Novel Functions of Silver on Superconducting Properties for RE123 Melt-Solidified Bulks

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Abstract. The intrinsic effects of Ag-addition on crystal structure and superconducting properties of Y123 melt-solidified bulks have been investigated. Increased c-axis length and decreases of maximum $T_c$ and carrier density caused by Ag-addition suggested the incorporation of Ag into the Y123 matrix, in which Ag$^+$ was considered to substitute for Cu ion of Cu-O chain. It was also found that Ag-addition enhanced $J_c$ properties all applied fields at 77 K. The distinct second peak of $J_c$ observed for the Ag-added bulk suggested that the Ag-incorporated regions acted as effective pinning centers under disordered vortex lattice.

1. Introduction

The RE123 (RE = Rare Earth elements, REBa$_2$Cu$_3$O$_y$) melt-solidified bulks are very attractive materials for strong bulk magnets trapping higher fields than the permanent magnets. The trapped fields and magnetic levitation force are simply proportional to the $J_c$ and size of the bulk. This is why intense studies were done to fabricate large-grain RE123 melt-solidified bulks, and succeeded in synthesis of the bulks with single domain as large as 140 mm in diameter for enhancement of trapping fields so far [1]. However, the trapped fields of the RE123 melt-solidified bulks at low temperatures are usually restricted by the mechanical properties rather than superconducting properties due to large electromagnetic force [2]. In addition, advance of cracks led by thermal cycle [3] is an inevitable problem for practical applications. For these problems, several methods, such as Ag-addition [4], external reinforcement by metal ring [5], resin or metal impregnation [6], have been developed for improving mechanical properties of the bulks. Although the Ag-addition is the simplest and most popular method among them, the effects of Ag on superconducting properties ($T_c$, $J_c$) of the RE123 melt-solidified bulks have not been well understood. The Ag has been usually considered as an inert impurity against the RE123 system.

In the present paper, we have carefully studied the intrinsic effects of Ag-addition for Y123 melt-solidified bulks through systematic control of carrier doping levels, and found that Ag-addition has the positive functions for high field trapping besides the improvement of mechanical properties.

2. Experimental

For the synthesis of Y-Ba-Cu-O melt-solidified bulks, Y123 and Y211 powders were prepared by calcination in air at 880°C for 24 h and 800°C for 120 h, respectively, starting from powder mixtures of Y$_2$O$_3$, BaCO$_3$ and CuO. The powders of Y123 and Y211 were mixed into a molar ratio of 7:3 and
0.5 wt% of Pt and 0 or 10 wt% of Ag2O were added to the mixtures. The mixtures were uniaxially pressed into pellets with 20 mm in diameter and 10 mm in thickness. Melt-solidification was performed by the cold seeding method using Nd123 single crystals in air. The rectangular specimens with 2 x 2 x 1 (// c) mm3 were cut from the same position of each bulk, 1 mm below the seed crystals in the c-growth regions. The microstructures of the samples were observed by a scanning electron microscope (SEM). Compositional analysis was performed by energy dispersion X-ray spectroscopy (EDS). Tc and Jc were evaluated by zero-field-cooled (ZFC) magnetization curves under 10 Oe and magnetization hysteresis loops at 77 K up to 5 T, respectively, using a SQUID magnetometer. Magnetic fields were always applied parallel to the c-axis. The oxygen content of the samples for these magnetization measurements was carefully controlled. At first, oxygen annealing was made at 250–300°C for more than 200 h in flowing oxygen to obtain carrier heavily overdoped samples. Then the samples were annealed at each predetermined temperature from 350 to 500°C for a long time enough to achieve the equilibrium state.

3. Results and Discussions
The both grown samples in present study were of single domain. The SEM observation revealed that Y211 particles with ~1 µm in size disperse homogeneously in the Y123 matrix independent of Ag-addition. The Ag particles with ~10 µm in size also segregated homogeneously in the Y123 matrix of the Ag-added sample. In cross sections of the ac-plane of the oxygen annealed samples, any apparent cracks were not found in the Ag-added sample, while many cracks running parallel to the ab-plane from the side surfaces were observed for the Ag-free sample. This corresponds to a typical effect of Ag addition, resulting in an improvement of mechanical strength as reported in ref. 4.

Figure 1(a) shows the XRD patterns for the samples annealed at 500°C in flowing oxygen. The 2θ angles of (200) and (020) peaks were almost unchanged for the both samples, while the (006) peak of Ag-added sample shifted to lower angle. This suggests an increase of c-axis length by Ag-addition. The lattice parameters of the samples annealed at several temperatures are shown in Figure 1(b). The a- and b-axes lengths were almost unchanged by Ag-addition and annealing temperature below 500°C. On the contrary, the c-axis length slightly decreased with a decrease of the annealing temperature for both samples due to oxygen absorption. Note that the Ag-added sample has longer c-axis than that of Ag-free sample, which is believed to originate from the Ag substitution for Cu site in Cu-O chain as reported for Y123 polycrystalline samples [7]. Although changes of lattice parameters by Ag-addition are different among each report, an increase of c-axis length is consistent with one another and this
work. The valence state of Ag ion in the Y123 is considered to be monovalent. The ionic radius of Ag\(^+\), is 0.67 Å with coordination number of 2 [8]. Since the Cu in the Cu-O chain tends to form CuO\(_4\) square along the bc-plane in the orthorhombic cell of Y123 with some oxygen deficiency, its ionic radius is smaller than 0.57 Å, which is for Cu\(^{2+}\) with a coordination number of 4. Therefore, the ionic size of Ag\(^+\) is larger than that of Cu ion in the Cu-O chain. The observed long c-axis length by Ag-addition can be explained by Ag\(^+\) substitution for Cu site in the Cu-O chain.

