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Investigation of $Y_1Ba_2Cu_3O_{6.9}$ and $Er_1Ba_2Cu_3O_{6.8}$ during cyclic temperature variations

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Gravimetric investigations of the superconductive ceramics $Y_1Ba_2Cu_3O_{6.9}$, $Y_1Ba_2Cu_{2.7}Al_{0.3}O_{7.1}$ and $Er_1Ba_2Cu_3O_{6.8}$ during cycling heating $\rightleftarrows$ cooling in the interval 293–1323 K at partial pressure of the oxygen 0.02 and 0.2×10^5 N m^{-2} are presented. Intervals of intense weight changes during heating and cooling are determined. Oxygen loss was shown to be the main reason for the weight changes. Structural characteristics and resistivity of the yttrium ceramics in the above-mentioned temperature interval are investigated. Experimental data are discussed within the framework of the models of the quasi-equilibrium and essentially nonequilibrium processes. Binding energy and diffusional parameters of the evolving gas are estimated.

1. Introduction

The determination of the thermal stability of High Temperature Oxide Superconductors (HTSC) and optimal thermal conditions for maximal oxygen content, an orthorhombic structure formation, etc. are the controlling factors in respect of usage of HTSC in various technologies. The above characteristics are studied in detail for $Y_1Ba_2Cu_3O_y$ [1–4].

In order to determine general trends in thermodynamic, kinetic and structural properties of HTSC the investigations on $Y_1Ba_2Cu_3O_y$ and $Er_1Ba_2Cu_3O_y$ are carried out in this work. Trivalent aluminium impurities, substituting for copper (Cu(I) in the copper chains of $Y_1Ba_2Cu_3O_y$ only) are shown not only to increase a thermal stability of $Y_1Ba_2Cu_3O_y$ up to the level of that of $Er_1Ba_2Cu_3O_y$ but to raise T_c (the temperature of superconductive transition) somewhat as well. The analysis of the oxide superconductor properties during thermal treatments were carried out by using the following methods: thermogravimetry, mass spectrometry, NMR and the X-ray and resistive ones as well.

2. Preparation of the samples and their characteristics

The casted $Y_1Ba_2Cu_3O_y$, $Y_1Ba_2Cu_{3-x}Al_xO_y$ and $Er_1Ba_2Cu_3O_y$ samples have been prepared by using a powder mixture of CuO, BaO, Y_2O_3, Er_2O_3 and Al_2O_3 to be pressed under a pressure of 5 ton cm^{-2}. The electron-microscopic images of the sample structures obtained in such a way are given in Figs 1 to 3. The average size of the grains in $Y_1Ba_2Cu_3O_y$ appeared to be about 18 μm (Fig. 1) but after addition of aluminium ($x = 0.3$) a continuous mesh of fine grains (0.5–5 μm) is realized and some coarse ones up to 10 μm in size are also observed. In this case the structure is similar to that of $Er_1Ba_2Cu_3O_y$. The porosity of the samples was about 25–30%. The temperature of the initiation of the superconducting transition (direct current was 30 μA) for $Y_1Ba_2Cu_3O_y$ and $Er_1Ba_2Cu_3O_y$ was 93.5 and 94 K and of the termination of it – 91 and 92.5 K, respectively. For the $Y_1Ba_2Cu_{2.7}Al_{0.3}O_y$ sample the temperature of the initiation of the superconducting transition was 99 K and of the termination of it – 97 K, but the superconducting transition, however, was incomplete (i.e. there was residual resistance at $T < T_c$). A fraction of the volume of the sample contributing in the diamagnetic response at 80 K in a field below 5 E for $Er_1Ba_2Cu_3O_y$, $Y_1Ba_2Cu_3O_y$ and $Y_1Ba_2Cu_{2.7}Al_{0.3}O_y$ was about 95, 90 and 10%, respectively. At $T > T_c$ the conductivity for all the synthesized samples was of a metallic nature but it had low temperature coefficient. This is typical for the systems having a short free path length of the carriers. X-ray structural analysis for the synthesized $Y_1Ba_2Cu_3O_y$ and $Er_1Ba_2Cu_3O_y$ superconductors yielded that they are in orthorhombic phase with the unit cell volume of 0.173 96 and 0.170 279 nm^3, respectively. For $Y_1Ba_2Cu_{3-x}Al_xO_y$

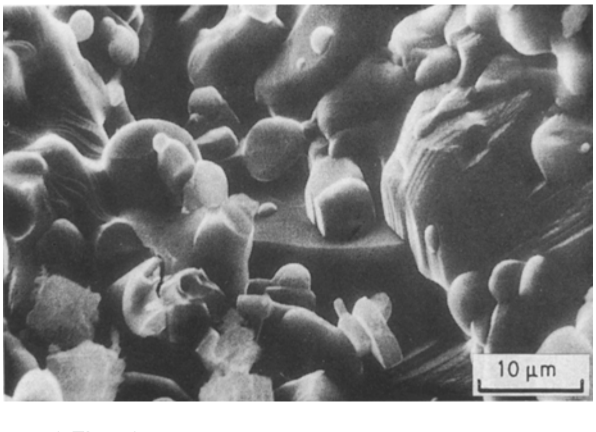

Figure 1 The microstructure of $Y_1Ba_2Cu_3O_y$.

