Crystallization features of $YBa_2Cu_3O_{7-\delta}$ in the Y_2BaCuO_5-$BaCuO_2$-CuO and $Y_2Cu_2O_5$-$BaCuO_2$ systems

N. A. Kalanda*[1], L. I. Gurskii[2], A. M. Saad[3], V. M. Truhan[1], and T. V. Haliakevich[1]

[1] Joint Institute of Solid State and Semiconductor Physics, NAS Belarus, Minsk, Belarus
[2] Belarusian State University of Informatics Science and Radioelectronics, Minsk, Belarus
[3] Al-Balqua Applied University, Salt, Jordan

Based on the data of X-ray phase and microstructure analysis, the sample composition was optimized in order to provide maximum size of the textured macrograins of $YBa_2Cu_3O_{7-\delta}$ and of the crystallites in the Y_2BaCuO_5-$BaCuO_2$-CuO, $Y_2Cu_2O_5$-$BaCuO_2$ systems. The growth rate has been studied and the $YBa_2Cu_3O_{7-\delta}$ growth activation energy has been calculated for the samples of Y_2BaCuO_5+$3BaCuO_2$+$2.3CuO$, Y_2BaCuO_5+$3BaCuO_2$+$0.6CuO$, and $Y_2Cu_2O_5$+$3.5BaCuO_2$ compounds in the temperature range of 1240-1270K for the case of use of the $Y_2Cu_2O_5$ and Y_2BaCuO_5 precursors with an average grain diameter of 10 μm and 1mm. A crystallization mechanism of $YBa_2Cu_3O_{7-\delta}$ in the Y_2BaCuO_5-$BaCuO_2$-CuO and $Y_2Cu_2O_5$-$BaCuO_2$ systems in the case of different sizes of Y_2BaCuO_5 and $Y_2Cu_2O_5$ precursor grains was proposed and validated.

1 Introduction

Despite of the huge amount of work performed up to now [1], it is difficult to obtain high-quality ceramics and yttrium-barium cuprate ($YBa_2Cu_3O_{7-\delta}$) single crystals because of crystallization peritectic character, active interaction of solution-melt with material of technological equipment, lack of oxygen in the liquid phase, crystallization of satellite phases, etc. [2-4]. At that, some reagents such as Y_2O_3, BaO and CuO form the chemically stable refractory compounds, which do not react completely, and, thus, are present in yttrium-barium cuprate in the form of separate inclusions, significantly worsening its superconductive properties. Due to that, the traditional techniques of getting $YBa_2Cu_3O_{7-\delta}$ in which feeds containing simple oxides like Y_2O_3, BaO and CuO are used are not effective [5,6]. The use of feeds containing Y_2BaCuO_5 and $Y_2Cu_2O_5$ precursors provides the $YBa_2Cu_3O_{7-\delta}$ synthesis without reactions intermediate with oxygen change in solution - melt [5,7,8]. Since the $YBa_2Cu_3O_{7-\delta}$ crystallization rate and its mechanism depend on the grain size of Y_2BaCuO_5 and $Y_2Cu_2O_5$ precursors, the study of the grains dispersity on peculiarities of crystallization processes of yttrium-barium cuprate becomes significant.

This work is devoted to investigation of the influence of the Y_2BaCuO_5 and $Y_2Cu_2O_5$ precursor grain size on the crystallization rate and mechanism as well as on the microstructure of $YBa_2Cu_3O_{7-\delta}$ in the Y_2BaCuO_5-$BaCuO_2$-CuO and $Y_2Cu_2O_5$-$BaCuO_2$ systems.

2 Experimental

To obtain Y_2BaCuO_5, $Y_2Cu_2O_5$ and $BaCuO_2$ compounds the Y_2O_3, BaO and CuO (99,99%) oxides were used. Oxides together with ethyl alcohol were grinded and mixed in vibrating mill for 3 h, dried at T=320 K and

* Corresponding author: e-mail: kalanda@ifttp.bas-net.by

pressed into tablets. Preliminary annealing was carried out in air at T=970 K (BaCuO$_2$) and T=1070 K (Y$_2$BaCuO$_5$, Y$_2$Cu$_2$O$_5$) for 24 h. The second grinding was used in order to increase the homogeneity. Final anneal of oxide mixtures was carried out in air at T=1240 K (for BaCuO$_2$) and T=1270 K (for Y$_2$BaCuO$_5$, Y$_2$Cu$_2$O$_5$) for 24 h.

