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Photoelectron spectroscopic study of $Ba_{1-x}Rb_xBiO_3$

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A photoelectron spectroscopic study to investigate the electronic structure of a noncuprate oxide superconductor $Ba_{1-x}Rb_xBiO_3$ ($0 \leq x \leq 0.4$) system is reported. Comparison of the results with those inconclusively reported for $Ba_{1-x}K_xBiO_3$ and $BaPb_{1-x}Bi_xO_3$ is discussed. It is concluded that the chemical environment of substituted Rb in this system is similar to that of Rb metal, core-level binding energies of Bi and Ba are unaffected by Rb substitution, and the shift of the valence band towards lower binding energy upon hole-carrier doping is observed. A characteristic change of the density of states in the vicinity of the Fermi level with composition x is observed, suggesting that the nonmetal-to-metal transition occurs through a continuous change of the electronic states of the system.

I. INTRODUCTION

The oxide superconductor $Ba_{1-x}Rb_xBiO_3$ was discovered at the same time as $Ba_{1-x}K_xBiO_3$.[1,2] At present, $Ba_{1-x}M_xBiO_3$ (M=K,Rb) has been found to have the highest transition temperature ($T_c \sim 28$ K at $x \sim 0.4$) among Cu-free superconductors.[1-3] This family of superconductors results from A-site substitution of the parent ABO_3-type perovskite $BaBiO_3$. It is closely related to the $BaPb_{1-x}Bi_xO_3$ which is one of the earliest high-T_c oxide superconductors, obtained by B-site substitution with Pb.[4] The parent compound of both families, $BaBiO_3$, is an exceptionally interesting material in the sense that it is found to be a semiconductor experimentally in spite of having an odd number of electrons in a unit cell. Already a number of explanations for $BaBiO_3$ itself and superconductivity in $BaPb_{1-x}Bi_xO_3$ have been proposed.[5] The occurrence of superconductivity in $BaPb_{1-x}Bi_xO_3$ and $Ba_{1-x}M_xBiO_3$ is likely to be physically equivalent from the fact that substitutions, though for different sites, similarly introduce carriers into the system.[6] The discovery of high-T_c superconductivity in the cuprate oxides which have both similarities and differences with the $Ba_{1-x}M_xBiO_3$ system has stimulated interest into the mechanism of superconductivity in these two systems.

For similarity, the parent materials of both oxide superconductors are half-filled band insulators, and superconductivity in both systems appears at the boundary of a metal-to-nonmetal transition.[3,7,8] Both have similar crystal structures: perovskite for $Ba_{1-x}M_xBiO_3$ and layered perovskite for cuprate superconductors. However, since $Ba_{1-x}M_xBiO_3$ contains no transition element and a muon-spin-resonance study has demonstrated the absence of magnetic order in $Ba_{1-x}K_xBiO_3$,[9] the magnetic mechanism, as proposed for the cuprate superconductors, is not plausible for superconductivity in $Ba_{1-x}M_xBiO_3$. Another important difference is that the two-dimensional metal-oxygen planes, which are believed to be an essential factor for a high-T_c in a cuprate system, do not exist in the $Ba_{1-x}M_xBiO_3$ system. From these features, understanding of the mechanism of superconductivity of the $Ba_{1-x}M_xBiO_3$ system will be directly helpful for the understanding of the superconductivity in the cuprate superconductors.

While there are already some reports on the theoretical[10-14] and experimental[15-19] electronic structure studies for $Ba_{1-x}K_xBiO_3$, there are none for $Ba_{1-x}Rb_xBiO_3$. It is also noted that disagreement still exists among those photoelectron spectroscopic studies. The following points are important for the understanding of the electronic structure. First, how does the density of states at the Fermi level, $N(E_F)$, change with the physical properties, such as conductivity, when the composition x changes? Second, does the valence band move toward lower binding energy when the system is hole doped and becomes metallic (superconducting) for $0.3 \leq x \leq 0.4$? This is of interest in that it indicates whether this system is understandable by a rigid-band picture. Third, how do the binding energies of inner core levels change, which in turn indicates the change of the chemical environment, as a function of x?

