Zeitschrift: Helvetica Physica Acta
Band: 61 (1988)
Heft: 4

Artikel: Crystal growth of the high T_C superconductor YBa_2Cu_3O_7-x
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DOI: https://doi.org/10.5169/seals-115951

Helvetica Physica Acta, Vol. **61** (1988) 470–477

0018–0238/88/040470–08$1.50 + 0.20/0

Crystal growth of the high T_c superconductor $YBa_2Cu_3O_{7-x}$

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(30. XII. 1987)

In honor of Martin Peter's 60th birthday.

Abstract. Some experiments on single crystals growth of the high T_c superconductor $YBa_2Cu_3O_{7-x}$ are discussed in particular one which allows us to grow small twin free single crystal. An original growth method by phase separation is presented as well as a simple device to measure the transition temperature of very small particle.

Since the recent discovery of high-T_c superconducting oxides by Bednorz and Müller [1], a huge number of papers has been published on these compounds. Most part of the experiments has been done on ceramics because they are relatively easy to synthesize. However very soon people try to grow single crystals of those compounds in order to observe anisotropic properties and also intrinsic properties which can be masked by a granular structure. For instance one needs single crystals to investigate the electronic structure by the two dimensional angular correlation of the positron annihilation radiation, a field where M. Peter is one of the world pioneer. Rapidly one has realized that it is not easy at all to grow single crystals of this type of compounds. They decompose before melting, are chemically very reactive with almost all crucible materials and show structural phase transformation. With such properties we can only use recrystallization, solution precipitation or vapour phase transport technics to grow single crystals. The first crystal growth experiments have been done on La–Sr–Cu oxides where Bednorz and Müller found superconductivity at 35 K. However very rapidly people turn on to the Y–Ba–Cu oxides where Wu et al. [2] found superconductivity above 90 K. In this system, Cava et al. [3] found that the superconducting phase is an oxide with formula $YBa_2Cu_3O_{7-x}$ which will be abbreviated by YBCO from now on. The crystal structure which is an orthorhombically distorted oxygen deficient perowskite has been first determined by François et al. [4] and Capponi et al. [5]. In this paper we will focus on crystal growth experiments of this compound.

Differential thermal analysis and X-ray diffraction on quenched YBCO ceramic shows that this compound melts peritectically at 1040°C [6]. The partially

melt high temperature state is a mixture of Y_2BaCuO_5 (the green phase), BaO et CuO. The room temperature crystal structure of $YBa_2Cu_3O_{7-x}$ is orthorhombique for $x < 0.5$ [7] but there is a reversible orthorhombique to tetragonal phase transition close 750°C [8]. This phase transition is responsible for the presence of twins if the crystal has been grown in the tetragonal state. In order to get twin free crystal one has to find a solvent which allows to perform the growth process below the transition temperature. At present time however, nobody has reported to have found such solvent. Moreover several authors (Holzberg et al. [9], Schell et al. [10], Zhou et al. [11]) report to have no success with the common low temperture fluxes like PbF_2, KF, PbO, B_2O_3 and Bi_2O_3. Schell [10] reports that vapour transport experiments via fluoride atmosphere were unsuccessful. The only fluxes which give, up to now, positive results are CuO or a mixture of CuO and BaO, that means that we have to start with off-stoichiometric mixture in the quasi-ternary diagram Y_2O_3–BaO–CuO. We found in the isothermal sections of this diagram, between 950 and 1000°C, a region of partial melting as shown in Fig. 1 [12]. At our knowledge, all growth process have been done in the intersection of this region and the triangle which has $YBa_2Cu_3O_{7-x}$–$BaCuO_{2+x}$–CuO as apex. Table 1 summarizes the growth parameters and main results that we have found in published papers or preprint directly sent to us.

