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Growth of Bi-Sr-Ca-Cu-O high-T_c superconfducting whiskers

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A synthesis technique of $Bi_2Sr_2CaCu_2O_{8+\delta}$ single-crystal whiskers was studied. The whiskers were synthesized by heating glassy melt-quenched Bi-Sr-Ca-Cu-O (3:2:2:4 in cationic ratio) plates. The atmospheric condition of the whisker growth, especially oxygen partial pressure and gas flow, was investigated. It was found out that the whisker growth rate shows a maximum at P_{O2}=2/3 bar. For the crystalline quality of the whiskers, the airtight condition was found to be useful as compared to the conventional oxygen stream condition. The crystalline quality, especially the straightness and morphology of the surface, could be improved by keeping the growing whiskers under the equilibrium P_{Bi} condition. Over 20-mm-long whisker crystals have been successfully synthesized by choosing optimum oxygen partial pressure around the P_{O2}=2/3 bar in the airtight condition. The growth condition and mechanism of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ whiskers were investigated by an *in-situ* high-temperature x-ray diffraction analysis and an *in-situ* high-temperature microscope observation. It was found that the whiskers grow in a partially melted state at a temperature of 10-40 degrees below the melting point. The result obtained demonstrates that $Bi_2Sr_2CaCu_2O_{8+\delta}$ whiskers grow at their bottom by the conventional liquid-phase growth mechanism, as was proposed by Matsubara *et al.* [1].

Key words: Superconductor, $Bi_2Sr_2CaCu_2O_{8+\delta}$, Whisker, Oxygen partial pressure

1.INTRODUCTION

The growth of superconducting $Bi_2Sr_2CaCu_2O_{8+\delta}$ whiskers has been identified and studied in detail by Matsubara *et al.* [1-3]. $Bi_2Sr_2CaCu_2O_{8+\delta}$ whiskers are the focus of much attention because of their peculiar dimensions (typically, 10mm, 10μm, and 1μm for *a, b,* and *c* axes of the whisker crystal, respectively.) and excellent crystallinities and superconducting properties. Therefore, whiskers are thought to be a good candidate for the fabrication of microwave devices based on the concept of intrinsic Josephson junctions [4].

The synthesis condition of whiskers has been studied in detail by Matsubara et al. [1-3]. The common sense right now is (1) long-time heating at around 840°C for several days, (2) under a stream of 1-bar oxygen, (3) of glassy melt-quenched Bi(Pb)-Sr-Ca-Cu-O plates, and (4) with right compositions (Ca-rich, Cu-rich, Pb-addition and excess Bi). However, the effect of oxygen partial pressure has not been studied. In this paper, we report a strong dependence of whisker growth on oxygen partial pressure in an airtight condition. We also demonstrate an advantage of the nearly airtight setting of the glassy plates in the furnace for the synthesis of straight and surface-smooth whiskers.

The growth of whiskers has not been studied *in-situ*. In this paper, we also present the results of an *in-situ* x-ray diffraction (XRD) analysis and an *in-situ* microscope observation. The growth mechanism and new aspects to grow high-quality whiskers are also discussed.

2.EXPERIMENTAL PROCEDURE

2.1 Preparation of whiskers

For the growth of the 2212 whiskers, we mostly followed the procedure of Matsubara et al. and Latyshev et al. [1-6]; (1) Bi_2O_3(99.9%), $SrCO_3$(99.9%), $CaCO_3$(99.9%), and CuO(99.9%) were weighted in the ratio of Bi:Sr:Ca:Cu=3:2:2:4 and mixed by an agate mortar and pestle for 2 hours under a nitrogen atmosphere. A batch of 20g was heated at 800°C for 12 hours in a recrystallized alumina crucible (99.7%) under oxygen (or air) flow in an electric furnace and subsequently melted at 1100-1200°C for 30 min to remove CO_2 and homogenize the melt. Then, the melt was poured onto a stainless steel plate and quickly pressed to prepare a glassy plate of a thickness of about 0.5 mm. The plates were crushed into small pieces of about 0.1-1 cm^2 because the longer whiskers mostly grow from the ruptured surface of the broken pieces. The glassy plates (~2.5g) were placed on a pure alumina (99.7%) crucible's lid (~70mmϕ), covered by another lid, and enclosed in a pure (99.7%) alumina container (100x100x50mm^3) with its lid and placed in a box furnace. The somewhat complicated setup described above is intended to provide uniform temperature distribution and no stream of gas at the growth position. A loss of Bi vapor is avoidable in this set up. O_2/N_2 mixed gas (250sccm) was flown into the box furnace so that it might ventilate the growth space through the

