Peritectic decomposition
of barium-yttrium cuprate $YBa_2Cu_3O_x$

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Precision X-ray diffraction analysis together with scanning electron microscopy, electron microprobe and thermal analysis have been used to study thermal decomposition of barium-yttrium cuprate $YBa_2Cu_3O_x$ above 900 °C in two ambients: air and vacuum (residual $p(O_2) = 700$ Pa). In air, $YBa_2Cu_3O_x$ undergoes peritectic decomposition at 1020 °C into Y_2BaCuO_5 and melt of barium and monovalent copper oxides. Y_2BaCuO_5 remains stable up to 1270 °C and at that temperature decomposes to Y_2O_3. In vacuum, at $p(O_2) \approx 700$ Pa, complete peritectic decomposition of 123 phase takes place at 965 °C and is preceded, starting from 925 °C, by nonequilibrium partial decomposition of $YBa_2Cu_3O_x$ into Y_2BaCuO_5, $YBa_3Cu_2O_y$ and $BaCu_2O_2$.

Методами прецизионной рентгенографии, сканирующей электронной микроскопии, локального электроннозондового и термического анализа изучены термические превращения при нагревании $YBa_2Cu_3O_x$ выше 900 °C по двум изобарам: на воздухе и в вакууме при $p(O_2) \approx 700$ Па. На воздухе $YBa_2Cu_3O_x$ претерпевает перитектический распад при 1020 °C на Y_2BaCuO_5 и расплав оксидов бария и одновалентной меди. Фаза Y_2BaCuO_5 остаётся устойчивой до 1270 °C, после чего подвергается перитектическому разложению до Y_2O_3. В вакууме при $p(O_2) \approx 700$ Па полный перитектический распад происходит при более низкой температуре 965 °C и ему предшествует, начиная с 925 °C, неравновесное частичное разложение фазы $YBa_2Cu_3O_x$ до Y_2BaCuO_5, $YBa_3Cu_2O_y$ и $BaCu_2O_2$.

The most promising results with respect to critical current density in bulk specimens of high-temperature superconductors have been obtained using the melt-texturing technology [1–4]. Higher critical current values are attributed to the reduction of weak-link effects as a consequence of grain growth, better grain alignment and increasing the number of centers for magnetic flux pinning formed, directly or indirectly, by precipitations of minor phases (such as Y_2BaCuO_5 in $YBa_2Cu_3O_x$) throughout the sample. At the same time, significant inhomogeneities in local distributions of critical current, chemical and phase composition have been observed in melt-textured specimens [5]. To understand the key features and control the melt-texturing process, it is important to know the mechanism of thermal decomposition of initial superconducting phase and of subsequent crystallisation under cooling from partially melted state.

The information available in literature on decomposition of barium-yttrium cuprate $YBa_2Cu_3O_x$ (123 phase) in the course of its heating is ambiguous. All authors agree that the main product of 123 decomposition is Y_2BaCuO_5 (211 "green" phase). Its formation is usually attributed to the peritectic reaction

$$YBa_2Cu_3O_x = Y_2BaCuO_5 + L + O_2.$$

where L is a melt enriched in barium and copper.

Serial versions on subsolidus decomposition resulting in the formation of other phases alongside with Y_2BaCuO_5 have been also reported: $Y_2BaCuO_5 + YBa_3Cu_2O_y + BaCu_2O_2$ [6], $Y_2BaCuO_5 + BaCuO_2 +$

Table. Results of X-ray phase analysis of products quenched after heat treatments at various conditions

Heat-treatment conditions			Phases in quenched samples
$p(O_2)$, Pa	T, °C	time, h	
$2{,}1 \cdot 10^4$	920	0.5	123
(air)	950	0.5	123
	990	1.0	123
	1010	0.5	123 (main phase) + 211 + $BaCO_3$ + $CuCO_3$
	1030	0.5	211 (main phase) + $BaCO_3$ + Cu_2O + $CuCO_3$
700±100	900	1.5	123
(vacuum)	925	0.5	123 (main phase) + 211 + 132 + $BaCu_2O_2$
	950	0.5	123 (main phase) + 211 + 132 + $BaCu_2O_2$
	950	0.75	123 + 211 + 132 + $BaCu_2O_2$
	970	0.5	211 (main phase) + $BaCO_3$ + Cu_2O + $CuCO_3$
	980	0.5	211 (main phase) + $BaCO_3$ + Cu_2O + $CuCO_3$

$BaCu_2O_2$ [7], Y_2BaCuO_5 + $BaCuO_2$ + Cu_2O [8], Y_2BaCuO_5 + $BaCu_2O_2$ + BaO [9], Y_2BaCuO_5 + $Ba_2Cu_3O_5$ + CuO [10]. It has been supposed that the controversy in reported data might be related to some uncertainties in equilibrium oxygen partial pressure $p(O_2)$ in gaseous ambient [11].

