



HAL
open science

ORIENTATION RELATIONSHIPS, MICROSTRUCTURE AND ELECTRICAL BEHAVIOUR OF GRAIN BOUNDARIES IN CERAMIC SUPERCONDUCTORS

J. Laval, C. Delamarre, M. Berger, C. Cabanel

► **To cite this version:**

J. Laval, C. Delamarre, M. Berger, C. Cabanel. ORIENTATION RELATIONSHIPS, MICROSTRUCTURE AND ELECTRICAL BEHAVIOUR OF GRAIN BOUNDARIES IN CERAMIC SUPERCONDUCTORS. *Journal de Physique Colloques*, 1990, 51 (C1), pp.C1-991-C1-996. 10.1051/jphyscol:19901154 . jpa-00230067

HAL Id: jpa-00230067

<https://hal.science/jpa-00230067>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

ORIENTATION RELATIONSHIPS, MICROSTRUCTURE AND ELECTRICAL BEHAVIOUR OF GRAIN BOUNDARIES IN CERAMIC SUPERCONDUCTORS

J.Y. LAVAL, C. DELAMARRE, M.H. BERGER and C. CABANEL

Laboratoire des Microstructures, CNRS-ESPCI, 10 Rue Vauquelin, F-75231 Paris Cedex 05, France

Abstract : The relationships between the crystallochemistry and the local electrical behaviour of grain boundaries in cuprate superconductors are considered. It is shown that the number of GBs with low electrical barriers should be drastically enhanced in order to increase the critical current. This could be reached by specific treatments to favour distributions of GBs including in particular low-energy coincidence [001] tilt boundaries.

Résumé : On considère les relations entre la cristallographie et le comportement électrique local des joints de grains dans les cuprates supraconducteurs. On montre qu'afin d'augmenter le courant critique la proportion de joints présentant des barrières électriques faibles doit être nettement augmentée. Il convient de favoriser une distribution de joints contenant en particulier des joints de flexion [001] de faible énergie grâce à des traitements spécifiques.

I. INTRODUCTION

There are reliable data which show that grain boundaries are detrimental for the superconducting properties of new ceramic superconductors. Particularly they induce a strong limitation for the critical current which is the key parameter for most applications. The first evidence is to be found in the comparison of the magnetization measurements for powder and sintered samples of $\text{YBa}_2\text{Cu}_3\text{O}_7$... It has been shown that, with or without an applied magnetic field, J_c remains 100 times greater in the powder than in the sintered samples. Similarly a comparison of thin films, either epitaxially grown on SrTiO_3 or textured with the c axis normal to the substrate and polycrystalline bulk samples brings out the bad performances of the latter relative to the former ($J_c \leq 10^3$ A/cm² versus 10^5 to 10^6 A/cm² for thin films). Moreover, the experiments of Dimos et al /1/ on YBaCuO bicrystals epitaxially grown on a SrTiO_3 bicrystal showed a catastrophic decrease of J_c with increasing misorientation between the two crystals.

One can assume however that for some special misorientations and specific interfacial planes the energy of the boundary will be minimized. Such minima should also occur in the chemical interfacial potential and consequently one could expect that these boundaries will exhibit low electric barriers, as has been found with other ceramics /2/, which is the first condition for obtaining favourable interfaces. The second condition is that the order parameter should be depressed only slightly at favourable interfaces. The last condition is that these boundaries should contain pinning centers to maintain a sufficient critical current under an applied magnetic field.

In order to check whether there could be some types of boundaries favourable for the transport of the supercurrent, we started to relate the microstructure of boundaries to their geometry (orientation relationships between grains, interface planes). The second stage of our comparison deals with the electrical behaviour of these different boundaries above T_c . The last stage considers the local behaviour of these boundaries in the superconducting state. In this paper, we first comment on the electrical behaviour of a grain boundary depending on its microstructure. Then we consider the microstructure of the different types of boundaries. Finally we discuss the possibility of adjusting the distribution of GBs.

