# Core-level electronic states of the $YBa_2Cu_3O_yBr_x$ superconductor studied by x-ray photoelectron spectroscopy

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Core-level electronic states of the $YBa_2Cu_3O_yBr_x$ superconductor, tetragonal, and orthorhombic $YBa_2Cu_3O_z$, and $BaBr_2$ have been studied with use of x-ray photoelectron spectroscopy. The intensity ratio of the satellite to Cu $2p_{3/2}$ line increases from 0.31 for the nonsuperconducting tetragonal phase to 0.46 for the brominated superconductor sample. The latter value is close to that for the superconducting orthorhombic phase (0.51), which strongly suggests that holes are doped by bromination into the tetragonal phase. Comparison of the binding energies of Ba $3d_{5/2}$ and Br $3d$ for the brominated sample with those of $BaBr_2$ shows that bromine in the former sample is strongly interacting with barium. The mechanism for the recovery of the superconductivity is discussed in terms of hole doping.

## I. INTRODUCTION

The recovery of superconductivity in a nonsuperconducting tetragonal $YBa_2Cu_3O_y$ (1:2:3) sample through halogen substitution is of interest from both a scientific as well as technological point of view.[1-5] It is well known that the charge carriers in the superconducting 1:2:3 sample are holes in the $CuO_2$ planes. If superconductivity in a halogen-substituted 1:2:3 sample is also due to holes, it would be expected that they are produced by substitution of two halogen ions into one oxygen vacancy in the chain, assuming a usual hole-doping mechanism.

The possibility of oxygen substitution by iodine in between the barium plane [Cu(I)-0(4)] was reported from x-ray-diffraction and Mössbauer measurements.[2] For bromine-substituted samples, studies of x-ray diffraction, Raman spectroscopy, and optical reflectance were carried out.[3,5] The possibility was discussed that Br ions randomly occupy interstitial sites.[3] From optical-conductivity results on a brominated single-crystal 1:2:3 sample,[5] it was concluded that the bromination leads to changes in the electronic structure in the $CuO_2$ planes. The speculation was presented that the planes are not substituted by Br ions and they may go into apical oxygen sites, transferring charge to the $CuO_2$ layers. However, the positions occupied by the Br atoms and changes in the electronic states due to the substitution are still unclear although the Br exists in the lattice.

It is very important to study the mechanism of hole doping for the elucidation of the superconducting mechanism in high-$T_c$ superconductors. The speculation that the hole-doping mechanism is due to the halogens was reported in Ref. 5. There, it was discussed that either a different charge-transfer mechanism without involving the chains is operating, or a restoration of the oxygen to

the chains is caused by bromination. However, no clear evidence has been found to explain the mechanism.

In this paper, we report on the core-level electronic states of $YBa_2Cu_3O_yBr_x$, tetragonal and orthorhombic 1:2:3 samples, and $BaBr_2$ for comparison studied with use of x-ray photoelectron spectroscopy (XPS).

## II. EXPERIMENT

Polycrystalline 1:2:3 samples with $T_c = 91$ K were prepared by solid-state reaction. A nonsuperconducting pellet sample was obtained by annealing in vacuum ($\sim 10^{-6}$ Torr) at 655 °C for 2 h. Bromination of the sample was carried out as follows: the pellet was degassed in vacuum ($\sim 10^{-6}$ Torr) at 260 °C and exposed to dried and deoxidized Br gas for 5 min–48 h. The surface layer of the pellets was scraped off by sandpaper in order to remove any impurity phases before x-ray-diffraction, ac-susceptibility, and XPS measurements. X-ray-diffraction patterns showed that the super- and nonsuperconducting samples were orthorhombic and tetragonal structures, respectively, and the brominated powder had an orthorhombic structure with $a = 3.84$, $b = 3.90$, and $c = 11.7$ Å. The ac susceptibility revealed that the brominated powder and pellet have $T_c = 91$ K, although the volume fractions that were superconductor were different for each.

The pellets were cleaned by scraping in an ultrahigh vacuum chamber ($1 \times 10^{-10}$ Torr) before the XPS measurements. XPS coreline for the tetragonal, orthorhombic, and brominated 1:2:3 samples were measured using a Mg $K\alpha$ source installed in a Phi-5100 ESCA system (Perkin-Elmer, U.S.A.). The spectra of $BaBr_2$ were also measured in order to compare it with that of the brominated sample. The binding energies of the core levels were referred to Au $4f_{7/2} = 84.0$ eV, except for $BaBr_2$.

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## III. RESULTS AND DISCUSSION

### A. Sample characterization

Changes of the ac susceptibility as a function of temperature are shown in Fig. 1. A starting tetragonal pellet sample for the bromination clearly shows no superconductivity above 15 K. On the other hand, the susceptibility indicates small and large superconducting fractions for the brominated pellet and powder, respectively, in which the former would be due to the slow diffusion rate of Br into the pellet.

