研　究　速　報

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Preparation of Bi-Sr-Ca-Cu-O System High Transition Temperature Superconductor by Laser-Melting without Crucible

Bi-Sr-Ca-Cu-O系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

Since the discovery of the oxide superconductor with high transition temperature by Bednorz and Müller[1] many works have been reported on $(La, Ba)_2CuO_4$ and $YBa_2Cu_3O_7$. Almost all of them were made on sintered polycrystalline materials, except for a few done on quite tiny single crystals. As the material was so exotic that it is, of course, necessary to grow high quality single crystals suitable for the fundamental measurements. However, the materials were rather reactive at higher temperatures to the crucible so that it was difficult to prepare high purity materials from the melt in a crucible[2,3]. Laudise et al.[4] examined the reaction of Pt, Au, Ir, Al_2O_3, ZrO_2 and ThO_2 to $YBa_2Cu_3O_7$. However, they failed to find satisfactory materials among them.

In this case, it is natural to try methods to grow crystals without using a crucible. For the purpose we found a new technique for the oxide superconducting materials by applying a laser-melting method. It was a kind of Verneuil process with laser beam as a heat source. Compared to the usual Verneuil process by flame fusion, the laser-melting is quite unique, as heat energy is supplied through a confined narrow cylindrical or conical path within diameter from several micrometers to several millimeters. Moreover, the temperature reaches several thousands degrees at which every materials could be melted.

For examination of the technique, we prepared Bi-Sr-Ca-Cu-O materials which was recently discovered by Maeda et al.[5] as a high transition temperature superconductor. The electrical and magnetic properties of the prepared materials were also measured.

2. Experimental

A carbon-dioxide laser, type NAL 50D fabricated by Nihon Kagaku Engineering Co. Ltd., was used as the heat source. The radiation power was controlled in a range from 1W to 50W by changing discharge current. The laser oscillated transversely not in a primary Gaussian mode but in compound modes of annular shape. The 4mmϕ area was heated uniformly under a direct illumination of outcoming laser beam. For melting $BiSrCaCu_2O_{5.5}$ the output power of the laser beam required was about 20W. It was not necessary to use a focussing lens.

For preparing the materials, commercial Bi_2O_3, SrO, CaO and CuO was used and mixed in a stoichiometric ratio of 1 : 1 : 1 : 2 to the total amount of about 15g. A cup-type alumina vessel about 10ml in volume was used as a container of the powder. Only the central region of the heap of powder was heated by laser beam. As the powder melted down and contracted, powder to be fed was supplied manually bit by bit with a small spoon. As the feeding continued a boule grew and increased the volume step by step.

In this experiment the diameter of the melt was about 5mm. As a merit of this method we could observe the melt at a close range with the naked eye. Thus we could control the manual feeding visually. At present any temperature control was not applied.

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Even under such a condition it was enough to prepare a boule.

The temperature of the melt was measured with an optical pyrometer. The melting point of the boule was 950±20°C. During the growth the temperature of the melt on the top of the boule was kept to 1050±10°C.

3. Results and Discussion

Our experiment was rather preliminary at present. We used neither rotating system to build a uniform temperature distribution in the boule nor an equipment for a stationary powder feeding. As a result the shape of the boule grown was irregular. However, this was enough for the characterization of the materials. An example of a boule was shown in Fig. 1. As the boule did not touch the container while growing, there was no fear for impurity contamination from outside.

Thus prepared boule was a polycrystal. The product was examined by a powder X-ray diffractometry. The chart pattern was shown in Fig. 2 with indices. The crystal was determined to be hexagonal with lattice parameters a=17.30Å and c=12.17Å. The density of the boule measured by a specific gravity bottle was 5.48g/cm³. This indicated that the unit cell contained 18.8 molecular units of $BiSrCaCu_2O_{5.5}$. Therefore, the crystal structure must be so complicated compared to $YBa_2Cu_3O_7$ for which the unit cell was composed of one molecular unit. However, as far as the X-ray diffractometry concerned, the material seemed to contain much amorphous phases as indicated by the high background scattering. Therefore, the above density as well as the number of molecular units in the unit cell would be corrected referred to the pure single phase material in future. We call this as a high-temperature-phase material.

