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Raman study of the effect of water vapor during low-temperature annealing on the structure and electrophysical properties of $YBa_2Cu_3O_v$



I.B. Bobylev^{*}, Yu.S. Ponosov, N.A. Zyuzeva

M.N. Miheev Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences, S. Kovalevskaya St., 18, Yekaterinburg 620990, Russia

HIGHLIGHTS

- Absorbing water at 200 °C, the Y-123 ceramics transforms to H_xYBa₂Cu₃O_y(OH)_z.
- \bullet The incorporation of water in the Y-123 (y ≥ 6.5) leads to the well magnetic peak.
- \bullet For the Y-123 with y < 6.5 the OH $^-$ -groups occupy the vacancies of several types.
- The OH⁻-groups are oriented along the *c*-axis.

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ABSTRACT

The effects of an interaction of $YBa_2Cu_3O_y$ (123) with water vapors at a temperature 200 °C on the structure and electrophysical properties of the compound have been examined by Raman spectroscopy. It has been found that the penetration of water into the 123-type causes the transition of the compound from an oxide to a hydride-oxide-hydroxide, which is accompanied with transformation to the 124 pseudotype phase. Direct evidence has been obtained for the incorporation of OH⁻-groups in the 123-structure. After the interaction with water, the materials with high oxygen content ($y \ge 6.5$) retain their superconductivity and exhibit two-magnon scattering in Raman spectra, which is not typical for them.

Short-term recovery annealing followed by oxidation removes the water from the compound structure, which leads to the disappearance of the spin fluctuation spectra. At the same time, the structural defects are partially preserved. These manifest themselves through some peculiarities in the Raman spectra and are apparently pinning centers of magnetic vortices. A model of a splitting of the Cu–O chains and a formation of the 124-like phase in water-intercalated 123-structure has been proposed. This mechanism supposes the dissociation of the OH⁻-groups and the filling in the copper vacancies by protons.

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* Corresponding author. *E-mail address:* bobylev@imp.uran.ru (I.B. Bobylev).

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1. Introduction

It is known that an YBa₂Cu₃O_y compound is unstable as regards water [1,2]. When interacting with water at near-room temperature, the compound exhibits amorphization of near-boundary grain regions; in addition, stacking faults being fragments of the 124-compound structure are formed. These defects emerge due to the splitting of the Cu–O chains. Besides, apart from oxygen the former appear to contain hydroxyl ions [2]. In Refs. [3–8], it is shown that, at a temperature of 200–300 °C, the 123-type compounds also interact with water vapors contained in the annealing atmosphere. In this case, the YBa₂Cu₃O_y structure absorbs water; the latter's absorption is the stronger, the smaller is the oxygen index of the compound [7]. The water absorption gives rise to a change in the structure of YBa₂Cu₃O_y, which transitions to the tetragonal phase of the 124-type with lattice parameters **a** = 3.883 A^o and **c** = 27.17 A^o [3,9,10].

Moreover, in [5,11], it was demonstrated by electron microscopy that, during low-temperature annealing of the oxygen nonstoichiometric compound $YBa_2Cu_3O_y$ under a humid atmosphere, the precipitation of nanoparticles takes place. This is explained by the decomposition of the compound into phases with different oxygen contents.

Current research is aimed at finding new ways to create artificial pinning centers and increase the critical current density of HTS materials such as 123-type in a wide range of magnetic fields. For this, one of the most commonly used methods is to enter complex oxides (Y_2BaCuO_5 , $BaZrO_3$, $BaSnO_3$, etc.), chemically non-interacting with the 123-type [12–17]. However, the endogenous structural defects may also be promising because these distort the structure of the materials and are capable of being effective pinning centers [18–20].

