Dramatically Enhanced Flux Pinning Properties of Cation Composition Controlled Bi(Pb)2212 Single Crystals

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Abstract. Single crystals of Bi2212 and Bi(Pb)2212 having various cation compositions were grown by the floating zone method and evaluated their \( J_c \) characteristics after control of oxygen content by post-annealing. \( J_c \) characteristics of Bi2212 and Bi(Pb)2212 were found to be improved by control of cation compositions towards stoichiometric, Bi:Sr:Ca:Cu = 2:2:1:2. This means that nonstoichiometric cation composition in these systems suppresses inherent superconductivity possibly due to considerably disordered crystal lattice, resulting in poor \( J_c \) characteristics. Dramatically enhanced \( J_c \) were achieved for cation stoichiometric and small amount of Y or Lu-doped Bi(Pb)2212 single crystals. The highest \( J_c \) at 20 K observed were ~0.85 MAc㎡ -2 in self-field and ~0.1 MAc㎡ -2 under 5 T with \( H // c \). The dilute Y and Lu-doping is considered to introduce locally lattice-distorted regions acting as effective pinning sites up to high fields.

1. Introduction

The Bi-based cuprates, such as Bi₂Sr₂CaCu₂O₈ [Bi2212] and (Bi,Pb)₂Sr₂Ca₃Cu₄O₁₀ [Bi(Pb)2223] are most promising materials for practical use among numerous high-\( T_c \) superconductors. In addition, Bi₂Sr₂CaCu₂O₈ (Bi2212) single crystals have been widely used for basic physical studies, because large and high quality single crystals can be grown by the floating zone (FZ) method. However, its poor flux pinning properties above 20 K in magnetic field due to its large electromagnetic anisotropy prevent the practical use above 20 K under high-fields. For this problem, a large amount of lead doping and additional oxygen content control were found to be effective for dramatic improvement of flux pinning properties [1,2]. Large reduction of electromagnetic anisotropy [3,4] and introduction of effective pinning centers, such as locally weak superconducting region corresponding to the inhomogeneous distribution of lead ions and interfaces of lamella structure parallel to \( ac \)-plane are believed to contribute to the enhanced flux pinning properties. Recently, further enhancement of \( J_c \) of Bi(Pb)2212 was achieved by dilute doping of 3d-elements, such as Fe, Ni and Co, to the Cu site in our previous study, suggesting that local weak superconducting regions introduced by dilute (~0.5 %) 3d-element substitutions acted as effective pinning site in spite of decrease in \( T_c \) [5].

On the other hand, the Bi2212 is well known to have nonstoichiometry in both cation and oxygen compositions. In particular, synthesis of Bi2212 single crystals with the stoichiometric cation composition (Bi₂Sr₂Ca₄Cu₆O₁₉) by FZ method is difficult and single crystals with Bi-rich and Sr-poor compositions, such as Bi₂₁Sr₁₄Ca₁₃Cu₁₀O₇, were commonly grown and used for various physical
studies. Therefore, dependences of \( J_c \) characteristics of Bi2212 and Bi(Pb)2212 single crystals on cation and oxygen compositions have not been systematically studied yet.

Based on these backgrounds, single crystals of Bi2212 and Bi(Pb)2212 having various cation compositions were synthesized and evaluated their \( J_c \) characteristics after controlling oxygen content by post-annealing in the present study. After optimization of cation composition for Bi(Pb)2212 single crystals in terms of \( J_c \), further enhancement of \( J_c \) properties were attempted by dilute Y or Lu doping to the Ca site, which are expected to increase pinning force by generation of new point-defect-like pinning centers originated from the local lattice distortions without decreasing \( T_c \).

