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Growth of $Bi_2Sr_2CaCu_2O_8$ Single Crystals and Etch Figures by Acetic Acid

$Bi_2Sr_2CaCu_2O_8$ 単結晶の作成と酢酸による食像

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1. Introduction

$Bi_2Sr_2CaCu_2O_8$ (Bi-2212) was discovered in 1988 by Maeda et al.[1] as one of the oxide superconductors with superconducting transition temperature at about 80K. The crystals of Bi-2212 phase grows directly from the melt developed in area. However, they are too thin to answer various requirements for experiments. As it is well known in crystal growth field larger crystals are grown from the melt in a crucible under a slow growth rate. However, for Bi-2212 this is not so suited as it reacts with crucible materials. In this case a self-sustaining method is recommendable and up to date both a Verneuil method and a floating zone method have been examined[2)~6)].

For Bi-2212 previously we have reported preliminarily about the Verneuil method[2]. However, the experiment has not been extended to the growth of single crystals. Afterwards the floating zone method is carried by several groups such as Takekawa et al.[3], Shigaki et al.[4], Menken et al.[5] and recently by Emmen et al.[6] Single crystals larger than $10\times10mm^2$ in areal dimension have been grown. However, the crystal texture is not satisfactory. The reason why only inferior single crystals grow may be due to the lack of a substantial research activity for the crystal growth. It may be said that the present growth of good Bi-2212 crystals is anticipated upon fortunate chances.

Observation by an interference contrast microscope (ICM) would be useful to the problem. Because micro-step-line structures on the as-grown surfaces are closely related to the crystal growth processes. Moreover, the inspection by optical microscopes embraces wide area and makes it easy to understand the comprehensive crystal growth processes.

We have grown single crystals by a horizontal travelling melt zone (HTMZ) method. As far as observations by ICM concerns crystals are qualified with less defects on their surfaces. On the other hand etching by acetic acid has revealed abundant etch figures due to built in defects in the crystal. The study of etch figures, therefore, would be useful to grow good crystals.

2. Experimental

In this experiment single crystals are grown by HTMZ method by CO_2-laser heating. The total system is illustrated in Fig. 1. The laser beam is generated by a gas flow type NAL 50D by Nihon Kagaku Engineering Co. as previously reported[2),7)]. The composition of the flow gas is CO_2: 10.6%, N_2: 18.5% and He: the rest. The flow rate is about 125 l/min atm. The nominal output power is 50W. The laser beam is about 4mm in diameter and led to the growth site by two mirrors. A polycrystalline bar about

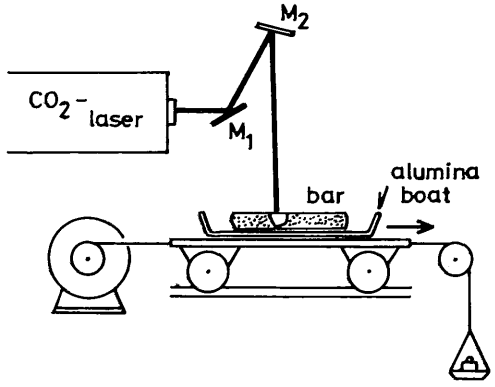

Fig. 1 Schematic illustration of the HTMZ system for Bi-2212 crystal growth with CO_2-laser heating.

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8mm in diameter and about 5cm in length is placed horizontally in an alumina boat and pulled by motor at a rate of 2.5mm/h. The laser beam is directed to the bar from above and a melt zone is formed in the bar. Travelling the melt zone through the bar tiny single crystals are produced bunched in the wake.

It has been recognized that the HTMZ method is equivalent to the self-sustaining method by reason as follows. The alumina boat itself lies in the shadow of the bar and interrupted against the laser beam. Therefore, it is not heated so hot. As the zonal melt hanging down approaches the boat, the bottom of the melt solidifies by natural cooling as shown in Fig. 2. Thus held by the crust the melt is separated from the boat.

As previously reported[2] the starting composition of $Bi_2Sr_2CaCu_2O_8$ produces only $Bi_2Sr_2CuO_6$ phase material. After heat treatment at 850°C in air overnight, it changes finally to $Bi_2Sr_2CaCu_2O_8$. After some trials, however, it is found that by shifting the composition Bi: Sr: Ca: Cu from 2: 2: 1: 2 it is possible to grow Bi-2212 crystals directly from the melt.

In our bar the composition is selected to $Bi_{2.2}Sr_{1.6}Ca_{1.2}Cu_{2.8}O_y$ as this has yielded better crystals. Commercially available 99.9% purity Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO are mixed in a mortar. Then the mixture is melted for chemical reaction by the above CO_2-laser and formed into a bar for the HTMZ processing.

The crystals are observed with ICM over their surfaces to decide the crystal growth processes. A Michelson-type interferometer microscope (MIM) is used to measure microstep heights as well as surface unevenness.

