First principles study on oxygen vacancy formation in rock salt-type oxides MO (M: Mg, Ca, Sr and Ba)

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Abstract

Oxygen vacancy formation energies in rock salt-type oxides MO (M: Mg, Ca, Sr, and Ba) were investigated using a first-principles projector augmented wave method based on a density functional theory. Finite-size cell interactions were corrected by calculating with several sizes of the supercells up to 512 atoms, and a band gap correction for a neutral oxygen vacancy was also performed. It was commonly found that the vacancy state induced by the oxygen vacancy is placed below the conduction band minimum (CBM) in all compounds. The position of the vacancy state is deep in MgO and becomes closer to CBM in CaO, SrO, and BaO in that order. By analyzing the oxygen chemical potential dependence, it was found that the formation of oxygen vacancy is preferable under the reduction atmosphere in all compounds. In addition, it was also found that the oxygen vacancy formation energies in MgO, CaO, and SrO are similar to each other, whereas BaO shows lower formation energy than others, indicating that the oxygen vacancy is more abundant in BaO as compared with other rock salt-type oxides. The reason for the lower oxygen vacancy formation energy in BaO is discussed.
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1. Introduction

Rock salt-type oxide is usually composed of oxygen and divalent cation (M), and a number of rock salt-type oxides have been studied for numerous applications. For instance, MgO is a typical rock salt-type oxide, and it has been used in many applications such as an insulator of electric devices, a support in catalysis, and a substrate for thin film depositions [1–4]. Due to its importance, material properties of MgO, such as grain growth behavior, diffusion behavior, grain boundary structure, surface structure, and so on, have been investigated experimentally and theoretically so far [5–8]. In addition to those properties, the defect formation behaviors in the rock salt-type oxides have been investigated because they affect the electric properties and the atomic migration behaviors of rock salt-type oxides. To investigate the defect formation behaviors in the rock salt-type oxides, theoretical calculations using a first principles method and an empirical

potential method have been used [8–12]. Especially, using the first principles method, the dependence of the defect energetics on atmospheres and Fermi energy, which are both important factors in actual applications, can be discussed. Thus, to obtain comprehensive information on the defect energetics in the rock-salt type oxides, use of the first principles calculation is important. On the other hand, although first principles calculations of the defect energetics in MgO have been reported by some groups, reports on other rock salt-type oxides, such as CaO, SrO, and BaO, are very limited.

In this study, the oxygen vacancy formation energies in four types of rock salt-type oxides, MgO, CaO, SrO, and BaO, were systematically investigated using a first-principles projector augmented wave (PAW) method based on a density functional theory (DFT), and the vacancy formation behaviors in those rock salt-type oxides were compared with each other. In the present study, the calculation error derived from a finite-size cell interaction was corrected by the method proposed by Makov and Payne [13]. This finite-size correction is known to be important to investigate the defect energetics of functional

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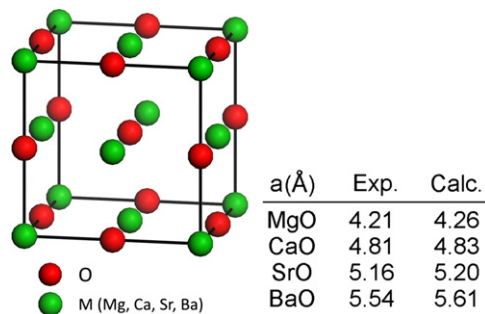| a(Å)	Exp.	Calc.
MgO	4.21	4.26
CaO	4.81	4.83
SrO	5.16	5.20
BaO	5.54	5.61

○ O
● M (Mg, Ca, Sr, Ba)

Fig. 1. Schematic view of unit cell of rock salt-type oxides, and experimental and calculated lattice constants of MO (M: Mg, Ca, Sr, and Ba).

materials [14–16]. In this study, the finite-size cell dependences were investigated by calculating with various sizes of supercells up to 512 atoms. In addition, the band gap correction for a neutral oxygen vacancy, which is also important for the calculation of wide gap materials, was also performed. Through this study, the formation energies of neutral and charged oxygen vacancies in MgO, CaO, SrO, and BaO were systematically investigated.