A striking feature that we observe in Table 1 is that apart Takei et al. [16], all authors get the same type of crystal having a platy form with size of the order of one millimetre and thickness of the order of 0.1 mm independently of solvent composition and growth temperature. As far as the crucible material is concerned it seems that contamination is more severe for alumina than for platinum above

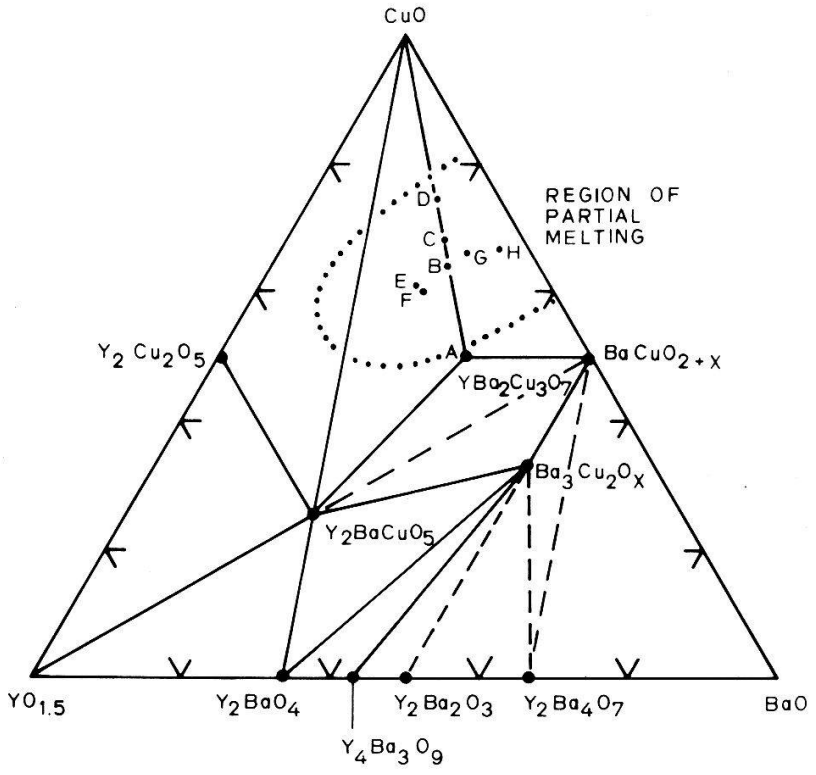

Figure 1
$YO_{1.5}$–BaO–CuO quasi-ternary phase diagram [12] between 950 and 1000°C.

Table 1

Authors (et al.) [ref.]	Composition [mole fraction]	Heat Treatment start/end [° Celcius] rate of decrease [°C/hour]	Material of the crucible Atmosphere	Crystal size [mm] T_c (as grown) [K]
Damento [13]	YBCO/CuO = 0.425	1150 then quenched 900 for 4 days	platinum air	1 × 1 × 0.2 89
Hayashi [14]	YBCO/CuO = 1/3	1250/1236 1	platinum air	1.5 × 1 × 0.2 78
Hidaka [15]	YBCO/CuO = 3/2	1400/? 3.3	platinum air	1 × 2 × 0.1 75
Takei [16]	YBCO/CuO = 1/3 to 3/1	1200–1050/700 15	alumina or platinum oxygen	5 × 5 × 5 91.3
Haneda [17]	Ba:Y:Cu =1.91:1.09:3.0	1400/600 11	alumina air	1.5 × 1.5 × 0.1 70 to 91
Kaiser [18]	YBCO–$BaCuO_2$–CuO Ba/Y = 9/I mole fraction CuO = 0.7	970/? 25	gold air	1 × 2 × 0.01 and 0.5 × 0.5 × 0.2 55 to 85
Scheel [10]	YBCO:BaO:CuO = 1:0.84:2.16	1040/? 10	alumina air	1.5 × 1.5 × 0.1 above 77
Schneemeyer [19]	$YO_{1.5}$–BaO–CuO Ba/Y = 4/1 with Ba + Y/Cu = 1/3, 5/12, 1/2, 2/3, 3/4 Ba/Y = 9/1 with Ba + Y/Cu = 1/2, 2/3 Ba/Y = 2/1 with Ba + Y/Cu = 1/2, 2/3	1000/880 4 to 15	alumina air	3.7 × 3.7 × ? 40
Zhou [11]	YBCO–BaO_2–CuO Ba/CuO = 1/3 to 2/5 YBCO/solvent = 0.6, 1.2, 2%	1000/850 4 to 10	alumina air	2 × 2 × 0.3 86

1100°C. The method of Takei et al. is a special case since these authors take care to avoid contact between the partially melt solution and the crucible. Finally one should notice that all crystals obtained were partially embedded in the flux and nobody has found a solvent which dissolve the flux but not the crystal.