In this study, we have succeeded in the synthesis of high-quality, single-phase $Ba_{1-x}Rb_xBiO_3$ for $0 \leq x \leq 0.4$. Photoelectron measurements were performed to investigate the electronic structure of this system for different x's, and the results are reported for the first time. Comparison of the results with those reported for $Ba_{1-x}K_xBiO_3$ and $BaPb_{1-x}Bi_xO_3$ is discussed.

II. EXPERIMENT

The samples used in this study were prepared by applying the synthesis procedure for $Ba_{1-x}K_xBiO_3$ of Hink *et al.*[3] Appropriate mixtures of $BaCO_3$, Rb_2CO_3, and Bi_2O_3 were calcined at 780 °C for 12 h in flowing N_2 gas, pulverized, and then annealed in O_2 at 400 °C for 1 h. X-ray-diffraction patterns revealed no impurity phases. Magnetization measurements were performed and superconductivity was observed for $0.28 \leq x \leq 0.44$, with $T_c \sim 29$ K and most independent of x. Sample preparation and characterization are described in detail elsewhere.[20]

High-quality polycrystalline $Ba_{1-x}Rb_xBiO_3$ samples ($x=0,0.1,0.2,0.3,0.4$) obtained by this method were used in this study. Measurements were made on the VG Scientific ESCALAB MkII spectrometer equipped with an Al x-ray source (1486.6 eV) for x-ray photoelectron spectroscopy (XPS) and a noble-gas discharge lamp for ultraviolet photoelectron spectroscopy (UPS). The energy distribution of the photoelectron was determined by an electron-energy analyzer, the resolution of which was set at 0.8 and 0.15 eV for XPS and UPS measurements, respectively. Core-level binding energies were referenced to the adventitious C 1s peak at 285.0 eV.[21] For the UPS measurement, the Fermi energy was determined directly from the zero binding energy of the analyzer because no charge-up was observed and the accuracy was better than 0.15 eV. The typical pressure during measurements was about 2×10^{-10} torr. The sample surface was scraped *in situ* by a diamond file to expose a fresh surface prior to each measurement. The surface cleanness was confirmed by the disappearance of both the adventitious C 1s peak and the impurity O 1s peak around 531 eV binding energy. After scraping, no appreciable changes in the spectra were observed over the period of measurements, which was typically 30 min. In this study, all of the spectra were taken at ambient temperature.

III. RESULTS AND DISCUSSION

A. Core-level spectra

Figure 1 shows the Rb 3*d* core-level XPS spectra from $Ba_{1-x}Rb_xBiO_3$. The shape of the spectra indicates the existence of additive peaks besides the two expected for a *d* core level. As shown for the case of $x=0.3$ in Fig. 1, we have analyzed the spectra and found that there may exist two inequivalent Rb species with different 3d binding energies in the samples: one with peaks 1 and 2 as $3d_{5/2}$ and $3d_{3/2}$ core levels, respectively, and another with peaks 3 and 4 as those core levels. Since there is only one site for Rb in this system and considering their intensity contribution, we conclude that peaks 1 and 2 were intrinsic and arose from the Rb substituted for Ba in the system, while peaks 3 and 4 arose maybe from the intergrain extrinsic Rb. This kind of intergrain Rb seemed to exist still in our samples; however, considering the results of various measurements done on this system, we conclude that it should have no effect on the results of this study. We will stress peaks 1 and 2 in the following discussion. The intensity of the Rb 3*d* peaks increased as x increased, indicating that the existence of Rb in the $Ba_{1-x}Rb_xBiO_3$ samples with quantity varied with x, as expected. The measured binding energy of Rb $3d_{5/2}$ in $Ba_{1-x}Rb_xBiO_3$ was about 109 eV for the nonsuperconducting composition with $x \leq 0.2$. For superconducting samples ($x=0.3$ and 0.4), this peak shifted toward lower binding energy for about 0.3 eV. Though the result is not shown here, we have also done the XPS measurement for insulating Rb_2O and found that the binding energy of the Rb $3d_{5/2}$ core level in Rb_2O is about 113 eV. This and the fact that, in general, core-level binding energies of a metallic element shift toward lower values under the environment with lower valency, the above results indicate that the substituted Rb in $Ba_{1-x}Rb_xBiO_3$ is monovalent *with a metallic environment* rather than the ionic one; i.e., the effective valency of the substituted Rb seems to be smaller than 1. This XPS result is direct evidence showing that substitution of Rb for Ba introduces hole carriers into the system.