In Refs. [21–25], it is claimed that the YBa₂Cu₃O_{6.9} compound, when annealed for a long time at t = 200 °C in a wet environment, deteriorates its superconducting properties up to its transition to a paramagnetic state. However, subsequent short-term annealing at a temperature of 930 °C after oxidation at 400 °C restores the superconductivity. Moreover, under certain conditions, such double heat treatment allows one to significantly improve the critical parameters of the 123-type as compared to the initial state [22–24,26]. In particular, the critical current density values in the intrinsic field increases 1.5–2 times. An even greater effect is achieved at high magnetic fields: j_c grows from 2 \cdot 10³ A/cm² to 10⁴ A/cm² in an external field of 10 T, applied perpendicular to the axis *c* [26]. The fact that the double heat treatment is most effective in the

Table 1		
Specification o	f YBa ₂ Cu ₃ O _v	samples.

У	H ₂ O, wt. %	Parameter c , Á	Т _с , К
6.9	0	11.707	90
6.9	0.1	11.711	88
6.8	0	11.782	82
6.8	0.29	27.09	88
6.8	1.19	27.10	84
6.8 (dry)	0	27.03	86
6.5	1.1	27.18	0
6.3	1.33	27.25	0

field perpendicular to the axis *c* indicates that the planar defects are pinning centers. The assumption has been made that the structural defects produced by interaction with water are partially conserved after short-term high-temperature annealing [27] and are effective pinning centers for magnetic vortices.

The objective of the present work is to investigate how the water absorption at low-temperature annealing affects the chemical and structural state of $YBa_2Cu_3O_{7-8}$ and its electrophysical properties. Moreover, there was of interest to reveal the water-absorbing mechanism underlying changes in the 123-structure and appearance of defects that may contribute to an improvement of the critical parameters of the materials. For this purpose, the Raman spectroscopy was used because it provides necessary information both on the local structural features of the material and its electronic and magnetic structure.

2. Experimental technique

A material to study was high-textured YBa₂Cu₃O_{6.9} ceramics, synthesized by the melt-textured growth (MTG) method [28,29] at the A. A. Bochvar High-Technology Scientific Research Institute for Inorganic Materials. The samples contained the Y₂BaCuO₅ phase (30 wt. %). The X-ray analysis showed that the *ab*-plane reflected only 00l lines, which indicates a high texture of the material. The bulk density of the material amounted to 5.2 g/cm³.

The YBa₂Cu₃O_y samples with the different oxygen contents were examined: y = 6.9, 6.8, 6.5, and 6.3. The required content of oxygen was attained during annealing at fixed temperatures of 400, 500, 700, and 900 °C, respectively [5]. Low-temperature treatment was carried out at t = 200 °C for ≥ 100 h in both a dry and water vapor saturated atmosphere. To achieve the oxygen index \approx 7, recovery annealing was performed at t = 930 °C for 2 h followed by oxidation at t = 400 °C in an oxygen atmosphere for 24 h.

The water content was controlled by a gravimetric method. The mass measurement error amounted to $\pm 0.005\%$. The compositions of the samples investigated are given in the Table 1. It should be noted that the water content in the samples is only nominal. Some



Fig. 1. An elementary unit cell of $YBa_2Cu_3O_7$. The arrows indicate the direction of the light polarization in the basal plane (XX) and along the axis *c* (ZZ).



Fig. 2. Raman spectra of YBa₂Cu₃O_{6.9} in the phonon region in polarizations (a) XX and (b) ZZ: (1) initial state, (2) after water intercalation to 0.1 wt % H₂O.



Fig. 3. Raman spectra of YBa₂Cu₃O_{6.8} in polarizations (a) XX and (b) ZZ: (1) initial state, (2) after treatment at 200 °C in a dry air, (3) after water intercalation to 0.29 wt % H₂O, (4) after water intercalation to 1.19 wt % H₂O, (5) after water intercalation to 1.19 wt % H₂O and after further drying, (6) after water intercalation to 1.19 wt % H₂O and after recovery at 930 °C.

crystallites absorbed water very weakly because their Raman spectra do not much differ from the spectra for the initial state. The given paper presents the spectra of the crystallites which reacted with water vapors.

