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Electronic states of $\text{BaBiO}_{3-\delta}$ and K-doping effects studied by photoelectron spectroscopy

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Abstract. Changes in the electronic states for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$ ($\delta = 0$ and 0.5) due to various surface treatments (fracturing, scraping and ion sputtering) have been studied by x-ray photoelectron spectroscopy. It is found that marked spectral changes occur as a result of scraping and sputtering; the core levels are broadened and the intensity at the top of the valence bands is reduced. These results are discussed in terms of the reduction of elements and damage in the surface region. The above results cause us to conclude that fracturing these samples is suitable as a cleaning procedure for this system.

The Bi 4f, Ba 4d and O 1s core levels have very low binding energies and are shifted by 0.2–0.4 eV to lower binding energies on 50% substitution of K for Ba. The Bi 4f line seems to contain a single chemical state for $\text{BaBiO}_{3-\delta}$, and more than one chemical state for $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$. The top of the valence band is found to be 0.5 eV below the Fermi level for $\text{BaBiO}_{3-\delta}$, while a clear Fermi edge appears for the K-doped material in the valence band spectra from both x-ray and ultraviolet photoelectron spectroscopy. The electronic states of $\text{BaBiO}_{3-\delta}$ and K-doping effects are discussed and compared with band calculations.

1. Introduction

The perovskite $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$ system is the only superconducting oxide having a transition temperature T_c above 25 K without the Cu–O₂ planes [1, 2]. Since the discovery of this material, the similarities and differences between the cuprates and the bismuthates including $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ [3] have been discussed in order to elucidate the mechanisms of high- T_c superconductivity in the oxides [4]. The main similarities are that the materials have a higher T_c even though they have a low density of states at E_F [4, 5] and that superconductivity appears near the metal–insulator transition regions. These properties probably refer to the roles of Cu 3d–O 2p and Bi 6s–O 2p hybridization in the cuprates and the bismuthates, respectively [4].

For the bismuthates, the end member $\text{BaBiO}_{3-\delta}$ is expected to be metallic because of the half-filled valence states. Experimental results show, however, that this material

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is a semiconductor [1, 2]. A three-dimensional charge-density wave (CDW) is one proposition to explain the semiconducting property of $\text{BaBiO}_{3-\delta}$, in which the valence disproportionation of Bi^{4+} ions into Bi^{3+} and Bi^{5+} is expected in the ionic limit [6, 7]. It was shown by a neutron diffraction study that the Bi atoms occupy two crystallographically inequivalent sites with different Bi–O bond lengths; this has been explained by the existence of two Bi valence states [6]. An optical study suggested that the CDW gap is accompanied by breathing-mode distortion in $\text{BaBiO}_{3-\delta}$ [8]. On the other hand, band calculations have predicted more covalent pictures with only minimal valence disproportionation rather than ionic pictures [9, 10].

Although photoemission studies have been performed on this material by many groups [11–22], the results differ widely and provided us with no consistent answer even on the question of whether inequivalent Bi states exist or not. For the Bi core levels, Kulkarni *et al* [14] and Jeon *et al* [21] reported the existence of two Bi 4f lines corresponding to Bi^{3+} and Bi^{5+} states in $\text{BaBiO}_{3-\delta}$ [14]. On the contrary, other groups [11–13, 17] found a narrow line in the Bi core level spectra. However, the explanations of the sharp line given by the various researchers were different. Hegde *et al* [13] mentioned that the single Bi line corresponds to Bi^{3+} and the existence of Bi^{5+} is denied, which was explained by two oxygen states (O^- and O^{2-}). On the other hand, Wertheim *et al* [11] and Shen *et al* [17] insisted that the sharp Bi core lines show that the charge disproportionation is too small to be identified by the photoemission.

Moreover, K- or Pb-doping effects on the Bi core levels of $\text{BaBiO}_{3-\delta}$ are also controversial. Bi 4f lines made sharper by the doping were reported by Kulkarni *et al* [14] for $\text{BaPb}_x\text{Bi}_{1-x}\text{O}_{3-\delta}$. On the other hand, broadening of the core lines was observed by Wertheim *et al* [11] but not discussed in detail. Hegde *et al* [13] and Jeon *et al* [21] reported that the Bi 4f spectrum is unchanged by the K doping. These differences in the core level photoemission results have prevented us from understanding the electronic structure of $\text{BaBiO}_{3-\delta}$ and the effects that doping has on it.

Although many photoemission studies were carried out for the valence bands of these systems, few studies found the Fermi edge for Ba–K–Bi–O using x-ray photoelectron spectroscopy (XPS) [16].