The furnace temperature was maintained by an RIF-101 precision temperature controller and monitored by Pt-Pt/Rh10 thermocouple with an accuracy up to ±0.5 K. X-ray radiometrical (XRA), X-ray phase (XRD) analyses were performed, and methods of electron microscopy, X-ray spectral microanalysis as well as optical microscopy were used to determine the mechanism of the YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals formation. Growth kinetics of yttrium-barium cuprate is determined by the change of the normalized intensity of the (103) X-ray line of YBa$_2$Cu$_3$O$_{7-\delta}$ compound. For detachment of the Y$_2$BaCuO$_5$ and Y$_2$Cu$_2$O$_5$ grains with average size d$_{av}$ ~ 1 mm, the sieve separation was used. The furnace thus contained not less than 90% of grains of Y$_2$Cu$_2$O$_5$ and Y$_2$BaCuO$_5$ with d$_{av}$ ~ 1 mm. The fine grinding of the Y$_2$BaCuO$_5$ and Y$_2$Cu$_2$O$_5$ furnace was carried out in a ball mill, using ethyl alcohol as the grinding medium. After fine grinding, the furnace contained grains of Y$_2$BaCuO$_5$ and Y$_2$Cu$_2$O$_5$ with d$_{av}$ ~ 10 μm in amount not less than 70%.

3 Results and discussion

The study of influence of the geometric dimensions of grains of Y$_2$BaCuO$_5$ and Y$_2$Cu$_2$O$_5$ precursors on YBa$_2$Cu$_3$O$_{7-\delta}$ crystallization kinetics and mechanism was carried out on the samples with the following compositions: Y$_2$BaCuO$_5$-BaCuO$_2$-CuO and Y$_2$Cu$_2$O$_5$-BaCuO$_2$. Three systems have been investigated: (I) - Y$_2$BaCuO$_5$+3BaCuO$_2$+2.3CuO, (II) - Y$_2$BaCuO$_5$+3BaCuO$_2$+0.6CuO, (III) - Y$_2$Cu$_2$O$_5$+3.5BaCuO$_2$. A MgO monocrystalline plate oriented in the (001) plane was chosen as a substrate. MgO is poorly wetting by the solution – melt. It also stimulates the nucleation of the YBa$_2$Cu$_3$O$_{7-\delta}$ phase on its surface and provides minimum loss of the melt forming in a diffusion pair [9]. The composition of the samples synthesized in the temperature range 1270–1320 K and having maximum size of the textured macro grains and YBa$_2$Cu$_3$O$_{7-\delta}$ crystallites, was determined by the phase and microstructure analysis of the surfaces of five sections of each tablet [8]. For estimation of composition with the greatest size of both textured YBa$_2$Cu$_3$O$_{7-\delta}$ macrograins and crystallites, the samples were heated up to the temperatures 1270 < T < 1320 K, and after two hours they were cooled down with the rate of 1 K/h to the temperature of 1170 K. Below this last temperature, all the chemical processes are frozen [7]. The calculation of the normalized area < S$_{mgrain}$ >/<S>, where < S$_{mgrain}$ > is the average area of the surface of five sections of the sample occupied by the textured YBa$_2$Cu$_3$O$_{7-\delta}$, macrograins, <S> is the average area of the total surface of five sections of the sample, was carried out based on results of the phase and microstructure analysis of the surface of the above mentioned five sections of the synthesized sample [8].

It was established that at synthesis of Y$_2$BaCuO$_5$+3BaCuO$_2$+xCuO samples with x$_1$=0, x$_2$=0.5, x$_3$=1.0, x$_4$=1.5, x$_5$=2.0, x$_6$=2.5, x$_7$=3.0 , with rising start temperature of the synthesis T$_s$ from 1270 K to 1305 K with the step of 5 K, the normalized areas <S$_{mgrain}$>/<S> and the average areas <S$_{mgrain}$> increase, while for T$_s$ from 1305–1320 K they decrease (Fig. 1a,b). From the plotted dependencies < S$_{mgrain}$ >/<S> = f(x, T), and from those for crystallite size <S$_{cr}$> = f(x, T) it was established that the highest values of < S$_{mgrain}$ >/<S> and of <S$_{cr}$> was observed in compositions Y$_2$BaCuO$_5$+3BaCuO$_2$+2.3CuO and Y$_2$BaCuO$_5$+3BaCuO$_2$+0.6CuO, respectively (Fig. 1 a,b).