The Raman spectra were excited in guasi-backscattering

geometry by the 514 nm (2.41 eV) line of an argon-ion laser with a power up to 0.5 mW, focused to a spot on the sample approximately 2 μ m in diameter. Under such conditions, the local heating of the sample was negligibly small. To eliminate the surface effects, the measurements were taken on freshly cleaved surfaces. In spite of



Fig. 4. Raman spectra of YBa₂Cu₃O_{6.5} in polarizations (a) XX and (b) ZZ: (1) initial state, (2) after treatment at 200 °C in a dry air, (3) after water intercalation to 1.1 wt % H₂O.



Fig. 5. Raman spectra of YBa₂Cu₃O_{6.3} in polarizations (a) XX and (b) ZZ: (1) initial state, (2) after treatment at 200 °C in a dry air, (3) after water intercalation to 1.33 wt % H₂O, (4) after further drying.

having the "green phase" (211) inclusions, the samples studied were essentially twinned single crystals. This made it possible to conduct full-fledged polarization measurements from both the basal plane (XX) and a plane containing the axis *c* of the crystal (ZZ). The scattered light was registered using a Renishaw RM 1000 spectrometer, equipped with edge filters to suppress low-frequency Rayleigh scattering and a thermoelectric cooling registration system based on a charge-coupled device. The spectral resolution was ~3 cm⁻¹. The measurements were taken at a single point of the end face of the single crystals whose typical size was 5–10 µm.

The temperature dependences of the magnetic susceptibility were measured with a Quantum Design MPMS-XL-5 SQUID magnetometer at a frequency of 80 Hz and at alternating field amplitude of 4 Oe. The X-ray diffraction study was carried out on a DRON-3M-typediffractometer in copper radiation (CuK_{α}).

3. Results

Figs. 2–5 represent the Raman spectra appearing in XX and ZZ polarizations in the phonon region for the samples undergone different heat treating operations (X and Z are directions of the light polarization in the basal plane and along the axis c, respectively (Fig. 1)).

In line with the literature [30], in the *XX* polarization for the samples with $y \ge 6.5$ in the initial state, 4 of 5 modes permitted by the selection rules can be observed. These correspond to vibrations of Ba (110 cm⁻¹), Cu (147 cm⁻¹), the planar O_{2,3} (~338 cm⁻¹) and apical O₄ (~495 cm⁻¹) oxygen. Furthermore, for the samples with $y \ge 6.5$ there are at least another three peaks at 185, 233, and 585 cm⁻¹ (Figs. 2a–4a, curves 1). Their emergence is explained by selection rule violations due to the non-stoichiometry in oxygen, which results in an activity of forbidden vibrations of the chain-oxygen O₁ [31]. For the sample with y = 6.3 in the initial state, a mode of the planar oxygen (450 cm⁻¹) is also seen (Fig. 5a, curve 1). In the *ZZ* polarization for all the compositions, besides the vibrations of Ba and Cu, there are only modes corresponding to the vibrations of the planar (421–445 cm⁻¹) and apical (488–500 cm⁻¹) oxygen (Figs. 2b–5b, curves 1).

After the samples with y = 6.9-6.5 were annealed at t = 200 °C in a dry atmosphere for 200 h, practically no changes were revealed in the spectra (Figs. 3 and 4, curve 2). In accordance with [32], this fact is evidence that the decomposition into phases with different oxygen contents proceeds very slowly under these conditions.

Similar treatment in an atmosphere saturated with water vapors

triggers significant changes in the spectra. In the XX polarization, the ratio of intensities of the modes responsible for the vibrations of Ba and Cu is modified in the spectra of the samples with y = 6.9-6.5 (Fig. 2a, curve 2; Figs. 3a-4a, curves 3). Such a ratio of these line intensities is inherent to the antiferromagnetic tetragonal phase with $y \approx 6$ [31,33,34]. In addition, the water absorption causes the modes of the planar (~450 cm⁻¹) and chain oxygen $(\sim 600 \text{ cm}^{-1})$ to emerge. In the ZZ polarization, the spectra have a mode of the chain oxygen $(596-609 \text{ cm}^{-1})$ (Figs. 2b-4b) and new lines (~210 and ~250 cm⁻¹) for the samples with y = 6.8 and y = 6.5(Figs. 3b-4b, curves 3). According to [35,36], one of them (250 cm^{-1}) may belong to the Cu₁-vibrations in copper-oxygen chains. The double chain oxygen vibrations at ~210 and ~600 cm^{-1} lines are allowed for the 124-type phase, therefore, their appearance indicates the occurrence of 124 fragments due to splitting of the Cu–O chains [9,10]. After recovery annealing at 930 °C followed by oxidation, the spectra of the sample with y = 6.8become similar to the appropriate spectra for the sample with the



