STUDY ON CRYSTALS OF HIGH-T<sub>c</sub> OXIDE SUPERCONDUCTOR
BY VERNEUIL METHOD WITH LASER-HEATING

Ichiroh NAKADA
Institute of research & development, Tokai University,
2-28-4 Tomigaya, Shibuya-ku, Tokyo, 151
TEL:03-3467-2211(EX.465) FAX:03-3467-6177
(Received 25, October 1990 Accepted 22, January 1991)

Abstract The crystals of high-T<sub>c</sub> oxide-superconductors YBCO are grown from the melt at higher temperatures. It is quite disadvantageous that the melt reacts with the crucibles in contact and contaminates the crystals. For the purpose to grow pure crystals a self-sustaining Verneuil method by laser-heating is examined. Unfortunately the oxide superconductors do not grow congruently from the melt. Therefore, further heat treatment is necessary to recover High-T<sub>c</sub> phases.

As for YBCO crystals the boule is capped with a melt in excess of BaCu<sub>2</sub>O<sub>3</sub> where the target crystals grow. This is a flux method in principle. The finished boule is heated at 910°C to melt away the flux to take out crystals. With an interference contrast microscope, it is confirmed that the crystal has grown by step growth process. The steps are rather heavily bunched. The domain structures have no correlation with the step structures. This suggests that the crystal growth is regular, while the domains are formed at the phase transition from the tetragonal to the orthorhombic phase after the crystal growth.

Key Words Superconductor, Crystal Growth, Verneuil Method

1. Introduction

Since the discovery of high-T<sub>c</sub> superconductors it has already passed more than four years 1). Still the nature of the extraordinary superconductivity has not been clarified. In order to promote the fundamental research activities, the preparation of single crystals is of the most importance. Nevertheless, the method has not been established. In the growth of oxide superconducting materials a liquid phase is involved at higher temperatures of 800-1000°C. Except for La-system materials they do not grow congruently from the melt. Therefore, the growth of single crystals does not occur directly from the melt.

Moreover, the melted materials are chemically reactive at higher temperatures against crucibles ever examined. Thus dissolved crucible materials in the melt contaminate the crystals grown. According to Raudise et al. 2) crucibles of Pt, Au, Al<sub>2</sub>O<sub>3</sub>, ThO<sub>2</sub> etc are damaged at higher temperatures by the melt.

As one of examples of contamination the experience by Sato et al. 3,4) would be
A single crystal of tetragonal YBCO(YBa$_2$Cu$_3$O$_x$).
Line configuration on the surface reveals the step structures due to a solution growth of the crystal.

The unit cell structure of the above crystal by the structure analysis. The occupancy of Cu(1) is 0.870(5)

They have made a structure analysis of the YBCO single crystal shown in Fig.1 by means of a four circle X-ray diffractometer. The resulted crystal structure is shown in Fig.2. In the unit cell a deficient occupation is found for Cu in site Cu(1). After long term examination they have come to the conclusion that the contacted alumina crucible contaminated the crystals during the growth. The diffusion of aluminum into the crystal is confirmed by careful analysis by means of atomic absorption spectrometry.

In order to develop a method to prepare pure crystals without using a crucible, the Verneuil process is one of the candidates which could fulfill the above purpose. Ordinarily the Verneuil growth is operated by detonating gas by mixing hydrogen and oxygen. In exceptional case, a plasma flame by electrodeless discharge is applicable. However, these flames are not easily maneuverable in a small scale. For a purpose to cover the disadvantage we have examined the applicability of laser-heating as illustrated in Fig.3.

However, there are some advantages and disadvantages in this method. First advantage is that it is a method without using a crucible. The melt is completely separated from the crucible wall as it is self-sustaining. Therefore, the melt would be free from contamination by crucibles. This is especially suited for the refractory materials.