II. ELECTRICAL BEHAVIOUR OF GRAIN BOUNDARIES IN CERAMIC SUPERCONDUCTORS

Fig 1 displays the three typical cases related to a specific microstructure. In case a, there is an intergranular phase which is thicker than the coherence length ξ ($s > 3\text{nm}$). Such a phase will always be a barrier for the supercurrent unless that phase is also superconducting. In case b, the intergranular phase is thinner than ξ : $0,3 < s < 3\text{nm}$. These boundaries will constitute Josephson junctions. The attenuation of the critical current

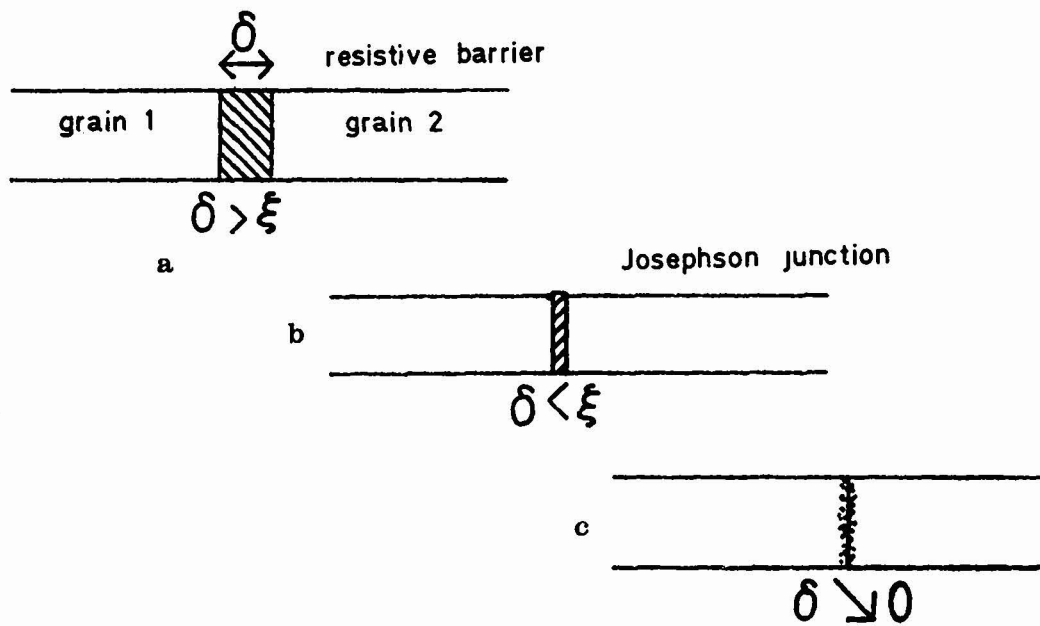


Fig. 1 : Schematic electrical behaviour of grain boundaries

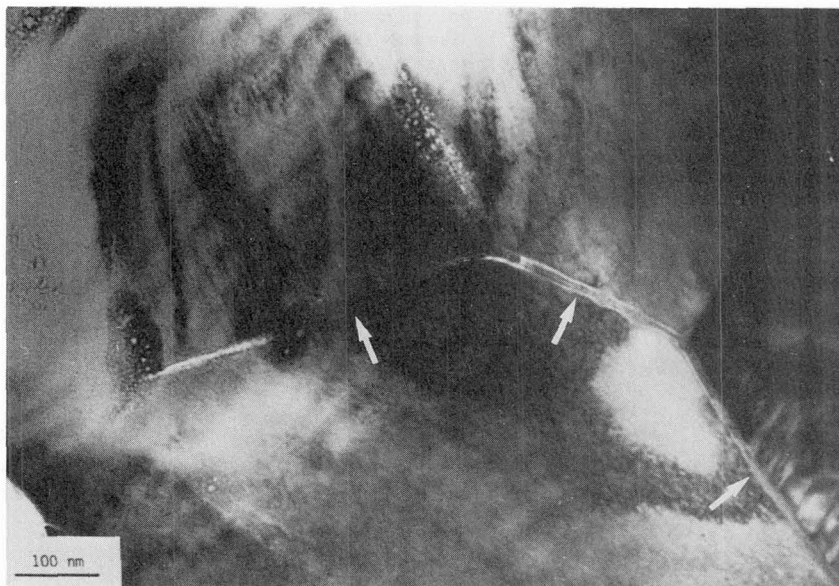


Fig. 2 : Intergranular phases on general boundaries

through such an interface is proportional to δ and to the resistivity of the second phase. Case c corresponds to the absence of an intergranular phase. This case is critical since in its "best" configuration (clean boundary, perfect registry between CuO planes), it could constitute "the" favourable path. In the other cases, the attenuation of the critical current will depend mainly on parameters such as segregation coefficient, interfacial atomic disorder and relaxation effects which are not easy to ascertain.

III. INTERGRANULAR MICROSTRUCTURE

The observations by transmission electron microscopy of samples coming from various laboratories evidence two types of GB's namely boundaries with or without a second phase. Furthermore, it appears that the presence and width of an intergranular phase depends on the orientation relationships between grains and on the interfacial plane. Thus, we attempted to relate the intergranular microstructure to the GB geometry.

In order to qualify the orientation relationships between grains we considered the occurrence of coincidence sites at GB's in the YBaCuO structure which are likely to give rise to low energy boundaries. Taking into account the high density of twinning within grains which correspond to the permutation between a and b, and the specific values of the parameters with $c \approx 3a$, we preferred to use a tetragonal cell Q with $a = b = 0.385$ nm and $c = 3a = 3b$ /3/. This cell equals a triple cubic cell a. It gives a closer idea of the real structure than an orthorhombic cell and, moreover, it is a good approximation which simplifies the determination of the coincidence index.

III.1. General boundaries

