First-principles Study on Defect Formation and Atomic Migration in Rhombohedral-LaAlO$_3$

Takashi Yamamoto[1] and Teruyasu Mizoguchi[1]

[1]Institute of Industrial Science, The University of Tokyo, Tokyo 153-8505, Japan

Lanthanum aluminate (LaAlO$_3$) is often used for functional electroceramic devices with a wide range of technological applications. Although defect formation behaviors and atomic migration behaviors influence critically on its electronic properties, there are few reports about defect formations and diffusion behaviors of LaAlO$_3$ [1-4]. In this study, intrinsic defect formation energetics and atomic migration behaviors in rhombohedral-LaAlO$_3$ are investigated by using a first-principles projector augmented wave (PAW) calculation.

First principles PAW calculations were carried out using VASP code. The cut-off energy for plane wave basis sets was set to 500eV. All of atoms were allowed to relax until their residual force converges to 0.1eV/Å with fixed lattice volume. LaAlO$_3$ has perovskite structure and shows phase transition from rhombohedral structure to cubic structure at 720K [5]. In this study, rhombohedral structure was employed because temperature effect is not considered in the calculation. In defect formation energy calculations, atmosphere dependence was taken into account by considering chemical potentials of each atom. Calculated defect species are single intrinsic vacancy, V_{O}, V_{La} and V_{Al}, partial Schottky defects, $2V_{\text{La}}^{3-} + 3V_O^{2+}$ and $2V_{\text{Al}}^{3-} + 3V_O^{2+}$, perfect Schottky defect, $V_{\text{La}}^{3-} + V_{\text{Al}}^{3-} + 3V_O^{2+}$ and cation antisite defects, La$_{\text{Al}}$ and Al$_{\text{La}}$. For each vacancy species, different charge states from neutral to fully ionized were considered. That is, from 0 to -3 for a La vacancy and an Al vacancy and from 0 to +2 for an O vacancy. In defect formation energy calculations of charged defects, finite-size cell effect induced by spurious coulomb interaction in periodic boundary condition was corrected by calculating with diverse of supercell size up to 480 atoms along with the method proposed by Makov *et al* [6,7]. Correction of finite-size cell effect showed L^{-1} (L is the shortest distance of each defects in periodic boundary conditions) dependence with good linearity. Correction directions were all downward for each single charged vacancy and these corrections leads that the defect formation energies increase from before corrections.

In the calculation with larger supercells than 180 atoms, numerical integrations over the Brillouin zone were performed at the Γ-point, whereas 7×7×7 k-points for 40 atoms, 5×5×5 k-points for 80 atoms and 2×2×2 k-points for 135 atoms were applied, respectively.

At reduction atmosphere, defect formation energy of neutral O vacancy is the lowest among the calculated defects. It was found that the oxygen vacancy formation energy in LaAlO$_3$ under reduction atmosphere, -0.12eV, is much lower than other perovskite oxides, 1.56eV and 1.72eV for SrTiO$_3$ and BaTiO$_3$, respectively [8,9]. In addition, it was found that $2V_{\text{Al}}^{3-} + 3V_O^{2+}$ and $2V_{\text{La}}^{3-} + 3V_O^{2+}$ partial Schottky vacancies are the most preferable species under La-rich oxidization atmosphere and Al-rich oxidization atmosphere, respectively.

Migration energy was estimated by calculating the energy of single atomic jump from the original position to the neighboring vacancy position with nudged elastic band method [10]. In addition to the migration energy of the single atom, effect of other vacancy on the migration energy was also investigated. The migration calculations were performed with 270 atom supercells constructed by a 3×3×3 expansion of a theoretically optimized rhombohedral-unit cell. Figure 1 shows atomic trajectory of migrating La, Al, and oxygen. It is found that all ions basically move straight to respective vacancy sites. In addition, present calculation revealed that the oxygen shows the lowest migration energy. Since oxygen vacancy in $LaAlO_3$ is preferentially formed under reduction condition, it can be considered that the oxygen migration is easily occurred in $LaAlO_3$ under reduction atmosphere, such as vacuum for thin film process. In contrast, migration energies of La and Al are much higher than O, and the migration energy of Al is approximately twice as that of La. This tendency, that the migration energy of B-site cation is much higher than that of A-site cation, is similar to the case of $SrTiO_3$ [11].
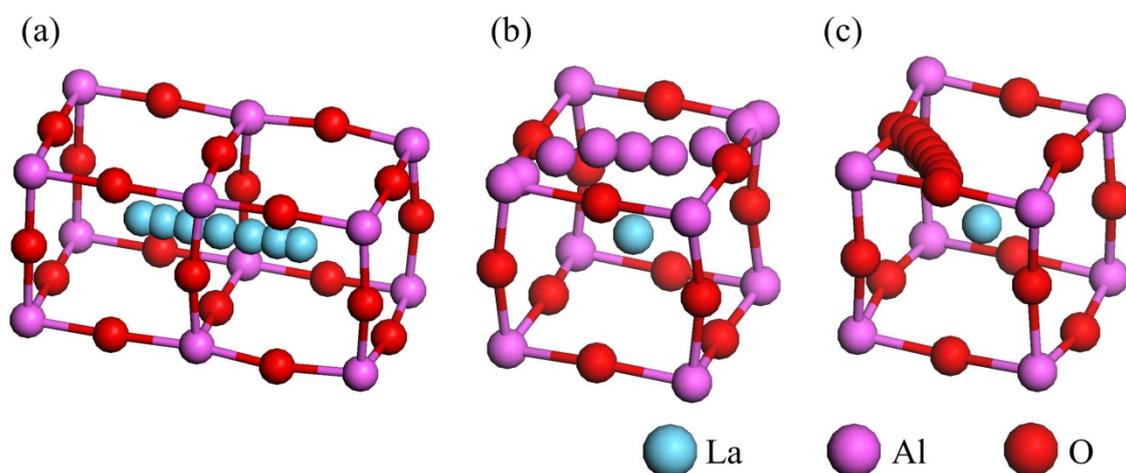
(a) (b) (c)

○ La   ● Al   ● O

FIG. 1. Atomic trajectories of migrating (a) La, (b) Al, and (c) oxygen. With the exception of the migrating ions, unrelaxed atomic configurations were used to simply show the migration path.

References
[1] X. Luo, et al., Phys. Rev. B **80** (2009) 104115.
[2] K. Xiong et al., Microelectron. Eng. **85** (2008) 65
[3] J. Q. Chen et al., Appl. Phys. Lett. **98** (2011) 041904
[4] M. Lonsti-Fomena et al., Comput. Mater. Sci. **44** (2008) 53.
[5] C. Y. Yang, et al., Acta Cryst. **A47** (1991) 703.
[6] G. Makov et al., Phys. Rev. B **51** (1995) 4014.
[7] F. Oba, et al., Phys. Rev. B **77** (2008) 245202.
[8] H. S. Lee, et al., Mater. Trans. **50** (2009) 977.
[9] H. S. Lee, et al., Acta Mater. **55** (2007) 6535.
[10] G. Henkelman, et al., J. Chem. Phys. **113** (2000) 9978.
[11] T. Mizoguchi, et al., Appl. Phys. Lett. **98** (2011) 091909.
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