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Introduction

All cuprate high-T_c superconductors are highly anisotropic layered systems, which implies high-quality single crystals are necessary to study their physical properties. To obtain crystals with cm-sizes the solute-rich-liquid crystal-pulling (SRL-CP) method was recently developed [1]. However, apart from the cases when the crystal size is the principal requirement, the flux growth with spontaneous nucleation remains to be the most simple and convenient method. This crystallization method performed under optimal conditions allows one to obtain high-quality crystals suitable for most physical studies.

In this work we have grown $RBa_2Cu_3O_x$ (R-123) crystals, where R=Y, rare earth, and have performed a crystal-morphology study to obtain information on the actual formation conditions which is vital for optimization of the growth process.

Crystal growth

$RBa_2Cu_3O_x$ crystals were obtained for almost all rare-earth elements (except La, Ce, and Tb) by spontaneous nucleation in high-temperature solutions of the R_2O_3-BaO-CuO system. An initial mixture prepared by careful grinding of oxides R_2O_3, BaO_2, CuO of high purity (99.99%) was heated in an alumina crucible at a rate of 20-40°C/h up to the temperature being by 30-40°C above the border of the $RBa_2Cu_3O_x$ crystallization

range. After the isothermal annealing the melt was slowly cooled with subsequent decanting of the residual flux at the temperature exceeding the flux freezing point by 5-10 °C. To prevent the R-123 crystals grown from the heat shock, the flux decanting was performed within the furnace and then crystals were cooled down to room temperature at a rate of 10-40 °C /h.

The crystals grown were characterized by various methods. To determine the cation composition, the rare-earth content was measured by the spectro-photometry, the copper content and Al-impurities - by the atomic absorption, and Ba - by the flame photometry [2, 3]. The scanning electron microscopy and microprobe analysis were used to control the homogeneity and reproducibility of the composition, and the X-ray powder diffraction - for the phase analysis of crystallization products. An electrical resistivity study was performed in the wide temperature range 4.2-450 K° to get information about the superconducting properties as well as about the normal-state electron transport. Anisotropic resistivity components were measured separately by the direct four-probe method with a resolution of 10^{-3} %. The crystal morphology investigation employed the optic and scanning electron microscopy.

The growth conditions and purity of some R-123 crystals grown are presented in Tab.1.

Table 1. Growth conditions and purity of crystals used

R,	Isothermal annealing		Cooling rate	Decanting	Crystal sizes	Al-impurities
rare earth	T (°C)	time (h)	(°C/h)	(°C)	(mm)	(wt.%)
Nd	1050	1 - 5	0.5	950	9x6x1.5	1.3
Gd	1000	1 - 5	0.3 - 0.5	940	10x6x1	1.2
Ho	990	5 - 10	0.3 - 0.5	920	8x8x0.6	~0.5
Er	980	5 - 10	0.3 - 0.5	920	8x7x0.6	~0.5
Tm	960	10	0.3	890	5x7x0.8	<0.1
Lu	950	10	0.2	880	5x3x0.2	<<0.1
Y	1000	5	0.3 - 0.5	920	5x5x1	0.6

The study was concentrated on the R-123 crystals with R=Tm and Lu, which have the smallest ionic sizes in the rare-earth raw. These compounds remain yet less studied though they are more attractive for investigating physical properties. R-123 compounds with Tm and Lu don't form $R_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions in contrast to those with rare earth elements having larger R^{3+} ionic radii. Tm- and Lu-based crystals are less

contaminated by impurities arising from the crucible material, which is mainly due to essentially lower temperatures required for their growth [4]. Moreover, substitution of magnetic Tm^{3+} or small Lu^{3+} ions for Y in the most studied Y-123 compound gives an opportunity to elucidate the role of rare-earth sublattice magnetism as well as the role of size effects in determining the physical properties of these systems.

