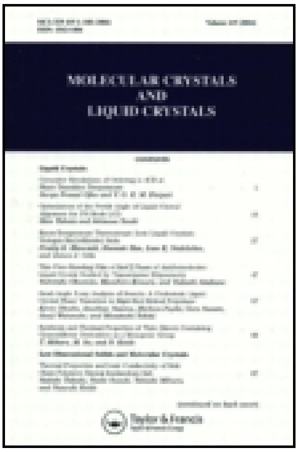

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Processing Effects on Microstructure, Flux Pinning and Critical Current Density of Cuprate Superconductors

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PROCESSING EFFECTS ON MICROSTRUCTURE, FLUX PINNING AND CRITICAL CURRENT DENSITY OF CUPRATE SUPERCONDUCTORS

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Abstract Magnetic hysteresis measurement on sintered Bi(Pb)SrCaCuO specimens consisting mainly of the 110 K phase and those partially or mainly containing the 80 K phase was performed. Their temperature and magnetic field dependences were compared in terms of the flux pinning behavior. At low temperatures near 4.2 K, magnetic hystereses were comparable to that observed in sintered $Ba_2YCu_3O_7$ and persisted, without significant degradation, up to 9 T. This suggested that the critical current density, J_c, can be intrinsically quite large. However, as the temperature was increased, the hysteresis and the corresponding J_c drastically decreased, possibly indicating its characteristic flux-lattice softening or melting behavior. In order to overcome this difficulty, we have examined doping of foreign ions such as Mg and Nb and found indications of clear improvement in the temperature and field dependence of the magnetization hysteresis.

INTRODUCTION

For the development of practical high-temperature superconducting materials, it is quite important to improve the critical current densities, J_c, under high magnetic fields. Since the J_c values of sintered bulk specimens are determined by the inter- as well as intra-grain critical currents, it is necessary to improve both parameters. It has been well known that the inter-grain J_c reflects the coupling strength of superconducting grains at grain boundaries and intra-grain J_c is determined by the pinning strength of magnetic flux lines by structural defects, such as twinning planes, dislocations and micro-precipitates within the grains. Therefore, J_c is expected to be strongly affected by the microstructure of the materials.

In a previous study[1] on the magnetization hysteresis measurements of Bi(Pb)SrCaCuO specimens heat-treated under various conditions, we have reported that the relative magnitude of the hysteresis or corresponding J_c values are larger for the 110 K high-T_c phase than those for the 80 K low-T_c phase, and that the former degrade more slowly than the latter with increasing temperature. Specimens containing both phases showed intermediate behavior of these two. In the present study, we discuss our previous data in a more or less quantitative manner in terms of flux pinning behavior and J_c. The second purpose of the present study is to examine the effect of introduction of foreign ions into the Bi(Pb)SrCaCuO system and to check whether the precipitated impurity phases could work as pinning centers for improvement of intra-grain J_c.

EXPERIMENTAL

Bi(Pb)SrCaCuO specimens were prepared by a conventional solid state reaction method using oxides or carbonates of each component metal as starting materials as described elsewhere[1]. For example, to prepare specimens having the highest content of the high-T_c 110 K phase, we adopted the starting composition[2] with a metals ratio of Bi:Pb:Sr:Ca:Cu:O as 0.90:0.21:1.0:1.0:1.6, respectively. This specimen was sintered at 850°C for 340 h. X-ray powder diffraction analysis indicated that it consisted of mostly the high-T_c phase and a small amount (about 10%) of lower-T_c 80 K phase plus some trace amount of other phases. The magnetic susceptibility measurement using SQUID showed T_c onset of 105 K and a Meissner fraction of about 60% (field cooling, 2.3 Oe) at 4.2 K.

