Intragrain pinning strength depth dependence of 2223 (Bi,Pb)-based high critical T_c superconducting ceramics made by a vitreous route

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Campbell's method for measuring the critical current in superconductors has been used to obtain the critical current density and the pinning strength in $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_{10-y}$ ceramics synthesized by a vitreous route. The intragrain critical current is much higher than 10^5 A/cm^2 at 40 K in zero dc magnetic field. A large increase of the pinning strength is observed near the grain surface. The decrease with depth is hyperbolic. The role of the precursors in the synthesis route is emphasized for introducing specific pinning centers. The analysis takes into consideration the ceramics granular nature, i.e., the existence of intergrain and intragrain currents. © *1995 American Institute of Physics.*

It is of great importance to increase the critical current of bulk 2223-based BiSrCaCuO ceramics (BSCCO) for many practical applications. The pinning strength of such BSCCO is known to be relatively low due to the lack of appropriate pinning centers in the bulk of the materials in contrast to point or line defects in YBCO ceramics. We have decided to use some material prepared by the so-called "multicomponent powder glass route."[1–5] This allows us to have some control on the geometry and also of the chemical nature on pinning centers, and on their distribution in the material.

We have measured the internal pinning strength inside the grains by applying a modified Campbell's method,[6] first obtaining the so-called flux profile[7] and then the critical current density. The effect of an external dc field has been investigated. The pinning strength is seen to decrease strictly hyperbolically in the grains. The role of *surface precipitates* is thus underlined. This points toward interesting possibilities for optimizing the pinning mechanism in such BSCCO systems. The obtained values are close to record high.

The vitreous route has already been used by our group in order to synthesize various 2223 Bi-based superconducting ceramics.[1–5] Other authors have also used the same kind of procedure. A large (nonexhaustive) list of references can be found in Ref. 5.

The process involves a so-called "crystalline precursor matrix" method based on the synthesis of separately quenched intermediate phases in a two-powder process. This procedure corresponded to "route 2" in Ref. 5.

The x-ray diffraction pattern of the resulting 2223 material showed a ~ *10%–90% mixture of 2212 and 2223 phases*. However, the 2223 phase was the main phase in the system.[5] The electrical resistivity curve[5] as a function of temperature showed a percolation path at 108 K, a residual resistivity of ~ 4 $\mu\Omega$ m, and a linear resistivity coefficient of 0.1 $\mu\Omega$ m/K.

Microstructural characterizations were performed on a Hitachi S2500 scanning electron microscope. The micrographs showed that the materials can be considered as a multitude of needle-like 2223 crystals of regular dimensions. (One should note that the 2212 phase only is present is the single phase $SrCaCuO_3$ crystalline precursor is prepared at 995 °C).[5] Close observation showed the presence of microscopic impurities incorporated in the main phase (indicated by a cross in Fig. 1). They are thought to be the 2212 intergrown phase in 2223 grains. Electron dispersive x-ray analysis can precise further the previous observations. It was found that precipitates at grain boundaries and in grains are Sr-, Ca-, and Cu-rich phases.[2]

In Ref. 5 we have reported the electrical, thermal, and thermoelectric properties of such systems. We concentrate here on the J_c and pinning strength values, their depth dependence and the related mechanism.

Campbell's method[6] consists in measuring the flux penetration (so-called "flux profile") for a cylindrical sample inserted in a magnetic field composed of a dc component and a small alternating superimposed signal.

The penetration depth p is defined as the difference between the radius R of the sample and the position reached by the magnetic flux in the sample. This penetration depth is easily obtained by considering the flux modification as a function of the magnitude of the ac field. We obtain the so-called Campbell's formula[6,7]

$$(p/R)=1-[1-(dS_{\text{supra}}/dh_{\text{ac}})/(2\pi\mu_0R^2)]^{1/2}, \qquad (1)$$

where S_{supra} is the signal measured by a small coil surrounding (wound on) the sample and h_{ac} the magnitude of the ac applied field. The inverse graph $h_{\text{ac}}(p)$ is known as the "flux profile."

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FIG. 1. Micrographs showing microscopic impurities incorporated in the main phase (indicated by a cross).