It was found that the highest value of the function f(y, T)=(<S$_{mgrain}$>/<S>) where y was changed step-like, namely y$_1$=2.0, y$_2$=2.5, y$_3$=3.0, y$_4$=3.5, y$_5$=4.0, y$_6$=4.5, in the samples consisting of the phase mixture Y$_2$Cu$_2$O$_5$+yBaCuO$_2$ corresponds to the composition Y$_2$Cu$_2$O$_5$+3.5BaCuO$_2$ (Fig. 2). It should be noted that for all compositions of the Y$_2$Cu$_2$O$_5$+yBaCuO$_2$ samples, after their synthesis, the structure of the textured macrograins was fine-grained, and, thus, the function <S$_{cr}$> =f(y, T) was not built. Thus, based on the above described results, for the study of the kinetics and mechanism of the YBa$_2$Cu$_3$O$_{7-\delta}$ crystallization, the samples with the following compositions were chosen: (I) - Y$_2$BaCuO$_5$ + 3BaCuO$_2$ + 2.3CuO, (II) - Y$_2$BaCuO$_5$ + 3BaCuO$_2$ + 0.6CuO, (III) - Y$_2$Cu$_2$O$_5$ + 3.5BaCuO$_2$.

Using the data of the change of the relative intensity of the (103) X-ray reflex, it was established that at the use of the Y$_2$Cu$_2$O$_5$ and Y$_2$BaCuO$_5$ precursors with the average grain size d$_{av}$ ~ 10 μm, the growth rate of YBa$_2$Cu$_3$O$_{7-\delta}$ in the systems (I) to (III) can be well described by the parabolic dependence (I/I$_{max}$)^2= k(t–t$_0$), where k is the constant of growth rate of YBa$_2$Cu$_3$O$_{7-\delta}$, I is the intensity of the (103) reflex measured through time intervals Δt =1h, I$_{max}$ is the maximal intensity of the (103) reflex line, t is the synthesis time of

$YBa_2Cu_3O_{7-\delta}$, t_0 is the time from the start of the furnace annealing to the appearance of $YBa_2Cu_3O_{7-\delta}$ in the furnace (Fig 3). It was established that the highest growth rate of $YBa_2Cu_3O_{7-\delta}$ was in the system (II). The values of the growth activation energy of $YBa_2Cu_3O_{7-\delta}$ were calculated by the formula $k = k_0 exp(-E/RT)$, where k_0 is the constant of growth rate at $t = t_0$, R is the gas constant (8.31 $J^*K^{-1*}gram-molecule^{-1}$). They are 31, 39 and 54 $K/J \cdot m$ for the systems (II), (I) and (III), respectively.
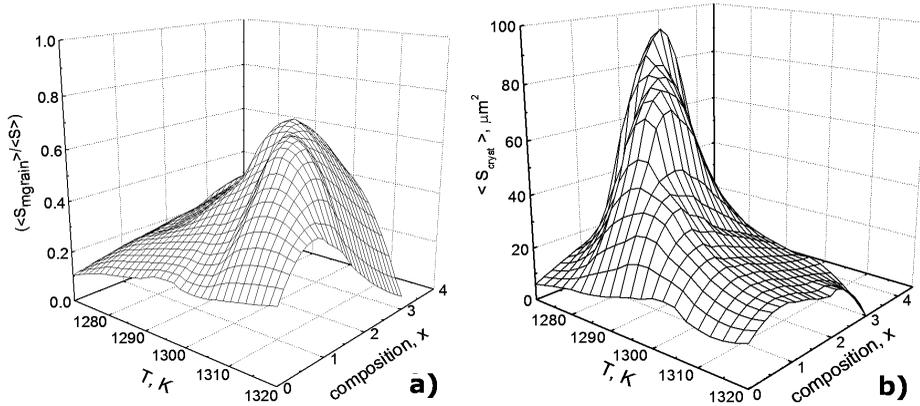
Fig. 1 a) Plot of $<S_{mgrain}>/<S>$ vs T, x - $(Y_2BaCuO_5+3BaCuO_2+xCuO)$ for $YBa_2Cu_3O_{7-\delta}$. B) Plot of $<S_{cryst}>$ vs T, x - $(Y_2BaCuO_5+3BaCuO_2+xCuO)$ for $YBa_2Cu_3O_{7-\delta}$.
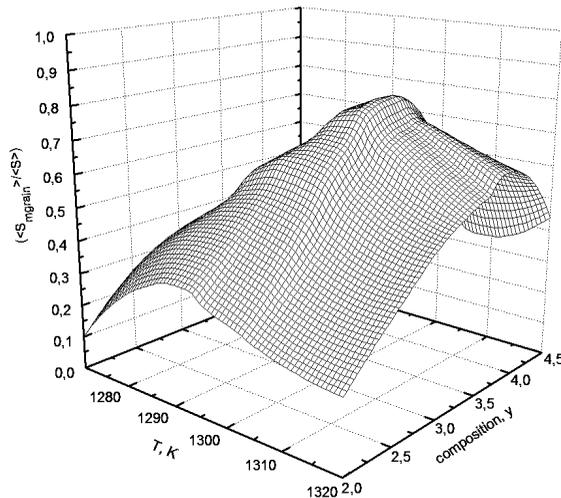
Fig. 2 Plot of $<S_{mgrain}>/<S>$ vs T, y - $(Y_2Cu_2O_5+yBaCuO_2)$ for $YBa_2Cu_3O_{7-\delta}$.
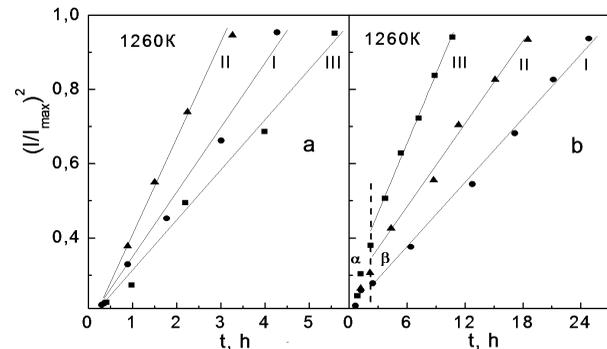
Fig. 3 Plot of $(I/I_{max})^2$ vs time for $YBa_2Cu_3O_{7-\delta}$ in the systems (I) to (III) (a – grains size $<d>\sim10\mu m$, b –$<d>\sim1$ mm).

