

Theoretical Calculations of Oxide-Ion Diffusion Pathway in Apatite-Type Lanthanum Silicate

Katsuyuki Matsunaga^{1,2}, Kazuaki Toyoura¹

¹ Department of Materials Science & Engineering, Nagoya University, Nagoya 464-8603, Japan

² Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

Oxide-ion conductors are important for their practical application to electrolytes in solid oxide fuel cell (SOFC). It is well known that typical oxide-ion conductors are Y₂O₃-stabilized ZrO₂ (YSZ) and strontium and magnesium doped LaGaO₃ (LSGM), but other rear-earth silicate and germanate having the hexagonal apatite-type crystal structure also exhibit excellent oxide-ion conductivities, which are comparable with those of YSZ and LSGM, depending on temperature.¹ In spite of their good oxide-ion conductivities, the detailed mechanism of the oxide-ion conduction is still unclear. This may be partly because these materials have a complicated crystal structure and it is rather difficult to understand the oxide-ion diffusion mechanism by experiment alone. It is thus desirable to clarify the diffusion pathway by using a highly accurate theoretical technique, for further improvement of the oxide-ion conductivity.

In this study, first-principles calculations of oxide ions in lanthanum silicate (La_{9.33+x}(SiO₄)₆O_{2+3x/2}) were performed to investigate the oxide-ion diffusion pathway and potential barrier. Electronic structure calculations were carried out by the projector augmented wave (PAW) method as implemented in VASP,^{2,3} and the minimum energy diffusion pathway was investigated by the nudged elastic band method.

In the case of $x > 0$ in La_{9.33+x}(SiO₄)₆O_{2+3x/2}, extra oxide ions contributing to the observed ionic conductivity are present at interstitial sites. First of all, therefore, the most stable and other low-energy interstitial oxide-ion positions were investigated. The present calculations showed that the most stable position is located close to the oxide-ion column along the c axis (see Figs. 1 and 2). Regarding the diffusion pathway along the c axis, the interstitialcy mechanism is likely to occur (see Fig. 1), which was also suggested by previous atomistic simulations.⁴ While it was found that, during diffusion normal to the c axis, an conducting oxide-ion is often bonded to SiO₄ groups, forming SiO₅-like distorted units, and subsequently one of the oxide ion in the SiO₅ unit is again released into interstitial sites. Namely, SiO₄ groups play a role for acting as relay points for the interstitial oxide ion to diffuse.⁵ The oxide-ion diffusion along and normal to the c axis gave rise to the calculated potential barriers for diffusion of around 0.3 eV to 0.4 eV, which suggests the rapid oxide-ion conduction in this class of materials.

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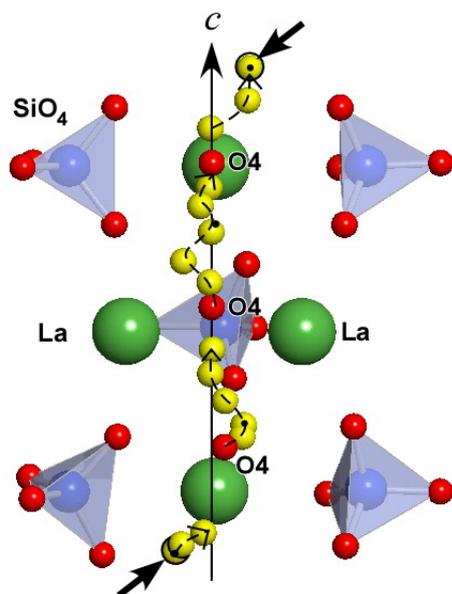


FIG. 1. Trajectory of oxide-ion diffusion along the c axis. Yellow balls indicate intermediate positions of the diffusing oxide ion, and the most stable position is indicated by the thick arrow.

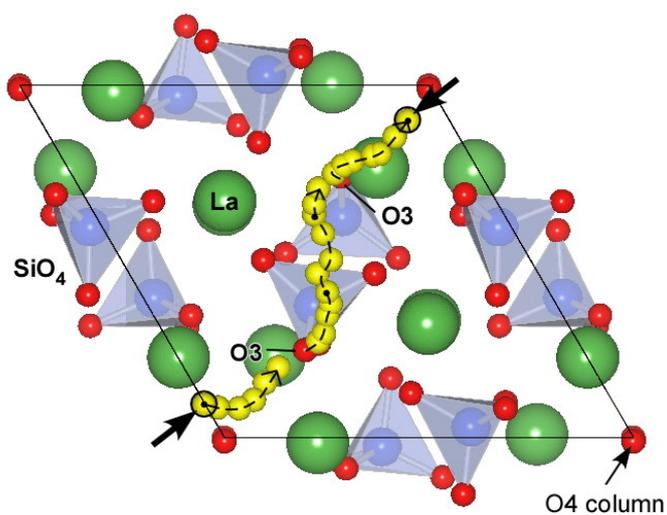


FIG. 2. Trajectory of oxide-ion diffusion normal to the c axis. This is drawn in the similar manner with FIG. 1.