Mem. Fac. Sci. Shimane Univ.,
21, pp. 83–87 Dec. 20, 1987

Effect of Compression Before Sintering on Superconductivity of High T_c Ba-Y-Cu-O

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(Received September 5, 1987)

Superconducting transition temperatures have been observed by electrical resistance measurements for the several samples of $Ba_2Y_1Cu_3O_{7-x}$ which prepared under compression up to 70 kbar before sintering. The onset and end points of the supercoducting transition decreased with increasing pressure. The temperature dependence of electrical resistance for high pressure samples showed a semiconducting behavior in the normal resistance region and the superconducting transition around 60 K indicating the existence of orthorhombic phase-II. The Meissner effect has been measured in order to confirm a superconducting state.

§I. Introduction

Since the discovery of the high-T_c superconductivity in Ba-La-Cu-o system with T_c higher than 30 K was reported by Bednorz and Müller,[1),2)] extensive studies have been carried out and as the second large advance, discovery of Ba-Y-Cu-O system with much higher and stable T_c around 90 K has been reported by Chu *et al.*[3),4)] Recently, the high T_c superconductor in the system Ba-Y-Cu-O was identified to be $Ba_2Y_1Cu_3O_{7-x}$,[5),6)] and its crystal structure was investigated by X-ray[7)-9)] and neutron diffraction method.[10)] The superconcucting compound has an orthorhombic perovskite-related 3-c structure. High-temperature X-ray diffraction study showed that the tetragonal phase is stable at high temperatures and transforms into the orthorhombic phase at temperatures below about 650°C. The high-temperature phase survives more or less on cooling in usual sample preparation. The two phases have nearly the same structure closely related to that of perovskite-type compounds. Neutron diffraction study showed that in the orthorhombic phase, the occupation factor of an oxygen atom on the *a*-axis differed greatly from that on the *b*-axis, which is the main reason why Ba-Y-Cu-O crystallizes in the orthorhombic phase. There exist the two types of orthorhombic superconductiog phase.[11)] One (ortho-I) is the superconducting phase with T_c above 90 K. The normal resistivity shows metallic and the lattice parameters are $a=3.825$ Å, $b=3.893$ Å and $c=11.676$ Å. The other (ortho-II) is the superconducting phase with T_c about 60 K. The normal resistivity shows semiconducting behavior and the lattice parameters are $a=3.835$ Å, $b=3.880$ Å and $c=11.744$ Å, appreciably different from those of the high T_c ortho-I phase. The tetragonal phase is nonsuperconducting above 1.3 K. These phases are concerning to change the concentration of oxygen vacanies with the formation tempeature of samples. The superconducting properties are also very sensitive to inhomogeneities in the superconducting phase itself. For example, the semiconducting green phase, whch is probably rich in yttrium and poor in copper, was found to be detrimental to the superconductivity.

It is interesting to measure the effect of compression before sintering on superconductivity in the sample preparation for Ba-Y-Cu-O.

§2. Experimental procedure

The compound $Ba_2Y_1Cu_3O_{7-x}$ was prepared from the appropriate mixture of $BaCO_3$ (purity 99.9%), Y_2O_3 (99.9%) and CuO (99.9%). First, the stoichiometric mixture was calcined in an alumina boat heated at 900°C for 16 hrs in air. After the first reaction, the pellet was taken out of the furnace. The pellet was ground to powder using mortar and pestle. The powder mixture was pressed at the applied pressure of 3 kbar, 35 kbar, 60 kbar and 70 kbar to produce pellets of 2.5 mm in diameter and 5 mm in hight. Subsequently, the pellets were sintered at 920°C for 45 hrs in air and cooled to room temperatute out of the furnace. The color of the pellet at this point was black.

The crystals structure of the synthesized oxides was examined by X-ray powder diffraction analysis with monochromated Cu K_α radiation. The Meissner effect was measured in the temperature range from 4.2 K to room temperature at the applied static field of 100 Oe by means of a vibrating-sample magnetometer.

