

Electronic structure of pure and substituted BaBiO_{3-δ} single crystals

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Abstract

The evolutions of the core level lines of pure BaBiO_{3-δ} or weakly Pb-substituted barium bismuthate are analyzed as a function of surface treatments. The air contamination and the Ar⁺ ion etching generate respectively one couple of high binding energy oxygen and bismuth satellites, while the barium line is weakly affected by these treatments. A well reconstructed surface and a fractured surface are characterized by a set of single Ba-, Bi- and O-lines, which indicate the absence of any measurable O- or Bi-disproportionation at the sample surface. Nevertheless, XANES spectra clearly show a valence of the bismuth higher than +3 and the presence of empty 6s Bi-states.

1. Introduction.

The copper-free high T_c superconducting oxides (Ba,K)BiO₃ and Ba(Pb,Bi)O₃ are derived from the insulating bismuthate BaBiO_{3-δ} by substitution with potassium or with lead. At low substitution rate, the compounds are semiconducting and by increasing the rate above ≈ 0.65 (respectively ≈ 0.35), the Pb-substituted (respectively K-substituted) compounds become metallic at room temperature and superconducting at low temperature [1,2]. These compounds have different crystallographic structures, depicted as distorted perovskite structure. Moreover, the 'undoped' monoclinic BaBiO_{3-δ} exhibits two nonequivalent Bi-sites, surrounded by environment where the Bi-O distances are different. This lattice distortion, attributed to a charge density wave state, leads us to consider a bismuth disproportionation, associated with the +3 and +5 valences, instead the +4 mean valence. This lattice distortion has been also detected by EXAFS in the semiconducting or metallic Pb-substituted phases [3].

Direct measurements of the valence of Bi-, O- and Ba-atoms should be performed by XPS or XANES spectroscopies, since the core level or the absorption edge structure should be shifted depending on the valence of the atoms. Some experiments on sintered samples have been reported, leading or not to the presence of a Bi-disproportionation or of a O-disproportionation. In order to contribute to this discussion, we present a study of the electronic structures of the pure and low Pb-substituted barium bismuthate performed on single crystals by XPS and XANES. Since XPS is particularly sensitive to the surface, a special care has been taken in the definition of the surface state of the samples .

2. Experiments.

BaBiO_{3-δ} single crystals were obtained by congruent melting from a bath of bismuth and barium oxides. Twinned or untwinned single crystals were selected with

(001) and (110) natural faces and studied at a base pressure of 8 x 10⁻¹⁰ mbar by XPS in a VSW-ESCA chamber using Mg Kα radiation. The chamber was equipped with a home-made heater, a 600 eV Ar⁺ ion gun, an oxidation chamber and a 150-hemispherical analyzer used with a energy resolution of 0.8 eV. XANES experiments at the Bi_{L3} edge have been performed on the same samples by electron detection, at LURE (Orsay).

XPS spectra have been recorded from untreated (Label: un.) or treated surface of some BaBiO_{3-δ} samples. These samples were sequentially annealed at 430° C in ultra high vacuum (UHV) (Label: an.) for 2 or 4 hours, etched with Ar⁺ ions (Label: et.) for 15 or 80 min., annealed a second time in UHV and finally in 5 mbar of pure oxygen (Label: ox.) for 1 hour. The annealing following an etching generally led to a reconstructed surface (Label: rec.), characterized by low energy electron diffraction patterns. One sample was also fractured in UHV and analyzed within the following hour (Label: frac.). The Pb-substituted samples were treated by the same way until the second annealing. To avoid any decomposition , they were annealed at 350° C only. Polycrystalline metallic bismuth and sintered or melted bismuth oxide were also used as references.

