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REPRODUCIBLE GROWTH OF LARGE FREE CRYSTALS OF $YBa_2Cu_3O_{7-x}$*

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Summary

By optimizing the experimental conditions for growth of yttrium barium cuprate (YBCO) from BaO–CuO solutions, free platelet crystals larger than $3 \times 3 \times 0.1$ mm^3 and bulk separated crystals larger than $3 \times 3 \times 1$ mm^3 could be achieved reproducibly. The thickness of the crystals depends on cooling rate, concentration of solution, impurities and (dissolved) crucible material.

1. Introduction

With the discovery of superconductivity above the boiling point of liquid nitrogen the need for single crystals arose for investigation of high-temperature superconductivity (HTSC). There are so far three classes of these cuprate superconductors: (1) $YBa_2Cu_3O_{7-x}$ and "1:2:3" rare earth barium cuprates, (2) bismuth alkaline earth cuprates and (3) thallium alkaline earth cuprates [1]. The bismuth and thallium compounds have various elemental ratios which are not easily obtained, compared with single-phase material. In contrast, $YBa_2Cu_3O_{7-x}$ (YBCO) has a well-defined stoichiometry and there is practically no solid solubility of constituent oxides. Therefore effort has been concentrated on crystal growth of YBCO to achieve crystals of sufficient size for positron annihilation experiments [2]. However, there are severe problems which have so far hindered the reproducible growth of large YBCO crystals and which are discussed in detail elsewhere [3, 4]. Here we mention only briefly that the thermal instability of YBCO does not allow growth from melts, vapor or high-temperature solutions using conventional molten salts as solvents [5, 6]. YBCO crystals can be grown only in small dimensions by solid state reactions and in somewhat larger dimensions from

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high-temperature solutions using excess of BaO–CuO as solvent [3, 4, 6 - 9]. The chemical instability of YBCO requires separation of the crystals from the residual flux while the latter is still liquid [3, 10, 11]. The twinning caused by the chemical–structural phase transformation from tetragonal non-superconducting $YBa_2Cu_3O_6$ (which is formed at high temperatures) to the superconducting orthorhombic phases $YBa_2Cu_3O_{7-x}$ with $x \approx 0 - 0.1$ has so far limited the size of single-domain crystal regions to about 100 μm [12, 13]. Another problem is the preferred growth of thin platelets instead of the desired bulk crystals. This paper describes the reproducible growth of either thin plates or free crystals 1 mm thick, of at least 3 mm lateral dimension.

2. Crystal growth experiments

The YBCO crystals were grown from high-temperature solutions using excess BaO and CuO in the molar ratio 28:72 as solvent [6, 11, 14, 15]. The concentration of YBCO in the solution was systematically varied between 5.6 and 30 wt.% to find the optimum conditions for obtaining large and/or thick crystals. The purity of the chemicals used in this preliminary study was more than 99% for CuO and $BaCO_3$, and 99.99% for Y_2O_3. Different starting mixtures ($BaCO_3 + Y_2O_3 + CuO$; $BaO + Y_2O_3 + CuO$; $YBCO + BaCO_3 + CuO$; and YBCO + pre-reacted BaO–CuO flux) gave similar results, so the $BaCO_3 + Y_2O_3 + CuO$ mixture was generally used. As crucible materials, Al_2O_3 (Degussa or Metoxit) and in a few cases ZrO_2 and tin oxide (Metoxit) were used. The volume of the crucibles varied from 15 to 200 cm^3 (the shape was either long-cylindrical or the conventional conical shape with a flat bottom). The preferred crucible had a volume of 60 cm^3 and was cylindrical. Kanthal chamber furnaces were used, and the temperatures were controlled with a precision of better than 0.5 °C by PtRh 6% *vs.* PtRh 30% thermocouples from Eurotherm 818P controllers/programmers. As no calibration thermocouples were available, the accuracy of the (absolute) temperature is estimated to be better than 10 °C only. The temperature gradient within the furnace, in the region of the crucible positions, is about 1 °C cm^{-1}, so that different crucibles used in the same run had relative temperature differences of at most 10 °C. The crucibles were positioned within fitting holes in firebricks or on top of firebricks so that liquid could be caught in case of crucible failure. The furnace atmosphere was air. After weighing, the chemicals were mixed in an agate ball mill, with acetone added to assist the mixing process. After drying the powder, the mixture was pressed (by hand) into the crucibles. Generally, four to six crucibles were placed in the furnaces for a crystal growth run which took 3 - 7 days. The typical procedure consisted of heating the furnace from room temperature to 1020 - 1030 °C at a rate of 300 °C h^{-1}. This soaking temperature was held for about 15 h, then the furnace was quickly opened to check completion of liquid formation. The process was then continued at the maximum temperature for another 12 - 15 h. After step-cooling to 960 - 980 °C, the cooling program was continued

