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Solid-Phase Synthesis of $LuBa_2Cu_3O_{6+x}$ Compound

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Abstract

Investigation of phase formation in the system Lu–Ba–Cu–O is performed within the temperature range of 750–950 °C in the air using different sources of lutecium. Specific features of the formation of 123Lu phase are revealed on the basis of X-ray and microscopic data. These features are: extremely narrow temperature range (875–890 °C), mass transfer performed mainly through the liquid phase, decomposition of the 123 phase under lengthy annealing of the sample at the synthesis temperature. Optimal parameters for the synthesis of $LuBa_2Cu_3O_{6+x}$ are determined. Ceramics with 123Lu phase content of 70 % is obtained for the first time.

INTRODUCTION

High-temperature superconductors (HTSC) of the composition $RBa_2Cu_3O_{6+x}$ (123R, R = Y, rare earths) were obtained for the first time by solid-phase synthesis. This method remains the major one for obtaining polycrystalline HTSC samples. Isostructural compounds were synthesized with all the rare earths except Ce and Tb, which form more stable compounds $BaCeO_3$ and $BaTbO_3$ [1]. Among 123R, the most substantial difficulties were connected with obtaining the phase with lutecium, which has the smallest ion radius among lanthanides. Many attempts of researchers to obtain $LuBa_2Cu_3O_{6+x}$ by solid-phase synthesis have lead either to negative result [2, 3] or to obtaining only small amounts of 123Lu phase in mixture with the accompanying compounds [4–6]. The authors of [3] performed synthesis of 123Lu at different temperatures within the temperature range of 900–1000 °C both in the air and in pure oxygen; in all cases, the synthesis product was represented by a mixture of compounds: $BaCuO_2$ (011), Lu_2BaCuO_5 (211) and CuO. On this basis, the authors concluded that the difficulties in obtaining 123Lu were caused not by kinetic reasons but by destabilization of the structure due to small ion radius of lutecium. The same conclusion was drawn from the experiments on partial substitution of yttrium by lutecium in polycrystalline samples of 123Y [7]: the lower limit of ion radius of R^{3+} providing the stability of 123 structure is close to the radius of Yb^{3+}.

However, in spite of these pessimistic expectations, high-quality 123Lu crystals were grown under the conditions of spontaneous solution-melt crystallization [8, 9]; the structure was refined [10]; single-phase films with high superconducting characteristics were obtained by means of MOCVD [11]. There are reasons to suppose that failures to perform a solid-phase synthesis of $LuBa_2Cu_3O_{6+x}$ are connected with the conditions under which the process was carried out.

The interaction in the ternary system R_2O_3–BaO–CuO during solid-phase synthesis is accompanied by the formation of intermediate phases: double and triple cuprates. The sequence of phase transformations during the synthesis of 123R depends on several parameters: temperature, rate of heating and cooling, time of thermal treatment, type of initial components. It is known that temperature and rate of the formation of $RBa_2Cu_3O_{6+x}$ phase in the system R_2O_3–BaO–CuO are substantially dependent on R; according to investigations performed in [4], the lowest ones are those for Lu. No systematic investigations of the mechanism and kinetics of phase formation in the system with lutecium have been reported.

The present work deals with the investigation of phase formation in Lu–Ba–Cu–O system, elucidation of problems connected with obtaining $LuBa_2Cu_3O_{6+x}$, and search for optimal conditions of solid-phase synthesis of this compound.

EXPERIMENTAL

Synthesis conditions

The reagents of specially pure grade (os.ch.) calcined preliminarily at 800, 400 and 700 °C, respectively, were used for the solid-phase synthesis. Isothermal annealing was carried out in the air in muffle furnace with resistance heating and temperature stabilization ±1 °C with the help of RIF-101 thermoregulator, which allowed also changing temperature in the furnace at a given rate. The same amounts of initial mixture (3 g) were used for all the syntheses. In order to homogenize the samples, they were thoroughly ground in agate mortar in the presence of acetone before annealing.