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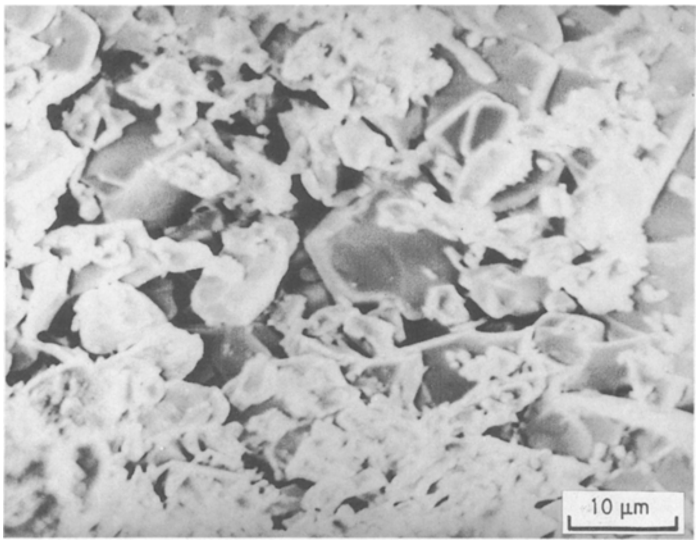

Figure 2 The microstructure of $Er_1Ba_2Cu_3O_y$.

there is a uniphase range ($x < 0.5$), for $x > 0.1$ the lattice is tetragonal with maximal $T_c \approx 98$ K at $x = 0.3$. The tetragonal cell volumes, V_c, corresponding to the superconducting tetragonal phases for $0.1 < x < 0.5$ depend on x slightly and are approximately equal to V_c for the orthorhombic phase of $Y_1Ba_2Cu_3O_{6.9}$. As follows from the work [5] this is due to the joining of the additional oxygen atom (as compared to Cu(I)) to Al^{+3} on *a*-axis without appreciable change in the initial phase volume. Removal of the oxygen from the superconducting $Y_1Ba_2Cu_3O_y$, $Y_1Ba_2Cu_{3-x}Al_xO_y$ and $Er_1Ba_2Cu_3O_y$ causes essential increase in the unit cell volumes of the above compounds. The oxygen deficiency y in $Y_1Ba_2Cu_3O_y$ and $Er_1Ba_2Cu_3O_y$ was determined by the data of the thermogravimetric analyses tabulated by the mass spectrometry data (the volume of the camera was an oxygen-calibrated one). It was taken into account that gas-evolution composition varied with the temperature. Within the temperature range of 300–400 K water (H_2O) was a dominating component in a gas evolution, however, low peaks of O_2, H_2 and N_2 were also present. With the increase in temperature (up to 1200 K) O_2 was the main component and there were also peaks of O, Ar, N, CO_2, BaO and CuO. It is worthwhile to note that the oxygen portion of the total weight loss $\Delta p/p$ depends essentially on the temperature. So at 700 K the contribution of oxygen to the total weight change $\Delta p/p$ is about 25%, and at 1200 K it is already about 47%. A detailed analysis of this method is given in [6]. According to the data obtained on the initial superconducting samples of $Y_1Ba_2Cu_3O_y$, $y = 6.9$, and on $Er_1Ba_2Cu_3O_y$, $y = 6.8 \pm 0.1$, respectively, we assume that for $Y_1Ba_2Cu_{2.7}Al_{0.3}O_y$ the parameter y may be estimated in terms of those considerations that the chemical potential of Cu(I) was not changed when impurity atoms of aluminium were introduced, and a quantity of oxygen conditioned by copper atoms under the similar synthesis parameters is $y = 6.9$. It was also taken into account that the total amount of aluminium substitutes only for Cu(I) as follows from the X-ray data [7] (at $x = 0.3$ aluminium substitutes for about 30% Cu(I) in chains). According to the data of NMR spectrum analysis the aluminium atom joins an additional oxygen atom as compared with Cu(I). This is natural as Al^{2+} has high oxygen affinity. Using such assumptions we carried out the estimations which yielded $y = 7.1$ for $Y_1Ba_2Cu_{2.7}Al_{0.3}O_y$. It should be noted that the above assumptions are confirmed by the values of the oxygen weight losses $(\Delta p/p)_{O_2}$ during heating from 300 to 1300 K: for $Y_1Ba_2Cu_3O_{6.9}$ we had $(\Delta p/p)_{O_2} = -1.65\%$, and for $Y_1Ba_2Cu_{2.7}$-$Al_{0.3}O_{7.1}$ there was $(\Delta p/p)_{O_2} = -1.22\%$. This corresponds to decrease in the value of y down to 6.2 both for yttrium ceramics and for ceramics having $x = 0.3$ of aluminium (here only losses of oxygen from Cu(I) chains are taken into account [6]).