In this paper we have used the precision X-ray diffraction technique together with analytical scanning electron microscopy and thermal analysis to study thermal decomposition of $YBa_2Cu_3O_x$ under conditions that hold the most interest for melt-texturing technology: $900 < T < 1280$ °C, $10^2 < p(O_2) < 10^5$ Pa.

The initial superconducting material was synthesized from Y_2O_3, $BaCO_3$ and CuO of "chemically pure" grade. A reagent mixture corresponding to the stoichiometric formula $Y_{1,00}Ba_{2,00}Cu_{3,00}O_x$ was compacted into pellets $\varnothing20{\times}5$ mm^3, fired at (930 ± 5) °C for 10 h and, after intermediate regrindings, at (940 ± 5) °C and (950 ± 5) °C for 30 h at each temperature. After the final firing, the pellets were cooled to 400 °C at 100 °C/h and oxidised at this temperature for 8 h before cooling to room temperature together with the furnace. The oxidation under these conditions aimed to obtain higher superconducting properties of initial barium-yttrium cuprate [12]. Chemical analysis and the comparison of measured and calculated mass losses were used to examine the preservation of cation stoichiometry after high-temperature treatments. By X-ray examination, the product of described synthesis was single-phased $YBa_2Cu_3O_{6.97}$ (the content of 211 phase < 0.5 mass %).

To obtain the samples for X-ray studies of thermal transformations in $YBa_2Cu_3O_x$,

two series of heat treatments were conducted in a tube furnace: in air flow and in vacuum under the residual oxygen pressure $p(O_2) = 700 \pm 100$ Pa. The samples pressed into disks or plates ≤ 1 mm thick were heated stepwise according to the schedules shown in the Table. The accuracy of temperature regulation in the heating zone was within ±1 °C. After each step of heat treatment, the next sample was extracted from the furnace within time a period not more than 5 s and then quenched in air. In this way, the sample quenched from a given temperature had passed all the previous steps of heat treatment shown in the Table. A Phillips PW 1710 based diffractometer was used for X-ray diffraction measurements using filtered Co K_α radiation. The diffraction patterns were taken at the scanning rate 0.5 to 2° per minute in 2θ interval from 20 to 80°, at accelerating voltage of 35 kV and generator current 30 mA.

The primary computer treatment of diffraction data was performed at the time of X-raying using standard software package provided for Philips PW 1710 diffractometer. That included the determination of the following values: d_{hkl} spacings calculated for both $K_{\alpha1}$ and $K_{\alpha2}$ components of X-ray radiation, diffraction peak width, integral peak intensity, background intensity, relative peak intensity, and statistical significance of a singled-out peak. The data treatment conducted after the experiment usually included the phase analysis and calculation of unit cell parameters.

To resolve very weak reflections, the Fourier transformation of initial diffraction
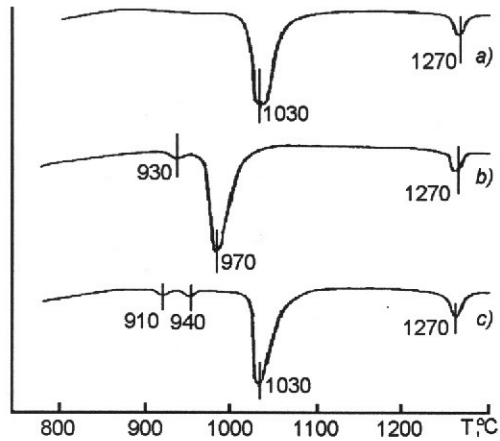
Fig.1. DTA curves of $YBa_2Cu_3O_x$: a ˚ homogeneous single-phased sample, heating in air; b ˚ the same sample, heating in vacuum, $p(O_2)$ = 700 Pa; c ˚ inhomogeneous sample (synthesised at 960 ˚C for 6 h), heating in air.