3. Results and discussion.

3.1 XPS spectra.

The smoothed XPS spectra related to O_{1s}, Bi_{4f7/2} and Ba_{3d5/2} core level lines, subtracted from a background contribution are reported on figure 1. The more or less structured lines have been decomposed with the minimum of lorentzian components and their parameters (position, amplitude, linewidth) were optimized by computer to adjust the fitted curve to the experimental spectra, as shown on figure 2. A set of main components is observed for the O_{1s}, Bi_{4f7/2} and Ba_{3d5/2} core level lines at 528.30 eV, 157.65 eV and 778.60 eV respectively, irrespective of the sample treatment. They are characterizing the barium bismuthate, and are found to

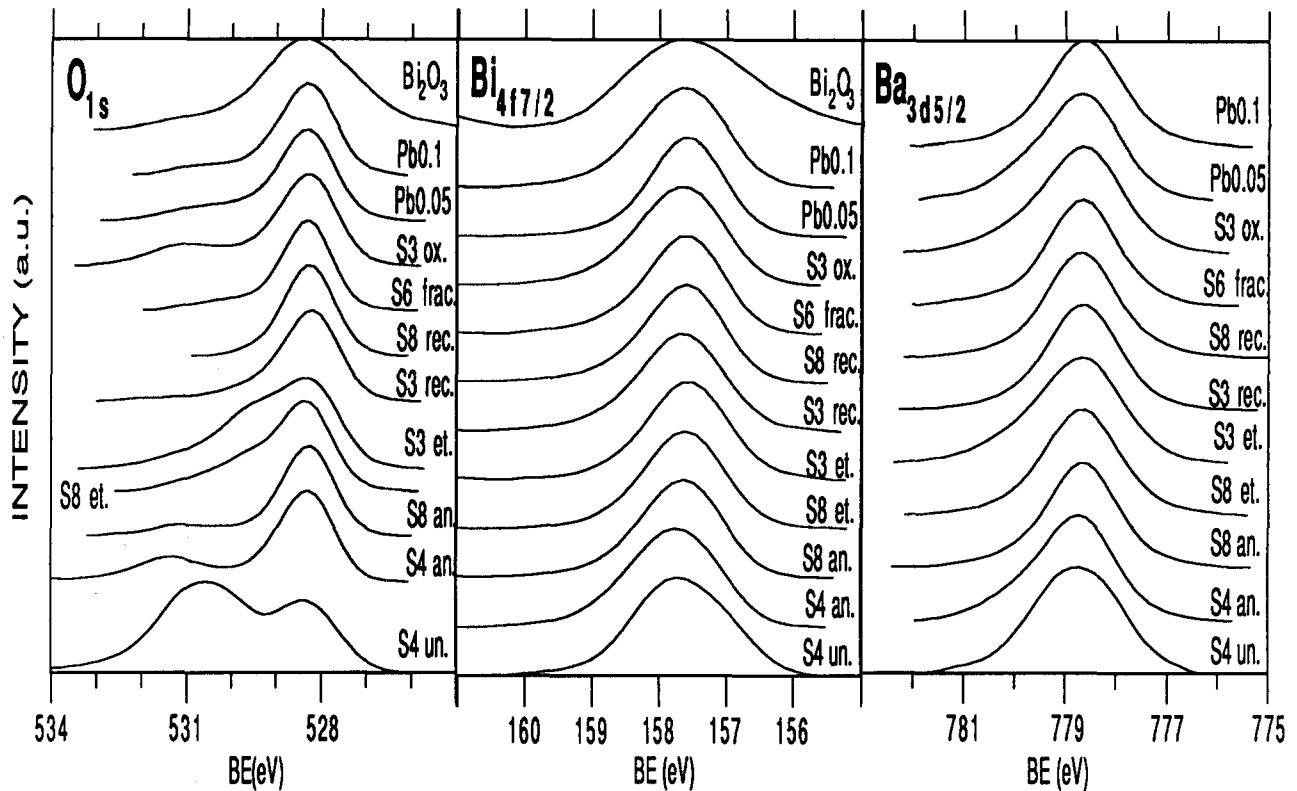


Figure 1. Evolutions of the O1s, Bi4f7/2 and Ba3d5/2 core level lines for four BaBiO_{3-δ} samples (S3, S4, S6, S8), recorded on a untreated (un.), annealed in UHV (an.), Ar⁺ ion etched (et.), reconstructed (rec.), fractured (frac.) and annealed in pure oxygen (ox.) surface. Core level lines of BaPb_{0.05}Bi_{0.95}O₃ (an.), BaPb_{0.1}Bi_{0.9}O₃ (rec.) and Bi₂O₃ samples are also shown.

be unchanged with a low Pb-substitution. In addition to the main peaks, high binding energy (HBE) satellites are detected, depending on the state of the sample surface. The parameters of all these components are listed in table 1.