We will now report on two experiments that have been done in our laboratory and which have given original results.

Twin free single crystals

When we have try the method proposed by Damento et al. [13], we have observed that after the heat treatment at 1150°C only a small fraction of the

charge seems to have been really liquid. In order to obtain a better melting we put the crucible in a RF furnace and increase the power without temperature control but observing the charge aspect. For a temperature estimated between 1200 and 1300°C, we had the feeling that the charge was fully liquid. We then shut down the RF power and let the curcible rapidly cool to room temperature. After this heat treatment we followed exactly the method of Damento et al. that means, holding the crucible at 900°C for 4 days followed by cooling at 1°C per minute to room temperature.

The upper surface of the solidified mass was found covered by small crystals with needle-like form and a typical size of $2 \times 0.1 \times 0.1\ mm^3$. Along almost each needle we found several very thin rectangular and square crystals (typically 100 μm edge and 1 to 3 μm thickness) with very flat and shiny surface as shown by the SEM picture of Fig. 2. By X-ray diffraction, the needles have been identified as CuO and the thin plates as YBCO. This has been confirmed by the typical colour observed under a polarized light microscope which also reveal the twin structure. Contrary to crystal grown under stress, many of those thin YBCO plates show only few domains such as it has been possible to isolate a twin free domain of manageable size. This peculiar structure has enabled Schmidt et al. to identify ferroelastic domain state and to study the optical properties.

As the oxygen environment in a twin plane maybe different than in the bulk, it should be interesting to measure the superconducting transition temperature on one of these thin plates. Unfortunately their volume ($<10^{-4}\ mm^3$) does not allow to use SQUID magnetometer or conventional inductive methods to detect the superconducting state. We have tried without success to measure the resistance

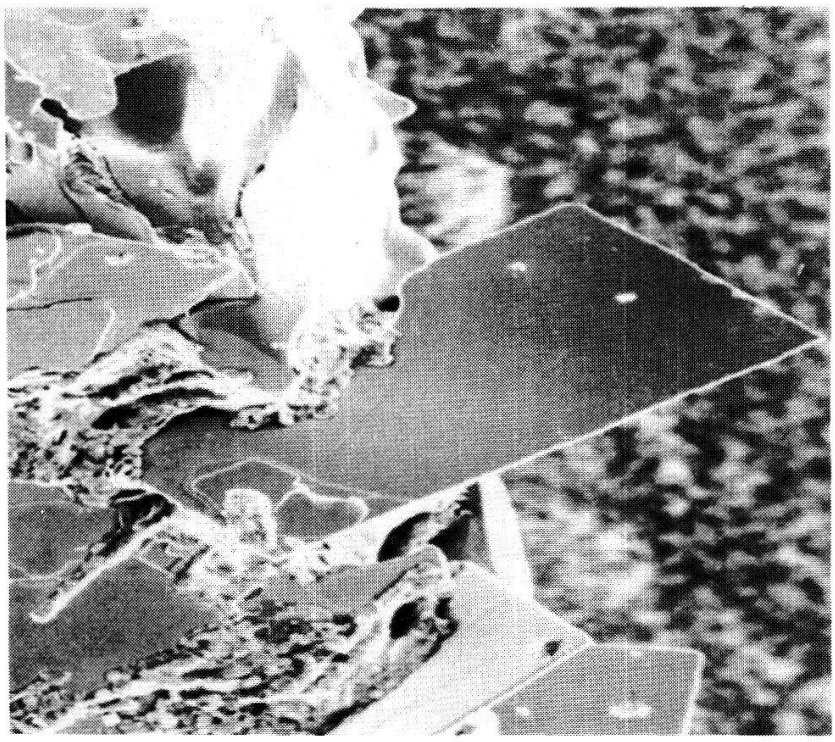

Figure 2
SEM picture of a $YB_2Cu_3O_{7-x}$ tiny plates which has grown on a copper oxide needle (size $100 \times 70\ \mu m^2$, thickness about 1–3 μm).

by the so-called 'flip ship' technics which consists to make 4 electric contacts by thermal diffusion between the crytal and 4 neighbouring metallic spots deposed by evaporation on an isolated substrate.