In order to see the effect of impurity doping on the magnetization behavior, several kinds of foreign elements such as Mg, Nb or Ti were added in excess by mixing their oxides into the starting powders. Their doping levels were fixed at 20% with respect to Cu molar content. These specimens were sintered between 840°C and 850°C for a period of 72 to 350 h. After the sintering, they were subjected to powder XRD analysis and observation of their microstructures by a X-ray microanalyzer (XMA).

Magnetization hysteresis measurements were performed under a wide range of temperature using a vibrating sample magnetometer (EG&G Princeton Applied Research, Model 4500) equipped with a 12 T cryostat (Janis Research). At each temperature, magnetization M was measured first by increasing the magnetic field to a maximum positive value then by sweeping down to a negative maximum value and finally again to a positive direction. A constant field sweep rate of 20 mT/s was used throughout the present study.

RESULTS AND DISCUSSION

Figure 1 shows magnetization hysteresis curves measured over a wide range of temperature for the 110 K phase Bi(Pb)SrCaCuO specimen. The hysteresis ΔM is defined as the difference of M between the increasing and decreasing branches of the curves under a given field. At the lowest temperature (4.2 K), the hysteresis is substantial and extends to 9 T, the highest field applied in this study, without significant degradation. However, as the temperature is increased, it is seen to decrease significantly. For example, at 40 K, after a magnetic field of 3 T is reached, the hysteresis seems to disappear in the present scale of Fig. 1. At 60 K, ΔM vanishes in a similar manner at a much lower field, about 1.5 T.

In order to interpret the observed hysteresis data in terms of flux pinning and J_c, we apply the standard critical state model first given by Bean[3] with a slight modification. In the critical state model of the type-II superconductors, the gradient of the local magnetic flux density B(x) within a sample is given by

$$dB(x)/dx = \mu_0 J_p(B) \qquad (1)$$

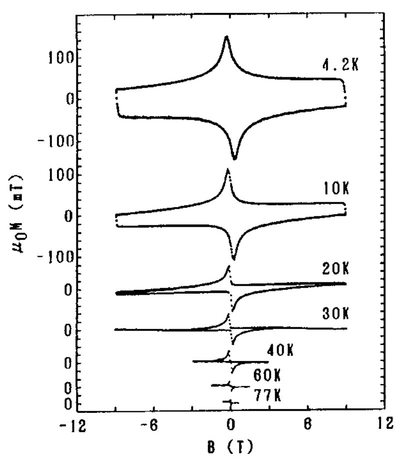

Fig.1: Magnetization Curves at various temperatures of the high T_c 110 K Bi(Pb)SrCaCuO.

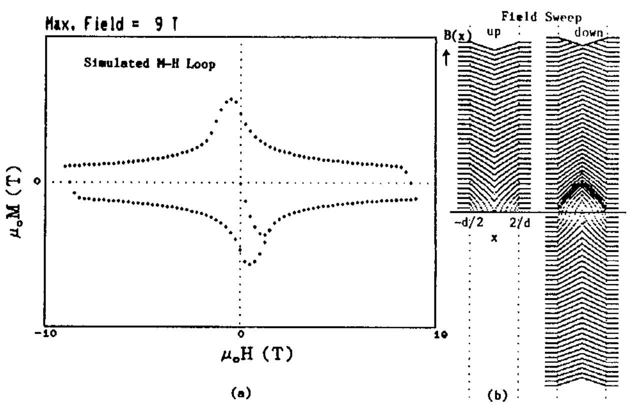

Fig.2: Simulation of magnetization hysteresis. (a)simulated M-H curve (b)distribution of magnetic flux density in a plate specimen with thickness d.

where μ_0 is the permeability of vacuum and $J_p(B)$ is the pinning current, under the local field B(x). In the original Bean's argument, J_p was assumed to be independent of B. In this case, if we consider the specimen is a flat plate of thickness d, it can be easily shown by integration of Eq.(1) along x,

$$J_p\ [A/m^2] = 2\ \Delta M\ [A/m]\ /\ d\ [m] \qquad (2)$$

where units are given in brackets for the sake of clarity.

