

High T_c Superconductor, YBa₂Cu₃O_{7-x} ; (I) Its Preparation and Physicochemical Characterization

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고온 초전도체 YBa₂Cu₃O_{7-δ} ; (1) 합성 및 물리화학적 특성 연구

최진호 · 변송호 · 홍승태 · 정덕영 · 최석용 · 김배환 · 김진태
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요 약

고온초전도체인 YBa₂Cu₃O_x를 고온 고상반응에 의해 합성하였다. 산소분압 1기압하에서 940°C, 40시간 열처리후 450°C까지 서냉하여 약 10시간 유지한 후 상온으로 냉각시켜 X-선 분석한 결과 사방결정계를 갖는 단일상 구조임을 탐했으며 초전도전이온도(T_c)는 90 K 이었다. 요드적정법으로 산화환원 적정을 행하여 YBa₂Cu₃O_x의 평균 산소함량(x)을 6.85 ± 0.02로 결정하였고 X-선 광전자분광 분석법으로 YBa₂Cu₃O_x내 Cu 전자의 바닥상태가 d⁸(Cu³⁺) 및 d⁹(Cu²⁺)의 혼합상태이며 시료 표면에 국부적으로 Cu³⁺의 농도가 높음을 알 수 있었다.

ABSTRACT

Almost single phase of Y₁Ba₂Cu₃O_x, which exhibits the onset of superconducting transition at 90K, has been prepared via a conventional ceramic processing route followed by an anneal for a period of 10 hours at 450°C in an atmosphere of 100% O₂. The mean value for the oxygen content has been determined as x = 6.85 ± 0.02 by an iodometric titration technique. X-ray photoemission spectra are found to be consistent with a mixture of the d⁸(Cu³⁺) and d⁹(Cu²⁺) as the ground state and reveals that the local concentration of Cu³⁺ decreases with depth from the surface where x corresponds to 7.0. This is explained as being associated with the intercalation of oxygen during cooling from the annealing temperature.

INTRODUCTION

Since Bednorz and Müller(1) first reported a possible high Tc superconductivity in the La-Ba-Cu-O system, many efforts have been made around the globe to raise the superconducting transition temperature. Above all, discovery of superconductivity in the Y-Ba-Cu oxide system by Wu et al. and Chu et al.(2) opened an era of superconductors which may be usable above the liquid nitrogen temperature.

It has been established later that the superconductive phase is $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ containing a large amount of oxygen vacancy which stabilizes the peculiar orthorhombic perovskite-derivative structure(3). According to the details of the structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ established by various techniques including X-ray diffraction(4), transmission electron microscopy, convergent beam electron diffraction(5) and neutron diffraction (6), Ba and Y ions are ordered in a fashion of Ba-Y-Ba sequence along the c-axis, and oxygen atoms at a $z=1/2$ level are completely deficient. Furthermore half of the oxygen atoms on a $z=0$ plane are lacking (7).

What is crucial for the realization of superconductivity in this system is likely to control the amount of oxygen vacancy as well as its ordering and/or the Cu^{3+} concentration, which is governed mostly by the thermodynamic condition of annealing, i.e., oxygen partial pressure and temperature(8). The oxygen content and $\text{Cu}^{3+}/\text{Cu}^{2+}$ ratio in the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been determined by iodometric titration and TG analysis(9). It has also been reported that the Cu-O chains along the b-axis of the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ play a critical role in superconducting transition either through the existence of mixed Cu^{3+} - Cu^{2+} ions and/or dimensional effects due to the presence of the one-dimensional Cu-O chains (10).

In this preliminary report we present results of the electrical resistivity measurement, iodometric titration, and X-ray photoelectron spectroscopic measurements made on an almost single phase $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ synthesized via a conventional ceramic processing route.