When the above material was annealed at 850°C in air overnight, the crystal structure changed to that of a low-temperature-phase. The chart pattern of an X-ray diffractometry was shown in Fig. 3 with indices.

The same X-ray pattern was also reported by

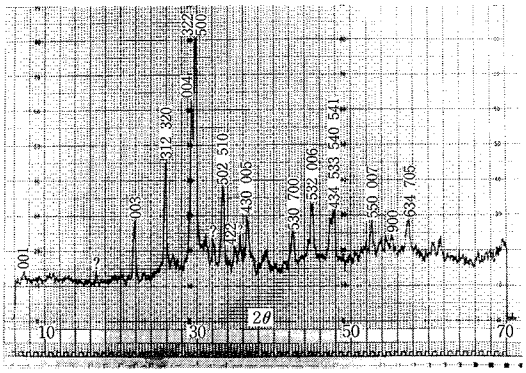

Fig. 2 Powder X-ray diffraction pattern of the high-temperature-phase $BiSrCaCu_2O_{5.5}$ for Cu-Kα radiation

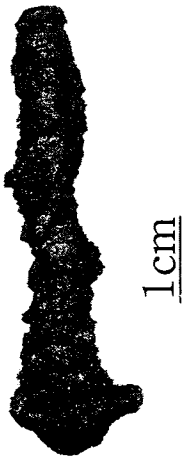

Fig. 1 A boule of $BiSrCaCu_2O_{5.5}$ grown by laser melting

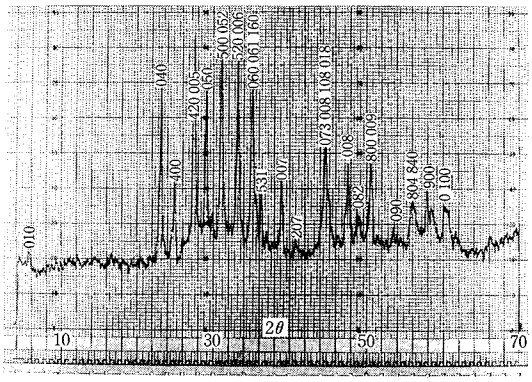

Fig. 3 Powder X-ray diffraction pattern of the low-temperature-phase $BiSrCaCu_2O_{5.5}$ for Cu-Kα radiation

Maeda et al.[5], Takayama-Muromachi et al.[6] and Tarascon et al.[7]. Maeda et al. related the structure to a molecular species of $BiSrCaCu_2O_x$. Takayama-Muromachi et al. determined the crystal system to compositions of either $Bi_2(Ca, Sr)_3Cu_2O_9$ or $Bi_2(Ca, Sr)_{3-\Delta x}Cu_2O_{9-\Delta y}$ as tetragonal with lattice parameters a=5.3983(3) Å and c=30.646(1) Å. Tarascon et al. claimed a tetragonal unit cell for $Bi_3Sr_4Ca_4Cu_3O_y$ with a=3.817Å and c=30.6Å.

As considered from a rather high background in the X-ray scattering, the materials prepared by various groups were not yet in a pure single phase. There remained unreasonable indexing for the diffraction patterns. Therefore, we believe that the reported crystal structures still includes ambiguity. In this paper we tentatively presented an orthorhombic crystal structure with lattice parameters a=14.40Å, b=15.32Å and c=16.25Å. The density of the boule was 5.67g/cm^3. This indicated that the unit cell contained 22.1 molecular units.

The dependence of the electrical resistance to temperature for the high-temperature-phase material was shown in Fig. 4 which suggested the superconductivity below 20K. However, the magnetic susceptibility presented only a paramagnetic response down to the liquid helium temperature as shown in Fig. 5. This showed that small region in the boule behaved superconductivity, probably due to the occurrence of the low-temperature-phase locally. Therefore, it should be concluded that the high-temperature-phase had no superconductivity.