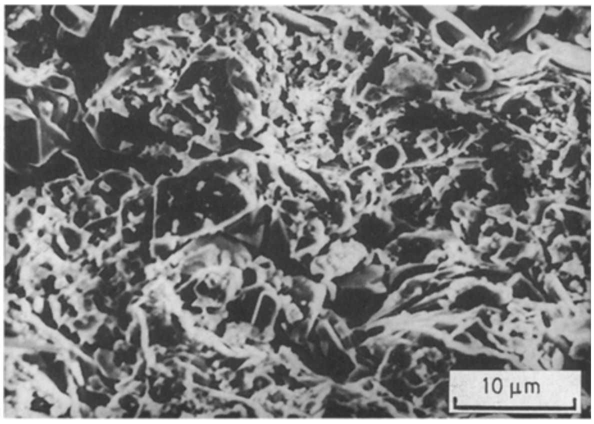

Figure 3 The microstructure of $Y_1Ba_2Cu_{2.7}Al_{0.3}O_y$.

3. Experimental results

Because of the essential superposition of the experimental data the changes in the weight $\Delta p/p$ of the initial superconducting samples $Y_1Ba_2Cu_3O_{6.9}$ during heating and air cooling at a rate of 5 K min^{-1} within the temperature range of 300–1323 K for two repeated cycles are given in Fig. 4a only schematically (qualitatively). The varying behaviour of $\Delta p/p$ as a function of T in air for Y_2O_3, CuO, and BaO unannealed compact, obtained under 5 ton cm^{-2}

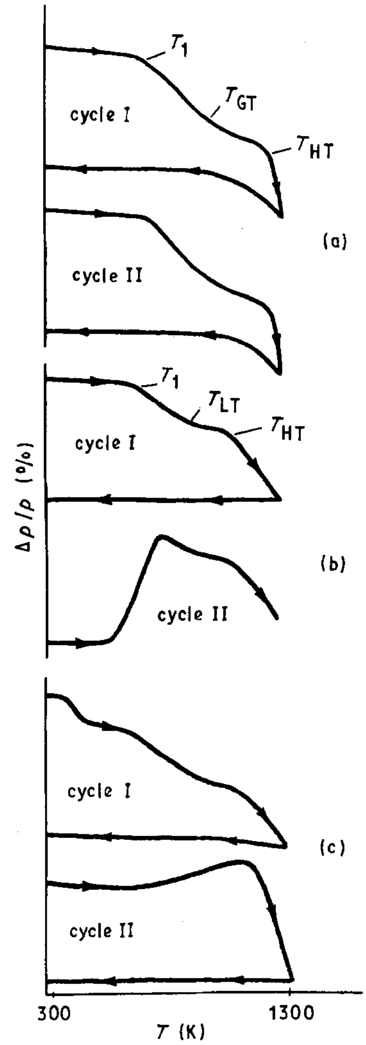

Figure 4 The changes in the weight $\Delta p/p$ during heating and cooling of the samples at the rate of 5 K min^{-1}. (a) the initial superconducting sample $Y_1Ba_2Cu_3O_{6.9}$: I and II cycles, air atmosphere; (b) the initial superconducting sample $Y_1Ba_2Cu_3O_{6.9}$: I cycle helium atmosphere, II cycle air atmosphere; (c) compact of Y_2O_3, BaO and CuO: I and II cycles, air atmosphere.

TABLE I Changes in the weight of the samples $\Delta p/p$ during thermocycling in the air atmosphere. The rate of the temperature variation is 5 K min^{-1}

Initial material	Cycle	Temperature range (T_1, T_x) (K)	($\Delta p/p$) (%)
Compact of Y_2O_3, BaO, CuO	I	313–471	− 0.58
		633–1053	− 1.43
		1093–1323	− 2.80
		1323–293	~ 0
	II	623–1163	+ 0.30
		1193–1323	− 2.49
		1323–293	~ 0
$Y_1Ba_2Cu_3O_y$ $y = 6.9$	I	717–1173	− 0.82
		1203–1323	− 2.44
		1323–923	+ 1.21
	II	708–1178	− 0.80
		1208–1323	− 2.40
		1323–923	+ 1.20

pressure is represented on Fig. 4c for comparison. The results of the performed experiments are given in Table I. Fig. 4b shows the $\Delta p/p$ "heating–cooling" variation at the rate of 5 K min^{-1} for the initial superconducting samples in the helium flow (flow rate $\dot{v} = 16$ cm^3 min^{-1}). In this case under the steady-state conditions, when the oxygen diffusive flow is compensated by the drift flow, the partial pressure of the oxygen according to the formula:

$$P = P_{O_2} \exp(-vz/D)$$

(here $v = \dot{v}/s = 1.33$ cm sec^{-1}, $s = 0.2$ cm^2 is the opening area for the helium flow, $P_{O_2} = 0.2 \times 10^5$ Pa is the partial pressure of the oxygen in the air, z is the distance between the sample and the outlet, $D \simeq 0.5$ cm^2 sec^{-1} is the oxygen diffusion coefficient), corresponding to $\bar{P} = 10^{-6} P_{O_2}$. These samples were subjected to the second "heating–cooling" cycle which was carried out in the air. During the second cycle the weight of the samples was being restored to the nearly initial values. Proceeding from that gaseous atmosphere composition during heating to 1323 K of the initial superconducting samples and ones obtained in the second cycle after reaching the maximal value of the weight (see Fig. 4b) coincided totally for O_2, N_2, Ar, CO_2, BaO, CuO, etc. except hydrogen (according to the mass spectrometry data which are given in the order of the diminution), the main impurity gaseous composition may be assumed to be restored to one of the initial samples during gaining the maximal weight in the second cycle. At the same time for the investigated samples, an increase in the absorption of hydrogen during the second cycle as heating rate increases is the general property. Thus, during heating at a rate near 20 K min^{-1} there is a great peak which becomes insignificant at a heating rate of 1.25 K min^{-1}. The observed effect of the strong relation between the hydrogen absorption and heating rate seems to exist due to that at sufficiently low rates at which an equilibrium state may be achieved, e.g. at 1.25 K min^{-1}, oxygen enters a lattice (this is supported by the fact that the samples with the weight restored in the second cycle are superconducting ones and have the orthorhombic lattice). As a result oxygen cannot bind hydrogen. At heating rates of 5 K min^{-1} and above an equilibrium state cannot be achieved, i.e. oxygen atoms do not achieve lattice vacancies and seem to remain in the grain boundaries, where they can bind hydrogen. This is supported by the fact that for the samples with the weight restored at such heating rates have the conductivity of semiconductor nature and the tetragonal lattice. Fig. 5 shows schematically the data of the variation of $\Delta p/p$ as a function of the rate of temperature change during heating in the helium flow and during air cooling for $Y_1Ba_2Cu_3O_{6.9}$, $Y_1Ba_2Cu_{2.7}Al_{0.3}O_{7.1}$, and $Er_1Ba_2Cu_3O_{6.8}$. The experimental results are given in Table II. It should be noted here that the observed variation of the temperature of the maximal weight gain as a function of the heating rate shows the limited rate of the processes of the weight gain [8]. During air heating ($P_{O_2} \simeq 0.2 \times 10^5$ Pa) as well as during heating in the helium ($P_{O_2} \simeq 0.02$ Pa) during the first cycles (Figs 4b and 5) two temperature intervals of changes in weight are observed.

TABLE II Changes in the weight of the samples $\Delta p/p$ during thermocycling: I–helium cycle; II–air cycle

Initial material	Atmosphere	Temperature variation rate, ($K\,min^{-1}$)	Cycle	Temperature range (T_1, T_x) (K)	($\Delta p/p$) (%)
$Y_1Ba_2Cu_3O_y$ $y = 6.9$	helium	5	I	653–1073 1083–1323 1323–293	− 0.86 − 2.64 0
	air	1.25	II	500–683 683–773 773–973 973–1050	+ 3.41 − 0.20 + 0.16 − 1.48
	air	5	II	530–763 763–1050	+ 3.40 − 1.50
	air	20	II	543–838 838–1050	+ 3.42 − 1.49
$Y_1Ba_2Cu_{2.7}Al_{0.3}O_y$ $y = 7.1$	helium	5	I	670–1098 1098–1323 1323–293	− 1.52 − 1.08 0
	air	5	II	500–728 728–1050	+ 2.55 − 1.29
$Er_1Ba_2Cu_3O_y$ $y = 6.8$	helium	5	I	663–1098 1098–1323 1323–293	− 1.34 − 0.92 0
	air	5	II	473–713 713–1050	+ 2.20 − 1.50

As follows from the X-ray structural analysis data, heating of the orthorhombic lattice samples of $Y_1Ba_2Cu_3O_{6.9}$ and $Er_1Ba_2Cu_3O_{6.8}$ to the temperatures not exceeding the first low-temperature interval of weight changes ($T_1\,T_{LT}$) results in formation of another phase. However, the above thermal treatment does not effect the monophaseness of HTSC $Y_1Ba_2Cu_{3-x}Al_xO_y$ which has the tetragonal lattice at the values of $x = 0.1$, 0.3, and 0.5. The processes proceeding within the interval (T_1, T_{LT}) are close to the equilibrium ones as at the heating rates of 1 to $20\,K\,min^{-1}$ the equilibrium state is achieved in 0.1 sec; during this period the temperature changes by no more than 0.04 K, i.e. by a negligible value.