General boundaries often contain an intergranular phase which is either vitreous or crystalline (Fig.2). Its width varies from a few nm to a few tens nm /4/. Even if no second phase is visible, the high energy of these boundaries as well as the existence of numerous host sites will favour a strong segregation over a distance which can easily be greater than 3 nm.

III.2. Boundaries admitting (a, b) as interface plane

GBs admitting (001) as an interfacial plane are frequently observed. Their microstructure is often very similar to the one described in III.1. The intergranular phase is again glassy or crystalline and 10 to 30 nm wide /4/. In such cases there is no direct orientation relationships between grains.

In some cases these boundaries are clean. A very special case which is a high coincidence boundary with $C_1 \perp C_2$ and $\langle 100 \rangle_0$ as common axis is frequently encountered. It corresponds to Σ_3 for the tetragonal structure (it would be Σ_1 in the cubic structure) (Fig. 3a). Such boundaries are free of second phase and moreover they tend to present, along the (001) interface, a defect-free zone which can be a few tens nm thick (Fig. 3b). From these data, it can be inferred that boundaries admitting (a,b) as interfacial plane can be second-phase-free most probably the result of them being coincidence boundaries.

III.3. Coincidence boundaries admitting an interfacial plane different from (a,b)

Coincidence boundaries are rather frequent in this material. The most common beyond Σ_3 are Σ_5 and Σ_{13} . They are particularly interesting since they both correspond to a rotation of the two lattices around c which leaves the Cu-O planes parallel. They are usually clean. In fig. 4, it is seen that the glassy phase at the triple junction does not wet the Σ_5 boundary which means that the energy of the boundary is small. The energy of these boundaries will depend on the misfit to coincidence. Moreover, it appears that the most favourable cases will correspond to interfaces containing a high density of coincidence sites since they have the lowest energy and won't promote a noticeable segregation.

The observed occurrence of Σ_5 and Σ_{13} boundaries is in good agreement with the results of Smith et al /5/ who found 5 types of orientation relationships between melt-grown single crystals /6/ corresponding to $\Sigma_5, 13, 17, 29$ and 41 coincidence boundaries with a specific percentage ranging from 8 to 17 %.

