



# Synchrotron-Radiation Photoemission Study of the Ba Atomic Layer Deposition on Multiferroic BiFeO<sub>3</sub>

G. Benemanskaya<sup>1</sup>, P. Dementev<sup>1</sup>, G. Iluridze<sup>2</sup>, T. Minashvili<sup>2, \*</sup>, G. Frank–Kamenetskaya<sup>3</sup>

<sup>1</sup>Department of Solid State Physics, Ioffe Institute, St. Petersburg, Russia

<sup>2</sup>Department of Engineering Physics, Georgian Technical University, Tbilisi, Georgia

<sup>3</sup>Department of Analytical Chemistry, St. Petersburg State Technological Institute, St. Petersburg, Russia

## Email address:

galina.benemanskaya@mail.ioffe.ru (G. Benemanskaya), tamazminashvili@rambler.ru (T. Minashvili),

kamenetskaya@yahoo.com (G. Frank–Kamenetskaya)

\*Corresponding author

## To cite this article:

G. Benemanskaya, P. Dementev, G. Iluridze, T. Minashvili, G. Frank–Kamenetskaya. Synchrotron-Radiation Photoemission Study of the Ba Atomic Layer Deposition on Multiferroic BiFeO<sub>3</sub>. *American Journal of Nano Research and Applications*. Special Issue: Nanotechnologies. Vol. 5, No. 3-1, 2017, pp. 18-21. doi: 10.11648/j.nano.s.2017050301.15

Received: December 6, 2016; Accepted: December 7, 2016; Published: January 6, 2017

**Abstract:** Electronic structure of ceramic BiFeO<sub>3</sub> surface and Ba / BiFeO<sub>3</sub> interface has been investigated *in situ* in an ultrahigh vacuum via synchrotron-based photoemission spectroscopy within the range of excited photon energy from 120 to 850 eV. The photo emission from the valence band and from Bi 4*f*, Fe 2*p*, and Ba 4*d* core-levels were studied. An effect of Ba atomic layer deposition is found to induce a significant change in all spectra that is originated from the strong interaction with charge transfer between Fe, Bi surface atoms and Ba adatoms. It is obtained that the Fe 2*p* 3/2 core-level spectrum for the clean BiFeO<sub>3</sub> sample contains both the Fe<sup>2+</sup> and Fe<sup>3+</sup> ion components with atomic ratio of Fe<sup>2+</sup> / Fe<sup>3+</sup> ~ 1. The Ba adsorption is found to increase the Fe<sup>2+</sup> / Fe<sup>3+</sup> ratio up to ~ 1.5 that clearly exhibits recharge between Fe<sup>3+</sup> ↔ Fe<sup>2+</sup> ions and possibility to enhance the ferroelectric polarization.

**Keywords:** Electronic Structure, Surface, Ba / BiFeO<sub>3</sub> Interface, Synchrotron-Photoemission Spectroscopy

## 1. Introduction

Multiferroics are the novel group of materials exhibiting coexistence of magnetic and ferroelectric ordering. Magnetism and ferroelectricity are essential to many forms of current technology, and the quiet for multiferroic materials, where these two phenomena are intimately coupled. Multiferroics have potential for applications in spintronics, datastorage, sensors and in tuneable multifunctional devices. BiFeO<sub>3</sub> (BFO) is considered as the multiferroic with high Curie point of ~ 1100 K, and high Neel temperature of 643 K [1, 2]. BFO is characterized by relatively simple crystal structure as the rhombohedrally distorted perovskite. Recently, photoemission studies for the clean BFO have been carried out [3 – 17]. Most of BFO works focused on core-level spectra. No study is devoted to the valence band spectrum and to the spectra of metal / BFO interfaces.

Data present first photoemission results obtained for the Ba ultrathin layer adsorbed on the ceramic BiFeO<sub>3</sub> surface and

shown possibility of photoemission method to study effect of Ba adsorption on the electronic properties of multiferroics. We perform first photoelectron spectroscopy (PES) study of electronic structure of the ultrathin Ba / BFO interface. Experiments were carried out *in situ* at BESSYII, Synchrotron, Berlin, using PES with photon energies in the range of 80 – 900 eV. The normal photoemission spectra from the valence band (VB) and Bi 4*f*, Fe 2*p*, and Ba 4*d* core-levels were recorded.

