研 究 速 報
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Verneuil Method by Laser-Fusion for High-T_c Oxide Superconductor

酸化物高温超伝導体用レーザー溶融ベルヌイ法

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1. INTRODUCTION

At present, the intensively studied high transition-temperature (T_c) oxide superconductors are chemically active to all the crucible materials at higher temperatures[1]. This is a serious neck to prepare high purity specimens in a crucible without contamination. With a purpose to solve this problem we have introduced a Verneuil method with laser-fusion as reported in previous papers[2,3] where $BiSrCaCu_2O_x$ and (La, Sr)$_2$CuO$_4$ were examined. The Verneuil method needs no crucible. Therefore, this is expected to be favorable to prepare high purity specimens.

By the Verneuil method as it includes a melt-growth process, it is necessary to keep a uniform and constant temperature distribution in the boule during growth to prepare high quality crystals. The most important point to be overcome is to establish a uniform powder feeding system, as irregular feeding disturbs the temperature at the liquid-solid interface seriously. By an ordinary Verneuil method[4], smoothly movable fine powder is being prepared and fed by mechanical vibration or hammering to the container. However, in the persent superconducting oxides, it is difficult to prepare powders in such a favorable condition. They are not dry and liable to coagulate together as to oppose a smooth flow. In previous reports[2,3] powder was fed by hand with a small spoon bit by bit. It was far from a uniform feeding. Recently we have located a small platform just above the growing boule and the powder to feed was placed on it and let fall down bit by bit. This method provided a uniform feeding. Further, the vessel supporting a boule was turned so that a uniform temperature distribution was built in it. The technique was applied to prepare (La, Sr)$_2$CuO$_4$ and the result was reported in this rapid communication.

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2. EXPERIMENTAL

The laser system in the present experiment was as reported in a previous paper[2]. Starting powder materials were commercial La_2O_3, $SrCO_3$ and CuO mixed in a stoichiometry of $(La_{0.93}, Sr_{0.07})_2CuO_4$. A part of the mixed powder was put in a cup-type alumina crucible 10ml in volume placed on a turn

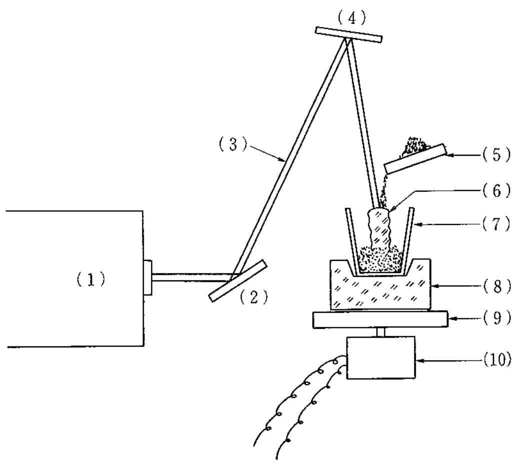


Fig. 1 Verneuil system by laser-fusion
(1) CO_2-laser, (2), (4) mirror, (3) laser beam, (5) platform for powder feeding, (6) growing boule, (7) alumina crucible for powder vessel, (8) supporter of the vessel cut from a brick, (9) turn table, (10) synchronous motor

table and melted from the above by lasser beam. Addidtional powder was dropped from a small platform placed above the boule. The system was shown schematically in Fig. 1.

The turn table was driven by a synchronous motor at 0.5rps. Owing to the rotation, a uniform melt was formed at the top of the boule about 4mm in diameter. The direction of the incident laser beam was tilted several degrees from the vertical, in order to avoid the platform from direct exposure to radiation. The location of the platform was adjusted vertically and horizontally with a supporting system.

The platform was quite simple as illustrated in Fig. 2. It is a small tray with a narrow beak. A powder placed on the flat was pushed to the beak bit by bit with a small spatula and dropped from there. Thus fed powder was caught at the top of the boule and vanished into the melt instantaneously. The growth rate was about 1 to 2cm/h.