Fig. 6. Raman spectra of YBa₂Cu₃O_y in the high frequency region: (1) initial state YBa₂Cu₃O_y ($y \ge 6.5$), (2) YBa₂Cu₃O_{6.9}, after water intercalation to 0.1 wt % H₂O, (3) YBa₂Cu₃O_{6.8}, after water intercalation to 0.29 wt % H₂O, (4) YBa₂Cu₃O_{6.8}, after water intercalation to 0.29 wt % H₂O, (4) YBa₂Cu₃O_{6.8}, after water intercalation to 0.1 wt % H₂O.

oxygen index y = 6.9(Fig. 3, curves 6). However, unlike them, the ratio of the line intensities of the planar and apical oxygen is dramatically different. This may stand for the preservation of some structural disorder. It should be emphasized that it is such double heat treatment, namely, low-temperature annealing and short recovery annealing at t = 930 °C followed by oxidation that improves the critical characteristics of the material.

As distinct from the samples with $y \ge 6.5$, the sample with y = 6.3 behaves otherwise. Annealing of the latter at a temperature of 200 °C in a dry atmosphere leads to the disappearance of the modes which are characteristic of vibrations of the chain (O₁) and apical (O₄) oxygen in the XX polarization (Fig. 5a, curve 2). Being initially almost absent, the ~600 cm⁻¹ line of the chain oxygen is enhanced in the ZZ polarization (Fig. 5b, curve 2). In the XX polarization, after treatment in an atmosphere saturated with water vapors, the spectra are free of the O₁ and O₄ modes but show a new asymmetric 667 cm⁻¹ line (Fig. 5a, curve 3).

When extra-treated at t = 200 °C under dry argon, the above sample losses the structural water, with the 667 cm⁻¹ line disappearing in the *XX* polarization. However, in the *ZZ* polarization, there remains 3 modes: a strong mode that is not peculiar to the initial state and responsible for the chain-oxygen vibrations (601 cm⁻¹) as well as modes ~210 cm⁻¹ and 250 cm⁻¹ (Fig. 5, curve 4). This indicates that the material is still in the same phase state (124-pseudo state) as well as after treatment in water vapors.

Treatment in a dry atmosphere also resulted in no changes in the spectra of the samples at higher frequencies. After annealing of the compound in an atmosphere saturated with water vapors, the spectra for the samples with y = 6.9-6.5 show a broad band at the ~2900 cm⁻¹ in the XX polarization (Fig. 6, curves 2–5). Such bands of B_{1g} symmetry have been firstly observed in undoped La₂CuO₄ and YBa₂Cu₃O₆ and have been attributed to the two-magnon scattering. Two-magnon Raman scattering directly probes shortwavelength magnetic fluctuations, which may exist even without long-range AF order. Subsequent treatment of the sample with y = 6.8 in a dry atmosphere significantly reduces the intensity of the broad band at 2900 cm⁻¹ (Fig. 6, curve 4). This implies that the presence of water in the structure is responsible for the increase of the magnetic correlation length, which leads to the occurrence of



Fig. 7. Raman spectra of $YBa_2Cu_3O_{6,3}$ in the high frequency region: (1) initial state, (2) after treatment at 200 °C in a dry air, (3) after water intercalation to 1.33 wt % H₂O, (4) after further drying.



Fig. 8. Raman spectra of YBa₂Cu₃O_Y in the high frequency region: (1) initial state, (2) YBa₂Cu₃O_{6.8} after water intercalation to 1.19 wt % H₂O, (3) YBa₂Cu₃O_{6.5} after water intercalation to 1.1 wt % H₂O, (4) YBa₂Cu₃O_{6.3} after water intercalation to 1.33 wt % H₂O.

two-magnon scattering even in the samples with high oxygen content.

