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Magnetic and Electrical Properties of High-Tc Superconductor $YBa_2Cu_3O_{6.87}$

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The structural, electrical and magnetic properties were investigated for the high-T_c superconductor $YBa_2Cu_3O_{7-x}$ where x was 0.13. The results of temperature dependence of the resistivity and the magnetization in $YBa_2Cu_3O_{6.87}$ whose structure and phase are confirmed by analysis of X-ray powder diffraction pattern have been reported. A very sharp superconductivity transition appears at 92K in the specimen whose chemical composition is determined from redox titration, strongly suggesting that this specimen consists of a single-phase superconductor. From the results of X-ray diffraction analysis, magnetization curves, levitation and resistance measurements, it is suggested that the observed superconductivity is bulk property in nature and that the $YBa_2Cu_3O_{6.87}$ phase is responsible for the superconductivity of the present reproducible specimen.

Introduction

Extensive studies have been made to clarify the nature of the high-T_c superconductivity, since Bednorz and Muller[1] reported possible high-T_c superconductivity in the Ba-La-Cu-O system. At ambient pressure a stable superconducting transition temperature between 77 and 93 K has been observed in Y-Ba-Cu-O systems[2,3]. Even for the Y-Ba-Cu-O system of the same composition, the magnetic and electrical properties vary depending on the method of specimen preparation. A mixing process of starting materials, sintering temperature and time, and cooling rate are expected to be important for obtaining homogeneous high-T_c superconductors. Although the diamagnetism due to the superconductivity has been reported by Wu *et al.*[2], the magnetic susceptibility has reached only about 25% of the complete Meissner effect. In the temperature dependence of the magnetic susceptibility, a great variety of specimen characteristics has been observed and reported around 90 K, depending on the sintering condition and starting composition[2,4]. From the resistivity and magnetic susceptibility data, it is suggested that the multi-phase in Y-Ba-Cu-O system exists even in the case that sharp superconducting transition is observed in resistance at around 90 K. Since the magnetic susceptibility is essential for the superconductivity and is sensitive to the multiphase, the magnetization curve in the low and the high fields is useful and important not only in the new scientific information concerning the high-T_c superconducting mechanism but also in the field of industrial applications. However, the full value of diamagnetic susceptibility expected from the Meissner effect was not observed, since impurity phases may exist in high-T_c superconductor. In the very recent experimental results, surprising results are in the high-T_c magnetic superconducting oxides[5,6]. Although the rare-earth ions are magnetic, rare-earth ions-Ba-Cu-O systems are still comparable in T_c with that of Y-Ba-Cu-O systems. The present work aims at synthesizing the reproducible high-T_c superconductor, refining its crystal phase, and determining the magnetic and electrical properties. In continuous work we will try to synthesize a new high-T_c superconductor which shows dry-ice transition temperature.

Experimental

Sample preparation and analysis. $YBa_2Cu_3O_{6.87}$ was prepared by an ordinary powder metallurgy technique. Starting powder materials of Y_2O_3(99.99%, Aldrich Co.), $BaCO_3$ (99.999%, Aldrich Co.) and CuO(99.999%, Aldrich Co.) were ball-mill-mixed and calcined at 880 °C for 10 hours in air. The well mixed powder was pressed into a pellet by 49 MPa and the pellet was sintered at 920 °C for 17 hours in air and then annealed at 700 °C for 12 hours. After annealing, specimen was furnace-cooled to room temperature in air at a cooling rate of 50 °C/hr. X-ray spectra obtained by a diffractometer (Philips, PW 1710, CuK_α) identified the specimen as an essential simple phase of the layered perovskite structure. The high-T_c superconducting phase of present compound as an orthorhombic and oxygen-defect perovskite was found to be chemical composition $YBa_2Cu_3O_{6.87}$ from redox titration[7].

Magnetization and resistance measurements. A powder specimen was used for magnetization measurement. Magnetizations were measured by using a vibrating sample magnetometer (EG & G Princeton Applied Research Co., Model 135) in the fields up to 5 KG at 79 K. A specimen of about 1.3 mm × 5 mm × 12 mm in size was cut from the pellet and was used for resistance measurements. For the resistance measurements, a standard four-probe AC and DC methods were employed and a silver paste(Dupont Co. 4929) was used as contact material. Platinum wires were used as electrical leads and were attached to the sample with conducting silver paste. The current density used for the measurement of electrical resistance was between 1 mA/cm^2 and 10 mA/cm^2, and resolution of the voltage measurement was 1×10^{-8}V. The resistance and transition temperature were