The superconductivity was confirmed by the magnetic susceptibility.

3. RESULTS AND DISCUSSION

An example of a boule grown was shown in Fig. 3 (a). It was revealed that the Verneuil method by laser-fusion provided quite a unique technique for crystal preparation. We can manipulate the growing boule at an extremely nearby place avoiding a risk of exposure to high energy density heating beam. With an ordinary Verneuil method by flame-fusion[4], the boule grown was surrounded by a high temperature flame. It is not possible to place a platform in the neighbourhood for powder feeding.

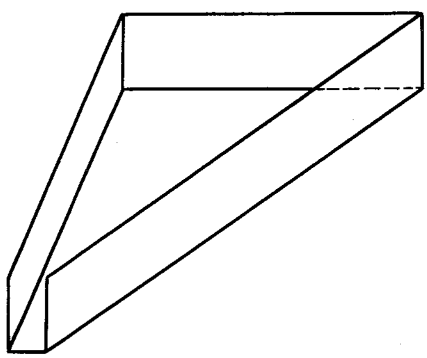
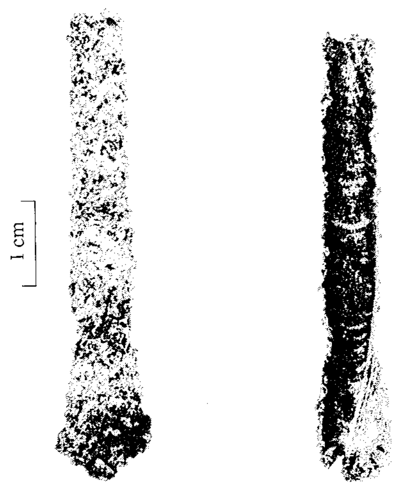


Fig. 2　Platform with a beak for powder feeding

As the diameter of the laser beam was confined to 4mm in this experiment, the outer side-face of the boule was attached by scattered powder in a semi-melt condition. A half-cut plane along the growth direction was shown in Fig. 3 (b). From the cross section, fringes concaved upwards showed the meniscus of the liquid-solid interface during the growth. The nonuniform appearance of the plane of cross section was produced by the instability of this material in air. In a previous[3] paper we have remarked that this boule was unstable to acid. However, recent experience revealed that this material is unstable even in air. Ordinarily, sintered as well as flux-grown $(La, Sr)_2CuO_4$ are stable even for a long standing time in air. The process for degradation with respect to our boule is under study at present.

The dependency of the magnetic susceptibility on temperature was shown in Fig. 4. The on-set temperature to superconductivity was about 35K. This was lower than the nominal T_c of 40K for this composition. The cause for inferiority may be related to the degradation of this material as it was kept in air overnight before the measurement of the susceptibility.

In conclusion, we have established a system of a Verneuil technique by laser-fusion for the high-T_c oxide materials. A combination of the laser heating



(a)　　(b)

Fig. 3　(a)　Melt-grown boule of $(La_{0.93}, Sr_{0.07})_2CuO_4$,
(b)　Section of the boule shown in Fig. 1 (a)

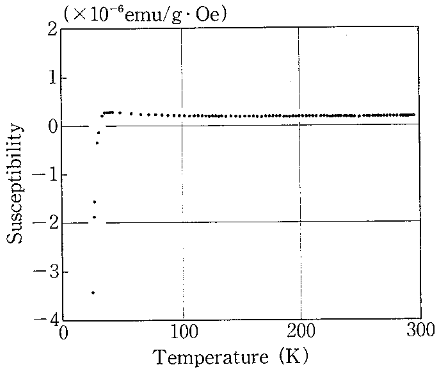


Fig. 4 Magnetic susceptibility of the as-melt-grown $(La_{0.93}, Sr_{0.07})_2CuO_4$

with a powder feeding platform and a turn table functioned effectively in the field of the interesting but complicated materials.

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