TABLE 1

Experimental data and results of selected crystal growth experiments

No.	*1* Wt.% *YBCO*	*2* *Crucible*	*3* *Soak temperatures/times* °C/h	*4* *Cooling rate* (°C/h^{-1})	*5* *Decanting temperature* (°C)	*6* *Flux separation*	*7* *Crystal*		*Remarks*
							Area (mm^2)	*Thickness* (mm)	
S 46	5.8	A N	1020/30	2	920	V	5 × 3	0.2	
S 52	26.2	A C	1020/24	1	910	V	5 × 4.5	0.07	
S 55	5.9	A C	1020/24	1	910	V	4 × 2	0.15	
S 61	[a]	A C	980/5	2	915	V	3 × 2	0.1	
S 65	10.2	Z C	1020/20	1.5	935	V	4 × 4	0.2	
S 84	7.8	A C	1000/about 24	1	920	V	3 × 3	0.1	Soak insufficient
S 88	24.7	A C	1030/16	0.6	915	V	2 × 2	0.4	*h0l* faces
S 89	30	A C	1030/16	0.6	915	V	2 × 2	0.4	*h0l* faces
S 90	20	A C	1030/16	0.6	915	V	2 × 2	0.4 intergrown	*h0l* faces
S 94	6.7	A C	1020/28	1	920	V	15 × 11	0.4	T 3 × 3 × 0.2
S 96	8.9	A C	1020/26	0.5	920	V	5 × 4.5	1.3	6 × 6 × 0.8; 3 × 3 × 1
S 97	8.9	A C	1020/26	0.5	920	V	4 × 3	2	
S 101–110	8	A N	1020/20	1	930	V	var.	var.	0.1 wt.% dopant[b]
S 111	8.7	Z N	1020/about 15	0.4	920	M	3 × 1.5	0.08	
S 112	8.7	Z N	1020/about 15	0.4	920	M	2 × 1	0.05	Max. 10 × 5[c]
S 116	6	A C	1020/about 15	0.4	920	V	8 × 3	1	T 3 × 2 × 1

1, Wt.% of YBCO in the solvent.
2, Crucible material and shape: A, Al_2O_3; Z, ZrO_2; C, cylindrical; N, normal shape.
3, Soaking temperature and time.
4, Cooling rate.
5, Temperature of decanting residual flux.
6, Degree of flux separation: V, complete; M, medium.
7, Crystal dimensions (maximal). T, typical dimensions of at least five crystals.

[a] Decanted flux from earlier experiments at 930 °C.

[b] 0.1 wt.% dopants: La_2O_3, In_2O_3, SnO_2, V_2O_5, Nb_2O_5, MoO_3, K_2CO_3 Li_2CO_3, B_2O_3, TiO_2; crystal dimensions variable.

[c] Surface: dendritic structure.

at rates between 0.4 and 2 °C h^{-1} until a temperature between 910 and 930 °C was reached. The hot crucible was then quickly removed from the furnace and the grown crystals were separated from residual flux by decanting. This procedure has to be carried out quickly and protection is required against splashing melt.

After the crucible was cooled to room temperature and crystal arrangement on its walls and bottom was analyzed, the crucible was carefully cracked in a vice bench and the crystals were mechanically removed and stored in desiccators. The a.c. susceptility measurements of virgin crystals indicated low transition temperatures or no superconductivity at all. Therefore, the crystals were annealed in pure oxygen in the temperature range 400 - 500 °C for 2 - 84 days and then checked for T_c. In Table 1 the conditions of specific experiments which yielded interesting results are given. These results are discussed further below or elsewhere [16, 17].