The superconductors of 123 system are usually obtained by multistep annealing of the stoichiometric mixture of simple oxides within the temperature range of 900–980 °C with an exposure of 15 h at each step. In order to establish the features of the behaviour of lutecium system and to optimize the synthesis regime, we changed one of the process parameters keeping the other constant. Taking into account the literature data on possible low thermal stability and low rate of the formation of 123Lu phase, the temperature of the first step of annealing was decreased to 750 °C, while the exposure was increased to 20 h and more. Heating rate was varied from 25 to 150 °C/h, cooling rate from 30 to 200 °C/h.

In order to reduce synthesis temperature, we used not $BaCO_3$ as the source of barium (since its solid-phase interaction in the system R_2O_3–BaO–CuO becomes complicated due its high thermal durability [12]) but more reactive BaO_2 (its monophase character was checked by XPA).

On the basis of the data on phase ratios in the system R_2O_3–BaO–CuO and the data on the system with lutecium [4, 13, 14], in addition to the usually used Lu_2O_3, other lutecium sources were tested for the synthesis of 123 phase: $Lu_2Cu_2O_5$ (202 phase) and $Lu_4Ba_3O_9$ (430 phase). Previously [4], it was discovered that the formation of 202 phase as an intermediate product is characteristic of the synthesis of 123R with R located at the end of rare earth row; the appearance of 430 phase was stated by us in preliminary experiments on the synthesis of 123Lu. Precursors were obtained by solid-phase synthesis within the temperature range of 900–920 °C in the case of $Lu_2Cu_2O_5$ and 800–1000 °C for obtaining $Lu_4Ba_3O_9$.

Investigation methods

The phase composition of synthesis products was monitored by means of XPA (DRON-3 diffractometer, CuK_α radiation); morphological features were characterized by means of optical (MBS-2) and scanning electron microscopy (JSM-T200, JEOL, Japan).

The problem of phase identification and measuring phase ratios in the system R–Ba–Cu–O using X-ray diffraction patterns is rather complicated since reference reflections of the occurring phases are situated very close to each other and frequently overlap each other. When working with lutecium-containing system, the difficulties increase because the diffraction data for the intermediate lutecium-containing phases are almost absent, except 211Lu [4]. On the basis of experimental diffraction characteristics obtained by us for the synthesized precursors, we revealed these phases during the investigation of phase formation with better reliability. The content of 123Lu phase with respect to 211 phase in the sample was estimated using the ratio of the most intensive peaks of these phases in the diffraction patterns according to equations proposed in [15]:

$$K = \frac{I_{103}(123\mathrm{Lu})}{I_{103}(123\mathrm{Lu}) + I_{131}(211\mathrm{Lu})}$$

Such an estimation is approximate; however, it allows revealing the trends by analyzing the results of a series of syntheses.

RESULTS AND DISCUSSION

At the preliminary stage of the work, we performed a multistep synthesis from simple oxides (Lu_2O_3, BaO_2, CuO) under the conditions close to those accepted for obtaining 123R ceramic samples. The reaction mixture corresponding to the stoichiometric composition of 123 was annealed starting from the temperature of 750 °C, the temperature of every subsequent step being higher than the previous one by 50 °C. Exposure at each step was about 20 h. Observations demonstrated that at 750 °C the sample gets black; according to XPA data (Fig. 1, *a*), it consists mainly of a mixture of Lu_2O_3, $BaCuO_2$ and CuO; traces of Lu_2BaCuO_5

