AMTC Letters
Vol. 1 (2008)

Atomic arrangement of δ-Bi_2O_3 with defective fluorite structure by first-principles calculations

Akifumi Matsumoto[1], Atsuto Seko[2], Yukinori Koyama[1] and Isao Tanaka[1,3]

[1]Department of Materials Science and Engineering, Kyoto University, Kyoto, 606-8501, Japan
[2]Pioneering Research Unit for Next Generation, Kyoto University, Kyoto, 615-8530, Japan
[3]Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan

Bi_2O_3 forms a monoclinic phase (α-Bi_2O_3) at room temperature, and transforms into a cubic phase (δ-Bi_2O_3) at about 1000 K [1, 2]. δ-Bi_2O_3 exhibits high oxide-ion conduction, while α-Bi_2O_3 does not [3]. Hence, the atomic structure of δ-Bi_2O_3, especially its relationship with the ionic conduction, is interesting. The framework of δ-Bi_2O_3 is the fluorite structure. Since the ratio of Bi atoms to oxygen is 2 to 3, a quarter of the oxygen sites is vacant for charge neutrality. The arrangement of the occupied and vacant sites on the oxygen sublattice has been reported as disordered [4, 5]. However, local structures of δ-Bi_2O_3 have been left open, although they are essential information to discuss the origin of the ionic conduction.

The difficulty in treating δ-Bi_2O_3 by first-principles calculations resides in the disordered arrangement of oxygen site vacancies. In the present study, we have examined many structural models with different arrangements of oxygen site vacancies. First-principles calculations within the generalized gradient approximation were made using the plane-wave basis projector-augmented wave method as implemented in the VASP code [6].

We first examine the defective structure within the unit cell of the fluorite (10 atoms). There are only 3 independent arrangements with the vacant sites ordered in <001>, <011>, and <111> directions, respectively. We hereafter call them 001-, 011- and 111-model, respectively. They have high symmetry if oxygen atoms are set at the ideal positions of the fluorite structure. However, when a small displacement is introduced for every atom to break the symmetry, their total energies are significantly decreased. For instance, the 111-model shows lower energy by 1.4 eV/formula-unit by the breaking of the symmetry. In order to overcome the restriction of the small cell, a set of larger supercells (80 atoms, 2×2×2 expansion of the unit cell) is examined. In addition, calculations of Y_2O_3 using the same set of models are made. Similar to some other rare-earth oxides, Y_2O_3 is known to form the bixbyite structure under ordinary conditions. The bixbyite structure is composed of octants that are identical to the 111-model of the defective fluorite structure as shown in Fig. 1. It can therefore be included in the 80-atom cell examined in the present study.

Figure 2 shows relative energies of different models for both δ-Bi_2O_3 and Y_2O_3. Energies of four corresponding structures are connected by dotted lines. Both of δ-Bi_2O_3 and Y_2O_3 show the lowest energy with the bixbyte structure. In δ-Bi_2O_3, the 001-model also shows the lowest energy. As can be seen in Fig. 2, δ-Bi_2O_3 shows much smaller variation in energy than Y_2O_3 among different models. This should be related to the significant disordering of the oxygen site vacancies in δ-Bi_2O_3. At high temperatures, configurational entropy contribution overcomes the small internal energy differences among different local structures, leading to the stabilization of the disordered structures.

This study was supported by Grant-in-Aid for Scientific Research on Priority Areas "Nano Materials Science for Atomic Scale Modification 474" from Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

References

[1] H. Harwig, A. Gerards, *Thermochim. Acta*, **28** (1979) 121.
[2] N. Sammes, G. Tompsett, H. Nafe, F. Aldinger, *J. Europ. Ceram. Soc.*, **19** (1999) 1801.
[3] T. Takahashi, H. Iwahara, T. Arao, *J. Appl. Electrochem.*, **5** (1975) 187.

