

The Growth of $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ Crystals from the Solution in Melt

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Abstract

$\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ crystals were grown by spontaneous crystallization from the solution in melt. Their characterization was performed. It was shown that the formation of Tm crystals takes place under the conditions of large relative supersaturations and occurs stage by stage. An important role in the formation of $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ crystals is played by the dendrite growth stage. Dendrite crystals were found in which separate branches grew by the normal mechanism along the $\langle 100 \rangle / \langle 010 \rangle$ directions. These crystals resembling whiskers are of extreme importance for the investigation of the anisotropy of electrical resistance.

INTRODUCTION

All the high-temperature superconductors of the type $\text{LnBa}_2\text{Cu}_3\text{O}_{6+x}$ (123-Ln) are known to have a layered structure, be crystallized as thin plates and exhibit strong anisotropy of physical properties along and across the layers. The role of anisotropy in superconductivity is still the subject of discussion. This is connected to a large extent with the fact that plate-like shape of crystals is a substantial obstacle for correct arrangement of the experiments aimed at the studies of anisotropy, in particular electrical resistance. In order to carry out such experiments, one needs single crystals from which it would be possible to make samples drawn along the c -axis. Attempts were made several times to prepare isometric crystals ($H = a + b$)/ $(2c) < 5$ where a , b and c are the dimensions of the crystal along the corresponding crystallographic axes [1, 2]) both by means of spontaneous crystallization [1] and by stretching onto an oriented seeding [3, 4]. There are fragmentary data concerning the growth of 123-Ln crystals as needles or whiskers along the [001] direction: $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ was obtained from gas phase [5], $\text{SmBa}_2\text{Cu}_3\text{O}_{6+x}$ was prepared on the surface of

partially ground ceramic pellets [6], $\text{Nd}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_{6+x}$ was prepared from BaO/CuO high-temperature solution in a crucible made of Nd_2O_3 [7]. However, even having overcome technical difficulties in preparing the samples of the required shape, researchers come across another problem, namely, the necessity to take into account the real structure of the obtained crystals when interpreting experimental data. Since the predominant growth mechanism for 123-Ln crystals is a layer-by-layer dislocation growth in the (001) plane, the crystals are pierced by a net of spiral dislocations shorting the pile of CuO_2 planes [8] which leads to a metal-type behaviour of electrical conductance and brings complications to the determination of real anisotropy of the system. A strict quantitative estimate of structural defects is not a simple task, so it is important to prepare the crystals of the required habitus that would grow according to some other mechanism, not dislocation one.

Having put forward the task of preparing $\text{LnBa}_2\text{Cu}_3\text{O}_{6+x}$ single crystals suitable for the investigations of electrophysical properties, we selected the most widely spread method of HTSC crystal preparation, *i. e.* spontaneous

crystallization from the solution in melt. The system which we selected as the subject of investigation was that with $\text{Ln} = \text{Tm}$. Preliminary experiments showed that thulium crystals can grow so that their habitus would be nearly isometric under definite conditions. They are stable (practically they do not undergo degradation when kept in the air for a long time and after repeated high-temperature annealing), exhibit perfect superconducting characteristics [9]. The cation ratio $\text{Tm} : \text{Ba} : \text{Cu} = 1 : 2 : 3$ is most strictly followed in the crystals of this compound since they do not form solid solutions of the type $\text{Ln}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{6+x}$ which are characteristic of the compounds with large ion radii of Ln^{3+} . Besides, it is known that the temperatures of peritectic melting of 123-Ln compounds decrease in the rare earths row, so the crystallization of phase 123 in the system with thulium occurs from lower-temperature (and thus more viscous) solution melts. An increase of the viscosity, in its turn, can lead to the change of growth mechanism [10] which allows one to hope that it would be possible to obtain the crystals grown according to a mechanism different from the dislocation one.