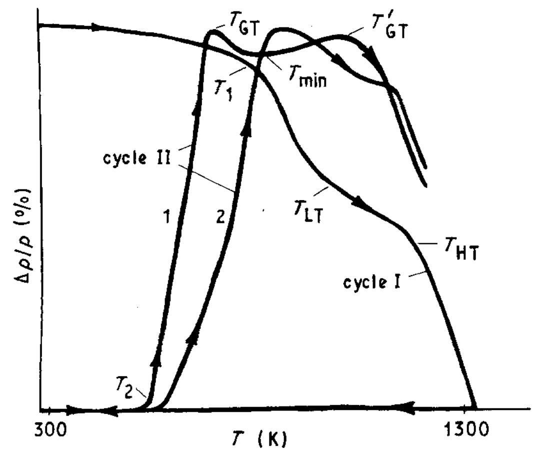

Figure 5 The changes in the weight $\Delta p/p$ during heating and cooling of the samples $Y_1Ba_2Cu_3O_{6.9}$: I cycle helium atmosphere, the rate of the variation of the temperature is $5\,K\,min^{-1}$; II cycle air atmosphere: the rate of the variation of the temperature is (1) $1.25\,K\,min^{-1}$; (2) $20\,K\,min^{-1}$.

The mass spectral analysis of the gas evolution of the samples during annealing shows that during heating up to 403 K there are low peaks of O_2, H_2, and N_2. During gas evolution, H_2O is the dominating component, however, its quantity is insufficient to be fixed by $\Delta p/p$ (Fig. 4a and b). During heating up to 471 K the Y_2O_3, BaO, and CuO compact the sharp peak of H_2O is mainly observed which results in the loss of $\Delta p/p \simeq 0.58\%$ (Fig. 4c) in this case. This follows from the data of mass spectral analysis of the gas evolution. The analogous losses $\Delta p/p$ of H_2O were observed during heating of BaO; during analogous heating of Y_2O_3 and CuO there were no perceptible losses. With following increase in temperature up to 1323 K O_2 was the main component in the gas evolution and the O, Ar, CO_2, CuO, and BaO peaks appeared as well.

4. Quasi-equilibrium processes

In Y_2O_3, CuO, and BaO compact in the first cycle at a temperature exceeding 623 K, in $Y_1Ba_2Cu_3O_{6.9}$, $Y_1Ba_2Cu_{2.7}Al_{0.3}O_{7.1}$, and $Er_1Ba_2Cu_3O_{6.8}$ in the I and II cycles during air heating and in the I cycle during helium flow heating (Figs 4 and 5) the first temperature interval (T_1, T_{LT}) of the intensive decrease in weight ($\Delta p/p < 0$) is observed. As follows from the data of gas evolution analysis during heating of the samples in the mass spectrometer with oxygen-calibrated volume the weight losses in HTSC under investigations due to the oxygen evolution during heating within temperature range (T_1, T_{LT}) in the helium atmosphere ($P_{O_2} \simeq 0.02$ Pa) $(\Delta p/p)_{O_2} \simeq -(0.3 + 0.35)\%$, in the air $(\Delta p/p)_{O_2} \simeq -0.25\%$ and for the compact in the air $(\Delta p/p)_{O_2} = -0.18\%$. It should be noted that a varying weight behaviour of

TABLE III

Material	Cycle	Process (5 K min^{-1})	Oxygen partial pressure P_{O_2} (Pa)	T_0 (K) exper.	T_0 (K) exper.	T_0 (K) theor.	h (eV) theor.
$Y_1Ba_2Cu_3O_{6.9}$	I	heating	0.2×10^5	945	220	147	1.05
		cooling		1123	172	171	1.27
	II	heating	0.2×10^5	943	221	146.8	1.04
		cooling		1125	171	171	1.27
	I	heating	0.02	863	181	87	1.48
		cooling		–	–	–	–
	II	heating	0.2×10^5	–	–	–	–
		cooling		1125	171	171	1.27
Compact of Y_2O_3, BaO, CuO	I	heating	0.2×10^5	392	68	69	0.38
		heating		818	150	129	0.9
		cooling		–	–	–	–
	II	heating	0.2×10^5	–	–	–	–
		cooling		–	–	–	–
$Y_1Ba_2Cu_{2.7}Al_{0.3}O_{7.1}$	I	heating	0.02	880	195	89	1.50
		cooling		–	–	–	–
$Er_1Ba_2Cu_3O_{6.8}$	I	heating	0.02	870	183	88	149
		cooling		–	–	–	–

the HTSC, i.e. the samples $Y_1Ba_2Cu_3O_{6.9}$, $Y_1Ba_2Cu_{2.7}Al_{0.3}O_{7.1}$, and $Er_1Ba_2Cu_3O_{6.8}$ after multiple air cycling was practically unchanged, but the nature of the conductivity of the samples became a semiconductor one.

