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Chemical states of Ba in $YBa_2Cu_3O_{7-\delta}$ studied by x-ray photoelectron spectroscopy

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X-ray photoelectron spectra of Ba 3*d* and O 1*s* were measured for BaO, $BaCO_3$, $Ba(OH)_2$, and $YBa_2Cu_3O_{7-\delta}$ in order to elucidate the chemical states of barium in $YBa_2Cu_3O_{7-\delta}$. It is revealed that the photoemission line at 780.4 eV corresponds to Ba^{2+} ions bonded to carbonate and hydroxyl groups, and that at 778.9 eV is due to Ba^{2+} ions in the orthorhombic structure. The O 1*s* lines at 531.2 and 528.4 eV are ascribed to carbonate and/or hydroxyl groups and oxygens in the superconducting oxide, respectively.

INTRODUCTION

Alkaline-earth elements such as Ca, Sr, and Ba play an important role in high-T_c superconducting oxides. It is well known that they are donors of holes to La_2CuO_4 and consequently that it becomes metallic.[1,2] Although their roles in Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, and Tl-Ba-Ca-Cu-O systems are not clear yet, recently it was pointed out that the BaO layer in Y-Ba-Cu-O may be very important because the spectroscopic data suggest the existence of holes on O(4) sites just beside Ba ions.[3]

Two x-ray photoemission spectroscopy (XPS) peaks of Ba $3d_{5/2}$ were found at about 780 and 778 eV for Y-Ba-Cu-O systems.[4-6] The 778-eV line was assigned to $Ba^{(2-\delta)+}$ at oxygen-deficient sites[4] since the value is less than that for BaO (780 eV) in the table in Ref. 7. The origin of the line was discussed in terms of coordination properties, final-state relaxation effects and inclusions, but they could hardly explain it.[5] It was pointed out that the different chemical states are due to the valence charge fluctuation of barium atoms.[8] Two chemically dissimilar barium ions were also identified in 4*d* core-level spectra.[9,10] On the other hand, the different chemical states of barium and oxygen in the Y-Ba-Cu-O (Ref. 11) and La-Sr-Cu-O (Ref. 12) systems were discussed in terms of impurities such as carbonate and hydroxyl groups coming from segregation or atmospheric gases.

Most of the previous results were discussed on the basis of the tabulated binding energy.[7] However, it should be emphasized that the determination of the precise core-level binding energy in insulators is very difficult because of unclear Fermi-level and charge-up shifts. Although the C 1*s* peak of "adventitious" carbon is employed as a reference for the determination of the core-level-binding energy for insulators, it was pointed out that an experimental error of a few eV is included in the methods.[13]

We measured XPS spectra of Ba 3*d* and O 1*s* for BaO, $BaCO_3$, and $Ba(OH)_2$ along with $YBa_2Cu_3O_{7-\delta}$ in order to elucidate the chemical states for two Ba $3d_{5/2}$ lines of Y-Ba-Cu-O systems without references. A new assignment of the lines at 778.9 and 780.4 eV will be presented here.

EXPERIMENT

Pelletized $Ba(OH)_2$ and $BaCO_3$ samples (13 mm diameter × 1 mm thickness) were prepared by pressing the corresponding powders. A BaO sample was prepared by firing a pelletized $BaCO_3$ sample at 1200 °C for 4 h in air. An orthorhombic $YBa_2Cu_3O_{7-\delta}$ sample was obtained as follows. The mixtures of barium, yttrium, and copper oxalates were prepared by coprecipitation of the corresponding nitrates with NH_4OH and an oxalic acid solution at $p\mathrm{H}=4.6$. The powders were heated in an oxygen stream (1 atm) and then ground. These treatments were repeated three times at 900 °C for 60 h, and 930 °C and 960 °C for 10 h.

Measurements of the XPS core-binding energy were carried out using an ADES-400 (V.G. Scientific). Mg $K\alpha$ and Al $K\alpha$ sources were employed for BaO and $BaCO_3$, $Ba(OH)_2$ and $YBa_2Cu_3O_{7-\delta}$, respectively. The BaO sample was cleaned by Ar^+ ion sputtering at 5 keV with 5 $\mu A/cm^2$ for 10 min in order to remove carbonate and hydroxyl groups. The surface of $YBa_2Cu_3O_{7-\delta}$ was scraped with a grinder to clean it *in situ* under UHV conditions ($\sim 1\times 10^{-8}$ Pa).