Fig.2. X-ray diffraction patterns after treatment $YBa_2Cu_3O_x$ in air at temperatures, ˚C: a ˚ 920; b ˚ 950; c ˚ 990; d ˚ 1010; e ˚ 1030.

data was performed. Splitting of a supposed peak into α_1 and α_2 components of X-ray radiation after such data treatment served as a criterion for the resolution of a very weak diffraction peak with an intensity close to the instrument detection threshold. That treatment allowed to increase the sensitivity of phase analysis in the system to 0.5–0.8 % by mass.

Local chemical composition and microstructure were studied by analytical scanning electron microscopy (SEM) using a JEOL JSM-35C microscope equipped with an electron microprobe with energy dispersive spectrometer. Thermograms were taken at heating rate 3 ˚C/min using a Paulik-Paulik-Erdey derivatograph.

First, the processes of thermal transformations in single-phased cuprate $Y_{1.00}Ba_{2.00}Cu_{3.00}O_x$ in two ambients: air ($p(O_2)$ = 2,1 · 10⁴ Pa) and low vacuum ($p(O_2)$ = 700 ±100 Pa) have been studied by means of thermal analysis.

Two strong endothermic peaks are evident in thermograms (Fig.1). When the sample is heated in air, these strong peaks are registered at 1030 ˚C and 1270 ˚C. According to visual observations and X-ray data (Table) the first of these two peaks corresponds to peritectic transformation of $YBa_2Cu_3O_x$ (123 phase) into Y_2BaCuO_5 (211 phase). The peak at 1270 ˚C is produced by consequent peritectic decomposition of 211 phase to yttrium oxide which is the most stable oxide component in this system. Decreasing the oxygen partial pressure $p(O_2)$ in the ambient causes the first endothermic

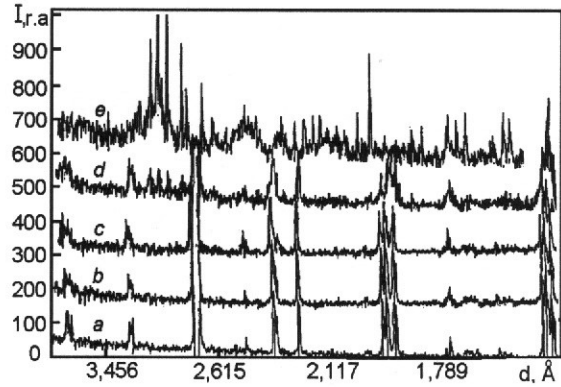peak (but not the second) to shift to lower temperatures. Under $p(O_2)$ = (700 ± 100) Pa, that effect is fixed at 970 ˚C (Fig. 1b). A weaker endothermic peak at 930 ˚C is also seen in thermograms taken in vacuum. There is no such effect on the thermogram taken in air from a single-phased sample that had been synthesized for an adequately long time (Fig. 1a). At the same time, small endoeffects at 900 – 940 ˚C are often observed in air for samples synthesised during shorter time periods (Fig. 1c). In such case, these effects become more pronounced when an excess of barium and copper oxides is added to the reaction mixture. This observation allows to relate those effects with eutectic melting of local areas enriched in barium and copper within not sufficiently homogeneous, although perhaps stoichiometric, samples.

X-ray diffraction patterns taken from the samples quenched after heat treatment at various temperatures in air and in vacuum ($p(O_2)$ = 700 ± 100 Pa) are shown in Fig.2 and Fig.3. In air, barium-yttrium cuprate $YBa_2Cu_3O_x$ remains single-phased in the course of heating up to 990 ˚C. After half an hour treatment at 1010 ˚C, a partial decomposition of 123 phase is observed (Table). At 1030 ˚C (the temperature of a strong endothermic peak on the thermogram) the decomposition of 123 is complete and it is accompanied with partial melting of the sample. The main decomposition product is Y_2BaCuO_5. Compact samples quenched from this temperature were greyish but after grinding into a powder their colour changed into bright green typical for 211 phase.
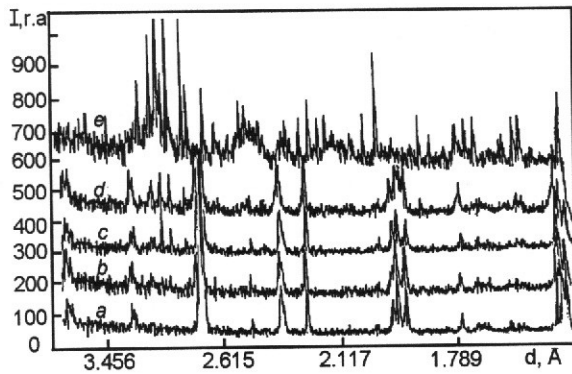
Fig.3. X-ray diffraction patterns after treatment $YBa_2Cu_3O_x$ in vacuum ($p(O_2)$ = 700 Pa) at temperatures, °C: a — 900; b — 925; c — 950, 0.5 h; d — 950, 1.25 h; e — 970.