We consider that the scattered photoemission data would originate mainly from the following two sources: firstly surface treatments for cleaning and secondly sample quality. The scraped surfaces of Bi–Sr–Ca–Cu–O are reliable for a photoemission study, because the surfaces are substantially stable even if not at a low temperature [23]. For Nd–Ce–Cu–O, the surfaces are damaged considerably by scraping, whereas fracturing is suitable for a photoemission study [24]. In the cases of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$ and $\text{BaPb}_x\text{Bi}_{1-x}\text{O}_{3-\delta}$, ion sputtering [12] and fracturing [17] have rarely been used while scraping has been carried out in many studies [11, 13–16, 18–22]. However, no detailed consideration of the surface treatments has been undertaken. So here we shall pay much attention to the surface stability of these systems.

To do this, sample characterizations on the structure, concentrations of metal elements and oxygen content are needed. The decomposition of K-doped materials into two phases (a K-rich phase and a K-poor phase) was reported, especially in the region of low K concentrations [25]. This shows the difficulty in synthesizing $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$ and the necessity of checking the sample quality.

In this paper, first, we describe the changes in electronic states of the surfaces treated by the various methods in order to check the suitability of the methods for the photoemission study. Taking these results into account, the electronic states of $\text{BaBiO}_{3-\delta}$ and the K-doping effects studied by XPS and ultraviolet photoelectron spectroscopy (UPS) will be presented in the following sections.

2. Experimental details

Polycrystalline $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$ was synthesized by solid state reaction of high-purity BaO_2 , KO_2 and Bi_2O_3 powders [26]. A mixture of the powders with the proper metal ratios was pelletized, sintered at 650 °C for 1 h in an N_2 stream and quenched to room temperature. The pellets were subsequently annealed at 450 °C for 4 h in an O_2 stream. This procedure was repeated three times in order to obtain good crystalline materials. $\text{BaBiO}_{3-\delta}$ was prepared by heating a mixture of BaCO_3 and Bi_2O_3 powders at 950 °C for 10–100 h in air after pre-heating treatments in the temperature range between 600 and 900 °C.

The materials synthesized were examined by x-ray powder diffraction (XPD), scanning electron microscopy (SEM) with energy-dispersive x-ray spectrometry (EDS), and electron probe x-ray microanalysis (EPMA) using a wave-dispersive x-ray spectrometer. The XPD patterns showed that these samples consist of a single monoclinic phase for $\text{BaBiO}_{3-\delta}$ and a single cubic phase for $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$. No impurity phases were observed by the SEM-EDS experiments. The mean composition obtained by the EPMA was $\text{Ba}_{0.47}\text{K}_{0.37}\text{Bi}_{1.00}\text{O}_{3-\delta}$ for $x = 0.5$, normalizing by taking $\text{Bi} = 1.00$, in which the scattering of data at 15 different measured points was within 10%. The temperature dependence of the resistivity showed that $\text{BaBiO}_{3-\delta}$ is a semiconductor and $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$ is a superconductor with a T_c of 20 K. The sample preparation and properties have been given in detail in [26].

X-ray photoemission experiments were carried out using an SSX-100 spectrometer (Surface Science Instruments) and a monochromated Al $K\alpha$ source (1486.6 eV) with a beam diameter of 300 μm . The total energy resolution of this system is 0.45 eV which was determined from the Fermi edge of pure Ni. The binding energy scale was calibrated using the Au $4f_{7/2}$ peak as 83.96 ± 0.05 eV. An ADES-400 spectrometer (VG Scientific) was used for He I (21.2 eV) and He II (40.8 eV) UPS measurements. The binding energy scale for UPS measurements was calibrated by referring the Fermi edge of pure Au to the Fermi level E_F and the total energy resolution of this system is 0.12 eV for the He I line. All measurements were performed under a UHV lower than 1×10^{-8} Pa at room temperature.

The sample surfaces studied here were cleaned by three different *in-situ* methods under UHV conditions (lower than 1×10^{-8} Pa) at room temperature:

- (i) scraping with a stainless steel file,
- (ii) fracturing and
- (iii) Ar^+ ion sputtering.

3. Results and discussion

3.1. Changes in electronic states due to various surface treatments

Figures 1(a), 1(b), 1(c) and 1(d) show the Ba 4d, O 1s, Bi 4f and valence spectra of $\text{BaBiO}_{3-\delta}$, respectively, for the fractured surface and the subsequently scraped surface. The Ba 4d line, which consists of a single spin-orbit split pair of $4d_{5/2}$ and $4d_{3/2}$, is broader for the scraped surface than for the fractured surface. The 528.5 eV line for the O 1s, which corresponds to oxygen atoms in the structure, and the Bi 4f lines are also wider for the scraped surface. The full widths at half-maximum (FWHMs) of the core lines for

