Journal of Korean Association of Crystal Growth
Vol. 9, No. 2 (1999) 137-140

Effects of annealing and impurities on the superconducting properties of $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystals

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(Received August 3, 1998)

$Bi_2Sr_2CaCu_2O_{8+\delta}$ 단결정의 초전도 특성에 미치는 열처리 및 불순물의 영향

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(1998년 8월 3일 접수)

Abstract Effects of annealing and impurities on the superconducting properties were investigated by the magnetization measurement in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) single crystals grown by flux method. It has been found that the superconducting properties are affected by Mg and Al impurities remarkably. The transition temperature (T_c) has been lowered by the impurity of Mg. However, the diamagnetism is remarkably increased in an annealed crystal grown in MgO crucible compared to that in Al_2O_3 crucible. The content of Mg impurity can not be considered as a principal parameter for the decay of superconducting properties probably because the diamagnetism is remarkably improved in annealed crystal containing Mg.

요 약 Flux법에 의해 성장된 $Bi_2Sr_2CaCu_2O_{8+\delta}$(Bi2212) 단결정의 초전도 특성에 미치는 열처리 및 불순물의 영향을 자화측정에 의해 조사하였다. 초전도 특성은 불순물인 Mg와 Al의 영향을 받음을 알 수 있었으며, 초전도 전이온도(T_c)는 Mg 불순물의 영향에 의해 보다 낮아졌다. 그러나 성장된 결정은 열처리에 의해 초전도 특성이 개선됨을 알 수 있었으며, 특히 MgO 도가니 사용에 의해 성장된 결정이 Al_2O_3 도가니에 비해서 반자계특성이 현저하게 증가되었다. 반자계 특성의 개선효과에 의해 Mg 불순물은 초전도 특성 열화의 주요 요소라고 생각될 수 없음을 알 수 있었다.

1. Introduction

It is well known that the $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (Bi-Sr-Ca-Cu-O) superconductors exhibit a strong anisotropic behavior [1, 2]. In many cases, the crystal growth, which is needed for measurement of superconducting characteristics of Bi-Sr-Ca-Cu-O system, is carried out by the flux method [3-5]. It is interesting to study the influence of the impurities introduced by the reaction of the flux with the crucible on the superconducting properties.

There is an increasing interest in the growth of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) phase with higher critical transition temperature (T_c), suitable for application such as a substrate for superconducting devices. It has been found that the crystal of Bi2212 phase grown in Pt crucible contains two kinds of precipitates, $(Ca,Sr)_2CuO_y$ and Sr-Pt-O [6]. Also, it has been reported that Sr-Pt-O has an influence on superconducting properties as flux pins. Furthermore, there is an interest in heat treatment which influences the superconducting properties of the grown crystal. The effect of annealing has been investigated for sintered materials of raw powders [7].

We have grown single crystals of Bi2212 phase by flux method using MgO and Al_2O_3 crucibles that are relatively cheaper to use compared to Pt crucible. In this paper the influence of the impurity and annealing on superconducting properties of grown crystals is studied.

2. Experimental procedure

Raw material powders of Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO were mixed, and sintered at 810℃ for 17 h. The starting composition was 30.8 mol% $BiO_{1.5}$, 26.4 mol% SrO, 19.8 mol% CaO and 23.0 mol% CuO, which has been used for growing relatively large single crystal [8]. The sintered materials were charged in MgO or Al_2O_3 crucible and melted at 1010℃. After melting, the temperature was cooled slowly at the rate of 2 and 0.5℃/h, respectively. The size of MgO and Al_2O_3 crucibles was 45 mmH×33 mmϕ and 50 mmH×33 mmϕ, respectively. The single crystals were obtained with dimensions of 1×2 mm^2 in area (c-plane) and about 20 μm in thickness from near the crucible wall.

The structure and composition analyses of the grown crystals were determined by X-ray diffraction (XRD) method and electron probe micro-analysis (EPMA). Qualitative and quantitative results of impurities were obtained by inductively coupled plasma (ICP) analysis. Furthermore, the temperature dependence of electrical resistivity was measured by four-terminal method. Magnetization measurement was performed by using the SQUID magnetometer (Quantum Design. MPM S-2) in magnetic field of 100 Oe that was applied perpendicular to the c-plane after zero field cool to 10 K. Resistivity and magnetization measurements were performed for both the as-grown and the crystals annealed at 700℃, for 100 h in ambient atmosphere.