IV. ELECTRICAL BARRIERS AT GRAIN BOUNDARIES

The voltage drops at grain boundaries were measured at room temperature with the same technique as that used for ferrite /7/. In order to avoid surface reactivity, the polishing of the samples ($1 \times 1 \times 6$ mm³) has been carried out in a non-aqueous medium (light oil). The samples were submitted to a dc voltage of a few volts. Voltage drops were in the

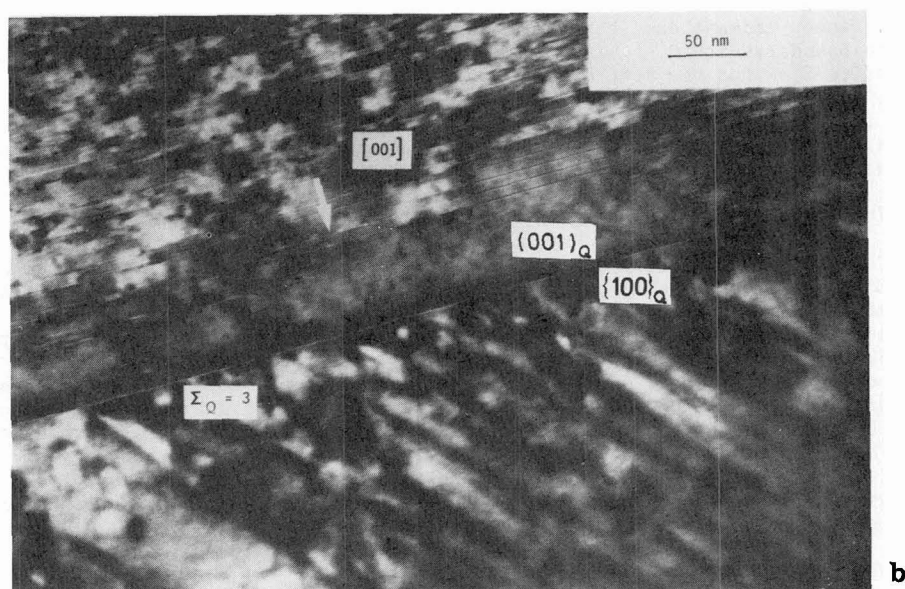
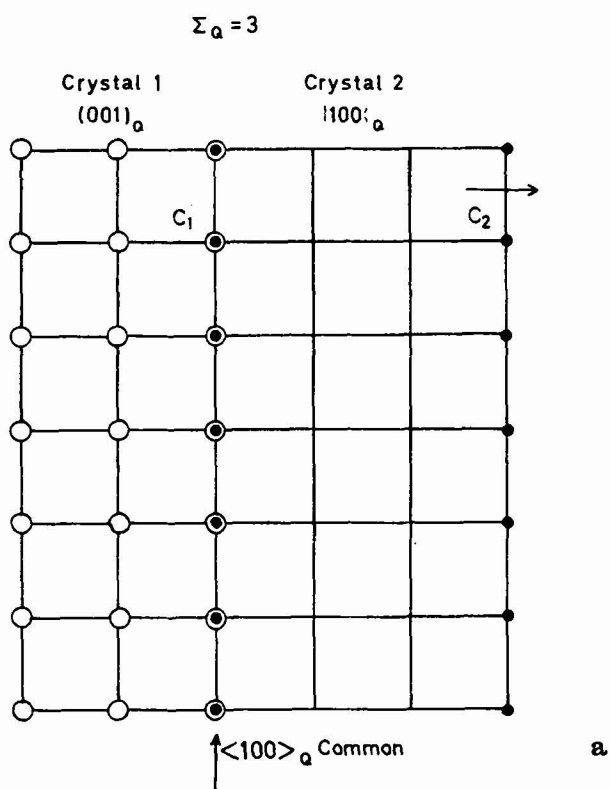