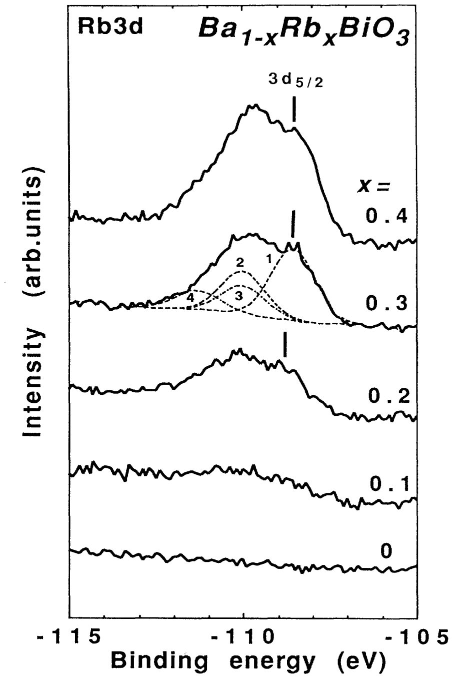

FIG. 1. Rb 3*d* core-level XPS spectra from $Ba_{1-x}Rb_xBiO_3$. See text for a detailed description.

Comparison of Bi 4*f*, Bi 5*d*, Ba 3*d*, and O 1*s* core-level XPS spectra from insulating ($x=0$) and superconducting ($x=0.4$) $Ba_{1-x}Rb_xBiO_3$ samples are shown in Fig. 2.

For Bi 4*f* core levels, our results show that the binding energies of Bi 4*f* do not change with x in the investigated composition range. This agrees well with the results of Hegde *et al.* for $Ba_{1-x}K_xBiO_3$.[15] Moreover, since the binding energies of Bi 4*f* are equal to those of Bi_2O_3,[15] this indicates that the chemical environment of Bi in $Ba_{1-x}Rb_xBiO_3$ is very similar to that of Bi_2O_3. However, it is also noted that a slightly broader feature of Bi 4*f* peaks for $x=0$ than that of $x=0.4$ could be observed. This might reflect the fact that there are two different Bi sites with slightly different binding energies in $BaBiO_3$ as was pointed out by the neutron-diffraction measurements of Thornton and Jacobson[22] and Cox and Sleight.[23]

Wagener *et al.* concluded from their XPS results for $Ba_{1-x}K_xBiO_3$ that while single chemical environments were observed for O, Ba, and K, inequivalent sites might exist for Bi, from the fact that the Bi 4*f* linewidth broadened when going from Bi_2O_3 to $Ba_{1-x}K_xBiO_3$.[17] If