The weight decrease processes occurring within the temperature range (T_1, T_{LT}) during heating and the weight increase during air cooling from 1323 K were close to the equilibrium ones, as they proceeded only during time interval $\tau < 0.6$ sec when the temperature was fixed. In these cases the temperature changed during τ no more than by 0.05 K, i.e. by a negligible value. Such fast processes cannot be connected with bulk diffusion (it will be shown subsequently, that the processes connected with a bulk diffusion takes tens of minutes even at the higher temperatures), but are much rather due to surface processes. This is supported by the fact that heating to the temperature range (T_1, T_{LT}) results in suppressing the d.c. superconductivity. However, a diamagnetic response is yet observed in the samples (a volume fraction providing for the diamagnetic response is $\Delta V/V < (5\text{–}10\,\%)$). On the basis of these data one may suppose that at heating the d.c. superconductivity failure take place, first of all, due to the failure of the superconducting properties of the grain boundaries. The grain-boundary nature of these processes responsible for the weight losses $\Delta p/p$ within the temperature range (T_1, T_{LT}) is supported also by the fact, that the HTSC weight losses $\Delta p/p$ is much larger in the fine grained $Y_1Ba_2Cu_{2.7}Al_{0.3}O_{7.1}$ (Fig. 2) and $Er_1Ba_2Cu_3O_{6.8}$ (Fig. 3), than in the coarse-grained $Y_1Ba_2Cu_3O_{6.9}$ (Fig. 1, see also Table II).

Taking into account, that within the temperature range under consideration from 293 to 1323 K, oxygen dominates during gas evolution within the first intensive change in $\Delta p/p$, let us consider the equilibrium of the gas O_2 with a solid. This area is within the temperature range, where only the translation and rotation of the molecules contribute into a chemical potential of the two-atomic gas. As quantum effects are essential for the oxygen only when

$$T \lesssim \hbar^2/kI = 4.2\,\mathrm{K}$$

(here $\hbar$ is the Planck constant, k is the Boltzmann constant, I is the moment of inertia of the molecule), the anharmonic effects ought to be taken into account at $T \gtrsim \hbar\omega/k = 2330$ K (ω is the oscillation frequency of the molecule) [9]. Within this temperature range the O_2 chemical potential is

$$\mu = kT \ln \frac{P_{O_2} \hbar^5 \pi^{3/2}}{I m^{3/2} (kT)^{7/2}} \qquad (1)$$

where P_{O_2} is the partial pressure of O_2 in atmosphere surrounding a solid, m is the mass of the atom of the gas. Let the gas atoms in solid may fill in some definite number of sites. The chemical potential of the gas atom in solid, when filling in the sites is random, may be written as [4]

$$\mu = -h + kT \ln \frac{c}{1-c} \qquad (2)$$

where h is the change in atomic enthalpy at gas molecule–solid transition, c is the degree of the filling in the sites in the solid. In the equilibrium state the chemical potential (1) equals to two chemical potentials (2), and it follows:

$$c = [1 + A(P, T)\exp(-h/kT)]^{-1}$$
$$A(P, T) = m^{3/4} I^{1/2} (kT)^{7/4} / \pi^{3/4} P_{O_2}^{1/2} \hbar^{5/2} \qquad (3)$$

At atmospheric pressure or lower one $A(P, T) \gg 1$. In this case the degree of the filling in at low T differs from 1 only slightly, at high T one is almost zero. A sharp change in $c(T)$ takes place in the vicinity of $T = T_0$, and $c(T_0) = 1/2$, i.e.

$$kT_0 \ln A(P, T_0) = h \qquad (4)$$

The interval around T_0 where c is changed $e = 2, 7, 8$ by tens or hundreds (i.e. from tens to hundreds) times

$$\Delta T_0 = 2T_0/\ln A(P, T_0) \qquad (5)$$

In view of the fact, that $A \gg 1$, $\Delta T_0 \ll T_0$, the sites are filled in a narrow range ΔT_0. As is seen from the Table III in a number of cases the experimental value of ΔT_0 exceeds the theoretical one. This may be explained by consideration, that in real objects the values of h may be scattered considerably. This scattering may be connected with inhomogeneous surface conditions in the case of surface states.

The value of h, moreover, for $Y_1Ba_2Cu_3O_{6.9}$ at heating is smaller than that at cooling. The varying structure of material during heating to 1323 K may be one of the reasons. A decrease in T_0 and ΔT_0 observed experimentally at lowering partial pressure of oxygen (see Table III) follows from the Equations 3, 4, as with decreasing $P_{O_2}A(P, T)$ increases resulting in decreasing T_0. In this case the transition interval ΔT_0 is decreased more considerably (due to both the decrease in T_0 and increase in a denominator in the right-hand side of the Equation 5). However, in a number of cases the scattering of the h values may disguise these effects. Discrepancy in h values for air heating and helium one (Table III) shows also, that the heating atmosphere seems to affect a composition of the impurities adsorbed on the surface.

As follows from Table III considering h for $Y_1Ba_2Cu_{2.7}Al_{0.3}O_{7.1}$ and $Er_1Ba_2Cu_3O_{6.8}$ the value of h depends not only on the structure but on the surface composition also. In particular, for $Y_1Ba_2Cu_{2.7}Al_{0.3}O_{7.1}$ HTSC an increase in h, as compared with the material without Al, may be explained by the fact, that aluminium, for example, binds more strongly oxygen than Cu(I).