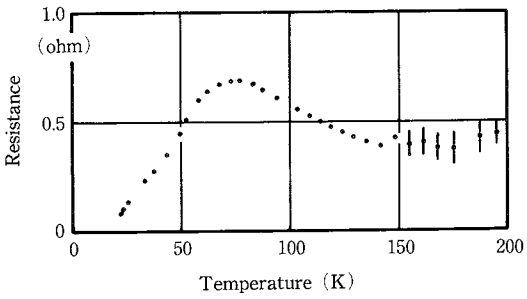

Fig. 4 Temperature dependence of the electrical resistance of the high-temperature-phase $BiSrCaCu_2O_{5.5}$

The dependence of electrical resistance of the low-temperature-phase material to temperature was shown in Fig. 6. It became a superconductor below 60K. From the magnetic susceptibility it is recognized that the superconductivity started at about 80K as shown in Fig. 7. It is to be remarked that from room temperature down to the superconducting transition temperature, the magnetic susceptibility revealed Pauli paramagnetism. This is a characteristic behaviour of high purity materials.

It became clear that it was possible to grow the oxide superconducting materials by modified Verneuil method by means of the laser-heating from melt without a crucible.

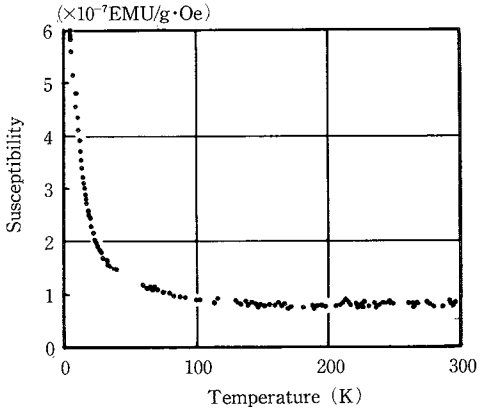

Fig. 5 Temperature dependence of the magnetic susceptibility of the high-temperature-phase $BiSrCaCu_2O_{5.5}$

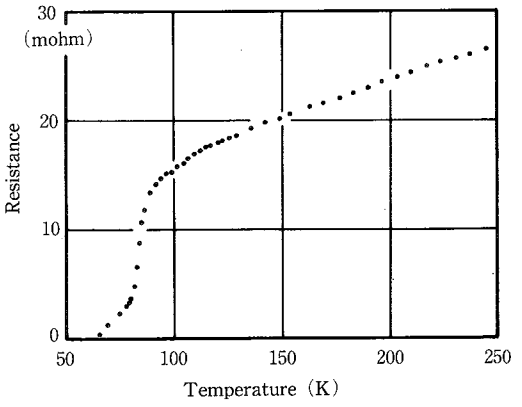

Fig. 6 Temperature dependence of the electrical resistance of the low-temperature-phase $BiSrCaCu_2O_{5.5}$

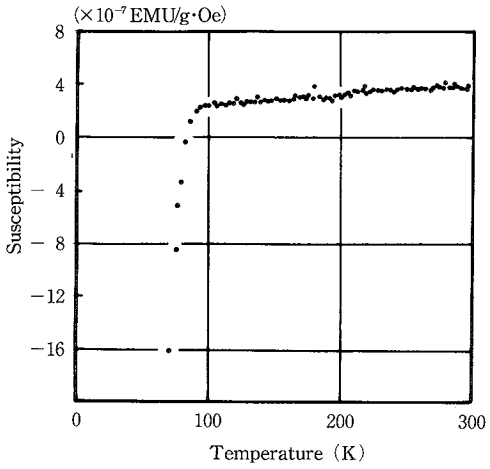

Fig. 7 Temperature dependence of the magnetic susceptibility of low-temperature-phase $BiSrCaCu_2O_{5.5}$

Sometimes the boules thus prepared from the melt needs annealing at lower temperatures in a furnace. By such treatment we must use a crucible as a container of the boules. In this case the role of the crucible is quite different from a container of the melt at higher temperatures. The reaction between the boules and the crucible is usually negligible.

At present the grown boules were polycrystals. However, it would be possible to grow single crystals by seeding as the case of ruby or sapphire single crystals by the ordinary Verneuil process. Even without a seed it would be possible to prepare polycrystals composed of small single crystals grown up in size available to the wide research fields.

As an example, the case of $BiSrCaCu_2O_{5.5}$ was reported. Papers to follow soon would present results for $YBa_2Cu_3O_7$ and $(La, Sr)_2CuO_4$ as well.

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