Some of the successful experiments have been repeated, and in two out of three cases the results could be reproduced.

3. Results

The dimensions of the crystals obtained are included in Table 1. Analysis of the observed crystal thicknesses indicates a relationship with cooling rate, as shown in Fig. 1. At cooling rates higher than 2 °C h^{-1} and up to 5 °C h^{-1} thin crystals are obtained, typically in the range of 0.05 - 0.2 mm thickness. At cooling rates between 5 and 10 °C h^{-1} much thinner plates, of the order of a few micrometres, are expected and have been found by several groups. On the other hand, thick plates of YBCO (of about 0.4 mm) can be obtained at cooling rates around 0.6 - 0.8 °C h^{-1}, whereas still lower cooling rates (of less than 0.5 °C h^{-1}) yield crystal thicknesses of more than 1 mm. This confirms the concept that growth instability is responsible for platelet

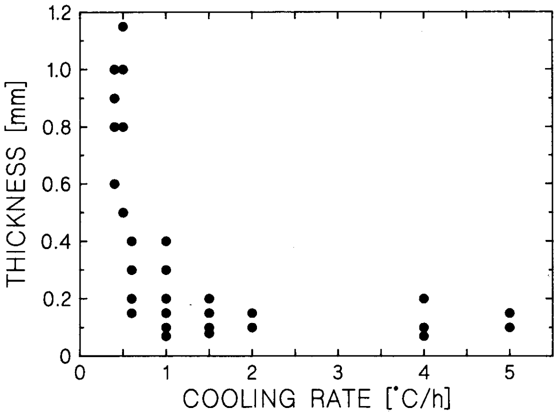
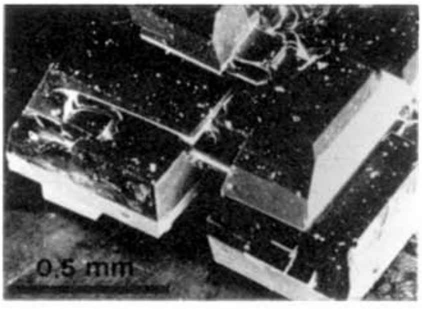


Fig. 1. Experimentally observed YBCO plate thicknesses for various cooling rates.

growth, as suggested earlier [3]. At extremely low growth rates we would therefore expect the development of the equilibrium form. However, other factors also have an influence on the thickness of the plates. Growth in ZrO_2 crucibles and also certain impurities (indium, tin and neodymium) favours thin crystals. On the other hand, high concentrations of YBCO in the flux lead to bulk crystals. Above 20 wt.% YBCO in the flux, additionally, $\{h0l\}$ faces are observed which are relatively rough (S-face?) and contaminated. Crystals with $\{h0l\}$ faces are shown in Fig. 2, whereas Fig. 3 shows a crystal of 1 mm thickness (S 96) where the $\{h0l\}$ faces are not observed. The largest crystal of S 116 ($8 \times 3 \times 1$ mm^3), has been cut for positron annihilation experiments and thus is no longer available for photography.

Other observations from the systematic crystal growth experiments are the occurrence of several undersired crystalline phases: long-prismatic black crystals of CuO with a typical surface domain structure, black cubes with small (101) faces of $BaCuO_2$, hexagonal, nearly colourless plates of barium aluminate and yellow transparent needles or whiskers of yttrium–barium aluminate which were not further investigated. The aluminate crystals indicate high aluminium concentration in the flux, originating from crucible corrosion [18], which leads also to aluminium contamination of the YBCO crystals as discussed in the next section. The occurrence of either CuO or $BaCuO_2$ indicates that the relevant phase fields in the pseudoternary phase diagram Y_2O_3–BaO–CuO_x are not remote from the small concentration field where YBCO can grow from liquid solution [19].