3. Results and discussion

When the flux method is used to obtain the Bi2212 phase single crystal, many nucleation sites are known to occur in the melt due to its narrow crystallization temperature range. Therefore, the size of obtained crystals is rather limited. The lattice constant of the grown crystal was a = b = 5.229 Å and c = 30.203 Å, and the composition ratio of Bi : Sr : Ca : Cu was determined to be 2.04 : 1.80 : 1.12 : 2.04 by XRD and EPMA.

Figure 1 shows the temperature dependence of resistivity of the crystals grown in Al_2O_3 crucible at cooling rate of 2℃/h. The resistivity of as-grown Bi2212 crystal behaves like a semiconductor below 200 K as shown in Fig. 1 (a). The temperature dependence of resistivity was quite irregular. This result was not fully understood in this stage and

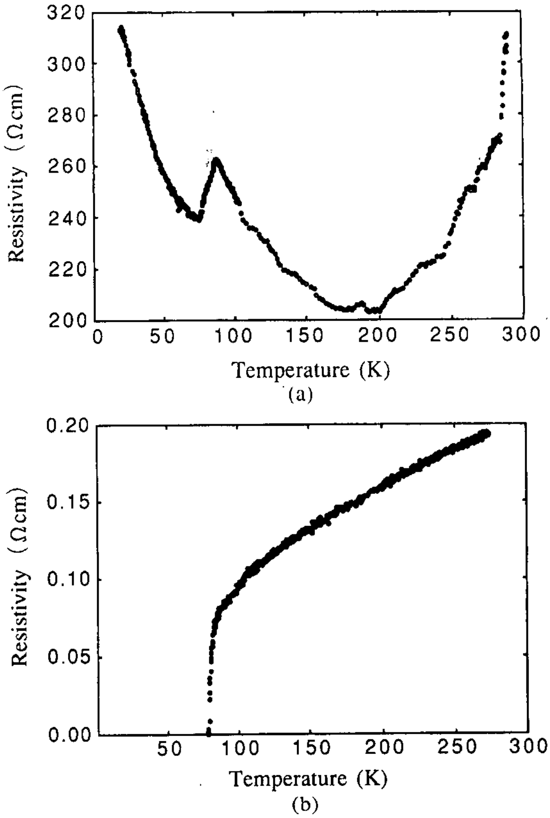

Fig. 1. Temperature dependence of the resistivity for (a) as-grown crystal, and (b) annealed crystal.

still under consideration. After annealing, the crystal shows superconducting behavior with the onset T_c of 85 K (Fig. 1 (b)), it may be due to the increase of carrier by taking O atom.

Figure 2 shows the temperature dependence of magnetization at 100 Oe, and it shows the effects of annealing. The crystals were grown by cooling at a rate of 0.5℃/h in each crucible material (MgO and Al_2O_3). The superconducting characteristics appeared both in as-grown and annealed crystals regardless of crucible materials. It indicates that the as-grown crystals could take O atom enough due to the slow cooling. However, T_c was changed by the use of different kind of crucible as shown in Figs. 2a and 2b, though T_c was not changed by annealing. T_c of the crystals grown in Al_2O_3 (Fig. 2a) and MgO (Fig. 2b) crucibles, were 85 K and 80 K, respectively.

It is well known [9, 10] that T_c is decreased seriously with increasing Mg concentration, which may explain the lower T_c for the crystal obtained in MgO crucible. However, we have found that the im-

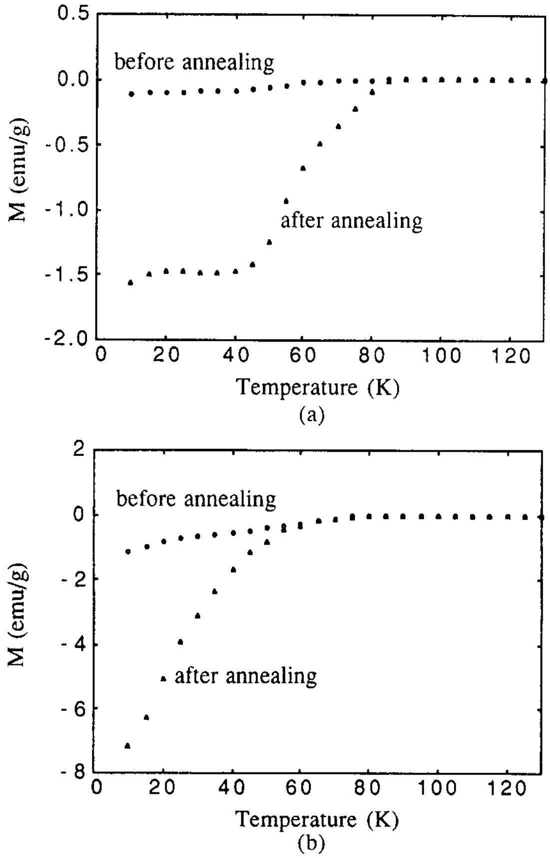

Fig. 2. Effect of annealing on the temperature dependence of the magnetization for the crystals obtained by a cooling at 0.5°C/h : (a) Al_2O_3 and (b) MgO crucibles were used.

