Ionic transport properties in doped $\delta$-Bi$_2$O$_3$

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Abstract. We have performed the first principles calculations on doped $\delta$-Bi$_2$O$_3$ to investigate ionic conductivity. The crystal structure and the ionic conductivity are discussed in total energy and density of states (DOS) from the calculations. The stabilized $\delta$-phase Bi$_2$O$_3$ doped rare-earth metal was explained from DOS data. By doping Ca, Sr, La, Gd or Sm, the ion conductivity monotonically decreases, while doping with impurity Y, Tb, Dy, Er or Tm, the ion conductivity firstly increases and then decrease. Our results support the effective oxygen vacancies mechanism.

1. Introduction
$\delta$-Bi$_2$O$_3$ is recognized as one of the most technologically important oxide ion conductors because it can be used as the solid electrolyte material in fuel cells, high temperature oxygen pumps and many different sensors[1-3]. So the pure and doped $\delta$-Bi$_2$O$_3$ have been extensively studied in experiments. The $\delta$-phase is one of the four known polytypes of Bi$_2$O$_3$ solid, and it is stable only in the temperature range from 730°C to its melting temperature of 825°C[4]. However, $\delta$-Bi$_2$O$_3$ can be stabilized by dopants which include rare-earth elements and many oxide impurities (from divalent to hexavalent oxides)[5]. The ionic conductivity of pure $\delta$-Bi$_2$O$_3$ is known to arise from the oxygen vacancies and the concentration of such vacancies can be as high as 25% of the total amount of anions. With such a high concentration of oxygen vacancies, the conductivity of $\delta$-Bi$_2$O$_3$ can be two orders of magnitude higher than that of the common oxide conductor, zirconia[6]. In addition, the conductivity can be further raised by the incorporation of appropriate dopants, particularly rare-earth dopants, into $\delta$-Bi$_2$O$_3$[7-11].

At the same time, the pure and oxide-doped $\delta$-Bi$_2$O$_3$ have already been studied theoretically. But these studies mainly concentrated on its atomic and electronic structures which are oxygen vacancy distributions and band structures in this crystal[12-14]. It is not enough to clearly understand the ionic transport properties of doped $\delta$-Bi$_2$O$_3$. To address the lack of theoretical data for alkaline-earth and rare-earth metals doped $\delta$-Bi$_2$O$_3$, we have calculated the crystal structure and ionic conductivity properties of supercell Bi$_{16-2x}$M$_x$O$_{24}$ ($x=1, 2, 4$) with the first principles method and with a large variety of doping elements for $M$.

2. Computational details
The total energy obtained from DFT calculations is used to analyze the ionic conductivity. In this calculation, we employ the highly precise full-potential linearized augmented plane-wave (FP-LAPW) method[15,16] which is carried out using a well-developed package WIEN2k code[17]. The exchange-correlation energy is treated in the generalized gradient approximations.
A cutoff energy of $-9.0$ Ry is used. The muffin-tin spheres radii are 2.0, 1.6, and 2.0 a.u. for Bi, O and impurity atom, respectively. These give a total energy that is converged within 0.1 mRy.

The lattice constant of $\delta$-Bi$_2$O$_3$ is taken from the experimental values of 5.6595 Å[19]. In several possible oxygen vacancy orderings, the $\langle 111 \rangle$ vacancy direction is adopted, for that $\delta$-Bi$_2$O$_3$ is stabilized by rare-earth metal doping[6]. Fig. 1 shows the unit cell and $2\times2\times1$ supercell used in this study. To investigate the conductivity due to the moving of oxygen ions, the oxygen atoms are displaced along anions axis and pass through saddle point between two Bi atoms in this supercell. During the moving of oxygen atoms, the total energy difference is calculated, which means that the diffusion barrier(or activation energy $\Delta E$) is obtained. Therefore the conductivity can be analyzed from the approximately describing: $\sigma = \sigma_0 \cdot \exp(-\Delta E/kT)$, where $\sigma_0$ is the pre-exponential factor. In this calculation, the relaxation is not taken into consideration because relaxation at saddle point can not be derived owing to the migration of oxygen ions to more stable position during optimization.

![Figure 1.](image)

**Figure 1.** (a) the unit cell for $\delta$-Bi$_2$O$_3$ with $\langle 111 \rangle$-direction vacancy. (b) supercell ($2 \times 2 \times 1$) chosen in the calculations. Big spheres and small spheres are Bi and O atoms, respectively.