EXPERIMENTAL

Growth conditions

123-Tm crystals were grown by means of spontaneous crystallization under slow cooling of the high-temperature solution melt in the system $\text{TmO}_{1.5} - \text{BaO} - \text{CuO}$ containing BaO and CuO in excess with respect to the $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ phase. A detailed description of the growth set-up was presented in [11]. The components were taken at a molar ratio of $0.007\text{Tm}_2\text{O}_3 - 0.289\text{BaO} - 0.704\text{CuO}$ which corresponds to 10.4 % (mass) of 123-Tm in the initial mixture; the components were then carefully mixed in an agate mortar, put into an alundum crucible and heated at a rate of 20–40 °C/h in an oven with Ohmic heating till the necessary temperature T_{max} which was somewhat above the point at which the crystallization of 123-Tm starts. Earlier we determined [12] that the crystallization of thulium-barium cuprate starts at $T \approx 925$ °C. After isothermal

exposure at $T_{\text{max}} = 960$ °C for 10 h, the system was cooled slowly (0.3–1 °C/h). At 890 °C which is close to complete solidification temperature, the grown crystals were separated from the residual liquid by decanting without taking the crucible out of the oven; then the cooling was continued till room temperature at a rate of ≤ 40 °C/h. Under these conditions 123-Tm crystals were obtained at good reproducibility and high yield. Typical dimensions of plate-like individuals were $5 \times 7 \times 0.8$ mm and of isometric ones $3 \times 3 \times 0.8$ –1 mm. Separate crystals were as large as $6 \times 12 \times 1.5$ mm. Mass fraction of the Al impurity was 0.1 %. The most important parameters of crystallization having substantial effect on the dimensions and quality of crystals are the composition of the initial mixture, maximum temperature of the experiment, and cooling rate during the growth of crystal. We studied the effect of these parameters for holmium system as an example [13], and it was then taken into account when optimizing the growth conditions for 123-Tm. For instance, in order to increase the thickness of crystals (the dimension along the *c*-axis), it is necessary to keep the slowest possible cooling rate (not more than 0.5 °C/h) within the selected temperature range.

Investigation techniques

In order to characterize the crystals, various methods were used. Morphological analysis of crystals and their splices was carried out with optical and scanning electron microscopes (NU-2E, Karl Zeiss Jena, and JSM-35, respectively). Diffraction patterns were obtained with a DRON-UM1 diffractometer (CuK_α radiation) and an automatic diffractometer ENRAF-NONIUS (MoK_α radiation). The homogeneity degree of the cation composition over the crystal and in different crystals from one and the same experiment was estimated using the scanning electron microscopy and microprobing (Cameca). In order to reveal structural defects possessing a component along the *c*-axis of the crystal, chemical etching with a mixture of acetic and nitric acids was carried out [14]. Superconducting properties were determined from electrical resistance data. The components of anisotropic resistance of crystals were deter-

mined within the temperature range 4.2–450 K by the direct 4-contact method [9, 15].

RESULTS AND DISCUSSION

According to the theoretical consideration of crystal morphology of the tetragonal phase $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [16], *F* shapes are the faces of the {001} basopinacoid and a series of tetragonal bipyramids {101}, {103}, {112} and {114}, among which the {101} is preferable. So, under the conditions close to the equilibrium, plate-like crystals faced with the {001} and {101} shapes should be formed. The faces of the {100} tetragonal prism are classified as *S* shapes. Since these faces grow much faster than *F* they should not be present in the facing of quasi-equilibrium crystals. However, the reported experimental material shows that the {001} and {100} shapes are predominant in the facing of the $\text{LnBa}_2\text{Cu}_3\text{O}_{6+x}$ phases. The growth of multi-faced voluminous crystals is believed to be dependent on the viscosity of the medium, adsorption of the solvent on separate faces of the crystal, the influence of impurities [17, 18]. In the opinion of the authors of [19], the decisive factor is critical supersaturation. Important information on the growth conditions can be obtained by means of the morphological analysis of the crystals, so it is reasonable to perform crystal morphological analysis of the individuals and splices grown in a low-temperature thulium system, and to estimate the degree of relative supersaturation in comparison with a higher-temperature system, for example holmium one.

In the optimal crystallization regimes, thin- and thick-plated individuals are crystallized in the Ho system (the predominant shape is {001} governing the development of {100}) [13, 14]. The {001} faces of crystals are usually smooth like mirrors; screw-like spirals, either round or square, are often present on these surfaces. The faces of the {100} tetragonal prism in thin-plate individuals are usually even. In thick-plated crystals (more than 0.3 mm thick) the relief of the {100} faces is more complicated: individuals occur that look like composed of a pile of thin packets parallel to (001); crystals with basopinacoid faces impeding as a roof over the faces of tetragonal prism are not rare (Fig. 1, a), as

well as hollow crystals formed by the {001} planes and (100) + (010) edges (see Fig. 1, b). These morphological features enable us to assume that both for thin- and thick-plated Ho crystals basopinacoid faces are the growth shapes. The faces of tetragonal prism should be considered as braking planes. Taking into account theoretical foundations considered above we can conclude that Ho crystals are formed under the conditions close to the equilibrium ones.