EXPERIMENTAL

The $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powders prepared by a conventional ceramic processing technique; the intimate ground mixture of BaCO_3 , Y_2O_3 and 3CuO was pressed into a pellet, calcined at 900°C in air for 16 hours, reground and pressed into a pellet, and sintered at 940°C in flowing O_2 for 40 hours. The sintered pellet was cooled to a temperature of 450°C at a rate of 100°C/hr , annealed in an atmosphere of 100% O_2 for 10 hours and then removed out of the furnace.

The structure of the prepared samples were examined by X-ray powder diffractometry with Ni filtered $\text{Cu-K}\alpha$ radiation. The conventional four-probe technique was employed to measure the electrical resistivity over a range of temperature, 20 to 300K. Iodometric titration was carried out in an O_2 free-nitrogen gas to avoid the oxidation of iodide ion. Sodium thiosulfate titrant was standardized against KIO_3 . Starch indicator was added immediately before the end point. X-ray photoelectron spectra were recorded as a function of sputtering time on a PHI 5100 Perkin-Elmer spectrometer. Unmonochromatized $\text{Mg-K}\alpha$ radiation of 1253.6 eV was used and the base pressure in the spectrometer was no greater than 2.0×10^{-9} Torr. Argon ion sputtering was made under the condition of 1kV, 25mA, and 2×10^{-9} Torr. The binding energies reported here were corrected from the known reference (BE of $\text{C}_{1s} = 284.6$ eV).

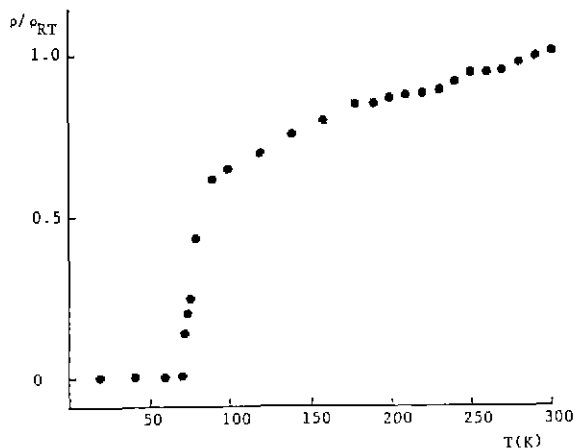
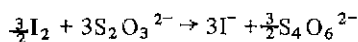
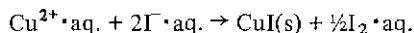
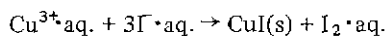


Fig. 1. Temperature dependence of the normalized electrical resistivity for YBa₂Cu₃O_{6.85}

RESULTS AND DISCUSSIONS

The X-ray powder diffraction patterns for the YBa₂Cu₃O_{7-δ} could be successfully indexed on the basis of an orthorhombic unit cell (Tab. 1) as reported by other investigators (3, 8, 11, and 12). The temperature dependence of the electrical resistivity for the YBa₂Cu₃O_{7-δ} is shown in Fig. 1. Superconducting transition with an onset temperature of 90K has been observed under ambient pressure.

We have determined the Cu³⁺/Cu²⁺ ratio of the superconducting phase and therefrom the oxygen nonstoichiometry(x) of a lattice molecule YBa₂(Cu_{3-2x}²⁺Cu_{2x}³⁺)O_{6.5+x} quantitatively by iodometric titration;



The x value has turned out to be 0.35 ± 0.02, which yields the formula of YBa₂Cu_{2.3}Cu_{0.7}²⁺³⁺O_{6.85}. The present result is in excellent agree-

Table 1. Powder X-ray data for YBa₂Cu₃O_{6.85}.