2. Methodology

First-principles PAW calculations with the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) functional were performed using the VASP code [17–19]. A plane-wave cut off energy (E_{cut}) of 500 eV was used. For oxygen, $2s^2$ and $2p^4$ electrons were considered as valence electrons, while $2p^6$ and $3s^2$ for Mg, $3p^6$ and $4s^2$ for Ca, $4s^2$, $4p^6$ and $5s^2$ for Sr, and $5s^2$, $5p^6$ and $6s^2$ for Ba were considered as valence electrons, respectively. Fig. 1 shows schematic structure of a unit cell of the rock salt-type oxides.

Before going to the supercell calculations for the vacancies, calculations of the perfect MO were carried out. The primitive cells were calculated using $24 \times 24 \times 24$ k-point mesh generated by the Monkhorst–Pack scheme (1300 irreducible k-points) [20]. Calculated and experimental lattice constants are shown in Fig. 1. It is found that the optimized lattice parameters are in good agreement with the experimental and previously reported theoretical values (Fig. 1) [21–24]. Based on the optimized structure of the perfect MO, the primitive cells and unit cells were expanded to make large supercells for the vacancy calculations.

To introduce an isolated oxygen vacancy, an interior oxygen atom was removed from the supercells. In order to take account of atomistic relaxation around the vacancy, all atoms in the supercells were allowed to be relaxed until the residual force becomes less than 0.05 eV/Å under the fixed volume condition. In the supercell calculations, numerical integrations over the Brillouin zone were performed at the Γ-point for every size of the supercells.

The formation energies of the vacancies in MO were calculated from total energies of the supercells, based on the standard formalism by Zhang and Northrup [25].

For compound systems, formation energies of vacancies depend on the atomic chemical potentials of atoms and the electron chemical potential i.e., Fermi energy. For a vacancy with a charge state q, the formation energy is given by

$$E_T = E_T(\text{defect}:q) - \{E_T(\text{perfect}) - \mu_O\} + n(\varepsilon_F + E_{VBM})$$

where $E_T(\text{defect}:q)$ and $E_T(\text{perfect})$ are the total energy of the supercell containing an oxygen vacancy in a charged state q and that of the perfect supercell, respectively. n_O is the number of oxygen atoms removed from the perfect supercell to introduce isolated vacancies. μ_O is the atomic chemical potential of oxygen, and ε_F is the Fermi energy measured from valence band maximum (VBM) [26]. For each vacancy species, its charge state q, varying from neutral to fully ionized, was considered, namely 0 and +2 for an oxygen vacancy. For charged defects, the total charge of supercells was neutralized by using background charge.

The formation energies of vacancies in MO also depend on the chemical potentials of the oxygen atom. The chemical potential of oxygen was determined from the equilibrium conditions of the phases containing M and oxygen. In order to consider the chemical potentials, the first-principles calculations were performed for primitive structure of each element. Then chemical potentials could be defined as

$$\mu_O(\text{O-rich}) = \mu_O(\text{O primitive cell}),$$

$$\mu_O(\text{M-rich}) = \mu_{MO} - \mu_M(\text{M primitive cell}).$$

The Fermi level ε_F was varied within the band gap. The calculated band gap was found to be 4.37 eV for MgO, 3.53 eV for CaO, 3.17 eV for SrO and 1.98 eV for BaO, by calculating the total energies of the charged and neutral cells. This value is lower than the experimental values of 7.6 eV for MgO, 6.9 eV for CaO, 6.4 eV for SrO, and 4.4 eV for BaO [27,28]. This difference between the calculated and experimental band gaps is hereafter called ΔE_g. By the presence of the oxygen vacancy, the vacancy state is usually generated below the conduction band minimum (CBM), and extra electrons are introduced to the vacancy state. Thus, this band gap error in the calculation often influences the formation energy of the neutral oxygen vacancy. To correct this band gap error, the formation energy of a neutral oxygen vacancy was adjusted to be the sum of the calculated value and ΔE_g multiplied by the number of electrons m at the donor levels, so that the m is 2 in the case of present study.

In addition, finite-cell size correction was also performed in this study. In the supercell calculation of the charged vacancies using periodic boundary conditions, Coulomb interactions are noted between the charged vacancy and anticlastic background charge, so called jellium, depending on the size of the supercells. It is necessary to correct this spurious interaction of charged vacancies to evaluate their formation energies. Errors in the defect formation energies due to the spurious electrostatic interaction in the finite-sized cells were corrected using the scheme proposed by