BaBiO$_3$ and the effect of potassium substitution using photoemission

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The electronic structure and surface stability of BaBiO$_3$ and Ba$_{0.6}$K$_{0.4}$BiO$_3$ are studied using photoemission. For BaBiO$_3$ and Ba$_{0.6}$K$_{0.4}$BiO$_3$, bonding and nonbonding valence-band features show good agreement with theoretical calculations reported by Takegahara and Kasuya, and Matthiess and Hamman, and Hamada et al. However, the magnitude of Bi 6$s$ and O 2$p$ antibonding states near the Fermi level are less than expected, and the Ba 5$p$ core levels are at a higher energy than reported by Wertheim et al. The Bi 5$d$ core levels show a single component for Ba$_{0.6}$K$_{0.4}$BiO$_3$ but show two components for BaBiO$_3$, and the large shift ($\sim$1.6 eV) of the second component to lower binding energy suggests the possible reduction of surface Bi to the metallic state. Examination of extended x-ray-absorption fine-structure data by Heald et al., obtained from these materials, shows that a weaker Bi$-$O bond exists in BaBiO$_3$ than in Ba$_{0.6}$K$_{0.4}$BiO$_3$, and this may explain why such bonds are easily broken in BaBiO$_3$.

I. INTRODUCTION

BaBiO$_3$-based lead and potassium superconductors show that high-temperature superconductivity can occur in non-copper-containing oxides and therefore pose important questions for this interesting field.$^{1,2}$ Pure BaBiO$_3$ exhibits a monoclinic distortion of the perovskite structure in which the oxygen octahedra around successive Bi sites rotate and undergo an 8% expansion of the Bi$-$O bond length.$^{3-6}$ Originally attributed to Bi charge ordering (between Bi$^{11+}$ and Bi$^{11+}$), this distortion can also be viewed in terms of a charge-density wave (CDW) on the oxygen site.$^{7,8}$ Ba$_{1-x}$Pb$_x$Bi$_2$O$_3$ can in some sense be called the first high-$T_c$ superconducting oxide because lead substitution enhances $T_c$ (near 13 K) in the composition range 0.05 $\leq$ x $\leq$ 0.3.$^9$ More recently, the discovery of the highest $T_c$ (29 K) in Ba$_{0.6}$K$_{0.4}$BiO$_3$, a non-Cu-containing material, suggests that the high-$T_c$ mechanism may not explicitly rely on the Cu 3$d$ orbitals.$^{1,2}$

In this paper, ceramic BaBiO$_3$ and Ba$_{0.6}$K$_{0.4}$BiO$_3$ are examined using photoemission. We compare our results with several recently published calculations and data published earlier for BaBiO$_3$.$^{10-12}$ Good agreement was found between some aspects of theory and experiment. However Ba core-level binding energies, a dearth of states near $E_F$, and line splittings in the Bi 5$d$ core levels suggest surface disruption or oxygen loss upon scrapping. BaBiO$_3$ was found to be more susceptible to surface modification or oxygen loss upon scrapping than Ba$_{0.6}$K$_{0.4}$BiO$_3$. Material from the same batch of samples was provided to Heald et al.$^{13}$ for extended x-ray-absorption fine-structure spectroscopy, and their study of the Debye-Waller factor indicates that BaBiO$_3$ has a weak Bi$-$O bond. We believe this explains why BaBiO$_3$ tends to lose surface oxygen more easily than Ba$_{0.6}$K$_{0.4}$BiO$_3$.

II. EXPERIMENTAL

The samples were prepared from a stoichiometric mixture of potassium, barium, and bismuth nitrates, calcined at 480$^\circ$C in air. The mixture was thoroughly ground, heated for 3 h at 780$^\circ$C in helium (which presumably contains less oxygen than argon), the cooled slowly over 1 h to 480$^\circ$C. The samples were held at 480$^\circ$C for 3 h under 1 atm oxygen pressure, and finally slowly cooled to room temperature. X-ray diffraction showed that the samples single phase.$^{14}$ Magnetic susceptibility measurements indicate that the Ba$_{0.6}$K$_{0.4}$BiO$_3$ sample is superconducting with a $T_c$ of $\sim$29 K.$^{14}$ The samples used in this study were cold pressed into a pellet.