sub-millimeter size gaps between the container and its lid and between crucible's lids. Then, it was heated at 830-860°C for 1-5 days. The lack of a gas stream is a difference from the conventional synthesis technique. The whiskers are expected to lose Bi atoms because they are kept at 840°C for several days. We chose equilibrium Bi vapor pressure instead of oxygen flow in order to prevent this Bi deficiency in the whiskers.

2.2 Sample characterization

The whiskers showed good crystalline qualities. A conventional θ/2θ x-ray diffraction of an aligned single piece of whisker shows sharp (00l) lines with fwhm of 0.09° for a (0020) line. Because the c-axis of the whisker was aligned parallel to the diffraction vector, only (00l) lines were observed. The amount of intergrowth in the whisker was examined by applying a lattice constant precision plot [7] developed for the intergrowth of Bi-Sr-Ca-Cu-O [8]. It was confirmed that the ratio of 2223 interleaved into the 2212 phase was less than 1%.

The resistance versus temperature curve was measured by a standard four-probe method. The resistance dropped at 100-110K for more than 99%, showing zero at around 75K as shown in Fig. 1. This means that a small amount of 2223 layers (less than 1%) exists in the whiskers grown here and contributes to the resistive drop at 110 K connecting the voltage electrodes.

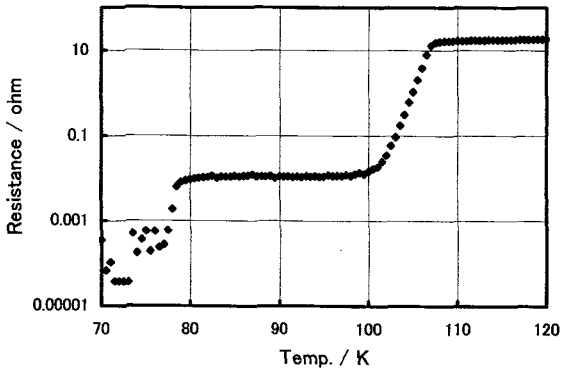

Fig. 1. Resistance of a whisker grown at 840 °C under 0.72 bar oxygen partial pressure.

3.RESULTS AND DISCUSSION

3.1 Oxygen partial pressure

In the solid-state reaction method of oxide materials, the heating atmosphere gives significant effects on the growing phases. It is well known that the lower oxygen partial pressure (7-10%) is effective for producing the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ (2223) phase [9-12]. We examined the influence of oxygen partial pressure on the growth of the 2212 whiskers. The oxygen partial pressure in the flowing O_2-N_2 mixed gas was kept to be p_{O2}=1, 0.8, 0.7, 0.6, 0.5, and 0.2 bar. The heating temperature was 840±2°C. During the first hour, the starting materials were heated up at 850°C so as to promote the melting of a partial amount and an appropriate size of the melting droplet. This process reduces the incubation time of whisker growth and increases the whisker size while reducing the number of whiskers per unit area.

Figure 2 shows the average lengths of 10 prominent whiskers from the 2.5-g batches grown under various oxygen partial pressures. It was found that the p_{O2}= 0.7 bar was preferable for the growth of the 2212 whiskers. It has been reported [13] that the degree of 2212 grain alignment on the Ag plate shows its maximum between 0.5 and 1.0 bar oxygen partial pressure during the melt processing of the 2212 tapes. The viscosity of the 'transient liquid' [14] might be minimum at that oxygen partial pressure. Here, on the growth of the 2212 whiskers, the role of the partial melt might be important. The less viscid melt promotes the diffusion and subsequent growth of 2212 whiskers.