X-ray diffraction revealed that the powder brominated for 5 min at 260 °C has an orthorhombic structure, which is in good agreement with previous results.[3] It was found that the orthorhombic and tetragonal structures coexist in the pellet brominated for 60 min at 260 °C. These results suggest that the bromination of the pellet sample occurs at the surface layer, while it occurs in crystalline form for the powder. In fact, the XPS intensity of Br $3d$ was decreased by deep scraping. The amount of Br was roughly estimated by weight gain to be about $y = 0.05$ and 1.37 for the brominated pellet and powder $YBa_2Cu_3O_6Br_y$ samples, respectively, assuming the starting sample as $YBa_2Cu_3O_6$. We found that the pellet exposed to bromine gas for 48 h at 260 °C becomes a powder which showed a large superconducting fraction. Since it was difficult to make the brominated pellet sample with a large superconducting fraction, we measured XPS spectra on the pellet brominated for 60 min at 260 °C, which is good enough to study electronic states of the core level because XPS is a surface-sensitive technique.

We find the compositions to be $YBa_{2.3}Cu_{3.8}O_{6.6}$, $YBa_{2.1}Cu_{3.3}O_{6.4}$, and $YBa_{3.3}Cu_{3.1}O_{5.3}Br_{5.1}$ for the orthorhombic, the tetragonal phases, and the brominated sample, respectively, in which these compositions were calculated using the XPS intensities. Although these values are not precise because quantitative analysis with XPS contains large errors, we could roughly compare changes in compositions. Oxygen content for the orthorhombic phase is close to 7 and, on the other hand, that for the tetragonal is less than for the orthorhombic, which is qualitative agreement with the stoichiometry, although

Ba and Cu contents deviate from the stoichiometry. Significant changes in composition due to the bromination are found for barium and oxygen: the former increases and the latter decreases. A large amount of Br is also found for the brominated sample. This value is too large in comparison with the previous results of x-ray fluorescence analysis,[3,5] which would be due to formation of $BaBr_2$ although no x-ray-diffraction patterns of $BaBr_2$ are obtained. The result could suggest that the bromination causes partial decomposition of the oxide, yielding restoration of oxygen in the oxygen vacancy sites. However, this idea cannot explain significant decrease in oxygen content because it is expected to remain almost constant.

In order to determine the position of bromine, Rietveld analysis of x-ray-diffraction data was performed.[3] The result suggested that the orthorhombic model best fit the experimental data and the most likely position for ordered bromine in this lattice is the oxygen deficient $(0, \frac{1}{2}, 0)$ site. However, fully occupying this site with bromine caused a poorer fit to the data. The result of Raman measurement suggested that bromine is incorporated into the $YBa_2Cu_3O_x$ lattice.[3] These results are all indirect evidence for the existence of bromine in the lattice. We are planning to perform high resolution electron microscopic measurements in order to determine the exact position of bromine.

### B. XPS study

We present Br $3d$ spectra for the brominated pellet [Fig. 2(a)] and $BaBr_2$ [Fig. 2(b)] for comparison with Fig. 2(a) in Fig. 2, in which the binding energy of $BaBr_2$ was corrected by referring to C $1s$ energy (285.0 eV) of adventitious carbon on the surface. The energies for Figs. 2(a) and 2(b) are found to be 68.3 and 68.4 eV, respectively, being in good agreement each other. This suggests a similar chemical environment of bromine in Fig. 2(a) and 2(b), that is, Br has $-1$ valence.
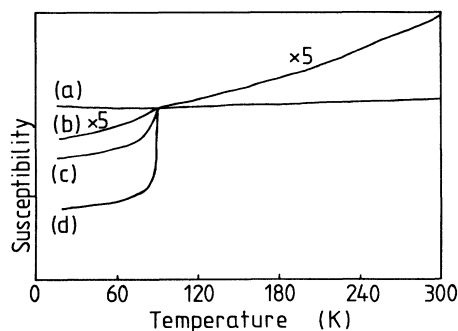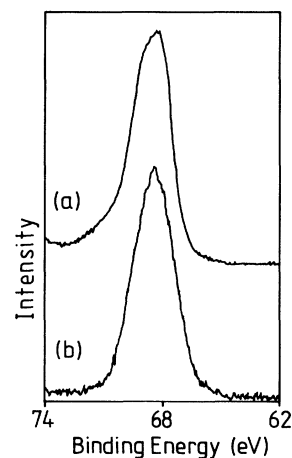


FIG. 1. Changes of ac susceptibility as a function of temperature for the tetragonal (a), brominated pellet (b) and powder (c), and orthorhombic (d) samples.