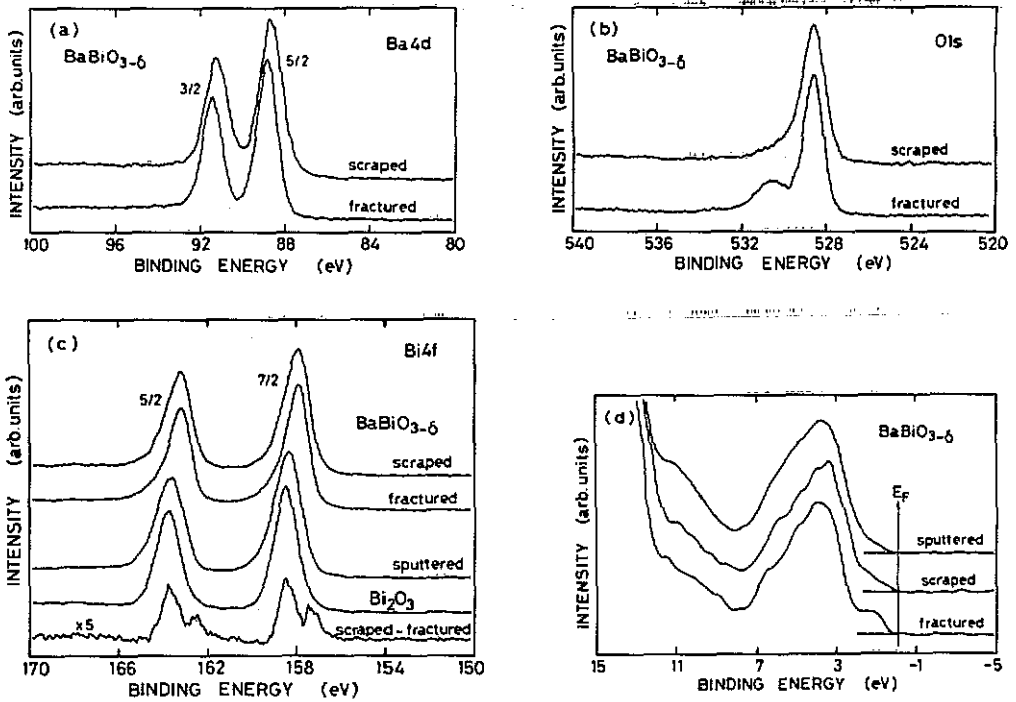


Figure 1. xps spectra of $\text{BaBiO}_{3-\delta}$ for fractured and scraped surfaces: (a) Ba 4d; (b) O 1s; (c) Bi 4f; (d) valence bands. In (c), the spectrum for Bi_2O_3 , the spectrum for the sputtered surface of $\text{BaBiO}_{3-\delta}$ and the difference spectrum between the fractured and the scraped surfaces are also shown. In (d), the spectra were smoothed with seven points in order to make the difference between the spectra clear. The valence spectrum for the sputtered surface is also shown in the figure.

Table 1. Full width at half maximum (FWHM) of Ba 4d_{5/2}, Bi 4f_{7/2}, Bi 4f_{5/2}, O 1s and K 2p_{3/2} peaks for $\text{BaBiO}_{3-\delta}$ and $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$ cleaned by various methods. The error is estimated to be smaller than ± 0.02 eV.

Specimen	Cleaning method	FWHM (eV)			
		Ba 4d _{5/2}	Bi 4f _{7/2}	O 1s	K 2p _{3/2}
$\text{BaBiO}_{3-\delta}$	Scraped	1.32	1.43	1.27	—
	Fractured	1.12	1.25	1.14	—
	Sputtered*	1.36	1.47	1.52	—
$\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$	Scraped	1.39	1.71	1.84	1.79
	Fractured	1.28	1.87	1.36	1.74

* Sputtered by Ar^+ ion with an energy of 3 kV for 60 s.

the surfaces treated by various methods are summarized in table 1. These values were obtained by taking the average of two experimental data in which good reproducibility was obtained.

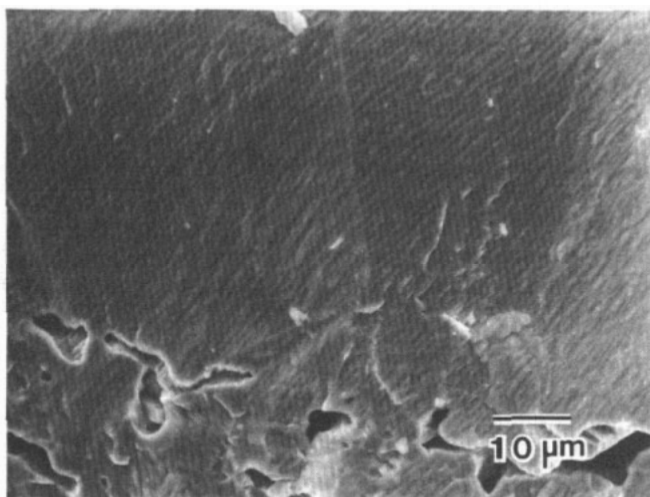


Figure 2. SEM image of a fractured surface of $\text{BaBiO}_{3-\delta}$, in which a number of fringes and some open voids are seen.