X-ray examination of melt droplets crystallised at the bottom of the sample quenched from 1030 °C revealed Cu_2O, $BaCO_3$ and small amounts of $CuCO_3$. No yttrium-containing phases have been found in the sample of the quenched melt. Barium and copper carbonates are evidently the products of interaction of the solidified melt with atmospheric carbon dioxide during cooling and consequent storage of the samples in air. The possibility of Cu (I) oxidation to Cu (II) during cooling should also take into account.

These results allow us to conclude that initially single-phased and stoichiometric with respect to cation content cuprate $YBa_2Cu_3O_x$, when heated in air undergoes the peritectic decomposition at (1020±10) °C according to the equation:

$$2\ YBa_2Cu_3O_{6.22}\ (s) = Y_2BaCuO_5(s)\ + 3\ BaO(m) + 2.5\ Cu_2O(m) + 0.97\ O_2\ (g)$$
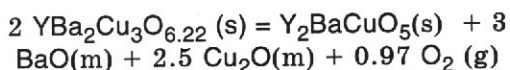
where letter indices stand for: (s) — solid crystalline phase; (m) — melt; (g) — gaseous phase. Oxygen index x = 6.22 in $YBa_2Cu_3O_x$ at 1020 °C is determined from $p(O_2)$ — T phase diagram presented in our earlier work [12].

The X-ray analysis of the sample quenched from the temperature of strong endothermic peak at 1270 °C shows that at that temperature Y_2BaCuO_5 phase undergoes peritectic decomposition according to reaction equation:

$$Y_2BaCuO_5(s)\ =\ Y_2O_3(s)\ +\ BaO(m) + 0.5\ Cu_2O(m) + 0.25\ O_2\ (g)$$
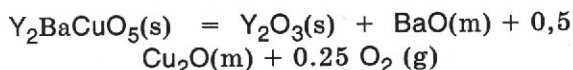
The sequence of $YBa_2Cu_3O_x$ thermal decomposition reactions changes essentially when oxygen partial pressure is lowered by

one and a half order of magnitude, down to $p(O_2)$ ≈700 Pa (Fig.3, Table). In that case, already after heat treatment of initially single-phased $YBa_2Cu_3O_x$ at 925 °C (the temperature of smaller endothermic peak on the thermogram) partial decomposition of 123 proceeds according to equation:

$$7YBa_2Cu_3O_{6.15}(s) = 3Y_2BaCuO_5(s) + + YBa_3Cu_2O_y(s) + 8\ BaCu_2O_2(s) + + (6.02 - 0.5y)\ O_2\ (g)$$
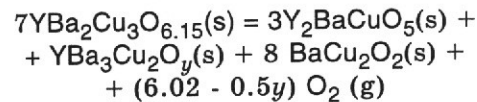
The subsequent heating in vacuum to 950 °C and holding the sample at that temperature cause gradual increase in amount of Y_2BaCuO_5 and of other decomposition products (Table) but initial phase $YBa_2Cu_3O_x$ does not decompose completely and remains a predominant one in the mixture. Therefore, the decomposition process does not reach its equilibrium: according to Gibbs phase rule, the number of condensed phases in equilibrium with a gaseous phase cannot exceed three for a four-component system. A slow rate of decomposition indicates most probably the diffusion control of the reaction. In the same time increasing temperature by another 20 deg (to 970 °C) results in rapid and complete decomposition of $YBa_2Cu_3O_x$ and $YBa_3Cu_2O_y$ and partial melting of the sample. Taking into account obtained X-ray data, decomposition of the 132 phase is described by reaction

$$2\ YBa_3Cu_2O_y(s) = Y_2BaCuO_5(s)\ + 5\ BaO+ + 1.5\ Cu_2O(m) +\ (y - 5.75)\ O_2\ (g).$$
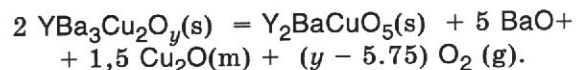
As seen from thermal analysis and X-ray data, lowering $p(O_2)$ from $2.1\cdot10^4$ down to $2\cdot10^2$ Pa does not produce any noticeable effect on the peritectic decomposition temperature of green phase Y_2BaCuO_5 at its consequent heating (1270 °C).

