### VOLUME 26, NUMBER 4

# Electronic structure of $BaPb_{1-x}Bi_xO_3$

## G. K. Wertheim, J. P. Remeika, and D. N. E. Buchanan Bell Laboratories, Murray Hill, New Jersey 07974 (Received 2 April 1982)

Vacuum-prepared surfaces of  $BaPb_{1-x}Bi_xO_3$  with x = 0, 0.25, and 1 were studied by xray photoelectron spectroscopy to elucidate the electronic structure and the valence states of bismuth in these compounds. Valence-band spectra give evidence for a shallow band in BaBiO<sub>3</sub>, which is depopulated as Pb is substituted for Bi. The lack of asymmetry of the Ba core-electron lines indicates that there is no Ba 5d or 6s character at  $E_F$ . The asymmetry of the O 1s line, especially in BaPbO<sub>3</sub>, indicates that this shallow band has largely O 2p character. The Bi 4f lines of BaBiO<sub>3</sub> were significantly broadened, but could not be unambiguously resolved into the two components expected on the basis of the crystal structure.

#### I. INTRODUCTION

The valence of Bi in BaBiO<sub>3</sub> has long been a subject of speculation. With few exceptions,<sup>1</sup> stud $ies^{2-4}$  have led to the conclusion that the formal valence of Bi(IV) implied by the composition is less likely than are equal amounts of Bi(III) and Bi(V). This conclusion has found support in recent crystallographic work<sup>5,6</sup> which has identified two inequivalent Bi sites in BaBiO<sub>3</sub>. It is worth noting, however, that the Bi - O bond lengths of the two sites do not differ by an amount commensurate with expectations based on a two-electron charge difference. In an early electron spectroscopy for chemical analysis study,<sup>4</sup> the Bi 4f lines were found to be broadened but unsplit, a result which was taken as indicative of mixed-valence behavior. Motivated in part by the discovery of superconductivity in the system<sup>7</sup>  $BaPb_{1-x}Bi_xO_3$ , we have undertaken a more detailed investigation of the electronic structure of these materials.

### **II. EXPERIMENTAL**

Samples consisted of a few large crystals of these compounds with x = 0, 0.25, and 1. (Details of the crystal-growth procedure will be published elsewhere.) The samples were mounted with conducting epoxy cement in sample holders so that the shiny top surface of the solidified melt was exposed. The holders were introduced into the preparation chamber of a HP 5950A spectrometer, which was evacuated until a pressure in the  $10^{-7}$ Pa range had been attained. The original sample surface was then removed with a diamond file. The progress of this cleaning procedure was followed by recording Ba, Bi, C, and O core-electron spectra. Filing was continued until carbon contamination could no longer be detected by x-ray photoemission spectroscopy. The vacuum in the preparation chamber gave no evidence of the evolution of oxygen from the sample during this procedure, indicating that these materials are stable in vacuum at room temperature.

The O 1s line showed profound changes in shape, sharpening, and moving to smaller binding energy during the cleaning pocedure. The O-Ba and O-Bi ratios decreased significantly as the top layer was removed, but the Ba-Bi ratio did not change appreciably, indicating that the air-exposed surface was partially hydrated. The Ba and Bi core-electron lines also narrowed and moved to smaller binding energy as the surface layer was removed.

The data were analyzed by a least-squares procedure in which lines with the Doniach-Sunjic shape<sup>8</sup> convolved with the well-established resolution function, and a calculated background are fitted to the data. The background was taken to be proportional to the integral of the fitted curve.

#### **III. RESULTS AND DISCUSSION**

#### A. Valence-band spectra

For insight into the electronic structure of these compounds the valence-band spectra are, of course, of major interest (see Fig. 1). The prominent structure near 14 eV is the essentially corelike Ba 5p spin-orbit doublet. It overlaps the feature between 8 and 12 eV which arises dominantly from

26

2120



FIG. 1. Valence-band spectrum of BaBiO<sub>3</sub>, BaPb<sub>1-x</sub>Bi<sub>x</sub>O<sub>3</sub> with x = 0.25, and BaPbO<sub>3</sub>. Bindingenergy scale is appropriate for BaBiO<sub>3</sub>, the other spectra are shown with the Ba 5*p* states aligned.

Bi or Pb 6s states. These states fall at approximately the same energy as they do in the elements, but are hybridized with the O2p states, and constitute part of the valence band. The broad structure between the Fermi level and 8 eV is the largely O2p derived part of the valence band.