After the chemical etching the as-grown surface is again examined by ICM. At first etching is made by acetic acid diluted by water to 1:50. With acetic acid alone, however, the etched surface is often covered heavily by dirty residue which hinders the observation of etch figures.

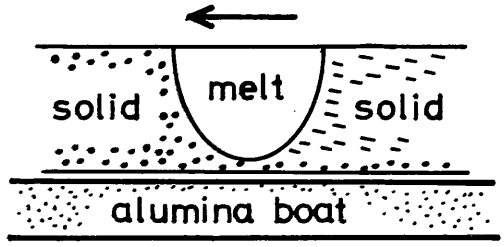


Fig. 2 Schematic cross section of Bi-2212 bar set on alumina boat under laser heating.

Searching further etchants it is found that commercially available fixer for photographic films such as Fuji superfix provides superior figures to acetic acid. Fixer solution generally contain acetic acid. Therefore, the superior performance for etching may be due to the ability of the rest chemical agents contained in the fixer to remove dirty residue. The etching time is 30–40 sec at room temperature. After etching, the surface is washed by water carefully and rinsed by methanol and aceton in turn and dried by softly pressing a filter paper.

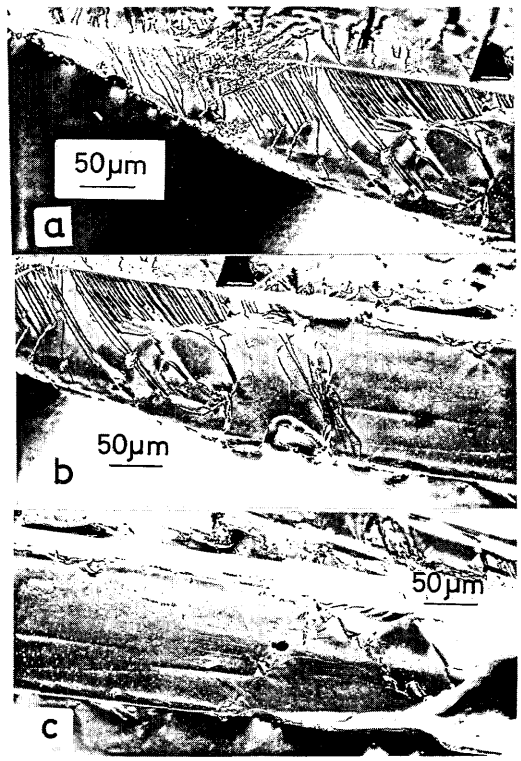
3. Results and Discussion

After trials for different compositions $Bi_aSr_bCa_cCu_dO_y$ it is decided that the composition $Bi_{2.2}Sr_{1.6}Ca_{1.2}Cu_{2.8}O_y$ provides better crystals as far as the optical inspection concerns.Still the grown crystals are tiny and extremely thin. Moreover, they are warped as to hinder high grade crystal structure analysis by X-ray methods.

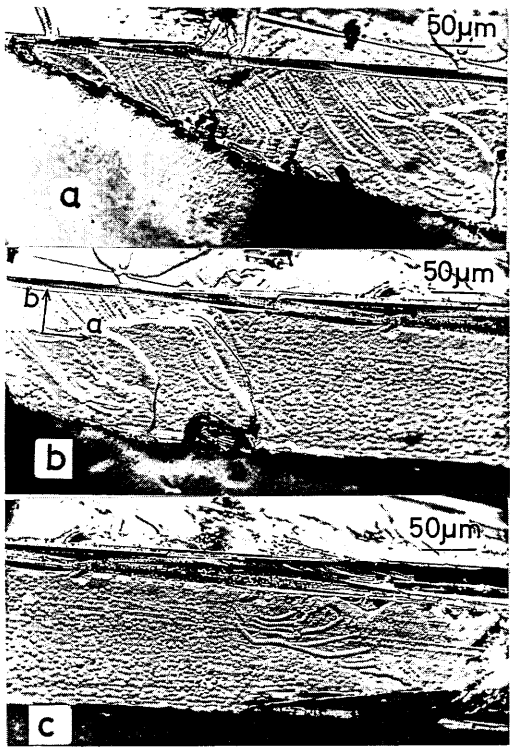
Generally the segregation coefficients of elements between the melt and the solid are different from 1 individually. At the start of HTMZ processing, therefore, the solid phase is regrown with different composition from the melt. Then the melt must adjust the composition subject to the composition in the regrown phase. As the melt zone travels the bar the melt would set to a stationary composition so that the regrown solid phase is held to $Bi_{2.2}Sr_{1.6}Ca_{1.2}Cu_{2.8}O_y$. Now there is a question to such an odd composition $Bi_{2.2}Sr_{1.6}Ca_{1.2}Cu_{2.8}O_y$ which is different from the generally accepted even composition $Bi_2Sr_2CaCu_2O_8$. If the main phase is $Bi_2Sr_2CaCu_2O_8$ then there should coexist other phases to cope with the composition change. If the grown phase is the same with the bar, then the lattice sites of the unit cell must be occupied by elements irregularly. In order to answer this question the high precision crystal structure analysis by X-ray is necessary. However, for warped crystals the analysis is difficult as the Bragg diffraction spots lack in sharpness.