RESULTS AND DISCUSSION

Figure 1 shows XPS spectra around 800, 540, and 300 eV for BaO, in which the binding energies are not corrected by subtracting the charge-up shift. The peaks at 792.3

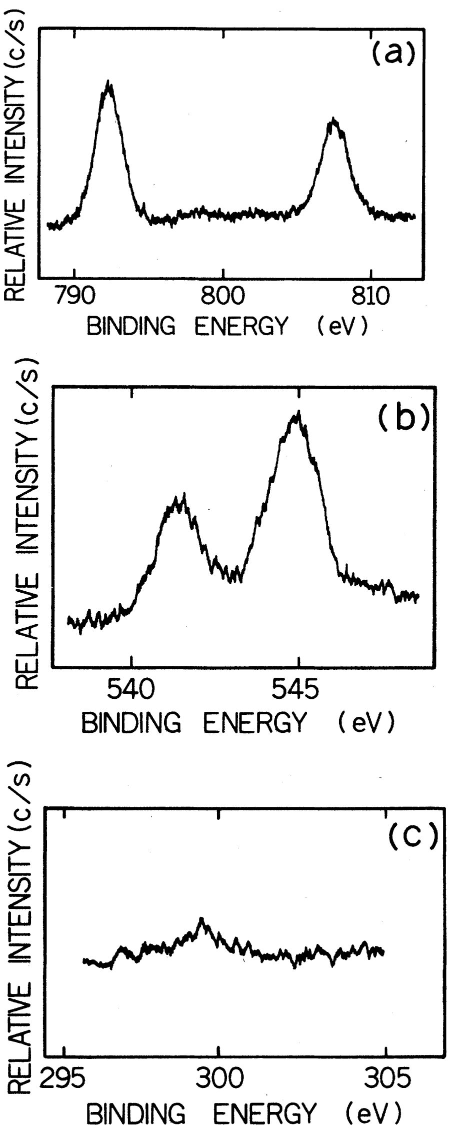

FIG. 1. XPS spectra of (a) Ba 3*d*, (b) O 1*s*, and (c) C 1*s*, for BaO. The binding energy is not corrected by subtracting charge-up shift.

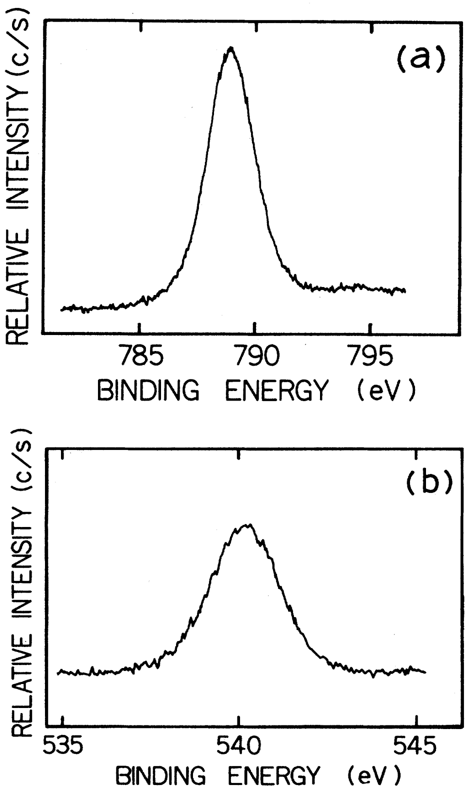

FIG. 2. XPS spectra of (a) Ba $3d_{5/2}$ and (b) O 1*s* for $BaCO_3$. The binding energy is uncorrected.

and 807.5 eV would correspond to Ba $3d_{5/2}$ and $3d_{3/2}$, respectively, which implies that the binding energy increases by over 10 eV due to the charge-up shift, assuming Ba $3d_{5/2}=779.8$ eV for BaO.[7] The 301.4-, 541.4-, and 544.8-eV peaks (uncorrected) could be ascribed to C 1*s* of carbonate, O 1*s* of oxide and that of carbonate, respectively. The latter C 1*s* is due to the carbonate not converted to BaO during sample preparation because of insufficient decomposition temperature of $BaCO_3$.

XPS spectra for $BaCO_3$ and $Ba(OH)_2$ are displayed in Figs. 2 and 3, respectively. For $BaCO_3$, the O 1*s* and Ba $3d_{5/2}$ peaks are found at 540.2 and 788.9; for $Ba(OH)_2$ at 540.4 and 789.4, respectively, in which they are also uncorrected.

Figure 4 shows XPS spectra of Ba 3*d*, O 1*s*, and C 1*s* for $YBa_2Cu_3O_{7-\delta}$ (orthorhombic) with and without scraping. The Cu 2*p* and Y 3*d* spectra were unchanged by scraping except for the intensity. For Ba $3d_{5/2}$, two peaks are identified at 778.9 and 780.4 eV in Fig. 4(a), curve 1. A big change is found in Fig. 4(a), curve 2 after scraping: The 780.4-eV peak is almost diminished and the 778.9-eV peak largely increases in intensity. On the other hand, the O 1*s* peak intensity at 531.2 eV decreases and that at 528.4 eV increases in Fig. 4(b). The C 1*s* peak at 284.7 and, approximately, 288 eV due to hydrocarbon contaminant and carbonate, respectively, almost disappear with scraping.

