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Growth and characterization of a Bi-Sr-Ca-Cu-O phase by crystal pulling method

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Crystal pulling법에 의한 Bi-Sr-Ca-Cu-O계의 결정성장과 특성평가

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Abstract The $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (BSCCO) phase is well known to be a superconductor having a strong anisotropic behavior. It can be seen that it is difficult to control the growth direction. In this study, we try to grow a Bi-Sr-Ca-Cu-O phase crystal by the crystal pulling method with a seed crystal and crucibel rotation. Relatively large crystals of the order of 5×5×5 mm^3 dimensions can be obtained. We also discuss the possible crystallization field of the $BiO_{1.5}$-(Sr, Ca)O-CuO ternary phase diagram, and present some results of the characterization and magnetic measurements on the grown crystal.

요 약 $Bi_2Sr_2Ca_{n-1}Cu_nO_y$(BSCCO)계는 강한 이방성의 움직임을 갖는 초전도체로서 잘 알려져 있으며, 결정육성시 성장방향의 제어에 큰 어려움이 있다. 본 연구에서는 종자 결정과 도가니의 회전을 이용한 crystal pulling법을 이용하여 Bi-Sr-Ca-Cu-O계의 결정성장을 시도하였으며, 이로부터 5×5×5 mm^3 크기의 비교적 큰 결정을 성장하였다. 또한 성장결정의 초전도 특성을 조사하였으며, $BiO_{1.5}$-(Sr, Ca)O-CuO 3원 상태도에서의 결정화 가능 영역을 검토하였다.

It is well known that single crystals of $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (BSCCO) phase are superconductors having a strong anisotropic behavior [1,2]. Especially, BSCCO superconductors have three phases with increasing n (n=1,2,3) which represents the number of

Cu-O layers [3,4]. The growth of single crystal is indispensable to study the physical properties of BSCCO. Several studies on the crystal growth of 7 K phase BSCCO (n=1) and 80 K phase BSCCO (n=2) had been carried out by the traveling solvent floating zone (TSFZ) method and either self-flux or KCl flux methods [5,7]. However, the major disadvantage of such growth methods is the failure to achieve large crystals. This limitation on the size of the crystal demand forcibly a restriction towards the pursuit of fundamental studies and practical applications of these crystals.

There is increasing interest in the growth of 80 K phase BSCCO single crystal which has higher critical transition temperature, suitable for application in substrate for superconducting devices. Although it is difficult to obtain large 80 K phase BSCCO single crystal when the crystallization field of $BiO_{1.5}$-(Sr,Ca)O-CuO ternary phase diagram is discussed [8], relatively larger single crystals can be grown by TSFZ method [9]. However, it is necessary to prepare a high quality and large single crystal. We have attempted to grow 80 K phase BSCCO crystals by the crystal pulling method with a seed crystal. In this paper, we describe the crystal growth and the superconductive characterization with magnetic measurements on the grown crystal.

A crystal pulling equipment, which is composed by a radio frequency generator (7 kHz), a MgO crucible (40 mmϕ×50 mmH) with Ni suscepter and driving system as shown in Fig. 1, was used for growth process. The raw materials are prepared by mixing and sintering (810℃, 17 h). The composition of starting material was fixed by a mixture of 35.8 mol%$BiO_{1.5}$, 22.4 mol%SrO, 14.9 mol%CaO and 26.9 mol%CuO.

When a BSCCO phase is grown by the crystal pulling method, its composition along the growth axis will change from the top to the bottom. Therefore, we tried to use crucible rotation, large crucible and large amount of starting material relative to the crystal

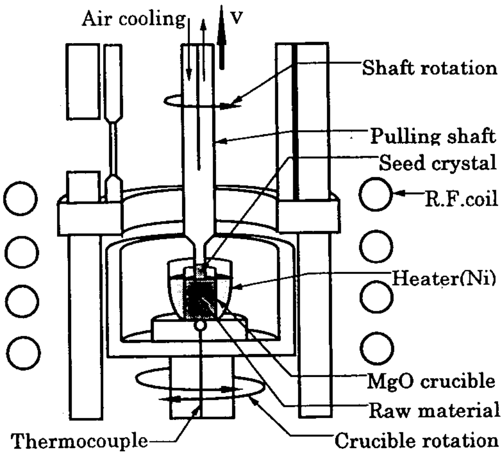

Fig. 1. Schematic diagram of the crystal pulling method.

