<table>
<thead>
<tr>
<th>Title</th>
<th>Ab-initio multiplet calculation of oxygen vacancy effect on Ti-L-2,L-3 electron energy loss near edge structures of BaTiO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Ootsuki, S.; Ikeno, H.; Umeda, Y.; Moriwake, H.; Kuwabara, A.; Kido, O.; Ueda, S.; Tanaka, I.; Fujikawa, Y.; Mizoguchi, T.</td>
</tr>
<tr>
<td>Citation</td>
<td>APPLIED PHYSICS LETTERS (2011), 99(23)</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2011-12</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/160633">http://hdl.handle.net/2433/160633</a></td>
</tr>
<tr>
<td>Copyright</td>
<td>Copyright 2011 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics. The following article appeared in APPLIED PHYSICS LETTERS 99, 233109 (2011) and may be found at <a href="http://link.aip.org/link/?apl/99/233109">http://link.aip.org/link/?apl/99/233109</a></td>
</tr>
<tr>
<td>Type</td>
<td>Journal Article</td>
</tr>
<tr>
<td>Textversion</td>
<td>publisher</td>
</tr>
</tbody>
</table>

Kyoto University
Ab-initio multiplet calculation of oxygen vacancy effect on Ti-L2,3 electron energy loss near edge structures of BaTiO3

S. Ootsuki, H. Ikeno, Y. Umeda, H. Moriwake, A. Kuwabara et al.

Citation: Appl. Phys. Lett. 99, 233109 (2011); doi: 10.1063/1.3663543
View online: http://dx.doi.org/10.1063/1.3663543
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v99/i23
Published by the American Institute of Physics.

Related Articles
High resolution electron energy loss spectroscopy of clean and hydrogen covered Si(001) surfaces: First principles calculations
Nazca Lines by La ordering in La2/3−xLi3xTiO3 ion-conductive perovskite
Dipolar transformations of two-dimensional quantum dots arrays proven by electron energy loss spectroscopy
Tuning the surface plasmon on Ag(111) by organic molecules
A study of the effect of iron island morphology and interface oxidation on the magnetic hysteresis of Fe-MgO (001) thin film composites

Additional information on Appl. Phys. Lett.
Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors

ADVERTISEMENT
Ab-initio multiplet calculation of oxygen vacancy effect on Ti-L2,3 electron energy loss near edge structures of BaTiO3

S. Ootsuki1,2,a), H. Ikeno,3 Y. Umeda,1 H. Moriwake,4 A. Kuwabara,4 O. Kido,1 S. Ueda,1 I. Tanaka,3,4 Y. Fujikawa,1 and T. Mizoguchi2,a) 

1Application & Analysis Center, TDK Corporation, 570-2 Matsugashita, Minamihatori, Narita City, Chiba 286-8588, Japan 
2Institute of Industrial Science, The University of Tokyo, 4-6-1, Komaba, Meguro, Tokyo 153-8505, Japan 
3Department of Materials Science and Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606-8001, Japan 
4Nanostructure Research Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan

(Received 17 August 2011; accepted 29 October 2011; published online 8 December 2011)

The effect of oxygen vacancy on Ti-L2,3 electron energy-loss near-edge structures (ELNES) of BaTiO3 was theoretically investigated through ab initio multiplet calculation. The presence of an oxygen vacancy influences spectral features not only at the nearest neighbor Ti site but also at Ti sites further from the oxygen vacancy. The effects of different oxygen vacancy concentrations were also investigated. Based on this study, it was concluded that the detection limit for oxygen vacancy with Ti-L2,3 ELNES is approximately 1%. © 2011 American Institute of Physics. [doi:10.1063/1.3663543]

BaTiO3 is used as the dielectric layers in the multilayer ceramic capacitors (MLCC).1 The MLCC device is usually heated in a reduction atmosphere during the fabrication process, and oxygen vacancies are introduced within the BaTiO3 layers. This oxygen vacancy has been known to influence the insulating property of the BaTiO3 layers.2–6 Thus, identification and control of the oxygen vacancy in the BaTiO3 layers are crucial for the MLCC devices.