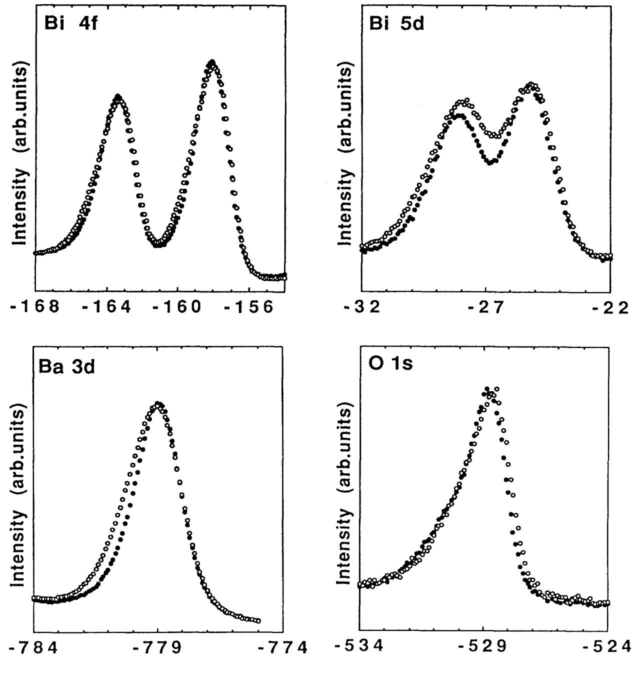

FIG. 2. Comparison of Bi 4f, Bi 5d, Ba 3d, and O 1s core-level XPS spectra from insulating [$x=0$ (○)] and superconducting [$x=0.4$ (●)] $Ba_{1-x}Rb_xBiO_3$ samples.

this is true, it seems that the peak width of Bi 4f is largest in $BaBiO_3$, smallest in Bi_2O_3, and in between in $Ba_{1-x}M_xBiO_3$, and that although the chemical environment became closer to being identical than that of $BaBiO_3$, inequivalent Bi sites still exist in $Ba_{1-x}M_xBiO_3$.

It is interesting to note that, while the binding energies of Bi $4f_{7/2}$ in $BaBiO_3$ and $Ba_{1-x}Rb_xBiO_3$ are equal, about 158 eV, the binding energies of Bi $4f_{7/2}$ in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ varied almost linearly with x, 158 eV for superconducting $Bi_2Sr_2CaCu_2O_y$, and about 158.6 eV for nonsuperconducting $Bi_2Sr_2YCu_2O_y$, respectively.[24] Although the explanation for this is not so clear, the fact that Bi sites in $Ba_{1-x}M_xBiO_3$ are surrounded by oxygen ions forming octahedra, while the Bi sites in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ form, not octahedra, but Bi-O planes, may be important. An octahedron structure might screen the change around it more effectively than a plane structure.

For Bi 5d, which are shallow core levels, a slight shift toward higher binding energy for increasing x might be pointed out; however, the amount of this shift is very small. Shen *et al.* pointed out that the binding energy of Bi 5d in $Ba_{0.6}K_{0.4}BiO_3$ reported by Ruckman *et al.*[16] is 0.5 eV larger than that in $BaBiO_3$ from their study, but speculated that the results of Ref. 16 might be affected by surface charging. Instead, they suggested that the binding energies of the Bi ions in $Ba_{1-x}K_xBiO_3$ should be lower than that of $BaBiO_3$.[25] However, our results showed that the binding energies of the Bi 5d levels were mostly independent of x as mentioned above.

For Ba 3d core levels, the $3d_{5/2}$ peaks were observed at 779 eV, independent of x within an accuracy of 0.1 eV. This result is consistent with that of Wagener *et al.* for $Ba_{0.6}K_{0.4}BiO_3$,[17] but inconsistent with that of Hegde *et al.*[15] for $Ba_{1-x}K_xBiO_3$ who observed this peak at 780 eV for $BaBiO_3$ and a shift of 0.4 eV to lower binding energy in superconducting $Ba_{0.6}K_{0.4}BiO_3$. We believe that our results for the high-quality samples with high signal-to-noise ratio and reproducibility are more reliable than those of Hegde *et al.* It is concluded that substituting Rb for Ba has little effect on the chemical environment of Ba atoms at least up to $x=0.4$. The effect of substitution of Rb for Ba sites may be screened by the BiO_6 octahedra surrounding the Rb/Ba atoms. We also agreed with Wagener *et al.* who pointed out that the Ba $3d_{5/2}$ binding energy in $Ba_{1-x}M_xBiO_3$ is lower than that in Ba metal. This indicates the metallic environment of the Ba sites in this system.[17,18]

The Ba $3d_{5/2}$ peak for $x=0$ was to some extent broader than that of $x=0.4$. This indicates the existence of an additive peak at higher binding energy around 780 eV and may be due to the existence of an extrinsic Ba compound in the $BaBiO_3$ sample.

