X-ray photoelectron spectroscopy analysis of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$

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Experiments on x-ray photoelectron spectroscopy of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ were performed to investigate the change of valence of each atom and the distribution of Y atoms on the cation sites. The core-level binding energies of Sr and Y increased with increasing Y content and that of Bi did not change. The average valence of Cu was above 2 for $0.0 \leqq x \leqq 0.5$ and below 2 for $0.8 \leqq x \leqq 1.0$. Y atoms were substituted for the cations between the adjacent Cu-O planes.

Since the discovery of high-T_c superconductivity in the La-Ba-Cu-O system by Bednorz and Müller,[1] superconducting oxides have been extensively examined in order to elucidate the mechanism of superconductivity. Maeda *et al.* reported a new class of superconducting oxides Bi-Sr-Ca-Cu-O (T_c=80 and 110 K).[2] The transition from a superconductor to an insulator was reported to be due to the substitution of rare-earth elements (R=Nd, Eu, and Y) for Ca ions in $Bi_2Sr_2RCu_2O_y$.[3,4] The distinct decrease of T_c with increasing Y content was also reported in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$.[5] In the previous study of electrical properties of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ at high temperatures, it has been suggested that the hole is stable in the region where both Cu^{1+} and Cu^{2+} ions exist.[6]

X-ray photoelectron spectroscopy (XPS) studies have been carried out to elucidate the electronic states of superconducting oxides.[7-12] Kohiki *et al.* demonstrated how XPS determined the distribution of Sr and Ca in the cation sites of $Bi_2Sr_{1.4}CaCu_2O_y$ single crystal[7,8] and $Bi_2Sr_2Ca_2Cu_3O_y$ thin films.[9,10] However, no prior XPS measurement of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ has been performed to our knowledge. In the present Brief Report, we report the change in the electronic states of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ systems with x, and the effect of the substitution of trivalent Y ions for the divalent Ca ions, on the basis of XPS results.

$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ compounds were prepared by the conventional solid-state reaction method. Powder samples with nominal compositions of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ (x=0.0, 0.5, 0.8, and 1.0 denoted by samples *A*, *B*, *C*, and *D*, respectively) were made by mixing powders of Bi_2O_3, $SrCO_3$, $CaCO_3$, Y_2O_3, and CuO. After having been calcined at 1123 K for 10 h in air, the mixed powders were ground and pressed into pellets. The pellet of sample *A* was sintered at 1121 K for 30 h in air, while the others were sintered at 1181 K for 30 h in air. All the samples showed almost single-phase x-ray-diffraction profiles. On the basis of quantitative analysis by energy-dispersive x-ray spectroscopy (EDX), the actual Y contents were determined to be 0.00, 0.52, 0.82, and 1.00 for x=0.00, 0.50, 0.80, and 1.00, respectively. It has already been reported that T_c decreases with increasing Y content and that superconductivity is observed at $x \leqq 0.5$.[13]

An x-ray photoelectron spectrometer (VG Scientific ESCALAB-MK II) was used to collect photoelectron spectra with Mg $K\alpha$ radiation. The spectrometer was calibrated by utilizing the Ag $3d_{5/2}$ peak (367.9 eV). The linewidth for the Ag $3d_{5/2}$ peak was 0.9 eV. The probable electron energy uncertainty amounted to ± 0.1 eV. The normal operating pressure was less than 1×10^{-7} Pa. The measurement of photoelectron spectra was carried out after scraping the samples in order to expose fresh surfaces. The electron binding energies were referred to the