To identify oxygen vacancy in BaTiO3 and related perovskite type compounds, Ti-L2,3 electron energy-loss near-edge structures (ELNES) observed with transmission electron microscopy (TEM) have been employed.7–13 It is known that the L3 and L2 edges are each split into two main peaks in the Ti-L2,3 ELNES of bulk BaTiO3 (peaks A, B, C, D in Fig. 2).7–13 When oxygen vacancies are introduced, the splitting between those two peaks at the Ti-L1 edge (peaks A and B in Fig. 2) and the Ti-L2 edge (peaks C and D in Fig. 2) becomes less apparent.7,8,11,13 These spectral changes have been interpreted as the valency change of Ti from +4 to +3, based on comparisons with the experimental spectra of reference compounds.

However, the oxygen vacancy induces not only extra electron but also structural distortions, and so the effect of the oxygen vacancy on the nearest neighbor Ti site is different from that on Ti sites further away from the oxygen vacancy. Such realistic effects of the oxygen vacancy on the Ti-L2,3 ELNES have not been investigated so far. In addition, how well the oxygen vacancy can be detected by Ti-L2,3 ELNES has not been fully understood. The lack of such basic knowledge is mainly because of the absence of good theoretical tools for calculating the transition metal (TM) L2,3 ELNES. For simulations of TM-L2,3 ELNES, the strong electronic correlation between the core-hole and excited electrons must be properly taken into account, which is beyond the ordinary one-particle density functional calculations.14

Recently, Ikeno et al. developed an ab initio multiplet calculation code for the L2,3 edges of TMs.14–19 In this paper, the Ti-L2,3 ELNES of BaTiO3 are theoretically investigated by the ab initio multiplet method. Moreover, the effects of the oxygen vacancy on the spectrum and the ability of Ti-L2,3 ELNES to detect oxygen vacancy are discussed.

Theoretical calculation of Ti-L2,3 ELNES was performed by the ab initio multiplet method that is based on the relativistic configuration-interaction theory.16,17 The calculation was performed with six- or seven-atom clusters embedded in an array of point charges to include the effects of the Madelung potential of BaTiO3. The theoretical transition energy was separately calculated by the Slater transition-state method.

The atomic arrangements around each oxygen vacancy were optimized by a first-principles projector augmented plane wave (PAW) calculation implemented in the Vienna Ab initio Simulation Package (VASP) code.20 The effect of oxygen vacancy on the Ti-L2,3 ELNES was investigated using cubic-BaTiO3. 153-atom supercells were used, and all atoms in the supercells were allowed to be relaxed. The optimized positions were used as those of the atoms in the clusters and those of the point charges of the Madelung potentials. To know the effect of extra electron introduced by the oxygen vacancy, both neutral and charged oxygen vacancies were calculated in the models with and without an extra electron.

In the cluster calculation, the effects of the extra electron induced by the oxygen vacancy were simulated by taking into account the change in the valency of the nearest neighbor Ti site to the oxygen vacancy. Namely, when the extra electron is present and localized to the oxygen vacancy, the closest Ti to the oxygen vacancy is considered a Ti3+ ion, whereas those further from the oxygen vacancy are considered Ti4+ ions. On the other hand, if the extra electron is far away from the oxygen vacancy, all Ti ions were set to Ti4+. The multiplet calculation of oxygen vacancy effect on Ti-L2,3 electron was investigated through ab initio multiplet calculation. The presence of an oxygen vacancy influences spectral features not only at the nearest neighbor Ti site but also at Ti sites further from the oxygen vacancy. The effects of different oxygen vacancy concentrations were also investigated. Based on this study, it was concluded that the detection limit for oxygen vacancy with Ti-L2,3 ELNES is approximately 1%. © 2011 American Institute of Physics. [doi:10.1063/1.3663543]
–4% to 10% are introduced by the oxygen vacancy.\(^{21,22}\) In addition, the effect of the extra electron on the lattice relaxation is approximately 1%.\(^{21,22}\) The Ti-L\(_{2,3}\) ELNES were calculated from Ti sites as shown in Fig. 1.

