研　究　速　報

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Preparation of $(La, Sr)_2CuO_4$ High-T_c Superconductor by Laser-Melting without Crucible

$(La, Sr)_2CuO_4$高温超伝導体の無るつぼレーザー溶融法による作成

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1. INTRODUCTION

In a previous paper[1] we have reported on a new growth technique for the high-transition-temperature (T_c) oxide superconductor $BiSrCaCu_2O_x$ from the stoichiometric melt produced by laser-heating. The as-melted material presented no superconductivity. Annealing at 830～850°C overnight in air induced a phase transition to the superconducting material.

As is well known Bednorz and Müller[2] first discovered a superconductor $(La, Ba)_2CuO_4$ as a superconductor with T_c of 30K. This was followed by $(La, Sr)_2CuO_4$ with a higher T_c of 40K[3] at La : Sr≡ 0.93 : 0.07.

Up to the present, most of the experiments were made using polycrystalline materials prepared by sintering of a stoichiometric mixture of oxide components at about 950°C. For the fundamental researches, of course, we need single crystals and for this purpose a flux method was applied using CuO as a flux[4,5]. According to the reports, synthesized $(La, Sr)_2CuO_4$ was dissolved in a melt of CuO at about 1300°C. Then the solution was slowly cooled. Single crystals nucleated on the melt surface at about 1160°C increased their size to 8×8×2mm. The crystals were dipped up by plutinum net from the melt and slowly cooled to room temperature.

With flux method, however, it was difficult to avoid contamination from the crucible. Such a problem could be solved by laser-melting method previously reported by us[1]. In this rapid communication we report on the application of laser-heating to grow $(La, Sr)_2CuO_4$ boules from a stoichiometric melt by selfsustaining method without using a crucible.

2. EXPERIMENTAL

The laser system used in the present experiment was as reported previously[1]. As a starting material, commercially available La_2O_3, $SrCO_3$ and CuO were weighted to a stoichiometric ratio of $(La_{0.93}, Sr_{0.07})_2CuO_4$ and mixed in a mortar. The mixture was then put in a cup-type alumina crucible 10ml in volume and melted from above by laser beam. Only the central confined area 4mm in diameter was heated. By an optical pyrometer the melting point of the mixture was 1050 ± 20°C. In our laser system, the temperature at a top of the melt rose to about 1600°C at the maximum output of 50W. Even with the maximum power, still the melting of the material was rather tedious. As a criterion the attainable temperature was estimated from a balance between the incident power and the energy loss by black body radiation. Neglecting the loss by heat conduction and convection to the surrounding, the highest temperature was 2600°C.

As the powder melted, it contracted extremely. Accordingly, the feeding was made manually with a small stainless spoon and the rate was controlled by visual observation. The growth rate of the boule was about 1cm/h.

The as-grown boule was electrically a conductor. The crystal structure was examined by powder X-ray diffractometry. The occurrence of superconductivity was confirmed by measuring a magnetic susceptibility.

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3. RESULTS and DISCUSSION

An example of a boule was shown in Fig. 1. The appearance was like a small lump of lava. The irregular form was produced by fused powders randomly attached to the surface.

The powder X-ray diffraction pattern was shown in Fig. 2 with net plane indices. It was clear that $(La, Sr)_2CuO_4$ was produced by merely melting the stoichiometric mixture. The crystal was tetragonal with lattice parameters $a=b=3.795$ Å and $c=13.300$ Å. The lattice parameters changed depending on the growth conditions.

In order to examine the inner parts of the boule, it was cut along the boule with a cutting-wheel. An example was shown in Fig. 3. While searching an etchant for the cut plane, it was found that this material was easily decomposed by diluted nitric acid. Previously Nakada et al.[6] found that $YBa_2Cu_3O_7$ was easily decomposed by warm water at 35°C. At the time, $(La, Sr)_2CuO_4$ was examined as well for the resistance to water and was confirmed to be stable even to the boiling water. However, $(La, Sr)_2CuO_4$ proved to be so unstable against the acid. Figure 3(a) showed the exterior, while Fig. 3 (b) showed the cut plane etched by diluted nitric acid for about a minute. As the etched plane was roughened so seriously that it appeared like an exterior face. From the photograph it could be recognized that there remained regions of incomplete reaction with white freckles. This suggested us to apply more slow growth rate to the boule.