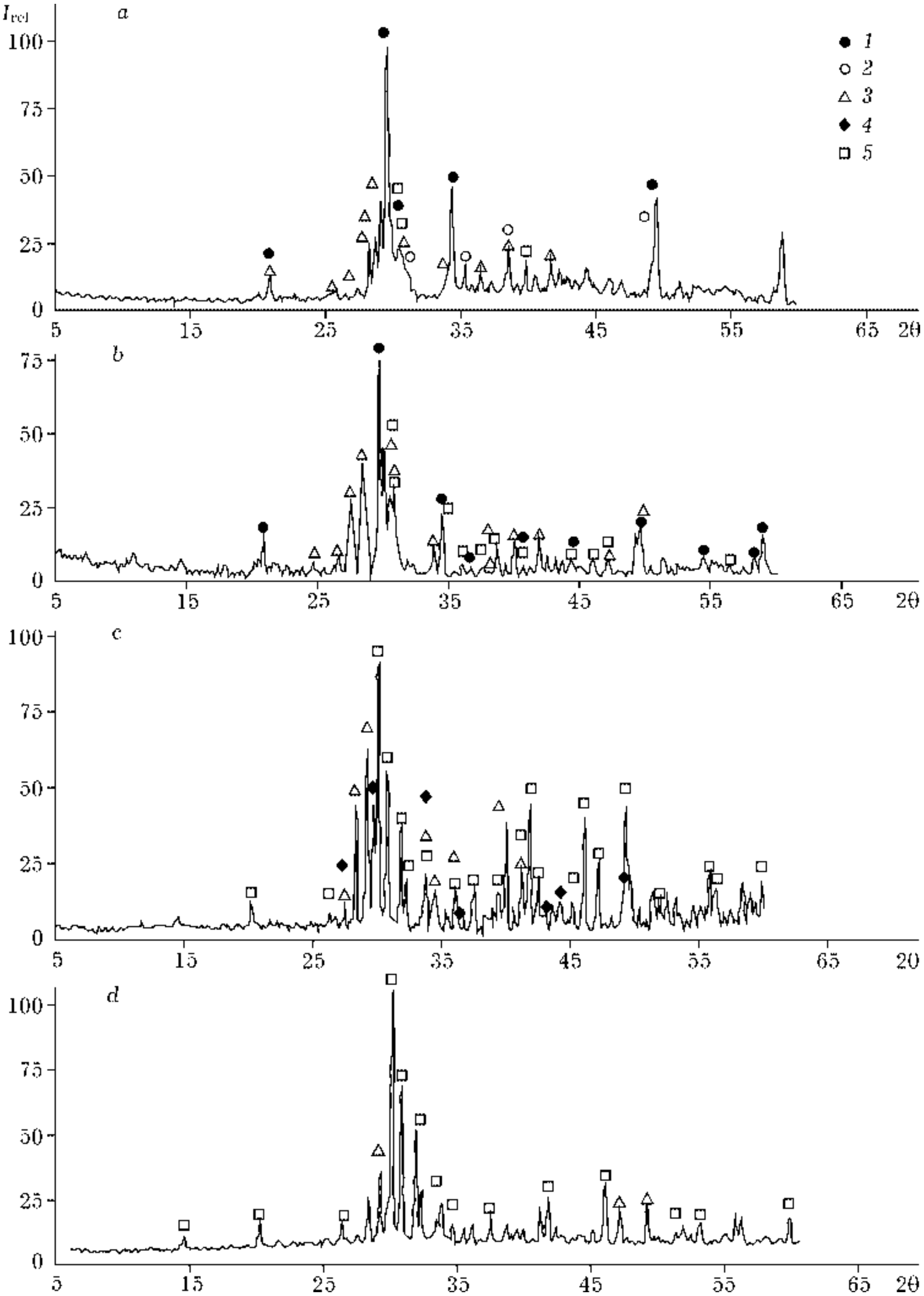

Fig. 1. Phase ratios for the multistep synthesis from simple oxides according to the standard scheme: *1* – Lu_2O_3, *2* – CuO, *3* – $BaCuO_2$, *4* – $Ba_3Lu_4O_9$, *5* – Lu_2BaCuO_5.. Temperature, °C: 750 (*a*), 800 (*b*), 850 (*c*), 900 (*d*).