In order to take into account the granular nature of the ceramics, we have extended the above model.[7] We have shown that the flux profile has a knee structure from which the critical current J_{cg} can be found in the grains of mean radius R_g, as

$$J_{cg}=(dh_{ac}/dp)_{(p=p^*)}(R/R_g)(1-p^*/R), \qquad (2)$$

where p^* is the intersection of the straight line fitted to the high $h_{ac}(p)$ data with the $h_{ac}=0$ axis. The value of p^* gives the order of magnitude of the penetration depth averaged over the grains. In order to do so the critical state model is used. One should also point out a recent article where the critical state model has been applied to granular superconductors.[8] The analysis is however limited to describe the susceptibility without extracting quantitative data.

The critical current J_{cj} in the weak links can also be found from

$$J_{cj}\approx(dh_{ac})/d(p/R)_{(p=0)}(1/R)(p^*/R)[2-(p^*/R)], \qquad (3)$$

i.e., from the data lowest value range. Furthermore, the grain superconducting fraction f_g can be obtained from $f_g=[1-(p^*/R)]^2$.

In so doing the flux profile inside the grain can be extracted from the global flux profile. In other words, we can measure the penetration of the magnetic flux on the average *inside the grains*. The critical current of the grains as a function of the distance p_g inside the grain, $p_g/R_g=1-[1-p/R)/(1-p^*/R)]$, can thus be obtained.

In order to obtain these critical currents we need a large number of points since the derivative should be computed. We have used a multiple profile acquisition scheme with five runs of twenty points and a shift in the initial value of the ac field in order to obtain a set of one hundred data points.

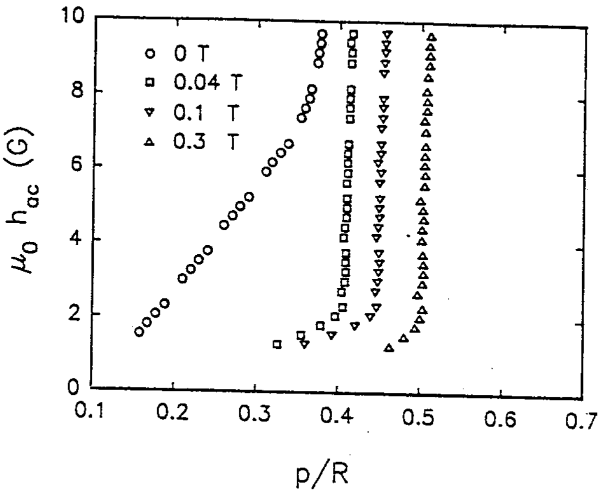

FIG. 2. Four flux profile for the $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_{10-y}$ sample taken at 40 K with dc fields ranging between 0 and 0.3 T. The knee structure is visible in this graph.

The flux profile for the $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_{10-y}$ sample prepared by the vitreous route was taken at 77 and 40 K in view of the superconductivity transition and of our cryostat limitations. For this measure the dc field was perpendicular to the ac field; the latter is maintained along the axis of the sample. The value of h_{ac} is at most 10 G. The 40 K results are shown in Fig. 2. Four flux profiles were taken for dc fields ranging between 0 and 0.3 T. The knee structure mentioned above is well visible in this graph. The slope in the low-field region is proportional to the critical current J_{cg} inside the grains.

In Fig. 3 the calculated critical currents in the weak links and in the grains are shown for both 77 and 40 K temperatures. The weak link critical current is greater than 600 A/cm^2 at low dc field and larger than 100 A/cm^2 at relatively large dc field at 40 K. The grain critical current is in the record high range for bulk materials (see values quoted for films in Refs. 9 and 10) between 10^4 and 5×10^4 A/cm^2 at 77

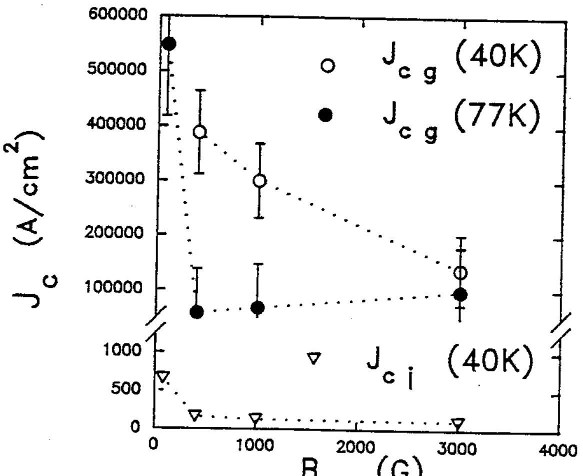

FIG. 3. Calculated critical currents in the weak links and the grains at 40 K and in the grains at 77 K. In all curves, an important increase of the intragrain critical current is seen at low dc field.