For the Tm system, the types of individuals and splices are more diverse than for the Ho system; along with the plate-like individuals, a

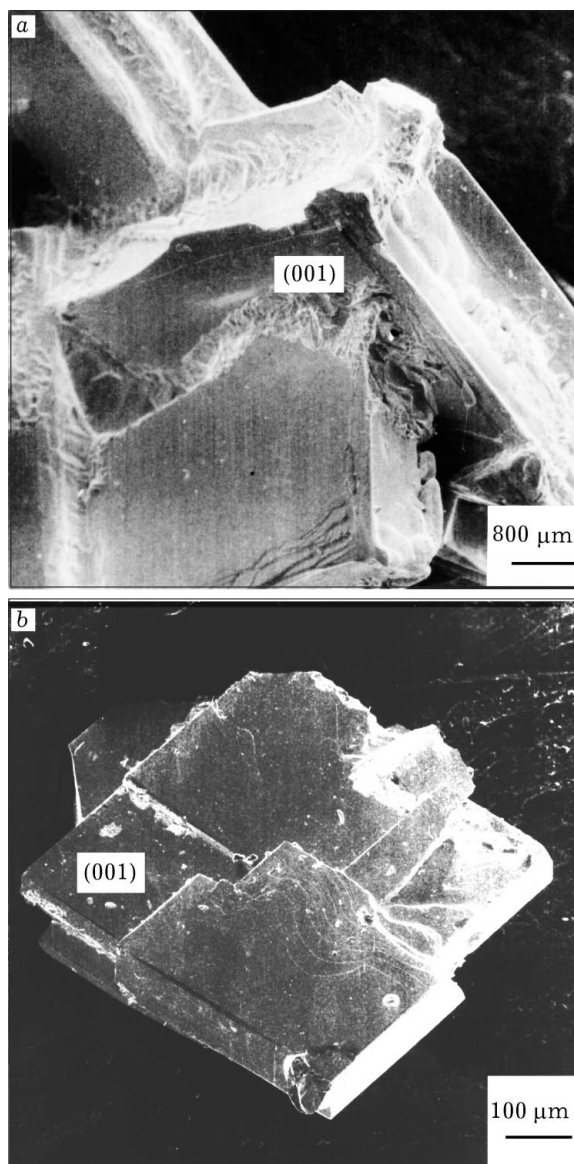


Fig. 1. Some features of the structure of $\text{HoBa}_2\text{Cu}_3\text{O}_{6+x}$ crystals: a – the transition from plain shapes to the summit and edge-shaped ones; b – a casing crystal.