| h | k | l | d(obs.)/Å | d(cal.)/Å | I/I ₀ |
|---|---|---|-----------|-----------|------------------|
| 0 | 0 | 1 | 11.72 | 11.69 | 4 |
| 0 | 0 | 2 | 5.85 | 5.84 | 4 |
| 0 | 0 | 3 | | 3.896 | |
| 0 | 1 | 0 | 3.879 | 3.889 | 12 |
| 1 | 0 | 0 | 3.827 | 3.824 | 4 |
| 0 | 1 | 2 | 3.236 | 3.237 | 5 |
| 1 | 0 | 2 | 3.203 | 3.200 | 5 |
| 0 | 1 | 3 | 2.753 | 2.752 | 58 |
| 1 | 1 | 0 | | | |
| 1 | 0 | 3 | 2.729 | 2.729 | 100 |
| 1 | 1 | 1 | 2.655 | 2.655 | 1 |
| 1 | 1 | 2 | 2.471 | 2.471 | 3 |
| 0 | 1 | 4 | | 2.336 | |
| 0 | 0 | 5 | 2.339 | 2.337 | 14 |
| 1 | 1 | 3 | 2.235 | 2.234 | 19 |
| 0 | 1 | 5 | 2.005 | 2.003 | 1 |
| 1 | 1 | 4 | 1.9943 | 1.9934 | 1 |
| 0 | 0 | 6 | 1.9497 | 1.9473 | 13 |
| 0 | 2 | 0 | 1.9434 | 1.9443 | 18 |
| 2 | 0 | 0 | 1.9117 | 1.9121 | 12 |
| 1 | 1 | 5 | 1.7758 | 1.7746 | 4 |
| 0 | 1 | 6 | 1.7416 | | |
| 0 | 2 | 3 | 1.7387 | 1.7396 | 2 |
| 1 | 2 | 1 | | 1.7144 | |
| 2 | 1 | 0 | 1.7146 | 1.7159 | 1 |
| 2 | 0 | 3 | | 1.7165 | |
| 1 | 2 | 2 | 1.6612 | 1.6616 | 1 |
| 1 | 2 | 3 | | 1.5835 | |
| 1 | 1 | 6 | 1.5845 | 1.5850 | 25 |
| 2 | 1 | 3 | 1.5705 | 1.5703 | 14 |
| 0 | 1 | 7 | 1.5333 | 1.5341 | 2 |
| 0 | 2 | 5 | 1.4947 | 1.4948 | 3 |
| 2 | 1 | 4 | | 1.4796 | |
| 2 | 0 | 5 | 1.4805 | 1.4800 | 3 |
| 1 | 1 | 7 | 1.4252 | 1.4239 | 2 |
| 0 | 2 | 6 | 1.3764 | 1.3761 | 5 |
| 2 | 0 | 6 | | 1.3645 | |
| 2 | 2 | 0 | 1.3634 | 1.3633 | 10 |

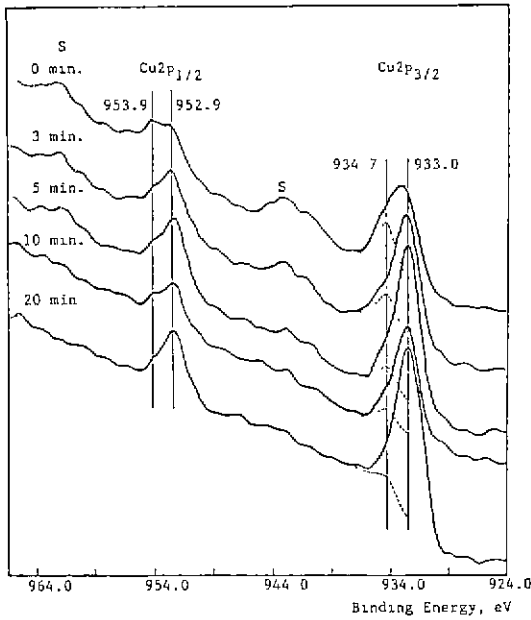


Fig. 2. XPE spectra in the region of the binding energy for Cu2p electrons in the $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$ against the Ar ion sputtering time.

ment with the equilibrium oxygen content predicted by Jorgensen et al.(10) at 450°C in 1 atm Po_2 .

