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Published online: 29 Jan 2016.

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Calculated XANES Spectra of Cation Off-Centering in Bi(Mg$_{0.5}$Ti$_{0.5}$)O$_3$

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The x-ray absorption near edge spectra (XANES) of Bi, Mg and Ti in BMT for different off-centering magnitudes, associated with different structural models, were calculated by using first-principles calculations. The models studied include the high symmetric structure, two experimental proposed structures (based on an x-ray diffraction experiment) and the calculated fully relaxed structure (based on the calculated energy optimization). The features in the XANES spectra that relates with the off-center shift of cations were identified. Our calculated XANES will aid future experimental identifications of the detailed structure of BMT.

1. Introduction

Bi(Mg$_{0.5}$Ti$_{0.5}$)O$_3$, henceforth BMT, is one of the promising high-temperature Pb-free antiferroelectric materials for future applications because of its antiferroelectric-like displacement of Bi cations and its octahedral tilting characteristics. Because the cation ordering of materials in this class directly affects their antiferroelectric properties, it is important to understand the actual structure of BMT. X-ray diffraction (XRD) experiment by Khalyavin and coworkers [1] reveals the crystal structure of BMT. They found that the oxygen cages of Mg and Ti are tilted, and the cations are proposed to move off-center from the center of their oxygen cages by 0.287, 0.086 and 0.086 Å for Bi, Ti, and Mg, respectively. Because it is unclear whether BMT is an ordered or disordered alloy, it is almost impossible to accurately resolve the fine structure (off-centering) of each cation

species based on the XRD data. Recently, Suewattana and coworkers [2] performed first principles calculations starting from the experimental structures in Ref. [1], and found that these structures are under internal strain and could be relaxed reducing the total energy by ~ 0.7 eV per Bi. The cations are shifted from the center of the oxygen cages by large values, i.e., by 0.505, 0.300 and 0.232 Å, for Bi, Ti, and Mg, respectively. BMT is known to be centrosymmetric. Therefore, the total polarization is expected to vanish. However, the large cation displacements can lead to a large polarization if the effects are not canceling each other. Among various experimental characterization techniques, x-ray absorption spectroscopy (XAS), which can selectively probe the local structure around each element, is highly powerful and suitable to identify elemental specific local structures. However, to aid experimental identification, especially for the near edge region of the XAS called x-ray absorption near edge spectra (XANES), the first principles calculations of plausible structural models are generally needed to simulate the spectra for comparison with the measured results.

In this work, we report our calculations of Bi, Mg and Ti-edges XANES spectra of BMT for different structural models, in order to aid identification of the actual structure of this material. The models studied include a high symmetric structure (the B-cations reside at the center of their respective octahedral oxygen cages), the experimental proposed structures (based on XRD measurements [1]) and the calculated structure (based on the energy optimization calculations [2]).