To establish the causes of different values of $YBa_2Cu_3O_{7-\delta}$ growth rates in the systems (I) to (III) with the average grain size of Y_2BaCuO_5 and $Y_2Cu_2O_5$ $d_{av}\sim10$ μm, let us consider the peculiarities of the crystallization mechanism of yttrium-barium cuprate in these systems. Based on the data of the local X-ray spectral microanalysis of the samples (I) - (III) tempered from T=1240-1270 K, it was established that the average concentration of yttrium ($<C_Y>$) in the solution- melt does not exceed 3 at. %. One may suppose that the maximal concentration of yttrium (max C_Y) will be on the border between the Y_2BaCuO_5, $Y_2Cu_2O_5$ grains and a solution-melt, and the heterogeneous nucleation and growth of $YBa_2Cu_3O_{7-\delta}$ should occur on the grain surfaces of the above mentioned solid phases [8,10]. However, during the investigation of the microstructure of the tempered samples, the formation of the $YBa_2Cu_3O_{7-\delta}$ compound was found to be not on the border between the grain surfaces and the solution-melt, but rather in the ellipsoid regions of the crystallized solution-melt (fig.4). In this case, the peritectic transformation reaction can be presented as: L + Y_2BaCuO_5 or (L + $Y_2Cu_2O_5$)→ L +$YBa_2Cu_3O_{7-\delta}$→$YBa_2Cu_3O_{7-\delta}$, L + Y_2BaCuO_5 → L + $YBa_2Cu_3O_{7-\delta}$ → $YBa_2Cu_3O_{7-\delta}$.