3.1.1 O-line.

The O-line related to the untreated surface exhibits, in addition to a relatively weak 'main' peak, a contribution of two HBE1 and HBE2 satellites shifted by 2.6 eV and 1.5 eV from the main line. If the HBE2-line is very small, the large relative weight of the HBE1-line (70%) indicates that this line is related to the surface contamination. The decrease of the weight of this line under the effect of an annealing at 430° C in UHV realized during 2 hours or 4 hours (spectra S4 an. and S8 an.) corroborates this interpretation, and the difference of the weight of this line (25% and 9%) illustrates the relative weak efficiency of the annealing used as cleaning process. As shown by the S8 et. spectrum, the total disappearance of the HBE1-component is obtained after a 15 min. Ar⁺ ion etching and at this stage, the surface can be considered to be free of any contamination. By the same way, the etching strongly increases the HBE2-component up to 40% of the total O-line. A 85 min. etching produces a reappearance of the HBE1-component (spectrum S3 et.) by decreasing the HBE2-component only. A post annealing in UHV erases these two components and the S8 rec. spectrum can be considered as

a single line. On the other hand, the S3 rec. spectrum exhibits a HBE3-component at 1.1 eV above the main peak. These variations lead to attribute the HBE1-line to a surface contamination and to stable oxides (like barium oxide) and the HBE2- and HBE3-lines to non stoichiometric or very ionic bismuthate. Indeed, HBE2-line results from the splitting of the main line - behavior already observed in YBa₂Cu₃O_{7-δ} [4] - and collapses into the main peak when the surface is reconstructed by a post annealing. The presence of a HBE3-line on the S3 rec. spectrum illustrates the progressive shifting of the satellite to the main peak. At that stage, the surface of the S3 sample is incompletely reconstructed and this results from the importance of the damage of the surface caused by the long etching. Very likely this etching decomposed the surface, generating stable oxides, as indicated by the presence of a HBE1- satellite. The oxygenation of the surface at 430° C enhances this HBE1-satellite, as shown on S3 ox. spectrum. This increase could be attributed to a over-oxygenation of the surface which makes this surface very similar to that one obtained after a short time UHV annealing.

The fractured surface is free of contamination signal and nevertheless exhibits a HBE tail corresponding to the HBE2-satellite. This corroborates the attribution of this satellite to the pure bismuthate and indicates a variation of ionicity at the breakage surface.

One should note also the variation of the linewidths

as a function of the state of the sample surface. The main line is relatively wide before any treatment and narrows when the surface is cleaned and reconstructed. At that stage, this line is ≈ 1.35 eV wide and only the fractured surface exhibits a narrower line. This parameter, which is nevertheless limited by the characteristics of the analyzer, is a direct quality factor of the surface of the samples. It is also deeply affected by the texture of the sample, as illustrated on figure 1, where the linewidth of the sintered Bi₂O₃ is found to be twice larger than that one of the reconstructed crystalline BaBiO_{3-δ} surface. The reconstructed surface, which was the unique surface allowing a LEED characterization, seems to be the thermodynamically stable surface and should be taken as reference to analyze the intrinsic electronic structure of BaBiO_{3-δ}.

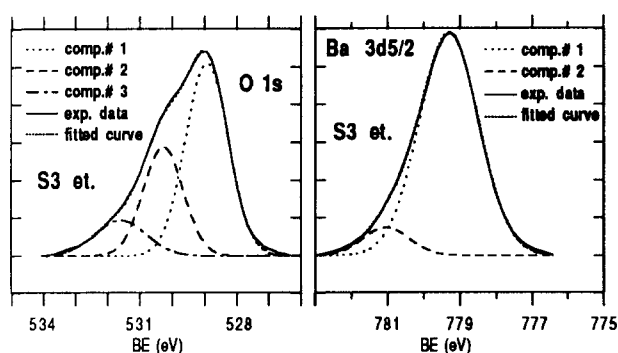


Figure 2. Decompositions of two core level lines, showing the amplitudes of the different components required to fit the experimental spectra (etched surface).