2. Calculation Details

We calculated the XANES spectra of four different BMT structural models. The first one is a high symmetric (ideal) structure with the B-cations in the middle of the non-tilted cages. The lattice constant is optimized by using first principle calculation based on local density approximation (LDA) as implemented in VASP code. The computational details of the first principles calculations are similar to [3]. The k-points mesh of $3\times3\times3$ was used. The cut-off energy was set at 500 eV. For the cases that required structural optimizations, the structure was relaxed until the residue force on each and every atom became less than 0.001 Ry/Å. Another two structural models are the experimental ones proposed by Khalyavin and coworkers [1], based on XRD experiments. One structure is in *Pbam* and another one in *Pnnm* space group with Glazer's tilt systems of $a_+^- b_0^0 a_+^-$ and $a_+^- b_0^0 a_-^-$ respectively (subscripts " +" and "–" denote cation displacements along a given axis and the superscripts have their usual Glazer's meaning). The main difference between the two models proposed by Khalyavin *et al.* is the tilting of the diagonal axis of the oxygen cages, one tilted on the x axis and another on the y axis (see Ref [1] for detail). These two structures have very similar lattice parameters and during the calculations they were fixed at their respective experimental values of a = 11.3196, b = 5.6423, and c = 7.8314 Å for *Pbam*; and a = 11.3325, b = 5.6501, and c = 7.8159 Å for *Pnnm* structures. Note that these two structures are very similar when they are viewed in a large cluster size. Last model is the relaxed BMT structure by Suewattana *et al.* [2], calculated by using first principle calculation to relax the experimental proposed *Pbam* structure. The schematic crystal structures of all models are shown in Fig. 1. First principles (*ab initio*) calculations of the XANES spectra based on the structures of all four models were calculated by FEFF 8.2 codes [4,5]. The codes utilize a full multiple scattering approach based on *ab initio* overlapping muffin-tin potentials. The *ab initio* muffin-tin potentials were obtained by using self-consistent calculations with Hedin–Lundqvist exchange – correlation functions [6]. The self-consistent calculations were performed in the sphere radius
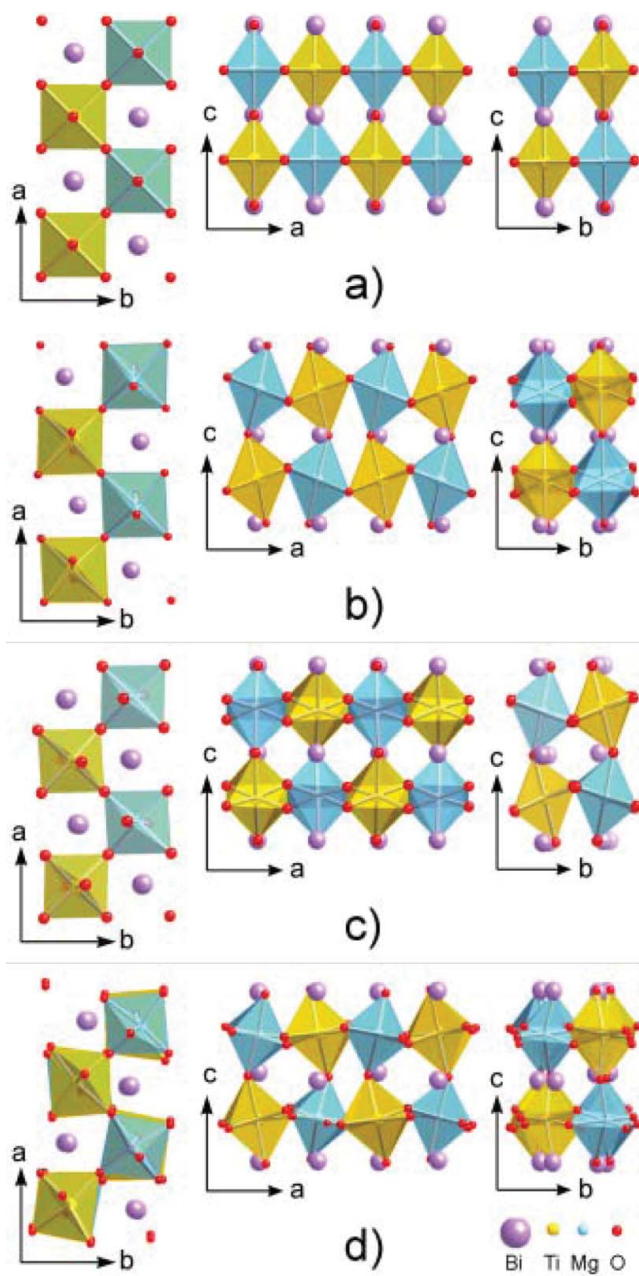
Figure 1. Structural models of BMT used in our calculation to calculate XANES spectra. a) Ideal cubic perovskite (high symmetric) structure – each cation is resided in the center of its oxygen cage, b) and c) the structural models proposed by Khalyavin et al. [1] based on their XRD data with the assumption of *Pbam* and *Pnnm* space group, respectively – the cations slightly shifted off-center, and d) the fully relaxed *Pbam* structure based on first-principles calculation proposed by Sue-wattana *et al.* [2].