[4] G. Gattow, H. Schroder, *Z. Anorg. Allg. Chem.*, **318** (1962) 176.
[5] M. Yashima, D. Ishimura, *Chem. Phys. Lett.*, **378** (2003) 395.
[6] G. Kresse, *Phys. Rev. B*, **54** (1996) 11169

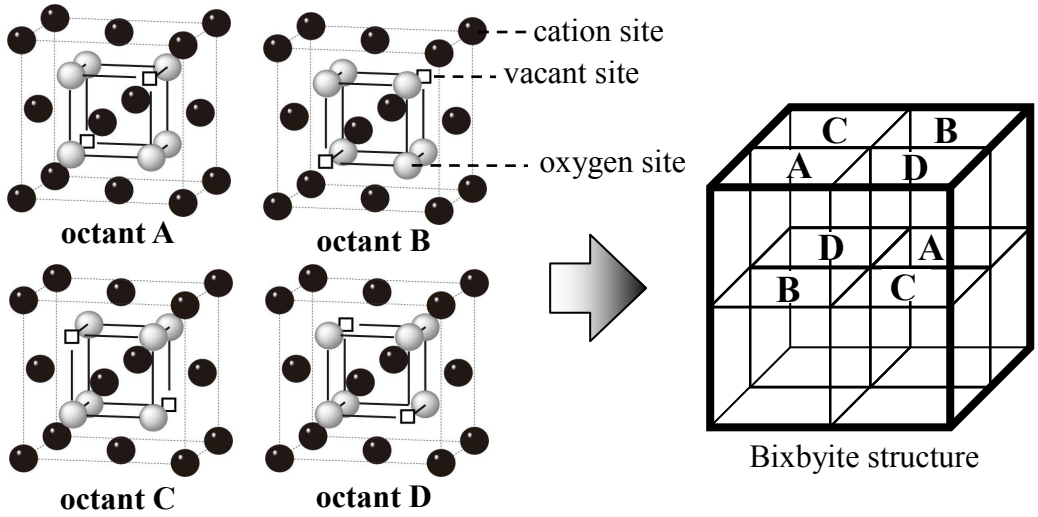

Fig. 1. The construction of the bixbyite structure by octants that are identical to the 111-model of the defective fluorite structure. Black, light-gray spheres and white square denote cation, oxygen, and vacant sites, respectively.

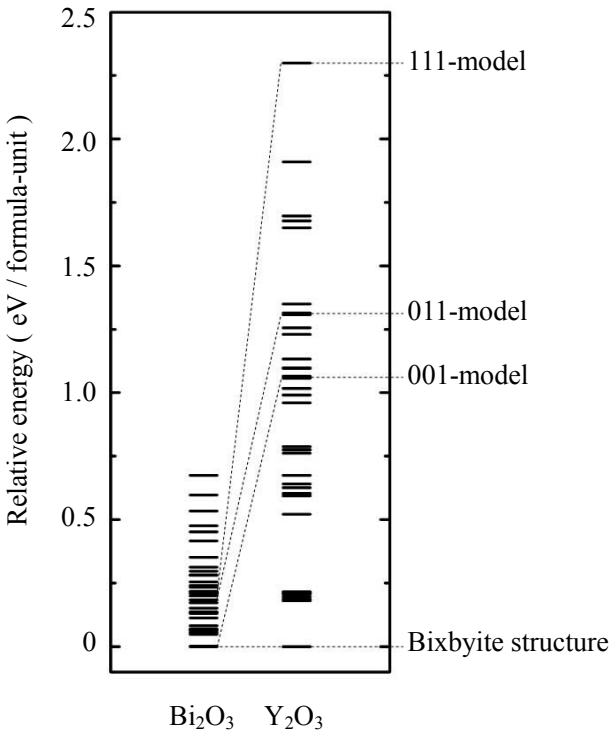

Fig. 2. Relative energies of a set of different models for δ-Bi_2O_3 and Y_2O_3 within the defective fluorite structure composed of 80 atoms.