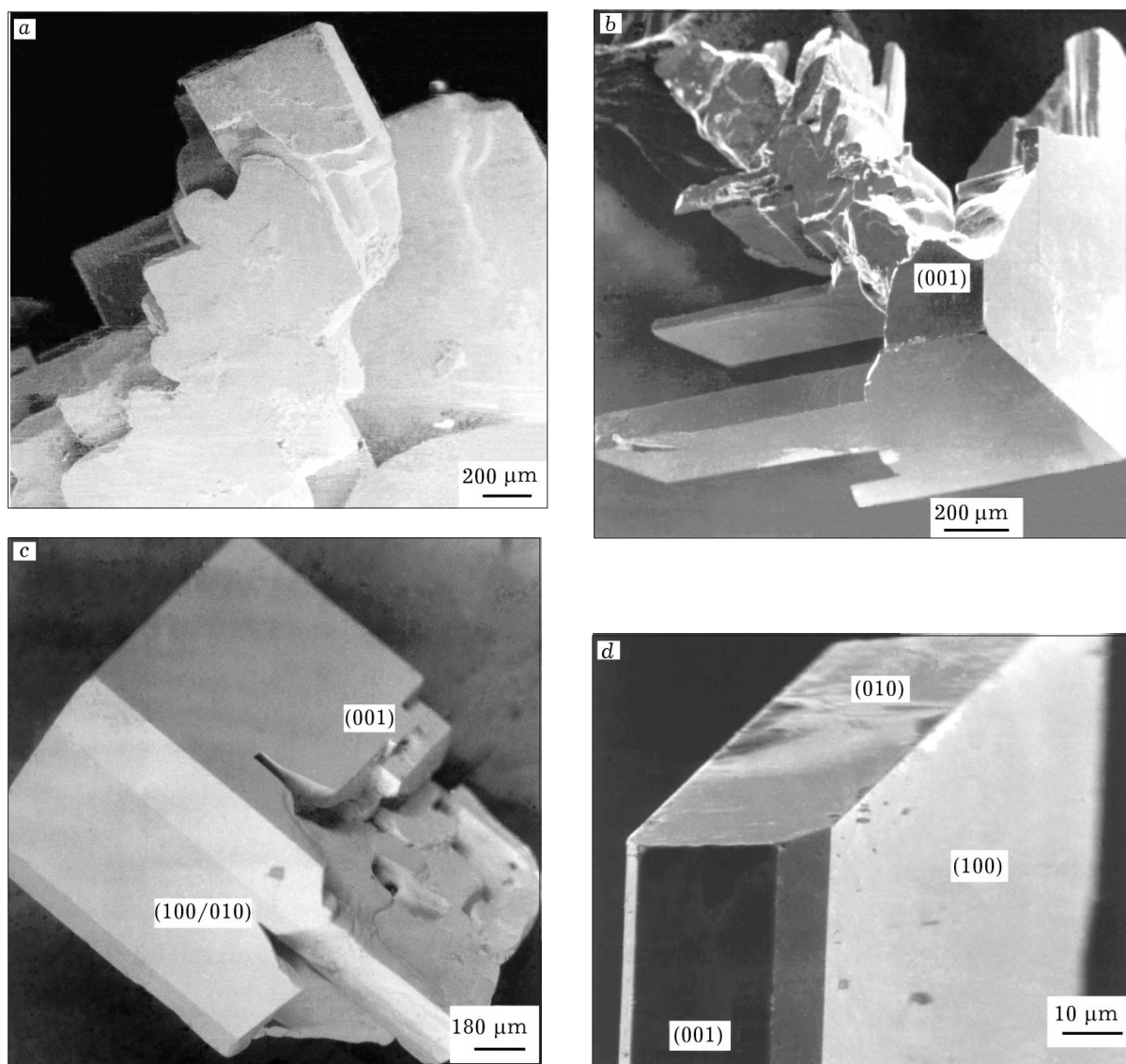


Fig. 2. Some features of the $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ crystal structure: *a* – a plain parallel summit splice, *b* – voluminous branched dendrite; *c* – an individual similar to single crystal with complete facing (regenerated crystal); *d* – a fragment of the faced dendrite branch.

substantial amount of nearly isometric crystals appears, with the thickness to width ratio close to 1. Besides typical faces $\{100\}$ and $\{001\}$, the faces of tetragonal bipyramid $\{101\}$ are also present. Micromorphology of the $\{100\}$ shapes of these individuals is more complicated than that of thick-plated crystals of the Ho system. Hopper-like structures are characteristic of them, as well as the presence of a horizontal band (junction) [20]. Dendrite shapes occur at the foundations of many crystals and regular splices (Fig. 2 *a* and *b*). As a rule, the dendrite, formed at the initial stage of growth, then gets

covered with plain faces, and the resulting individual can be a completely faced crystal (shapes $\{001\}$, $\{100\}$ and $\{101\}$), the so-called regenerated crystal (see Fig. 2, *c*).

Now we shall consider the structure of dendrite crystals in more detail (see Fig. 2, *b*). The main trunk of the dendrite (the main direction of fast growth) runs along $\langle 110 \rangle$ which agrees with the existing theory of dendrite growth [21]. An evidence of the high rate of growth along this direction is an indefinite contour of the summit. The individuals in which only the main dendrite trunk is formed and branches

are only spotted occur along with those with relatively large branches. The branches grow along the $\langle 100 \rangle$ directions. They either are adjacent to each other or separated by gaps. Open branches of the dendrites can have either round surface or well-faced crystal one (see Fig. 2, *d*) with the developed prism planes $\{100\}$ governing the development of basopinacoid $\{001\}$.

The structure of dendrite crystals can serve as the section of crystal volume growth and render information concerning the growth mechanisms at different stages. The existence of dendrite growth shapes at the beginning of $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ spontaneous crystallization is the evidence of relatively high supersaturation at this stage. High frequency of nuclei formation near the summits leads to the formation of the main trunk of the dendrite crystal. Then under the conditions of lower but still high supersaturation, the branches develop by the normal mechanism of $\{100\}$ faces growth. At this stage, the $(100)/(010)$ face can become the habitus-forming one. At the last stage, the layer-by-layer growth of the $\{001\}$ faces occurs from the summits.