Secondly as
the heating energy is transferred by a thin pencil of the laser-beam, it is markedly convenient to design devices for the crystal growth. Because just outside the beam it is at room temperature. Therefore, the feeding orifice can be set near the top of the crystal only if attention is payed to keep out of the laser beam. As a result the equipment is built into a compact size. Regarding the oxide materials it works in air and the control of the environment, for example, from the oxygen excess to the oxygen deficiency would be easily carried surrounding the growing boule with a simple wall. Thirdly it is possible to prepare crystals for test with only a small amount of materials. Ordinarily about 10g of the raw materials are enough to prepare a test boule.

The disadvantages are as follows; Firstly the temperature control during the crystal growth is not easy. Therefore, the crystals grow under irregular temperature circumstances. For the uniform powder feeding, it is required for the raw materials to be dry and smoothly movable by vibration. This is a rather severe condition to fulfill. The reacted YBCO is rather suited for feeding, while the starting raw oxides are not.

As remarked above, in the case of oxide superconductors they do not grow congruently from the melt. By cooling of the melt, the solids are either composed of several excess phases or different forms from the target material. Therefore, after solidification, further heat treatments are necessary to come to the target material.

In the second section, the Verneuil process with laser-heating is introduced together with a schematic representation and shown how the method is applied to YBCO. The characterization of the grown crystals by means of the optical microscopy, especially by the interference contrast microscopy are presented. In the third section observation of grown crystals and the response to the thermal treatment is presented and discussed.

2. Experimental

Experimental system for YBCO is described in detail elsewhere 8) and some further elaborations are described below. The Verneuil system with laser-heating is as illustrated in Fig.4 schematically. CO₂-laser beam from the generator is guided by two mirrors to a top of the boule to which powdered YBCO is thrown down by a vibrator. The merely mixed Y₂O₃, BaCO₃ and CuO is not suited for feeding as it would not flow. The mixture once melted
and reacted beforehand by laser-melting is suited for smooth feeding after pulverization. The melting of the mixture must be made carefully so that the melt does not touch the crucible wall. Thus prepared material in a solid rod is crushed and pulverized into a fine powder in a stainless mortar. Then the powder was grown into a boule by Verneuil process. The composition of the reacted material consists of YBCO and BaCu2O3 in molar ratio of about 1:10. The effect of the composition variation to the grown crystals is examined based on the phase diagram presented by Raudise et al. 2) The grown boule is shown in Fig.5.

The boule is divided into small pieces and placed in a quartz tube as shown in Fig.6 and put in a furnace at 910°C overnight so that the flux is swept away as a melt leaving YBCO crystals as they have grown. The melted flux spreading over the inner wall is fixed as a glassy material combined with quartz, while YBCO crystals are left as a swarm of tiny crystals as shown in Fig.7. Grown crystals are 0.1–0.8mm in areal dimension, while the thickness is in the range of several tens of micrometers. As the crystal is so brittle and thin that it is quite difficult to isolate crystals without breaking them into pieces.

After heating at 910°C overnight they are cooled down to 600°C in several hours and taken out of the furnace.

The crystals are examined under the interference contrast microscope.

Fig.5 Boule prepared by laser-heating

Fig.6 Schematic representation how to extract the YBCO crystals out of the boule. (1) quartz tube, (2) alumina boat, (3) a piece from the boule.

Fig.7 Crystals of YBCO left after heating at 910°C overnight. The scale is 1mm/div.
3. Results and Discussion

By the preparation of the Verneuille boule the composition of YBCO and BaCu$_2$O$_3$ in the feeding powder is changed intentionally to see the effect of their ratio. However, there is no marked difference to note.

Nearly all the crystals reveal domain structures as illustrated in Fig.8. The crystals up to 0.2mm in surface dimension is rather qualified. However, grown up over 0.5mm, crystals are in a state of coagulation with a common orientation. It is clear that most of the crystals are a single crystal in the higher temperature region, i.e., the tetragonal form. The crystals are covered by step structures revealing the crystal growth by step growth process.

With respect to domain structures, the contrast in the interference contrast microscope (ICM) is compared to the crystal orientation determined from the lattice parameter measurement by X-ray. The result is shown in Fig.9. In the figure the contrast in ICM is related to the rise and fall of the geometrical steps to the clockwise turn of the contrast lever of the microscope. Corresponding to this, the domains also respond in their contrast as shown in the figure. The dark and the bright contrast regions are related to the crystal axes as indicated in the figure.

