# ELECTRONIC STRUCTURE OF MONOCLINIC $BaBiO_3$

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## ABSTRACT

We present the results of photoemission studies of "valence disordered" monoclinic $BaBiO_3$ in the photon energy range 15-120 eV. The line-shapes of the valence band photoemission spectra and the Ba contributions to the valence band are very similar to the line shapes of the total density of states and Ba partial density of states, respectively. Oxygen resonance is observed, demonstrating the existence of empty O 2p states. These results support a more covalent rather than a simple ionic picture for the electronic states of $BaBiO_3$.

## I. INTRODUCTION

The recently discovered superconductor $Ba_{1-x}K_xBiO_3$ is the only known compound without Cu which has a transition temperature as high as 30K[1]. This new family of superconductors results from A-site K doping of the parent $ABO_3$-type perovskite $BaBiO_3$ and is closely related to the $BaBi_{1-x}Pb_xO_3$ system, which was one of the earliest high transition temperature oxide superconductors and was produced by B-site doping with Pb[2,3,4]. The parent compound $BaBiO_3$ for both families is extremely interesting. Cubic $BaBiO_3$ has an odd number of electrons in each unit cell and is expected to be a metal. However, experimentally it is found to be a semiconductor. An explanation invoking valence disproportionation between the two Bi ions to give $Bi^{III}$ and $Bi^{V}$ has been proposed to account for this discrepancy[5]. Thus, A- or B- site doping suppresses the charge density waves to produce the metallic superconducting phases[1,4]. On the other hand, band calculations have been performed

to study the electronic structure of $BaBiO_3$ and predict only minimal valence disproportionation in the monoclinic phase[6,7]. More recently, a new monoclinic "valence disordered" $BaBiO_3$ is found, whose structure remains monoclinic but the two Bi-O distances become nearly equal. In this case, it is argued that the two Bi cations are nearly totally valence disordered with an approximate valence corresponding to $Bi^{IV}$ [8]. Therefore, an investigation to distinguish the simple ionic picture and the more covalent picture proposed by band calculations will provide some insights into the electronic state of $BaBiO_3$. In this paper, we present the results of our resonance photoemission study of the monoclinic "valence disordered" $BaBiO_3$ which is also a semiconductor. The experimental results are compared with the predictions of one electron band calculations. The line-shapes of the valence band total density of states (DOS) and the Ba partial DOS agree with the predictions of the band calculations. An oxygen resonance behavior is observed at 19 eV photon energy, which clearly demonstrates the existence of empty O 2p states (or O 2p holes) in the compound. This indicates that the average valence of the Bi cations is not necessary $Bi^{IV}$, which is required in a simple ionic picture of the compound by assuming O to be $O^{II}$. These results support the more covalent picture proposed in the band calculations.

## II. EXPERIMENTAL

Crystalline samples of "valence disordered" $BaBiO_3$ were prepared using the procedures outlined by Chaillout et al.[8]. More details of the photoemission experiments are presented in another publication[9].

## III. RESULTS AND DISCUSSION

The panel (a) of Fig. 1 presents a photoemission spectrum of the valence band and the shallow core levels of the $BaBiO_3$ compound at 70eV photon energy. The inset is a magnification of the valence band spectrum. This compound does not have a clearly defined Fermi edge, which is consistent with the semiconducting nature of the material. No emission is observed until 0.2 eV below the Fermi level, which means that the Fermi level ($E_F$) lies at least 0.2 eV above the valence band maximum. We can compare the valence band spectrum with the total density of states (DOS) from a band calculation. The comparison shows that the experiment agrees well with the theory except for a shift in energy to higher binding energy[9]. Both the experimental EDC and the calculated results show low DOS at small binding energies. As the binding energy

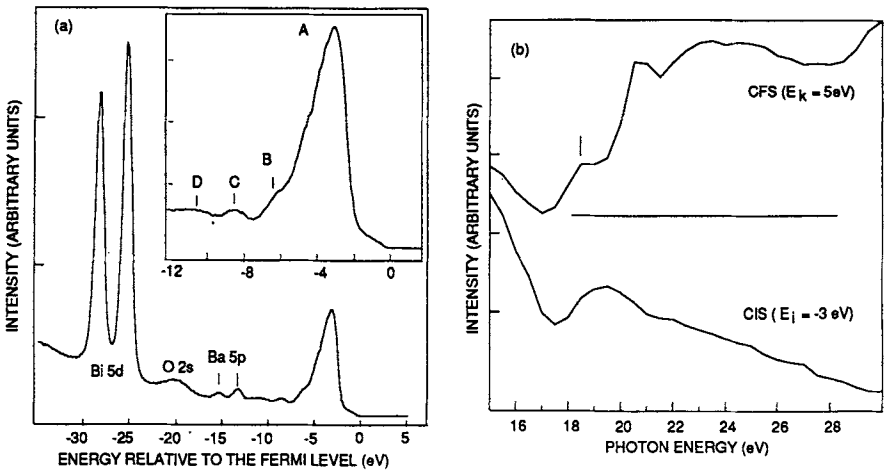


Figure 1. (a) Valence band and shallow core levels photoemission spectrum recorded at 70 eV. The insert is a magnification of the valence band spectrum. (b) CIS and CFS spectra of $BaBiO_3$ in the vicinity of the O 2s to O 2p transition threshold.

