimental result can be explained in the context of a concept on $\text{YBa}_2\text{Cu}_3\text{O}_d$ as on a virtual ferroelectric, the critical temperature of which varies in the field of negative values. Under certain conditions, this temperature may increase up to high positive values. In so doing, modification of the chemical state of $[\text{BaO}_2]$ structural group occurs from formal peroxide compound to formal oxide with strengthening of one Ba-O bond and with weakening of another one.

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