Detailed optimization of the growth conditions was carried out for the Tm-based system, and the best results were obtained for the 0.007Tm$_2$O$_3$ - 0.289BaO - 0.704CuO composition of the initial mixture. The temperature at which Tm-123 crystals start to form has been determined to be about 925 °C from a set of growth experiments interrupted at different points of the cooling process. An exact value of this temperature is of primary importance to set the growth conditions. Growth experiments performed under conditions listed in the table reproducibly resulted in a high yield of Tm-123 crystals with average sizes of 5x7x(0.8-1.3) mm^3, Fig.1, and some crystals grew up to 6x12x1.5 mm^3.

Similar conditions were used for the preparation of Lu-based crystals. In this case we met the same problems as other investigators [5]: the growth of Lu-123 crystals was very unstable which required all technological parameters to be exactly set and controlled.

To obtain the required oxygen stoichiometry x, RBa$_2$Cu$_3$O$_x$ crystals grown were subjected to secondary annealing in air or flowing oxygen. Tm-123 and Lu-123 crystals oxygenated in flowing oxygen at 475°C, $x \approx 6.9$, had low electrical resistivity ρ_{ab}(100K)=65-90 $\mu\Omega$cm, high superconducting transition temperatures T$_c$=90-92 K, and rather narrow superconducting transitions (ΔT$_c$~0.2-0.4 K). The obtained values are characteristic of high-quality R-123 single crystals, which implies the crystals grown have high structural perfection at the microscopic scale.

Morphology.

The crystal morphology analysis performed by Sun and Schmid [6] for the Y-123 system has shown that at nearly equilibrium conditions plate-like crystals shaped with the {001} and {101} facets should grow. However, extensive experimental data demonstrate that the shape of R-123 crystals is dominated by the {001} and {100} facets. Such factors as the viscosity and absorption of the flux, dissolved impurities have an essential influence on the crystals' habit and surface morphology, but the key parameter is the oversaturation degree [7]. So, the evolution of the crystals' shape, formation of various facets within the process of crystal growth under particular conditions provide

one with the information on oversaturation in the R-Ba-Cu-O system.

We have carried out a comparative analysis of the crystal morphology for two systems, Ho-123 and Tm-123, which differ in such principle parameter as the crystallization temperature.

In general, both systems demonstrated the same morphology type. Plate-like crystals of different thickness were mostly observed, and their shape was dominated by the basal-pinacoid facets {001} with less developed tetragonal prism facets {100}, Fig.1. The most perfect crystals were thin plate-like individuals with both basal-pinacoid facets being shiny. In such thin crystals the {100} prism facets were usually also rather smooth. The main growth mechanism was the layer-by-layer dislocation growth of the (001) plane.

The Ho-Ba-Cu-O system

In the holmium system, crystals grew mainly in a form of single plates ≤ 0.3 mm thick, and the {001} and {100} facets determined their habit. The following types of the micromorphology were observed for the {001} faces.

1) both facets of the basal pinacoid had shiny surfaces;
2) one facet was shiny, while a screw dislocation appeared on another;
3) one of the {001} facets demonstrated a single screw dislocation, while another had a rough relief of the surface being formed by numerous round growth kinks.

In contrast to thin crystals, thick-plate (> 0.3 mm) ones had more complex relief of the {100} facets. It is worth noting that some "notches" could be often observed on these facets giving evidence that crystals were constituted of several thinner parts. In some cases these manifestations of the "layered" or "sandwich" structure were almost completely covered by a thin shiny layer, which formed at the final stage of the crystal growth, Fig.2. Individuals with the {001} basal-pinacoid facets hanging over the tetragonal-prism facets were also observed fairly often in the Ho-system. At the subsequent stage of formation such crystal became overgrown by the same phase giving rise to a "case-like" crystal with a complete set of facets, {100}+{001}. At this stage the tops behaved as generating points, Fig.3.

The as grown Ho-123 crystals were tetragonal (P4/mmm) with the lattice parameters a=3.8688 Å and c=11.765 Å.

