

## Determination of the Copper Valency and the Oxygen Deficiency in the High Tc Superconductor, $YBa_2Cu_3O_{7-x}$

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The ratio of trivalent to divalent copper has been determined by the redox titration for two superconducting phases of  $YBa_2Cu_{2x}^{3+}Cu_{3-2x}^{2+}O_{6.5+x}$  with the onset temp. of 60K ( $x = 0.23 \pm 0.01$ ) and 90K ( $x = 0.35 \pm 0.02$ ), and for the insulating one ( $x \approx 0$ ) which was kept in an ambient atmosphere for 72 hrs. It is found that  $T_c$  and the ratio of  $Cu^{3+}/Cu^{2+}$  depend strongly on the annealing temperature and time. A typical orthorhombic phase can easily be obtained by a slow cooling or stepwise cooling at  $P_{O_2} = 1$  atm, and shows a high  $T_c$  (ca. 90K) superconductivity.

### Introduction

The finding of high  $T_c$  superconductors<sup>1,2</sup> has stimulated a great scientific interests not only in the field of physics but also in those of chemistry and material science. Most of papers appeared in the literature describe the physical characterization only on the high  $T_c$  superconductors, but few papers have determined the  $Cu^{3+}$  and  $Cu^{2+}$  contents present in the  $YBa_2Cu_3O_{7-x}$  superconducting phase<sup>3-5</sup>. As far as we know, the ratio of  $Cu^{3+}/Cu^{2+}$ , the extent of oxygen vacancy, and its ordering play an important role not only in the superconductivity but also in the normal state properties. Recently Takagi, *et al.* reported that the formation of oxygen vacancy in  $Ba_xLa_{2-x}CuO_{4-y}$  could make a significant influence on the high  $T_c$  superconductivity<sup>6</sup>. According to Saito, *et al.*<sup>5</sup>, on the contrary, there might be no clear correlation between the  $T_c$  and oxygen deficiency in superconductor  $Sr_xLa_{2-x}CuO_{4-y}$ . Harris and Hewston<sup>7</sup> determined the oxidation state of copper in superconducting  $YBa_2Cu_3O_{7-x}$  phase by iodometric titration along with TG analysis. But no systematic chemical characterization on the Y-Ba-Cu-O system has ever been appeared in the literature.

In this paper, we report the detailed procedure of iodometric titration, the analytical error sources, the correlation among the synthetic condition, the superconducting transition temperature and the  $Cu^{3+}/Cu^{2+}$  ratio in  $YBa_2Cu_3O_{7-x}$  system.

### Experimental

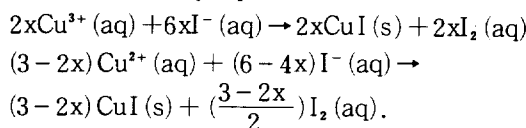
**Synthesis and physical characterization.** A mixture of  $Y_2O_3$ ,  $BaCO_3$  and  $CuO$  was ground and calcined at 900 °C in air for 16 hours. The product was reground, pressed into a pellet, sintered at 940 °C in  $O_2$  atmosphere for 40 hours. Finally, the sample(I) was annealed at 650 °C and the sample (II) at 450 °C in flowing  $O_2$  for 18 hours. The sample(III) was obtained by exposing the ground sample(II) into an ambient atmosphere for 72 hours.

Structural analysis has been performed by Jeol X-ray powder diffractometer with Ni-filtered  $Cu-K\alpha$  radiation. The electrical resistivity was measured by the conventional four-probe technique over the temperature range from 20 to 300K.

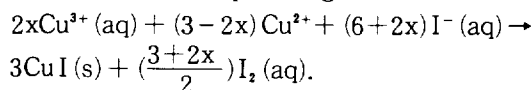
X-ray photoelectron spectroscopy(XPS) measurement with the monochromatic  $Mg-K\alpha$  radiation was performed with

a PHI 5100 Perkin-Elmer spectrometer at Materials device research center, Samsung Advanced Institute of Technology. The base pressure in the spectrometer was in the high  $>2.0 \times 10^{-9}$  Torr region.

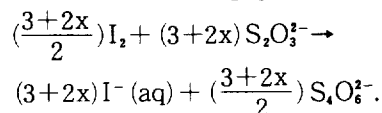
**Iodometric titration.** The determination of  $Cu^{3+}/Cu^{2+}$  ratio and the oxygen deficiency in the  $YBa_2Cu_{2x}^{3+}Cu_{3-2x}^{2+}O_{6.5+x}$  could be schematically represented as follows.