Y$_2$BaCuO$_5$+L $\rightarrow$ L $\rightarrow$ YBa$_2$Cu$_3$O$_{7-\delta}$. In the same conditions, in the II-system both the Y$_2$BaCuO$_5$ and the YBa$_4$Cu$_3$O$_{9-\delta}$ compounds were discovered. Since the content of Y$_2$BaCuO$_5$ and YBa$_4$Cu$_3$O$_{9-\delta}$ decreases during the crystallization of YBa$_2$Cu$_3$O$_{7-\delta}$. hence, the formation to the YBa$_2$Cu$_3$O$_{7-\delta}$ compounds should take place according to the scheme: L + Y$_2$BaCuO$_5$ $\rightarrow$ L + Y$_2$BaCuO$_5$ + YBa$_4$Cu$_3$O$_{9-\delta}$$\rightarrow$L + YBa$_2Cu_3O_{7-\delta}$ $\rightarrow$ YBa$_2$Cu$_3$O$_{7-\delta}$ YBa$_4$Cu$_3$O$_{9-\delta}$+Y$_2$BaCuO$_5$+L$\rightarrow$L$\rightarrow$YBa$_2$Cu$_3$O$_{7-\delta}$.

Thus, the YBa$_2$Cu$_3$O$_{7-\delta}$ crystallization in the (I)–(III) systems with the grain size of the Y$_2$BaCuO$_5$ and Y$_2$Cu$_2$O$_5$ precursors <d>~10 μm occurs in the solution-melt. In this case, the growth rate of YBa$_2$Cu$_3$O$_{7-\delta}$ in the systems (I), (III) is limited by the Y intake speed from the Y$_2$BaCuO$_5$ grains to the YBa$_2$Cu$_3$O$_{7-\delta}$ growing grains through the liquid, because of the relatively low value of <C$_Y$> ~ 3 at.% in the solution-melt. In the system (II), the growth rate will be limited by the Y intake speed also from the grains of the intermediate phase YBa$_4$Cu$_3$O$_{9-\delta}$ additionally. The obtained experimental results coincide well with the theory.

Fig. 4 Ellipsoidal areas in the tempered solution – melt of the samples of system II (a), I (b), and III (c), for the case of use of Y$_2$BaCuO$_5$ and Y$_2$Cu$_2$O$_5$ with average grain size d$_{av}$ ~10 μm in the initial furnace.

It is known that density of yttrium (J$_Y$) flow to the YBa$_2$Cu$_3$O$_{7-\delta}$ grains surface is proportional to the gradient of its concentration (ΔC$_Y$) in the liquid phase, which can be conditionally divided into two areas with various concentration Y [3]. The first area (C$_{Y1}$) is located on border of L/Y$_2$BaCuO$_5$ Y$_2$BaCuO$_5$/L grains. The second area (C$_{Y2}$) is located on border of L/YBa$_2$Cu$_3$O$_{7-\delta}$ YBa$_2$Cu$_3$O$_{7-\delta}$/L grains. Suppose that yttrium concentration in a solution-melt is a constant (C$_{Yo}$). It is well known (Fick's first law) that substance stream from unit of Y$_2$BaCuO$_5$ grains surface is described as: J$_{Y1}$= k$_1$D$_{Y1}$/$\delta_1$$\Delta$C$_{Y1}$, where D$_{Y1}$ –is the chemical diffusion- factor of yttrium through boundary layer, δ_1- is the thickness of boundary layer between Y$_2$BaCuO$_5$ grains surface and conventional border outside of which the solution-melt structure is constant. At crystallization YBa$_2$Cu$_3$O$_{7-\delta}$ the gradient stream on unit of crystal surface makes J$_{Y2}$=k$_2$D$_{Y2}$/$\delta_2$$\Delta$C$_{Y2}$, where D$_{Y2}$ - is the chemical diffusion- factor of yttrium through boundary layer, δ_2 is the thickness of boundary layer between Y$_2$BaCuO$_5$ crystals surface and conventional border outside of which the solution-melt structure does not change. Streams J$_{Y1}$ and J$_{Y2}$ are equal in (I) and (III) systems at quasi-equilibrium conditions of YBa$_2$Cu$_3$O$_{7-\delta}$ crystallization. The growth rate equation can be presented as: v$_{2(cryst.)}$ = v$_{1(dec.)}$$\Delta$C$_2$/$\Delta$C$_1$, where v$_{2(cryst.)}$= kD$_{2L}$/$\delta_2$ –is the growth rate