For the O 1s level, a main peak at about 528.6 eV and a weak peak at about 531 eV were observed for all samples with a tendency for the main peak to shift toward higher binding energy for superconducting samples. Hegde *et al.* discussed the existence of several species of O 1s in the $Ba_{1-x}K_xBiO_3$ system and their relations to superconductivity.[15] However, we believe that only the main peak is intrinsic and the weak peak is an extrinsic feature since the intensity of the weak peak depended on the sample quality and cleaning procedure prior to measurement; i.e., the intensity of this peak decreased significantly by surface filing. Although we could not remove this peak entirely, the effect of it on the results of this study seemed negligible.

The O 1s XPS spectrum can be used to check the quality of a sample and its surface under measurement. Utilizing this, our study indicates that with the utilized synthesis conditions, the superconducting composition ($0.3 \sim x \sim 0.4$) seemed to be of better quality and more stable than the nonsuperconducting composition ($x < 0.3$). Under measurement, this 531-eV O 1s peak seemed to become prominent after scrapping faster for nonsuperconducting compositions than for superconducting compositions. This is consistent with the report of Jeon *et al.* who argue that $BaBiO_3$ is more susceptible to surface modification or oxygen loss upon scrapping than $Ba_{0.6}K_{0.4}BiO_3$.[19]

Hegde *et al.* have argued that the binding energy of the main peak at 528.5 eV became lower for the superconducting composition.[15] This is inconsistent with our results, which contrarily observed a very slight shift toward higher binding energy for superconducting compositions. Because this shift was very small and comparable to the experimental accuracy, we must leave this point for further study. However, we believe that the observation of the shift toward lower binding energy of the O 1s level in the superconducting compositions should be considered to be erroneous.

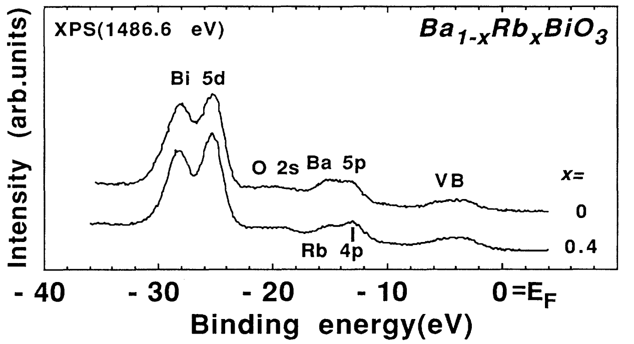

FIG. 3. XPS spectra in the valence band and shallow core-level region from $Ba_{1-x}Rb_xBiO_3$ samples with $x=0$ and 0.4.

Figure 3 shows the XPS spectra in the valence band and shallow core-level region of $Ba_{1-x}Rb_xBiO_3$ with $x=0$ and 0.4. Besides the broad valence band centered at about 3–4 eV binding energy, Ba $5p_{3/2}$ and Ba $5p_{1/2}$ core levels were observed around 13 and 15 eV, respectively. For Rb-substituted samples, the Rb $4p_{3/2}$ level superposed on the Ba $5p_{3/2}$ level at about 13 eV, resulting in an increase of the spectrum intensity at this energy relative to that of the Ba $5p_{1/2}$ level at 15 eV. Features at about 20, 25, and 28 eV are due to O 2*s*, Bi $5d_{5/2}$, and Bi $5d_{3/2}$ core levels, respectively. The results agreed well with those reported by Wagener *et al.* for $Ba_{1-x}K_xBiO_3$.[17]

B. Valence-band spectra

Figure 4 shows the UPS spectra in the valence-band region of $Ba_{1-x}Rb_xBiO_3$ for different *x*'s. The overall feature of each spectrum was similar, showing one broad structure between the Fermi energy ($E_F=0$ eV) and 7 eV binding energy. Besides the dominant peak at about 3.5 eV, peak features at about 5 and 6.5 eV can also be observed. Since these peaks were observed also for $Ba_{1-x}K_xBiO_3$,[26] they should be considered to be intrinsic features of the $Ba_{1-x}M_xBiO_3$ system.