It is very difficult to determine the exact binding energy for insulators such as BaO, $BaCO_3$, and $Ba(OH)_2$ because of the charge-up shift. Therefore, we here compare the binding-energy differences between Ba $3d_{5/2}$ and O 1*s*, which can cancel out the charge-up shift. The various binding-energy differences between Ba $3d_{5/2}$ and O 1*s* for BaO, $BaCO_3$, $Ba(OH)_2$, and $YBa_2Cu_3O_{7-\delta}$ are listed in Table I, in which the 778.9-, 780.4-, 528.4-, and 531.2-eV peaks for $YBa_2Cu_3O_{7-\delta}$ are denoted by Ba $3d_{5/2}$ (I), Ba $3d_{5/2}$ (II), O 1*s* (I), and O 1*s* (II), respectively. It is found that the binding-energy difference of Ba $3d_{5/2}$–O 1*s* for BaO is 250.9 eV, which is nearly equal to that of Ba $3d_{5/2}$ (I)–O 1*s* (I) $=250.5$ eV for $YBa_2Cu_3O_{7-\delta}$. The energy differences of Ba $3d_{5/2}$–O 1*s* for $BaCO_3$ and $Ba(HO)_2$ are 248.7 and 249.0 eV, respectively, which are very close to that (249.2 eV) of Ba $3d_{5/2}$ (II)–O 1*s* (II).

It was reported that Ba ions in Y-Ba-Cu-O systems are located in two different electronic environments since two

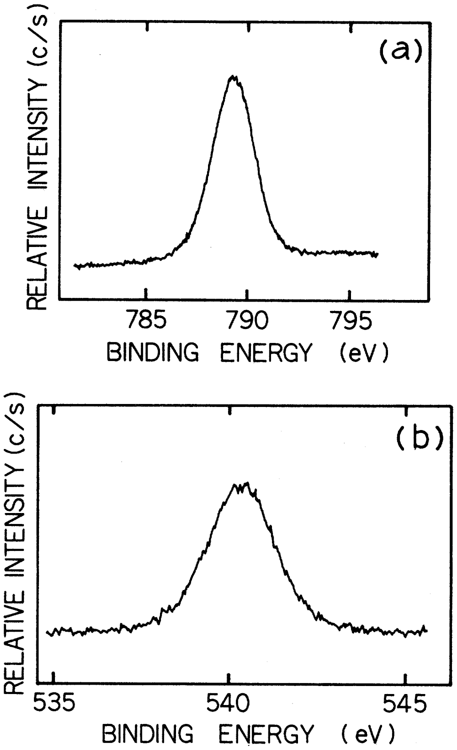

FIG. 3. XPS spectra of (a) Ba $3d_{5/2}$ and (b) O 1s for Ba$(OH)_2$. The binding energy is uncorrected.

peaks for Ba $3d_{5/2}$ were observed.[4,5] Therefore, it was concluded[4] that the lower binding-energy (777.8-eV) peak is due to a lower oxidation state $Ba^{(2-\delta)+}$ because it is lower than the tabulated value (779.8 eV) for BaO.[7] The above two Ba $3d_{5/2}$ peaks were found by changing the detection angle: The strong latter peak was observed at the take-off angle at 15° and the former increased in intensity at the angle of 85°.[6] These angular-dependent chemical shifts were also observed in the Ba 4d spectra.[10] It was concluded[6] that the 780- and 778-eV peaks associated with the O 1s line at 531 and 528.5 eV, respectively, are due to some form of barium oxide at the surface and the superconducting 1:2:3 phase, respectively. It was pointed out from the results of heating experiments[9] that oxygen defects in or near Cu—O chains lead to two chemically dissimilar barium atoms even in single-orthorhombic-phase samples.

Our results in Table I reveal that the 778.9-eV peak in the Y-Ba-Cu-O system does not correspond to $Ba^{(2-\delta)+}$ but to Ba^{2+} and the 528.4-eV peak is due to oxygens in the orthorhombic structure. Our assignment of the peak is consistent with the results (Ba $3d_{5/2}=779.1$ eV) in barium oxidation.[14] We could ascribe the 531.2-eV peak to carbonate and hydroxyl groups, which is in agreement with the results of water adsorption on $YBa_2Cu_3O_{7-\delta}$.[15] The 780.4-eV peak of Ba $3d_{5/2}$ for $YBa_2Cu_3O_{7-\delta}$ strongly relates to the 531.2-eV peak since both peak intensities were simultaneously reduced by scraping, which implies that the higher-binding-energy peak (780.4 eV) corresponds to that of barium bonded to carbonate and hy-

