27p-B8-6　First-principles Study on Oxygen Vacancy Migration in Alkaline-earth Doped Monoclinic Lanthanum Germanate

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1. Introduction

Solid oxide fuel cells (SOFCs) are recently gaining interests in expectation of their contributions to realization of energy supplies with low emissions of sulfur, nitrogen oxides and hydrocarbon pollutant, and significantly reduced CO_2 emissions. However, the requirement of high operating temperatures (above 850^0C) for conventional SOFCs lead to difficulties in thermal cycling, chemical and microstructure degradation and expensive constituents in interconnects and heat exchangers[1]. The limitation of operating temperatures is mainly due to reduction of oxygen ion conductivity of electrolyte membranes in low temperatures. Therefore it is a crucial subject to find out new solid electrolyte materials that remain high ionic conductivity at reduced temperatures.

In 2001, monoclinic La_2GeO_5 was experimentally found by T. Ishihara et al.[2,3] to have a higher ionic conductivity than usually used electrolyte made of yttria-stabilised zirconia. Then a theoretical analysis followed for clarification of the stable structures and electronic properties of a perfect La_2GeO_5 crystal and preferable sites of oxygen vacancy formation in it[4]. Activation barrier for oxygen hopping to the vacancy was elucidated by first-principle calculation[5] and the average value well agreed with experiment. However, doping a small amount of alkaline-earth metals (M = Ba, Sr, Ca) with lower valance number 2+ to La sites will help charge compensation by the formation of ionic defects, viz., oxygen ion vacancies, and hence increase the ionic conductivity. Ishihara *et. al.*[3] showed the ionic conductivity increased in the following order: Ca>Sr>Ba in N_2 atmosphere. In this work, by applying simulation technique based on the density functional theory, we elucidate the vacancy migration mechanism in terms of the relationship between cation size and activation barrier.

2. Calculation method

The calculations were performed using Vienna Ab-initio Simulation Package (VASP). Electron-ion interactions were described by the projector augmented wave method with plane waves up to an energy of E_{cut} = 900 eV. For the exchange-correlation energy, the generalized gradient approximation was employed within the Perdew–Burke–Ernzerhof (PBE) functional. The Brillouin zone was sampled using 3 × 3 × 3 Monkhorst-Pack k-point grids. Activation barriers for diffusion were evaluated by climbing image nudged elastic band (CI-NEB) method.

3. Result

Total density of states of La_2GeO_5 revealed the insulator properties with a band gap of 4 eV. Creation of a neutral oxygen vacancy leaves two electrons localized close to the vacancy location. Substituting La^{3+} with dopant 2+ cations creates one hole resulted in emergence of spin-polarized localized occupied and unoccupied states. Consequently, for the doped systems $La_{1.75}M_{0.25}GeO_{4.75}$ (M = Sr, Ba, Ca), majority and minority spin states exhibit insulating and semiconducting properties, respectively. The partial charge density of this emerged states shows localization on the Ge atom neighboring the vacancy site. As compared to Ba and Sr, Ca is found to have a lower activation barrier due to its almost same ionic radius as the host atom La.
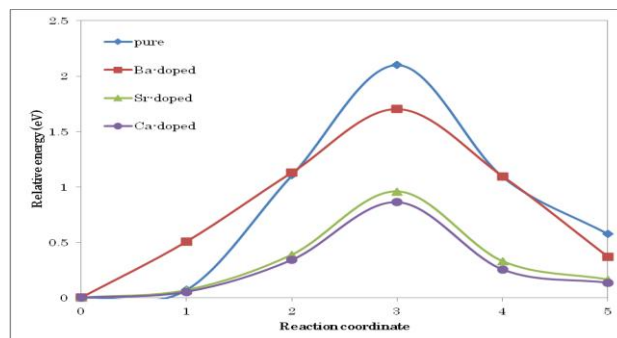

Fig. Activation barrier for oxygen hopping in undoped and alkaline-earth metals doped La_2GeO_5.

4. Conclusion

Doping to La site with lower oxidization number atoms such as alkaline-earth metals (Ba, Sr, Ca) results in lowering the activation barrier. Ca dopant causes lower activation energy for oxygen hopping compared to Ba and Sr dopants, well matching with experimental results. Therefore, doping with Ca is the most effective for increasing the ionic conductivity. And it can be concluded that $La_{1.75}Ca_{0.25}GeO_{4.75}$ is an attractive fast oxide ion conductor.

References

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