Crystals grown from ZrO_2 crucibles are more easily oxidized and are less contaminated than crystals grown from Al_2O_3 crucibles. On the other hand, the ZrO_2-grown YBCO crystals showed an enhanced surface contamination by flux droplets. This might be explained by either a reduced surface tension of the liquids caused by ZrO_x surface segregation of the melts, or by a reduced viscosity (compared with aluminate-containing melts) leading to an enhanced dynamic wetting effect, which favours liquid droplet separation.



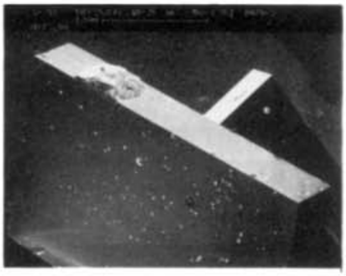


Fig. 2. YBCO crystals with major {001} and minor {100} and $\{h0l\}$ faces (S 89).

Fig. 3. Thick plate of YBCO without $\{h0l\}$ faces (S 96).

The dopant experiments showed that even small additions (0.1 wt.%) of various dopants had significant effects on the crystal growth results. From this observation we conclude that the starting chemicals should be of at least 99.9%, or better, of 99.99% purity to reduce accidental (positive or negative) dopant effects and to achieve reproducibility. The specific dopants have effects on number, size and shape of the YBCO crystals and on the formation of undesired crystalline phases. Indium, tin and neodymium favour growth of few thin crystals of YBCO; potassium and lithium enhance formation of large crystals which, however, show a tendency for flux droplets to adhere; boron enhances formation of large YBCO crystals, and of crystals of $BaCuO_2$ and aluminates; and titanium, molybdenum and vanadium facilitate flux separation from the crystal surfaces which have typical dimensions of $5 \times 5\,mm^2$. The effect of dopants needs to be studied more systematically before an optimized "recipe" for growth of large clean crystals of YBCO can be given. Also, the effect of dopants on the superconducting properties should be analyzed.

4. Characterization

The relevant features of YBCO crystals for use in physical measurements are (1) the superconducting properties such as T_c, the width of T_c, critical current density, Meissner and specific heat effects, and (2) the factors which have an influence on these superconducting properties. Therefore numerous crystals of different size grown in Al_2O_3 and ZrO_2 crucibles were annealed in oxygen to obtain the superconducting phase and the highest-possible T_c. A few of these annealing experiments have been selected for Table 2, in which the oxidation parameters, crystal size and superconducting transition temperatures are given.

Analysis of the data in Table 2 and of other data confirms that oxidation kinetics is anisotropic, as one would expect from the layer aspect of the YBCO structure. Oxidation along $\langle 001 \rangle$ is much slower than along the $\langle 100 \rangle$ directions so that mainly the lateral dimensions of the YBCO $\{001\}$ plates determine oxidation, whereas a crystal thickness effect has not been observed so far. Significant differences were found between crystals grown in Al_2O_3 and ZrO_2 crucibles. If it is assumed that oxidation is quasi-completed (for that crystal fraction which contributes to the a.c. susceptibility signal discussed further below) when the width of the superconducting transition temperature is about 1 K or less than this, then the YBCO ZrO_2 crystals require about 1 week for the first 1 mm to be oxidized, and the YBCO Al_2O_3 crystals require about 1 week for 0.5 mm and about 10 weeks for the first 1 mm to be fully oxidized. This may be explained by a combined effect of high aluminium concentration in the YBCO crystals (typically 2.2 - 2.9 at.%) and a specific aluminium effect on oxidation kinetics, whereas the zirconium concentration measured by energy-dispersive X-ray analysis lies between 0 and 1 at.%, typically at 0.25 at.%.

