GROWTH OF SEPARATED $YBa_2Cu_3O_{7-x}$ CRYSTALS

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ABSTRACT

The problem of separating YBCO crystals from solidified residual melts could be solved by systematic growth experiments. Free crystals up to 7x7 mm^2 area and about 0.1 mm thickness could by obtained from a BaO-CuO solvent and small alumina crucibles. Superconductivity was revealed by levitation and Meissner effect.

INTRODUCTION

The peritectic melting of YBCO at around 1020°C excludes crystal growth from melts. Growth at tempertures below the decomposition temperature from high-temperature solutions, from the gas phase or from solid state is possible in very small ranges of experimental parameters only. In growth from high-temperature solutions the delicate nature of the oxidation states of copper imposes severe restrictions to the choice of solvents. The relatively low growth temperatures correspond to low YBCO concentrations in the solvents and thus to low growth rates in the generally diffusion-limited growth from solutions. However, the greatest difficulty in growth of YBCO was the problem to separate the crystals from residual flux. This limited the size of free crystals obtained in cavities within the solidified flux to a few tens or hundreds of microns. Large crystals of a few mm dimensions were occasionally found at the surface of the solidified flux [1] but could not be removed by dissolution of the flux due to the extreme sensitivity of YBCO to solvents and even to water. Another problem with the crystals cooled to room temperature is severe cracking which frequently leads to splitting off parts of the YBCO crystal plates. Perhaps this is due to the difference of thermal expansion coefficients of YBCO and flux.

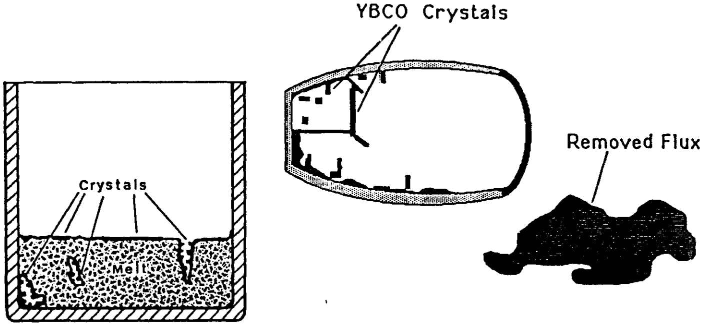
This paper describes the systematic approach for finding the optimum solvent and to establish the conditions for growth of relatively large crystals which can be separated from the growth solution as long as it is liquid. Magnetic susceptibility measurement and levitation experiments are briefly reported. When using platinum crucibles and relatively high temperatures a new platinum-rich phase was found which explained the severe corrosion of the platinum crucibles.

SOLVENTS FOR YBCO GROWTH EXPERIMENTS

The very high melting points of Y_2O_3 (2400° C), of $Ba_3Y_4O_9$ (2160°C), and of other Ba-Y-oxides and of ternary Ba-Y-Cu-oxides suggest to choose a solvent, in the ternary phase diagram BaO-Y_2O_3-CuO [1], which shows lower melting and which therefore is CuO- and BaO-rich. The eutectic at 870° C [2] between $BaCuO_2$/$BaCu_2O_2$ on the one side and CuO/Cu_2O on the other was chosen as the first solvent candidate. The complex melting and stoichiometry behavior of the YBCO compound [3] and the so far unexplainable results of preliminary DTA investigations suggested systematic crystal growth experiments for solving the flux-separation problem. Starting from the composition 25 mole % YBCO and 75 mole % solvent consisting of 28 mole % BaO ($BaCO_3$) and 72 mole % CuO, the composition was systematically changed for several series of growth experiments. The best result of the starting composition and the procedure described elsewhere [1] is shown in Fig. 1: the crystal of about 8x6 mm^2 area and 0.1 mm thickness was floating on the flux and thus shows cracks and mosaic. The temperature program of soaking the well-mixed mixture of the starting materials Y_2O_3, $BaCO_3$ and CuO, within small (8 ml) alumina crucibles, was fixed by the peritectic of YBCO and by the eutectic YBCO-flux: soaking was done at 1020° to 1040°C for 15 to 20 hours followed by slow cooling at a rate between 2°/hour and 10°/ hour to 900° ± 20°C where the residual melt was decanted. The final situation for the initial procedure when crystals were found in cavities and on the surface of the

Fig.1:YBCO crystal (mm grid)

Fig.2: Schematic view of first (a) and new (b) crystal growth experiment showing separation of flux from crystals.