Although the intensity of each spectrum at the Fermi energy was remarkably weak, as shown in Fig. 5, careful measurements in this region showed that the intensity of the spectrum changed systematically as a function of *x*. For $x=0$ and 0.1, the spectra almost overlapped each other with no clear edge and very low intensity at the Fermi energy. This indicates the nonmetallic character of the materials. For $x=0.2$, somewhat greater intensity compared with that of $x=0$ and 0.1 at and below the Fermi level could be observed. This reflects that the $x=0.2$ composition is semiconducting with larger conductivity than that of the $x=0$ and 0.1 compositions. For the $x=0.3$ and 0.4 superconducting samples, the spectra are almost identical with greater intensity at the Fermi level than that of $x=0$, 0.1, and 0.2 together with a structure at about 0.2 eV below the Fermi energy.

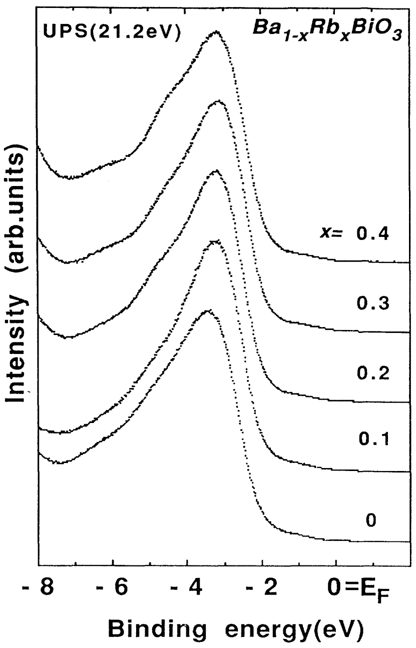

FIG. 4. Valence-band UPS spectra from $Ba_{1-x}Rb_xBiO_3$ with different *x*'s.

In Fig. 6, the resistivity curves of the samples used in this study are shown. This resistivity result indicates that the $x=0.1$ and 0.2 samples are semiconducting with the resistivity of the $x=0.2$ sample lower than that of the $x=0.1$ sample for about 3 orders of magnitude. For $x=0.3$ and 0.4, the samples are metallic with almost the same resistivity and become superconducting at the same temperature, about 29 K.

It is clear that the UPS results described above agreed completely well with the resistivity measurements. It is plausible to conclude that the systematic change of the density of states at the Fermi energy observed in the UPS spectra corresponds to the transport properties and is responsible for the metallic behavior and superconductivity of the system for the superconducting composition.

In Fig. 7, comparison of the valence band of the $x=0$ and 0.4 $Ba_{1-x}Rb_xBiO_3$ samples is shown. It is clear that

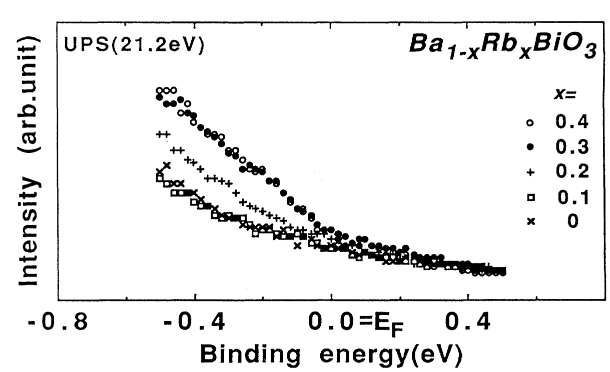

FIG. 5. Enlargement of the UPS spectra of Fig. 4 in the Fermi-level region. The systematic change of the spectrum with composition *x* and finite density of states for superconducting compositions ($x=0.3$ and 0.4) can be observed.

