

## CRYSTAL GROWTH PROBLEMS OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

Hans J. SCHEEL\*

Istituto MASPEC of C.N.R., Via Chiavari 16-18, I-43100 Parma, Italy

The problems for growth of bulk single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  "YBCO" and of high-quality layers are: unknown phase diagrams and difficulty to obtain equilibrium data, the low thermal and chemical stabilities of YBCO, the low solubility of YBCO in the corrosive BaO-CuO melts, and the twinning problem. Based on a tentative phase diagram and systematic growth experiments, conditions could be found were nearly cm-crystals of YBCO could be separated from growth solutions by decanting.

### 1. INTRODUCTION.

Simultaneously with the discovery of high temperature superconductivity (HTSC) at the IBM Zurich Research Laboratory and especially after finding the real high-temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  "YBCO" by Chu and coworkers, worldwide attempts started to produce single crystals and high-quality epitaxial films. However, it was soon realized that there is an enormous difference between the ease of fabricating superconducting ceramic samples on one hand and the great difficulty to grow single crystals and high-quality layers on the other hand.

The question of the required crystal and layer perfection seems to be clearing up now. Although it had been argued that twinning and/or the phase transition and/or grain boundaries are necessary for high temperature superconductivity, there is the growing evidence for the detrimental effect of these defects on HTSC. For instance twin boundaries seem to have a pinning effect for the HTSC flux, and the intragranular and thin-film current densities are reported to be  $10^6 \text{ A} \cdot \text{cm}^{-2}$  in contrast of  $10^4 \text{ A} \cdot \text{cm}^{-2}$  for intergranular values.

Therefore the goals for crystal growth of YBCO have to be 1. Bulk single-domain crystals of at least 5 mm dimensions in all directions and of high structural perfection (free of

grain boundaries, low dislocation density),  
2. Single-crystalline compact epitaxial films of various thicknesses and of high structural perfection.

The bulk crystals of YBCO and of related phases where the constituent cations are substituted, individually or in combination, partially or completely, by other cations which fit into the structure, are necessary for investigation of the effect of twins, grain boundaries, point and line defects on HTSC. In particular, the lack of understanding of the HTSC phenomenon as such demands numerous physical and structural investigations for which well-characterized single crystals are required. Whereas for single crystals of HTSC no direct application in technology is evident, the thin layers are expected to have applications in a variety of devices and structures.

Despite the obvious need for high-quality crystals and epitaxial layers, no reproducible process for their fabrication could yet be found. It is the goal of this paper to analyze published results and other information as well as own findings for the obstacles to growth of large and high-quality crystals and layers, to present the status of the art, and to indicate suggestions for eventually achieving the set goals. Specifically, the limited thermal and chemical stabilities of

\* Present address: Department of Physics, University of Geneva, 24 quai Ernest - Ansermet, CH - 1211 Geneve 4, Switzerland.

YBCO and their consequences, the difficulties in investigations of phase diagrams and with finding corrosion-resistant crucibles, the thin-plate problem and the twinning problem will be discussed.

In view of the great difficulties encountered with YBCO, the search for compounds and structures with improved thermal and chemical stabilities and without twinning problem may be an alternate route to achieve understanding and facilitate applications of HTSC.

## 2. PHASE DIAGRAM DATA AND CONSEQUENCES FOR CRYSTAL GROWTH

Phase diagrams are extremely valuable for planning crystal growth experiments and for achieving high yields and sizes of crystals. However, in the ternary phase diagram  $BaO - Y_2O_3 - CuO$  only the binary system  $BaO - Y_2O_3$  (1), certain aspects of the binaries  $BaO - CuO$  and  $CuO - Y_2O_3$ , and a few ternary phases are known (2-4). Phase equilibria containing copper are very sensitive to the oxygen partial pressure, so that the system  $BaO - Y_2O_3 - CuO$  should contain oxygen as the fourth component which has a significant effect on the melting behaviour and on the stability regions of Cu-containing phases. However, equilibrium for a given temperature and oxygen partial pressure is difficult to achieve and requires extended times, so that the dynamic DTA and TG methods may lead to misleading and contradictory results, for instance for the melting behaviour of YBCO as a function of oxygen pressure (5-7). The majority of works report incongruent melting of YBCO in air and in oxygen above 1000°C and below 1050°C, so that this temperature range has to be regarded as the **upper limit** for any crystal growth technique. It also means that growth from melts can be excluded, only growth from liquid or gaseous solutions or solid state recrystallization can be used for growth of YBCO crystals. This upper limit for growth of YBCO may be shifted to somewhat higher temperatures by application of high oxygen pressures or by substitution of yttrium by other rare earth ions or other large three-valent cations and by substitution of Ba by Ca, Sr, Cd or Pb. However, there is an ultimate temperature limit due to the valency requirement of copper (+2) at around 1200°C depending on the oxygen pressure.