Thermal analysis and X-ray diffractometry were supplemented with the study of microstructure and local elemental composition of quenched samples using scanning electron microscopy. The grain microstructure of initial single-phased sample is homogeneous with sharp and clean grain boundaries (Fig. 4a). Electron microprobe has not revealed grains with elemental composition different from that of $YBa_2Cu_3O_x$. After treatment at 925 °C, smaller grains appear in the sample and microprobe identifies majority of them as $BaCu_2O_2$ (Fig.4b). The further heating to 950 °C results in the appearance of larger $BaCu_2O_2$ grains (Fig.4c). Micrographs evidence clearly the partial melting — rounded boundaries of
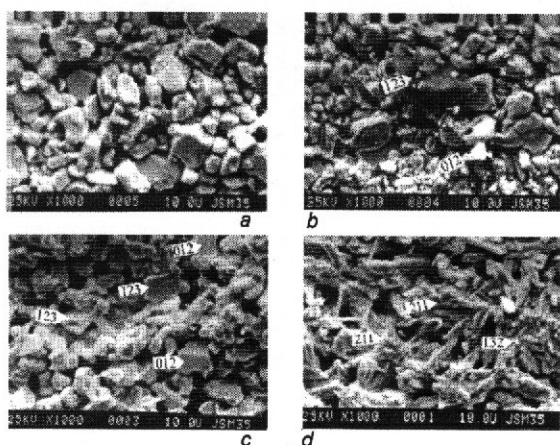
Fig.4. Electron microphotographs of samples after treatment in vacuum at temperatures, °C: a — 900; b — 925; c — 950, 0.5 h; d — 950, 1.25 h. Phases identified by electron microprobe: 123 — $YBa_2Cu_3O_x$; 211 — Y_2BaCuO_5; 132 — $YBa_3Cu_2O_y$; 012 — $BaCu_2O_2$.

initial grains, the appearance of needle-shaped grains. At longer treatment times at 950 °C, the transformation of grains is enhanced and the number of needles increases. The needle-shaped grains, according to electron microprobe, are formed mainly by Y_2BaCuO_5 and, in fewer cases, by $YBa_3Cu_2O_y$ (Fig.4d).

Identification of $YBa_3Cu_2O_y$ и $BaCu_2O_2$ by means of electron microprobe was an especially useful supplement of X-ray data as many peaks from these phases overlapped those of main one $YBa_2Cu_3O_x$ on diffractograms.

Thus, the results obtained allow to conclude that:

1. In air, $YBa_2Cu_3O_x$ undergoes the peritectic decomposition at 1020 °C into Y_2BaCuO_5 and melt of barium and monovalent copper oxides. Under subsequent heating, Y_2BaCuO_5 remains stable up to 1270 °C and decomposes into Y_2O_3 and melt of BaO and Cu_2O at that temperature.

2. In vacuum, at $p(O_2) \approx 700$ Pa, the peritectic decomposition temperature of 123 phase decreases to (965 ± 5) °C and this decomposition is preceded, by nonequilibrium partial decomposition of $YBa_2Cu_3O_x$ into Y_2BaCuO_5, $YBa_3Cu_2O_y$ and $BaCu_2O_2$ starting from 925 °C.

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Перитектичний розклад купрату барію-ітрію $YBa_2Cu_3O_x$

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Методами прецизійної рентгенографії, скануючої електронної мікроскопії, локального електроннозондового і термічного аналізу вивчено термічні перетворення під час нагрівання $YBa_2Cu_3O_x$ вище 900 °С за двома ізобарами: на повітрі та у вакуумі при $p(O_2) \approx 700$ Па. На повітрі $YBa_2Cu_3O_x$ перитектично розкладається при 1020 °С на Y_2BaCuO_5 та розплав оксидів барію і одновалентної міді. Фаза Y_2BaCuO_5 залишається стабільною до 1270 °С, після чого зазнає перитектичного розкладу до Y_2O_3. У вакуумі при $p(O_2) \approx 700$ Па повний перитектичний розклад відбувається при нижчий температурі 965 °С і йому передує, починаючи з 925 °С, нерівноважний частковий розклад фази $YBa_2Cu_3O_x$ до Y_2BaCuO_5, $YBa_3Cu_2O_y$ і $BaCu_2O_2$.