We performed also X-ray photoelectron spectroscopic measurements on $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$ to confirm the coexistence of Cu^{3+} and Cu^{2+} . Figure 2 shows the X-ray photoelectron spectra against the Ar ion sputtering time in the region of the binding energy for the Cu2p electrons. The intensity of the minor shoulder peak ($2p_{3/2} = 934.7$ eV) decreases gradually and the major one ($2p_{3/2} = 933.0$ eV) increases sharply with the increased sputtering time. The peak separation was based on the reference spectra for the $\text{La}_2\text{Cu}^{2+}\text{O}_4$ and the $\text{La}_4\text{LiCu}^{3+}\text{O}_8$ (prepared under the high oxygen pressure(13)). The binding energies for the Cu2p_{3/2} electrons in the La_2CuO_4 having only Cu^{2+} ions and the $\text{La}_4\text{-LiCuO}_8$ in which only the Cu^{3+} ions exist were 933.2 and 934.6 eV, respectively. Compared

with these results, the present spectra for $\text{YBa}_2\text{-Cu}_3\text{O}_{6.85}$ are consistent with a mixture of the $d^8(\text{Cu}^{3+}) 2p_{3/2}:934.7$ eV and the $d^9(\text{Cu}^{2+}) 2p_{3/2}:933.0$ eV configurations as the ground state. The band in the region of the binding energy for the Cu2p_{3/2} electrons was separated by using a reiterative curve fitting computer program provided by Perkin-Elmer. The content of Cu^{3+} ion calculated from the area of the separated bands before the Ar ion sputtering is approximately 1.0 which is almost identical with a chemical formula of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and this is slightly higher than that (0.7) from the redox titration. This indicates that Cu^{3+} ions present in the sample are more or less concentrated on the surface of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ phase. It may be ascribed to the preferential oxidation at the surface of the specimen during cooling from the annealing temperature of 450°C . The possibility of being associated with the local hydration due to the atmospheric humidity is ruled out because hydration proceeds consuming Cu^{3+} ions of the superconducting phase (14).

According to the crystallographic structure determined (15-17), the copper coordination number should change from 6 in an ideal stoichiometric perovskite-type compound to 4 and 5 in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ whose local symmetries are D_{4h} and C_{4v} , respectively. It has also been proposed that most of the Cu^{3+} ions present in the sample are located in the one-dimensional chains. That is, as the $d^9(\text{Cu}^{2+})$ electronic configuration is more stable in C_{4v} symmetry as shown in Figure 3, the $\text{Cu}^{3+}(d^8)$ ions may be enriched in the site of D_{4h} symmetry which is located in one-dimensional chains. According to the simple calculation of crystal field stabilization energy(CFSE) in the reduced symmetry of $C_{4v}(-18.28$ Dq) and $D_{4h}(-24.56$ Dq) for $\text{Cu}^{3+}(3d^8)$, it is quite clear the all Cu^{3+} ions prefer the square-planar site (D_{4h}) than square pyramidal

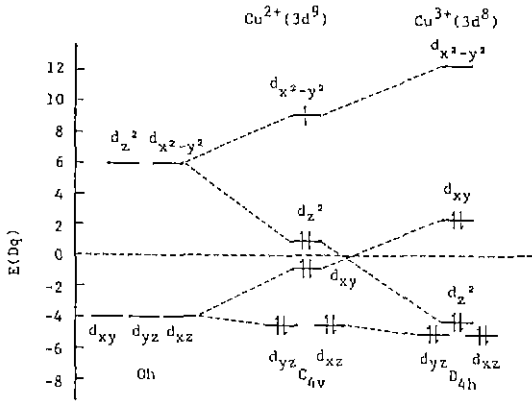


Fig. 3. Relationship of crystal-field energies for d-orbitals in octahedral (O_h)-, square-pyramidal (C_{4v})- and square planar (D_{4h})-symmetry.

one (C_{4v}) due to high D_{4h} site preferential energy. And presumably the Cu²⁺ ion with a CFSE of -12.28 Dq in D_{4h} site will fail in the competition with the Cu³⁺ ion in the same site and, therefore, be forced to occupy the C_{4v} site in YBa₂Cu₃O_{7-δ} system. From this consideration of CFSE, it should be apparent why square planar complexes are much more common for d⁸ electron configurations than for d⁹ and actually, most square planar complexes known involve Ni²⁺, Pd²⁺, Pt²⁺, and Au³⁺, all of which are d⁸ configuration(18). A study on the quantitative depth profile, which would give the exact information for the distribution of Cu³⁺ ion present in the superconductor YBa₂Cu₃O_{7-δ}, has already been under way.