## 2. Experimental Details

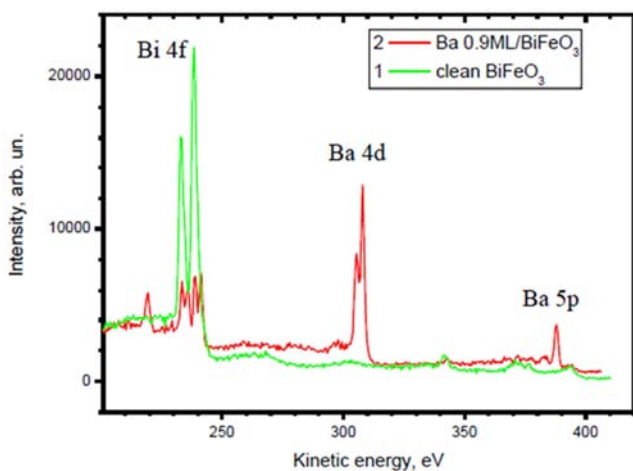
Experiments were carried out at the Russian–German beam line using HIRES station, synchrotron BESSYII, Helmholtz Zentrum, Berlin, by means of PES during synchrotron radiation with photon energies in the range of 60 – 1200 eV. Photoemission studies were performed *in situ*

in an ultra high vacuum of  $5 \cdot 10^{-10}$  Torr at room temperature. Ceramic polycrystalline sample of  $\text{BiFeO}_3$  (BFO) was obtained from initial fine-dispersed powder by sintering process in a furnace at a temperature of  $\sim 1200$  K. The BFO sample was preliminarily heated *in situ* at a temperature of  $\sim 1000$  K. Photoelectrons in a cone oriented along the normal to the surface were detected. The normal photoemission spectra from the valence band (VB) and from Bi 4*f*, O 1*s*, Fe 2*p*, and Ba 4*d* core-levels were recorded. The total energy resolution was 50 meV.

Step-by-step deposition of Ba submonolayer coverage from 0.1 to 1 monolayer was performed onto the BFO surface. To ascertain the Ba coverage, the atomically pure barium source was preliminarily calibrated to dosage using the original technique [18]. This made possible to determine the Ba dosage deposited onto the sample to better than 20%. The Ba over layer is presented in monolayer (ML) units because of Ba sticking coefficient could be supposed to equal to one at least up to 1 ML. Note that 1 ML is defined as one complete layer of Ba atoms and equal to  $\sim 6.5 \cdot 10^{14}$  atoms  $\text{cm}^2$ . Moreover, the amount of 1 ML of Ba atoms was determined from the intensity saturation of the Ba 4*d* core-level-peak.

### 3. Results and Discussion

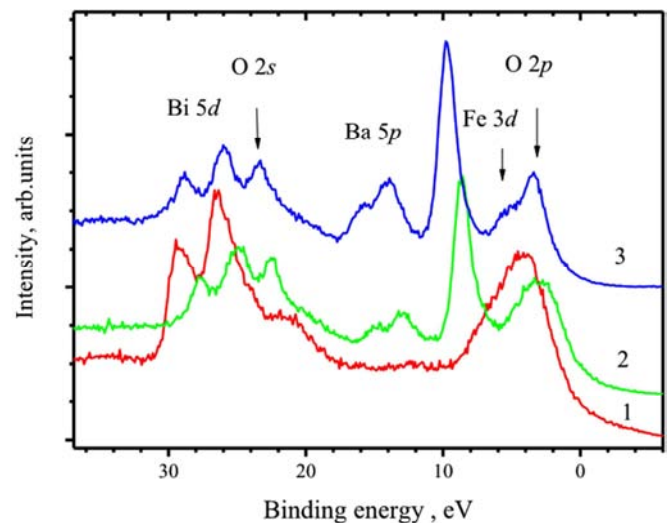
Overview of the normal photoemission spectrum for the clean  $\text{BiFeO}_3$  ceramic sample at excitation energy of  $h\nu = 400$  eV is presented in Fig. 1, Curve 1. The spectrum clearly shows the principal Bi 4*f* peak and denotes a lack of foreign contaminations. As can be seen, the photoemission in the valence band region (VB) has too little intensity and could be studied at lower excitation energies (see Fig. 2). After Ba adsorption at 0.9 ML the initial spectrum undergoes the significant change in all region showing appearance of Ba 5*p* and Ba 4*d* core-level spectra and increasing Bi 4*f* core-level doublet (Fig. 2, Curve 2).



**Figure 1.** Normal photoemission spectra for the clean  $\text{BiFeO}_3$  ceramic sample (1) and for the  $\text{Ba/BiFeO}_3$  interface at Ba coverage of 0.9 ML (2). Excitation energy  $h\nu = 400$  eV.