With respect to several pieces of single crystals the lattice parameters measured by X-ray oscillation photography are a=5.37Å, b=27.1Å and c=30.7Å. It is noticed at once that a superstructure is built in the crystal along the b-axis stretched nearly five times to that of the normal lattice parameter.

The largest single crystal in a strict sense is about $0.5\times0.2\times0.03mm^3$. Crystals formed by merging several



Figs. 3(a), (b) and (c) A single crystal of Bi-2212 photographed devided into three sections (a), (b) and (c).



Figs. 4(a), (b) and (c) Corresponding areas of Figs. 3 etched by Fuji superfix.

single crystals by small-angle-of-misfit grain boundaries are about 2-3×0.5-1×0.03mm^3. The superconducting transition temperatures measured by electrical resistance for merged crystals are at about 85K. Therefore, with built-in superstructures and grain boundaries they behave as an ordinary Bi-2212 superconductor.

Under ICM the most of the as-grown surface areas are finished to atomic flat faces with small number of microstep-line structure. The crystal growth is recognized as due to the lateral growth process. Rather low microstep-line density may explain the slow growth perpendicular to the faces. As the surface is microscopically so flat that important clues for crystal growth are not difinitely provided.

Now the chemical etching seems to have opened an epoch for the research of the crystal growth processes in Bi-2212. Figures 3(a), (b) and (c) show example for the as-grown surfaces observed by ICM. In Fig. 3(a) and to the left of Fig. 3(b) swarmed high steps are seen. The step height is about 300A. In the right part of Fig. 3 (b) and Fig. 3(c), the surface is rather smoothly finished to an atomic scale. Figures 4(a), (b) and (c) indicate the corresponding areas to Fig. 3. Characteristic etch pits are digged along the corresponding stepped structures in Fig. 3. It is recognized that a vast number of etch pits are produced by spontaneous dissolution and not related to outcrop of dislocations. Therefore, it is known that the crystal structure is rather qualified. Figures 5(a) and (b) show a qualified area under ICM before and after the etching. Remarkable etch pits and fine straight line etch-grooves along the a-axis are seen. It clearly indicates that etching has digged out unexpected defect structures built in the crystal. These defect structures would provide clues to the crystal growth processes and contribute to the improvement of the crystal growth technology.

It is to be marked that with respect to the pseudo-square etch pits, for example, in Fig. 5(b) their face diagonals are either parallel to the a-axis or the b-axis. Therefore, the orientation of the crystal is determined at a glance referred to the fine straight line etch-grooves running along the a-axis.

Fig. 5(a) As-grown single crystal of Bi-2212.

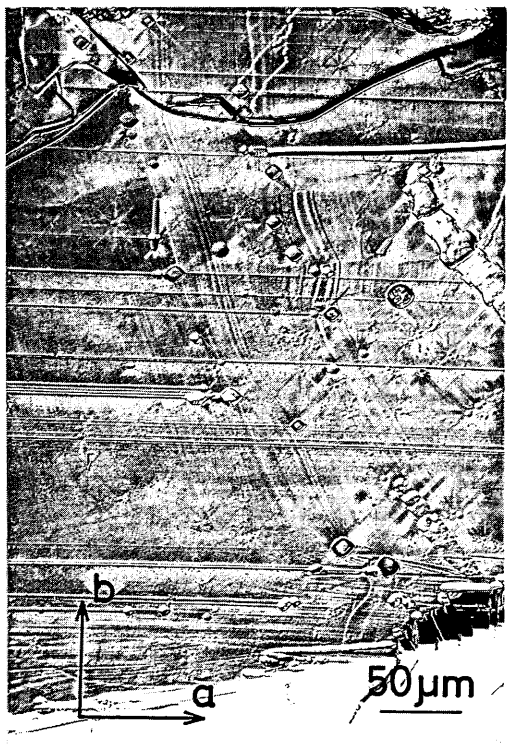


Fig. 5(b) The corresponding area of Fig. 5(a) etched by Fuji superfix.

This is a rapid communication stressed to etch figures of Bi-2212 crystals by acetic acid. It is to be remarked that the etch figures of Bi-2212 by Br_2-ethanol has already been reported by Vasquez and Housley[8] concerning cleaning of the surface for electrical contacts. However, they have not discussed about the correlation as well as the usability of etch figures to the crystal growth.

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