For the sample with y = 6.3, the double spin-flip excitation was seen in the initial state as well but after the water absorption its intensity increased markedly (Fig. 7, curve 3). Previously, high-frequency spin fluctuations were observed in some underdoped superconducting cuprates by means of inelastic x-ray scattering [37].

Only in the ZZ polarization, a weak line at ~3450 cm⁻¹ appeared in the spectra of the samples with y = 6.8 and 6.5. It is attributed to the OH⁻-group stretching vibrations (Fig. 8, curves 2 and 3). In agreement with [3,4,7,8], this fact proves that



Fig. 9. X ray diffraction patterns of $YBa_2Cu_3O_y$ (y = 6.9 for curves 1,2 and y = 6.8 for curves 3–6): (1) initial state (reduced intensity is 5 times), (2) after water intercalation to 0.1 wt % H₂O, (3) after water intercalation to 0.29 wt % H₂O (indexing 124), (4) after water intercalation to 1.19 wt % H₂O, (5) after water intercalation to 0.29 wt % H₂O and after further drying, (6) after water intercalation to 1.19 wt % H₂O and after recovery at 930 °C, followed by oxidation.



Fig. 10. Temperature dependences of (a) the real χ' and (b) imaginary χ'' parts of the magnetic susceptibility of YBa₂Cu₃O_{6.9}: (1) initial state; (2) after water intercalation to 0.1 wt % H₂O; (3) after water intercalation to 0.1 wt % H₂O and after recovery at 930 °C.

the water enters the YBa₂Cu₃O_y structure. After heat treatment of the sample with y = 6.3 in a humid atmosphere, this line become very intense (Fig. 8, curve 4). In this case, it is asymmetrical and consists of at least three bands. This testifies to the incorporation of OH⁻- groups into different structural positions. The absence of this line in the XX polarization indicates that the O–H bond is directed along the **c**-axis of the crystal. Subsequent annealing of the sample with y = 6.3 at t = 200 °C under dry argon causes the 3450 cm⁻¹ line to vanish, which indicates the water removal. Along with the above mentioned line, the line at 667 cm⁻¹ also disappears in the phonon part of the spectrum (Fig. 5a, curve 4). From this it follows that the line is also related to the vibrations of OH⁻-groups, which are probably of a deformational type.

The X-ray analysis shows that poor water absorption by the sample with y = 6.9 does not affect the structure of the compound (Fig. 9, curve 2). However, higher water absorption by the samples with y = 6.8 causes a phase transformation of 123–124 pseudo with a parameter c = 27 Å, at least on the surface of the sample (Fig. 9, curves 3–4). In this case, the sample texture remains unchanged, however, the line intensities sharply drop, and their expansion occurs. This may be due to stresses generated by the phase transformation. It should be noted that the water absorption leads to an increase in the parameter c (see Table 1).

Extra annealing at t = 200 °C in a dry atmosphere removes the water, but as the spectroscopic data show, the 124-type phase is

conserved (Fig. 9, curve 5). During recovery annealing at t = 930 °C, the compound transitions back to the 123-phase, exhibiting partial recrystallization, and deteriorating its original high-texture (Fig. 9, curve 6).

The results of the magnetic susceptibility measurements show that for the samples (y = 6.9) absorbed ~0.1 wt. % water, the critical temperature goes down from 90 K to 88 K, and the transition width increases significantly (Fig. 10, curve 2). However, recovery annealing at t = 930 °C followed by oxidation gives rise to a growth of T_c to 90 K and the transition width diminishes to identical to the initial state (Fig.10, curve 3).

After similar treatment of the sample (y = 6.8) absorbed 0.29 wt.% water, the critical temperature, on the contrary, goes up from 82 K to 88 K (Fig. 11, curve 2). Thus, whatever the oxygen content, the water absorption provokes the structural state for which $T_c = 88$ K is typical. As the water content rises to 1.19%, both T_c and the diamagnetic response come down (Fig. 11, curve 3).