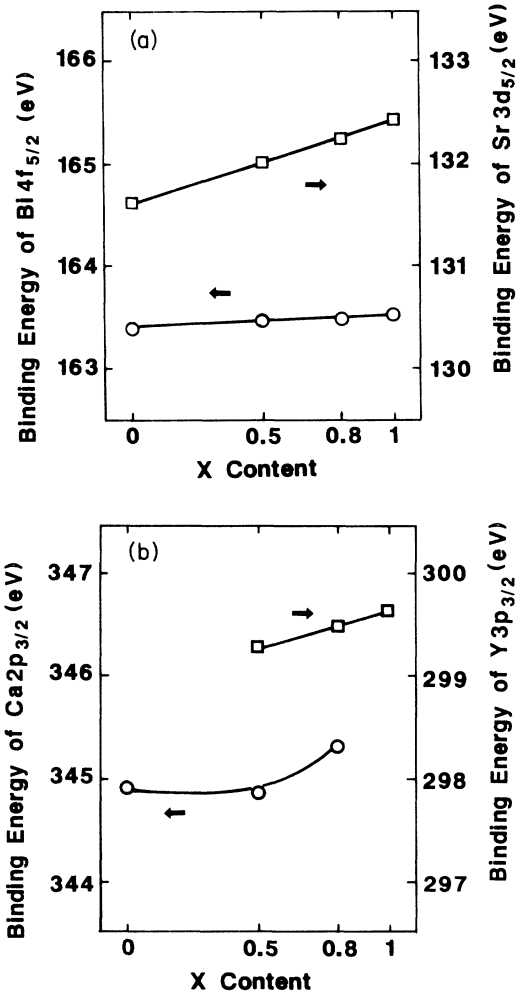

FIG. 1. Y content dependence of the binding energy of Bi $4f_{5/2}$, Sr $3d_{5/2}$, Ca $2p_{3/2}$, and Y $3p_{3/2}$ in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$.

C 1s line of contaminating carbon, whose value was 284.6 eV.

Figure 1 shows Y content dependence of binding energies of Bi $4f_{5/2}$, Sr $3d_{5/2}$, Ca $2p_{3/2}$, and Y $3p_{3/2}$. The Bi $4f_{5/2}$ binding energies (E_{Bi}) do not change for all Y content and are about 163.4 eV, which is almost identical to that of $Bi_2(Sr,Ca)_3Cu_2O_y$ (163.3 eV) (Ref. 7) and $Bi_2Sr_2Ca_2Cu_3O_y$ (163.4 eV).[9,10] The Bi $4f_{7/2}$ peak was not taken into account in this system because it coincides with the Y $3d$ peak. The Ca $2p_{3/2}$ binding energy (E_{Ca}) of sample C (345.3 eV) is higher than that of sample B (344.8 eV), which is similar to that of sample A. The Y $3p_{3/2}$ binding energy (E_Y) increases with increasing Y content. E_Y of sample D is 299.6 eV, which is similar to that of Y_2O_3 (299.8 eV). The Sr $3d_{5/2}$ binding energy (E_{Sr}) also increases with increasing Y content.

Figure 2 shows the Sr $3d$ spectra of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ system. The Sr $3d$ spectra can be decomposed into two components shown in Fig. 2. The Sr $3d$ peak "a" having lower binding energy changed from 131.7 eV for sample A to 132.3 eV for sample D. The Sr $3d$ peak "b" had higher binding energy, 133.1 eV, for all the samples. Kohiki *et al.* have determined that the peaks a and b are due to the Sr atoms located between Bi-O and Cu-O planes and between the adjacent Cu-O planes, respectively.[7] In sample A, the intensity ratio ($R_{ab}=I_b/I_a$) of the peak areas I_a and I_b of the Sr $3d_{5/2}$ spectra is 0.32, which is slightly larger than that of the $Bi_2Sr_{1.4}CaCu_2O_y$ single crystal ($R_{ab}=0.25$).[7] This is considered to be due to the difference in Sr content between Kohiki's sample and ours. In samples B, C, and D, R_{ab} became smaller. Thus, Sr atoms predominantly occupy the lattice sites between Bi-O and Cu-O planes with increasing Y content. On the basis of the above result and the fact that E_{Bi} is constant for all the samples, it is considered that Y atoms are selectively substituted for the cations between the adjacent Cu-O planes. Since the trivalent Y ions are substituted for the divalent Ca ions, the average valence of the Cu ions becomes lower, and thus the average valence of the Sr ions, which locate between Bi-O and Cu-O planes, tends to become higher.

The Cu $2p_{3/2}$ binding energy (E_{Cu}), Cu LVV Auger-electron kinetic energy (E_k), and the intensity ratio of the Cu $2p_{3/2}$ satellite-peak area to the Cu $2p_{3/2}$ main-peak area (R_{ms}) are shown as a function of Y content in Fig. 3. The Cu $2p_{3/2}$ electron spectra are shown in Fig. 4. E_{Cu} and E_k decrease with increasing Y content. E_{Cu} of samples A and D are 932.8 and 932.6 eV, respectively, which