Angle-integrated photoemission measurements were carried out at the National Synchrotron Light Source (NSLS) U14 beam line, using a plane grating grazing monochromator (PGM). Valence-band and core-level studies were conducted in the photon energy range 14 to 135 eV. The kinetic energy of photoelectrons was analyzed by a double-pass cylindrical mirror analyzer (CMA). The base pressure during the experiment was $6 \times 10^{-10}$ Torr and samples were introduced into the spectrometer from a preparation chamber equipped with a load lock. The sample normal was 42$^\circ$ from the CMA axis and the photon beam was incident at an angle of 47$^\circ$ from the sample normal. The CMA pass energy was set
at 15 eV during the valence-band and core-level measurements and at 25 eV during the constant-initial-state (CIS) and the constant-final-state (CFS) measurements. The samples were mounted on Al blocks with ultrahigh-vacuum-compatible conducting epoxy and sample surfaces were prepared by scraping at room temperature with a stainless steel rasping tool.

III. RESULTS AND DISCUSSION

A. The valence band of BaBiO$_3$

We begin our discussion with a comparison of our photoemission result for BaBiO$_3$ to a theoretical band-structure calculation. In Fig. 1, we show the theoretical density of states (DOS) calculated by Takeghara and Kasuya$^{11}$ for BaBiO$_3$ along with our photoemission energy-distribution curve (EDC) at $h\nu=80$ eV. The overall correspondence between theory and experiment is quite good. Similar conclusions were also drawn from comparison of our data with that calculated by Hamada et al.$^{15}$ for an EDC taken at 70-eV photon energy. The dominant feature (centered at $-4$ eV) in the calculated DOS is due to nonbonding O-p orbitals. Our photoemission results for these O-p orbitals agree well with the theory in terms of the bandwidth, center energy, and general distribution of states. The flanking lower DOS features in the calculated results are bonding (at $-10$ eV) and antibonding (at $-5$ eV) Bi-s/O-p states. We can identify the Bi-O bonding band, and its binding energy is again in good agreement with the calculation of Takeghara and Kasuya.$^{11}$ The antibonding states of Fermi level ($E_F$), on the other hand, are missing in our photoemission spectrum. Failure to observe a significant DOS near $E_F$ would have serious implications for proposed high-$T_c$ models in this oxide because $T_c$ depends on the density of states at $E_F$ in the Bardeen-Cooper-Schrieffer (BCS) theory.$^{16}$ However, studies on other high-$T_c$ oxides like YBa$_2$Cu$_3$O$_{7-x}$ and La$_{0.85}$Sr$_{0.15}$CuO$_4-x$ show that oxygen removal reduces $T_c$. Observation of a sharp Fermi level is difficult, in part, because the surfaces in those materials lose oxygen in a vacuum at room temperature.$^{17-20}$ For the case of the 1:2:3 material, List et al.$^{21}$ show that the absence of DOS features at $E_F$ is due to surface oxygen loss. This problem can be mitigated by conducting photoemission observations at cryogenic temperatures. In the Bi-Sr-Ca-Cu-O superconductors that are less susceptible to O loss because there are few oxygen vacancies, the Fermi-level features are readily observed.$^{22-24}$ Thus, we attribute the lack of Fermi-level states in our spectra to surface oxygen loss.

B. The Ba 5p core levels, Ba 4d-5p giant resonance, and O 2p valence-band resonance

The sharp spike in the theory DOS (near $-12$ eV) is the Ba 5p core level. In our EDC’s this core level is found at a substantially higher-binding energy (near $-14$ eV); however, this is not unexpected since the theory would not be expected to reproduce the binding energy of such core levels. However, x-ray photoemission spectroscopy (XPS) data published by Wertheim et al.$^{12}$ shows that these core levels should be near $-13$-eV binding energy. Electron spectroscopy for chemical analysis (ESCA) results obtained by Hegde et al.$^{14}$ for our materials show a component near $-13$ eV in addition to the higher binding energy component that dominates the surface sensitive EDC’s obtained for this study. In copper containing high-$T_c$ oxides that contain Ba, photoemission studies show that the Ba 5p and 4d core levels move to higher binding energy where oxygen is removed from the surface.$^{21}$ The unambiguous assignment of the Ba-5p orbital features is greatly facilitated by resonant enhancement in the narrow range of photon energies close to the “giant” Ba 4d $\rightarrow$ 4f resonance.$^{25}$ The 94-eV spectrum shown in Fig. 2(a) precedes the Fano resonance whereas the 105-eV spectrum is nearly on resonance. The Fano-like line shape photoemission cross section near this resonance is illustrated in Fig. 2(b) with CIS spectrum collected with $E_k=3$ eV. The 4d absorption edge is clearly apparent in this CIS spectrum as is the shape preedge multiplet feature (near $h\nu=95$ eV). The multiplet structure is due to splitting of the $^3D_1$ state of the exchange coupled $4d^94f^1$ photoinduced final state.$^{26,27}$ A similar lower energy, $^3P_1$ multiplet feature is not visible above the noise level in our data. Also shown in Fig. 2(b) is a CIS photoyield spectrum with the initial-state energy set at the center of the Ba 5p features (i.e., $E_0=-15$ eV). The CIS spectrum illustrates the strong Ba-5p Fano enhancement and interestingly also shows a sharp pre-4d threshold feature associated with the $^3D_1$ multiplet feature seen in the CIS spectrum.