Another consequence of the low thermal stability of YBCO compared to high-melting compounds surrounding this phase in the ternary phase diagram shown in Fig. 1 is the limited applicability of solvents in crystal growth from high-temperature solutions (8).

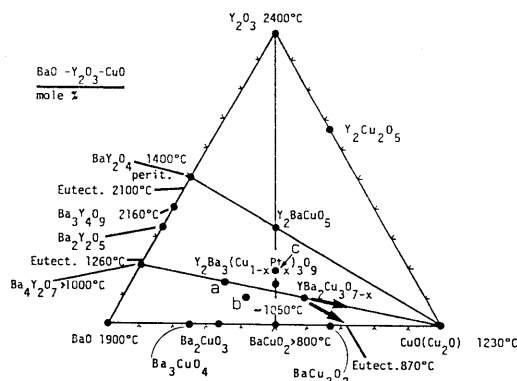


Fig.1 Phase diagram  $BaO - Y_2O_3 - CuO$  with the YBCO phase  $YBa_2Cu_3O_{7-x}$ , with the new phases  $YBa_2Cu_5$  (a),  $Y_2Ba_3Cu_0$  (b), and with the Pt-containing phase  $Y_2Ba_2CuPt_6$  (c).

It was found (4,9) that the popular solvents like fluorides lead to crystallization of  $CuO$  whereas  $PbO$  and  $Bi_2O_3$  are incorporated into the YBCO lattice with the corresponding effect on lattice constants and superconducting properties. The preferred solvents for growth of YBCO should contain mainly  $CuO$  and  $BaO$  (see the arrows in Fig. 1) and have a relatively low melting point. Therefore a tentative phase diagram based on DTA data and melting experiments was established (10) which indicates a eutectic around 40 m%  $BaO$  at about 935°C, that means between the compounds  $BaCuO_2$  and  $CuO$ . Another report (11) indicated the eutectic at 28 m%  $BaO$  and 870°C. This temperature range of 905 + 30°C indicates the **lower limit** for crystal growth of YBCO from  $BaO - CuO$  solutions. Other solvents (molten salts like nitrates, halides) may be found which allow to grow YBCO at still lower temperatures, preferably below the tetragonal-orthorhombic phase transition around 700°C, in order to solve the twinning problem discussed further below.

The relatively low growth temperature and possibly also the difference of bonding between YBCO and the BaO-CuO melts lead to a low **solubility** which in combination with the narrow temperature range for crystal growth has negative consequences which are discussed in the section on growth stability. Preliminary investigations (10) indicate a solubility of 2 to 3 m % YBCO in melts of 28 m% BaCO - 72 m % CuO at around 1000 °C. The knowledge of solubility and melting behavior was important for solving the crystal separation problem discussed below.

### 3. CRYSTAL SEPARATION

Despite its thermodynamic stability at room temperature YBCO is chemically very unstable. It is easily dissolved in diluted and weak acids, and it is attacked by water and humidity and CO of the air. Therefore YBCO samples should be kept in desiccators. A consequence of this **chemical instability** is that the grown crystals can not be separated from the residual flux by its dissolution in acids. Other methods of crystal separation have to be applied which are described in the following.

The most generally applied approach is to heat YBCO with excess of BaO/CuO or just excess CuO in Pt or alumina crucibles, achieve partial melting and find after solidification and cooling to room temperature cavities within or at the surface of the solidified mass. The crystals found in these cavities have sizes between 0.1 to 4 mm and perhaps have been separated from the growth solution by its contraction during solidification. This approach can be used for production of many small crystals up to 1 mm. However, the growth of larger crystals of say 4 mm is not reproducible, and a further significant increase of crystal size seems difficult. Occasionally large crystal plates up to 8 mm can be found on the surface of the melt or crucible (4,9), but these deteriorate during oxygen annealing, perhaps due to differences of thermal expansion coefficients of YBCO and solidified flux.

Another approach of separating crystals uses the pronounced wetting and creeping of the liquid solutions on metals like gold and platinum (12, 13), so that free crystals up to 2.5x2.5x0.08 and 0.5x0.5x0.2 mm<sup>3</sup> remain in the gap between pellet and crucible or between the

gold crucible and support sheet.

Accidental separation of flux may occur when crucibles of mullite/sillimanite soak up the liquid, or when metal crucibles develop a leak (by corrosion) through which the liquid penetrates. A somewhat similar effect is used by a sieve, contained within the crucible, which allows the liquid to drop or creep to the crucible bottom, where crystals can grow and then be separated by tilting the hot arrangement (14).