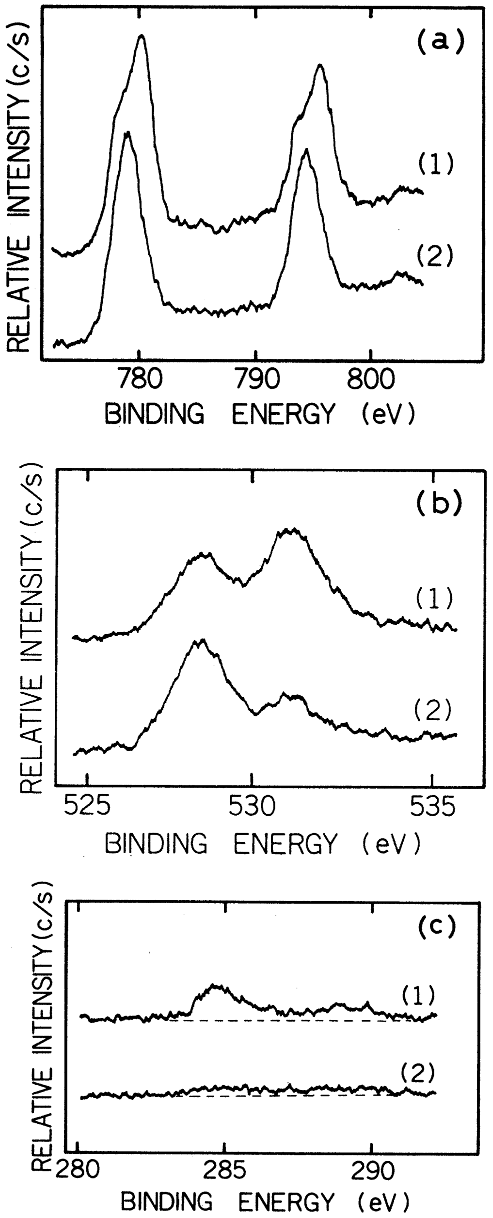

FIG. 4. XPS spectra of (a) Ba 3d, (b) O 1s, and (c) C 1s for orthorhombic $YBa_2Cu_3O_{7-\delta}$ with (curve 2) and without (curve 1) scraping.

TABLE I. Binding-energy difference between Ba $3d_{5/2}$ and O 1s for BaO, $BaCO_3$, $Ba(OH)_2$, and $YBa_2Cu_3O_{7-\delta}$.

Sample	Energy-level difference (eV)
BaO	Ba $3d_{5/2}$–O 1s = 250.9
$BaCO_3$	Ba $3d_{5/2}$–O 1s = 248.7
$Ba(OH)_2$	Ba $3d_{5/2}$–O 1s = 249.0
$Ya_2Cu_3O_{7-\delta}$	Ba $3d_{5/2}$(I)–O 1s(I) = 250.5
	Ba $3d_{5/2}$(II)–O 1s (II) = 244.7
	Ba $3d_{5/2}$(II)–O 1s (I) = 252.0
	Ba $3d_{5/2}$(II)–O 1s (II) = 249.2

droxyl groups.

There still exists the C 1*s* band for carbonate in Fig. 4(c) after scraping. The peak-intensity ratio of O 1*s* (531.2 eV)/C 1*s* (around 288 eV) was about 5.4. On the other hand, the ratio for barium carbonate was 3.2, which means that the O 1*s* band at 581.2 eV for Y-Ba-Cu-O contains extra components, most likely the OH group. For this higher-binding-energy peak, another interpretation was proposed that it is due to peroxides.[16–18] However, the cleaning method of the sample surfaces described in the literature was completely different from ours: They did not employ to scrape or cleave the samples *in vacuo*, but heated them. The latter procedure could not lead to cleaning the sample surfaces. We emphasize here that the only one O 1*s* line was reported on scraped or cleaved La-Sr-Cu-O,[19] Y-Ba-Cu-O,[20–26] and Bi-Sr-Ca-Cu-O (Ref. 27) surfaces *in vacuo*.

In summary, we have measured XPS spectra of Ba $3d_{5/2}$, O 1*s*, and C 1*s* for BaO, $BaCO_3$, $Ba(OH)_2$, and $YBa_2Cu_3O_{7-\delta}$. We conclude by comparing the binding-energy differences between Ba $3d_{5/2}$ and O 1*s* for various compounds containing barium that (i) the 778.9-eV peak is not due to $Ba^{(2-\delta)+}$ but to Ba^{2+} in the superconducting-oxide structure, (ii) the 780.4 line corresponds to barium bonded to carbonate and/or hydroxyl groups, and (iii) the O 1*s* lines at 531.2 and 528.4 eV are due to mainly carbonate and/or hydroxyl groups, and the superconducting oxide, respectively.

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