5. Nonequilibrium processes

The processes proceeding with the weight losses ($\Delta p/p < 0$) in the second higher temperature range (T_{HT}, 1323 K) on air heating to 1323 K in the first and second cycles and on helium one in the first cycle and the processes proceeding with gaining the weight ($\Delta p/p > 0$) on air heating within the temperature range (T_2, T_{GT}) after the thermal treatment of the samples in helium flow (see Figs 4 and 5 and Table II) are more intensive than quasi-equilibrium ones (see section 4). The typical values of $|\Delta p/p\Delta T|$ (here $\Delta T = T_{LT} - T_1$ is the interval of the proceeding of the process) for quasi-equilibrium processes are 2×10^{-3} % K^{-1}, at the same time the weight losses in the second temperature range (T_{HT}, 1323 K) both in air and in helium $|\Delta p/p\Delta T| \simeq 10^{-2}$ % K^{-1} ($\Delta T = 1323\ K - T_{HT}$), and the intensity of the weight gain within the range of (T_2, T_{GT}) is $|\Delta p/p\Delta T| \simeq 1.5 \times 10^{-2}$ % K^{-1} ($\Delta T = T_{GT} - T_2$). According to the data obtained in this work the interval of the proceeding of the processes in isothermal conditions within the temperature range (T_{HT}, 1323 K) and (T_2, T_{GT}) takes tens of minutes. In this case during these intervals when the samples are heated at a rate (1.25–20) K min^{-1} the temperature is changed by tens of hundreds of degrees centigrades. These changes are very essential and the processes are, therefore to be considered as unequilibrium ones.

A. Let us consider the processes causing the weight losses within the temperature range (T_{HT}, 1323 K) in more detail. According to the X-ray data for $Y_1Ba_2Cu_3O_{6.9}$ and $Er_1Ba_2Cu_3O_{6.8}$ heated up to 1323 K the superconducting phase lines have almost totally disappeared, but in the case of $Y_1Ba_2Cu_{2.7}Al_{0.3}O_{7.1}$ the reflexes corresponding to the tetragonal initial lattice became more narrow. As follows from the above results on analysis of the gas evolution composition (see section 2) the decrease in the weight within the temperature range (T_{HT}, 1323 K) seems to be connected with the oxygen going out of the bulk of the sample and limited by the bulk diffusion. That is why heating of the sample at considerable rate leads to the proceeding of the processes being shifted to higher temperatures than those at which oxygen equilibrium filling in the sites in the bulk of the sample decreases. Such processes may be described by kinetic equation [10]

$$\partial(c - c_e)/\partial t + (c - c_e)/\tau = 0 \qquad (6)$$

where, c is the actual filling, c_e is the equilibrium filling, τ is the relaxation time of the process. From Equation 6 for the isothermal process we obtain:

$$\ln\frac{c(t) - c_e(T)}{c(0) - c_e(T)} + \frac{t}{\tau(T)} = 0 \qquad (7)$$

Let us analyse the experimental data for $Y_1Ba_2Cu_3O_{6.9}$, as an example. Treating the experimental data at two temperatures of isothermal annealing, $T_1^0 = 1233$ K and $T_2^0 = 1268$ K, according to Equation 7, the values of τ for these temperatures may be obtained: $\tau(T_1^0) = 952$ sec and $\tau(T_2^0) = 734$ sec. To estimate the diffusion parameters we shall approximate the samples by a spherical model. In this case the solution is of the form [11]

$$c(r, t) = c(0, 0)\frac{\sin 2\pi r/d}{2\pi r/d}\exp(-4\pi^2 Dt/d^2) \qquad (8)$$

where D is the gas diffusion coefficient in the solid, d is the diameter of the sphere, r is the distance from the centre of a ball. Using the expressions $D = d^2/4\pi^2\tau$ and $D(T) = D_0\exp(-u/kT)$ for D (u is the diffusion activation enthalpy) and determining $D(T_1)$ and $D(T_2)$ from Equation 8 for $\tau(T_1)$ and $\tau(T_2)$, the diffusion parameters were estimated (a size of the sample was $d = 0.1$ cm): $u = 1$ eV, $D_0 = 2.53 \times 10^{-2}$ cm^2 sec^{-1}. For the samples of the same sizes the kinetic parameter estimations carried out analogously by using the experimental data yielded the following values: $u = 1.3$ eV and $D_0 = 8 \times 10^{-2}$ cm^2 sec^{-1} for $Y_1Ba_2Cu_{2.7}Al_{0.3}O_{7.1}$ and $u = 1.1$ eV, $D_0 = 10^{-1}$ cm^2 sec^{-1} for $Er_1Ba_2Cu_3O_{6.8}$, respectively. The values of u are somewhat lower than the corresponding ones obtained for $Y_1Ba_2Cu_3O_y$ in works [12, 2, 3] at the temperatures lower than 730 K and are closer to the values of u at 900 K [12]. On the basis of this the authors of the work [12] supposed the temperature dependence of the activation enthalpy during gas diffusion out of the sample within the regarded temperature range.