The normal photoemission spectrum of the BFO sample in

the valence band (VB) region and Bi 5*d* core-level is shown in Fig. 2 (Curve 1). The excitation energy is 120 eV. The position of the valence band maximum  $E_{VBM} = 0$  eV. A broad band between binding energies of 0 and 10 eV below the  $E_{VBM}$  is obtained. Calculations show that the width of the VB is about 8 eV [4, 5]. It is slightly less than obtained experimentally. Two small features located at binding energies of  $\sim 4$  and 6 eV are corresponded to the photoemission from the O 2*p* and Fe 3*d* core-levels. The broad feature between 20 and 30 eV is believed to consist of two separate structures, of which at least one is due to the Bi 5*d* core-level doublet located at a slightly higher binding energy (Bi 5*d* 5/2 at 26 and Bi 5*d* 3/2 at 29 eV). An unresolved shoulder at about 22 eV can be attributed to the O-related state, namely, O 2*s* as shown in [19].

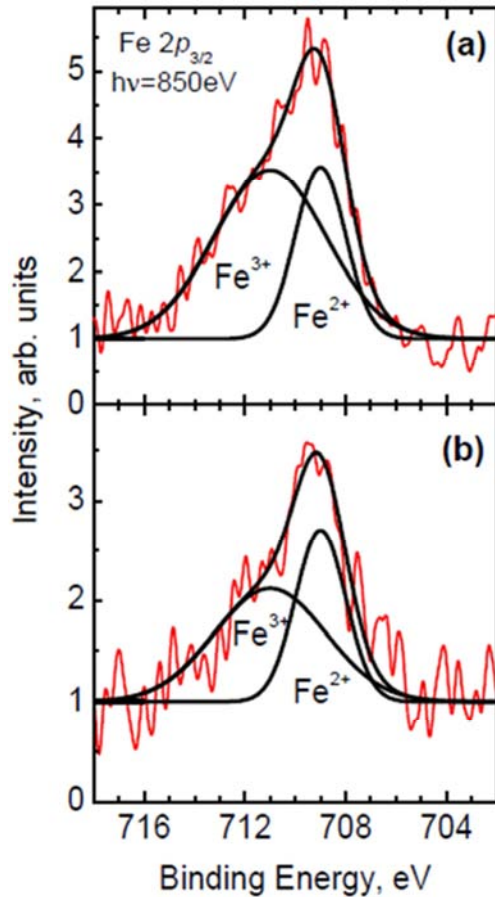


**Figure 2.** Normal photoemission spectra in the valence band region of the  $\text{BiFeO}_3$  ceramic sample at different Ba coverages: (1) clean sample, 0.5 ML, and (3) 0.9 ML. Excitation energy  $h\nu = 120$  eV.

The modification of the spectrum upon Ba adsorption is presented in Fig. 2, Curves 2 and 3. As can be seen, Ba adsorption on the clean BFO is evident to modify throughout the spectrum. The more drastic change occurs at initial stage of Ba deposition at small submonolayer coverage up to 0.5 ML. An evolution of the VB spectrum and an appearance of the Ba 5*p*  $\frac{1}{2}$  and Ba 5*p*  $\frac{3}{2}$  core-level doublet at energies of 9.5 and 8.0 eV are observed. The Bi 5*d* core-level peak is shifted slightly to lower binding energy and reduced in intensity under increasing Ba coverage. The O 2*s* shoulder at  $\sim 22$  eV is now clearly resolved. Completely unexpected result was that a new additional feature at  $\sim 10$  eV is appeared in spectra (Fig. 2, Curves 2 and 3). Since the intensity of this peak is drastically enhanced by Ba adsorption, it is natural to associate this feature with Ba-related states, for instance, with a Ba surface plasmon.

The Fe 2*p*, O 1*s*, and Bi 4*f* core-levels were studied after the same series of Ba adsorption in order to gain further insight into the reaction of Ba adatoms with BFO surface. The Fe 2*p* core-level is split into the 2*p*  $\frac{1}{2}$  and 2*p*  $\frac{3}{2}$  components on account of the spin-orbit coupling [6 – 8, 17]. The 2*p*  $\frac{3}{2}$  core-level for the  $\text{Fe}^{2+}$  ions is observed at binding energy of  $\sim$