Although the 4d to 4f resonance at the 4d threshold dominates both the 5p-CIS and the CIS spectra in Fig. 2(b), their disparity in line shape and peak energy are worth noting. The peaking of the 5p partial cross section below the resonance energy and the large negative Fano shape parameter (q) used to fit the 5p cross section have been discussed both theoretically and experimentally in the past.$^{25,28}$ These effects have been attributed to a combination of two effects: (1) the field driving the 5p photo-
emission being a superposition of the external and resonantly oscillating 4d shell dipole field; and (2) the external and 4d dipole fields superimposing constructively (hence maximizing the driving field for 5p photoemission) below resonance but cross over to a destructive superposition above resonance.

O-related features in the photoemission spectrum show resonant cross-section enhancement near the O-2s threshold. In Fig. 3 we show the photoabsorption spectrum for BaBiO$_3$ near the O-2s absorption edge. Also shown in Fig. 3 is the CIS spectrum with $E_b = -4$ eV (at the maximum of the O-2p valence-band states). The similarity of this enhancement process to that just exploited for the Ba-5p orbital should be noted. Discussion of the comparative valence-band features of the pure and K substituted compound will be deferred to later in this paper.

![Image](image_url)

**FIG. 2.** A comparison of an EDC taken at the pre-Ba-4d resonance energy of 94 eV to an EDC collected at 105 eV (near the resonance energy). Note the large resonant enhancement of the Ba-5p orbitals indicated by an arrow. (b) A CFS curve for BaBiO$_3$ in the validity of the giant Ba 5d $\rightarrow$ 4f Fano-like resonance. Note that this CFS spectrum represents the net photoabsorption coefficient for the material. The CIS spectrum reflects the resonant behavior of the photoemission cross section of the states located at a binding energy of 15 eV, (i.e., the Ba-5p core levels). The sharp preresonance $^3D_1$ multiplet features in both spectra should also be noted.

![Image](image_url)

**FIG. 3.** CFS and CIS ($E_b = -4$ eV) spectra for BaBiO$_3$ in the vicinity of the O-2s threshold. The binding energy of the CIS spectrum was chosen so as to lie in the O-2p valence-band states. The O-2s threshold is clearly visible in both of these photo-cross-section measurements.

**C. Bi-5d core levels and Bi–O bond instability**

The core levels with the greatest oscillator strength in the vacuum ultraviolet range for these materials are the Bi-5d states.$^{29}$ Accordingly these levels offer the best opportunity for studying the differing Bi sites in these materials. Structural and chemical studies indicate that BaBiO$_3$ contains bismuth in different oxidation states.$^{5,30}$ Thus, photoemission core level spectra should be complex and show two or more chemically shifted components. However, unambiguous identification of Bi 5d core-level features with specific Bi oxidation states is complicated by evidence of surface modification or oxygen loss, which was detected in conjunction with the Ba core level components.

In Fig. 4, we compare the Bi-5d levels at $h\nu = 80$ eV for Ba$_{1-x}$K$_x$BiO$_3$, $x = 0.0$ and $x = 0.4$ in this series. The BaBiO$_3$ 5d core-level spectrum (middle spectrum) in Fig. 4

![Image](image_url)

**FIG. 4.** The Bi-5d$_{3/2}$ and 5d$_{1/2}$ core-level spectra for Ba$_{1-x}$K$_x$BiO$_3$, $x = 0.4$, $x = 0.0$ prepared under moderate scraping conditions and $x = 0.0$ prepared under vigorous scraping conditions.
was taken on a surface we will identify as being moderately scraped (MS). The peak positions of the most intense Bi-5d level are seen to be (see Fig. 4) essentially unchanged between \( x = 0.0 \) and \( x = 0.4 \). We wish to note, however, that a small second Bi 5d component is evidence in the MS-BaBiO\(_3\) spectrum in two ways: an unresolved shoulder is present on the low binding energy side of the lower 5d (5d\(_{5/2}\)) feature; and the depth of the minimum between the doublet is reduced (relative to the K substituted material) indicating a similar low binding energy shoulder for the 5d\(_{3/2}\) feature also.