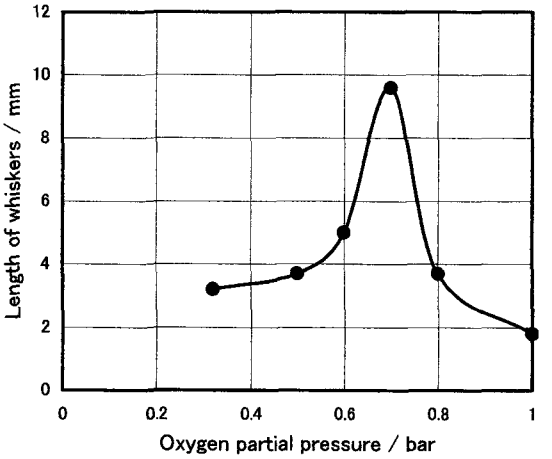

Fig. 2. Oxygen partial pressure dependence of whisker length after heating at 840 °C for 120 h.

3.2 Oxygen flow

The need for an oxygen stream (>5 sccm per cm^2 for the cross section of a tube furnace) is reported [3]. In the tube furnace, the gas temperature might have a certain contour distribution along the radial direction. When a gas stream of 2000 sccm was introduced into a tube furnace whose diameter is 60 mmϕ, the temperature of the center of the tube was 10°C lower than that near the tube wall at 850°C. The temperature of the boat was almost close to that of the furnace tube because of a heat transfer from the tube. If the glassy plates were placed on a boat, the temperature of the plates would also be close to that of the tube. Contrary to this, at the tip of the growing whisker towards the center of the furnace tube, the temperature is slightly lower because of cooling by the gas stream. Therefore, the temperature of the whiskers might be somewhat lower than that of the plates. Cooling of grown whisker tips might help the stability of these whiskers.

The advantage of the temperature gradient along the tube length is also reported [15]. This also cools down the whisker tips from their growth sites (their roots). However, in this synthesis, both the temperature gradient and the oxygen gas stream were excluded in the growth condition. Still, a certain size of whiskers was obtained. The whiskers were quite straight, uniform in width, and with fewer droplets at the top or side, as shown in Fig. 3(a). Contrary to these grown in the airtight condition, those whiskers grown under a gas stream were thicker and had irregular shapes, as shown in Fig. 3(b). The

density of the whiskers was higher under the gas stream. By placing the glassy plates under the nearly airtight condition, P_{Bi} might be kept at its thermally equilibrium value. This P_{Bi} protects the whiskers from the loss of Bi atoms from their surface during the long-time heating in the growth schedule, resulting in straight and surface-smooth products.

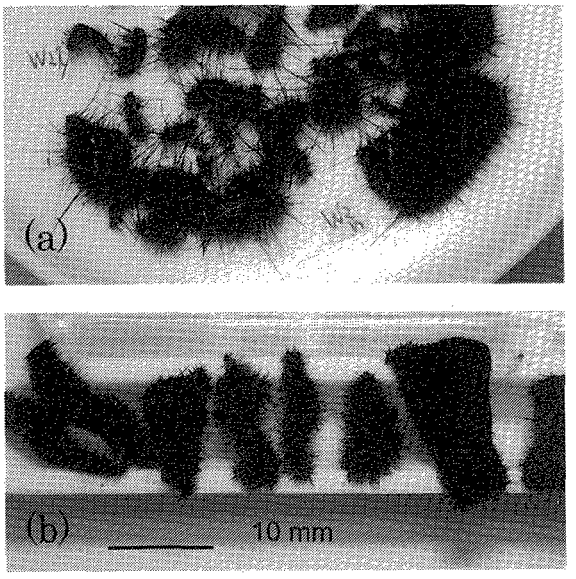

Fig. 3. (a) $Bi_2Sr_2CaCu_2O_{8+\delta}$ whiskers grown in a nearly airtight space under 0.72 bar oxygen partial pressure and (b) in a 1.00 bar oxygen stream.