Figure 2 shows Ti-L\(_{2,3}\) ELNES of cubic and tetragonal BaTiO\(_3\). The experimental spectrum of tetragonal BaTiO\(_3\) is shown in the same figure. The experimental spectrum was taken by TEM (JEOL 2200FS with Omega filter), and the energy resolution was around 1 eV. It can be seen in Fig. 2 that the present ab initio multiplet calculation reproduces the experimental spectrum well. It is also found that the calculated Ti-L\(_{2,3}\) ELNES of cubic and tetragonal BaTiO\(_3\) are almost identical. A high energy resolution of better than 0.1 eV is clearly necessary to distinguish between the two different structures merely by Ti-L\(_{2,3}\) ELNES.

Figures 3(a) and 3(b) show, respectively, the calculated Ti-L\(_{2,3}\) ELNES of the vacancy models without and with an extra electron, namely, with Ti\(^{4+}\) or Ti\(^{3+}\). With respect to the oxygen vacancy, Ti-L\(_{2,3}\) ELNES were calculated for the nearest neighboring Ti sites (Ti\(^{4+}\)\(_{1\text{stNN}}\) or Ti\(^{3+}\)\(_{1\text{stNN}}\)), second nearest neighboring Ti sites (Ti\(^{4+}\)\(_{2\text{ndNN}}\) or Ti\(^{3+}\)\(_{2\text{ndNN}}\)), and third nearest neighboring Ti sites (Ti\(^{4+}\)\(_{3\text{rdNN}}\) or Ti\(^{3+}\)\(_{3\text{rdNN}}\)). In the case of Ti\(^{4+}\)\(_{1\text{stNN}}\), the spectrum shifts to lower energy and peaks B and D are each split. This peak splitting and spectral shift can be ascribed to dangling-bond formation and decreased Ti ionicity, respectively. In the case of Ti sites further away from the oxygen vacancy, the spectra are similar to that of perfect BaTiO\(_3\), though the spectrum of the Ti\(^{4+}\)\(_{2\text{ndNN}}\) site is shifted to lower energy by 0.9 eV. By analyzing the chemical bonding, it was found that the Ti\(^{4+}\)\(_{1\text{stNN}}\) site has lower ionicity than other sites, indicating that the oxygen vacancy influences the electronic structure at the Ti\(^{4+}\)\(_{1\text{stNN}}\) site. Although the spectra of the Ti\(^{4+}\)\(_{2\text{ndNN}}\) and Ti\(^{4+}\)\(_{3\text{rdNN}}\) sites are slightly shifted to higher and lower energy, respectively, the magnitude of either shift is almost negligible.

By introducing an extra electron into the nearest neighbor Ti site, the spectral features are completely changed (Ti\(^{3+}\)\(_{1\text{stNN}}\) site). The spectrum features correspond well to experimental spectrum of Ti\(^{3+}\) compounds.\(^{11-13,23}\) However, it is found that the effect of the extra electron does not reach the Ti sites further away from the oxygen vacancy. Namely, the spectral features of Ti\(^{4+}\)\(_{2\text{ndNN}}\), Ti\(^{4+}\)\(_{3\text{rdNN}}\), and Ti\(^{3+}\)\(_{3\text{rdNN}}\) sites are almost identical to those without the extra electron (Figs. 3(a) and 3(b)). From Figs. 3(a) and 3(b), it is found that both structural distortion and extra electron induced by the oxygen vacancy mainly affect to close Ti to the oxygen vacancy. This localized effects can be ascribed to that the Ti-L\(_{2,3}\) edge is caused by spatially localized orbitals, Ti-2p and 3d.

To consider the oxygen vacancy concentration, a weighted sum of spectra was calculated from the relation that a lone oxygen vacancy is surrounded by eight Ti\(^{4+}\)\(_{3\text{rdNN}}\) ions, eight Ti\(^{4+}\)\(_{2\text{ndNN}}\) ions, two Ti\(^{4+}\)\(_{1\text{stNN}}\) ions, and two Ti\(^{3+}\)\(_{1\text{stNN}}\) ions. The much further Ti sites were considered the same as those in perfect BaTiO\(_3\). By taking these conditions into account, the effect of oxygen vacancy was simulated with different vacancy concentrations of 0.52%, 1.04%, and 1.56%.