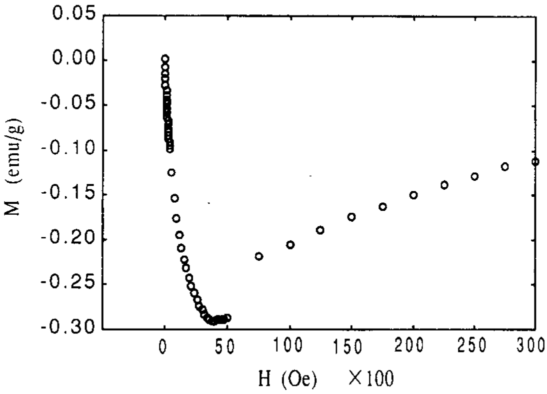

Fig. 3. Magnetization for the as-grown crystal using Al_2O_3 crucible at 10 K.

purity concentration of Mg was not particularly high in the crystals as shown in Table 1. Contradictory to this, the diamagnetism signal for Meissner effect was remarkably increased in annealed crystal obtained from MgO crucible compared to that from Al_2O_3 crucible as shown in Fig. 2.

The fraction of diamagnetization related to superconducting diamagnetism value can be obtained by measurement of magnetization dependence of magnetic field. Figure 3 shows the magnetization for as-grown crystal in Al_2O_3 crucible at 10 K. Diamagnetization was shown to change linearly until the magnetic field is 100 Oe. When the crystal is all superconducting with diamagnetism (B = 0), the magnetization value M is indicated by the following equations,

$$B = H + 4\pi M \quad (1)$$

$$M = -H/4\pi \quad (2)$$

where B is the magnetic flux, and H is the applied magnetic field.

Therefore, magnetization value M was calculated to be -7.957 emu/g at 100 Oe. Furthermore, the magnetization values due to superconducting property at 10 K, which are shown in Fig. 2, was indicated M'. The fraction of diamagnetization can be obtained from the ratio of M' to M by the following equation 3,

$$(M'/M) \times 100 \quad (3)$$

Table 2 shows the fraction of diamagnetization

Table 1
Analysis of impurities for grown crystals dependent on crucible material

Crucible	Impurity	Concentration (wt%)
Al_2O_3	Al	0.15
	Mg	<0.01
MgO	Al	0.03
	Mg	<0.01

Table 2
Fraction of diamagnetization value for as-grown and annealed crystals dependent on crucible material

Materials	Fraction of diamagnetization (%)
As-grown crystal in Al_2O_3 crucible	1.33
Annealed crystal in Al_2O_3 crucible	19.69
As-grown crystal in MgO crucible	14.60
Annealed crystal in MgO crucible	89.83

value for as-grown and annealed crystals with different crucible materials. The fraction of the superconducting part was reduced in Al contained crystals. It is characterized that the diamagnetization in Bi2212 crystals is decayed more remarkably by Al than by Mg impurity. In annealed crystals, the superconducting diamagnetism value of the Mg contained crystal was improved effectively. It is believed that the content of Mg impurity is not a principal parameter for the decay of superconducting properties, based on the measured diamagnetization value in Table 2.

4. Summary

The superconducting properties of Bi2212 depending on the impurity and annealing effect were investigated by the measurement of resistivity and magnetization of single crystals. It is characterized that the Mg and Al impurities affected superconducting properties remarkably. T_c was observed to be 85 K and 80 K for the crystals obtained from using Al_2O_3 and MgO crucibles. However, the content of Mg impurity can not be considered as a principal parameter for the decay of superconducting properties probably because the diamagnetism was remarkably improved in annealed crystal of Mg contained.

Acknowledgements

The authors wish to thank Dr. S. Tachibana (Iwate Prefectural Industrial Research Institute) for technical assistance in measurements of ICP analysis, and M. Nakamura (Department of Materials Science and Technology, Iwate University) for his support in experiment.

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