3.1.2 Bi-line.

The variations of the Bi-line are relatively reduced. The broad structure related to the untreated surface can be decomposed with a main peak at 157.65 eV and an HBE1-satellite shifted by 1.4 eV. The weight of this satellite is weakly reduced by annealing in UHV and the Ar⁺ ion etching is required to remove it. The reconstructed surface is characterized by an absence of such a component, which reappears after the reoxygenation. Although this HBE-line always remains relatively weak, one should note that it is detected on the fractured surface. This satellite is not directly correlated with any O-satellite and can not be attributed to any surface contamination, since its weight is unchanged after UHV annealing. It is related to thermally stable bismuth compounds or, more likely, represents an asymmetry of the Bi-core level line for some states of the surface. This asymmetry may be in relation with the valence band of BaBiO_{3-δ}, which is built by hybridization of O-2p and Bi-6s states. The absence of the energy loss satellite characterizes the etched and reconstructed surfaces, which can be suspected to be more or less oxygen deficient, since the etching is known to be a reducing process for weakly stable oxides.

As for the O-main line, the line width of the Bi-main line is deeply affected by the surface treatments. The annealings narrow the main line and the presence of any

surface contamination is indicated more by the value of the linewidth than by the weight of the HBE1-satellite. The reconstructed surface exhibits the narrowest linewidth among the treated surfaces and the weakest linewidth is found to be associated with the fractured surface. By a similar way, only a long time etching broadens the O- and Bi-main lines, and this essentially expresses a deep modification of the roughness of the surface.

Using the O-main line as reference, the position of the Bi-main line is found to be unchanged when the surface is treated and located at the position of a Bi³⁺. The chemical shifts between Bi³⁺, Bi⁴⁺, Bi⁵⁺ ions were published by few authors, and ranges from 70 meV up to 1eV [5,6]. Since it seems to us very hazardous to measure energy shifts as small as 70 meV on carbon free insulating surfaces, we prefer to consider the width of the Bi-line to estimate the presence of any bismuth disproportionation. The evolution of the linewidth from a dirty surface to a well reconstructed is a narrowing and the fractured surface is related to the narrowest line: these two observations indicate the absence of disproportionation on well defined surfaces, and lead to conclude that the bismuth is only trivalent. This conclusion is corroborated by the calculation of the stoichiometry at the surface of the fractured and reconstructed samples based on the intensities of the XPS lines. Using Bi₂O₃ as reference, we found a large oxygen deficiency for these surfaces, leading to the chemical formula BaBiO_{3-δ}, with $\delta > 0.5$.

3.1.3 Ba-line

The Ba-line exhibits only weak modification as a function of the different treatments. Generally, the Ba-line is found to be single. The linewidth of the Ba_{3d5/2} main line is relatively large for an untreated surface (2.00 eV) and is decreased continuously to 1.66 eV when the surface is progressively cleaned by annealing in UHV (Tab.1). Inducing a destruction of the surface, the Ar⁺ ion etching broadens the line, while the surface reconstruction produced by a post-annealing narrows the line to 1.65 eV, limit obtained also with the fractured surface. The oxygenation slightly broadens the line which remains single contrarily to the Ba-line of YBa₂Cu₃O_{7-δ} which splits into two lines [4], indicating nevertheless the presence of a different superficial oxide.

Generally the Ba-line is found to be symmetrical and only after some treatments a very weak HBE component is introduced to account for a loss energy tail. According to [4], the symmetry of the Ba-line suggests that the states in the valence band are exclusively O- and Bi-types.

3.1.4 Influence of the Pb-substitution

At weak substitution, no change related to Pb is observed on the core level lines. Similar evolutions of the electronic structure as a function of surface treatment are measurable on Pb-substituted compounds, as shown in figure 1: the oxygen HBE1-satellite is detected in the UHV annealed BaPb_{0.05}Bi_{0.95}O₃ while it completely disappears in the reconstructed BaPb_{0.1}Bi_{0.9}O₃. In

Table 1. Relative weight and full width at half maximum of the different components of the O_{1s}, Bi_{4f7/2} and Ba_{3d5/2} core level lines as a function of surface treatment. S3, S6, S4 and S8 correspond to several BaBiO_{3-δ} samples.