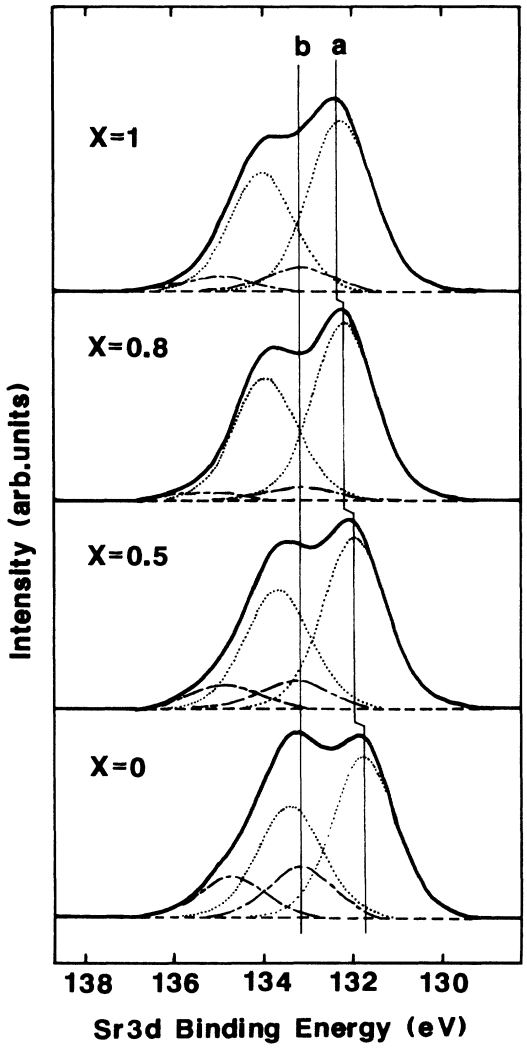

FIG. 2. The Sr $3d$ electron spectra of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ ($x=0.0$, 0.5, 0.8, and 1.0) samples. The peaks "a" and "b" are due to the Sr atoms located between the Bi-O and Cu-O planes and between the adjacent Cu-O planes, respectively.

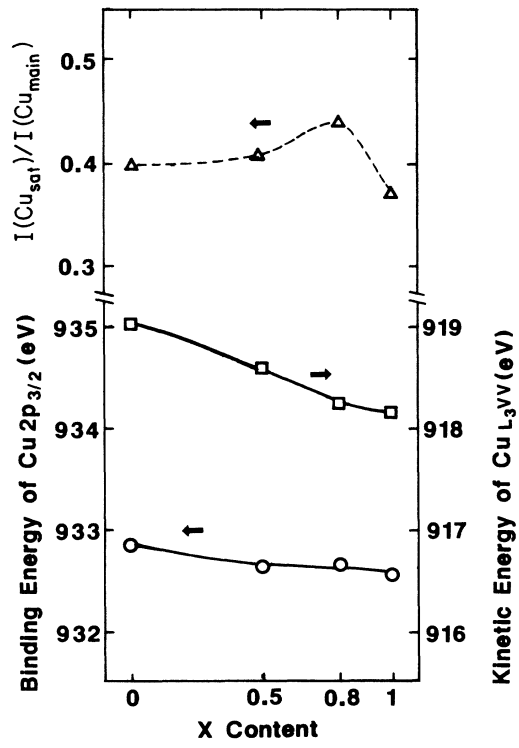

FIG. 3. Y content dependence of the binding energy of Cu $2p_{3/2}$, the kinetic energy of Cu LVV, and the intensity ratio of the Cu $2p_{3/2}$ satellite peak to the Cu $2p_{3/2}$ main peak.

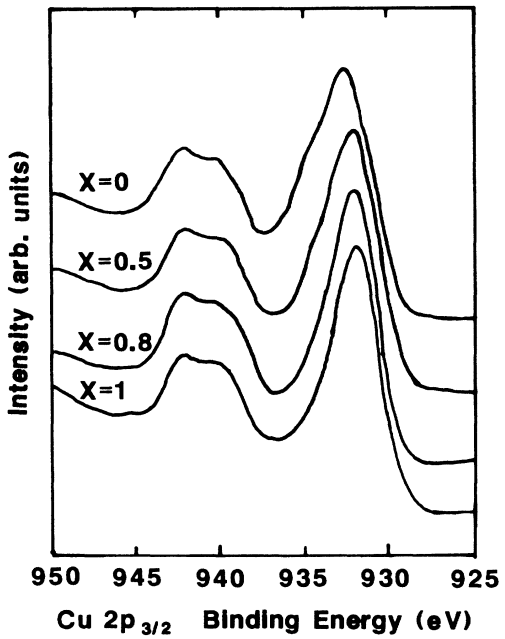

FIG. 4. The Cu $2p_{3/2}$ electron spectra of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ ($x=0.0$, 0.5, 0.8, and 1.0) samples.