Fig. 3 : $\Sigma_3 = 3$ coincidence boundary
 a) projection of sites for crystal 1, 2 and common sites
 b) transmission electron image

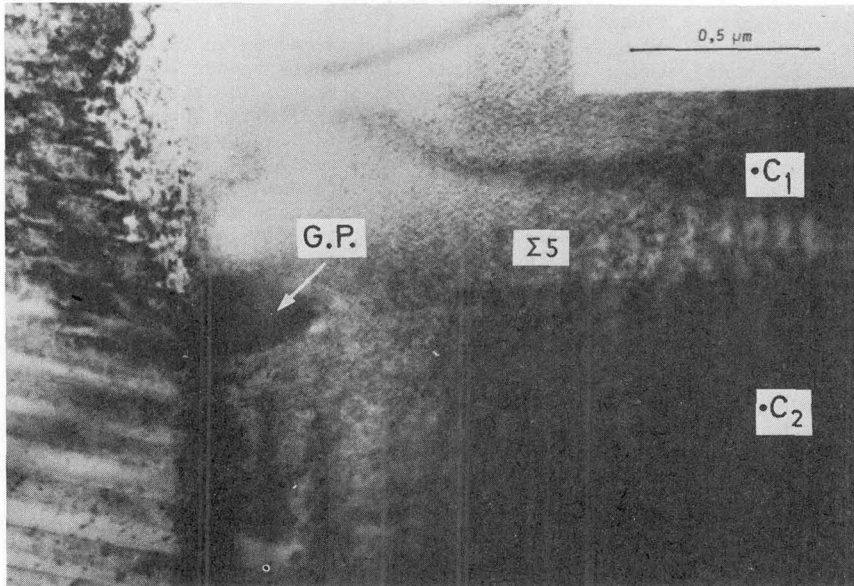


Fig. 4 : $\Sigma=5$ coincidence boundary. The boundary is "clean" : no wetting by the glassy phase (G.P.) at the triple junction

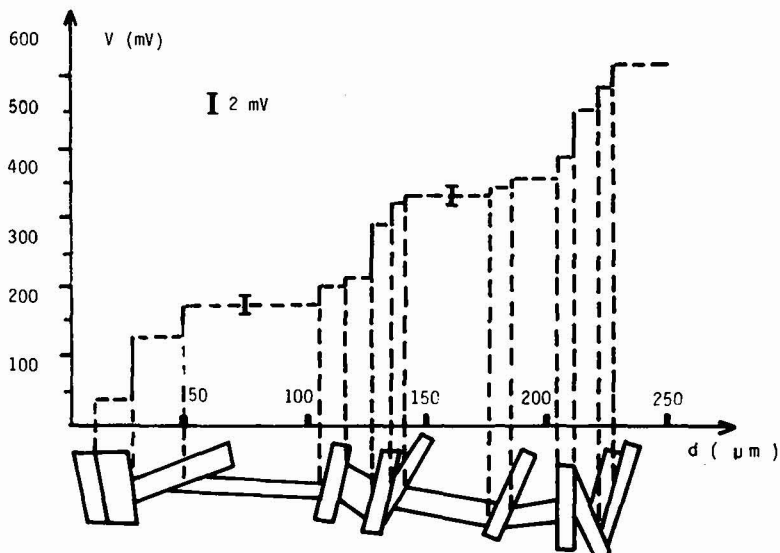


Fig. 5 : Voltage drop profile across consecutive boundaries on a YBaCuO ceramic prepared via the mixed oxide route

range 1-100 mV and were measured by means of tungsten microprobes. The sample microprobes were observed by optical microscopy.