Summation of the two equations gives



If the generated  $I_2$  is titrated by  $S_2O_3^{2-}$ , then



From the above relation, the content of the excess oxygen ( $x$ ) in  $YBa_2Cu_{2x}^{3+}Cu_{3-2x}^{2+}O_{6.5+x}$  can be calculated by the following equation.

$$x = \frac{658.2vy - 3w}{2w - 15.9994vy}$$

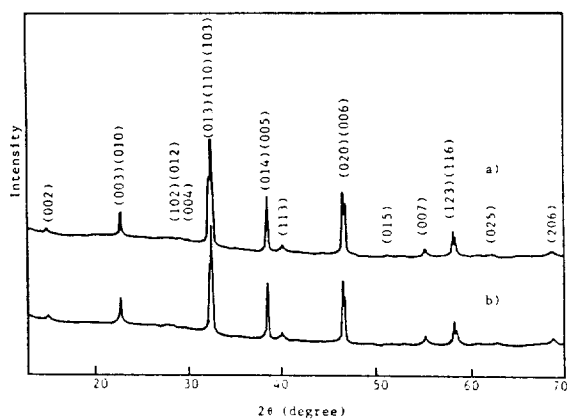
where  $y$ : normality of thiosulfate solution (N)

$w$ : sample weight (mg)

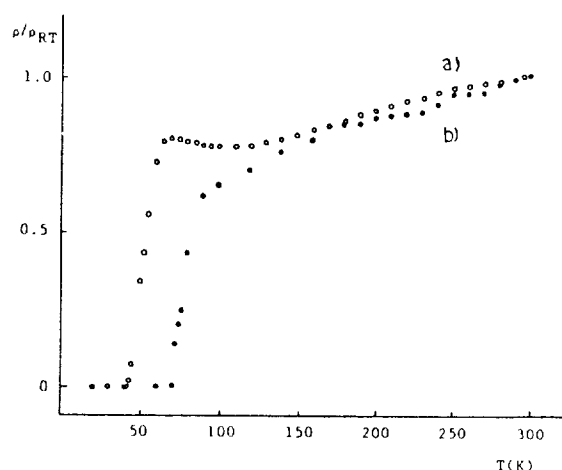
$v$ : volume of the added titrant (ml)

### Results and Discussion

As shown in Figure 1, XRD patterns for the sample(I) and (II) agree very well with that reported by Cava, *et al.*<sup>8</sup> No difference between the XRD patterns for the sample(I) and (II) could be observed, which may indicate that the annealing temperature around 450 and 650 °C does not greatly change the structural symmetry of Y-Ba-Cu-O system. However, there was a considerable difference in the electrical resistivity. Figure 2 shows the temperature dependence of the electrical resistivity for the sample(I) and (II). The sample(I) shows a superconducting transition at onset temp. of 60K, while the sample (II) at 90 K which is approximately 30 K higher than



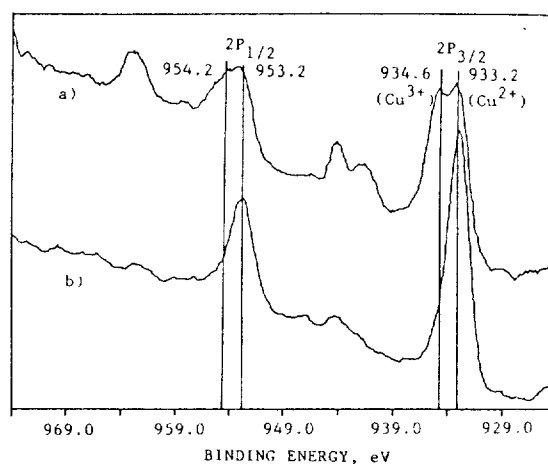
**Figure 1.** X-ray diffraction patterns for a) the sample (I),  $\text{YBa}_2\text{Cu}_3\text{O}_{6.73}$  and b) the sample (II),  $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$ .



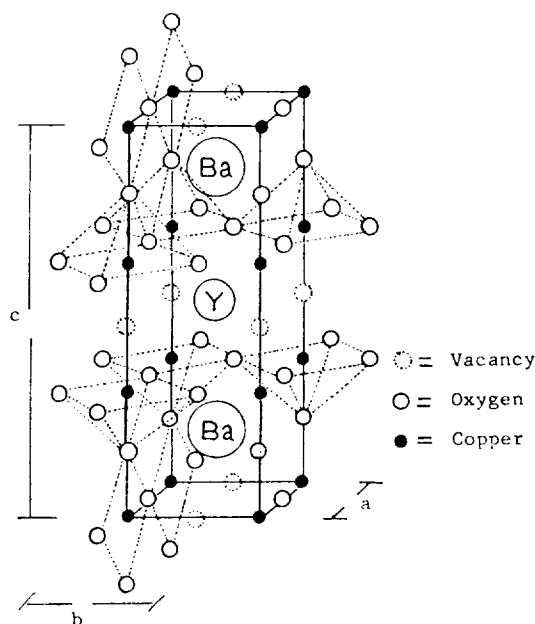
**Figure 2.** Temperature dependence of the normalized electrical resistivity for a) the sample (I) and b) the sample (II).