The best way of separating crystals consists of achieving concentration and temperature conditions for complete dissolution of YBCO, and to remove the hot liquid from the crystals grown by decanting or by pouring the liquid through a hot sieve or by using tilting or rotating of the crucible. This has been achieved by systematic DTA investigation in conjunction with melting experiments, and by systematic variation of growth parameters in crystal growth experiments (9, 10). This complete flux separation is the presupposition for achieving larger crystals and liquid-phase epitaxy of YBCO.

### 4. CHOICE OF CRUCIBLES

Platinum crucibles are usually applied in crystal growth of oxide compounds from high-temperature solutions (8). Therefore, this was the first choice for the oxide superconductors until it was realized that Pt is heavily corroded by the Y -Ba-Cu - oxide melt even at temperatures below 1000 °C. Also the formation of new phases like  $Y_2Ba_2CuPtO_8$  and gives evidence of Pt dissolution. Another evidence comes from the phase diagram Ba-Pt-O (15) which indicates formation of  $4 BaO * PtO_2$  and of solid solutions up to a temperature of 1260 °C. Therefore, Pt crucibles could be used only above this temperature or at significantly lower temperatures where the dissolution kinetics is sufficiently slow. An alternative metal crucible is gold which seems less heavily attacked (12, 13) and leads to incorporation of 0.007 to 0.008 mole fraction of Au which had no significant effect on the superconducting properties (13). A severe disadvantage of these metal crucibles is the strong creeping effect so that long-time experiments for growing large crystals seem not feasible.

High-melting oxide crucibles like  $Al_2O_3$ ,

MgO, ThO<sub>2</sub> and ZrO<sub>2</sub> seem to be more favourable although severe wetting and creeping has also been reported for Al<sub>2</sub>O<sub>3</sub> crucibles. Al seems to substitute for copper in the chains (16) of  $YBa_2Cu_{3-y}Al_yO_{7-x}$  up to y values of 0.22. However, the melting and creeping behavior of the Y-Ba-Cu-O melts on alumina crucibles seems to be influenced by numerous factors like melt composition, temperature, time, oxygen partial pressure, grain size and porosity of the alumina, and is not understood. It is even difficult to achieve non-wetting conditions reproducibly. A reliable control of wetting creep and corrosion will be the presupposition for growth of large crystals for which long-time experiments are required. Possibly, the use of the other high-melting oxides or of single-crystalline crucibles will give some improvement.

#### 5. GROWTH STABILITY

The YBCO crystals generally are extremely thin plates  $\{001\}$  with  $\{100\}$  as side faces, and only rarely plates of large thickness or more isometric crystals of 0.5 x 0.5 x 0.2 mm have been observed (13). Occasionally, also dendrites and hopper-like growth could be seen. The question is whether thin plates are due to the structure, or whether they are representing a special form of growth instability, for instance in the series starting from cubes to whiskers with increasing degree of instability as shown in Table 1.

Table 1. Crystal forms as a function of the degree of growth instability.

CUBES & THICK SQUARE PLATES

CUBES WITH INCLUSIONS

HOPPER GROWTH

DENDRITES

THIN PLATES

WHISKER

DEGREE OF

INSTABILITY



There is a striking analogy with the

perovskite BaTiO<sub>3</sub> which has the equilibrium form of a cube  $\{100\}$  and which initially was grown as the famous butterfly twin consisting of extremely thin plates. The condition for twin formation was the presence of polycrystalline material in the flux and a high supersaturation, and twin-plane reentrant edges explained the mode of growth.

If this analogy applied to YBCO the maximum stable growth rates and the required times for growth of large YBCO crystals can be estimated in two ways: 1. From the known growth rates of crystals grown from high-temperature solutions of various concentrations (for example SrTiO<sub>3</sub>/50% in TiO<sub>2</sub>, 800 Å · s<sup>-1</sup>; GdAlO<sub>3</sub> / 15% in complex flux, 250 Å · s<sup>-1</sup>) one arrives at about 30 Å · s<sup>-1</sup> for YBCO growing from a 2 to 3% solution. 2. Since YBCO crystals of about 1 mm size grown in 5 days show already hopper growth and plate growth, the maximum stable growth rate is of the order of 1 mm per week or 20 Å · s<sup>-1</sup>, in reasonable agreement with the first estimate. For cm size crystals growing from 100 cm<sup>3</sup> solution this would correspond to a cooling rate of 0.02° · h<sup>-1</sup>, to a required temperature stability of 0.05°C, and to a duration of the experiment of 3 months (8,17). Thus it will be difficult (though not impossible) to grow bulk crystals of YBCO in view of crucible corrosion, power stability, and so on.