Fig. 5 shows an example of the profile observed on an YBaCuO sample sintered the usual "mixed oxide" route. First, it is seen that boundaries usually present a potential barrier and that only a very small percentage of barriers (a few %) are less than 2 mV. It is therefore mandatory to reduce drastically the number of high barriers to now, the data obtained on non-textured polycrystalline samples show clearly that the number of boundaries with low barriers is always too small whichever process is used. On the other hand textured YBaCuO ceramics such as the one prepared by Jin et al /8/ must contain a high number of low barrier boundaries corresponding to low angle [001] tilt boundaries in order to exhibit high J_c ($J_c > 10^4$ At/cm² at 77 K at zero field).

V. DISCUSSION

From TEM observations it appears that general boundaries will be always detrimental for the transport of supercurrent. Since the supercurrent flows preferentially along planes, the favourable boundaries will be the one which preserve the parallelism and tie to one registry of these planes. Moreover they must concurrently -1) present low energy barriers at room temperature -2) depress only slightly the order parameter -3) be free of vortices. Such conditions could be matched only with low energy boundaries such that their effective width (corresponding to the distance where the chemical potential varies) should be smaller than the coherence length in a-b planes (< 3 nm). Low angle coincidence [001] tilt boundaries can be good candidates depending on the type of interfacial planes. Moreover, from our data on SrTiO₃ /9/, ferrite /2/ and WC /10/ and the results of Roshko et al on MgO /11/ one can assume that there is still some segregation on coincidence boundaries and particularly on secondary dislocations, which accommodate misfit to coincidence. Furthermore, from Chisholm et al /12/, it can be inferred that dislocation cores on [001] tilt boundaries are probably wider than 3 nm. Therefore dislocations which are likely to be decorated will act as pinning centers for flux lines.

Furthermore from the data of Smith et al (4) it can be seen that ≈ 50 % of tilt boundaries are coincidence boundaries. If a granular texture with 4 co-surrounding neighbours around each grain is assumed, then to insure a percolation path of favourable boundaries are needed. With 6 surrounding neighbours, 35 % of favourable boundaries only are required. It can thus be concluded that [001] tilt coincidence boundaries deserve a careful look. In order to test the superconducting properties of energy [001] tilt boundaries one must figure out their local behaviour from room temperature down to 5 K. We are now developing this local characterization capability by means of an electrical microprobe fitted in a helium-cooled cryostat.

There are probably other means than melt growth that could be successful in favouring [001] tilt low energy boundaries e.g. powder processing in a high magnetic field doping and liquid phase sintering as found in ferrite /2/. One can hope that by obtaining a specific distribution of GBs with a sufficient number of flux-pinning boundaries, critical currents as high as in single crystals could be obtained.

- /1/ D. Dimos, P. Chaudhari, J. Mannhart, F.K. LeGoues, Phys. Rev. Lett. 61 (1988) 21
- /2/ M.H. Berger and J.Y. Laval These Proceedings
- /3/ M.H. Berger, C. Delamarre et J.Y. Laval, à paraître Rev. Phys. Appl. (1989)
- /4/ J.Y. Laval, M.H. Berger, C. Delamarre, H. Zeng et A. Dubon, Revue Phys. Appl. 24 489
- /5/ D.A. Smith, M.F. Chisholm and J. Clabes, Appl. Phys. Lett. 53 (23) (1988) 2444
- /6/ D.L. Kaiser, F. Holzberg, M.F. Chisholm and T.K. Worthington, J. Cryst. Growth 85 (1987), 393
- /7/ J.Y. Laval and M.H. Berger-Pinet, J. de Physique (1986) C1-329
- /8/ S. Jin, T.H. Tiefel, R.C. Sherwood, M.E. Davis, R.B. Van Dover, G.W. Kammlott, F. Fastnacht, H.D. Keith, Appl. Phys. Lett. 52 24 (1988) 2074
- /9/ M.H. Berger, thèse (1989) Caen
- /10/ J. Vicens, A. Dubon, J.Y. Laval, M. Benjdir, G. Nouet, these Proceedings
- /11/ A. Roshko and W. D. Kingery, J. Am. Ceram. Soc. 68 (1985) C-331
- /12/ M.F. Chisholm and M.A. Smith, Phil. Mag. 59 (1989) 181