With manual feeding of the powder, it would be difficult to avoid serious temperature fluctuation at the melt-solid interface. Therefore, it would be unfavourable to grow larger single crystals. In our

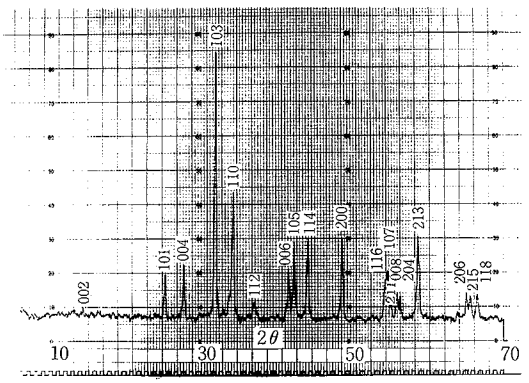
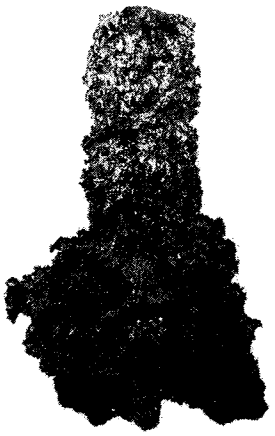
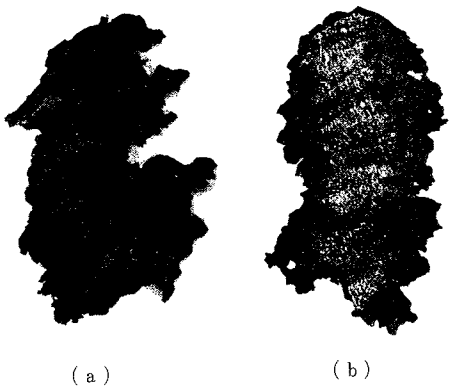


Fig. 2 Powder X-ray diffraction pattern of melt-grown $(La, Sr)_2CuO_4$ for Cu-Kα radiation.



1 cm

Fig. 1 A melt-grown boule of $(La, Sr)_2CuO_4$.



(a)　(b)

1 cm

Fig. 3 (a) Exterior of a boule.
(b) Section of the boule etched by dil-HNO_3.

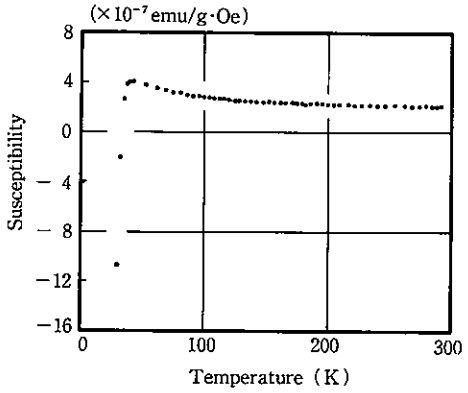


Fig. 4 Magnetic susceptibility of the as-melt-grown $(La, Sr)_2CuO_4$.

case, however, the examination by back-Laue photography revealed that even with the boule shown in Fig. 3, tiny single crystals grew larger than 1mm in dimension. In principle it would be possible to grow larger single crystals if we would use a stationary powder feeding system.

The dependency of magnetic susceptibility on temperature was shown in Fig. 4. The on-set temperature to superconductivity was about 35K. This was a little lower than the nominal transition temperature of 40K. The reason for the inferiority would not be due to the principal fault of this method. Probably the involved incompletely reacted material might have influenced the superconductivity.

In conclusion it became clear that the direct melt method by laser of the stoichiometric $(La)_2CuO_4$ including Ba or Sr could provide method to prepare sizable and qualified single crystals without using a crucible.

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