In an attempt to define the nature of the states responsible for the superconductivity of  $BaPb_{1-x}Bi_{x}O_{3}$  we compare the valence-band spectrum of this compound with x = 0.25 with those of BaBiO<sub>3</sub> and BaPbO<sub>3</sub> (see Fig. 1). The bindingenergy scale in this figure is appropriate for Ba- $BiO_3$ . The data for the other compounds were placed so as to align the Ba 5d lines. The Fermi level of BaBiO<sub>3</sub> was assumed to fall at the top of the occupied valence band because the compound is known to be a small-gap semiconductor. That of BaPbO<sub>3</sub> can be similarly placed at the cutoff of the strong valence-band feature. The Fermi level of  $BaPb_{1-x}Bi_xO_3$  is more difficult to assign because the valence band has a low density-of-states tail, but it clearly lies higher than in BaPbO<sub>3</sub>.

The most significant differences between the three spectra are found near  $E_F$ . The spectrum of BaBiO<sub>3</sub> clearly shows an occupied band in the interval between the Fermi level and 2 eV, which is

largely or entirely empty in  $BaPb_{1-x}Bi_xO_3$  and  $BaPbO_3$ . This band could, in principle, be made up of Ba 5d 6s, O 2p, or Bi 6sp states. From the calculations of Scofield<sup>9</sup> we know that the photoelectric cross section of the 6s states of Ba is comparable to that of O 2p, while that of the 5d states is estimated to be somewhat larger, based on the values quoted for La and Gd. The cross sections of the Bi 6s and 6p states are both 4.4 times larger than that of O 2p, so that any of these states could, in principle, be responsible for the observed shoulder. Further information concerning the states near  $E_F$  is obtained from the core-electron spectra.

#### B. Core-electron spectra

A fit to the Ba4d lines in BaBiO<sub>3</sub> is shown in Fig. 2. The model function is clearly capable of representing the data in detail, without significant misfit. The most important numerical result is that the singularity index is essentially zero (see Table I). This indicates that there are no electronic excitations at  $E_F$  when an electron is emitted from a Ba atom, i.e., the compound behaves like an insulator. This provides direct proof that there are no Ba states at the Fermi energy of BaBiO<sub>3</sub>. The Ba 4d spectrum of BaPbO<sub>3</sub>, although significantly broader, leads to the same conclusion.



FIG. 2. Least-squares fit to the x-ray photoemission spectrum of the Ba 4d core electrons in BaBiO<sub>3</sub>. Two spin-orbit components as well as the calculated back-ground are shown.

Core level	$E_B^{a}$	so <sup>b</sup>	$\Gamma^{c}$	$\alpha^{d}$
Ba 4d		2.59	~0.2	0.004
Bi $4f^{e}$ O 1s	157.8 528.5	5.31	$\sim 0.2$ $\sim 0.1$	0.10

TABLE I. Properties of some core electrons in BaBiO<sub>3</sub>.

<sup>a</sup>Core-electron binding energy of the l+s state measured from the top of the occupied valence band.

<sup>b</sup>Spin-orbit splitting.

<sup>c</sup>Lifetime width.

<sup>d</sup>Singularity index.

<sup>e</sup>Average values from a two-site analysis.

An attempt to use the same model function to fit the Bi 4f lines gave a decidedly unsatisfactory result. Since it is known from crystallographic studies that there are two inequivalent Bi lattice sites, the model function was then generalized to contain two spin-orbit pairs, constrained to have the same lifetime width, spin-orbit splitting, and intensity ratio. Much better fits could now be obtained, but the intensity ratio of the two spin-orbit doublets was typically far from the value of unity expected on the basis of the crystal structure. Moreover, the magnitude of the residuals indicated that the model function was not capable of representing the data in detail. The best fits were typically obtained with a small nonzero singularity index, suggesting that there is some Bi 6s character at  $E_F$ , but the quality of the fits does not justify detailed interpretation. The magnitude of the observed broadening is, however, in line with that reported earlier.<sup>4</sup>

An interpretation of the Bi4f core-electron binding energy rests ultimately on measurements for well-characterized compounds. Measurements on powders, using contamination carbon as a reference,<sup>10</sup> show shifts relative to elemental Bi of 2.2 eV for NaBiO<sub>3</sub>, 2.3 eV for Bi<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, and 2.4 eV for Bi<sub>2</sub>O<sub>3</sub>, i.e., there appears to be a weak retrograde dependence on formal oxidation state. Larger shifts were found only for more electronegative ligands like fluoride or sulfate. A systematic dependence of core-electron binding energy on ligand electronegativity was also found in the bismuth sesquichalcogenides with shifts of 0.7, 0.8, and 1.9 eV for the telluride, selenide, and oxide, respectively.<sup>11</sup> The results of Ref. 10 certainly suggest that one should not expect to be able to define the oxidation state of Bi in oxygen coordination in terms of the core-electron binding energy. However, the realization that the Bi line shifted significantly in the present experiments when the surface layer was removed makes it clear that a calibration with vacuum-prepared surfaces is needed before an interpretation of the Bi core-electron binding energy can be attempted.