The composition and structure of crystals

For morphological analysis, we focused on the individuals in which the influence of growth conditions was most vividly depicted. In order to study superconducting properties, we selected well-faced isometric crystals with pure even surfaces, without any noticeable block structure, and the fragments of dendrite crystals. Chemical and microprobe analyses showed that the ratio of Tm : Ba : Cu cations in the crystals of different morphological types is 1 : 2 : 3 within the determination accuracy. Mass fraction of the Al impurity entering the melt due to the interaction with the crucible is not more than 0.2 % in thulium crystals (for comparison, holmium compounds crystallized at higher temperatures contain Al up to 0.6 %). According to the X-ray diffraction patterns of the powder, isometric as-grown crystals $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ are rhombic (cell parameters are, Å: $a = 3.829$, $b = 3.877$, $c = 11.699$, sp. gr. P/mmm) and $\text{HoBa}_2\text{Cu}_3\text{O}_{6+x}$ crystals are tetragonal ($a = 3.868$, $c = 11.765$, sp. gr. $P/4mmm$). As recorded by the Lauer method, well faced den-

drite branches are single crystals. Perhaps they should be more precisely called skeleton crystals [22]. The crystallographic orientation of such crystals was determined by means of X-ray diffraction. The direction in which the crystal becomes longer coincides with the b -axis; the predominant face is (010) . Cell parameters of the as-grown crystal are, Å: $a = 3.801(1)$, $b = 3.842(1)$ and $c = 11.674(2)$. In order to reveal structural defects possessing a component along the c -axis of the crystal, selective chemical etching was used. On the (001) faces of 123-Tm plate-like crystals, etching leads to the appearance of etch pits as sharp pyramids; the edges of their square bases are directed along the crystal edges. Their density is 10^3 cm^{-2} reaching 10^8 cm^{-2} at the sites of accumulation (in the region of a visible defect, *i. e.* ingrowing slices or cracks). The pits of this type are usually conditioned by screw-like dislocations [8]. No pyramidal etch pits were observed at the (001) faces of skeleton crystals which is very likely to be the evidence of the absence of screw-like dislocations along $[001]$ and confirms the conclusion based on morphological analysis that the growth mechanism of the skeleton crystals differs from the layer-by-layer growth at dislocations which is characteristic of plate-like crystals.

Superconducting characteristics

Isometric crystals $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ annealed in oxygen flow at 475–500 °C in order to obtain oxygen content $x = 0.9$ (which is optimal from the viewpoint of superconductance) exhibited the transition temperature $T_c = 90\text{--}92 \text{ K}$. According to the data on resistance, the width of the transition $\Delta T_c = 0.2\text{--}0.5 \text{ K}$ which is the evidence of high uniformity of the crystal composition.

The measurements of temperature dependence of electrical resistance across and along the layers made using the samples obtained from well faced branches of skeleton crystals allowed to exclude the influence of defects like screw-type dislocations on the transport of electrons along the c -axis and to obtain novel data on undistorted anisotropy of resistance [15].

CONCLUSIONS

1. Under the conditions of spontaneous crystallization from the solution in melt, $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ crystals have been grown; crystallization regimes optimal for the preparation of crystals with a large dimension along the *c*-axis have been selected experimentally.

2. The cations ratio in the crystals of the 123-Tm compound independently of the habitus is practically corresponding to the stoichiometry. Al impurity content is small and has no effect on superconducting properties of the crystals.

3. Morphological analysis of the 123-Tm crystals allowed to conclude that the supersaturation in the thulium system is increased, which provides a high probability for the voluminous skeleton crystals to be formed due to the normal growth of {100} faces.

4. Separate branches of the skeleton crystals faced by the (010)/(100) planes having no structural defects like screw-type dislocations along the *c*-axis were used to manufacture unique samples with which the investigation of real anisotropy of electrical conductance in $\text{LnBa}_2\text{Cu}_3\text{O}_{6+x}$ crystals was performed.

The investigation has been partially supported by the Russian Foundation for Basic Research (Grant No. 00-02-17914), Federal Government Programme (Grant No. K0042), The State Scientific Programme on the Physics of Condensed Materials (Superconductivity Section) (Grant No. 98009) and the Programme "Universities of Russia" (Grant No. 1785).

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