SAMPLE # and TREATMENT	O1s line					Bi4f7/2 line		Ba3d5/2 line	
	MAIN	MAIN	HBE3	HBE2	HBE1	MAIN	HBE1	MAIN	HBE1
	fwhm	weight	weight	weight	weight	fwhm	weight	fwhm	weight
	(eV)	(%)	(%)	(%)	(%)	(eV)	(%)	(eV)	(%)
S4 untreated	1.42	27	-	~ 3	70	1.70	10	2.00	-
S4 annealed (2 h.)	1.38	72	-	~ 3	25	1.55	6	1.80	8
S8 annealed (4 h.)	1.38	83	-	8	9	1.44	10	1.66	-
S8 etched (15 min.)	1.36	60	-	40	-	1.45	-	1.78	-
S3 etched (85 min.)	1.48	57	-	30	13	1.49	-	1.90	9
S3 part. reconstructed	1.35	69	31	-	-	1.49	-	1.69	-
S8 well reconstructed	1.36	97	-	~ 3	-	1.40	-	1.68	-
S6 fractured	1.27	83	-	17	-	1.35	9	1.64	-
S3 oxygenated (1 h.)	1.47	73	-	-	27	1.43	10	1.80	9
BaPb _{0.05} Bi _{0.95} O ₃ (an.)	1.38	71	17	-	12	1.35	~ 5	1.74	10
BaPb _{0.1} Bi _{0.9} O ₃ (rec.)	1.42	81	-	19	-	1.46	9	1.78	-
Bi ₂ O ₃	2.45					2.38			

addition, a large HBE2 O-satellite and a Bi-satellite are observed in the reconstructed BaPb_{0.1}Bi_{0.9}O₃, like in the fractured BaBiO_{3-δ}.

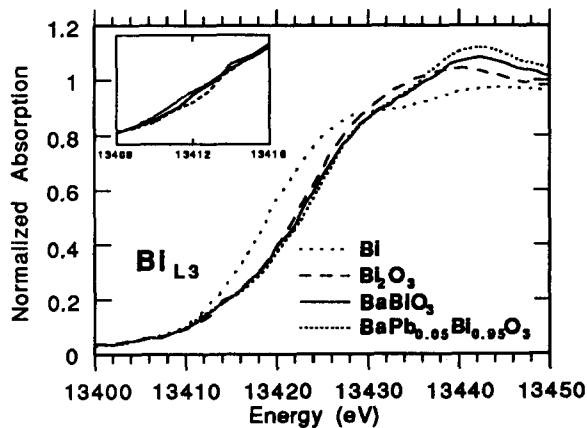


Figure 3. Bi_{L3} x-ray absorption edge for Bi, Bi₂O₃, BaBiO₃ and BaPb_{0.05}Bi_{0.95}O₃. The insert shows the 6s states.

3.2 XANES spectra

Since the Bi_{L3} absorption edge is located close to 13400 eV, these spectra are less surface sensitive and no surface treatment is necessary to obtain relevant spectra. As shown on figure 3, the absorption edge is also sensitive to the valence of the bismuth and a significant energy shift is observed between Bi⁰ and Bi³⁺. The positions of the Bi₂O₃, BaBiO_{3-δ} and BaPb_{0.05}Bi_{0.95}O₃ spectra clearly indicate that in the barium bismuthates the mean valence of the bismuth is higher than +3. In addition, a small bump located at 13413 eV near the onset of the edge (insert, fig. 3), expresses the presence of empty 6s states in the barium

bismuthates, which is the signature of Bi⁴⁺ or Bi⁵⁺.

4. Conclusion

The XPS study have shown the presence of different O-satellites, the weights of which are related to the presence of contamination or of stable oxides or to a change in the covalence of the bismuthates. The reconstructed and fractured surfaces are oxygen deficient and do not exhibit any disproportionation. But the presence in the bulk of Bi⁵⁺ is demonstrated by XANES.

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