The Tm-Ba-Cu-O system

An apparent peculiarity of the Tm-system was that a lot of bulk crystals having

almost equal sizes along all directions existed side by side with platelets. They were shaped by tetragonal-bipyramid facets {101} besides the {001} and {100} facets, Fig.4. As a rule there were 2 or 4 such facets rather than 8, i.e. the actual crystal symmetry was less than tetragonal. According to the x-ray powder diffraction, the as-grown Tm-123 crystals were orthorhombic (P/mmm) with the lattice constants a=3.829 Å, b=3.877 Å, c=11.699 Å.

Tm-crystals demonstrated one more distinction from the Ho-system, namely the presence of two types of skeletal agglomerates - crystals grown together by tops, and branchy dendrites, Fig.5.

Morphology peculiarities of Ho- and Tm-based single crystals give evidences for their formation under different oversaturation conditions. Ho-based crystals formed at a weak oversaturation, and their {001} facets are the growth forms, while the {100} ones are the passive forms. The skeletal forms, which are characteristic of the Tm-system, and an occurrence of rough {100} facets together with smooth {001} and {101} ones are indicative of higher oversaturation realized in this system.

A comparison of the crystal-morphology data obtained with technological parameters of the growth experiments has allowed us to determine the optimal conditions for obtaining perfect R-123 single crystals.

Acknowledgements

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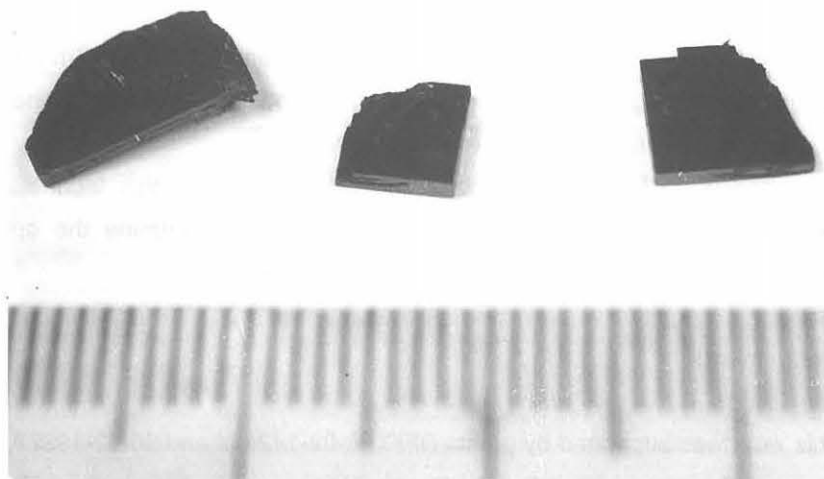7] Y. Yamada, M. Nakamura, Y. Shiohara and S. Tanaka ; J. Cryst. Growth 148 (1995) 241.
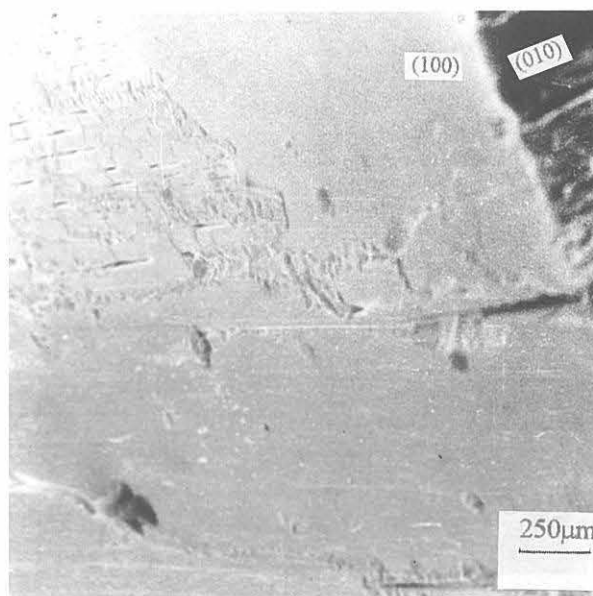
Fig.1. Tm-123 crystals.