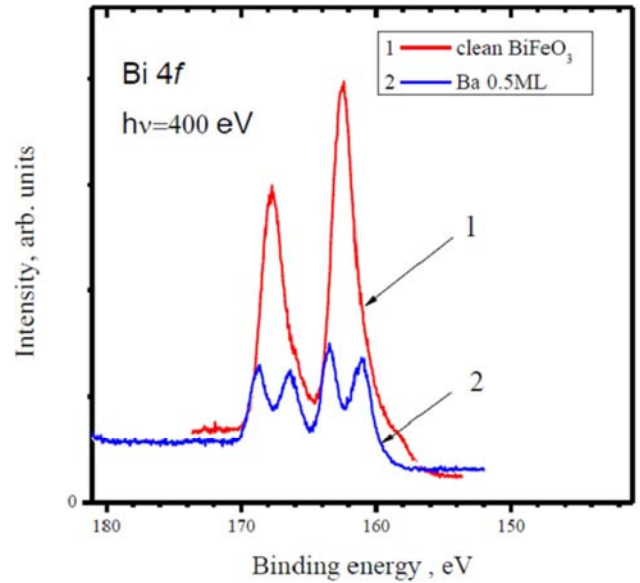
709 while for the Fe<sup>3+</sup> ions it appears at 711 eV [8, 17]. The crystal structure of BFO is composed of the chains of octahedral FeO<sub>6</sub> complexes connected by vertexes, while the Bi ions are in cavities between the octahedrons. The magnetic and ferroelectric properties of BFO are due to the Fe ions octahedrally surrounded with the oxygen ions and due to not only Fe<sup>3+</sup> ions but especially also due to Fe<sup>2+</sup> ions [6, 17]. So, studies of the photoemission from the Fe 2*p* core-level can be used diagnostically to identify the presence both the Fe<sup>3+</sup> and Fe<sup>2+</sup> ions.



**Figure 3.** Decomposition of normal photoemission spectra of Fe 2*p* 3/2 core-level for clean ceramic BFO (a) and for Ba / BiFeO<sub>3</sub> interface at Ba coverage of 0.9 ML (b). Thin red lines represent experimental data and thick black lines represent fitting results with fitting components. Excitation energy  $h\nu = 850$  eV.

According to the fitting result, the atomic ratio of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions corresponds to Fe<sup>2+</sup> / Fe<sup>3+</sup>  $\approx 1$  in clean BFO. The Ba adsorption on the BFO surface is found to cause significant change in the Fe 2*p* 3/2 core-level spectrum (Fig. 3b). As can be seen, the atomic ratio is increased up to the value of Fe<sup>2+</sup> / Fe<sup>3+</sup>  $\approx 1.5$  or Ba/BFO interface at Ba coverage of 0.9 ML. The observed effect of Ba adsorption signifies the improving ferroelectric polarization [6]. The Ba ultrathin layer on the BFO is found to produce the strong interaction between Ba adatoms and Fe ions that leads to increase the ratio Fe<sup>2+</sup> / Fe<sup>3+</sup>  $\approx 1.5$ . The Fe 2*p* 3/2 core-level evolution is obviously caused by the recharge between Fe<sup>3+</sup>  $\leftrightarrow$  Fe<sup>2+</sup> ion sand may be one of the reasons for enhanced ferroelectric and magnetic properties

of BFO due to increasing in the amount of the Fe<sup>2+</sup> ions.



**Figure 4.** Normal photoemission spectra of the Bi 4*f* core-level of the clean BFO sample (1) and for the Ba / BFO interface at Ba coverage of 0.5 ML. Excitation energy  $h\nu = 400$  eV.

The Ba atomic layer deposition on the BFO surface is found to cause splitting the double structured spectrum of Bi 4*f* core-level (Fig. 4, Curve 1) into two double structured ones (Fig. 4, Curve 2). The initial Bi 4*f* core-level peaks is shifted and reduced in intensity with increasing Ba coverage. The appearance of extra fine structure demonstrates the obvious chemical shift of the Bi 4*f* core-level peaks corresponding to the photoemission from Bi atoms in the interface area. We can attribute the positive shift to the partial redistribution of the Ba adatom charge to the Bi surface atoms and charge transfer from the Ba adlayer to the Bi atoms with increasing both the Bi-ionicity and electron density in the interface area.

## 4. Conclusions

To summarize, the Ba adsorption is found to modify the VB spectrum as well as the Fe 2*p* and Bi 4*f* core-level spectra. It is revealed that the atomic ratio of the Fe<sup>2+</sup> / Fe<sup>3+</sup> ions increases from  $\sim 1$  up to  $\sim 1.5$  through the formation of the Ba / BFO interface. The result points out that the BFO ferroelectric polarization could be hanced due to in crease in the amount of the Fe<sup>2+</sup> ions under Ba adsorption. The Ba adsorption is found to induce splitting of the double structured spectrum of Bi 4*f* core-level into two double structured ones accompanied by the chemical shift. It could be attributed to the charge transfer from the Ba adlayer to the Bi surface atoms with increasing both the Bi-ionicity and electron density in the interface area.