It is well known for various oxides that the FWHM of the XPS core line is increased by structural changes, i.e. strain and defects, and chemical changes, i.e. reduction of elements [27–29]. The core lines of $\text{BaBiO}_{3-\delta}$ taken for the sputtered surface have larger FWHMs than those for the scraped and fractured surfaces. An example is shown for the Bi 4f line in figure 1(c). This broadening would be due to the damage induced by sputtering, which is in agreement with the results for SiO_2 and Al_2O_3 [27, 29, 30]. From the analogy of these results, we consider that the broadening of the core lines found for the scraped surface could also be attributed to the structural and chemical changes in the surface region.

For the binding energy of the core lines, the Ba 4d lines are shifted to lower binding energies by scraping (figure 1(a)). This probably implies partial reduction of the Ba ions according to the general tendency of the chemical shifts for the core levels. The difference spectrum between the fractured and the scraped surfaces is shown at the bottom of figure 1(c). We find a peak at 158.5 eV which is close to the binding energy of Bi 4f_{7/2} for Bi_2O_3 (158.57 eV). This result shows the partial reduction of the Bi ions. The binding energy of the Bi 4f line for the sputtered surface is also close to that for Bi_2O_3 , which implies that the Bi ions were strongly reduced by sputtering.

Figure 1(d) shows the XPS valence spectra for the fractured, scraped and ion-sputtered surfaces of $\text{BaBiO}_{3-\delta}$. In order to make the differences clear, the spectra were smoothed with seven points. A sharp edge structure is observed at about 0.5 eV below E_F for only the fractured surface, while it is remarkably dulled by scraping and sputtering. The latter shows that the valence states are strongly modified, which is consistent with the changes in the core level spectra. It is roughly estimated that the chemical and structural changes induced by scraping and sputtering would occur at least 50 Å below the surface according to the escape depth of photoelectrons with kinetic energies of 1486 eV (Al K α XPS) [31]. These results indicate that the photoelectron spectra taken from the scraped and ion-sputtered surfaces do not reflect the electronic states of bulk $\text{BaBiO}_{3-\delta}$ any longer.

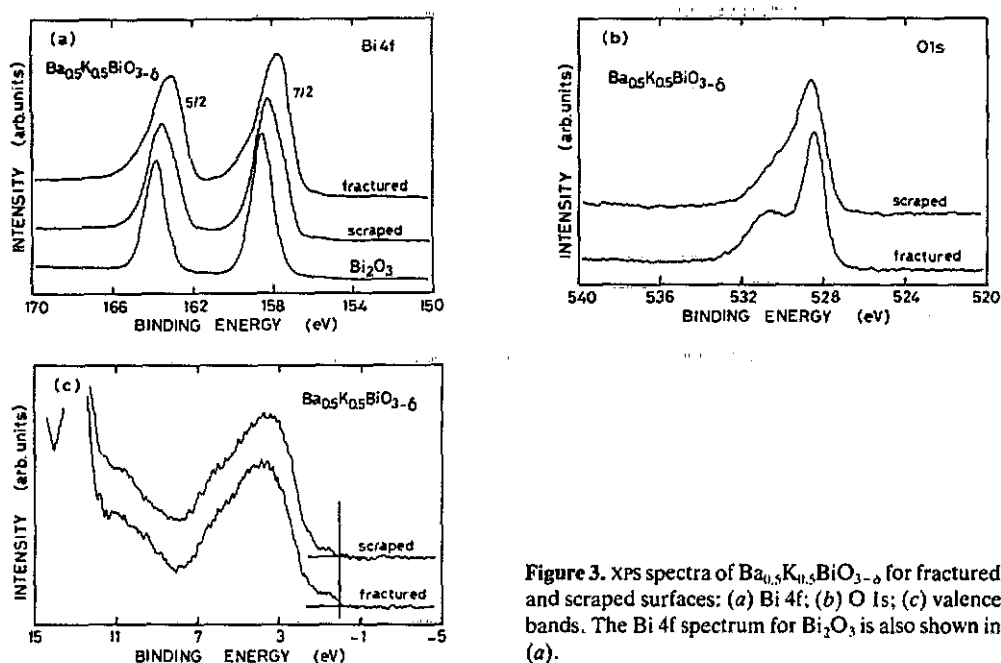


Figure 3. XPS spectra of $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$ for fractured and scraped surfaces: (a) Bi 4f; (b) O 1s; (c) valence bands. The Bi 4f spectrum for Bi_2O_3 is also shown in (a).

Figure 2 shows the SEM image of a fractured surface of $\text{BaBiO}_{3-\delta}$. A number of fringes, which were observed all over the fractured surface, reveal that the fracture occurred at intra-grains except for void surfaces.