of $YBa_2Cu_3O_{7-\delta}$, $v_{1(dec.)} = kD_{1L}/\delta_1$ –is the decomposition rate of Y_2BaCuO_5 grains. Growth rate of $YBa_2Cu_3O_{7-\delta}$ is characterized by yttrium streams from Y_2BaCuO_5 – (J_{Y3}), $YBa_4Cu_3O_{9-\delta}$ – (J_{Y4}) grains through a phase liquid to $YBa_2Cu_3O_{7-\delta}$ surface in (II) system. The growth rate equation of $YBa_2Cu_3O_{7-\delta}$ can be formulated as: $v_{(cryst.)} = \Delta C_2 \{ v_{3(dec.)}/\Delta C_3 + v_{4(dec.)}/\Delta C_4 \}$, where $v_{3(dec.)}$, $v_{4(dec.)}$– is the decomposition rate of Y_2BaCuO_5 and $YBa_4Cu_3O_{9-\delta}$, ΔC_3, ΔC_4 – is the gradient of yttrium concentration on section border of L/Y_2BaCuO_5 Y_2BaCuO_5/L and $L/YBa_4Cu_3O_{9-\delta}$ $YBa_4Cu_3O_{9-\delta}/L$. Thus, growth rate of $YBa_2Cu_3O_{7-\delta}$ in (I), (III) systems is determined rate of Y_2BaCuO_5 grains decomposition and supersaturation degree on interface section a solid phase. Growth rate of $YBa_2Cu_3O_{7-\delta}$ in (II) system was determined rate of decomposition of $YBa_4Cu_3O_{9-\delta}$ grains additionally. Growth rate of $YBa_2Cu_3O_{7-\delta}$ in (I), (III) systems was determined Y mobility in solution-melt at absence of artificial homogenization. The greatest growth rate of $YBa_2Cu_3O_{7-\delta}$ in (II) system is caused by two streams of Y to a crystal surface. Formation and subsequent decomposition of $YBa_4Cu_3O_{9-\delta}$ provides, in our opinion, chemical homogenization of reagents in a solution-melt. In (III) system formation and growth of $YBa_2Cu_3O_{7-\delta}$ grains occurs, as well as in (I), but at greater growth rate that can be explained by the chemical homogenization caused by peritectic reaction of $L + Y_2Cu_2O_5 \rightarrow L + YBa_2Cu_3O_{7-\delta} \rightarrow YBa_2Cu_3O_{7-\delta}$ $Y_2Cu_2O_5 + L \rightarrow Y_2BaCuO_5$. At increasing size of the grains of Y_2BaCuO_5 and $Y_2Cu_2O_5$ and Y_2BaCuO_5 up to $d_{av} \sim 1$ mm, the change of the growth rate of $YBa_2Cu_3O_{7-\delta}$ in the systems (I)-(III) can be divided into two stages (α, β), which can be described by the quasi-linear and parabolic dependencies, respectively (Fig. 3).

The greatest growth rate of $YBa_2Cu_3O_{7-\delta}$ was observed in the (I) system. Growth activation energy of $YBa_2Cu_3O_{7-\delta}$ increased up to 183, 197 and 201 kJ/mol at the second growth stages for (I), (III) and (II) systems accordingly. To explain these peculiarities, the following additional experiment was carried out. The polycrystalline high-density ($\rho \sim 0.94\rho_{reop}$) tablets of Y_2BaCuO_5 and $Y_2Cu_2O_5$ 8 mm in diameter and 3 mm thick were immersed in $L(BaCu_{1.8}O_z)$, $L(BaCu_{1.2}O_z)$, and $L(BaCuO_z)$ liquid at 1240-1290 K for 2 h. Then the tablets were cooled with the rate of 1 K/h down to the different temperatures in the range of 1240-1290 K, with the subsequent tempering. It was established by the X-ray spectral and X-ray radiometrical (XRA) analyses that Y was absent in liquid phase at 1240-1270 K, but the Y was detected in the vicinity of the Y_2BaCuO_5 and $Y_2Cu_2O_5$ tablets at 1270-1290 K. Microstructure analysis showed that Y_2BaCuO_5 tablet tempered from melt $L(BaCu_{1.8}O_z)$ at 1240-1270 K has a textured layer of $YBa_2Cu_3O_{7-\delta}$ (Fig. 5).
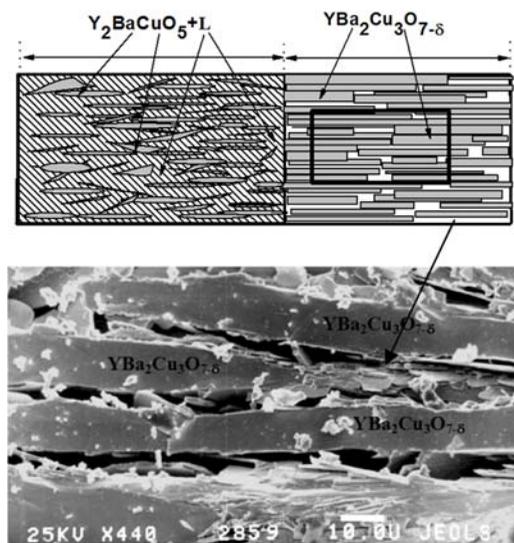
Fig. 5 Diffusion layers of Y_2BaCuO_5+L ($BaCu_{1.8}O_z$) system.
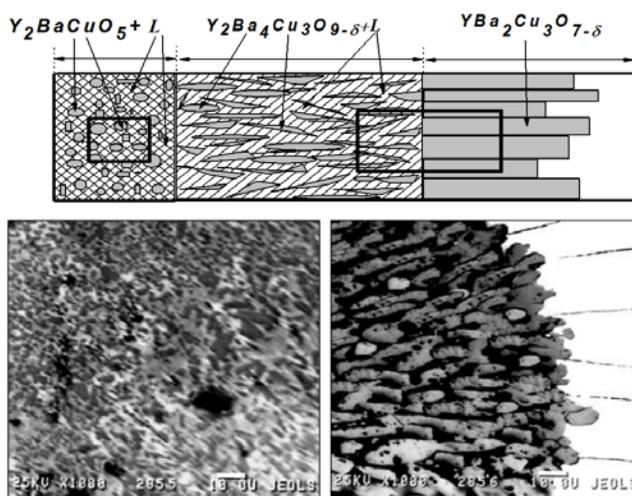
Fig. 6 Diffusion layers of $Y_2BaCuO_5 + L$ ($BaCu_{1.2}O_z$) system.