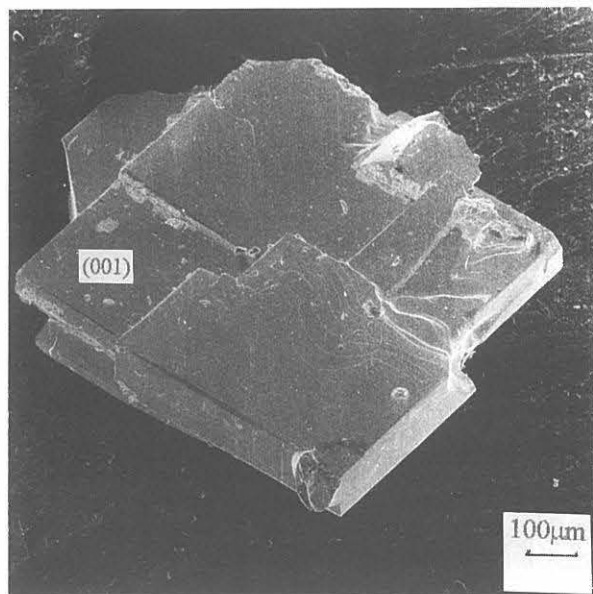Fig.2. "Layered" structure of bulk Ho-123 crystal, the (100) face.
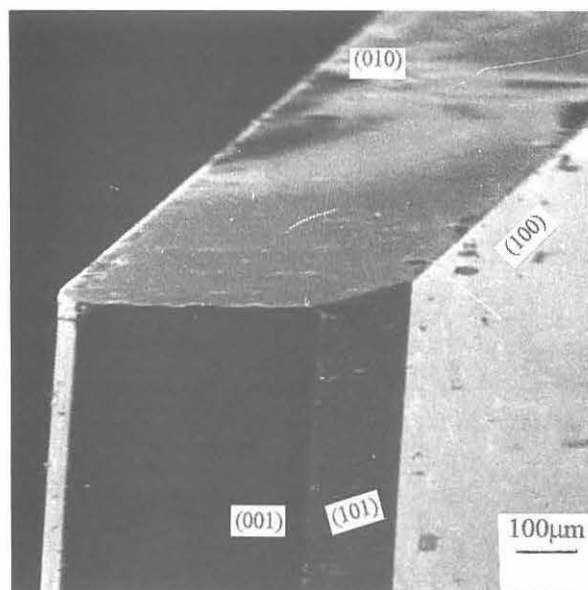

Fig.3. "Case-like" crystal Ho-123.

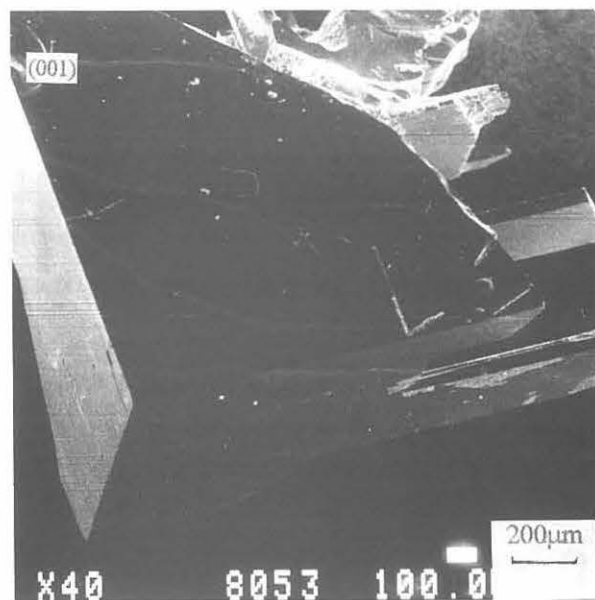Fig.4. Isometric Tm-123 crystals demonstrating the {101}, {001}, and {100} facets.

Fig.5. Branch dendrite becoming overgrown by the {001} and {100} planes at the final stage of formation.