Fig.9
The relation between domain contrast and the crystallographic orientation in (ab)-plane. The domain contrast is also related to the geometrical step structure as illustrated in the case of Nomarski-type interference contrast microscope. N indicates the shear direction of the Nomarski prism equipped in the microscope.
Both sides of the orthorhombic YBCO. The macro-domains A are seen common to both sides. (The reversed contrast on both sides is a mere technical problem) Micro-domains are indicated by B. D is an overgrowth of a misoriented crystal.

There occur two kinds of domains. The one is a wide domain and the other is a thin needle-like domain. In Figs. 10(a) and (b) both sides of the same crystal is shown where regions A belong to a wide domain, while regions B belong to a thin domain. The wide domains (A) are passing through the crystal, while thin domains (B) are localized as illustrated in Fig. 11. The origin of the thin domains seems to be related to the stress involved in the crystal, as often misoriented overgrowth is observed on the reverse face of the crystal. The example shown in Figs. 10 by D is just the case for such a situation.

By heat treatment at about 600°C thin domains are apt to vanish. This is one of the proofs that thin domains are related to the stress in the crystal which is annealed away by the heat treatment. As shown in Figs. 12(a) and (b), wide domains also respond to the heat.
treatment at about 600°C overnight. Though the response is rather tedious, there is a tendency for domains to coagulate among them. To clarify a condition of the most favorable heat treatment for reforming into a unified domain in the crystal is our purpose of the research.

![Fig.12(a) Before annealing](image)

![Fig.12(b) After annealing at 600°C overnight. Change of domain patterns are seen.](image)

In Fig.13(a) contrasted line configurations indicate stepped structures developed on the surface. The steps are as illustrated in Fig.14. The steps are decorated by heat treatment at 600-700°C. Surface is damaged by heat treatment. Fortunately steps are decorated beautifully.

![Fig.13(a) Before annealing.](image)

![Fig.13(b) After annealing at 600-700°C. Surface is damaged by heat treatment. Fortunately steps are decorated beautifully.](image)

![Fig.14 Schematic illustration of steps.](image)
treatment at about 600°C as shown in Fig.13(b). Thin step lines not seen in Fig.13(a) is clearly brought into reliefs in Fig.13(b). In Fig.13(a) the fine steps would be about 100Å high, while clearly observed steps are from 500 to 1000Å in height. These are, of course, the heavily bunched steps.

As seen in Figs.10(a) and (b) step structures have no correlation to the domain structures. Also domain pattern shows that the crystal is twinned in the orthorhombic phase. However, it also proves that the crystal has been a single crystal in the preceding tetragonal phase which is directly grown from the melted flux. Under the ICM the steps are seen with exaggeration due to the extremely high contrast revealed by the microscope. However, in practice, the step height is markedly low compared to the thickness of the crystal. The former is about 0.1 micrometer at the highest, while the latter is 30-40 micrometers.

Furthermore, as remarked in Figs.10(a) and (b) the step line structure on both sides of the same crystal has no correlation at all. This clearly indicates that the crystal has grown on both faces independently. This is an important information by the discussion of the crystal growth process involved.

4. Conclusion

The Verneuil method with a laser-heating is proved to be effective in principle to prepare oxide superconductors. However, at the same time it is recognized that there is a technical barriers to be overcome to reach target crystals. The problems would be solved together with the elucidation of the crystal growth processes involved.

Acknowledgement

This is a part of the work being carried in our laboratory. The author thanks to Mr. K. Ishida and Mr. T. Yoshimura for the cooperative work. Also, the author is sincerely grateful to Prof. M. Iida, Prof. T. Kuros, Dr. Y. Akiba of Tokai University as well as Prof. I. Ogura and Prof. K. Kuroda, Dr. M. Itoh and Dr. T. Shimura and Mr. M. Chihara for encouraging discussions and helps to carry experiments.

References:

This paper was presented in the Satellite Conference on Superconductors at Tokai University, Oct. 25, 1990.