Table 1
The distribution of Bi concentration inside of the crucible after the growth with and without crucible rotation

Distance from the crucible bottom	Bi content (at%)	
	with rotation	without rotation
5 mm	36.53	40.53
15 mm	33.79	41.07
25 mm	34.30	30.40
35 mm	31.87	17.48

size to obtain relatively homogeneous samples. Table 1 shows the distribution of Bi concentration, which is measured by electron probe micro-analysis (EPMA), inside the crucible separated from the bottom after the growth with and without crucible rotation of 6 rpm. A clear inhomogeneity of Bi concentration was observed in without crucible rotation, but a melt homogeneity of Bi element was observed in with crucible rotation. This denotes that a strong convection is necessary for facilitating the melt transfer in the growth of BSCCO single crystals.

The crystal growth of BSCCO phase was attempted to have crystal rotation. The pulling rate and rotation speed of seed were typically 0.3 mm/h and 35 rpm. The seeds used for the crystal pulling were made of $SrTiO_3$ with [110] orientation by a flame fusion technique [10], and cooled through the pulling shaft by an air flow rate of about 10 ℓ/min during growth. Therefore, the temperature gradient above the melt surface is about 20℃/cm

Figure 2 shows an as-grown BSCCO crystal by the crystal pulling method. Relatively large crystal of the dimension of 5×5×5 mm^3 can be obtained. The crystal was grown along the [001] orientation, resulting in (00$\underline{10}$) peak observed by X-ray diffraction (XRD) pattern. Facet plane was also elongated along the a-axis. It was found that the concentration ratio of the pulled crystal measured by EPMA was typically $Bi_{2.19}Sr_{1.76}Ca_{1.15}Cu_{1.89}O_x$. However, growth of crystals without crucible rotation were also attempted, crystals were not obtained. We assume that the decreased Bi content as shown in Table 1 affects the growth mode with the change of melting temperature compared to the $BiO_{1.5}$-(Sr,Ca)O-CuO phase diagram [8].

The critical temperatures of grown crystal were measured by resistivity and DC susceptibility measurement. The resistivity was measured by a four probe method in the c-plane on an as-grown crystal from 270 K to 60 K. Figure 3 shows the temperature de-

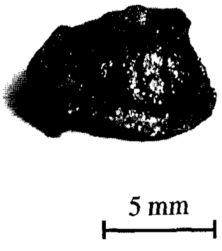

Fig. 2. Photograph of a Bi-Sr-Ca-Cu-O phase single crystal.

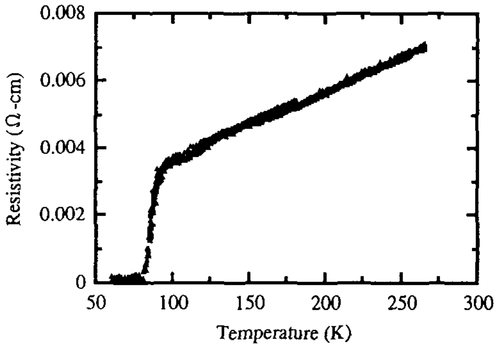

Fig. 3. Temperature dependence of resistivity of as-grown $Bi_{2.19}Sr_{1.76}Ca_{1.15}Cu_{1.89}O_x$ crystal.

pendence of the resistivity for the as-grown crystal. It shows that superconducting resistivity behavior which have zero-resistance temperature was about 80 K. The resistivity shows a typical metallic-like behavior which is a pronounced linear decrease with decreasing temperature in the normal state. The DC magnetization measurement was carried out using a Quantum Design SQUID magnetometer at a field of 100 Gauss parallel to the c-axis for the crystal. Figure 4 shows the result of a typical superconducting magnetic transition. The superconducting onset transition temperature is also about 80 K consistent with the resistive measurement as shown in Fig. 3. The results of superconducting transition indicate the crystal pulling method with crucible rotation is effective for the growth of BSCCO phase.

In summary, the single crystals of 80 K phase BSCCO, which have the dimensions of 5×5×5 mm^3, have been grown by the crystal pulling method with a seed crystal and crucible rotation. Melt homogeneity of Bi element can be achieved by crucible rotation. The superconducting transition was found to be measuring the resistivity and magnetization of the as-grown crystal.

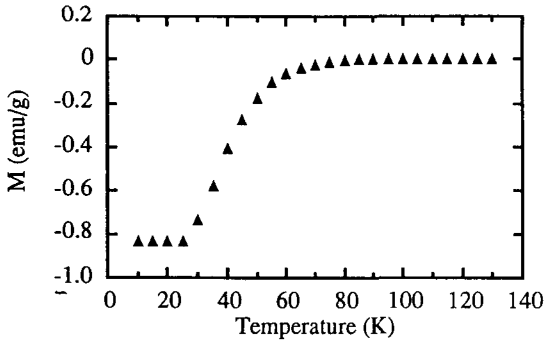

Fig. 4. Magnetization measurement of as-grown $Bi_{2.19}Sr_{1.76}Ca_{1.15}Cu_{1.89}O_x$ crystal at a field of 100 Gauss.

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