2. Experimental

Crystal boules with nominal compositions of Bi\(_{2.1}\)Sr\(_{1.9-x}\)Ca\(_{0.9+x}\)Cu\(_{2.0}\)O\(_y\) (\( x = 0, 0.1, 0.2, 0.3, 0.4 \)) and Bi\(_{2.0}\)Sr\(_{2.0}\)Ca\(_{1.0}\)Cu\(_{2.0}\)O\(_y\) were grown by the FZ method in air and under flowing mixed gas of 5%O\(_2\)/Ar, respectively. The obtained boules were annealed at 800°C in air for improving homogeneity of cation composition in the crystals. Plate-like crystals with typical dimensions of 1×1×0.05mm\(^3\), which were obtained by cutting and cleavage of the grown boules, were annealed at 400°C in air and quenched. The resulting crystals were in the carrier overdoped state. For the Bi(Pb)2212 system, crystal boules with nominal compositions of Bi\(_{1.6}\)Pb\(_{0.6}\)Sr\(_{1.8}\)Ca\(_{1.0}\)Cu\(_{2.0}\)O\(_y\) and Bi\(_{1.5}\)Pb\(_{0.6}\)Sr\(_{2.0}\)Ca\(_{1-x}\)RE\(_x\)Cu\(_{2.0}\)O\(_y\) (RE : Y \( x = 0, 0.001, 0.002, 0.003, 0.005 \); Lu \( x = 0, 0.002, 0.005, 0.01 \)) were also grown by the FZ method under flowing mixed gases of 20%O\(_2\)/Ar and 5%O\(_2\)/Ar, respectively. The obtained plate-like crystals from these boules were annealed at 400°C in \( P_{O_2} = 2.1 \) atm or at 600°C in \( P_{O_2} = 2.7 \times 10^{-4} \) atm and quenched in order to achieve the carrier heavily overdoped or the carrier lightly overdoped states, respectively. Cation composition of each single crystal was analyzed by the inductively-coupled-plasma (ICP) method. Superconducting properties were measured by a SQUID magnetometer (Quantum Design MPMS-XL5s) under applied fields parallel to the \( c \)-axis. \( J_c \) was calculated from the width of magnetization hysteresis loops using the extended Bean model. In-plane \( J_c \) anisotropy (\( J_c^a / J_c^b \)) of the Bi(Pb)2212 single crystals due to the interfacial pinning effect of the lamella structure was evaluated by the magneto-optical (MO) observations.

3. Results and discussion

3.1. Relationship between cation composition and \( J_c \) for Bi2212 and Bi(Pb)2212 single crystals

The ICP analyses revealed that cation compositions of Bi2212 and Bi(Pb)2212 single crystals were almost unchanged from their nominal compositions including the nearly stoichiometric one. Figure 1(a) shows the \( J_c-H \) curves at 20 K for the Bi2212 single crystals having various cation compositions. Both \( J_c \) and irreversibility field (\( H_{irr} \)) of Bi2212 were systematically improved by increasing Sr and decreasing Ca compositions at all the measured temperatures below \( T_c \). This suggested that the Sr/Ca ratio is one the crucial factors for determining \( J_c \) characteristics of Bi2212. The single crystal starting from the stoichiometric composition exhibited the best \( J_c \) performance. Although large difference in \( J_c-H \) properties between the single crystals and melt-textured tapes has been discussed for Bi2212 so far, our present results strongly indicated that the nonstoichiometric cation composition in the conventional Bi2212 single crystals seriously degraded their essential \( J_c \).

\( J_c-H \) curves for the heavily lead doped Bi2212 single crystals having different Bi and Sr compositions are shown in Figure 1(b). The Bi(Pb)2212 single crystal starting from nearly stoichiometric composition showed apparently higher \( J_c \) and \( H_{irr} \) similarly in the case of the Bi2212.
3.2. Dilute rare-earth metal doping effect on critical current density