At the use of L ($BaCu_{1.2}O_z$), a textured layer $YBa_4Cu_3O_{9-\delta}$, was formed initially on the tablet of Y_2BaCuO_5, then the $YBa_2Cu_3O_{7-\delta}$ was formed (Fig. 6). The $YBa_2Cu_3O_{7-\delta}$ and $YBa_4Cu_3O_{9-\delta}$ crystallites were grown perpendicularly to the frontal surface of the sample. For the $Y_2Cu_2O_5$ tablet placed into $BaCuO_z$ melt at T=1270 K, the sequence of crystallization of layers $Y_2Cu_2O_5/Y_2BaCuO_5/YBa_2Cu_3O_{7-\delta}/L$ was established (Fig 7).
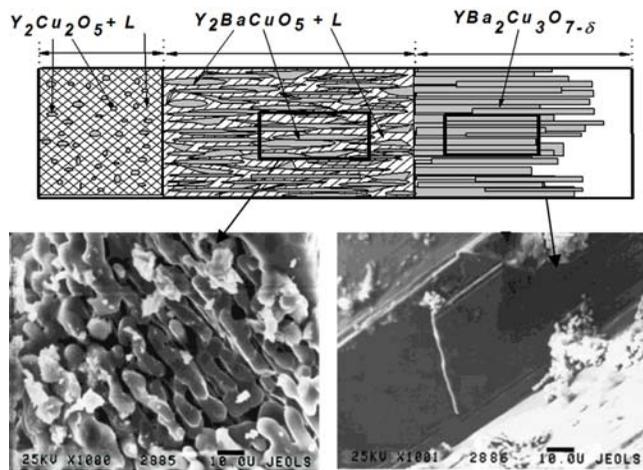
Fig. 7 Diffusion layers of Y$_2$BaCuO$_5$ + L(BaCuO$_2$).

Hence use of firm phases grains of Y$_2$BaCuO$_5$ and Y$_2$Cu$_2$O$_5$ with size <d>~1 mm aroused the greatest growth rate of YBa$_2$Cu$_3$O$_{7-\delta}$ in system Y$_2$BaCuO$_5$+3BaCuO$_2$+2.3CuO, as a limiting stage of growth rate YBa$_2$Cu$_3$O$_{7-\delta}$ is mutual diffusion of reagents through a layer of firm phase of YBa$_2$Cu$_3$O$_{7-\delta}$. Interdiffusion of reagents occurs through layers of firm Y$_2$BaCuO$_5$/YBa$_4$Cu$_3$O$_{9-\delta}$/YBa$_2$Cu$_3$O$_{7-\delta}$/L phases and Y$_2$BaCuO$_5$/YBa$_2$Cu$_3$O$_{7-\delta}$/L for Y$_2$BaCuO$_5$+3BaCuO$_2$+0.6CuO and Y$_2$Cu$_2$O$_5$+3.5BaCuO$_2$ systems accordingly.