increases, the DOS quickly reaches to its maximum, and then decreases. The general line-shape of the experimental spectrum agrees with the theoretical DOS but is shifted to higher binding energy. Feature C is very weak on a fresh surface as seen in Fig.1, but slowly grows stronger as the sample ages in the vacuum. It is very similar to the -9 eV feature observed in most of the cuprate superconductors fractured at room temperature[10], and is extrinsic to the stoichiometric material. Unlike the cuprate superconductors, no high energy satellite structure was observed, which is consistent with the delocalized nature of the valence states. We also notice that the binding energies of the shallow core levels Ba 5p, O 2s and Bi 5d are shifted as compared with the results from band calculations[7].

To acquire a better understanding of the valence band features, we have also recorded Constant-Final-State (CFS) and Constant-Initial-State (CIS) spectra which are presented in the panel (b) of Fig.1. The CFS spectrum was recorded at a kinetic energy of 5 eV and thus reflects the photoabsorption signal as a function of the photon energy. As indicated by the arrow, an absorption process occurs at a photon energy near 19 eV which is most likely due to the oxygen 2s --> 2p absorptions. It should be pointed out that the oxygen 2s core level in Figure 1 is located at -20 eV. The 1 eV difference

between the absorption threshold and the O 2s binding energy is not presently fully understood[9]. Now let us look at the CIS curves which reflect the photoemission intensity of the valence band features as a function of photon energy. For $E_i$ = - 3 eV, which corresponds to feature A of the valence band, a clear intensity modulation is observed at the 19 eV threshold. We think that the most reasonable explaination about this intensity modulation is the oxygen resonance, which suggests the existence of empty oxygen 2p states.

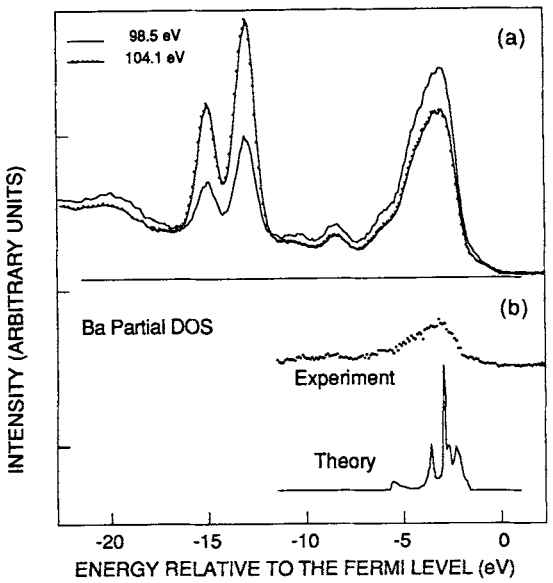


Figure 2.
(a) Photoemission spectra recorded below and above the Ba $^1P_1$ absorption threshold. (b) The Ba partial density of states in comparison with the prediction of band calculation.

Utilizing the Ba resonance photoemission process, we are able to differentiate the Ba partial density of states from the rest of the valence band. Figure 2a presents photoemission spectra of the $BaBiO_3$ compound at photon energies of 98.5 and 104.1 eV, which are the photon energies just below and above the $^1P_1$ threshold of the Ba 4d --> 4f absorption. It is clear that the Ba 5p emission is enhanced while the main valence band emission is suppressed at 104.1 eV photon energy. Figure 2b shows the difference curve of the two spectra in Figure 2a. Such a difference curve reflects the Ba partial density of states. ( Note that we have neglected the cross section change of the oxygen states at the two photon energies.) Also presented in Figure 2b is the Ba partial density of states from the band calculation[6]. The comparison shows that the experimental and the theoretical results agree well except for a ~0.5 eV shift.

The comparison between theory and experiment for both the valence band total DOS and Ba partial DOS shows that the band theory gives a good description of the electronic structure of $BaBiO_3$. As discussed elsewhere, the charge fluctuation between the two unequal Bi ions is small, in consistence with the predictions of the band calculations also[9]. The ionic picture with $Bi^{III}$ and $Bi^{V}$ at the two unequal Bi sites appears oversimplified. This success of the band calculations is not completely unexpected because of the delocalized valence states.

## IV. SUMMARY

We have performed a photoemission study on the "valence disordered" monoclinic $BaBiO_3$ compound. The valence band spectrum is consistent with the semiconducting nature of the compound. The line-shapes of the valence band total density of states and the Ba partial density of states agree with the predictions of the one-electron band calculations. Empty O 2p states (or O 2p holes) were observed by both CFS and CIS spectra. Our results support the more covalent picture proposed by the band calculaions.

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