High Critical Current Density in the High-Tc Superconductor: Generation of Efficient Pinning Centers (SOLID STATE CHEMISTRY-Multicomponent Materials)

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High Critical Current Density in the High-$T_c$ Superconductor: Generation of Efficient Pinning Centers

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We have found novel flux pinning centers in high-$T_c$ oxide superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ with $T_c = 80$ K that dramatically increase the critical current density ($J_c$). Single crystals with a large amount of Pb substituting for Bi were grown by the floating zone method, and their magnetic properties and microstructures have been studied by means of SQUID magnetometry and electron microscopy. $J_c$ increases remarkably beyond a critical Pb content of ~0.4 per formula unit, where characteristic two-phase microstructures are revealed by high-resolution electron microscopy: The “single” crystals consist of alternating thin (several tens of nanometers) lamellar plates of two phases with the (010) interface; one with lower Pb content (~0.4) and a modulated structure and the other with higher Pb content (~0.6) and a modulation-free structure.

Keywords: Copper oxide superconductor/ $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ / Pb substitution/ Microstructure

High temperature copper oxide superconductors (HTSCs) exhibit an unusual magnetic field - temperature ($H - T$) phase diagram which is quite different from that of conventional superconductors [1]. The major origin is strongly two-dimensional characters of HTSCs, as well as short coherence lengths and elevated critical temperatures ($T_c$’s), which substantially change the vortex state in magnetic fields perpendicular to the CuO$_2$ layers; vortex lines become ill-defined and transform into pancake vortices confined within the CuO$_2$ layers which couple only weakly between the layers. Then, the role of thermal fluctuation on the dynamics of vortices is enormously enhanced, and flux flow and flux-lattice melting occurs in a wide temperature range below $T_c$, resulting in a finite resistivity. From the viewpoint of practical applications it is particularly important to increase $J_c$.

Among the many HTSCs studied up to date, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Bi-2212) has been considered to be one of the most promising materials to be used as wires for cables and magnets because of its chemical stability and flexibility in manufacturing processing: the melt-texture growth technique has sufficiently improved superconducting coupling between polycrystalline grains, which is another factor limiting the actual $J_c$ value, and enabled to produce wires with relatively high $J_c$ values below 20 K. However, one serious problem is that $J_c$ decreases drastically above 20 K in magnetic fields. This arises from the breakdown of the zero-resistive state due to thermally activated flux flow. Suppression of the flux flow is particularly serious for this compound because of
its inherent 2D anisotropy. There is no doubt that large-scale applications would be accelerated by finding an appropriate solution to overcome this obstacle.

A key to increase $J_c$ is to generate efficient pinning centers in crystals. Recent studies using heavy ion irradiation have clearly exemplified that aligned columnar defects serve as flux pinning centers. However, these methods are rather formidable and not useful in practical material processing. We believe that an alternative breakthrough to generate efficient pinning centers in a more practical and useful way is necessary for future large-scale applications.

We have studied the single crystal growth of Bi-2212 and found that the partial replacement of Bi by a large amount of Pb remarkably affects the magnetic properties of Bi-2212 [2]. Single crystals of Pb-substituted Bi-2212 were grown from starting compositions $\text{Bi}_{2.2-x}\text{Pb}_x\text{Sr}_{1.8}\text{CaCu}_2\text{O}_8\delta$ ($x = 0, 0.4, 0.6, 0.7, 0.8$) by the conventional floating zone (FZ) method with an infra-red heating furnace. The atmosphere used was 20% O$_2$ / 80% N$_2$, and the growth rate was 0.5 mm h$^{-1}$. Plate-like crystals of dimensions $1.0 \times 1.0 \times (0.03 \sim 0.04)$ mm$^3$ were cleaved from each rod and used for magnetization measurements. A remarkable enhancement in $J_c$ was found for large Pb content of $x \geq 0.6$. In addition, a characteristic lamellar structure was observed by means of high-resolution electron microscopy (HREM) only in crystals with $x \geq 0.6$. Figure 1 presents the HREM images of a typical fragment from the $x = 0.7$ crystal, where is seen a well-ordered zebra pattern composed of two kinds of lamellar plates; $\alpha$-phase plates with Pb poor composition (~ 0.4 per formula unit) as examined by EDX microanalysis and a modulated structure (periodicity of 11 ~ 12b) and $\beta$-phase plates with Pb rich composition (~ 0.6) and a modulation-free structure. Each plate has a thickness of several tens of nanometer, and the interface is always perpendicular to the b axis. It is noted that structural modulations in the $\alpha$-phase domains is considerably disordered, compared with those seen in uniform (Bi,Pb)-2212 crystals with less nominal Pb content. The lamellar microstructures found in the present study reminds us of eutectics and eutectoids cooled unidirectionally. They usually form either alternating lamellar plates or rods embedded in a matrix. Many examples have been known for metallic systems, while recently a large number of oxide-oxide eutectics have also been studied. As for cupric oxides, Revcolevschi et al. prepared an aligned eutectic structure made of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and CuO by a FZ technique. The lamellar morphology observed in our study is quite similar to those found in Pb-Sn, NiO-ZrO$_2$, and Fe(C)-Fe$_3$C.

The improvement in $J_c$ in the present heavily Pb-doped Bi-2212 single crystals must be due to an automatic, unintended generation of efficient pinning centers. The observed specific two-phase microstructures must be related to it. Since the interface always crosses the CuO$_2$ planes, the present microscopic two-phase structures must suppress the thermal fluctuation of pancake vortices more efficiently than randomly distributed point defects.

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Figure 1. Electron micrographs showing typical microstructures of the $x = 0.7$ crystal. The incident electron beam was parallel to the [101] direction so that the b axis was perpendicular to the incident beam. The zebra pattern seen in (a) is due to alternating stacking of two kinds of lamellas along the b axis, resulting from phase separation at high temperature. The dense fringes seen in the $\alpha$ domains in (b) visualize the structural modulations.