Following this argument, if J_p is assumed to be really constant under any applied field, ΔM should also be expected to be constant. However, observed magnetization curves clearly show field dependences, reflecting the expected field dependence of $J_p(B)$. Let us assume alternatively that $J_p(B)$ is a function of B. As a trial, we have assumed that J_p is inversely proportional to the square root of B in Eq.(1) and performed a numerical simulation. The result is shown in Fig. 2. Fig. 2(b) represents the calculated distribution of B(x) along x direction for various external field during the sweep and Fig.2(a) is the expected M-H hysteresis loop by the present simulation.

It is readily understood that the calculated points explain the qualitative feature of the field dependence of magnetization reasonably well, as long as the hysteresis is finite. Another point to be noticed is that the dB(x)/dx which is proportional to $J_p(B)$ under a given external field is approximately constant except at very low fields. This means that we can still apply Eq.(2) to calculate J_p under various fields. Using the observed ΔM value of Fig. 1, for example, J_p at 4.2 K and under 5 T is calculated to be $6.3x10^5$ or $6.3x10^6$ A/cm^2, if we take d as 2 or 20 μm, respectively, from the examination of the microstructure discussed later.

By the preceding argument, it is now clear that experimentally observed $\Delta M(B)$ can be considered to be proportional to $J_p(B)$ except at very low fields. $J_p(B)$ appearing here is also regarded as the intragrain critical current density, $J_c(B)$. Therefore it is equivalent to consider $\Delta M(B)$ or $J_c(B)$ and their temperature and field dependences for a given specimen, while the distribution of grain size affect in the determination of the absolute value of J_c. Keeping this in mind, we proceed the discussion of J_c for different specimens in terms of ΔM.

Figure 3 demonstrates field dependence of ΔM at various temperatures for 80 K phase and 110 K phase samples. Since the grain sizes and their distributions are different between these samples, it is not possible to directly compare J_c values. However, it is quite clear that the 110 K phase sample has much weaker temperature dependence than the 80 K phase sample at high fields of several Tesla. This means that J_c of the 110 K phase degrades with increasing magnetic field more slowly than that of the 80 K phase.

Figure 4 shows temperature dependence of ΔM of the 110 K phase under various fields in a semi-logarithmic scale. ΔM is seen to decrease in an approximately exponential manner at low temperatures. However, as the temperature is increased, they start to deviate downwards around 20 to 30 K. It should be noted that the inflection temperature is a function of the applied field; it deviates at lower temperature in higher fields.

In order to compare this behavior with other high-T_c systems, a similar plot was made for various samples under a fixed field of 1.5 T and presented in Fig. 5. The figure contains data for the 110 K phase, 80 K phase as well as a $Ba_2YCu_3O_7$ (denoted as BYCO hereafter) sintered

