

Mechanism of Oxygen Transport in La-Based Perovskites from First Principles

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Highlights

- The rate for oxygen diffusion depends on the oxygen vacancy formation energy.
- The perovskites that involve late transition metals exhibit better catalytic performance.
- The covalent character of the M-O bond has a major effect on the vacancy formation.

1. Introduction

Perovskite-type oxides have attracted great academic and industrial interest for the many technological applications that can be built upon their peculiar electronic and magnetic structures¹. In particular, LaMO₃ (M = Sc ~ Cu) has been widely used as catalysts both in conventional heterogeneous catalysis and in some emerging areas such as electrocatalysis. However, the lack of a fundamental understanding of oxygen migration in these materials severely limits their development and optimization. In this work, density functional theory calculations have been carried out to examine the evolution of the geometrical and electronic structures of LaMO₃ during oxygen vacancy formation and oxygen ion migration.

2. Methods

DFT+U calculations were performed using the Vienna ab-initio simulation package (VASP 5.3.5). Pseudocubic (consisting of 40 atoms), orthorhombic and rhombohedral supercells (consisting of 80 atoms) were employed to represent the crystal structures of La-based perovskites. Both the PBE & BEEF-vdW exchange-correlation functionals were used in the present calculations to estimate the effect of the long-range dispersion force on the structural properties of the materials. Oxygen vacancy formation energies were calculated, and the minimum energy pathways for oxygen migration were identified by using the climbing-image nudged elastic band (CI-NEB) method².

3. Results and discussion

3.1 Oxygen vacancy formation

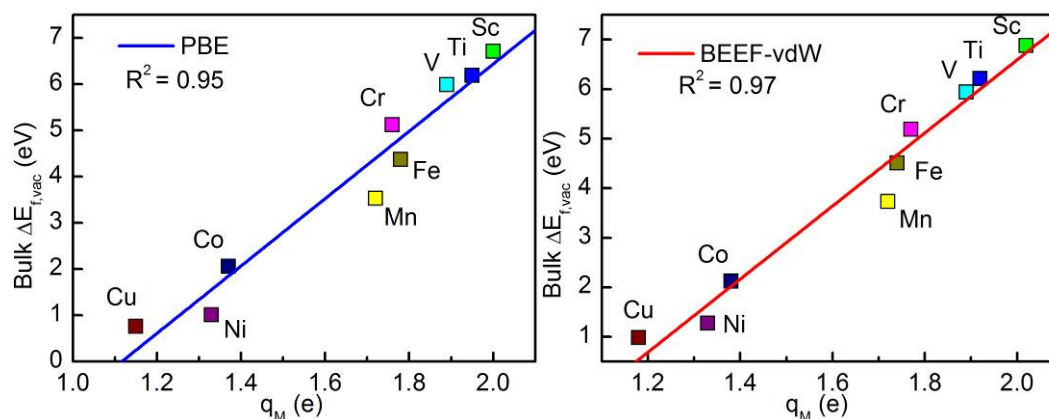


Figure 1. Oxygen vacancy formation energy as a function of effective Bader charge on transition-metal cation in perfect perovskites.

As oxygen ion migration takes place following the vacancy-hopping mechanism³, oxygen vacancy formation energy in perovskites is calculated as:

$$\Delta E_{f,vac} = E_{defective} - E_{perfect} + 0.5O_2 \quad (1)$$

Calculated results indicate that the $\Delta E_{f,vac}$ does not decrease monotonically with the atomic number of the transition metals involved in $LaMO_3$. This has been rationalized by the particularly stable electron configuration of the Fe^{3+} , which has a half-filled 3d subshell^{4,5}. Then, charges on the transition-metal cations (qM) in the perfect perovskites were calculated according to Bader's analysis and correlated with the $\Delta E_{f,vac}$. As can be seen in Fig. 1, a straight line is given. The smaller the qM, the higher the covalent character of the M-O bond, and hence the more readily the oxygen vacancy is formed.

3.2 Oxygen ion migration

As suggested in previous work, migration of oxygen ions in perovskites follows a vacancy-mediated hopping mechanism and proceeds along a curved line. With the local Jahn-Teller distortion taken into account, six elementary steps for oxygen ion migration are identified in the pseudocubic and orthorhombic crystal structures, while there are only two elementary steps present in the rhombohedral model because of their high structural symmetry. The lowest energy barriers for the elementary steps are given in Fig. 2. In general, the perovskites that involve the late transition metals have relatively low energy barriers.

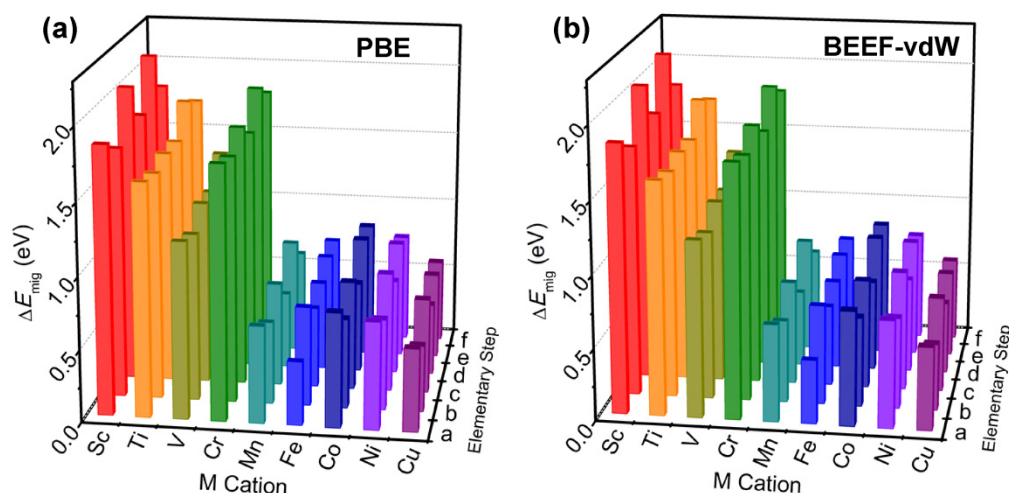


Figure 2. Energy barriers for different oxygen migration steps in $LaMO_3$ ($M = Sc \sim Cu$).

4. Conclusions

The rate for oxygen bulk diffusion depends dominantly on the oxygen vacancy formation energy rather than the energy barrier for oxygen migration. The perovskites that involve late transition metals have relatively low oxygen vacancy formation energies, low energy barrier of oxygen migration, and thereby exhibit better catalytic performance in redox reactions.

References

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Keywords

Perovskites; DFT; Oxygen vacancy; Oxygen migration