FIG. 2. XPS spectra of Br $3d$ for the brominated pellet sample (a) and $BaBr_2$ (b) whose binding energies are corrected by referring to adventitious carbon $1s$ level (285.0 eV).
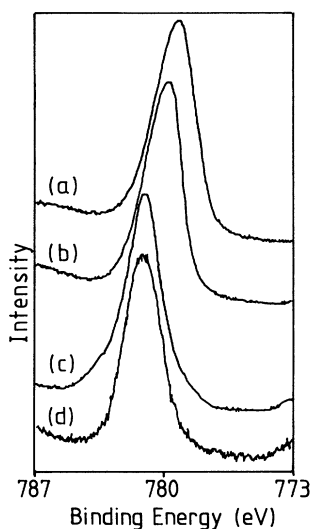
FIG. 3. XPS spectra of Ba $3d_{5/2}$ for the orthorhombic (a), tetragonal (b), brominated (c) samples, and $BaBr_2$ (d).

Figure 3 shows Ba $3d_{5/2}$ spectra for super- [Fig. 3(a)] and nonsuperconducting [Fig. 3(b)] 1:2:3 samples, the brominated pellet [Fig. 3(c)] and $BaBr_2$ [Fig. 3(d)]. The binding energies are 779.7, 780.0, and 781.3, and 781.3 (corrected) eV for Fig. 3(a)–3(d), respectively, in which the last two are in good agreement. The chemical environment of Ba in the brominated sample and $BaBr_2$ are also suggested to be similar. However, coincidence of the Ba $3d_{5/2}$ binding energies for the two sample would not imply the formation of $BaBr_2$ by the bromination, because of lack of impurity phases in the x-ray-diffraction pattern.

Cu $2p$ spectra for super- [Fig. 4(a)] and nonsuperconducting [Fig. 4(b)] samples and the brominated pellet [Fig. 4(c)] are shown in Fig. 4, in which $2p_{3/2}$ binding energies are 934.7, 933.9, and 934.7 eV, respectively. The FWHM (full width at half maximum) of the lines is
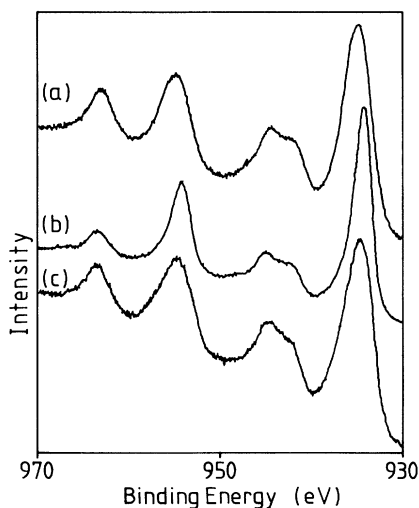


FIG. 4. XPS spectra of Cu $2p$ for the orthorhombic (a), tetragonal (b), and brominated (c) samples.

significantly different between Figs. 4(a) and 4(b): 3.6 eV for the former and 2.2 eV for the latter, which is characteristic for the orthorhombic and tetragonal phase of the sample. Other characteristics are different intensity of satellite between Figs. 4(a) and 4(b) at about 943 eV. We find that the intensity ratio of the satellite to the main line $(2p_{3/2})$ is about 0.51 and 0.31 for Figs. 4(a) and 4(b), respectively, and the bromination of Fig. 4(b) leads almost to recovery of the ratio (0.47) and the FWHM (0.36). The binding energies of O $1s$, Y $3d_{5/2}$, Cu $2p_{3/2}$, and Br $3d$ for Figs. 4(a)–4(c) and $BaBr_2$ are listed in Table I.

The Cu $2p_{3/2}$ core-level spectra of copper oxide superconductors show a main line at about 934 eV due to well-screened core hole final state of the $2p^5 3d^{10}L$ configuration, in which the $L$ denotes a ligand hole, and a broad satellite centered at about 943 eV due to the poorly screened final state of the $2p^5 3d^9$ configuration. For the 1:2:3 sample, the satellite intensity is strongly dependent on oxygen content:[6] less for the tetragonal phase than the orthorhombic because of oxygen deficiency in Cu-O chains for the former, which is in good agreement with our result. We find that the intensity ratio increases from 0.31 to 0.47 which is close to the value (0.51) for the orthorhombic phase, by bromination of the tetragonal phase. This suggests that the valence state of Cu in the chain becomes similar to that for the orthorhombic sample, that is, holes are doped by the bromination.

