AMTC Letters
Vol. 2 (2010)

Local distortion in defective fluorite Bi_2O_3 derived by first principles lattice dynamics calculations

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δ-Bi_2O_3 is known as a high oxide-ionic conductor. It forms a defective fluorite (df) structure in which a quarter of O sites are vacant. The structure has been investigated both by experiments and calculations to obtain guiding principles of good ionic conductors. However, most of theoretical results in the past are inconsistent to experimental data [1,2]. Firstly, they show metallic or semimetallic electronic structure, while δ-Bi_2O_3 exhibits a clear band gap experimentally [3]. Secondary, the formation energy of δ-Bi_2O_3 relative to α-Bi_2O_3 is too high to explain the phase transition behavior. In this paper, structures and energetics of df-Bi_2O_3 are pursued on the basis of first principles lattice dynamics calculations.

Structure models were constructed by introducing vacant sites into a quarter of O sites of a fluorite structure and each structure model was optimized. Plane-wave basis PAW method with GGA as implemented in VASP code [4] was used for the first-principles calculations. After the optimization, lattice vibrations were calculated by the frozen phonon method with *fropho* code [5,6].

Figure 1 shows the phonon dispersion curves of a df-Bi_2O_3 with the vacant sites aligned along a <111> direction (<111> model). The imaginary value of the frequency illustrated below zero indicates that the structure is at a local maximum of the potential surface and unstable against the corresponding lattice vibration. It is clear that this structure is dynamically unstable against a wide variety of vibrations. Therefore, a new structure is constructed by introducing displacement along the strongest imaginary frequency vibration mode at the R point ($\boldsymbol{k}$=(1/2, 1/2, 1/2)) and optimized again. Although the original and new structures have different symmetry and different size of unit cells, the atomic arrangement in the O sublattice is the same. Hereafter, we call the original and new structures high symmetric (HS) and low symmetric (LS) structures, respectively. Both structures have one Bi site, surrounded by eight O sites where two of them are vacant. Figure 2 shows the distance between the Bi atom and the eight O sites in the HS and LS structures. The center of the four nearest Bi atoms is considered as the position of the vacant site. All of the distances are the same in the HS structure, while in the LS structure a half of them is shortened and the others are elongated owing to the local distortion. The local distortion lowered energy by 1.6 eV/formula-unit. The electronic structure also changes dramatically. Figure 3 is the electronic density of states of the HS and LS structures. The Fermi energy and the top of the valence band are set to zero on the vertical axis for the HS and LS structures, respectively. As is shown in Fig. 3, while no band gap can be seen in the HS structure, clear band gap appears in the LS structure.

Such a local distortion with a reduction of energy can also be seen in other arrangements of df-Bi_2O_3. The local distortion and the symmetry break should be the nature of df-Bi_2O_3. The appropriate inclusion of the local distortion is therefore essential in reproducing atomic and electronic structures.

This study was supported by both a Grant-in-Aid for Scientific Research (A) and a Grant-in-Aid for Scientific Research on Priority Areas “Nano Materials Science for Atomic Scale Modification 474” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. A.M. thanks the Japan Society for the Promotion of Science.

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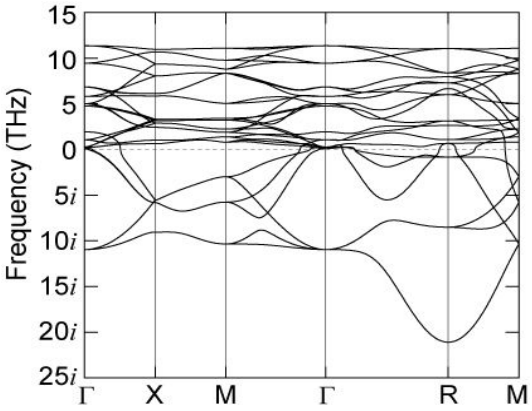

FIG. 1. Phonon dispersion curves of a df-Bi_2O_3 with the vacant sites aligned along a <111> direction

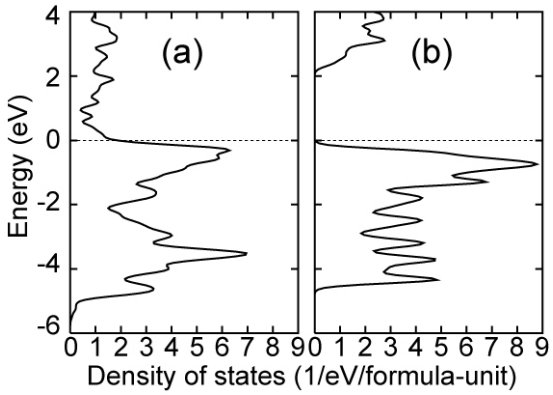

FIG. 3. Electronic density of states in (a) HS and (b) LS structures in the <111> model.

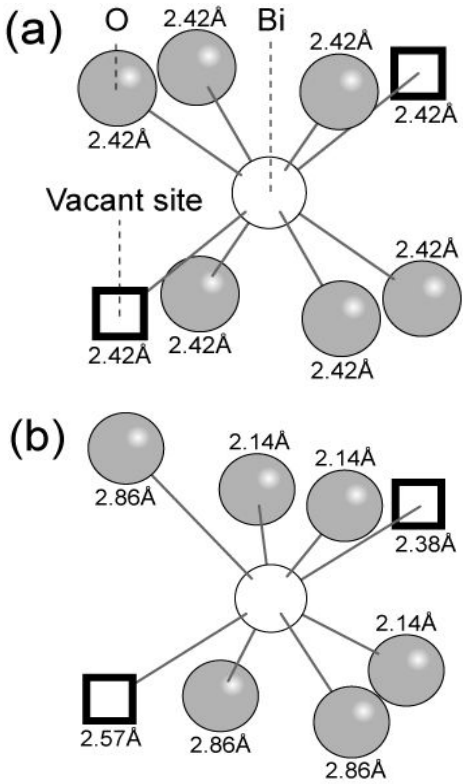

FIG. 2. The distance between the Bi atom and the nearest eight O sites in (a) HS and (b) LS structures in the <111> model.