Correlations between the Oxygen Ionic Conductivity of Sr- and Mg-doped $LaGaO_3$ and Its Crystal Structure

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Abstract. Oxygen vacancy formation and migration in $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) with various crystal symmetries (cubic, orthorhombic and monoclinic) are studied by employing first-principles calculations based on density functional theory (DFT). The calculated vacancy formation energy of the cubic LSGM is 3.96 eV, much lower than those of orthorhombic and monoclinic LSGM. The calculated averaged migration energies increase in the order of $E_m^C < E_m^O < E_m^M$. There is a clear trend towards higher migration energies as the crystal symmetry becomes lower. That is to say that the oxygen ion conductivity increases in the order of $\sigma_M \le \sigma_O << \sigma_C$, accompanied a clear trend towards higher oxygen ion conductivity as the lattice becomes closer to the ideal cubic symmetry. The much lower formation and migration energies of oxygen vacancies in C-LSGM than in the other two structures imply the best oxygen ion conductivity of C-LSGM among the three crystal structures. The results obtained in this paper can not only elucidate the correlations between the ion conductivity and crystal structures of the LSGM, but also predict rational crystal structures of LSGM for solid oxide fuel cell applications.

Introduction

Fast oxygen ion conductors are important materials because of their prospective applications in oxygen pump, oxygen sensor and solid oxide fuel cells (SOFC). Recently, Sr- and Mg-doped $LaGaO_3$ has attracted extensive attention owing to its higher oxygen ionic conductivity than the standard oxygen ionic conductor yttria-stabilized zirconia and stability in a wide range of oxygen partial pressures [1-6]. It is expected to be one of the best candidates as solid electrolyte in SOFC. The incorporation of Sr and Mg dopants with lower density to form the system $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (denoted as LSGM) gives rise to the highly mobile oxygen vacancies that are responsible for the observed ionic conductivity.

An electrolyte material for the SOFC application requires its oxygen ionic conductivity as high as possible. The ionic conductivity is controlled by the formation and migration energies of oxygen vacancies, which are closely related to its crystal structures. However, the crystal structure of LSGM has been reported to be cubic[5,6], orthorhombic[1,2] and monoclinic[3,4] at room temperature (RT). Therefore, it is important to study the correlations between the oxygen ionic conductivity of Sr- and Mg-doped $LaGaO_3$ and its crystal structure, it can help to predict rational crystal structures of LSGM for solid oxide fuel cell applications. First-principles calculations are an important tool for the detailed understanding of the transport mechanisms of the electrons and oxygen vacancies [7,8]. In this paper, we systematically study the oxygen vacancy formation and migration in cubic, orthorhombic and monoclinic LSGM by first-principles calculations. Our aim is to elucidate the correlations between the ion conductivity and crystal structures of the LSGM.

Calculation methods

Dmol^3 are employed, which is based on density functional theory (DFT). The virtual crystal approximation (VCA) was employed in the small amounts of Sr- and Mg- doping in $LaGaO_3$ (LSGM). Three symmetries, i.e., cubic (C-LSGM), orthorhombic (O-LSGM) and monoclinic (M-LSGM) structures were considered in the study. Lattice constants and internal positions in the primitive cell of each crystal structure were fully optimized under the condition of residual force $\leqslant$ 0.1 eVÅ $^{-1}$.

The supercells containing an oxygen vacancy were constructed using the fully optimized primitive cell of C-LSGM, O-LSGM and M-LSGM, respectively. They are 2×2×4 for C-LSGM, O-LSGM and M-LSGM. Each supercell with an oxygen vacancy has 79 atoms. Complete linear synchronous transit/quadratic synchronous transit (Complete LST/QST) tools in DMOL^3 code is used, which shows also the transition-state in a simple manner and get the barriers of oxygen vacancy migration (E_m) immediately.

Structure

Figs. 1a~c show the schematic structures of the LSGMs with cubic ($Pm\bar{3}m$), orthorhombic (Imma) and monoclinic (I2/a) symmetries using ball-and-stick primitive cell models, respectively. $Pm\bar{3}m$ is an ideal cubic perovskite structure while Imma and I2/a contain a network of corner-sharing GaO_6 octahedra and belong to the family of rotationally distorted perovskites.

Before carrying out vacancy calculations, the crystal structures of the LSGM with various symmetries were simulated using energy minimization procedures. The calculated lattice parameters are listed in Table 1 and the experimental values were also presented for comparison. Our calculated results are in good agreement with experiment, providing support for the reliability and validity of the subsequent defect simulations.