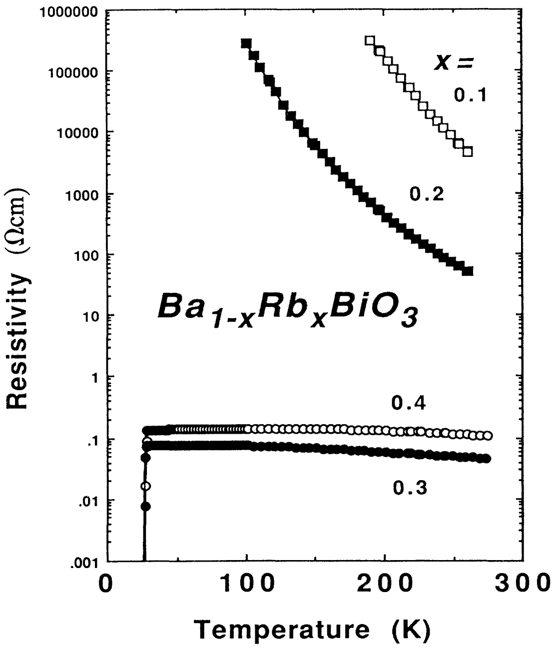

FIG. 6. Resistivity data for the $Ba_{1-x}Rb_xBiO_3$ samples used in this study.

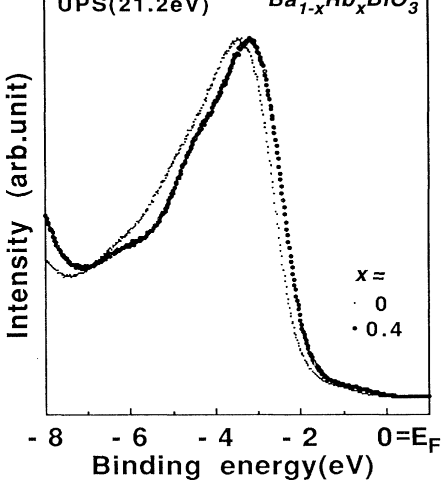

FIG. 7. Comparison of the valence band of the $x=0$ and 0.4 $Ba_{1-x}Rb_xBiO_3$ samples, the valence band of the $x=0.4$ lower binding energy with respect to that of the $x=0$ nonsuperconducting sample.

the valence band of the $x=0.4$ superconducting composition shifted toward lower binding energy for about 0.3 eV compared with that of the $x=0$ nonsuperconducting composition, while the overall feature of the valence band was essentially unchanged (except in the vicinity of the Fermi level as described above). The same shift of the valence band compared with that of the $x=0$ sample was also observed for the $x=0.3$ sample. This shift was also observed in the UPS spectra excited by He II (40.8 eV radiation). It is concluded that the valence band of the superconducting $Ba_{1-x}Rb_xBiO_3$ shifts toward lower binding energy compared with that of $BaBiO_3$.

Hegde *et al.* have also reported the observation of the Fermi edge and a similar shift of the valence band of superconducting $Ba_{0.6}K_{0.4}BiO_3$.[15] Though we agree with their conclusion, however, the results obtained by those authors were poor in both signal-to-noise ratio and energy resolution since they were recorded by XPS and thus should be interpreted carefully.

For the $BaPb_{1-x}Bi_xO_3$ system, recently, the observation of a clear Fermi edge for superconducting $BaPb_{0.75}Bi_{0.25}O_3$ was reported by Lin *et al.* [27] Matsuyama *et al.* have also reported on the observation of a Fermi edge together with a rigid shift of the valence band toward lower binding energy by 0.3–0.4 eV of superconducting $BaPb_{1-x}Bi_xO_3$ ($x=0.15$) with respect to that of $BaBiO_3$.[28]

These facts indicate the similarity of physics in the two families $Ba_{1-x}M_xBiO_3$ and $BaPb_{1-x}Bi_xO_3$, although the substitutions from the parent material are different: *A* site in the former and *B* site in the latter. Considering that substitution of Rb/K for Ba or Pb for Bi introduces hole carriers into the system and supposing the system to be understandable by a rigid-band picture, one expects the shift of the valence band toward the Fermi level upon hole-carrier doping. The results of our study and others for $Ba_{1-x}M_xBiO_3$ and $BaPb_{1-x}Bi_xO_3$ seemed to support this picture, at least qualitatively. However, since the one-electron model fails to describe the electronic structure of the parent material $BaBiO_3$, the situation is certainly not so simple as that for doping in semiconductors.