10 Å (containing approximately 325 atoms) around the absorber cations. The electronic transitions associated with the XANES measurements must follow the dipole selection rule. An X-ray absorbance can be calculated by the Fermi's golden rule,

$$\mu \infty \sum_f \mid \langle f \mid D \mid i \rangle \mid^2 \delta(E_i - E_f + \hbar\omega)$$

where $\mu(\omega)$ is an x-ray absorbance, $|i\rangle$, $|f\rangle$, E_i, and E_f are the initial and final states and their corresponding energies, respectively, ω and D are the photon frequency and the dipole operator.

In this work, we chose to calculate Ti and Mg K-edge and Bi L_3-edge XANES. The choices are based on the x-ray energy range that is suitable for actual XAS measurement at most synchrotron facilities. At the Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima, Thailand, the XAS beamline can measure in the energy range of 1,250 – 10,000 eV; making it possible to measure Mg and Ti K-edge (Bi L_3-edge requires higher photon energy and is needed to be measured elsewhere). As a consequence of the selection rule, K-edge XANES corresponds to the dipole transition from $|s\rangle$ to $|p\rangle$ state, and L_3-edge corresponds to that of $|p\rangle$ to $|d\rangle$ and $|p\rangle$ to $|s\rangle$ states.

3. Results and Discussion

XANES technique is a powerful tool to investigate the local structure of the materials by speculating each element separately. Each element's x-ray absorption spectra take place at its characteristic x-ray energy and contain information of its neighboring arrangements. For BMT, there are three cations, Bi, Ti, and Mg. Therefore, the XANES measurement for their respective absorption edges can be used to reveal the local structure of this material. Here we calculated the expected spectra of all three cation absorbers for four BMT structural models. For the spectra of individual cation (Bi, Ti and Mg), the main features related with the off-center shifts of the cation will be discussed.

3.1 Bi L₃-edge XANES of BMT

The commonly known L_3 absorption edge energy of Bi is 13.418 keV. Therefore the Bi-L_3 edge XANES spectrum has the edge around this value. The calculated Bi L_3-edge XANES spectra of the four model structures of BMT are shown in Fig. 2. The XANES spectrum of the ideal structure is clearly different from those of other models in general. The high symmetry of the ideal structure leads to the clear and distinct features. There are three broad peaks at three main regions. The two spectra, generated from the structural models proposed by the experiment (henceforth "experimental models"), have very similar features due to their similarity in the local structure around the Bi absorber. The spectra contain a shoulder A around the edge area followed by the main peak B and broader peaks C, D and E at the energy of 13430, 13439, 13450, 13473, and 13516 eV, respectively. The spectrum from the calculated model with fully relaxed structure contains almost all features observed in the experimental spectra with some slight differences. In comparison with the experimental model spectra, the spectrum of the fully relaxed structure shows reduction in shoulder A and stronger peak B with the peak position slightly shifted toward higher energy by about 1 eV. Peak C moves closer to peak B and appears
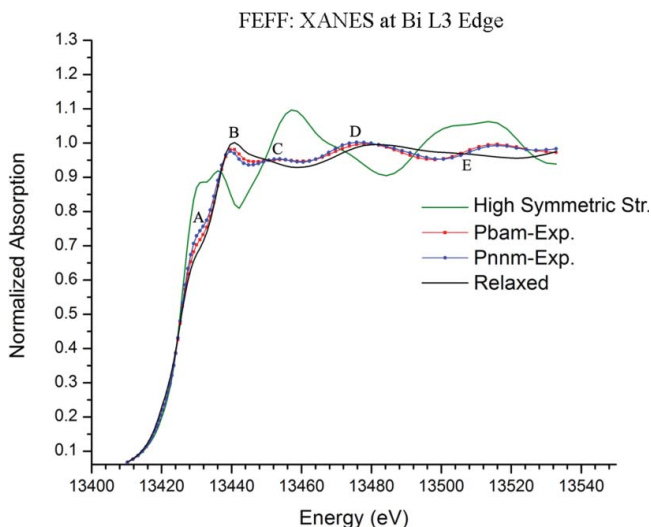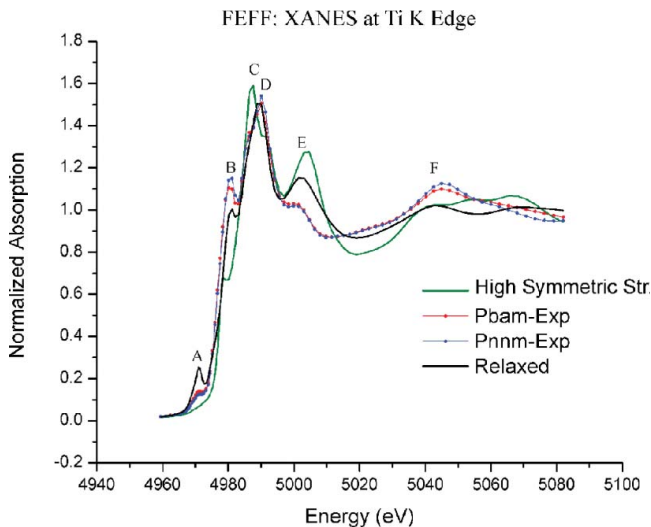
Figure 2. Bi L_3-edge XANES spectra of four different structural models of BMT.