that of the sample (I). This result means that the oxygen content is a very important factor to improve the superconducting properties. From the neutron powder diffraction measurements<sup>9</sup>, it has been reported that there is the orthorhombic-to-tetragonal phase transition in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  which occurs near 700 °C in a pure oxygen atmosphere, and the transition temperature is lowered to about 670 °C in 20% oxygen and to about 620 °C in 2% oxygen. The observed depression of the superconducting transition temperature and an anomaly at around 60~90K in curve(a) in Figure 2 may indicate the presence of a trace amount of tetragonal phase which can not be detected by the X-ray diffraction analysis.

According to the XPS spectrum (Figure 3-a) before Ar-ion sputtering for the sample (I),  $\text{YBa}_2\text{Cu}_{2.54}\text{Cu}_{0.46}\text{O}_{6.73}$ , annealed at 650 °C for 18 hrs under  $P_{\text{O}_2} = 1 \text{ atm.}$ , the  $\text{Cu}^{3+}$  ions seem to be rich on the surface of the sample. The metal ion content below 10 a/o is, in common, hardly detectable in XPS analysis, it is generally thought to be difficult to observe the  $2\text{P}_{3/2}$  signal of  $\text{Cu}^{3+}$  in sample (I) (BE = 934.6 eV). But the chemical analysis shows that  $\text{Cu}^{3+}$  and  $\text{Cu}^{2+}$  contents in sample (I) are estimated as approximately 3.6 and 20.0 a/o, respectively. It is, therefore, speculated that no equilibrium was reached in the bulk due to the limited rate of oxygen diffusion in this experimental condition. And this consideration has been confirmed by observing the strong depression of



**Figure 3.** Cu 2P core-level XPS spectra for the sample (I) a) before and b) after the Ar-ion sputtering.



**Figure 4.** The idealized orthorhombic crystal structure for  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

$2\text{P}_{3/2}$  signal of  $\text{Cu}^{3+}$  ion (BE = 934.6 eV) and the enhancement of  $2\text{P}_{3/2}$  one of  $\text{Cu}^{2+}$  ion (BE = 933.2 eV) in the Ar-ion sputtered spectrum (Figure 3-b).

Figure 4 represents the crystal structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .<sup>10</sup> There are two types of copper atoms stabilized in the corner shared  $[\text{CuO}_4]_{\infty}$ -chains ( $D_{4h}$ ) between two (Ba-O) planes, and  $[\text{CuO}_5]_{\infty}$ -layers ( $C_{4v}$ ) between (Ba-O) and Y-planes, perpendicular to the c-axis direction. Considering the crystal field stabilization energy (CFSE) in the reduced symmetry of  $C_{4v}$  (-18.28 Dq) and  $D_{4h}$  (-24.56 Dq) for  $\text{Cu}^{3+11}$ , it is quite evident that  $\text{Cu}^{3+}$  ions favor the square planar sites than  $C_{4v}$  sites, due to the high  $D_{4h}$  site preferential energy. The  $\text{Cu}^{2+}$  ion with CFSE of -12.28 Dq in the  $D_{4h}$  site will presumably be forced to occupy the  $C_{4v}$ -sites. As mentioned above, the concentration of  $\text{Cu}^{2+}$  (20%; occupancy of  $C_{4v}$  sites) is relatively higher than that of  $\text{Cu}^{3+}$  (3.6%; occupancy of  $D_{4h}$  sites) and so  $2\text{P}_{3/2}$  signal (BE = 933.2 eV) for ( $\text{Cu}^{2+}$ -O) bond seems to be stronger. The main peak at 933.2 eV can be assigned as a  $2\text{p}3\text{d}^{10}\text{L}$  final state ( $2\text{p}$ : core hole in the 2p state;  $\text{L}$ : hole in the ligand state) and the satellite at 942 eV as a  $2\text{p}3\text{d}^9$  final