The O 1s line shown in Fig. 3 is best fitted by an asymmetric line of the type associated with electron-hole pair excitations at  $E_F$  in metals. Similar line shapes also arise in semimetals<sup>12</sup> due to the modification of the density of states by the core hole. A fit to the data of Fig. 3 yields a singularity index of 0.10 (see Table I). The asymmetry of the O 1s line is a direct indication that the oxygen core hole is screened by electron-hole pair excitations in the final-state valence band. The absence of comparable asymmetry on the Ba or Bi lines indicates that the states at  $E_F$  have dominantly O 2p character, because only an O core hole is capable of modifying the density of states so as to allow a pseudometallic screening response. A comparable asymmetry was also found in the O 1s electron spectrum of BaPbO<sub>3</sub>.

The O 1s spectrum also contained a weak subsidiary peak at  $\sim 530$  eV which grew with time in the spectrometer. Since the Ba and Bi lines remained unchanged, this secondary oxygen peak is assigned to contamination, a common observation for samples mounted with epoxy. A C 1s line also developed on the initially clean surface supporting this assignment.

The Pb 4f lines of BaPbO<sub>3</sub> could be well fitted with a vanishing singularity index, suggesting that



FIG. 3. O 1s spectrum of BaBiO<sub>3</sub>.

26

there is little Pb 6s character at  $E_F$ . Data analysis in this case was complicated by a weak component at smaller binding energy which was evident even by inspection. Least-squares analysis placed it 0.85 eV toward smaller binding energy. It is tentatively identified as divalent Pb in Ba sites. It seems likely that this substitution is responsible for the broadening of both the Ba and O core levels in this compound.

In  $BaPb_{1-x}Bi_xO_3$ , all core-electron states were found to be significantly broadened, presumably by the random occupancy of the *B* site by Pb and Bi. The effect on the Pb and Bi core-electron spectra was sufficiently great so that they could not be fitted with the conventional line-shape function.

#### **IV. CONCLUSIONS**

The present experiments lead to the conclusion that the Bi atoms in the two lattice sites of BaBiO<sub>3</sub> are, electronically, only marginally distinguishable. The occupancy of a band at  $E_F$ , identified as being dominantly of O 2p character, is decreased by the substitution of Pb for Bi. In BaBiO<sub>3</sub>, this band, or a subband split off by the lattice distortion, is completely filled, resulting in a semiconductor. The small difference in binding energy for the two Bi sites in BaBiO<sub>3</sub> is then largely a reflection of the fact that this band makes only a small contribution to the charge densities at the two inequivalent sites.

#### **ACKNOWLEDGMENTS**

We are indebted to B. Batlogg and C. Methfessel for valuable discussions, to L. F. Mattheiss and D. R. Hamann for communicating the results of their band-structure calculations prior to publication, and to A. S. Cooper for x-ray identification of phases.

- <sup>1</sup>J. Th. W. de Hair and G. Blasse, Solid State Commun. <u>12</u>, 727 (1973).
- <sup>2</sup>T. Nakamura and J.-H. Choy, J. Solid State Chem. <u>20</u>, 233 (1977).
- <sup>3</sup>R. Arpe and H. Muller-Buschbaum, Z. Anorg. Allg. Chem. <u>434</u>, 73 (1977).
- <sup>4</sup>A. F. Orchard and G. Thornton, J. Chem. Soc. Dalton Trans. <u>1977</u>, 1238.
- <sup>5</sup>D. E. Cox and A. W. Sleight, Solid State Commun. <u>19</u>, 969 (1976); Acta Crystallogr. Sect. B <u>35</u>, 1 (1979).
- <sup>6</sup>G. Thornton and A. J. Jacobson, Acta Crystallogr. Sect. B <u>34</u>, 351 (1978).

- <sup>7</sup>A. W. Sleight, J. L. Gillson, and P. E. Bierstedt, Solid State Commun. <u>17</u>, 27 (1975).
- <sup>8</sup>S. Doniach and M. Sunjic, J. Phys. C <u>3</u>, 285 (1970).
- <sup>9</sup>J. H. Scofield, J. Electron Spectrosc. Relat. Phenom. <u>8</u>, 129 (1976).
- <sup>10</sup>W. E. Morgan, W. J. Stec, and J. R. Van Wazer, Inorg. Chem. <u>12</u>, 953 (1973).
- <sup>11</sup>Z. Hurych and R. L. Benbow, Phys. Rev. Lett. <u>38</u>, 1094 (1977).
- <sup>12</sup>P. M. Th. M. van Attekum and G. K. Wertheim, Phys. Rev. Lett. <u>43</u>, 1896 (1979).