---

**Fig. 1.** (Color online) Structure of BaTiO\(_3\) with oxygen vacancy and Ti positions of calculation.

**Fig. 2.** Experimental Ti-L\(_{2,3}\) ELNES of tetragonal BaTiO\(_3\) and theoretical Ti-L\(_{2,3}\) ELNES of cubic and tetragonal BaTiO\(_3\).

**Fig. 3.** (Color online) Theoretical Ti-L\(_{2,3}\) ELNES of the perfect BaTiO\(_3\) and the Ti near oxygen vacancy (a) without and (b) with extra electron.
changes in Ti-L2,3 ELNES caused by the presence of the oxygen vacancy result from not only the nearest neighboring Ti sites. The spectral changes induced only by the oxygen vacancy concentration exceeds 1%, and those peaks become doublets when the oxygen vacancy concentration is +4 (without extra electron), (b) Ti next to oxygen vacancy is +3 (with extra electron). Deep and light red and gray colors mean high and low concentrations, respectively.

The spectra simulated with different oxygen concentrations are shown in Fig. 4. The calculated spectra were broadened with different broadening factors of 0.5 eV and 1.2 eV to represent the spectral changes in experiments with different energy resolutions. It is clearly found that spectral features are changed by the presence of the oxygen vacancy. In particular, small shoulders appear at the lower energy sides of peaks B and D when the oxygen vacancy concentration exceeds 1%, and those peaks become doublets when the concentration is 1.5%. Although these extra features are less apparent with low energy resolution, the present theoretical calculation suggests that the Ti-L2,3 ELNES affords the potential to identify a 1% oxygen vacancy by observing the spectrum with high energy resolution. This detection limit obtained by the present calculation is nicely consistent with that proposed by Muller et al. from experiments.11

From Figs. 3(a), 3(b), 4(a), and 4(b), it is found that the effect of the extra electron on the averaged Ti-L2,3 ELNES is very small, except that the local Ti4+ and Ti3+ yield largely different spectral features. This is because the nearest neighboring Ti sites are four times smaller in number than the second nearest neighboring Ti sites. The spectral changes described above can thus mainly be ascribed to the relatively large chemical shift of the Ti-L2,3 ELNES from the second nearest neighboring Ti sites, Ti_{Horizontal}. That is, the spectral changes in Ti-L2,3 ELNES caused by the presence of the oxygen vacancy result from not only the nearest neighboring Ti sites but also the neighboring Ti sites further away from the oxygen vacancy.

Finally, it should be mentioned that Mizoguchi et al. and Shao et al. discussed the effect of the extra electron, namely Ti^{3+}, to the Ti-L2,3 edge.14,23 From their results, more than 10%~20% of Ti^{3+} is necessary to observe clear spectrum changes. And the spectral changes induced only by the extra electron mainly appear around the first and third peaks of Ti-L2,3 edge, while that by the structural distortion appear around the second and fourth peaks (Fig. 4). By the presence of oxygen vacancy, both extra electron and structural distortions are introduced. Present study demonstrated that consideration of both effects is indispensable to correctly interpret the spectrum.

In summary, the effect of oxygen vacancy on the Ti-L2,3 ELNES of BaTiO3 was investigated through ab initio multiplet calculation. It was found that spectral differences between cubic and tetragonal BaTiO3 are quite small. From the present analysis, it was concluded that those Ti sites that are further away exert a greater influence on the spectral. Specifically, it was concluded that Ti-L2,3 ELNES has the potential to detect an oxygen vacancy concentration of 1%.

This study was supported by a Grant-in-Aid for Scientific Research 19053001, 22686059, and 23656395 from the MEXT of Japan. Some calculations were performed in Supercomputing system in ISSP-Univ. Tokyo.


FIG. 4. (Color online) Linear combine spectra of Ti-L2,3 of BaTiO3 that include oxygen vacancy:Vo. Broadening width of the black (thick) and red (thin) lines are 0.5 eV and 1.2 eV, respectively. (a) Ti next to oxygen vacancy is +4 (without extra electron), (b) Ti next to oxygen vacancy is +3 (with extra electron). Deep and light red and gray colors mean high and low concentrations, respectively.