**Table 1. Analytical Results for  $YBa_2Cu_{3-2x}Cu_{2x}O_{6.5+x}$** 

Synthetic Condition	Tc, O <sup>a</sup>	X <sup>b</sup>	Formula	$\frac{Cu^{3+}}{Cu^{2+}}$
650 °C				
Sample(I) O <sub>2</sub> -annealed/ furnace-cooled 450 °C	60 K	0.23(1)	YBa <sub>2</sub> Cu <sub>2.54</sub> <sup>2+</sup> Cu <sub>0.46</sub> <sup>3+</sup> O <sub>6.73</sub>	0.18
Sample(II) O <sub>2</sub> -annealed/ air-quenched kept in an ambient atmosphere for 72 hrs.	90 K	0.35(2)	YBa <sub>2</sub> Cu <sub>2.30</sub> <sup>2+</sup> Cu <sub>0.70</sub> <sup>3+</sup> O <sub>6.85</sub>	0.30
	insulating	-0.03(1)	YBa <sub>2</sub> Cu <sub>2.94</sub> <sup>2+</sup> Cu <sub>0.06</sub> <sup>3+</sup> O <sub>6.47</sub>	0

<sup>a</sup> On-set transition temperature. <sup>b</sup> Numbers in parentheses are standard deviations in the last digit from 2 to 4 determination.

state<sup>12</sup>. The appearance of the satellites indicates that although the ground state of Cu ions has nominally 3d<sup>9</sup> configuration, 3d<sup>10</sup> configuration has considerable weight in the final state due to a charge transfer from ligands to Cu ions. Above all, we propose that the main peak in the higher energy region (934.6 eV) should be the contribution from Cu<sup>3+</sup> ions. This interpretation could be confirmed by the comparison with the spectra for the La<sub>2</sub>Cu<sup>2+</sup>O<sub>4</sub> and the La<sub>4</sub>LiCu<sup>3+</sup>O<sub>8</sub>, where the binding energies of the Cu<sup>2+</sup>2P<sub>3/2</sub> and the Cu<sup>3+</sup>2P<sub>3/2</sub> electrons are 933.2 and 934.0 eV, respectively<sup>13</sup>.

In order to obtain the relation among the critical temperature, the oxygen vacancy, and the effect of atmospheric H<sub>2</sub>O, which can not be easily detected by the X-ray analysis, iodometric titration was carried out for the sample (I), (II) and (III). The followings should be noticed in this titration;

- (1) Re-distilled water should be boiled and then cooled just before titration in order to remove the effect of dissolved O<sub>2</sub> or CO<sub>2</sub> on the oxidation of the iodide ions and the side reactions like carbonate formation.
- (2) To prevent the effect of O<sub>2</sub>-liberation, KI should be added in prior to HCl addition.
- (3) In the presence of Cu(I) ion, hydrogen ion concentration higher than ~0.3 M must be avoided in order to prevent air oxidation of the iodide ion. The hydrogen ion concentration chosen in this experiment was less than 0.05 M and the titration was carried out under O<sub>2</sub>-free nitrogen atmosphere.
- (4) The sample should be kept well closed under the dry atmosphere before titration because the superconducting phase is sensitive to water.
- (5) When KIO<sub>3</sub> is weighed out in order to standardize thio-sulfate, a significant weighing error may occur because of the hygroscopic nature of KIO<sub>3</sub>. For example, if there is an error of 0.6 mg in weighing of 15 mg of KIO<sub>3</sub>, the x value may deviate about 0.07. To reduce such an error, drying of KIO<sub>3</sub> and the use of a balance with high accuracy and precision is recommended.

The calculated x values for the sample (I), (II), and (III) were 0.23 ± 0.01, 0.35 ± 0.02 and 0.00, respectively. Table 1 shows the summary of the superconducting transition temperature (Tc) and the results of the iodometric titration against the preparation conditions. On the basis of ex-

perimental results, it is evident that the higher the Cu<sup>3+</sup>/Cu<sup>2+</sup> ratio is, the higher the superconducting transition temperature becomes. Particularly, the analytical results for the sample (III), which is not only an insulator, but also has no Cu<sup>3+</sup> ions, give the important information for the water effect on the Tc in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> system. From the XRD pattern for the sample (III) with x ≅ 0, no significant change compared with the sample (I) and (II) was observed except for the enhancement of tetragonal phase. This observation may indicate that the Cu<sup>3+</sup> ions present in the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> are preferentially reduced to Cu<sup>2+</sup> ions due to the high hydration enthalpy of Cu<sup>3+</sup><sup>11</sup>. Therefore it can be postulated that the decomposition reaction of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> in humid atmosphere proceeds in three steps: reduction, hydroxylation and the formation of carbonate successively. A detailed study on the interaction between YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> and H<sub>2</sub>O will be published<sup>14</sup>.

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