Since the discovery of superconductors with transition temperature above liquid nitrogen temperature, levitation has been very often used to demonstrate the superconductivity. This method allows only to know that the T_c of a sample is certainly above 77 K if the sample levitates or is perhaps below 77 K if it does not levitate. There is a similar method to detect superconductivity which consists to move a permanent magnet in the neighbourhood of the sample. This induces dynamically superconducting screening currents and as result of this diamagnetic effect there is a translational force in the field gradient of the magnet. Based on this principle we have designed the apparatus shown in Fig. 3 which allows to determine the temperature at which this translational force appears. The particle lays on a copper surface which can be cooled with liquid nitrogen or liquid helium. It is enclosed in a small vacuum-tight chamber where we can introduce helium gas to ensure good thermal contact with the crystal. We have found indeed that if the crystal is in vacuum, its temperature is higher than that of the cold surface due to poor thermal contact. The tightness at low temperature is ensured by a ultra-vacuum copper gasket. The magnet near the crystal is moved

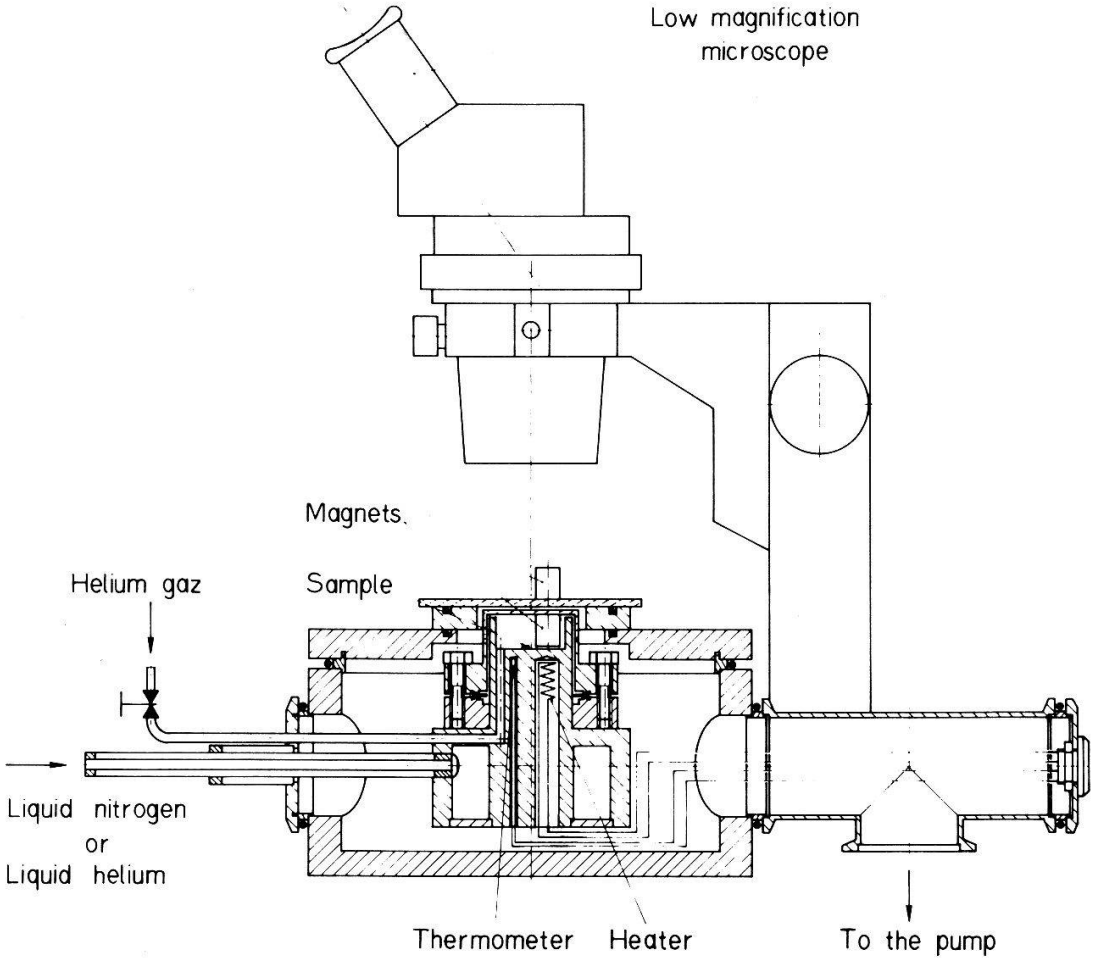

Figure 3
Device to measure transition temperature of a very small sample.

by influence with an external magnet through the two isolating windows. The crystal movements are observed by means of a low magnificafition microscope. The temperature is measured with a platinum resistance and can be stabilized by means of a heater. The reproducibility of the temperature at which the particle starts to move is better than one degree. By calibrating our apparatus with samples that have been measured which a conventional ac susceptibility method, we find that the temperature obtained corresponds to the lower beginning of the inductive transition, that means about 1 degree below