It should be noted finally, that at air and helium flow heating of HTSC materials the weight losses within the temperature range (T_{HT}, 1323 K) are accompanied by an endothermal effect. For the thermal effect due to only the evaluation of oxygen we had $Q_1 \approx 48$ kcal g^{-1} and at cooling within the same temperature range one had $Q_2 \approx 23.2$ kcal g^{-1}, respectively. As the processes resulting in evolution of Q_2 are the surface ones and of Q_1 are the bulk ones and thermal insulation conditions were not fulfilled during experiments, the relation $|Q_1| > |Q_2|$ may be explained by the thermal losses from the surface of a sample. It is worthwhile to note that the value of Q is close to the thermal dissociation for the copper oxide.

B. The weight recovery processes investigated in the work in $Y_1Ba_2Cu_3O_{6.9}$, $Y_1Ba_2Cu_{2.7}Al_{0.3}O_{7.1}$, and $Er_1Ba_2Cu_3O_{6.8}$ (Figs 4b and 5) during air heating within the temperature range (T_2, T_{GT}) and after thermal treatment in helium flow (as was shown in section 3) take place due to recovery of the main impurity gas composition to the initial one. As follows from the X-ray structural analysis data heating up to the temperature T_{GT} at which the maximal weight gain at the heating rates of 1.25–20 K min^{-1} takes place, does not result in formation of the superconducting phase. At further increase in temperature up to T_{min} the weight losses seem to take place mainly due to losses of the oxygen owing to its increased mobility at the temperatures about 700 K [12], i.e. of the order of T_{GT}.

As to the physical nature of the second observed maximum of $\Delta p/p$ (Fig. 5) occurring at $T'_{GT} > T_{min}$ (for example, during heating at a rate of 1.25 K min^{-1}, when the proceeding processes are separated the most clearly) there is no prevailing opinion about the mechanisms leading to it [4]. Taking into account, however, that at the temperatures T_{min} (as the X-ray investigations show) in oxide ceramics under investigations the superconducting phase is beginning to appear and the interfaces also appear, where gases, including oxygen, may be sorbing. In this case it ought to be taken into account, that at the initial transformation stages the boundary area is increasing. With phase transformation proceeding, the value of area is going through the maximum, then decreases, and vanishes when the transformation is completed. The total amount of the atmospheric gases absorbed on the phase boundaries being proportional to the boundary area, follows the same dependence. This may serve as an explanation why the gas contents in oxide ceramics have a maximum at the temperatures of T'_{GT}.

As Fig. 5 shows the peaks $\Delta p/p$ at T_{GT} and T'_{GT} are the most clearly separated at the low heating rates (1.25 K min^{-1}). This allows us to conclude, that at such a heating rate the rates of the diffusion processes of the gas saturation of HTSC is not a limiting element. With the increase in the heating rate up to 20 K min^{-1} gas does not succeed in migrating from the atmosphere to the boundaries, and the peaks are shifted to the more higher temperatures, where gas desorption cannot take place. This results in a diffusion of the above mentioned peaks.

The gas diffusion parameters, determining the weight gain in the samples, calculated by the formulae 7 and 8 as in the subsection A, using isothermal annealing procedure within the temperature range of (T_2, T_{GT}) have the following values: for $Y_1Ba_2Cu_3O_y$ $u = 0.16$ eV and $D_0 = 2.5 \times 10^{-6}$ cm^2 sec^{-1}; for $Y_1Ba_2Cu_{2.7}Al_{0.3}O_y$ $u = 0.39$ eV and $D_0 = 3.8 \times 10^{-5}$ cm^2 sec^{-1}; for $Er_1Ba_2Cu_3O_y$ $u = 0.45$ eV and $D_0 = 1.7 \times 10^{-4}$ cm^2 sec^{-1}. Comparing the results of section 5 (A and B), the activation energy u during gas diffusion from HTSC is much lower than that during diffusion of the gas into the HTSC. This is determined by the fact, that the activation energy u in gas loss processes (diffusion from HTSC) consists of the breaking of the bond energy between oxygen atom and an occupied site, the migration energy, and the energy barrier on the surface [2]. However, as to the weight recovery processes (diffusion into the HTSC), the activation energy is only determined by the migration energy. Finally, it should be noted, that the weight recovery processes proceed at relatively low temperatures. Therefore, the penetration of the gas impurities into the sample is determined by the diffusion along the grain boundaries. In view of the fact, that in this case fraction of the volume part of the sample, where diffusion takes place, is small, the value of the effective measured diffusion coefficient together with D_0 is essentially lower than that for the cases when the diffusion proceeds all along the whole bulk of the sample during process of the weight losses within the temperature range (T_{HL}, 1323 K).

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