Table 1. Powder X-ray data for $YBa_2Cu_3O_{0.87}$

h.k.l	d_{obs}	2θ	Compound. d_{calc}	I/I_o
0 0 3	3.913	22.7	3.912	22
0 1 3			3.897	
1 0 3	2.741	32.6	2.731	100
1 1 0			2.736	
0 1 4	2.345	38.4	2.344	37
0 0 5			2.347	
1 1 3	2.239	40.3	2.239	16
0 1 5	2.031	44.6	2.010	10
0 0 6	1.949	46.6	1.956	48
2 0 0	1.915	47.5	1.913	17
1 0 6	1.741	52.5	1.741	11
0 2 3			1.744	
1 1 2	1.669	55.0	1.665	10
1 2 3	1.586	58.5	1.587	33
2 1 3	1.572	58.7	1.573	18
1 1 7	1.436	64.9	1.428	6
0 2 6	1.377	68.1	1.380	12
2 0 6	1.365	68.7	1.368	24
2 2 0			1.365	
0 0 9	1.300	72.7	1.298	7
1 2 6			1.304	

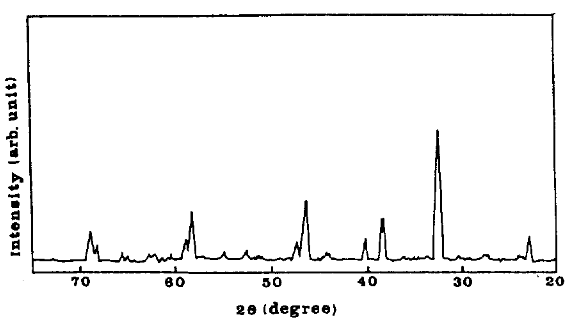

Figure 1. X-ray diffraction pattern of $YBa_2Cu_3O_{6.87}$.

not affected by the current density in this range. The measurements were made at several fixed field in the process of decreasing the temperature. The temperature was measured by Au-7% Fe-chromel thermocouples calibrated by standard platinum resister. The frequence was changed from 20 Hz to 1 KHz. No frequence dependence and no essential difference between both AC and DC four-probe methods were observed.

Results and Discussion

X-ray diffraction data taken at room temperature with a Philips 1710 diffractometer equipped with a curved graphite monochrometer in the scattered beam path are listed in Table 1. Intensity data shown in Figure 1 were collected with CuK_α radiation over a 2θ range from 20° to 75°. The reflections in the X-ray powder pattern of the sample can be successfully indexed on the basis of an orthorhombic unit cell with a = 3.8243 Å, b = 3.8885 Å, and c = 11.687 Å. The lengths of the a and b axes are very close to the cell dimensions of typical perovskite-type compounds, and the length of the c axis is approximately three times as large as that of the a or b axis. This long unit cell tripled along the c-axis is responsible for an orthorhombic structure with an ordering of Y and Ba. The ordering of Y and Ba implies that there are correspondingly two distinctive sites for Cu: one between a pair of the Ba layers and the other between the Y and Ba layers. Each site of Cu is accompanied by a different position of oxygen vacancies around it, indicating the orthorhombic symmetry of the crystal structure[8]. From this fact it is strongly suggested that the crystal structure of $YBa_2Cu_3O_{6.87}$ is closely related to that of perovskite-type compounds[8]. The adapted space group is Pmmm with the highest symmetry.

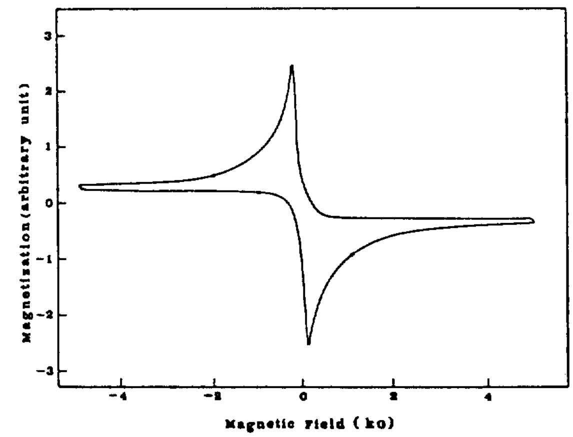

Figure 2. Magnetization curve for $YBa_2Cu_3O_{6.87}$ measured at 79K. First and second runs are shown.