TABLE 1

Temperature and temporal modes of the synthesis of mixtures with different sources of lutecium, and phase composition of the sample

Stage	Sample No.	T, °C	τ, h	Visual characteristics	Basic phase composition (according to XPA data)
I	1	830	86	Black powder	211 + $BaCuO_2$ + CuO
	2	830	86	The same	211 + $BaCuO_2$ + CuO
	3	830	24	Black powder with admixture of blue colour	211 + $BaCuO_2$ + $Lu_2Cu_2O_5$
II	1	840	17	Black-green powder	–
	2	840	17	Black powder	–
III	1	850	23	Black-green powder	211 + $BaCuO_2$
	2	850	23	Black powder	211 + $BaCuO_2$
	3	850	23	The same	211 + $BaCuO_2$
IV	1	865	17	Black-green powder	211 + $BaCuO_2$
	2	865	17	Black powder	211 + $BaCuO_2$
V	1	880	44	Submelting, agglomeration into black pellet	123 (10 %) + 211 + $BaCuO_2$
	2	880	44	The same, with green bottom	123 (15 %) + 211 + $BaCuO_2$
	3	880	44	Weak agglomeration into a black pellet	211 + $BaCuO_2$
VI	1	880	36	No submelting, weak agglomeration into a black pellet	211 + $BaCuO_2$, 123 disappeared
	2	880	36	The same	211 + $BaCuO_2$, 123 disappeared
	3	880	36	Black pellet	211 + $BaCuO_2$

Note. Lutecium source: Lu_2O_3 (sample No. 1), $Lu_4Ba_3O_9$ (No. 2), $Lu_2Cu_2O_5$ (No. 3). Heating rate: 150 °C/h, cooling rate: 200 °C/h.

phase are also detected. When the synthesis temperature is raised to 800 °C, the main phases remain Lu_2O_3 and barium cuprate, the content of the green phase Lu_2BaCuO_5 increeases (see Fig. 1, *b*). At the third stage (T = 850 °C), a complete disappearance of the initial products occurs; the fraction of 211 phase increases and becomes close to the $BaCuO_2$ phase content (see Fig. 1, *c*). After annealing at 900 °C, the sample is composed of the 211 phase and barium cuprate (see Fig. 1, *d*), their ratio remaining unchanged during subsequent annealing. So, under these experimental conditions, no formation of 123Lu phase is observed. The use of other sources of lutecium within this temperature-time scheme did not lead to success, too.

Analyzing the obtained data and literature on the synthesis of related 123R phases for the closest to lutecium R (for example, in [15], 123Yb was synthesized at 830 °C), we made an attempt of more thorough investigation of the temperature range of 830–900 °C. The results of experiments of this series are shown in Table 1. In the lutecium system, even annealing for 86 h at 830 °C, no traces of 123 phase were detected. Further annealing within the temperature range of 830–865 °C with different exposure at each step did not lead to the formation of 123Lu phase, too. The samples obtained at these stages were black or black-green powders; according to XPA data, they were mixtures of 211, $BaCuO_2$ and CuO. Only after annealing at 880 °C, the appearance of the samples changed (a decrease in volume was observed along with submelting and densification); reflections of 123 phase were detected in the diffraction patterns; its content with respect to the 211 phase did not exceed 10 % (for synthesis from Lu_2O_3) and 15 % (for synthesis from $Lu_4Ba_3O_9$). An increase in annealing time at the same temperature leads not to an increase in 123 phase content but, to the contrary, to its disappearance from both samples. One can see in Table 1 that the use of Lu_2O_3

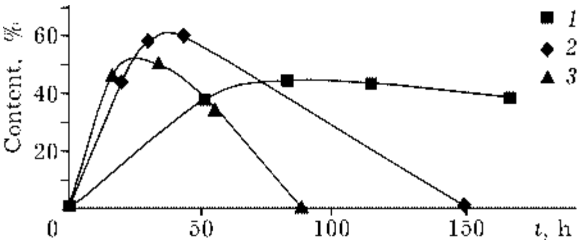

Fig. 2. Content of 123Lu phase as a function of time of isothermal exposure. Temperature, °C: 875 (*1*), 890 (*2*), and 900 (*3*).

or $Lu_4Ba_3O_9$ as a source of lutecium gives almost the same result. When lutecium is introduced into the initial mixture as $Lu_2Cu_2O_5$, no formation of the 123Lu phase is observed under these conditions.