3.3 High-temperature x-ray observation

Whisker growth was observed by an x-ray diffractometer equipped with an atmosphere-controlled sample heating stage. The P_{O2} was kept at 0.67 bar where the maximum growth rate was expected [5]. From room temperature to 500 °C, no diffraction line was observed. In the XRD spectrum measured at 600 °C, broad peaks appeared at 26.0° and 33.2°. In the XRD spectrum measured at 700 °C, around 10 diffraction peaks clearly appeared. These peaks were identified as those of $Bi_2(Ca,Sr)O_4$. At 800 °C, the $Bi_2Sr_2CuO_{6+\delta}$ phase appeared, and the $Bi_2(Ca,Sr)O_4$ phase almost disappeared. At 820 °C and 840 °C, the $Bi_2(Ca,Sr)O_4$ phase completely disappeared. Although the composition of the $Bi_2(Ca,Sr)O_4$ phase is not close to that of the glassy precursor (Bi:Sr:Ca:Cu=3:2:2:4), the $Bi_2(Ca,Sr)O_4$ phase crystallized prior to the $Bi_2Sr_2CuO_{6+\delta}$ phase. The results suggest that the relation between the $Bi_2(Ca,Sr)O_4$ phase and the $Bi_2Sr_2CuO_{6+\delta}$ phase is eutectic in the phase diagram [16]. In such a case, a phase far from the prepared composition first crosses the extrapolation of liquidus line in the supercooled glassy material. The intensities of the XRD peaks corresponding to the $Bi_2Sr_2CuO_{6+\delta}$ phase indicate no textured growth of $Bi_2Sr_2CuO_{6+\delta}$. The sample was kept at 850 °C for 500 min. The first measurement was done as soon as the temperature was increased to 850 °C.

The XRD lines corresponding to the $Bi_2Sr_2CuO_{6+\delta}$ phase disappeared abruptly, and those of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ phase appeared. The sequence of the phase formation can be explained by the peritectic reaction of the liquid phase and the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ phases (n=1,2) [16].

The XRD line observed at 2θ=33.04° corresponding to the (200) or (020) was quite strong. It is known that whiskers grow along their a-axis (preferred growth direction) [4]. Therefore, the XRD peak is determined as that of (200). The a-axis alignment indicates that the whiskers tend to grow normal to the plate surface.

3.4. High-Temperature Microscope Observation

The initial stage of whisker growth (0-12h) was observed by an optical microscope equipped with an atmosphere- controlled sample heating stage. When the glassy melt- quenched plate was heated, nothing changed until 800 °C. Above 800 °C, black dots were observed on the surface of the plate. In the XRD spectra mentioned in the previous section, the $Bi_2Sr_2CuO_{6+\delta}$ phase appeared in this temperature range. At above 840 °C, bright dots were observed, possibly corresponding to the partially melted phase whose top is normal to the light axis of the microscope. The black dots mentioned above disappeared. The growth of whisker whose tip part is narrower in the width was observed by keeping the temperature in this range. The shape and size of the tip part did not change with the increase of heating time, while the length between the tip part and the root of the whisker increased. By this *in-situ* observation of the whisker growth, it is concluded that the growth site is at the bottom of the crystal.