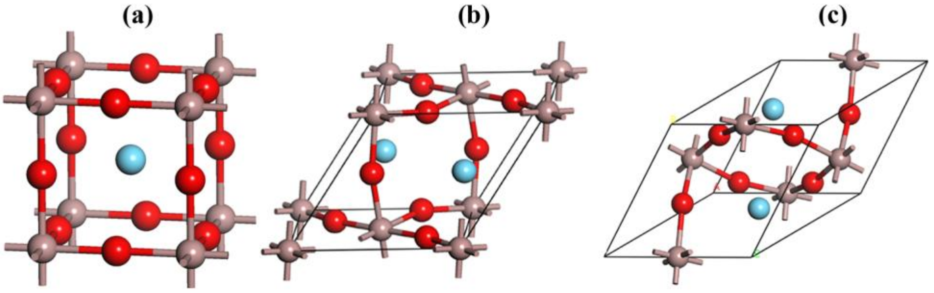

Fig. 1 Ball-and-stick primitive cell models of LSGMs with different crystal symmetries (the blue, brown and red spheres represent La/Sr, Ga/Mg and O ions, respectively): (a) C-LSGM ($Pm\bar{3}m$); (b) O-LSGM (Imma); (c) M-LSGM (I2/a).

Table 1. Calculated and experimental structural parameters of cubic, orthorhombic and monoclinic LSGM

LSGM system	Lattice parameter	
	Calc.	Expt.
C-LSGM	a =3.9000Å α=β=γ=90°	a =3.9760 Å α=β=γ=90°
O-LSGM	a=5.5085 Å b=7.7973 Å c=5.5756 Å α=β=γ=90°	a=5.5179 Å b=7.8200 Å c=5.5394 Å α=β=γ=90°
M-LSGM	a=7.8135 Å b=5.5742 Å c=5.5108 Å α=γ=90° β=90.121°	a=7.8160 Å b=5.5393 Å c=5.5147 Å α=γ=90° β=90.060°

Oxygen Vacancy Formation and Migration

Oxygen vacancy Formation Energy. The formation energies of an oxygen vacancy with respect to the calculated energy for an oxygen atom in the molecule ($\frac{1}{2}E_{O_2}$) for the cubic, orthorhombic and monoclinic LSGM were computed and shown in Fig. 2. Only one vacancy site was studied for the cubic and rhombohedral structures due to all equivalent oxygen sites in them, while two oxygen vacancy formation energies were calculated for the orthorhombic and monoclinic structures owing to two nonequivalent oxygen sites (named O1 and O2, respectively). The oxygen vacancy formation energy for the O2 site is higher than that for the O1 site but the difference is rather small (0.06-0.07 eV). Fig. 2 shows that the vacancy formation energy of the cubic LSGM is 3.96 eV, much lower than those of orthorhombic and monoclinic LSGM, both of which are about 5.50 eV. It means that the oxygen ions in the C-LSGM may be more easily to be activated for transportation.

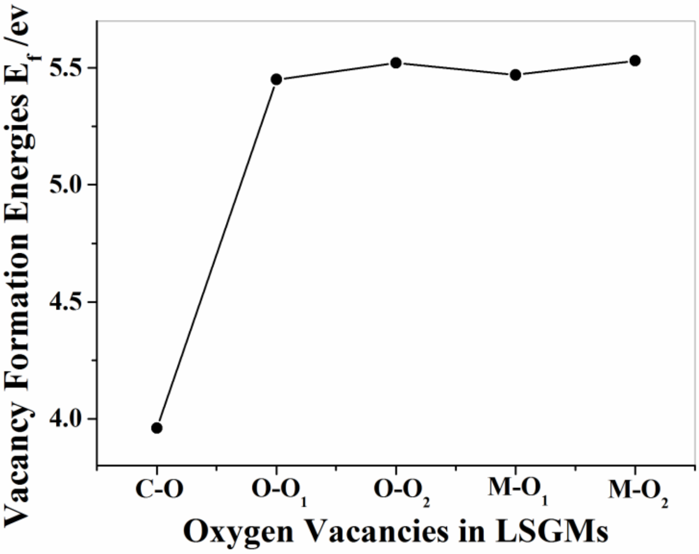

Fig. 2. Calculated vacancy formation energies (E_f) of LSGMs with respect to the calculated energy (1/2)EO_2 for an oxygen atom in the molecule. C-O corresponds to oxygen vacancy in cubic LSGM. O-O1, O-O2, M-O1 and M-O2 correspond to oxygen vacancy at O1 or O2 site in orthorhombic and monoclinic LSGM, respectively.