## Acknowledgements

The authors thank B. Senkovskiy, Synchrotron BESSYII, for his help during the experiments and the Russian–German

Beamline, Synchrotron BESSYII, Helmholtz Zentrum, Berlin, for providing the facilities to perform the experiments.

## References

- [1] L. W. Martin, S. P. Crane, Y.-H. Chu, M. B. Holcomb, M. Gajek, M. Huijben, C.-H. Yang, N. Balke, and R. Ramesh, *J. Phys. Condens. Matter*, vol. 20, no. 434220, 2008.
- [2] P. Baettig, C. Ederer, and N. A. Spaldin, *Phys. Rev. B*, vol. 72, no. 214105, 2005.
- [3] J. Li, J. Wang, M. Wuttig, R. Ramesh, N. Wang, B. Ruetter, A. P. Pyatakov, A. K. Zvezdin, and D. Viehland, *Appl. Phys. Lett.*, vol. 84, p. 5261, 2004.
- [4] Y. P. Wang, G. L. Yuan, X. Y. Chen, J.-M. Liu, and Z. G. Liu, *J. Phys. D*, vol. 39, p. 2019, 2006.
- [5] T. Higuchi, Y.-Sh. Liu, P. Yao, P.-A. Glans, J. Guo, Ch. Chang, Z. Wu, W. Sakamoto, N. Itoh, T. Shimura, and T. Yogo, *Phys. Rev. B*, vol. 78, no. 085106, 2008.
- [6] F. Gao, C. Cai, Y. Wang, S. Dong, X. Y. Qiu, G. L. Yuan, and Z. G. Liu, *J. Appl. Phys.*, vol. 99, no. 094105, 2006.
- [7] S. Mandal, C. K. Ghosh, D. Sarkar, U. N. Maiti, and K. K. Chattopadhyay, *Solid State Sci.*, vol. 12, p. 1803, 2010.
- [8] A. T. Kozakov, A. G. Kochur, K. A. Googlev, A. V. Nikolsky, I. P. Raevski, V. S. Smotrakov, and V. V. Yermkin, *J. Electron Spectrosc. Rel. Phenom.*, vol. 184, p. 16, 2011.
- [9] I. C. Infante, J. Juraszek, S. Fusil, B. Dupe, P. Gemeiner, O. Dieguez, F. Pailloux, S. Jouen, and E. Jacquet, *Phys. Rev. Lett.*, vol. 107, no. 237601, 2011.
- [10] R. Schafrank, J. D. Baniecki, M. Ishii, Y. Kotaka, and K. Kurihara, *New J. Phys.*, vol. 15, no. 053014, 2013.
- [11] J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, and K. M. Rabe, *Phys. Rev. B*, vol. 71, no. 014113, 2005.
- [12] S. J. Clark and J. Robertson, *Appl. Phys. Lett.*, vol. 90, no. 132903, 2007.
- [13] K. Liu, H. Fan, P. Ren, and Ch. Yang, *J. Alloys Comp.*, vol. 509, p. 1901, 2011.
- [14] Sh. Li, J. Morasch, A. Klein, Ch. Chirila, L. Pintilie, L. Jia, K. Ellmer, M. Naderer, K. Reichmann, M. Grotting, and K. Albe, *Phys. Rev. B*, vol. 88, no. 045428, 2013.
- [15] B. Ramachandran, A. Dixit, R. Naik, G. Lawes, and M. S. Ramachandra Rao, *Phys. Rev. B*, vol. 82, no. 012102, 2010.
- [16] Z. V. Gareeva and A. K. Zvezdin, *Phys. Status Solidi RRL*, vol. 3, p. 79, 2009.
- [17] B. Yu, M. Li, J. Wang, Zh. Hu, X. Liu, Y. Zhu, and X. Zhao, *Thin Solid Films*, vol. 520, p. 4089, 2012.
- [18] G. V. Benemanskaya, M. N. Lapushkin, and S. N. Timoshnev, *Surf. Sci.*, vol. 603, p. 2474, 2009.
- [19] Y. Jeon, G. Liang, J. Chen, M. Croft, M. W. Ruckman, D. Di Marzo, and M. S. Hegde, *Phys. Rev. B*, vol. 41, p. 4066, 1990.