Resistance measurement was made by the four probe method over the temperature range of 48 K to 250 K. Electrical contact was made to the sample by using the ultrasonic vibration soldering system. The temperature was measured using a calibrated Lake-Shore-Cryotronics-Inc. platinum resistance thermometer with accuracy better than 0.1 K.

§3. Results and Discussion

Figure 1 shows the X-ray powder diffraction pattern of $Ba_2Y_1Cu_3O_{7-x}$ sample. All the reflection peaks can be indexed as an orthorhombic phase with lattice parameters of a=3.820 Å, b=3.888 Å and c=11.673 Å. Effect of compression before sintering was not observed by the X-ray diffraction patterns. The temperature dependence of the magnetic susceptibility for the sample compressed at 3 kbar is shown in Fig. 2. A sharp transition was observed at 84 K and the Meissner signal indicates that the sample is in superconducting state.

The electrical resistances of Ba-Y-Cu-O system measured with the dc current of 10 mA at various pressures are plotted as a function of temperature in Fig. 3. The values of resistances are normalized at that of 250 K. The resistance at 3 kbar decreases monotonously with decreasing temperature showing the metallic resistance in the

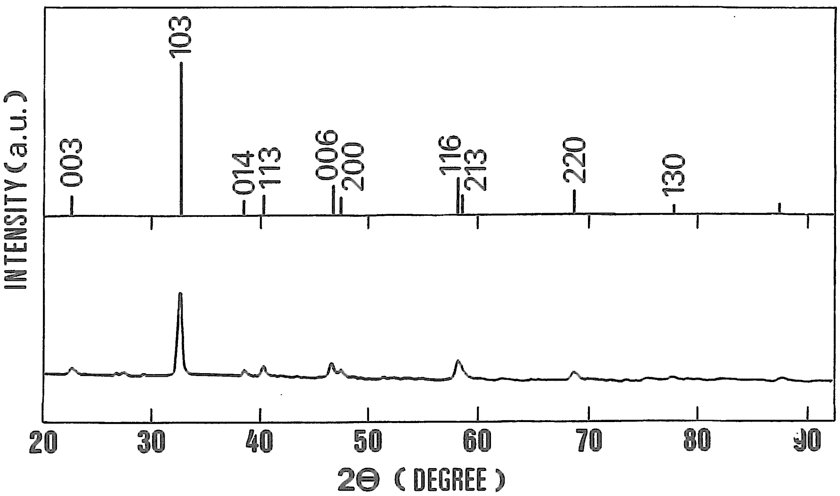

Fig. 1. X-ray powder diffraction pattern of $Ba_2Y_1Cu_3O_{7-x}$ at room temperature.

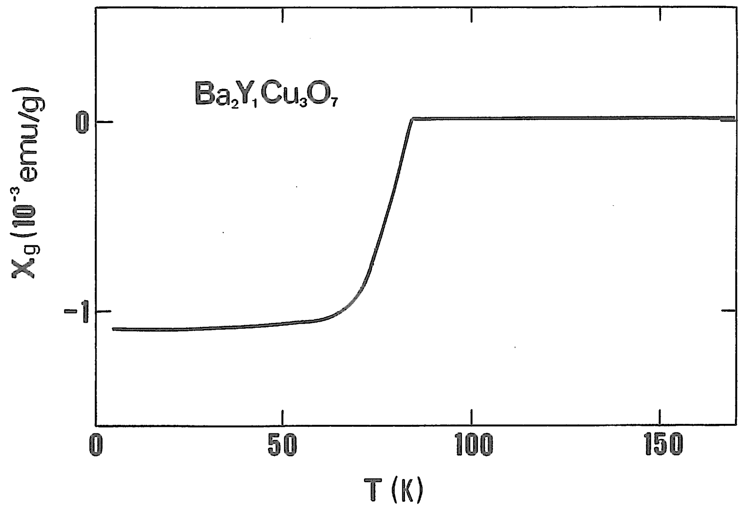

Fig. 2. Temperature dependence of the magnetic susceptibility of $Ba_2Y_1Cu_3O_{7-x}$.

