Structure and Dynamics of Oxide Crystals at High Temperatures by First Principles Calculations

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Phonon modes of a given crystal can be computed by a set of first principles calculations with finite atomic displacements from those in the original crystal. When the crystal is dynamically unstable, imaginary modes appear. According to the eigenvectors of the imaginary modes, the crystal symmetry can be lowered and the atomic positions can be displaced until the positions where all of the imaginary modes disappear. Dynamically stable structures and the transition pathway from the original structure can be thereby given.

Bi_2O_3 is known to exhibit high oxide-ion conduction in the δ-phase. It forms a cubic defective fluorite (df) structure in which a quarter of O sites are vacant. An example of imaginary modes that appears in a df structure with an array of vacant oxygen sites along <111> direction is shown in Fig.1(a). The crystal symmetry is lowered by introducing a set of displacements along the eigenvectors of imaginary modes. The resultant low symmetry structure is shown in Fig. 1(b). The local distortion has lowered energy by 1.6 eV/formula-unit. The low symmetry structure is isomorph to arsenolite that is known to be formed in As_2O_3 and Sb_2O_3, but yet-unknown in Bi_2O_3 [1].

In order to examine the average structure of the disordered δ-Bi_2O_3, first principles molecular dynamics simulation is performed at 1100 K for 1 ns [2]. Figure 2 shows the cross section of the averaged oxygen distribution density in an octant in the 80-atom simulation cell. The cross section is made on the plane that includes two 32*f* oxygen sites as shown by black balls in the figure. The elliptic shape of the distribution implies that oxygen atoms occupy not only the central 8*c* sites but also 32*f* sites. The site occupancy and the internal coordinates of two sites are found to be fairly close to those obtained by *in-situ* neutron diffraction analysis at 1051 K [3].

Both of two different kinds of calculations indicate the formation of the locally distorted low symmetric structures in Bi_2O_3. The appropriate inclusion of the local distortion is therefore essential on the examination the structure-property relationships.

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References

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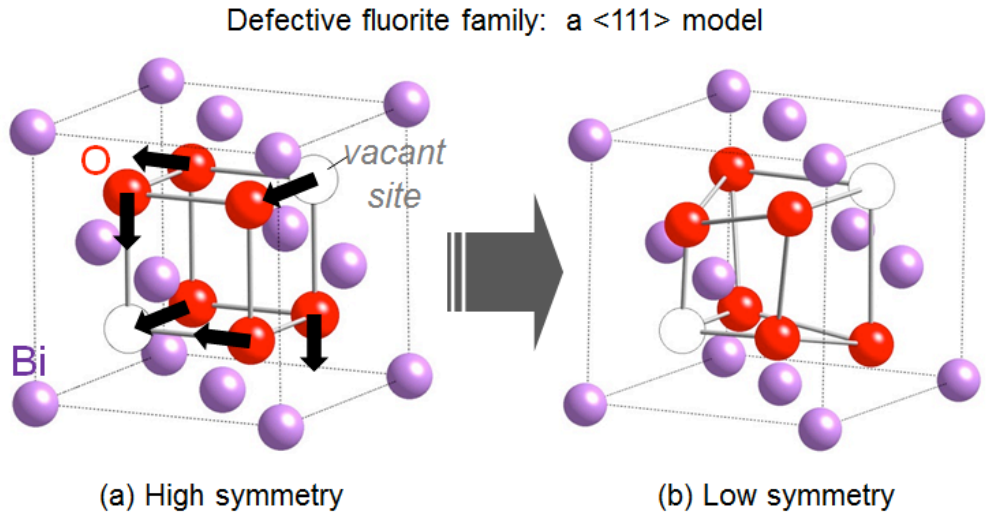

FIG.1. A <111> model of the defective fluorite family. Black arrows show the eigenvectors of an imaginary mode that appears in the high symmetry crystal.

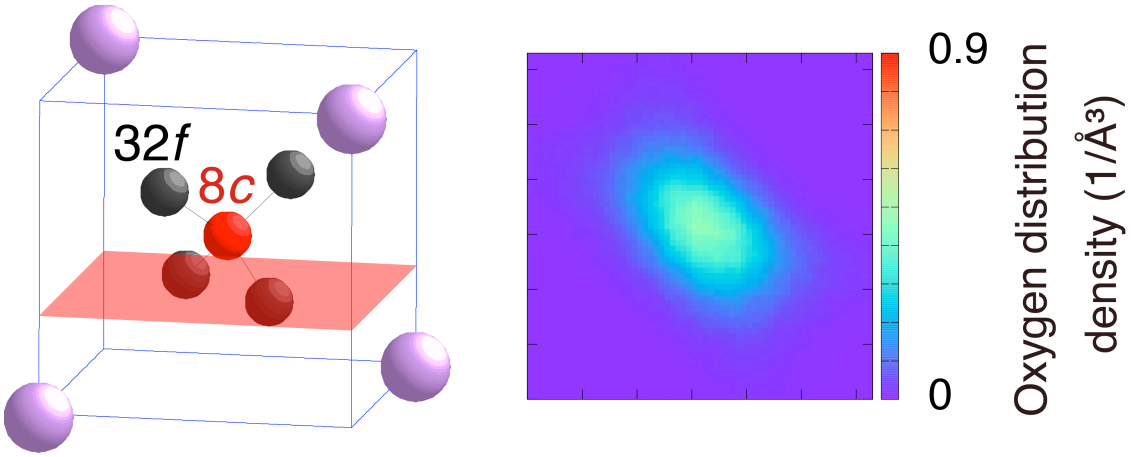

FIG.2. A cross-sectional view of the averaged oxygen distribution density in octants that is obtained by the first principles molecular dynamic simulation. 32*f* and 8*c* denote Wyckoff positions in the cubic fluorite structure.