The presence of Bi sites with low 5d binding energy is underscored when a vigorously scraped (VS) BaBiO\(_3\) surface is studied (see Fig. 4, top spectrum). For the VS surface the Bi-5d core levels show a clearly resolved low binding energy component. The 1.6-eV shift of this low binding energy component, relative to the oxide, suggest that Bi in these sites interacts weakly with O. We wish to emphasize at this juncture that the K-substituted sample showed only one Bi site after vigorous scraping. Our Bi 5d result for BaBiO\(_3\), like that for the Ba core levels, indicates that surface preparation has a strong effect on the chemical state of the surface and that conclusions about the oxidation state of Bi should be examined critically using complimentary data. Before discussing the meaning of these differing Bi-core-level components further, we will review some recently obtained extended x-ray-absorption fine-structure spectroscopy (EXAFS) results, which may be of relevance to this question.

Heald and co-workers\(^{13}\) carried out careful temperature dependent EXAFS studies of the Bi sites in Ba\(_{1-x}\)K\(_x\)BiO\(_3\) for \( x = 0.0 \) and 0.4 using the same material studied by photoemission. Besides yielding structural information, this study provides site specific lattice dynamical information, which is useful in developing an interpretation of our photoemission results. As expected this EXAFS study yielded two Bi sites for BaBiO\(_3\) one site [Bi(1)] with a short Bi—O bond length of 2.13 Å and another site [Bi(2)] with a long Bi—O bond length of 2.28 Å. For Ba\(_{0.6}\)K\(_{0.4}\)BiO\(_3\) a single Bi—O bond length of 2.15 Å (close to the shorter value in the pure compound) was observed. Both thermal vibrations and static disorder introduce a Debye-Waller dampening of the EXAFS amplitudes. The temperature dependence of the mean square deviation of the bond length between the absorbing atom (Bi) and its neighbors (\( \sigma^2 = \sigma_{vb}^2 + \sigma_{stat}^2 \)) for the Bi sites in BaBiO\(_3\) and Ba\(_{0.6}\)K\(_{0.4}\)BiO\(_3\) is reproduced from Heald et al.\(^{13}\) and shown in Fig. 5. Also included in the figure are Einstein model fits to the data. The central point to note here is that the long Bi—O bond has a substantially larger thermal amplitude of vibration than does the shorter Bi—O bond in BaBiO\(_3\). The Bi—O bond in the K-substituted material has a still smaller \( \sigma^2 \) thermal variation. Thus, the long Bi—O bond is quite soft (or weaker) (\( \Theta_E = 388 \text{ K} \)) relative to the short Bi—O bond (\( \Theta_E = 489 \text{ K} \)) in BaBiO\(_3\), and the Bi—O bond in Ba\(_{0.6}\)K\(_{0.4}\)BiO\(_3\) is somewhat harder still (\( \Theta_E = 528 \text{ K} \)). In our discussion in the following, we will relate this observation to the relative ability of Bi surface sites in retaining surface O atoms.

Oxygen desorption and bond breaking at surfaces of high-\( T_c \) oxides has been a recurrent theme in the photoemission spectroscopy of these materials.\(^{17,18,22,31,32}\) The EXAFS results reviewed show the relative softness of the long Bi—O bond [around the Bi(2) sites] in the BaBiO\(_3\). The scraping technique often used in preparing pressed sintered oxide powder pellets for photoemission measurements probably causes the local surface temperature to rise. The scraping process typically induces a transient rise in chamber vacuum pressure due to the desorption of gases. The soft Bi—O bonds about the Bi(2) sites are more vulnerable to the thermomechanical stresses of the scraping process than are the harder Bi—O bonds about the Bi(1) sites. Specifically, we speculate that the sites with low Bi 5d binding energy (noted earlier) are surface Bi(2) sites that have been stripped of oxygen. The more vigorous the scraping process the larger the thermal transients and the larger the fraction of such oxygen-poor Bi(2) surface sites. This is consistent with the increase of such sites between the moderately and vigorous scraped BaBiO\(_3\) surfaces. Since the Bi—O bonds in Ba\(_{0.6}\)K\(_{0.4}\)BiO\(_3\) are all of short and hard type [like the Bi(1) in BaBiO\(_3\)] the apparent immunity of the substituted component to the creation of such low Bi 5d binding energy sites is understandable.