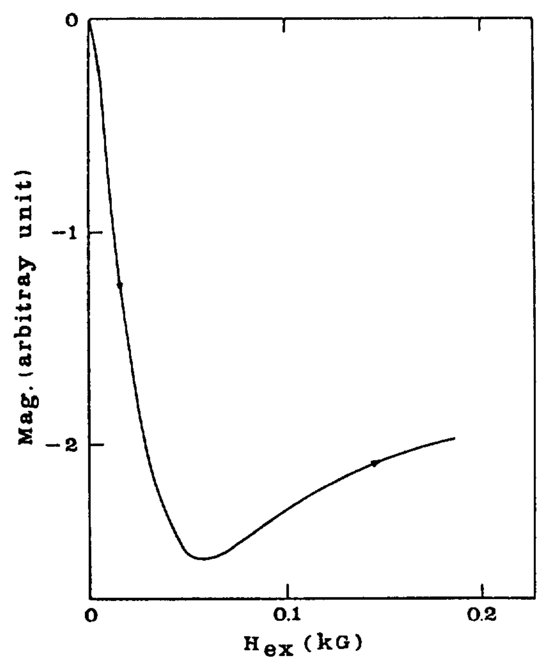

Figure 3. Magnetization curve for $YBa_2Cu_3O_{6.87}$ measured at 79K under low magnetic field.

An extremely large diamagnetism is observed at a temperature as high as 79 K in superconducting $YBa_2Cu_3O_{6.78}$. The magnetization measurements of a powder sample were performed by using a vibrating sample magnetometer in the fields up to 5 KG. A field of 5 KG produced by an electromagnet is seen to be adequate even at 79 K for this superconductor. Magnetization curves at 79 K were measured in

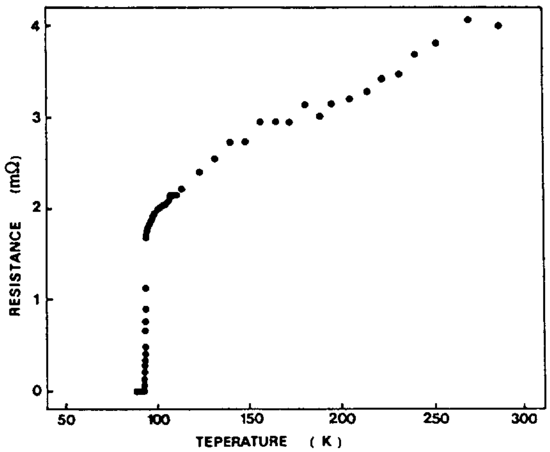

Figure 4. Temperature dependence of the resistivity of $YBa_2Cu_3O_{6.87}$. The onset Tc and the zero-resistance Tc are 98K and 92K, respectively.

constant sweeping rate of applied field of 250 G/min. The magnetization curves obtained at 79 K are shown in Figure 2 and 3, respectively. In Figure 2, results of first run and second run are shown. For the sample of $YBa_2Cu_3O_{6.87}$ with T_c = 92 K, large hysteresis was observed at 79 K in a field up to 5 KG. A typical superconducting magnetization curve for a single phase is shown in Figure 2. Magnetization curves at 79 K clearly indicate that $YBa_2Cu_3O_{6.87}$ is typical type-II superconductor. As shown in Figure 3, lower critical field (H_{c1}) is roughly estimated from magnetization using the concept of the critical state, and H_{c1} is obtained based on extraporating the magnetization curve of an ideal type-II superconductor in the lower fields. From the linear part of the initial magnetization curve in the low-field region the magnitude of the lower critical field at 79 K is estimated to be about 65 Oe for $YBa_2Cu_3O_{6.87}$ superconducting phase. From the results shown in Figure 2 and 3, it is suggested that the magnetism should be attributed to d-electrons of copper atomic orbitals, since yttrium and barium atoms are non-magnetic. However, further study has to be designed to investigate what the magnetic behavior will be in the superconducting state, since copper atoms will play an essential role in metallic conduction of the present material.

Magnetic levitation of the $YBa_2Cu_3O_{6.87}$ disc was carried out at liquid nitrogen boiling point(77 K) in air. The resistance of $YBa_2Cu_3O_{6.87}$ is similar to that of metallic in the normal state at temperatures higher than 98 K and it is decreased almost linearly from the room temperature with decreasing temperature followed by a sharp transition to zero resistance between 98 K and 92 K. The temperature dependence of the resistance of $YBa_2Cu_3O_{6.78}$ is shown in Figure 4. The onset critical and the zero-resistance critical temperatures are 98 K and 92 K, respectively.

In an ideal structure of the present Y-Ba-Cu oxide system, it is known that the Cu^{2+} ions occupy the edge positions forming the norminal square planar (CuO_4)-units and the Cu^{3+} ions occupy the centers of the perfect octahedral at the corners[8]. When the half of the axial oxygen ions is missing from the lattice and all the Cu ions are bivalent Cu^{2+}, the extreme composition may be represented as $YBa_2Cu_3O_{7-x}$ with $0<x<0.5$. The present sample gives the value of $x = 0.13$. The oxygen vacancies can be formed due to the missing of oxygen ions, and the electrons trapped at these vacancies should migrate by the essay ordering of the Cu^{2+} and Cu^{3+} ions through an electron hopping.

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