First-principles analyses of proton incorporation in calcium phosphate

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Proton-conducting phosphates, which are reported to exhibit protonic conductivity at intermediate temperatures (473-973 K) [1], are candidate materials for solid electrolytes in fuel cells operating in the temperature range. According to the theoretically investigation [2,3], protons mainly reside around oxide ions and migrate by rotation around oxide ions and hopping between adjacent oxide ions. Therefore, the arrangement and types of oxygen ions, in other words, oxygen polyhedral network, in the crystals should be a key factor in the proton conduction. In this study, we focused on the calcium phosphate β-CaP_2O_6, which has one-dimensional PO_4 tetrahedral network, to evaluate the stability of protons in the crystal lattice by first principle calculations.

All first-principles calculations were performed based on the projector augmented wave (PAW) method implemented in the VASP code [4,5]. A supercell consisting of $2 \times 2 \times 1$ unit cells (288 atoms) was employed here.

First of all, the potential energy surface (PES) of a proton in the rigid host lattice was evaluated. Figure 1 shows the calculated PES of a proton superimposed on the crystal structure of β-CaP_2O_6. This crystal has twelve oxygen sites (O1~O12), where four types of PO_4 tetrahedral units form zigzag chains along the a axis by four corner-shared oxide ions (O1, O5, O9, O12). The yellow domain denotes that the potential energy with reference to the global minimum is less than 1 eV. From the result of the PES analysis, the potential energy of a proton around oxide ions is relatively low, which is consistent with the conventional view mentioned above.

Then, the most-stable and metastable sites (proton sites) were determined by structural optimizations using the energy local minima in the PES as the initial structures. The determined twenty proton sites are shown in Fig. 2. The distances from the proton sites to the first-nearest-neighbor oxide ions (O_{1NN}) are nearly 1 Å at all the proton sites, approximately equal to that in water. Nineteen proton sites are located around non-shared oxide ions with low potential energies below 0.6 eV, while only one proton site around corner-shared oxide ion has the highest energy, 1.11 eV. This

indicates protons prefer non-shared oxide ions to corner-shared oxide ions.

Focusing on the second nearest-neighbor (O_{2NN}) oxygen sites, the O_{2NN}-H distances are 1.4 ~ 1.8 Å at the proton sites around non-shared oxide ions; therefore, protons are more stabilized by formation of a hydrogen bond with O_{1NN} and O_{2NN}. By contrast, the O_{2NN}–H distance at the proton site around the corner-shared O12 ion is 2.48 Å. This suggests that the O_{2NN}–H bond is no longer available and proton exists in a less stable state. Consequently, types of oxide ions and formation of hydrogen bonding are important factors in the proton incorporation and migration behavior in phosphates.

References
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[4] P.E. Blöchl, Phys. Rev. B **50** (1994) 17953.
[5] G. Kresse et al., Phys. Rev. B **54** (1996) 11169.

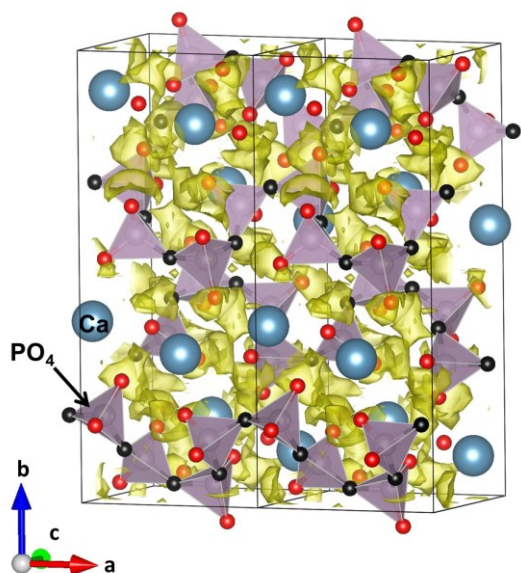Fig. 1. Crystal structure of β-CaP$_2$O$_6$ and the calculated PES in the rigid host lattice. The red and black balls are non-shared and corner-shared oxide ions, respectively. The yellow domain denotes that the potential energy with reference to the global minimum is less than 1 eV.
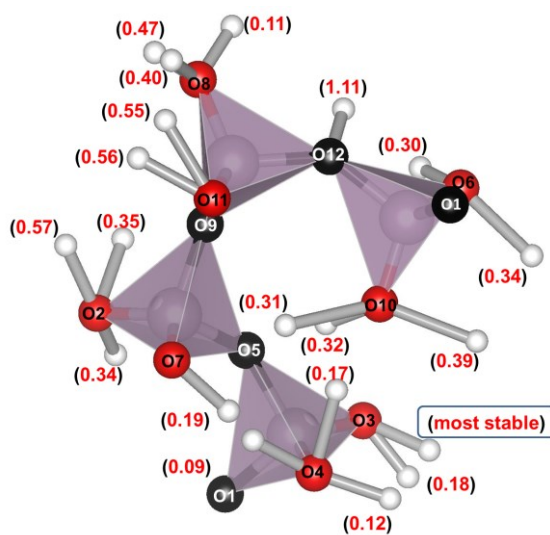
Fig.2. Determined proton sites around each oxide ion. The energies in parentheses are the potential energies (in eV) with reference to that at the most stable site.