For the K-doped materials, the study was carried out in the same way as for $\text{BaBiO}_{3-\delta}$. The FWHMs of the core levels for $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$ are also listed in table 1. Although the Bi 4f_{7/2} line is narrower for the scraped surface than for the fractured surface contrary to the results for $\text{BaBiO}_{3-\delta}$, the lineshapes are quite different for the two surfaces, as shown in figure 3(a). The binding energy of Bi 4f_{7/2} is shifted, by scraping, from 157.8 eV (for the fractured surface) to 158.4 eV, which is close to the peak position for trivalent Bi (158.6 eV); this could be attributed to the partial reduction of Bi [32].

Figure 3(b) shows the O 1s spectra for the scraped and the fractured surfaces of $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$. The main peak at about 528.5 eV is sharper for the fractured surface than for the scraped surface (table 1), which implies that damage would be induced in the surface region of the K-doped material as well as in the surface region of $\text{BaBiO}_{3-\delta}$. On the other hand, the fraction of the peak at about 531 eV is larger for the former than for the latter. This is due to contamination at pore regions of the fractured surface; the contamination could be carbonates and/or hydrates, analogous to the results for cuprate superconductors [33, 34]. Moreover, a clear Fermi edge is observed for only the fractured surface of $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$, whereas there is little spectral intensity at E_F for the scraped surface as shown in figure 3(c). This result shows that the electronic states of the surface are considerably changed from a metallic to an insulating nature by scraping.

From the above results, it is clarified that the fractured surfaces of the $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$ systems are less damaged than the scraped and ion-sputtered surfaces, although the former contains more contaminants than the latter at pore surfaces (figures 1(b), 2 and 3(b)). We would like to emphasize here that the fractured surfaces are also more suitable for studies on the electronic states of the sintered $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$ using photoemission,

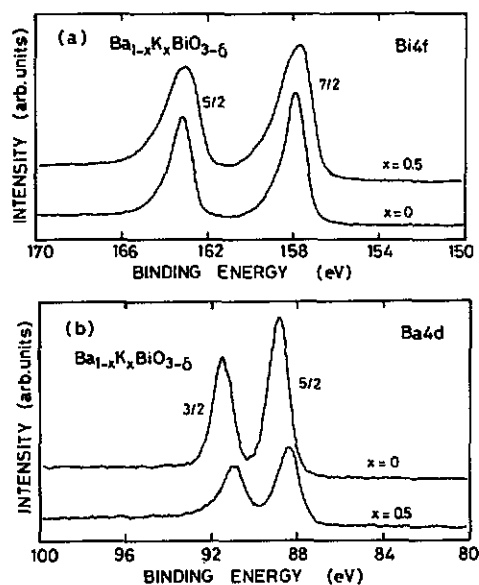


Figure 4. (a) Bi 4f and (b) Ba 4d core level spectra taken from fractured surfaces for $BaBiO_{3-\delta}$ and $Ba_{0.5}K_{0.5}BiO_{3-\delta}$.

because the effects of void surfaces on the electronic states are not detrimental compared with the effects of degradation of the surfaces by scraping and sputtering as clearly shown in the valence band spectra (figures 1(d) and 3(c)). It should be noted that many previous results [11, 13–15, 18–22] were obtained from scraped surfaces of the bismuthates. In the next section, therefore, we shall describe the electronic states of $Ba_{1-x}K_xBiO_{3-\delta}$ ($x = 0$ and 0.5) investigated by XPS and UPS for fractured surfaces.

3.2. Electronic states of $BaBiO_{3-\delta}$

3.2.1. Core levels. The Bi 4f spectra for $BaBiO_{3-\delta}$ and $Ba_{0.5}K_{0.5}BiO_{3-\delta}$ are shown in figure 4(a). We compare the FWHM of the Bi 4f_{7/2} line for $BaBiO_{3-\delta}$ with that for the oxides containing Bi. The FWHMs measured under the same experimental conditions are found to be 1.10 eV and 1.15 eV for Bi_2O_3 and $NaBiO_3$, respectively. The FWHM for $BaBiO_{3-\delta}$ (1.25 eV, shown in table 1) is close to these values within the deviation of 0.05 eV, which suggests that the Bi 4f line is composed of a single Bi state.

It was suggested as a result of the highly asymmetric lineshapes of the Bi 4f [14, 22] and Bi 5d [21] lines that the Bi atoms in $BaBiO_{3-\delta}$ have two different states. It should be emphasized here that these results were obtained for scraped surfaces on which the electronic states are considerably altered. Our result is in good agreement with that for the fractured surface where a single state of Bi was suggested from the Bi 5d line [17]. The Bi 4f line of $BaBiO_{3-\delta}$ obtained here for the fractured surface is a little asymmetric. We consider that the tail at the high-binding-energy side of the main peak could be attributed to the component of Bi^{3+} induced by a small amount of oxygen defects and to energy loss components accompanied by inter-band excitations (see figure 6(a)). The fact that δ -values of 0.05–0.15 were obtained for the $BaBiO_{3-\delta}$ sample by an iodometric titration [26] supports the former. For the latter, a small activation energy (about 0.3 eV) was reported from the results of resistivity measurements [8, 35].