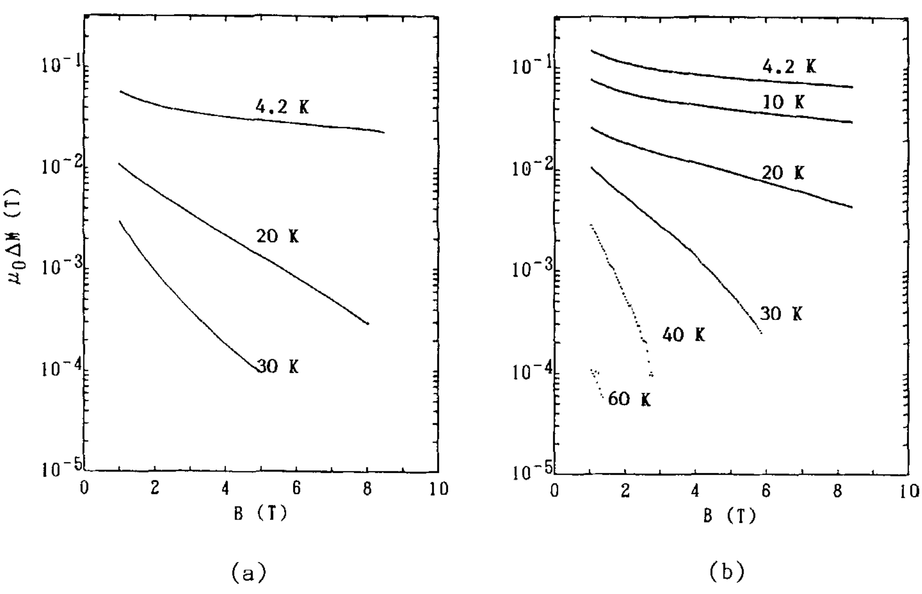

Fig.3: ΔM vs. magnetic field at various temperatures of (a) 80 K low T_c sample and (b) 110 K high T_c sample.

specimen prepared in a standard procedure. Also included is a data for a BYCO single crystal reported by Senoussi et al.[4] It is quite interesting that the slopes of ΔM (in the logarithmic scale) vs. temperature are not particularly different for these specimens, although closer examinations reveal that they increase in the order of the Bi-80 K phase, the Bi-110 K phase and the BaYCuO system. This implies that at low temperatures below 20 K, all systems exhibit quite similar flux pinning behavior. However, more important difference is the deviation of ΔM from the exponential behavior at high temperatures. More specifically, in the BYCO single crystal the inflection is seen at over 50 K, much higher temperature than the Bi system.

According to Gammel et al.[5], the so called flux-lattice melting occurs at around 75 K in a BYCO crystal and at 30 K in a Bi 80 K crystal. Since our observation of the break-down of logarithmic temperature dependence of magnetization hysteresis is fairly consistent with their study in terms of temperature ranges, it is considered that we are observing the same phenomena, flux lattice melting or at least softening of the flux lattice in our measurements.

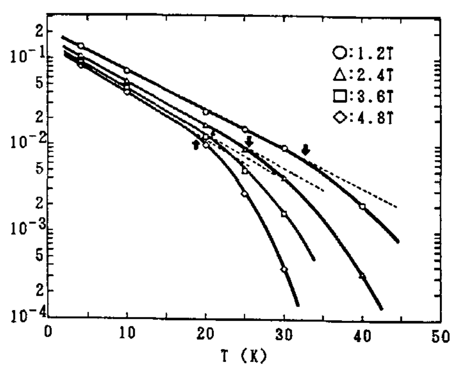

Fig.4: ΔM vs. temperature of 110 K phase sample at various applied fields.

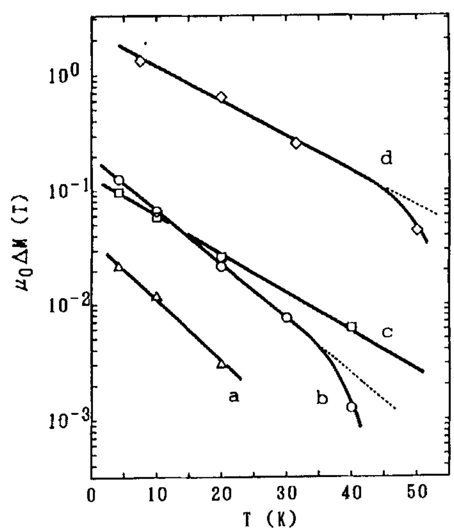

Fig.5: ΔM vs. temperature at an applied field of 1.5 T.(a)80 K phase (b)110 K phase (c)sintered BYCO (d)single crystal BYCO (after Senoussi et al.[4])

In the case of the Bi system, therefore, the flux pinning is rather weak at higher temperatures over around 30 K and it is crucial to introduce some pinning centers in order to improve J_c. Figure 6 shows the experimental results for the temperature dependence of ΔM obtained in the MgO and NbO doped Bi(Pb)SrCaCuO samples. In the case of MgO doping shown in Fig. 6(a), it is seen that the temperature and field dependence of ΔM is improved when it is compared to the non-doped sample shown in Fig. 3(b). For example, at 40 K under 3 T, ΔM of the MgO-doped sample is about three times compared to the non-doped sample. While the Nb-doped sample exhibits much smaller ΔM at 4.2 K, it becomes comparable to non-doped sample at 60 K as shown in Fig. 6(b). Therefore, we have concluded that the doping of impurity ions to introduce microprecipitates should be effective in improving the flux pinning.

