Photoemission from single-crystalline Bi-Sr-Ca-Cu-O

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An x-ray photoemission experiment was performed on high-T_c superconducting Bi-Sr-Ca-Cu-O single crystals with $T_c \sim 80$ K. It is found that Sr and Ca are interchangeable on the lattice sites of the crystal and that they are electronically distinguishable. This is consistent with the structure model for the crystal with formula unit $Bi_2(Sr,Ca)_3Cu_2O_y$. We demonstrate how the distribution of Sr and Ca in the cation sites is determined by x-ray photoemission, which cannot be done by x-ray diffraction.

Bednorz and Müller[1] first reported high-temperature ($T_c \sim 30$ K) superconductivity in the La-Ba-Cu-O system. Other workers[2,3] recorded higher T_c's (~ 40 K) in the La-Sr-Cu-O systems. Wu et al.[4] discovered 90-K superconductivity in the Y-Ba-Cu-O system. Recently, Maeda, Tanaka, Fukutomi, and Asano[5] reported that a new class of oxides Bi-Sr-Ca-Cu-O has T_c's ranging from 105 to 70 K.

In the present x-ray photoemission experiment on single-crystalline Bi-Sr-Ca-Cu-O ($T_c \sim 80$ K) we study the valence electronic state of each cation that should involve the information about its environment such as the position in the crystal structure, charge transfer with surrounding anions, and so on.

The preparation method of the single crystals used in this experiment has been described elsewhere in detail.[6] Single crystals were grown in Bi_2O_3-$SrCO_3$-$CaCO_3$-CuO solution. Typical dimensions of the crystals were 1.5 mm×0.7 mm×0.1 mm. The crystals were 80-K superconductors. In order to avoid complications arising from the coexistence of two superconducting phases, crystals without any trace of 105-K superconductivity were selected for this work. The crystals possess an orthorhombic unit cell with lattice parameters $a = 5.453$ Å, $b = 27.26$ Å, and $c = 31.04$ Å. The c axis is perpendicular to the surface of the thin plate. Transmission electron microscopy revealed that the plate samples possessed a perfect basal cleavage, similar to that of clay minerals. The chemical composition of the crystal was determined by electron microprobe analysis corresponding to $Bi_2Sr_{1.4}Ca_1Cu_2O_y$.

An SSI SSX-100 electron spectrometer was used to collect photoemission spectra with monochromatic Al $K\alpha$ radiation. The linewidth for the Ag $3d_{5/2}$ photopeak was 0.56 eV. The spectrometer was calibrated by utilizing the Au $4f_{7/2}$ electron binding energy (83.93 eV). The probable electron energy uncertainty amounted to 0.05 eV. The normal operating vacuum pressure was less than 5×10^{-9} Torr. Measurement of the electron spectra was carried out after scraping the sample surface with a diamond file to eliminate the effect of adsorbates on the photoemission spectra and to obtain reliable results. We can perform reliable photoemission experiments on the freshly scraped surface since the crystals have a perfect basal cleavage and there is no influence of artifacts. The electron binding energies were referred to the C $1s$ line of impurity carbon, which had a value of 284.8 eV. This value was consistent with a zero binding energy for the Fermi level.

$Bi_2(Sr,Ca)_3Cu_2O_y$ has been reported to have an orthorhombic structure with unit-cell lattice parameters $a \sim 5.4$ Å, $b \sim 27$ Å, and $c \sim 30$ Å (Refs. 7–10). The transmission electron microscope observation demonstrated that the material possesses a layered structure like the La-Sr-Cu-O and Y-Ba-Cu-O systems where two Cu-O layers are isolated by Bi-O layers.[11,12] From the proposed alternating layered structure of -[Bi-O]-[(Sr,Ca)-O]-[Cu-O]-[(Ca,Sr)-O]-[Cu-O]-[(Sr,Ca)-O]-[Bi-O]-, we can expect to observe two inequivalent electronic states of Sr and Ca and a different Cu valence from that observed in the Y-Ba-Cu-O system, due to lack of the Cu-O chain in the $Bi_2(Sr,Ca)_3Cu_2O_y$ structure.