A whisker associated with stripes (mosaic structure) was also observed. The wider whiskers are mostly composed of a mosaic of several crystals. The length of the white-stripe part, seen at the left side edge of the whisker, increased with the heating time, while that between the tip and top of the stripe did not. This tendency was systematically observed with increase of time. This is similar to the growth mode mentioned above. It was found that the direction of this whisker changed considerably. Namely, the root of this whisker was not concretely fixed. Such a rotation was observed quite frequently if the melt quenched plate was heated under 0.67-bar oxygen partial pressure. Under the 0.67-bar oxygen, whiskers grow quite fast (up to 250 μm/hr) but turn around, become entangled with each other, and finally stop their growth. Some whiskers disappeared from the view of the optical microscope. Contrary to this, under 1-bar oxygen, the root of the whiskers was quite rigid. Therefore, we could keep observing the whiskers for several tens hours. The weak root, observed at 0.67-bar oxygen partial pressure, might be caused by the less viscid molten phase surrounding the whiskers. Due to the less viscid molten phase, the whisker growth rate shows a maximum at 0.67 bar; however, the less viscid molten phase makes the lifetime of whiskers short at the growth temperature.

3.5. Growth Mechanism

Concerning the growth mechanism of the whiskers, there are several proposals. They are classified into two categories: one is the tip-growth model, and the other is the bottom growth- model (end-base growth). As the tip-growth model, the Vaper-Liquid-Solid growth

mechanism (VLS) [17] is proposed by Mozhaev *et al.* [18]. Other tip-growth models are the screw-dislocation model (vapor deposit at the tip by the step-flow mechanism) [19] and the surface-diffusion model (the diffusion of atoms along the whisker surface) [20]. Zhou *et al.* reported that a temperature gradient of about 2-5 °C/cm in the tube furnace along the tube axis helped the growth of whiskers [21] and support the tip-growth model because the temperature gradient is thought to be the driving force of whisker growth. However, the vapor pressures of Sr and Ca are not high enough to support the vapor mechanism under the oxygen atmosphere. Nor the diffusion length of atoms along 10mm-long whiskers.

Matsubara *et al.* and Lee *et al.* proposed a bottom-growth model in which the whiskers grow out from the root part nourished through the liquid phase near the plate surface [1,22,23]. In this model, the glass precursor forms a Bi-Sr-Ca-Al-O complex oxide (solid) and a liquid phase. The former works as a micro crucible by forming a skeleton structure. The latter produces whiskers [1].

From the high-temperature microscope observation discussed in the previous section, we have directly confirmed that the growth mechanism obeys the model of Matsubara *et al.* [1]. The existence of a melted phase at the pedestal of the whiskers, which is suggested by the change of the whisker direction, also shows agreement with this model. It is concluded that the growth mechanism is the conventional liquid-solid type.

In this model, the molten phase plays a major role. It has been reported that the viscosity of the molten phase becomes small under the P_{O2}=0.67 bar [5]. In the liquid-solid mechanism, the rate-determining step is the diffusion of elements through the liquid phase. Therefore, the smaller viscosity of the liquid phase is thought to promote the growth and thus the quality of the whiskers. If the growth rate is higher, a prolonged synthesis period can be avoided. This also contributes to the quality of the whiskers because the tips of whiskers are exposed at around 840°C throughout the growth period which results in the loss of Bi atoms from the surface.

4.SUMMARY

We have identified an effect of oxygen partial pressure on the $Bi_2Sr_2CaCu_2O_{8+\delta}$ whisker growth rate, which might be caused by the change in viscosity of the liquid phase at the growth temperature. The whisker growth rate shows a maximum at P_{O2}=0.67 bar where the viscosity of the melting phase is minimum. We have also demonstrated the advantage of a nearly airtight set up on the growth of straight and surface-smooth whiskers.

The growth of whiskers was studied *in-situ* by XRD and microscope observation. The XRD results suggest that the relation between the $Bi_2(Ca,Sr)O_4$ phase and the $Bi_2Sr_2CuO_{6+\delta}$ phase is eutectic and that between the $Bi_2Sr_2CuO_{6+\delta}$ phase and the $Bi_2Sr_2CaCu_2O_{8+\delta}$ phase is peritectic in the phase diagram. The microscope observation directly confirmed that the growth mechanism of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ whiskers is the conventional liquid-solid type. In this mechanism, the whiskers grow at their bottom part nourished through the liquid phase near the plate surface.

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