are higher than that of Cu_2O (932.2 eV).[14] The higher binding energy corresponds to a higher valence of Cu in these oxides. The Auger parameter, which was defined as the sum of the Cu $2p_{3/2}$ electron binding energy and the Cu *LVV* Auger-electron kinetic energy, changed from 1851.9 eV for sample *A* to 1850.7 eV for sample *D*. The Auger parameters reported for Cu_2O and CuO are 1849.2 and 1851.8 eV, respectively.[14] The linewidth of the main peak gradually decreased with increasing Y content. Shoulder peaks around 934.5 eV, observed in samples *A* and *B* in Fig. 4, correspond to the Cu^{3+} ions.[9,10] Fermi edges for samples *A* and *B*, which were superconductors, were observed clearly by ultraviolet photoelectron spectroscopy (UPS), but it was difficult to observe Fermi edges for samples *C* and *D*.[15] Thus, it is suggested that the average Cu valence decreases with increasing Y content and that the average Cu valences of samples *A* and *B* are higher than +2. Table I summarizes the satellite-to-main-peak ratios of CuO, Cu_2O, and samples *A*, *B*, *C*, and *D* according to the report by Kohiki and co-workers[8-10] The satellite-to-main-peak ratios of CuO and Cu_2O are 0.54 and 0, respectively. The probability of the existence of Cu^{2+} ions can be derived from the satellite-to-main-peak ratios, assuming that the probability of existence of

TABLE I. Satellite-to-main-peak ratios (R_{ms}) of CuO, Cu_2O, and samples *A*, *B*, *C*, and *D*. Contents of Cu^{2+} ion and average valence of Cu are also listed.

	Sample					
	CuO	*A*	*B*	*C*	*D*	Cu_2O
R_{ms}	0.54	0.40	0.41	0.44	0.37	0
Cu^{2+} content (%)	100	74	76	81	69	0
Average valence of Cu	2.0	2.3	2.2	1.8	1.7	1.0

Cu^{2+} depends linearly on the satellite-to-main-peak ratio. The R_{ms} of sample *C* is 0.44, which is the largest value within our samples. The R_{ms} of sample *A* is 0.40, which indicates that 26% of the Cu ions are trivalent, and that the average valence of Cu corresponds to 2.3, if valences of Cu are assumed to be +3 and +2. The R_{ms} of sample *D* is 0.37, then it comprises 31% Cu^{1+} and 69% Cu^{2+} ions, and the average valence of Cu corresponds to 1.7, assuming that the valences of Cu are +1 and +2.

It was reported that the oxygen content (y) obtained by thermal decomposition was 8.31 for $Bi_2Sr_2CaCu_2O_y$ and 8.37 for $Bi_2Sr_2YCu_2O_y$.[5] Assuming that the valence of Bi, Sr, Ca, Y, and O are +3, +2, +2, +3, and −2 on the lattice sites, respectively, the Cu average valences derived from oxygen contents were 2.31 for $Bi_2Sr_2CaCu_2O_y$ and 1.88 for $Bi_2Sr_2YCu_2O_y$.[5] In sample *A* ($Bi_2Sr_2CaCu_2O_y$), which is a superconductor, the analyzed valence (2.3) of Cu is nearly equal to the value estimated above (2.31). Takahashi *et al.* reported that the superconductivity could be driven by the formation of Cooper pairs of O $2p$ holes in Fermi-liquid states on the basis of the results of angle-resolved UPS.[16] From these results, it is considered that the decrease of T_c by the substitution of Y for Ca in this system is caused by the decrease of the hole concentration in the Cu−O bond. In sample *D* ($Bi_2Sr_2YCu_2O_y$) which is a nonsuperconductor, the analyzed average valence (1.7) of Cu is lower than the above estimated value (1.88). It is suggested that holes on the oxygen site may exist in sample *D*. This is consistent with the results derived from the electrical properties of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ at high temperatures.[6]

In conclusion, Y atoms are substituted for the cations between the adjacent Cu-O planes for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ systems. As the Y content increases, the binding energies of Sr and Y increase and that of Bi does not change. The average valence of Cu is above 2 for $0.0 \leqq x \leqq 0.5$ and below 2 for $0.8 \leqq x \leqq 1.0$ for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ systems.

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