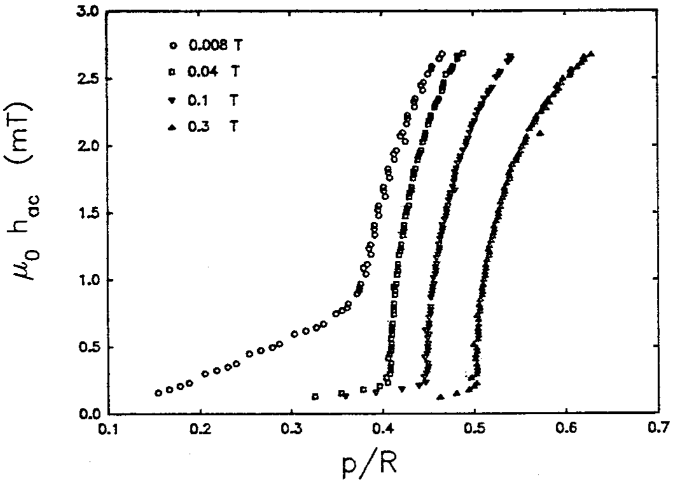

FIG. 4. Flux profile with high ac fields up to 30 G. A curvature of the flux profile in the grain region after the knee can be observed.

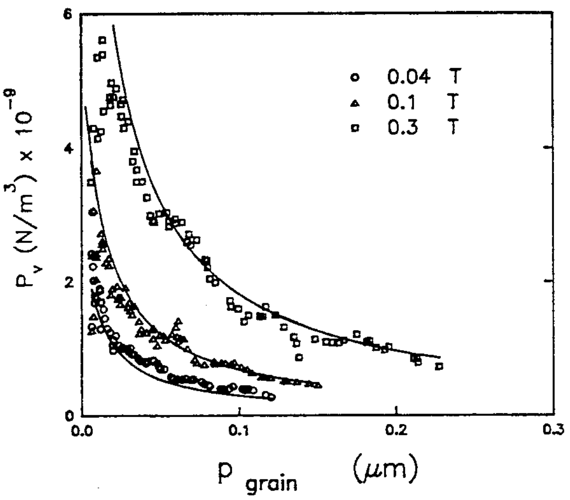

FIG. 5. Pinning strength P_v obtained by derivating the flux profile curves (proportional to the critical current J_{cg}). P_v increases when the dc field increases. A very large rise of P_v near the grain surface is observed.

K and $B=0$. In all curves, a large increase of the intragrain critical current is well marked at low dc field.

We also made other flux profile acquisition runs but with high ac fields up to 30 G. Furthermore, a large dc field was applied in the perpendicular direction. Obviously, the higher the dc field, more deeply the ac field influence is marked inside the grains. Figure 4 shows these results. A marked curvature of the flux profile in the grain response can be observed after the knee. We argue that such a feature is due to a reinforcement of the pinning mechanism near the surface of the grains, and confirm the importance of local micro and macrostructure[10] for improving pinning strength values. In order to do so, we subtract the weak link region and analyze the data. Since the derivative of the flux profile curves is proportional to the critical current J_{cg} and if we identify J_{cg} with the pinning strength P_v by $P_v=J_{cg}B$, where B is the dc flux density, we obtain the data of Fig. 5 which allows us some information on the depth dependence of J_c and of the pinning strength. It is seen that P_v increases when the dc field increases, as expected. More interestingly the very large rise of P_v near the grain surfaces should be noticed. We argue that the increase in pinning strength only arises from the presence of $SrCaCuO_3$ precipitates near the grain surface. These particles may thus act directly or indirectly as pinning centers.

The inverse of the pinning strength P_v vs p_g is almost a straight line given by $1/P_v=\kappa p_g+\psi$. The values of κ and ψ decrease when the dc field increases. In Fig. 5 we have shown the resulting data fit with these κ and ψ parameters. The pinning strength near the grain surface reaches a value $\sim 2.66\times 10^9$ N/m^3 at 0.04 T.

We have thus demonstrated that a reinforcement of the pinning strength near the surface of grains is observed. This is likely due to the presence of a $SrCaCuO_3$ crystalline phase near the grain boundaries.

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