normal state region, and then starts to drop around 90 K. As clearly seen in the figure for a specimen at 3 kbar, a sharp onset of superconducting transition is observed at $T_{co}=94$ K while zero resistivity state (end point) is achieved at $T_{ce}=84$ K. The temperature dependence of the electrical resistance of high pressure samples were found to be semiconductor-like in the normal state region. The superconducting transition temperatures decrease with increasing pressure before second sintering. The effect of compression before sintering on the superconducting transition temperatures are shown in

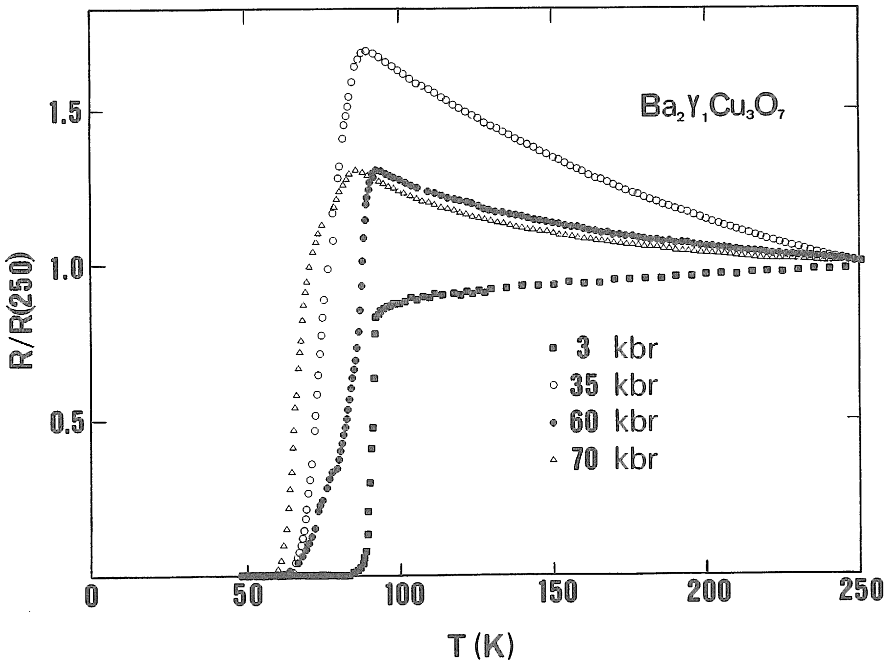

Fig. 3. Temperature dependence of the electrical resistances for $Ba_2Y_1Cu_3O_{7-x}$ at various pressures.

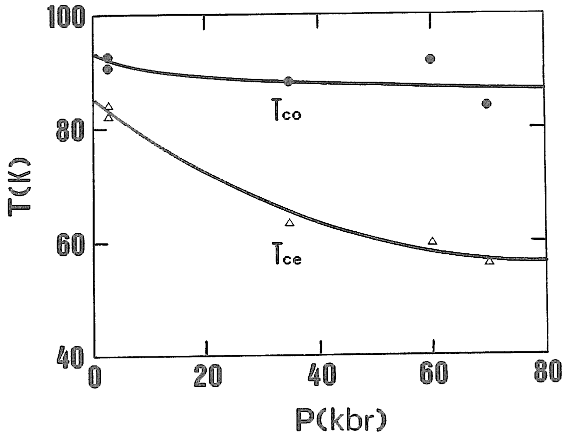

Fig. 4. Effect of compression before sintering on the superconducting transition temperatures T_{co} and T_{ce} for $Ba_2Y_1Cu_3O_{7-x}$.

Fig. 4. The onset temperature T_{co} and end point T_{ce} decrease with increasing pressure. High pressure samples which are high density and hard showed semiconducting behavior and end point of about 60 K. These resuslts show that the high pressure samples have

ortho-II phase in which the concentration of oxygen vacancies increase more than ortho-I phase. After the second sintering, we got out the sample from the furnace. It is fairly difficult to enter the oxygen into the high density and hard samples in a few minutes to cool down from 920°C to room temperature. The superconducting state is very sensitive to the concentration of oxygen vacancies concerning to the valence state of Cu ions.

Acknowledgments

The authers are grateful to T. Hatta, T. Ishikawa and Y. Suzuki for their help with the sample preparations and the resistance measurements.

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