After the sample (y = 6.8) absorbed 0.29 wt. % water was heattreated at a temperature of 200 °C in a dry atmosphere, the transition behavior becomes more complicated. Three peaks observed in the dependencies $\chi'' = f(T)$ belong to the 70–80 K region (Fig. 11b, curve 4), which implies a structural heterogeneity of this transition. However, after double heat treatment of the 123 sample the transition to a superconducting state shrinks and T_c corresponds to the composition of YBa₂Cu₃O_{6.9} (Fig. 11, curves 5).



Fig. 11. Temperature dependences of (a) the real χ' and (b) imaginary χ" parts of the magnetic susceptibility of YBa₂Cu₃O_{6.8}: (1) initial state; (2) after water intercalation to 0.29 wt % H₂O; (3) after water intercalation to 1.19 wt % H₂O; (4) after water intercalation to 0.29 wt % H₂O and after further drying; (5) after water intercalation to 1.19 wt % H₂O and after recovery at 930 °C.

4. Discussion

The problem of the effect of both water and hydrogen on the structure and properties of the 123-type holds a certain place in the literature [1,9,37-39]. In Ref. [39], it was shown that inelastic neutron scattering spectra have no O-H bonds after hydration. The assumption has been made that this is because of a short lifetime of the proton near the oxygen ion as it resides mostly in the interstices. On the basis of our results, it can be supposed that the OH⁻-groups involved in the 123-structure for the compositions with y > 6.5 when hydrating the latter largely dissociate into a proton and O^{2-} . This is evidenced by a very weak intensity of the OH⁻-group stretching vibrations in the spectra for the samples with $y \ge 6.5$ (Fig. 8, curves 2, 3). As for the sample with y = 6.9, it is non-existent at all. An indirect proof for the dissociation of the OH⁻-groups is the fact that the hydration should have bound the proton to the oxygen ion and formed the OH⁻-group, which in fact does not happen [39].

As has already been noted above, the water absorption greatly affects the critical temperature and diamagnetic response. As to the YBa₂Cu₃O_{6.8} compound absorbed 0.29 wt. % water, the T_c rises apparently due to the phase decomposition, which leads to the formation of an oxygen-rich matrix phase [7]. Earlier, the critical temperature was found to increase after water and hydrogen intercalation [3,38,40].

Attention should be paid that for the compositions y = 6.8-6.3 absorbed water, the frequency of oscillations of the apical oxygen is enhanced in the *ZZ* polarization. According to the accepted concepts [41], this can be a proof for an increase in the oxygen content. However, for the sample with y = 6.9 the frequency softens. The shift of the apical oxygen line correlates with the change of T_c and may indicate a change in the electronic structure and the number of free charge carriers.

Despite the variations of T_c as YBa₂Cu₃O_{6.8} absorbs water, its diamagnetic response decreases (Fig. 11a). This may be explained either by the grain-boundary degradation because of hydrolysis (grain-boundary amorphization [2]) or by the decrease of the fraction of the superconducting phase due to the formation of structural defects and stresses emerging around the latter [42].

Comparison of the magnetometry data with the Raman spectroscopy measurements shows that the 123-samples intercalated with water possess simultaneously both T_c -superconductivity that is typical for the samples with $y \cong 7$ and short-range antiferromagnetic fluctuations (Figs. 6 and 11). This can be accounted for the heterogeneity of the water absorption by various grains and even by an individual single crystal [42], which may be a subject of special study.

On the basis of the results secured, the following model can be proposed to illustrate the interaction of the 123-compound with water and hydrogen. It was concluded in [2] that the adsorbed water molecules dissociate at the crystallite surface. Penetrating the 123-structure, the newly formed OH^- -groups partially dissociate into a proton and O^{2-} :

$$O_1^{2-} + \Box_5 + H_2O = 2OH^- \leftrightarrow 2H^+ + 2O^{2-}$$

During hydrogenation, another process passes; it is accompanied by reduction of copper:

$$H_2 + 2Cu^{3+} (Cu^{2+}) \rightarrow 2H^+ + 2Cu^{2+} (Cu^+)$$

 $H^+ + 0^{2-} ↔ 0H^-$

Thus, regardless of whether water or hydrogen is intercalated,

the same equilibrium is established. For $y \ge 6.5$, it is shifted towards the formation of a proton and O^{2-} . In both cases, the YBa₂Cu₃O_y compound intercalated with water or hydrogen turns into a hydride-oxide-hydroxide H_{2x-z}YBa₂Cu₃O_{y+x-z} (OH) _z and transitions to the 124-type phase as a result of the splitting of the Cu–O chains.