only as a shoulder. Peak D is broader and is shifted to the higher energy; merging with peak E thus appears as a small shoulder. Among the four models, the Bi atom stays at the center of the oxygen cage for the ideal structure model, but shifted off-center by 0.287 Å for the experimental models and by 0.505 Å for the fully relaxed model. If we investigate the main features that varied as the Bi atom moves off-center we can associate the off-center shift with (1) the reduction in shoulder A – the ideal structure spectrum has this shoulder appear almost as a first peak (2) the enhancement and shifting toward higher energy of peak B – the ideal structure spectrum has peak B at about 13436 eV.

3.2 Ti K-edge XANES of BMT

The commonly known K absorption edge energy of Ti is at 4965 eV. Therefore the Ti K-edge XANES of BMT has the absorption edge around this value. The calculated Ti K-edge XANES spectra of the four model structures of BMT are shown in Fig. 3. All spectra can be characterized with a few common features. At 4971 eV, there is a pre-edge peak A followed by a shoulder/small peak B at 4981 eV and main peaks C and D at 4988 and 4990 eV. At higher energy, there are broad peaks E and F at 5004 and 5043 eV, respectively. Among four models, the Ti atom stays at the center of the oxygen cage for the ideal structure model, shifted off-center by only a small amount of 0.086 Å for the experimental models and by a large amount of 0.300 Å for the fully relaxed model. From Fig. 3, it is clearly seen that for the fully relaxed structure the pre-edge peak A is significantly enhanced. For the experimental model spectral, the peak only appears as a small bump while for the ideal structure peak A vanishes. These indicate that the magnitude of the pre-edge peak A goes with the off-centering of Ti. The increase in the pre-edge peak A as the Ti shifts off-center is consistent with the finding of Vdrinskii and co-workers [7]. Vdrinskii and co-workers calculated Ti K-edge XANES of various perovskite ATiO$_3$ and suggested that the pre-edge feature in Ti K-edge XANES spectrum can be used to identify Ti off-center shift. Beside the pre-edge peak A, the main peaks C and D are also affected by the off-center shift of Ti. When there is no off-center shift (the ideal structure
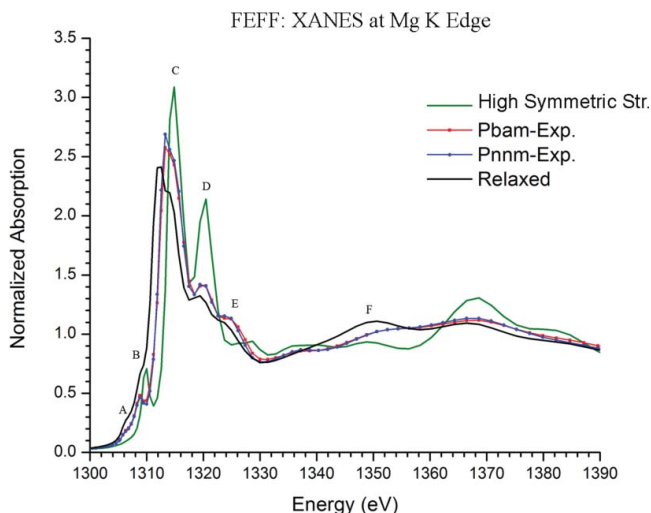
Figure 3. Ti *K*-edge XANES spectra of four different structural models of BMT.