Table 2. Binding energies of Bi $4f_{7/2}$ for the Bi oxides. The error in the binding energy is within ± 0.05 eV.

Material	Nominal valence	Binding energy of Bi $4f_{7/2}$ (eV)
Bi	0	156.90
Bi_2O_3^*	+3	158.57
NaBiO_3	+5	158.64
BaBiO_3	+4	157.80

* The binding energy was calibrated using the C 1s peak.

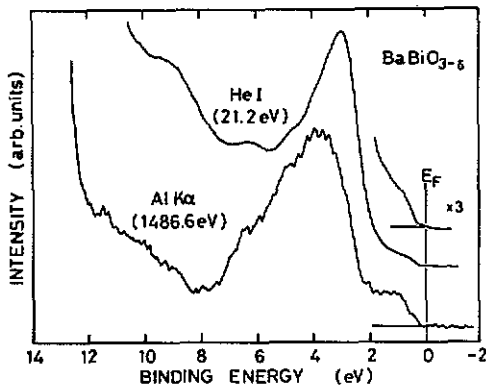


Figure 5. Valence band spectra taken from a fractured surface for $\text{BaBiO}_{3-\delta}$ measured by Al $K\alpha$ XPS and He I UPS.

The binding energy of the Bi $4f_{7/2}$ line for various bismuth oxides is summarized in table 2. The shift of Bi $4f_{7/2}$ seems to follow the general tendency of the chemical shifts except for $\text{BaBiO}_{3-\delta}$ whose binding energy is lower by about 0.8 eV than for Bi_2O_3 (Bi^{3+}) and NaBiO_3 (Bi^{5+}). If a strong ionicity were assumed in this system, the mean valence of the Bi ions would be estimated to be lower than 3+ from the chemical shift. However, a Bi valence lower than 3+ is unlikely on the basis of the electroneutrality rule. We consider that the low binding energy of Bi $4f$ for $\text{BaBiO}_{3-\delta}$ could be attributed to strong covalency in the Bi–O bonds because it could reduce the binding energy of the core levels [36]. This covalent picture agrees with the result for the valence spectra which will be mentioned later. The binding energy of the Ba $4d_{5/2}$ line (figure 4(b)) is 88.9 eV for $\text{BaBiO}_{3-\delta}$ which is lower than that for BaO (89.7 eV) [37]; this also suggests covalency in the Ba–O bonds.

3.2.2. Valence bands. The valence band spectra of $\text{BaBiO}_{3-\delta}$ measured by Al $K\alpha$ XPS and He I UPS are shown in figure 5. It is found that there is no spectral intensity at E_F and the top of the valence bands appears at about 0.5 eV below E_F in both the XPS and the UPS spectra. This is in good agreement with the semiconducting nature of this material. The photoionization cross sections of Bi 6s and O 2p, respectively, are 0.0013 Mb and 0.00024 Mb at 1486.6 eV (Al $K\alpha$ XPS) and 0.027 Mb and 10.67 Mb at 21.2 eV (He I UPS) [38]. The relative photoionization cross sections of Bi 6s to O 2p are 5.4 for Al $K\alpha$ XPS and 0.0025 for He I UPS, which means that the Bi 6s and O 2p characters dominate the XPS and UPS valence spectra, respectively. The lineshapes near E_F in the XPS and UPS

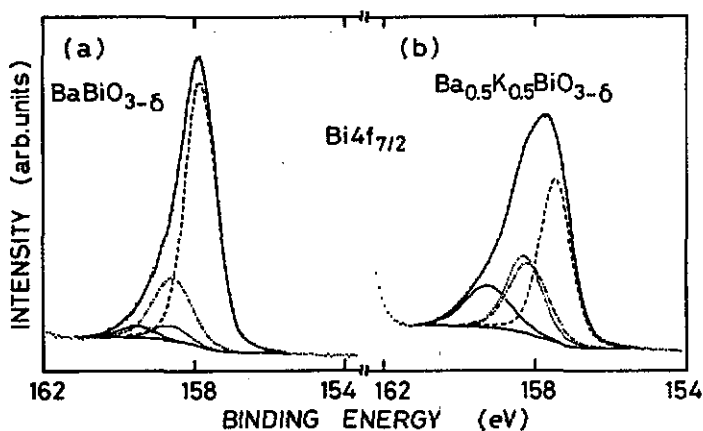


Figure 6. Deconvoluted Bi $4f_{7/2}$ lines for (a) $\text{BaBiO}_{3-\delta}$ and (b) $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$: ---, Bi^{4+} component; - · -, Bi^{3+} component; · · ·, Bi^{5+} component; —, energy loss component.

valence spectra, which resemble each other, suggest that the Bi 6s and O 2p levels are hybridized in this region, i.e. a highly covalent picture.