Figure 3 shows the temperature dependence of normalized ZFC magnetization for the samples annealed at 400 °C in flowing oxygen. Although both samples exhibited sharp transitions with \(\Delta T_c\) of less than 0.5 K, \(T_c\) of the Ag-added sample, 92.3 K, was higher than that of Ag-free sample, 90.6 K. These samples were confirmed to have each equilibrium oxygen content, therefore, the difference of \(T_c\) was due to an intrinsic change occurred in the Y123 matrix. The \(T_{\text{onset}}\)'s measured by magnetization of the samples annealed at several temperatures were shown in Figure 4. The maximum \(T_c\) of the Ag-added sample, 92.7 K, was slightly lower than that of the Ag-free sample, 93.3 K. It was indicated that the decrease of maximum \(T_c\) of Ag-added sample resulted from Ag substitution. It should be noted that the annealing temperature giving the optimally doping state is lower by ~50°C for the Ag-added sample than that of the Ag-free sample. The result suggests that Ag-addition caused the decrease of the carrier doping level somehow. This can be also explained by the incorporation of Ag\(^+\) into Cu-O chain with forming the dumbbell bond O-Ag-O along the c-axis, resulting in a slight decrease in oxygen content in the Cu-O chain. Although Ag\(^+\) has lower valence than Cu ion in the Cu-O chain, a decrease in oxygen content due to Ag substitution leads to a decrease in the carrier concentration compared to the Ag-free Y123. Since the difference in oxygen content of the Ag-free Y123 between 425 and 475°C in flowing oxygen was 0.031, the concentration of Ag at Cu site in the CuO chain is roughly estimated to be 1.5%.

Figures 5 show \(J_c\)-B properties at 77 K for the optimally doped and overdoped samples. As for an overdoped samples, Ag-free and Ag-added samples annealed at 450 °C and 350 °C, respectively, were chosen to show typical properties. It was found that \(J_c\) of Ag-free sample at the optimally doped state decreased monotonically with fields. In contrast, Ag-added sample exhibited prominent second peak with \(J_c\) of 55 kAcm\(^{-2}\) under 1 T, which is twice as high as that of Ag-free sample. The substituted Ag\(^+\) for Cu in the CuO chain changes local structure by a decrease of oxygen content and difference in the ionic size. Therefore, local lattice distortion around Ag\(^+\) must be occurred. Since the local regions around the substituted Ag\(^+\) is supposed to be weak superconductor, they can induce order-disorder transition of the vortex system and such weak superconducting areas can act as pinning centers, resulting in the large second peak effect. Similar phenomena have been reported for oxygen deficient or small amount of impurity, such as Zn, Ga and Co doped Y123 [10,11]. It is noteworthy that oxygen defects and low level impurity doping often cause low \(J_c\) under low fields and low irreversibility fields,
while, the Ag-added sample showed the improved \( J_c \) all over the fields. Moreover, it was proved that the enhancement of \( J_c \) led by Ag substitution were exhibited even for the overdoped samples. In order to discuss more detail on the enhanced pinning properties, the quantitative studies on the Ag substitution and its distribution would be required.

![Figures 5. \( J_c-B \) curves at 77 K for Ag-free and Ag-added Y123 bulks at optimally doped state(a) and overdoped state(b).]

4. Conclusions

We have fabricated Ag-added Y123 melt-solidified bulk and investigated the crystal structure and superconducting properties in order to clarify the influence of Ag on the Y123 matrix. It was found that Ag-addition slightly increased the \( c \)-axis length and decreased of maximum \( T_c \) with a shift of corresponding annealing temperatures. These facts indicated that Ag was incorporated into Y123 matrix. The decrease of carrier density by Ag-addition can be explained by partial substitution of Ag\(^+\) for Cu of the Cu-O chain with forming the dumbbell bond. Furthermore, Ag-addition led to the distinct second peak of \( J_c \) even in the overdoped state. This means that effective pinning sites under magnetic fields were introduced by the dilute Ag-incorporation. The enhancement of \( J_c \) properties was observed in all fields despite the slight decrease in \( T_c \), which cannot be achieved by other impurity doping. Therefore, the Ag-addition is concluded to be a more effective and promising method for the enhancement of \( J_c \) properties than ever reported techniques.

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