In the x-ray photoemission the chemical bond possessing less (more) ionic character gives lower (higher) binding energy for the electrons. The electronegativity difference of the Bi-O bond (1.7) is slightly larger than that of the Cu-O bond (1.6). Thus the effective electron population on the Sr or Ca atoms between the Bi-O and Cu-O sheets is slightly larger than that sandwiched between the adjacent Cu-O sheets. If we can partition the core-level electron spectra of Sr and Ca of the single-crystalline Bi-Sr-Ca-Cu-O samples, the binding-energy difference of the partitioned peaks is in relation to the change of effective electronic charge on Ca or Sr atoms due to the difference in lattice sites in the $Bi_2(Sr,Ca)_3$-Cu_2O_y crystal structure. The valence of a cation should be determined by both the distances between the cation

TABLE I. Interatomic distances (Å) and bond valence sums.

Cation site	Interatomic distance[a]	Bond valence sum Sr	Bond valence sum Ca
Between the Bi-O and Cu-O sheets	2.56(5)×4	1.21	0.81
	2.74(2)×4	0.74	0.50
	2.91(11)×1	0.12	0.08
	⋮	⋮	⋮
		2.07	1.39
Sandwiched with the adjacent Cu-O sheets	2.52(5)×8	2.70	1.79

[a]Reference 9.

and surrounding anions and the coordination numbers of the anions. Average bond valences were calculated using the method of Brown and Altermatt[13] and they are listed in Table I. The values for the cation sites between the Bi-O and Cu-O sheets are 2.07 for Sr and 1.39 for Ca and those for the cation sites sandwiched with the adjacent Cu-O sheets are 2.70 for Sr and 1.79 for Ca. These values suggest that the cation sandwiched between the adjacent Cu-O sheets possesses a larger valence than that between the Bi-O and Cu-O sheets.

The Sr $3d$ and Ca $2p$ spectra of the Bi-Sr-Ca-Cu-O samples are shown in Figs. 1 and 2. Both spectra can be partitioned into two components as shown in these figures. The Sr $3d_{5/2}$ peak having lower binding energy (L_{Sr}) is located at 131.7 eV and that of higher binding energy (H_{Sr}) positioned at 132.9 eV. The Ca $2p_{3/2}$ peak with lower binding energy (L_{Ca}) is shown at 344.7 eV and that with higher binding energy (H_{Ca}) positioned at 345.9 eV. Since less (more) ionic character gives lower (higher) binding energy for the electrons, L and H peaks are obtained from the Sr and Ca atoms located between the Bi-O and Cu-O sheets and those located between the adja-

FIG. 2. The Ca $2p$ electron spectrum of the single-crystalline Bi-Sr-Ca-Cu-O samples. The separated peaks have a shape of 100% Gaussian and 1.35 eV full width at half maxima. The binding energy difference between L and H peaks was 1.2 eV.

cent Cu-O sheets, respectively. The proposed crystal structure of the $Bi_2(Sr,Ca)_3Cu_2O_y$ with inequivalent Sr and Ca lattice sites also gives the separation in each peak of the Sr and Ca core-level electron binding energies.

The difference of divalent ion radius between Sr and Ca is 0.21 Å. In spite of the such a difference, the result indicates that Sr and Ca atoms can occupy both sites in the proposed $Bi_2(Sr,Ca)_3Cu_2O_y$ structure. The intensity ratios of H to L peaks of the Sr $3d$ and Ca $2p$ spectra are 0.25 and 0.59, respectively. The H to L ratios expected from the proposed $Bi_2(Sr,Ca)_3Cu_2O_y$ structure are 0.50, if Sr and Ca are randomly distributed among two possible sites. Thus Sr atoms predominantly occupy the lattice sites between the Bi-O and Cu-O sheets and Ca atoms occupy two inequivalent lattice sites (between the adjacent Cu-O sheets and between the Bi-O and Cu-O sheets) almost evenly in the Bi-Sr-Ca-Cu-O samples. This suggests
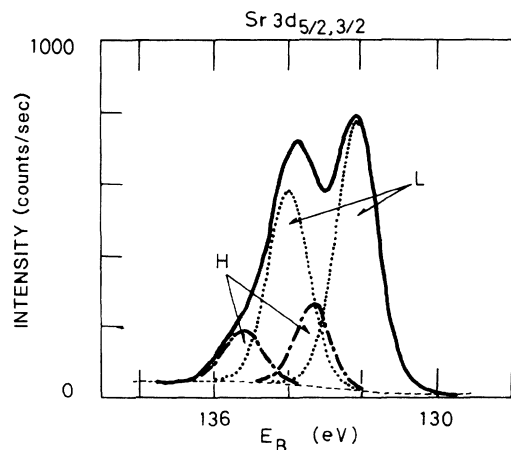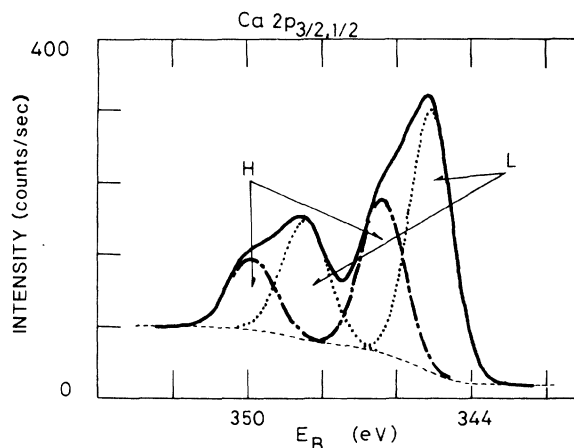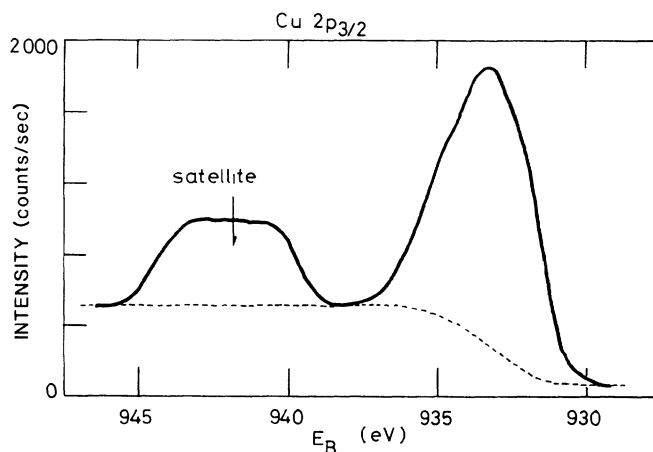