#### 6. EPITAXY

Deposition of thin layers of YBCO by sputtering, "MBE" or other techniques leads to amorphous or polycrystalline layers which are transformed into epitaxial layers by annealing at 900° to 950°C. This means, that the epitaxial relationship is achieved by solid-state epitaxy (for layers of exact stoichiometry  $YBa_2Cu_3O_{7-x}$ ) or by a liquid-assisted epitaxy process in case of non-stoichiometry. Single-crystalline substrates of SrTiO<sub>3</sub> and of MgO were mainly applied although there are other compounds which might be utilized: these are listed, along with important properties and the misfit with YBCO, in table 2.

So far, Verneuil-grown SrTiO<sub>3</sub> has been available only, that means high dislocation densities and low-angle grain boundaries will be mostly present (18). In a later stage, substrates of higher quality may become necessary, which then could be fabricated by

Table 2. Substrates for epitaxy of YBCO

Substrate	Lattice constant Å	Misfit %	Thermal Exp. Coeff. $10^{-6} \cdot K^{-1}$	$T_C$ K	
SrTiO <sub>3</sub>	3.9053	1	9	105	310
MgO	4.20	8	8(40°C) 14(700°C)	---	10
Al <sub>2</sub> O <sub>3</sub>	Hex. 4.76, 12.93	--	5(40°C)	---	---
KTaO <sub>3</sub>	3.9885	3	2.6(<300K) 6.8(>300K)	---	---
KNbO <sub>3</sub>	4.018(mean)	3.9	5(20-200°C)	708	---
KTa <sub>1-x</sub> Nb <sub>x</sub> O <sub>3</sub> with $x=0.37$	3.9941	3.3	5.6(25-46°C)	300	---
BaTiO <sub>3</sub>	Tetr. 3.986, 4.03	3.5	7	393	4100
ThO <sub>2</sub>	5.6	(45)	6(20°C) 10(700°C)	---	---
ZrO <sub>2</sub> cubic	5.07	(31)	4.5	---	---
YBCO	3.866 (mean)	--	13(<400°C) 11(>635°C)	92	---

top-seeded solution growth or by growth from borate fluxes (8, 19).

In sputter epitaxy or in "MBE" the surface mobility of the arriving species required for high-quality epitaxial growth can only be achieved by high substrate temperatures. Perhaps vapour-phase epitaxy or liquid-phase epitaxy using solutions of YBCO as described in section 2 should be tried for direct epitaxy of YBCO layers.

#### 7. TWINNING PROBLEM

YBCO crystals and layers are grown as the high-temperature phase  $YBa_2Cu_3O_{6.2}$  which is tetragonal and not superconducting. During annealing at 500+100°C in oxygen the sample is oxidized to  $YBa_2Cu_3O_{6.8}$  and transformed to the orthorhombic phase which is superconducting at around 92K. This structural phase transition (which also involves chemical change and thus should be regarded as a special case of topotaxy) leads to twinning within the tetragonal {001} plane, so that the tetragonal axes  $a_1$  and  $a_2$  distort to the orthorhombic  $a$  and  $b$  axes.

For detailed physical and structural investigations of HTSC, untwinned respectively single-domain crystals of at least mm-dimensions and of high structural perfection are required. Possibilities to achieve single-domain crystals are a) application of uniaxial pressure along one of the tetragonal  $a$  axes during the oxygen annealing procedure and when passing the tetragonal crystal through the phase transition, b) growth of the orthorhombic YBCO phase below the phase transition, and c) epitaxial deposition of YBCO onto an anisotropic substrate which forces the alignment of the domains, at least to a certain critical thickness. In view of the great difficulties in growth of tetragonal YBCO at relatively high temperatures, the second possibility to grow directly the orthorhombic YBCO phase at temperatures below about 650° perhaps will be faced with still larger problems, mainly arising from expected very low solubility of YBCO in low-melting fluxes.

## 8. CONCLUSIONS.

The problems in crystal growth and epitaxy of YBCO based on its limited thermal and chemical stability and on its low solubility explain why so far only relatively small and thin crystals could be obtained. In comparison, the  $La_{0.85}Sr_{0.15}CuO_4$ -phase has higher thermal stability and a very high solubility (in excess CuO) so that large crystals could be achieved by top-seeded solution growth in acceptable time.

Another problem for YBCO is the non-availability of the relevant phase diagrams and the difficulty to determine them. Therefore it was only recently possible to achieve fully liquid solutions and to separate the grown crystals from residual flux. With this result it should be in principle possible to obtain large crystals and layer deposition by LPE, possibly by applying new technologies.

Perhaps the biggest problem is twinning for which the possible solutions were indicated. In view of the great difficulties in connection with YBCO it may be worthwhile to look for an alternate way to obtain superconducting crystals and layers with a similarly high (or still higher)  $T_c$  and with the potential of high current densities for applications: to an interdisciplinary search for a compound and a structure with high thermal and chemical stability and without twinning problem.

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