4   Conclusions

1. To obtain the yttrium-barium cuprate with large sizes of textured macrograins and crystallites the following compositions of furnace have been proposed: Y$_2$BaCuO$_5$+3BaCuO$_2$+2.3CuO) – system (I); (Y$_2$BaCuO$_5$+3BaCuO$_2$+0.6CuO) – system (II); (Y$_2$Cu$_2$O$_5$+3.5BaCuO$_2$) – system (III);

2. The peculiarities of the crystallization of yttrium-barium cuprate at using of peritectic reaction from the furnace of systems (I), (II) and (III), containig precursors Y$_2$BaCuO$_5$ and Y$_2$Cu$_2$O$_5$ with grain sizes of 10 µm and 1 mm have been established. It was shown that in the temperature range of 1240-1270 K in the case of the grain size 10 µm the activation energy of the growth of YBa$_2$Cu$_3$O$_7$ compound has the values of 31, 39 and 54 kJ/mol for systems (II), (I) and (III), respectively, and in the case of the grain size 1 mm – the values of 183, 197 and 211 54 kJ/mol for systems (I), (III) and (II), respectively.

3. During the analysis of the growth rate of yttrium-barium cuprate in systems (I), (II) and (III), where the average grain size of solid phases of Y$_2$BaCuO$_5$ and Y$_2$Cu$_2$O$_5$ was d$_{av}$~10 µm, it was found that the maximum growth rate of YBa$_2$Cu$_3$O$_{7-\delta}$ takes place in the system (II) , which is caused by the relatively small value of <C$_Y$> ~ 3 at. % in the solution-melt. At the same time, the growth rate of yttrium-barium cuprate in systems (I) and (III) is limited by the entry of Y from the grains of Y$_2$BaCuO$_5$ and Y$_2$Cu$_2$O$_5$ to the growing grains of YBa$_2$Cu$_3$O$_{7-\delta}$ via the liquid phase, and in system (II) also from the grains of intermediate phase YBa$_4$Cu$_3$O$_{9-\delta}$.

4. At increasing grain sizes of solid phases of Y$_2$BaCuO$_5$ and Y$_2$Cu$_2$O$_5$ up to the d$_{av}$~1 mm, the highest growth rate of yttrium-barium cuprate was observed in the system (I), because in this case the limiting factor of the growth rate is the interdiffusion of reagents through the layer of solid phase of yttrium-barium cuprate, while in the case of (II) and (III) the interdiffusion of reagents takes place through the solid phase layers of Y$_2$BaCuO$_5$/YBa$_4$Cu$_3$O$_{9-\delta}$/YBa$_2$Cu$_3$O$_{7-\delta}$ and Y$_2$BaCuO$_5$/YBa$_2$Cu$_3$O$_{7-\delta}$, respectively.

5. By the analysis of the microstructures of the microstructures of hardened samples it was established that the mechanisms of crystallization of yttrium-barium cuprate in systems (I) (II), and (III) have differencies at different sizes of Y$_2$BaCuO$_5$ and Y$_2$Cu$_2$O$_5$ precursor grains. It was shown that the growth of yttrium-barium cuprate in the case of precursor grain size of 10 µm occurs not on their surface but on the certain distance from it, with creation of ellipsoidal areas during the solution-melt crystallization. At that, in the systems (I) and (III) peritectic transformation occurs according to the scheme L + Y$_2$BaCuO$_5$ or (L + Y$_2$Cu$_2$O$_5$)→ L +YBa$_2$Cu$_3$O$_{7-\delta}$→YBa$_2$Cu$_3$O$_{7-\delta}$, and in the system (II) the scheme of the peritectic transformation is the following: L + Y$_2$BaCuO$_5$ → L + Y$_2$BaCuO$_5$ + YBa$_4$Cu$_3$O$_{9-\delta}$ → L + YBa$_2$Cu$_3$O$_{7-\delta}$. →YBa$_2$Cu$_3$O$_{7-\delta}$, in this case the intermediate compound YBa$_4$Cu$_3$O$_{9-\delta}$ is formed.

References

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