It follows from the experimental data (see Table 1) that lengthy (for more than 80 h) exposure at 865 °C does not lead to the appearance of 123Lu phase, while at 880 °C its decomposition is already observed. Hence, the lower temperature limit of the formation of 123Lu phase is most likely situated within the range of 865–880 °C. The behaviour of change in 123Lu phase content depending on time of isothermal exposure of the sample (a mixture of oxides) at different temperatures near this region is shown in Fig. 2. At 875 °C, the amount of 123 phase at first increases rather rapidly (not less than 1 % per hour), then the growth decelerates (~0.2 % per hour) and reaches maximum (45 % with respect to 211 phase content) after 80 h of isothermal exposure. During the further annealing, the content of 123Lu phase in the sample starts to decrease slowly due to its decomposition. For the temperature of isothermal annealing increased up to 890 °C, the content of 123 phase reaches its maximum (~60 %) within 18 h and immediately after this starts to decrease at a rate much higher than that at 875 °C. After exposure for 150 h, the 123Lu phase disappears completely; the samples are mixtures of the green phase and barium cuprate. The change in 123 phase content at 900 °C depicts even more unstable character of synthesis process at this temperature.

So, we come to a conclusion that the rate of formation of 123 phase with Lu, unlike that predicted in [4], is rather high (the obtained data are comparable with the results of [1] for 123Yb); however, obtaining monophase sample is complicated by instability of 123 phase within the temperature range where it is formed at a noticeable rate.

In the subsequent series of experiments, by varying temperature (near 880 °C) and duration of annealing (taking into account the data of Fig. 2), as well as character and rate

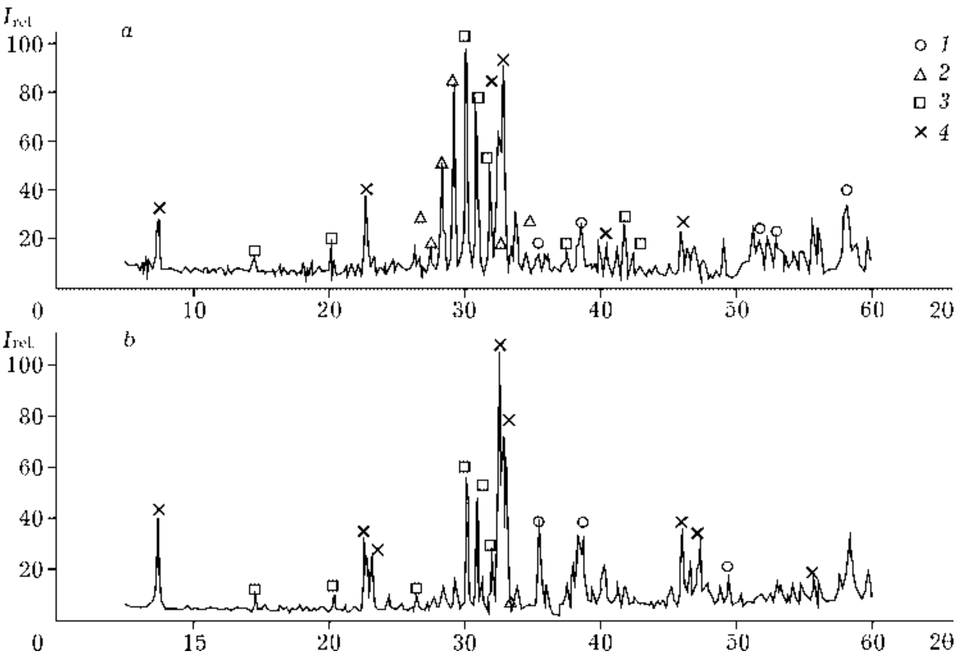

Fig. 3. Diffraction patterns of samples obtained in the synthesis mode close to the optimal one: *a* – stoichiometric initial mixture; *b* – initial mixture with excess CuO (15 %); *1* – CuO, *2* – $BaCuO_2$, *3* – Lu_2BaCuO_5, *4* – $LuBa_2Cu_3O$.