the middle of the transition. This lowering of T_c is due to the magnetic field of about 200 gauss applied to the sample as shown by Junod et al. [21]. In the case of the thin crystals we obtain a transition temperature of 57 K. However one should notice that the crystals have been severely damaged by humidity during the 6 months between crystal growth and the measurements. Earlier experiments in liquid nitrogen have shown that T_c at the beginning was higher than 77 K [20].

Crystal growth by liquid phase separation

The growth mechanism in all methods cited at the beginning of this paper is still not well understood. It is different from the conventional solution growth since in this case the system is never completely liquid. Many authors suppose that the low-melting liquid acts to transport materials to the growing crystal rather than the crystals being formed by precipitation. With the goal to see what happens if we try to separate the liquid phase, we have done growth experiments in alumina crucible having the geometry shown in Fig. 4. In case a, we place a reversed small crucible in the main crucible and put the mixture in the space between the two crucibles. In this way the liquid phase can flow through the slits which are present at the contact between the two crucibles. In case b, the mixture is put in a crucible which has a conical bottom and a small hole at the lower part. The liquid phase has then the possibility to flow in the lower crucible which supports the first. Geometry a has been applied to mixtures corresponding to point *B, F, G* in the composition triangle of Fig. 1 while geometry b has been applied to the mixture *E*. For each composition, the crucible was heated to temperature between 1150 and 1200°C at 100°/h and held at this temperature for two hours. After a rapid cooling to 1050°C, the temperature is slowly decreased

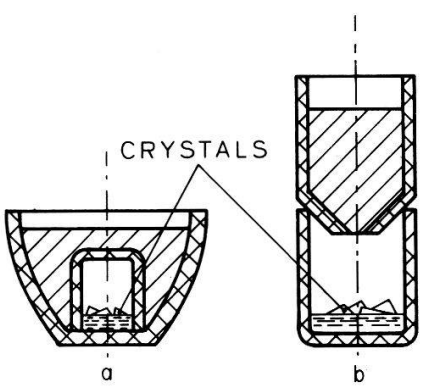

Figure 4
Crucible geometry to grow crystal by liquid separation.