spectrum) peak C is the largest and peak D appears to be a shoulder. When off-center shift takes place (the other three spectra) peak C is reduced to be a shoulder and peak D becomes dominant. However, the switching of the C and D peaks does not appear to go proportionally with the magnitude of the off-centering as the off-center shift for the case of experimental models are much smaller than the fully relaxed model be the C and D features are almost the same for these cases. We may conclude Peak B also appears to enhance and peak E appears to reduce as a consequence of off-center shift of Ti. However, the magnitude of the enhancement and reduction does not directly related with the amount of the shift of Ti. As we can see from the spectra, the fully relaxed model has the Ti shifted off-center the most but the enhancement in peak B and reduction in peak E (compared to that of the ideal structure spectrum) are smaller than the experimental model spectra.

3.3 Mg **K**-*edge XANES of BMT*

The commonly known *K* absorption edge energy of Mg is at 1305 eV. Therefore the Mg *K*-edge XANES of BMT has the absorption edge around this value. The calculated Mg *K*-edge XANES spectra of the four model structures of BMT are shown in Fig. 4. All spectra can be characterized with a few common features. At 1307 and 1309 eV, there are pre-edge shoulders A and B followed by the main peak C at 1314 eV and smaller peaks D and E at 1320 and 1324 eV. At higher energy, there is a broad peak F at 1350 eV. Among the four models, the Mg atom stays at the center of the oxygen cage for the ideal structure model, shifted off-center by only a small amount of 0.086 Å for the experimental models and by a large amount of 0.232 Å for the fully relaxed model. From Fig. 4, it is apparent that the pre-edge shoulder A is related to the off-center magnitude of Mg. The pre-edge shoulder A disappears in the ideal structure where there is no off-centering. It is getting stronger in the experimental spectral and is strongest in the relaxed structure as the Mg off-centering shift increases. Main peak C and peak D also change with respect to the off-center shift of Mg. As Mg shifts off-center (starting from at the center in the ideal

Figure 4. Mg *K*-edge XANES spectra of four different structural models of BMT.

model to slightly shifted off-center in the experimental model to the most off-center shift in the fully relaxed model) peak C is getting broader and shifted toward the lower energy while peak D is reduced. Note that, instead of viewing the main peak C to shift toward the lower energy, one can view the shift as the shift of the absorption edge position down to the lower photon energy as Mg shifts off-center. A small hump at E is also the result of the off-center shift of Mg. However, the magnitude of the enhancement and reduction does not directly relate to the amount of the shift of Mg. Finally the peak F, only occurs in the relaxed model and appears as a broad shoulder in the experimental model; suggesting that it is associated with the Mg off-center shift.

4. Conclusion

The Bi L_3-, Ti *K*- and Mg *K*-edges XANES spectra of Bi(Mg$_{0.5}$Ti$_{0.5}$)O$_3$ were calculated based on first principles calculations. Four different crystal structure models were used for the simulation of the XANES spectra ranging from (1) the high symmetric structure where the cations are located perfectly at the center of oxygen cages, to (2) the model proposed based on XRD measurements that has the cations shifted off-center, and (3) finally the fully relaxed structure model based on first principles calculations that found the cations significantly shifted off-center. Because different models have different off-center shift of the cations, the identification of the features in the XANES spectra that relates with the off-center shift can be identified.

- For Bi L_3-edge XANES, the reduction in the first shoulder (A) at 13430 eV and the enhancement and shifting toward higher energy of the main peak (B) at 13439 eV are the main features associated with the off-center shift of Bi.
- For Ti *K*-edge XANES, the off-center shift of Ti leads to the increase in the pre-edge peak (A) at 4971 eV.
- For Mg *K*-edge XANES, the off-center shift of Mg leads to the shift of the edge energy down to the lower photon energy.

These observed features would aid future experimental identification of the cation local structures in this material.

Acknowledgment

Funding

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