Dilute doping of Y or Lu for Bi(Pb)2212 single crystals with nearly cation stoichiometric composition was discovered to lead further improvement of \( J_c \) characteristics. Their \( T_c \)'s were high above 85 K independent of the doping levels of Y or Lu. This is in contrast to the case of dilute 3d-element doping to the Cu site, in which \( T_c \) decreased largely with an increase of the doping level. Figure 2 shows the critical current properties for the Y and Lu doped Bi(Pb)2212 at 20 K. Doping levels lower than 0.2% for Y, and 0.5% for Lu were quite effective for enhancement of \( J_c \) of the nearly cation stoichiometric Bi(Pb)2212, while larger doping levels lowered \( J_c \) properties partially due to degradation of crystallinity. The best performance was recorded by the Lu 0.5% doped Bi(Pb)2212 crystal, which showed a high \( J_c \) of \( 8.5 \times 10^5 \) A/cm\(^2\) at 20 K in self field, and maintained high \( J_c \) above \( 10^5 \) A/cm\(^2\) even in 50 kOe. These \( J_c \) values apparently exceeded those of the melt-textured Bi2212/Ag tapes.

![Figure 1. \( J_c-H \) properties of (a)Bi2212 and (b)heavily lead doped Bi2212 single crystals with various cation compositions.](image)

![Figure 2. \( J_c \) characteristics of Y and Lu doped Bi(Pb)2212 single crystals at 20 K](image)

![Figure 3. Magnet optical images of Bi(Pb)2212 single crystals at 30 K in 1260 Oe, (a)Y-free and (b)Y-0.2% doped.](image)
The characteristic second peak effect in $J_c$-$H$ curves of the Bi(Pb)2212 are considered to be due to the field-induced pinning sites originated from the inhomogeneous distribution of Pb ions at 20 K. For this particular crystal, 0.5% Lu-doped Bi(Pb)2212, the second peak effect was almost hidden by large enhancement of $J_c$. In-plane magneto-optical images of Y-free and Y-0.2% doped Bi(Pb)2212 single crystals at 30K are shown in Fig. 3, which are taken under an external magnetic field of 1260 Oe applied parallel to the c-axis after cooling to 30 K in zero field. The angle of current discontinuity line, for the Y-free single crystal was 62.3°, meaning the in-plane $J_c$ anisotropy ($=J_c^a/J_c^b = \tan\beta$) of ~1.9. This is due to the interfacial pinning of the lamella structure effective below ~1500 Oe. On the other hand for a 0.2% Y-doped single crystal, the observed $J_c$ was 58.8°, which corresponded to $J_c^a/J_c^b$ ~1.65. The observed small in-plane anisotropy indicated that the interfacial pinning of the lamella structure is not predominant in the dilute Y-doped crystal. Above these results strongly suggests that strong point-defect-like pinning sites were successfully introduced by the moderately dilute Lu or Y doping for the Bi(Pb)2212.

The $J_c$ characteristics of the Bi(Pb)2212 single crystals was dramatically improved when the Y or Lu concentration was far lower than 1 %. This concentration corresponds to the mean distance of these rare-earth elements longer than twice of coherence length ($d > 2 \sqrt{ab}$). In other words, local weak superconducting regions dispersed in the inherently strong superconducting matrix acted as effective isotropic pinning centers. Slight difference in the optimal doping levels for Y and Lu in the starting compositions was found to be explained by the their actual concentrations in the grown Bi(Pb)2212 crystals through by the careful ICP analyses. The actual Y concentration was found to be approximately double in the grown crystal, while it was almost unchanged in the Lu-doped crystals.

4. Conclusions

Effects of compositional control of cations on the flux pinning properties of undoped and heavily lead doped Bi2212 single crystals were systematically studied. Nonstoichiometry in cation composition is found to strongly affect both $J_c$ and $H_{irr}$ and crystals with nearly cation stoichiometric compositions exhibited the highest critical current performance. Furthermore, approximately 0.5% doping of Y or Lu to the Ca site dramatically improved $J_c$ characteristics of Bi(Pb)2212 single crystals from low fields to high fields. The highest $J_c$, $8.5 \times 10^5 \text{ A cm}^{-2}$, was recorded by the Lu 0.5% doped Bi(Pb)2212 single crystal. Magneto-optical images taken for Y-free and dilute Y-doped Bi(Pb)2212 crystals suggested that strong isotropic pinning center were successfully introduced by the dilute rare earth doping for Ca site.

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