TABLE 2

Details of oxygen annealing experiments and observed superconducting transition temperatures

No.[a]	*Crystal dimensions* (mm)	O_2 *Annealing temperatures/times* (°C/days)	T_c *onset* (K)	ΔT_c (K)	*Remarks*
S 52	4.9 × 3.2 × 0.07	As-grown	28	Large	Al_2O_3 crucible
	1.5 × 1 × 0.1	500 - 400/7	73	1	
	1.5 × 1 × 0.1	500 - 400/7	63	2	
	2 × 2 × 0.8	485/84	66	1.5	
S 84	1.5 × 2.5 × 0.1	485/10	40	7	
	3 × 2.5 × 0.1	485/85	40	3	
S 116	2 × 2 × 0.7	As-grown	25	Large	
	2.5 × 2.5 × 0.8	465/13	66	4	
S 55	n.m.[b]	As-grown	no	—	Nominal 0.7% strontium
	3 × 2 × 0.1	485/84	60	2.5	
S 65	n.m.[b]	As-grown	no	—	ZrO_2 crucible
	2 × 1 × 0.1	470/11	86	0.8	
	3 × 2 × 0.08	485/70	87.3	1	

[a] Crystal growth experiment number. Measured impurities were 2.2 - 2.7 at.% for S 52; 3.5 at.% aluminium for S 84; and about 0.25 at.% zirconium for S 65.

[b] Not measured (about 2 × 1 × 0.1).

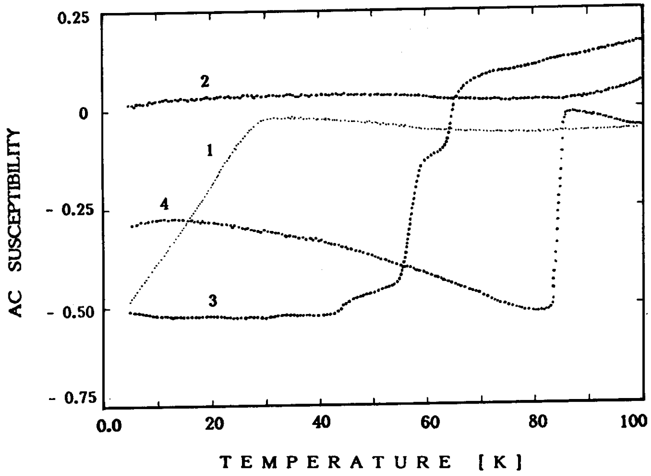


Fig. 4. The susceptibilities of crystals grown from Al_2O_3 (S 52) and ZrO_2 (S 65) crucibles as-grown (1, S 52; 2, S 65) and after oxidation treatment (3, S 52; 4, S 65) at 470 °C for 11 days.

The T_c values of the completely oxidized YBCO crystal fractions may be correlated with the measured aluminium and zirconium concentrations and thus indicate that high-purity chemicals of about 99.99% purity are required when optimum T_c is to be achieved, and that the crucible contamination problem has to be solved [18].

Measurements of a.c. susceptibility in a low external field (about 0.01 Oe) were used for determination of the transition temperatures and the widths of the superconducting transitions as given in Table 2. The susceptibility curves of selected crystals grown in Al_2O_3 and ZrO_2 crucibles are shown in Fig. 4. The as-grown YBCO (ZrO_2) shows no superconductivity, and the as-grown YBCO (Al_2O_3) shows a low-temperature broad transition only. The oxidized YBCO (Al_2O_3) crystal shows a broad transition with shoulders indicating uncomplete oxidation, whereas the YBCO (ZrO_2) crystal has a sharp transition with T_c (onset) of 86 K, indicating that oxidation is more or less completed.

5. Conclusions

Reproducible growth of free crystals of YBCO has been achieved. However, this requires careful preparation of the experiments and proper control of actual crucible temperatures. According to the growth stability concept the thickness of the YBCO plates could be varied between values of less than 0.1 mm (for cooling rates over 1 °C h^{-1}) and about 1 mm for cooling rates below 0.5 °C h^{-1}. Dopants have detrimental or beneficial effects on crystal growth at low concentrations (0.1 wt.%). Crucibles of Al_2O_3 and ZrO_2 are corroded, and this leads to crystallization of undesired phases and to incorporation of typically 2 - 3.5 at.% of aluminium and 0.25 at.% of zirconium in YBCO. This has a significant effect on oxidation kinetics and the maximum achievable T_c. The contamination effects from the crucibles and influence of small dopant concentrations indicate that the problem of crucible corrosion must be solved and that chemicals of at least 99.99% purity have to be used if large crystals of YBCO with optimized superconducting properties are to be grown.

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