D. Comparison of photoemission results for Ba\(_{0.6}\)K\(_{0.4}\)BiO\(_3\) and BaBiO\(_3\)

In Fig. 6, spectra for Ba\(_{0.6}\)K\(_{0.4}\)BiO\(_3\) and BaBiO\(_3\) are compared, and the effect of scraping is seen to have a impact on the data and conclusions that may be drawn from it. The shallow core levels for O(2s), Ba(5p), and K(3p) are clearly seen and identified. The appearance of the K 3p and the weakening of the Ba 5p core levels in the K-substituted material is clear by comparison with the pure material. The O 2s levels near -21-eV binding energy are common to both compounds. K substitution
causes the O 2p derived valence-band state to shift slightly towards the Fermi level and changes are seen in the Bi-O bonding states (i.e., a small peak near −9 eV is observed in the K containing sample). A rigid shift of the valence band toward the Fermi level upon K substitution is expected since K contributes fewer electrons to the valence band than barium. Hamada et al.\textsuperscript{15} find that the Fermi level shifts downwards by 0.43 eV. Their calculations also show that potassium addition reduces the density of states near the Fermi level because BaBiO\textsubscript{3} shows a saddle-point singularity at the X point, which causes a peak at $E_F$. (Note that our results do indicate a shift of valence-band intensity toward the Fermi level vicinity in the immediate vicinity of the Fermi level.)

We also compare the photoemission spectrum of a moderately scraped BaBiO\textsubscript{3} (MS BaBiO\textsubscript{3}) to that of a vigorously scraped sample (VS BaBiO\textsubscript{3}). Relative to MS BaBiO\textsubscript{3}, VS BaBiO\textsubscript{3} exhibits several valence-band modifications. It has a higher density of states in the region within 2 eV of $E_F$; the center and peak of the valence band are shifted to higher binding energy and the valence band is broader. The dearth of bonding O neighbors at the Bi(2) sites should result in nonbonding Bi states close to $E_F$. This could be responsible for the excess states within 2 eV of $E_F$ for the VS-BaBiO\textsubscript{3} surface. Our results for MS-BaBiO\textsubscript{3} and the changes upon going to Ba$_{0.4}$K$_{0.4}$BiO\textsubscript{3} are in good agreement with the calculation of Hamada et al.\textsuperscript{15} However, since more vigorous working of the surface does induce modifications, this effect should be taken into account before the result shown in Fig. 6 is accepted as a true representation of the differences between BaBiO\textsubscript{3} and Ba$_{0.4}$K$_{0.4}$BiO\textsubscript{3}.

IV. CONCLUSIONS

Angle-integrated photoemission spectra of BaBiO\textsubscript{3} and Ba$_{0.6}$K$_{0.4}$BiO\textsubscript{3} have been measured using synchrotron radiation photon energy range from 14 to 135 eV at room temperature. CFS spectra taken through the O-2s and Ba 4d thresholds show resonant enhancements at 21 and 105 eV. CIS spectra show that this resonant enhancement is connected with interference between direct emission from O 2p or Ba 5p and the decay of core excited O 2s or Ba 4p states, respectively. Agreement between the photoemission spectra for BaBiO\textsubscript{3} and calculations of several groups is relatively good.\textsuperscript{10,11,15} Emission near $E_F$ is smaller than expected from calculations, and a shift of Ba core levels to higher binding energy suggests the surface may be oxygen deficient. Oxygen loss induces the similar modifications of photoemission spectra in other high-$T_c$ oxides. This surface instability leads to a splitting of the Bi 5d core levels which correlates with scraping. A pressure increase during scraping strengthens the belief that oxygen is lost during surface preparation. We find that BaBiO\textsubscript{3} is less stable than Ba$_{0.6}$K$_{0.4}$BiO\textsubscript{3} because the same shift of the Bi 5d core level is not observed for the K-substituted material. We believe this instability is due to the fact that Bi has two sites in BaBiO\textsubscript{3} [Bi(1) and Bi(2)] and that the Bi—O bond is weaker at one of the sites Bi(2) when compared to the other site Bi(1) or Bi—O in Ba$_{0.6}$K$_{0.4}$BiO\textsubscript{3}. Apart from the instability detected for BaBiO\textsubscript{3} surface, reasonable agreement between theory and experiment is found when potassium is substituted for Ba in BaBiO\textsubscript{3}. In light of experience with the cuprate high-$T_c$ materials, experiments employing peeled crystals or conducted at cryogenic temperature are an obvious and necessary extension of this work.

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