However, observation of microstructure of several samples studied here by XMA revealed that they contain various phases, 80 K phase, native impurity oxides or complex compounds in addition to the desired 110 K phase in a very complicated manner.

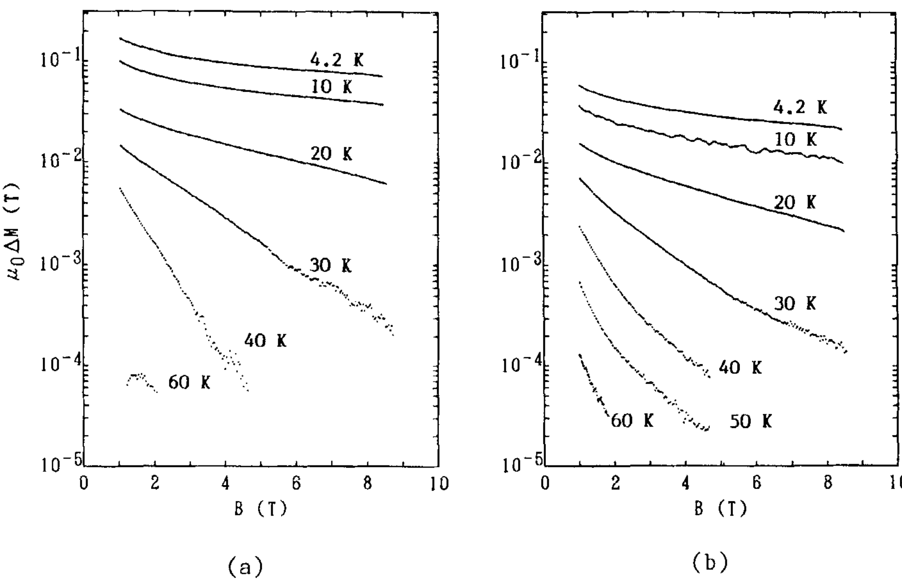

Fig.6:ΔM vs. magnetic field at various temperatures of (a) Mg doped and (b) Nb doped Bi(Pb)SrCaCuO samples.

Among them, the best sample in terms of microstructural appearance has been the MgO-doped system shown in Fig. 7. In this specimen, the 110 K phase was well developed and distributed, as in the case of the non-doped sample. The typical grain size of each crystal was about 20 to 30 μm long with 2 μm in thickness. Pure MgO oxide was found to be distributed as typically 2 μm spherical particles. Although XMA analysis cannot detect much finer particles within the 110 K phase grain, it is well expected that they do exist in a more microscopic scale. More efforts in search of effective impurity ions through optimization of the heat treatment and submicroscopic observation of specimens such as by transmission electron microscopy, should be necessary.

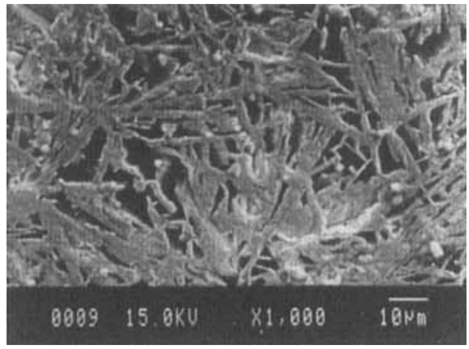

Fig.7: Secondary electron image of microstructure of Mg doped Bi(Pb)SrCaCuO sample.

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