Proton transfer mechanism in lanthanum orthophosphate

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Proton conducting materials are of interest as solid electrolytes of fuel cells at intermediate temperatures (400-700 °C).[1] Lanthanum orthophosphate, $LaPO_4$, has been recently focused on as a candidate material with high proton conductivity in the temperature range. The present study has theoretically addressed the proton transfer mechanism, which has not been clearly understood so far.

All the computational studies were based on first-principles calculations, which were performed using the projector augmented wave (PAW) method implemented in the VASP code.[2,3] The generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerhof was used for the exchange-correlation term.[4] Prior to finding proton conduction paths, proton sites in the crystal were determined by evaluation of the potential energy surface (PES) with the fixed atomic positions and the following structural optimization. Then, conduction paths and their energy profiles were evaluated using the nudged elastic band (NEB) method.[5] The kinetic Monte Carlo (KMC)[6] simulations were finally performed to estimate the proton diffusion constants in $LaPO_4$.

Figure 1 (a) shows the crystal structure of $LaPO_4$. Oxygen and phosphorus atoms form isolated PO_4 tetrahedra in the monazite structure. Oxygen sites are crystallographically classified into four (O1~O4), shown by colour in the figure. According to our calculations on the PES and the structural optimization, protons can reside around all the oxygen sites in $LaPO_4$. Figure 1 (b) shows the calculated energy local minima of protons with the potential energies with reference to the most stable. There are two or three energy local minima around each oxygen site.

Energy profiles for possible conduction paths within 3.5 Å distance connecting the determined proton sites were evaluated using the NEB method. As the results, twenty-one direct paths were found with low potential barriers below 1 eV. Then, the KMC simulations were performed using these paths. The mean jump frequency, ν, for each path was estimated based on the following equation, $\nu = \nu^* \exp(-\Delta E_{mig}/k_B T)$, where ν^* is the pre-exponential factor considered as the jump trial frequency, ΔE_{mig} is the potential barrier, k_B is the Boltzmann constant, and T is the temperature. The pre-exponential factor was assumed to be 10^{13}/s, which is a typical value for the jump trial frequency. Figure 2 shows the displacements of protons after 50000 KMC steps at 1000 K, in which all the protons migrate from the center position independently. The dispersion of the displacements corresponds to the diffusion constant, D, as follows: $D_i = < r_i(t)^2 / 2t >$, where i denotes x, y, or z coordinate, t is the time, and r_i is the i-component of the displacement vector. The dispersion is almost isotropic in bc-plane, while that along a-axis is comparatively small. This results in anisotropy in the calculated diffusion constants, 4.0×10^{-6} cm^2/s in bc-plane vs. 1.5×10^{-6} cm^2/s along a-axis.

This study was supported by the Elements Science and Technology Project from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan and Grant-in-Aid for Young Scientists (B) from Japan Society for the Promotion of Science.

References

[1] T. Norby, Solid State Ionics 125 (1999) 1.
[2] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953.
[3] G. Kresse and J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
[4] P. J. Perdew, K. Burke, and M. Ernzerhof Phys. Rev. Lett. 77 (1996) 386.
[5] G. Henkelman, B. P. Uberuaga, and H. Jónsson, J. Chem. Phys. 113 (2000) 9901.
[6] A. Van der Ven et al., Phys. Rev. B 64 (2001) 184307.

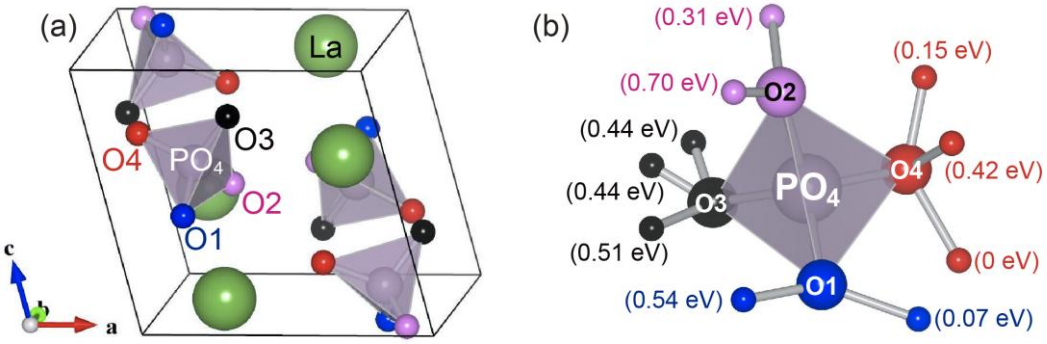

FIG. 1. (a) Crystal structure of $LaPO_4$. The green balls and purple tetrahedra denote lanthanum atoms and PO_4 tetrahedra, respectively. The oxygen atoms are crystallographically divided into four types (O1: blue, O2: pink, O3: black, and O4: red). (b) Energy local minima of protons in $LaPO_4$. The potential energies with reference to the most stable are shown in the parentheses.

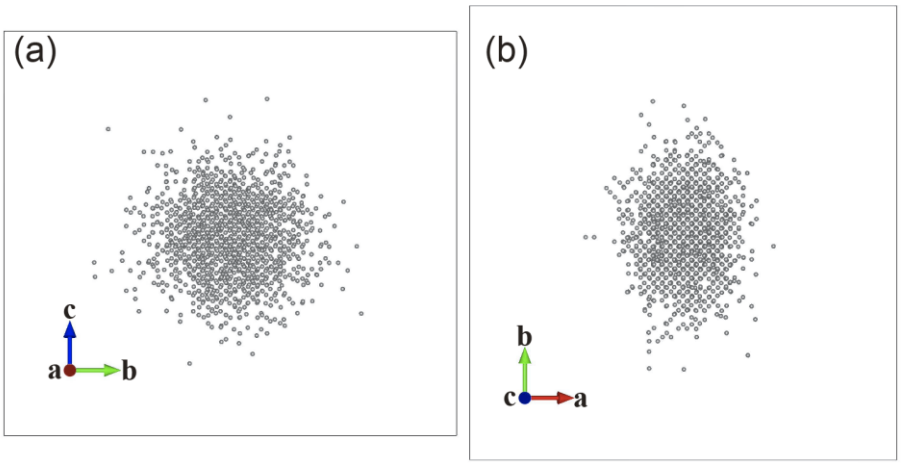

FIG. 2. Displacements of protons from the center after 50000 KMC steps at 1000 K (a) from *a*-axis and (b) from *c*-axis views. A supercell of 50×50×50 unitcells was used for the KMC simulations. The lengths of *a*-,*b*-, and *c*-axes are 346.69 Å, 357.26 Å, and 327.13 Å, respectively.