FIG. 1. The Sr $3d$ electron spectrum of the single-crystalline Bi-Sr-Ca-Cu-O samples. The separated peaks have a shape of 100% Gaussian and 1.25-eV full width at half maxima. The binding energy difference between L and H peaks was 1.2 eV.

FIG. 3. The Cu $2p_{3/2}$ electron spectrum of the single-crystalline Bi-Sr-Ca-Cu-O samples.
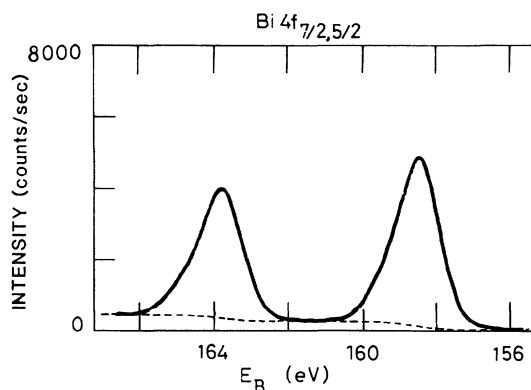
FIG. 4. The Bi $4f$ electron spectrum of the single-crystalline Bi-Sr-Ca-Cu-O samples.

that the smaller Ca ion can interchange lattice site with the Sr ion, whereas the Sr ion selectively occupies the unique site.

From the Cu and Bi core-level electron spectra, which are shown in Figs. 3 and 4, the Cu $2p_{3/2}$ and the Bi $4f_{7/2}$ electron binding energies are estimated to be 932.9 and 158.0 eV, respectively. For comparison, the Cu $2p_{3/2}$ binding energy in $YBa_2Cu_3O_{6.9}$ is 933.6 eV (Ref. 14) and the Bi $4f_{7/2}$ binding energy is 157.8 eV for $BaBiO_3$,[15] 158.8 eV for $NaBiO_3$, and 158.6 eV for Bi_2O_3.[16] These similar values for Bi indicate that one should not expect to define the oxidation state of Bi in terms of the core-electron binding energies.

In the Cu $2p_{3/2}$ spectrum a clear satellite structure is observed about 8 eV below the main structure. The satellite structure corresponds to a d^8 electronic configuration, while the main one corresponds to a $d^9\underline{L}$ charge-transfer state. Therefore the result confirms the Cu^{2+} ionic state as well as the charge transfer between Cu and O atoms in the present system and thus quite confirms a similar electronic configuration to the previous cuprate superconductors.

The main conclusion of the present experiment is that the Sr and Ca atoms are interchangeable in the lattice of single-crystalline Bi-Sr-Ca-Cu-O samples. These are electronically distinguishable as expected on the basis of the $Bi_2(Sr,Ca)_3Cu_2O_y$ crystal structure.

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