As was pointed out in [9,10], the materials subjected to either hydrogenation or hydration are substantially similar in structure and their electrical properties. This fact allows us to make the assumption that in both cases the same topotactic process takes place. In contrast to [2,3], in the hydration process, the Cu–O chains are split by the reaction

 $CuO + H_2O \rightarrow HCuO_{2-v}(OH)_v + (1-y)H^+$ in the interstices,

where a proton appears to occupy every second vacant position of copper.

Let us consider two extreme cases. At high oxygen content, $y \approx$ 7 the water enters the structure according to the reaction

In this case, there are practically no OH⁻-groups, in accordance with the Raman spectroscopy data. Also, in agreement with the spectroscopic data, at low oxygen concentrations ($y \cong 6$) the OH⁻-groups almost never dissociate and are embedded in the oxygen vacancies.

In the case of hydrogenation of the 123-type with $y \approx 7$, a different reaction is in progress.



The fact that a proton attaches to the vacant position of copper is consistent with its preference to be in positions with low coordination number [43].

The difference between hydrogenation and hydration is that in

the former case, the Cu–O chains are formed with considerable oxygen deficiency. This is probably because the hydrogenated 123type is able to absorb oxygen [9,38]. In the water intercalation process, the shortage oxygen is considerably less because the system contains oxygen along with water. Common to both processes is that the hydrogen involved in the 123-structure occupies not only the interstices near the copper-oxygen chains [38] but also creates its own positions by splitting them up. It can be assumed that this is the reason for the transition of the 123-type to the 124type phase to occur where the proton replaces the vacancies of Cu⁺ in the Cu-O chains.

Recovery annealing at a temperature of 930 °C also removes the water. Then, the inverse transition of the 123-type from the hydride-oxyhydroxide in the oxide form happens. During the oxidation process at t = 400 °C, the 123-type is saturated with oxygen, and the antiferromagnetic fluctuations disappear.

5. Conclusions

Absorbing water during annealing at t = 200 °C, the YBa₂Cu₃O_v ceramics transforms from an oxide to an $H_{2x-z}YBa_2Cu_3O_{y+x-z}(OH)_z$ hydride-oxyhydroxide. According to the results of the X-ray diffraction studies of the compound, the changes in the Raman spectra stand for the splitting of the Cu–O chains and the transition of the 123-type to the tetragonal phase of the 124-pseudo type. For the compositions with high oxygen content (y > 6.5), H₂O-molecules dissociate into a proton and O^{2-} . The proton takes up a vacant position of copper in the split Cu-O chains or resides in the interstices.

The incorporation of water in the structure of YBa₂Cu₃O_v with y > 6.5 leads to the transformation of broad structureless background in the initial state to the well shaped magnetic peak. With relatively low water content, the samples are in a two-phase state, simultaneously exhibiting both high-temperature superconductivity and antiferromagnetic short-range order.

For the water-intercalated materials with the oxygen index v < 6.5, the OH⁻-groups dissociate little and occupy the oxygen vacant positions of several types. In doing so, they are oriented along the *c*-axis.

Despite the water removal, low-temperature annealing of the 124-type in a dry atmosphere leaves its structure unchanged. At the same time, short-term annealing at t = 930 °C followed by oxidation initiates the inverse transition of the 124-type from the hydride-oxyhydroxide phase to the orthorhombic one of the 123type. In this case, the planar structural defects are partially preserved. These may improve the electrophysical properties of the material, especially in a magnetic field applied perpendicular to the axis c.

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