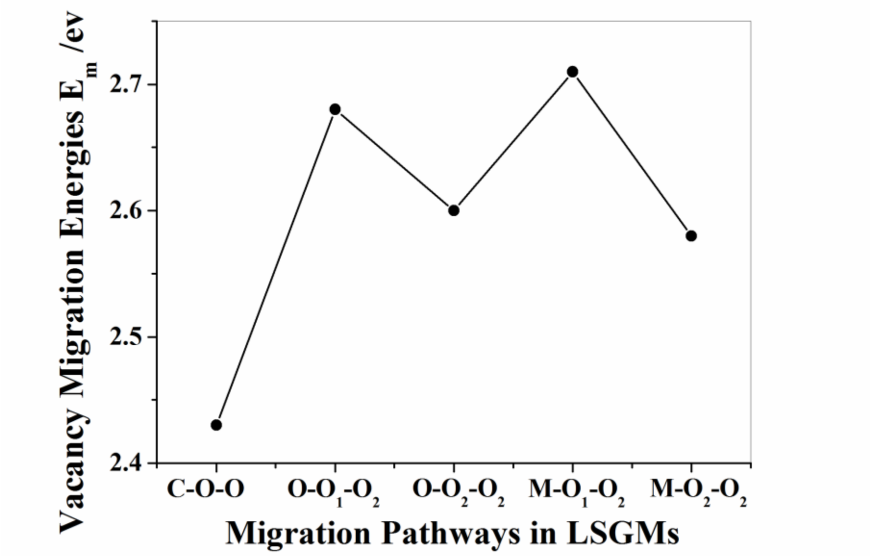

Fig. 3. Calculated vacancy migration energies (E_m) of LSGMs along different migration pathways, C-O-O corresponds to the migration pathways of oxygen vacancy between two neighboring oxygen sites in cubic LSGM. O-O1-O2, O-O2-O2, M-O1-O2 and M-O2-O2 correspond to the migration pathways of oxygen vacancy between neighboring O1 and O2 sites or two O2 sites in orthorhombic and monoclinic LSGM, respectively.

Oxygen Vacancy Migration Energy. The calculated oxygen vacancy migration energy E_m along the migration pathway for each structure is shown in Fig. 3. It shows clearly that the migration energy in the C-LSGM is much lower than those of the other two structures. The migration energies increase in the order of $\boldsymbol{E_m^C} < \boldsymbol{E_m^O} < \boldsymbol{E_m^M}$ (E_m^O and E_m^M were averaged migration energies along O1-O2 and O2-O2). There is a clear trend towards higher migration energies as the crystal symmetry becomes lower, which is in agreement with other reported perovskite materials [7,8]. Besides, in the O-LSGM and M-LSGM the migration energies along the pathway linking two O2 sites are obviously lower than those along the pathway linking O1 and O2 sites. It indicates that the oxygen vacancies can be more easily activated to migrate along the O2-O2 than along the O1-O2 pathways and at lower temperatures the former migration pathways is probably in operation alone.

Conclusion

First -principles calculations have been employed to investigate oxygen vacancy formation and migration in cubic, orthorhombic and monoclinic $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ to reveal the correlations between the ion conductivity and crystal structures of the LSGM. The following points have emerged from our results:

1. The calculations reveal that C-LSGM has much lower vacancy formation and migration energies than O-LSGM and M-LSGM whose vacancy formation and migration energies are much larger and similar each other.
2. The calculated averaged migration energies increase in the order of $\boldsymbol{E_m^C} < \boldsymbol{E_m^O} < \boldsymbol{E_m^M}$. There is a clear trend towards higher migration energies as the crystal symmetry becomes lower. In the O-LSGM and M-LSGM, the migration energies along the pathway linking two O2 sites are obviously lower than those along the pathway linking O1 and O2 sites.
3. The much lower formation and migration energies of oxygen vacancies in C-LSGM than in the other two structures imply the best oxygen ion conductivity of C-LSGM among the three crystal structures. The oxygen ion conductivity increases in the order of $\boldsymbol{\sigma_M} \leq \boldsymbol{\sigma_O} << \boldsymbol{\sigma_C}$, there is a clear trend towards higher oxygen ion conductivity as the lattice becomes closer to the ideal cubic symmetry.

Acknowledgements

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