X-ray-absorption results suggest that holes in $YBa_2Cu_3O_y$ with $\sigma$ symmetry are present in all Cu-O bonds at $y=6.9$ and those in O(4) and O(1) sites are affected by oxygen loss, while the holes in the planes remain mostly unperturbed.[7] In the Ref. 5 doping mechanism due to the bromination was speculated to be that the bromine ions directly add 0.2 holes per plane (Ref. 8) to the $CuO_2$ planes by a different charge-transfer mechanism without involving the chains, or that they might cause a restoration of oxygen to the chains, leading to a recovery of the superconductivity. If the latter is true, the satellite structure of Cu $2p_{3/2}$ for the brominated and orthorhombic samples would have the same intensity ratio for the two peaks at 944 and 942 eV,[9] because the Cu valence and the structure would be almost the same for both. The ratios are 1.49 and 1.35 (see Fig. 5, in which the backgrounds of the spectra were subtracted and the satellite was divided into two components[9]) for the former and the latter, respectively. Therefore, our analysis of the satellite suggests other doping mechanisms although it is still unclear.

TABLE I. The binding energies of Br $3d$, Y $3d$, O $1s$, Ba $3d_{5/2}$, and Cu $2p_{3/2}$ for super-( $A$ ), nonsuperconducting ( $B$ ), and brominated ( $C$ ) 1:2:3 samples and $BaBr_2$ ( $D$ ).

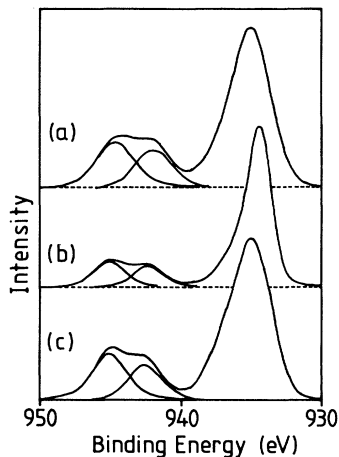| Core level \ Sample | Binding energy (eV) | | | |
|---|---|---|---|---|
|  | $A$ | $B$ | $C$ | $D$ |
| Br $3d$ |  |  | 68.3 | 68.4 |
| Y $3d$ | 156.0 | 156.2 | 156.3 |  |
| O $1s$ | 528.7 | 529.3 | 529.4 |  |
| Ba $3d_{5/2}$ | 779.7 | 780.3 | 781.3 | 781.3 |
| Cu $2p_{3/2}$ | 934.7 | 934.2 | 934.7 |  |

FIG. 5. XPS spectra of Cu $2p_{3/2}$ and satellite for the ortho-rhombic (a), tetragonal (b), and brominated (c) samples, in which the satellite was divided into two components.

It was pointed out that the binding energy of Ba $3d$ is strongly dependent on the bond length of Ba-O in the 1:2:3 sample,[10] that is, the longer the bond, the larger the energy. For the tetragonal 1:2:3, since the distance of Ba-O(4) becomes longer than that for the orthorhombic because of O(1) vacancy,[11] the Ba $3d_{5/2}$ energy would be higher, which is in good agreement with our result. If Br ions are inserted in the O(1) sites, the distance of Ba-O(4) would be between that for the tetragonal and orthorhombic, because of −1 valence for the Br ion, although it is also dependent on the covalency of the Ba-Br bond.[9] Our result is not in agreement with the above prediction, which suggests that the O(1) site is not simply substituted

by one Br ion, although the Br ions are strongly interacting with the Ba ions. Even though one Br ion occupies the one O(1) vacancy site, enough holes to create superconductivity would not be formed, assuming the usual manner of hole doping. Studies on the local structure of Br ions in the brominated sample are required in order to determine the position of Br ions.

In summary, we have studied the core-level electronic states of the brominated 1:2:3 sample, in which superconductivity was recovered by bromination of the nonsuperconducting tetragonal sample. The binding energies of Ba $3d_{5/2}$ and Br $3d$ for the brominated sample are in good agreement with those for BaBr$_2$. This result suggests similar chemical environments for Ba and Br in both samples, that is, Ba ions are strongly interacting with Br with −1 valence in the former sample. From comparison of the intensity ratios of the satellite to the Cu $2p_{3/2}$ line for the super- [Fig. 5(a)], nonsuperconducting [Fig. 5(b)], and brominated [Fig. 5(c)] samples, we find that the value is changed by bromination from 0.31 for [Fig. 5(b)] to 0.47 for [Fig. 5(c)] which is almost identical with 0.51 for [Fig. 5(a)]. This indicates enough hole doping to create superconductivity with bromination. It is pointed out that the mechanism of the hole doping is due to neither the substitution of one Br ion into one O(1) vacancy site, nor the recovery of oxygen in the site with bromination, although the mechanism is still unclear.

## ACKNOWLEDGMENTS

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