To date, there is no X-ray photoelectron spectroscopic evidence for the coexistence of Cu³⁺ and Cu²⁺ ions. Fujimori et al. (19) suggested that the Cu³⁺ is screened by a ligand-to-metal atom charge transfer and becomes nearly d⁹-like in its ground state. This may appear inconsistent with our observation. But taking into consideration that the Y-Ba-Cu-O system is very sensitive to the ambient H₂O(14), the con-

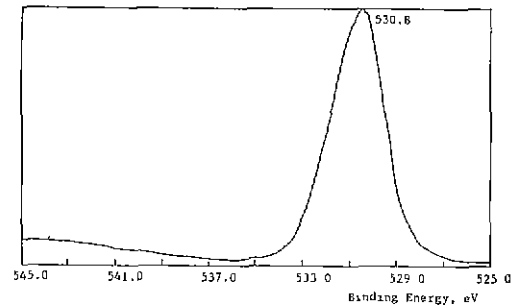


Fig. 4. Oxygen O_{1s} singlet spectrum for YBa₂-Cu₃O_{6.85}.

dition in which the sample was handled might be a considerable factor changing the XPE spectra. Besides above observation, it is very interesting that the satellite peak at about 943 eV diminishes gradually with increasing the Ar ion sputtering time as shown in Figure 2. Van den Laan et al.(20) and Larsson(21) pointed out that, in the Cu2p region of the photoelectron spectra of copper dihalides, the main peak corresponds to transitions to a 2p3d¹⁰L-like final states (2p: core hole in the 2p state, L:hole in the ligand state) and the satellites to a 2p3d⁹-like multiplet of final states. The satellite structure can appear from a ligand-to-metal atom charge transfer(22) as well as the coexistence of the d⁹ and d⁸ configuration in the ground state(23). Thus we can propose that, since the temperature of the sample is increased during the Ar ion sputtering at extremely low oxygen pressure, the intensity of the satellite peak is decreased remarkably because of decreased charge transfer from the ligand which results from the increased oxygen vacancy, the Cu³⁺ and Cu²⁺ ions are reduced to Cu⁺ ions (3d¹⁰) which show no measurable Cu2p3d⁹ satellite peaks at all. However, the fact that there is little shift of the main peak to lower energy region does not confirm the possibility of the reduction of the Cu³⁺ and Cu²⁺ to the Cu⁺. As shown in Figure 4, the oxygen

O_{1s} line position of 530.8 eV with FWHM = 1.3 eV in $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$ phase is more or less consistent with the binding energies observed in the CuO (BE of O_{1s} ; 529.6 ± 0.15 eV with FWHM = 1.3 eV) and the $\text{Cu}(\text{OH})_2$ (530.9 ± 0.2 eV with FWHM = 1.8 eV) (24).

In summary, the prepared sample can be formulated as $\text{YBa}_2\text{Cu}_{0.69}^{3+}\text{Cu}_{2.31}^{2+}\text{O}_{6.85}$ as a spatial average from $\text{Cu}^{3+}/\text{Cu}^{2+}$ ratio determined by the iodometric titrations. XPE spectra has revealed that the content of oxygen(x) or Cu^{3+} ion decreases with depth over a narrow extent beneath the surface exposed to atmosphere. It is interpreted as being due to the preferential oxidation at the surface during cooling. The strong Jahn-Teller distortion due to Cu^{2+} ions stabilized in C_{4v} -sites and the lattice contraction because of the existence of Cu^{3+} in D_{4h} -ones might be responsible for the high temperature superconducting transition temperature in Y-Ba-Cu-O system.

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