(a) (b)

solidified flux only, is shown in Fig. 2a. The optimized procedure allowed decanting of the liquid so that crystals were in-situ separated from the flux: this is schematically shown in Fig. 2b. The maximum area of separated YBCO crystals obtained from the small crucibles so far is 7x7 mm^2. The surface morphology of the crystals reveals spiral growth mechanism; on (001) faces of small crystals of 2x2 mm^2 frequently a single growth pyramid and regularly spreading growth layers could be observed. This also indicates that in principle thick YBCO crystals can be grown.

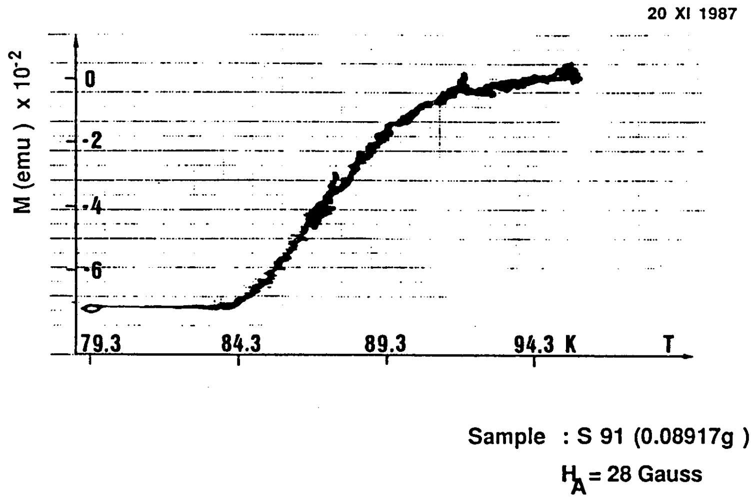
A pronounced cracking and twinning behavior was observed in the YBCO crystals, especially after the oxygen annealing procedure. This phenomenon was rarely observed in crystal growth of perovskites like $SrTiO_3$ or $KTaO_3$, only in cases of pronounced phase transitions like in $LaAlO_3$ and $NdAlO_3$ the formation of twin domains and occasionally cracks could be observed [4].

EVIDENCE OF SUPERCONDUCTIVITY

Single crystals and crystalline aggregates were annealed in oxygen following the usual procedure. Thereby it was realized that the temperatures and times used for ceramic pellets were sufficient for small and thin crystals whereas thick "large" crystals did not levitate. Perhaps they require much more time. Investigation of the optimum annealing procedure is planned; and also a dependence of oxygen diffusion on ordering and structural perfection can be expected.

An aggregate of crystals was tested for Meissner effect because the thin single crystals were still too small for the sensitivity of the available Foner vibrating-sample

Fig.3: Temperature dependence of magnetic susceptibility of a YBCO crystal aggregate at an applied field of 28 Gauss.



magnetometer. The magnetization of a sample cooled in an external field of 28 Gauss from 120 K to liquid nitrogen temperature is shown in Fig. 3. The negative susceptibility indicates superconductivity with a T_c of about 91 K.

Levitation experiments were carried out by the procedure published earlier [1]. An improved levitation test consisted of cooling a sample within a copper chamber mounted onto a helium-pumped cryostat. A $SmCo_5$ magnet lifted the crystalline sample which could be observed through gold-plated windows. By an intensive light source the black sample could be heated so that levitation was suppressed.

CONCLUSION

Separation of flux-grown YBCO crystals of nearly cm size from the residual melt was achieved, thus eliminating the barrier towards growing large crystals. The crystals were, after annealing procedure in oxygen, superconducting as revealed by both magnetic susceptibility measurements and levitation. One of the remaining problems now is twinning and cracking of large crystals when being oxidized and passing through the tetragonal-orthorhombic phase trasition. Possibly, epitaxial procedures or uniaxial stress on bulk crystals in the a or b direction during the cooling procedure could reduce the twinning problem in case twinning is not a condition for superconductivity.

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REFERENCES

1. H.J. Scheel and F. Licci, J. Crystal Growth, Special Issue on High-Temperature Superconductors, to be published in December 1987.
2. G. Balestrino, S. Barbanera, P. Paroli and G. Paterno, presented at the European Workshop on High-Tc Superconductors and Potential Applications July 1-3, 1987, Genoa, Italy (unpublished).
3. J. Hauck, K. Bickmann, F. Zucht, Z. Physik B - Condensed Matter 67, 299 (1987).
4. D. Elwell and H.J. Scheel, Crystal Growth from High-Temperature Solutions, (North-Holland Publishing Company, London-New York 1985) chapters 4 and 5.