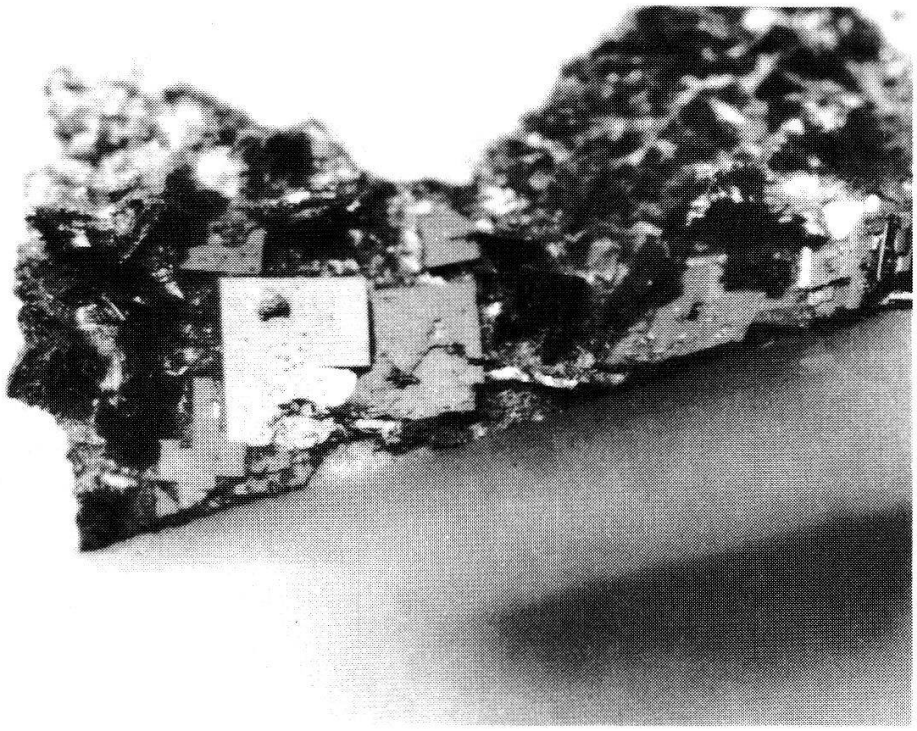

Figure 5
Photograph of $YBa_2Cu_3O_{7-x}$ (up to $2 \times 2 \times 0.3\,mm^3$) which have grown above the separate liquid.

at a rate between 7 and 60°/h with 2 hours plateaux every 50°. In all experiments we have observed that there was a separation of liquid and we found at the surface of the solidified liquid several platy square crystals with maximum size of $2 \times 2 \times 0.3\,mm^3$ as shown by the picture of Fig. 5. Unfortunately the crystals were either partially embedded in the flux or one face was totally glued to the flux and we could not determine a suitable solution to make these crystals free. The same experiments have been done without phase separation and in all cases we found much smaller crystals. This could indicate that crystallisation takes place really by precipitation from the liquid phase and that with our geometry, there is a smaller number of nucleation sites. The same type of phase separation has been tried with platinum crucible but in this case we get only small crystals. This difference can be understood since the liquid wets the platinum surface as it is now generally known.

With the apparatus of Fig. 3 we have found a transition temperature of 54 K for the crystals grown by phase separation. We have tried to increase this temperature by annealing the crystals under oxygen flow at temperature between 580 and 780°C. We do not observe a substantial increase as reported by many authors but have similar results as Haneda et al. [17] who report that the oxygen annealing degrades the T_c of their single crystals. At present time we do not understand why 2 similar growth process done in alumina crucible give such different transition temperature. It is possible that it is due to the purity of the alumina crucible. Powder X-ray diffraction done on our crystals shows tetragonal symmetry. However under the polarized light microscope we observe a small region which is anisotrope. That means that a small part of our crystal has the

orthorhombique structure responsible for superconductivity but this fraction is too small to be seen with the X-ray.

To conclude we have succeeded to grow very small crystals which are almost twin free and we have designed a simple apparatus to measure the transition temperature on only one of these very small crystals. The phase separation technique that we have developed to grow bigger crystals is promising but there are still some problems to solve.

We thank Dr. François for X-ray diffraction measurements, F. Liniger for the crystal picture, C. Chevalier for technical assistance and Prof. H. Schmidt for his help and stimulating discussions.

We are specially grateful to Professor Martin Peter for his constant interest and support to crystal growth which is a vital tool in solid state physics.

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