### 3. Results and discussions

To reduce the crystal distortion, we mainly study the dopant whose ionic radius is close to that of Bi ion, such as Ca, Sr, Y and partial rare-earth elements. Fig. 2 shows the variation of activation energy with doping number $x$. From $x = 1$ to $x = 4$, the doping leads to ionic conductivity enhancing. There are two tendencies on activation energy variations with dopant concentration. Firstly, containing impurity Ca, Sr, La, Gd, Ho or Sm, the activation energy increases monotonically with increasing the dopant concentration. Secondly, for impurity Y, Tb, Dy, Er and Tm, the activation energy exhibits the variation from decreasing to increasing with the concentration. We may understand these behaviors by analyzing the variations of oxygen vacancy.

The ion conductivity arises from orienting jump of oxygen ions among effective oxygen vacancies under electric field. The conductivity increases along with oxygen vacancies. However, if the number of oxygen vacancies reaches a certain value, the oxygen vacancies begin to become ordering. So that under the Coulombic interaction and defect associates[21], the cations form the defect pairs and this results in the weakening of oxygen ionic diffusion because of the decrease of effective vacancies.

Among oxygen vacancies in $\delta$-Bi$_2$O$_3$, except for 25% of intrinsic ones, in addition, vacancies come from the substitution of impurities. When the trivalent Bi is replaced by divalent Ca and Sr, the nonequivalent substitutional incorporation will result in positive oxygen vacancies as charges compensating defects. At the same time, each Bi atom has one lone pair electron whose volume is approximately equal to that of one oxygen anion. So doping induces the increase of oxygen vacancies. For trivalent Y or rare-earth metal, the compensation of charges does not
exist at substituting. The oxygen vacancies mainly result from the space of lone pair electron in Bi atom or crystal distortion.

The plot of density of states is shown in Fig. 3. The ionic bond is formed in the range of \(-5.5 \sim 0\) eV. Due to charge transferring from Bi to O upon doping, the width of bonding states becomes narrow and the ionic interaction of Bi and O becomes weak. This leads to the enhancement of the ion conductivity.

For the case of Ca doping, the number of density of states at Fermi level \(N_{E_F}\) of oxygen are about 12.5, 14 and 19.5 states/eV for three concentrations \((x=1, 2, 4)\), respectively. The rise of \(N_{E_F}\) means the increase of oxygen defects so that the vacancies concentration increases with dopants in the case of Ca. As discussed above, since the large number of vacancies exceed the saturation value, big crystal distortion occurs and defect associates form. Actually the effective vacancy decreases, which leads to the decrease of ion conductivity. This is the reason we see the monotonously increased activation energy in Fig. 2.

While a different behavior is presented in the case of Y doping (Fig. 3). The \(N_{E_F}\), which value is less than that of Ca doped system, slightly increases and then decreases from 8.5 to
9.0 then to 3.0 states/eV. Its crystal distortion is smaller than that of Ca doping. The small change of $N_{\text{EF}}$ for Y doping leads to that the oxygen vacancies concentration does not reach the saturation. The variation of oxygen vacancy from increasing to decreasing induces a maximum of ion conductivity. In our calculations, the same variation of activation energy is also obtained in this system by doping Tb, Dy, Er or Tm.

For La and Sm doping, their variation of activation energy are similar seen in Fig. 2. The DOSs are obviously migrating toward lower energy and the $N_{\text{EF}}$ gradually decreases with the impurity content increasing: 9.4, 6.3 and 2.1 states/eV for La and 8.5, 4.4 and 3.9 states/eV for Sm. This implies that the system becomes more stable because the defect of oxygen vacancy decreases. The ion conductivity gradually decreases with the impurity La, Sm concentration increasing, which is in agreement with the experiments[8-10]. Furthermore, the less occupation of $\delta$-phase by rare-earth metal doping is another evidence of that this system is more stable than that by Ca or Sr doping.

4. Summary
Briefly, the more stable system doping with rare-earth metal is established. The effective oxygen vacancies mechanism is used to explain ion conductivity in doped Bi$_2$O$_3$ materials. We conclude that one maximum of conductivity can be obtained at least with increasing the dopant concentration. The results exhibit that: doping with Ca, Sr, La, Gd or Sm, the monotonically decreasing ion conductivities are presented; while doping with Y, Tb, Dy, Er or Tm, the ion conductivities firstly increase and then decrease, therefore a maximum value is obtained. These calculation results agree well with the known experimental data.

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5. References
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