The valence band intensity obtained here could be compared with the result of the band calculation taking the photoionization cross sections into account [39]. It is found that the calculated density of states is in qualitative agreement with the spectral intensity measured by XPS and UPS. The energy positions of the centroid of the main bands measured by XPS and He I UPS are close to those of calculated partial densities of states for Bi and O, respectively. The only disagreement is that the electronic states obtained by calculation and the experiment are metallic and insulating, respectively.

3.3. K-doping effects

3.3.1. Core levels. The Bi 4f peak is markedly broadened by doping with K; the FWHM increases from 1.25 to 1.87 eV for Bi $4f_{7/2}$ (figure 4(a) and table 1). This suggests that the Bi state in $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$ consists of more than one component. Therefore, we divided the Bi $4f_{7/2}$ lines into four Gaussian lines which correspond to Bi^{3+} , Bi^{5+} , Bi^{4+} (Bi^{4+} denotes the Bi state dominating in $\text{BaBiO}_{3-\delta}$) and energy loss components. The Bi $4f_{7/2}$ lines of Bi_2O_3 , NaBiO_3 and $\text{BaBiO}_{3-\delta}$ were used as the standards for Bi^{3+} , Bi^{5+} and Bi^{4+} , respectively, where the FWHMs and the separations of the binding energies among them were kept constant. The backgrounds of the spectra were subtracted using the Shirley method. The results for $\text{BaBiO}_{3-\delta}$ and $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$ are shown in figure 6, in which satisfactory fitting is achieved.

The following results are obtained for the K-doping effects by analysis of the Bi $4f_{7/2}$ line.

- (1) The binding energies of all lines are decreased by 0.4 eV.
- (2) The fraction of Bi^{4+} is reduced.
- (3) The components of Bi^{3+} and Bi^{5+} are increased.
- (4) The high-binding-energy component is also increased.

The binding energy shift obtained here is close to that for the valence bands which will be shown later; this suggests that these shifts could be attributed to that of E_F

downwards in this system because of hole doping by the substitution of K^+ for Ba^{2+} and because of the small density of states at E_F [4]. It should be noted here that the fraction of Bi^{4+} decreases with the substitution, while the fractions of Bi^{3+} and Bi^{5+} are increased. The former suggests that the ordered electronic states which would construct the semi-conducting nature are reduced in the superconducting material. The increase in Bi^{3+} and Bi^{5+} fractions would be due to the break in the ordered electronic states. A similar picture was obtained by an optical study of the Ba–Pb–Bi–O system, in which an energy gap remains even in the metallic phase [8, 35]. However, it was pointed out that the energy gap would almost vanish with the insulator–metal transition by K doping in contrast with the situation in Ba–Pb–Bi–O [40]. The broadening of the Bi 4f line might be due to inhomogeneity of the K concentration in the sample or to the presence of contamination at pore surfaces of the fractured surfaces. Although the XPD pattern showed a single phase, inhomogeneity or contamination would have a strong effect on the XPS spectra if it appeared at sample surfaces. Since $BaBiO_{3-\delta}$ is transformed to metallic by the substitution, the conduction electrons would be excited by the Bi 4f_{7/2} photoelectrons, which leads to a high-binding-energy broad peak beside the Bi 4f_{7/2} line [36] and contributes to broadening of the line.

The Ba 4d line shifts towards a lower binding energy by about 0.4 eV with the substitution of K for Ba as does the Bi 4f_{7/2} line (figure 4(b)). A shift of about 0.2 eV was also observed for the O 1s line. The binding energy of the K 2p_{3/2} line was 291.6 eV (the spectrum is not shown here), which is lower by about 1 eV than that for K^+ ionic compounds such as KCl and KBr [41]. The low binding energy implies covalency in the K–O bonds.

3.3.2. Valence bands. The valence band spectra of $Ba_{0.5}K_{0.5}BiO_{3-\delta}$ and $BaBiO_{3-\delta}$ measured by XPS and He I UPS are shown in figures 7(a) and (b), respectively. The Fermi edge is clearly seen in both XPS and UPS spectra for $Ba_{0.5}K_{0.5}BiO_{3-\delta}$, which agrees with the metallic nature of this material. It should be emphasized that we, for the first time, observe a clear Fermi edge for the fractured surface using He I UPS. Upon taking the photoionization cross section into account, the O 2p and Bi 6s characters would dominate the valence spectra measured by He I UPS and XPS, respectively. The result that a clear Fermi edge is observed in both XPS and UPS spectra implies that the Bi 6s and the O 2p levels are mixed at E_F . Therefore, conduction occurs through a three-dimensional network containing the Bi 6s and O 2p states.