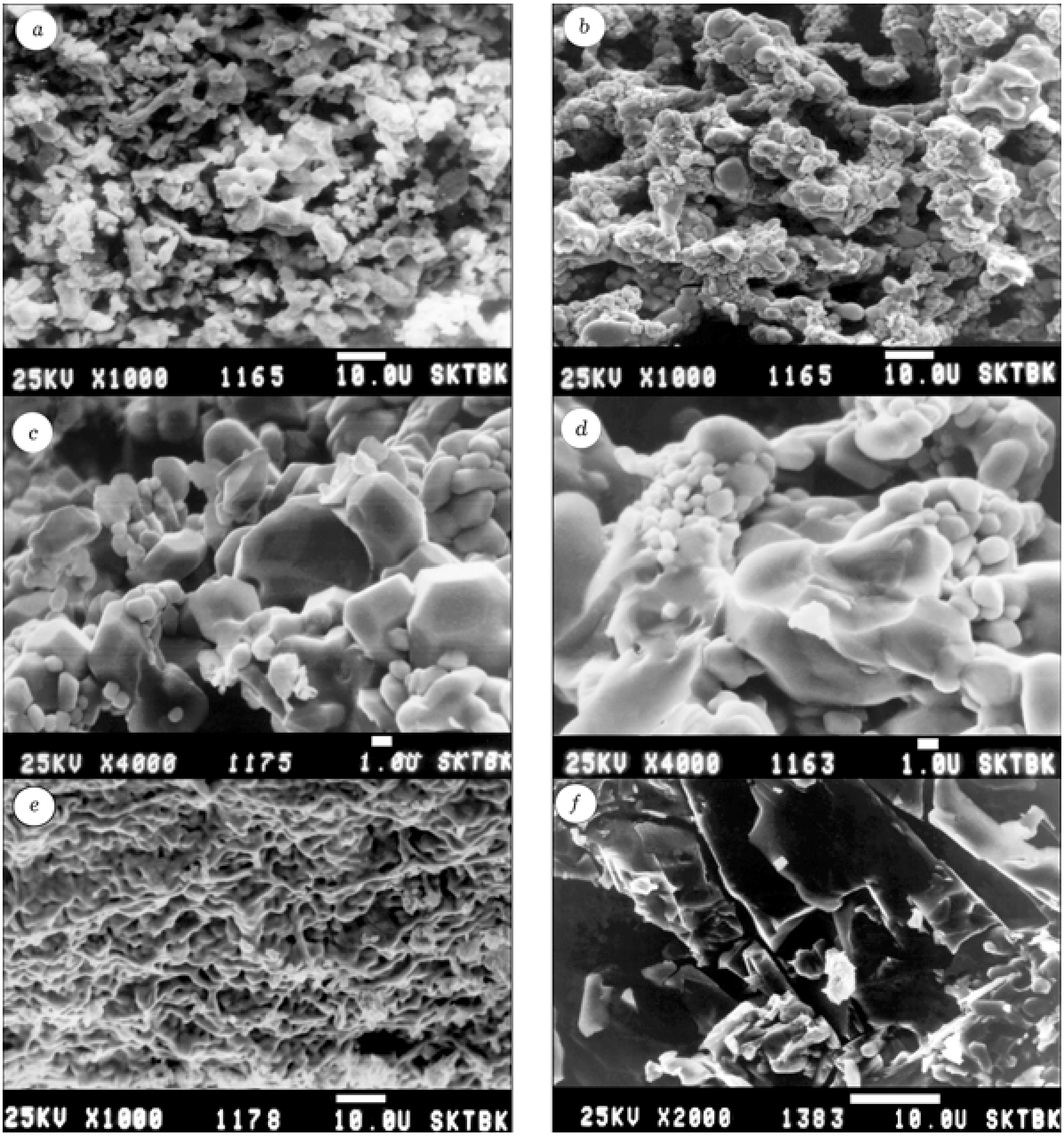

Fig. 4. Changes in the microstructure of sample during synthesis. Annealing at temperature, °C: 830–850 (*a*), 865 (*b*–*d*), 875 (*e*, *f*).

of heating and cooling, we selected conditions under which the products with 123Lu phase content of 50 to 60 % were obtained within 10–15 h (Fig. 3, *a*); the product contained admixture of 211Lu and barium cuprate.