Next, we discuss the comparison of the band calculations and experimental results. From the rather small amount of the observed valence-band shift of the $BaPb_{1-x}Bi_xO_3$ system compared with the estimation from a rigid-band calculation, Matsuyama *et al.* propose a modified electronic band picture, arguing that new electronic states are created in the vicinity of the Fermi level by doping and the Fermi level is pinned in these states.[28] However, it is noted that Hamada *et al.* [12] estimated from their band calculations that for $Ba_{0.6}K_{0.4}BiO_3$ the Fermi level shifts downward by 0.43 eV compared with that of $BaBiO_3$, which is in good agreement with the experimental results obtained for $Ba_{1-x}Rb_xBiO_3$ in this study and of Hegde *et al.* [15] Very recently, Papaconstantopoulos *et al.* [13] reported on the band calculation of Ba(K)Pb(Bi)O_3 and argued that upon substitution either for the Ba or Bi sites, the position of the Fermi level moves qualitatively according to the rigid-band approximation. However, the widening of the oxygen-dominated bandwidth is also associated; i.e., the rigid-band model does not hold rigorously upon doping. At present it seems that further electronic calculation studies are needed to explain the existed experimental results.

To summarize, although it is still unclear whether $Ba_{1-x}M_xBiO_3$ and $BaPb_{1-x}Bi_xO_3$ systems can be well described by a one-electron band picture or not, experimentally it is clear that (i) the valence band of the superconducting composition shifts toward the Fermi level, and (ii) although a clear Fermi edge was not observed for the superconducting composition in this study due maybe to the samples used being polycrystalline, a finite density of states at the Fermi energy reflecting the existence of the Fermi edge was observed. The magnitude of the density of states at the Fermi energy changes systematically as a function of x, corresponding with the transport properties of the samples and indicating that the transition from nonmetal to metal in this system occurs through a continuous change of the electronic states.

It is interesting to compare the results of this system with those of the cuprate superconductors. It is now well established that a clear Fermi edge exists in cuprate superconductors. However, no common consensus on the change in shape and the binding energy of the valence band as a result of carrier doping exists at present. Most of the results reported no significant difference between the overall feature of the valence band of superconducting and nonsuperconducting compositions. However, recently, we have reported on the observation of a systematic change of the density of states at the Fermi energy and also a shift of the valence band toward lower binding energy when the system undergoes a nonmetal-to-metal transition in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ system similar to the $Ba_{1-x}M_xBiO_3$ system.[29] These characteristics of the cuprate superconductors were not pointed out before and might be important for the elucidation of the mechanism of high-T_c superconductivity in both cuprate and noncuprate oxide superconductors. Confirmation of the results and more studies are required to gain plausible conclusions.

IV. CONCLUSION

A photoelectron spectroscopic study to investigate the electronic structure of a noncuprate oxide superconductor $Ba_{1-x}Rb_xBiO_3$ system was reported for the first time. Comparison of the results with those reported for $Ba_{1-x}K_xBiO_3$ and $BaPb_{1-x}Bi_xO_3$ was discussed. It was concluded that the chemical environment of substituted Rb in this system is similar to that of Rb metal, core-level binding energies of Bi and Ba were unaffected by Rb substitution, and a shift of the valence band toward lower binding energy upon hole-carrier doping was observed. A characteristic change of the density of states in the vicinity of the Fermi level with composition x was observed, suggesting that the nonmetal-to-metal transition occurs through a continuous change of the electronic states of the system.

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