The photoemission of the valence bands for $Ba_{1-x}K_xBiO_{3-\delta}$ has been studied using XPS [13, 16] and synchrotron radiation (50–120 eV) [18, 21], in which the Fermi edge was found for only XPS. The latter results are in good agreement with our UPS He II (40.8 eV) spectrum with an invisibly weak Fermi edge (not shown here). The Fermi edge found here at 21.2 eV would be due to the resonance enhancement of O 2s → O 2p since the ionization cross section of O 2p at 21.2 eV is not very different from that at 40.8 eV [38]. However, inverse photoemission results showed no enhancement of the O 2p-derived band just above E_F at an incident electron energy between 20 and 14 eV [16, 42].

Band calculations of this system have been reported [10, 39, 43], where the overall shape of the densities of states resemble each other: the main band centred at 2–3 eV and a weak density of states at E_F . Our results are in qualitative agreement with the calculations except for the binding energy of the valence bands; the centre of the main band measured by XPS and He I UPS has a binding energy higher by about 1 eV than that of the calculated results.

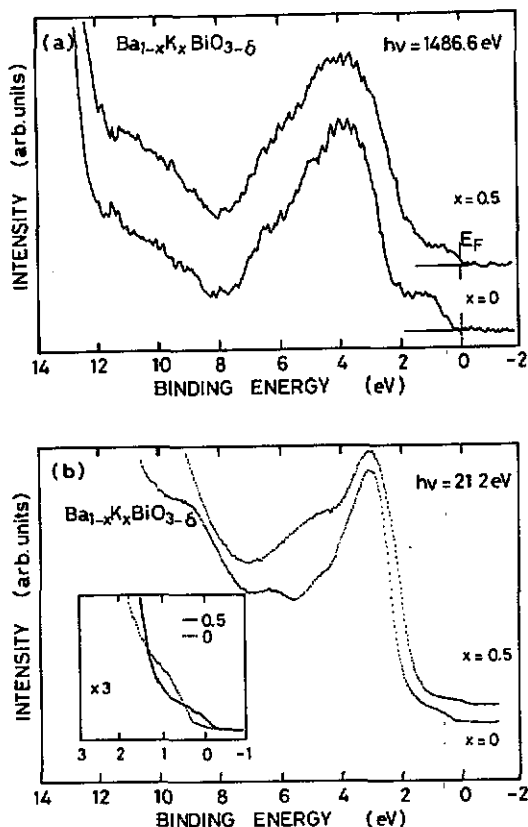


Figure 7. Valence band spectra of $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$ and $\text{BaBiO}_{3-\delta}$ measured by (a) Al $K\alpha$ XPS and (b) He I UPS. The inset in (b) shows the enlarged spectra near E_F . A clear Fermi edge is observed for $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$ in both XPS and UPS spectra.

Upon comparing the valence band spectra of $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$ and of $\text{BaBiO}_{3-\delta}$, a large difference between densities of states at E_F is seen: a small intensity for the former and nothing for the latter. It should be noted that the threshold of the main bands is shifted by about 0.4 eV towards E_F by doping. The shift of E_F due to K doping calculated by LAPW [10], FLAPW [39] and APWCPA [43] is between 0.4 and 0.5 eV, which corresponds to the shifts of the core lines and valence bands obtained here. The spectral intensity at the top of the valence bands, which was estimated by measuring the height of the edge, is decreased by the doping; this is also in agreement with the calculations. However, the band theory cannot explain the semiconductor-metal transition as due to the doping. Mattheiss and Hamann [9, 10] showed that it was possible for the energy gap to be induced by only a small charge disproportionation due to a distorted structure including the frozen-phonon-breathing mode of oxygen octahedra. In order to solve the problem, further experimental and theoretical investigations on the semiconducting nature of $\text{BaBiO}_{3-\delta}$ will be needed.

4. Summary

In this paper, it was shown that the photoelectron spectra of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$ are remarkably varied by the surface treatments (fracturing, scraping and ion sputtering): the FWHM

of the core lines is broadened and the intensity at the top of the valence bands is reduced by scraping and ion sputtering. We would like to emphasize that the inconsistency among previous results was due to the different surface preparations used, even though they were carried out under UHV conditions. We pointed out from the systematic experiments on the various surface treatments that the fractured surface is suitable for photoemission studies on sintered $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$.

It seems that the chemical states of Bi in $\text{BaBiO}_{3-\delta}$ and $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_{3-\delta}$ are a single state and more than one state, respectively. The $\text{Bi } 4f_{7/2}$ line was divided into four components which correspond to Bi^{3+} , Bi^{5+} , Bi^{4+} and inter-band transitions. The top of the valence band for $\text{BaBiO}_{3-\delta}$ was found to be about 0.5 eV below E_F . On the other hand, a clear Fermi edge was found using XPS and He I UPS for the K-doped material. These results are in good agreement with the semiconducting and the superconducting (metallic) properties. Hybridization between the Bi 6s and the O 2p orbitals was suggested by taking the photoionization cross section into account. XPS and UPS valence band spectra are in qualitative agreement with the band calculations except for the band gap for $\text{BaBiO}_{3-\delta}$.

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