Some additional information on the specificity of phase formation in lutecium system was obtained from microstructural observations of samples during synthesis (Fig. 4).

Though the diffraction patterns of samples annealed at temperature 830 °C $< T <$ 865 °C are almost identical and, according to XPA, correspond to a mixture of 211 phase and barium cuprate, the microstructure of samples differs. After annealing at 830 and 850 °C, the sample is an accumulation of weakly bound grains of unclair acute-angled shapes (see Fig. 4, *a*). At 865 °C, the particles tightly stick together, pores between them increase (see Fig. 4, *b*). At this stage of annealing, the difference in the morphology of samples obtained from initial mixtures of different composition manifests itself.

In the sample obtained from Lu_2O_3 (see Fig. 4, *c*), two types of grains are distinguished: coarse ones (3–5 μ in cross section), that have quite well formed facing typical for barium cuprate microcrystals, and small, almost spherical or shaped as elongated prisms, corresponding to the microcrystals of 211 phase. A sample obtained from $Lu_4Ba_3O_9$ looks more uniform at this stage of annealing (see Fig. 4, *d*), which is likely to provide subsequently more stable growth of the 123 phase in the case when this precursor is used. Attention should be paid to the fact that after observing the microstructure, we better understand the discovered influence of character and rate of heating on the synthesis result. The application of lengthy stepwise exposure at a temperature below the point of 123 phase formation promotes the growth of relatively large crystallites of intermediate phases 211 and $BaCuO_2$; their competitive formation occurs within the same temperature range, while slow continuous rise in temperature at a constant rate leads to the formation of smaller particles, which simplifies their chemical interaction.

A view of the sample at the stage of the formation of 123 phase is shown in Fig. 4, *e*. The basic microstructural motif is represented by the so-called leak structures, which is an evidence of the appearance of a substantial amount of liquid in the samples. An image of the sample in which the content of 123 phase is about 50 % (according to XPA data) is shown in Fig. 4, *f*. One can clearly see large (more than 10 μ) flat particles of 123Lu phase, barium cuprate grains (up to 3 μ), and elongated microcrystals of 211 phase (up to 5 μ).

It is likely that, in contrast to the yttrium system in which the formation of 123 phase starts in true solid state, while the appearance of the liquid phase only activates chemical interaction and accelerates mass transport of components [16, 17], a noticeable formation of 123Lu phase occurs only in the presence of the liquid phase. Taking this fact into account and keeping in mind that an increase in liquid formation in the system can be promoted by an excess of CuO due to the appearance of double ($BaCuO_2$ + CuO) or triple ($LuBa_2Cu_3O_{6+x}$ + $BaCuO_2$ + CuO) eutectics, we performed experiments adding an excess of CuO (15 %) with respect to the nominal composition into the initial mixture. It should be noted that such an approach [7] allowed obtaining single-phase 123Yb. In our case, an increase in the yield of 123Lu phase up to 70 % with respect to 211 phase content was achieved; barium cuprate admixture was almost absent (see Fig. 3, *b*). Possible means to achieve higher yield of 123Lu phase can be mechanical activation of the initial mixture [18] or the use of $Ba(NO_3)$ as barium source [19].

CONCLUSIONS

In order to determine the conditions of obtaining $LuBa_2Cu_3O_{6+x}$ by solid-phase synthesis, we performed investigation of phase formation in the Lu–Ba–Cu–O system within the temperature range of 750–950 °C in the air. It was stated that the formation of 123Lu proceeds through Lu_2BaCuO_5 and $BaCuO_2$ phases, similarly to the yttrium-containing system. The synthesis goes on within the narrow temperature range (875–890 °C) and is unstable by its character. The decisive requirement for the formation of 123Lu is the presence of liquid phase in the reaction system.

The conditions for obtaining $LuBa_2Cu_3O_{6+x}$ compound were optimized; ceramics with 123Lu phase content of 70 % was obtained for the first time.

Acknowledgements

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