

Observation of the proton migration path in protonic conductor $\text{Rb}_3\text{H}(\text{SeO}_4)_2$

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The materials represented as $\text{M}_3\text{H}(\text{XO}_4)_2$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{X} = \text{S}, \text{Se}$) are known to exhibit a super protonic conductivity at high temperature. The mechanism of the proton conduction has been predicted to be hopping of the protons between neighboring hydrogen-bonds driven by the disorder of the hydrogen-bonds. However, no direct observation of the migration path has been reported. The protonic conductivity is induced by a structural phase transition. Through the transition, the hydrogen-bond, which is isolated within a dimer of $\text{XO}_4\text{-H-XO}_4$, becomes disordered. Despite much effort to reveal the origin of the phase transition, the detailed mechanism is still open to question. In this study, single crystal neutron diffraction experiments were conducted on $\text{Rb}_3\text{H}(\text{SeO}_4)_2$ in order to investigate the proton migration path and the structural variation toward the phase transition.

The experiments were performed on the neutron four-circle diffractometer, FONDER. The data were measured at several temperature points below and above the phase transition temperature. With the obtained data, the structural parameters such as atomic positions and temperature factors were refined with the program, RADIEL. In addition, the Fourier synthesis method was utilized in order to investigate the proton conduction path. The results revealed that the configuration of SeO_4 tetrahedron was found to remain unchanged, while the increase of the hydrogen-bond length, the distance between SeO_4 tetrahedrons, was observed as the temperature increased. As the hydrogen-bond length increased the hydrogen atom in the hydrogen-bond approached the oxygen atom in the hydrogen-bond. This may imply the weakening of the hydrogen-bond, which

may foster the phase transition. Above the phase transition temperature, the apical oxygen of SeO_4 tetrahedron becomes disordered occupying three equivalent sites. Meanwhile as for the other atoms in SeO_4 tetrahedron, no unusual behavior was observed. Therefore, it is considered that only the apical oxygen is disordered in the SeO_4 tetrahedron.

The nuclear density distribution in the high temperature phase obtained by the Fourier synthesis clearly showed a continuous density distribution which corresponds to the density of the proton. The distribution spreads two dimensionally connecting the hydrogen-bonds, suggesting the proton conduction path. The two dimensional feature is in a good agreement with a macroscopic conductivity data. In the density distribution, there found small bumps at the middle of the neighboring hydrogen-bonds. This may corresponds to a metastable site for the proton and may be indicative of the existence of a monomer, $[\text{H}(\text{SeO}_4)]^-$, as an intermediate state of the proton conduction.

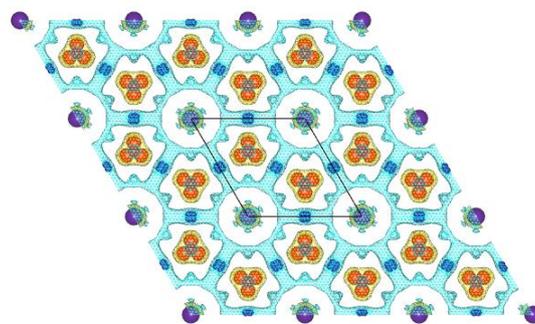


Fig. 1. Proton conduction path in $\text{Rb}_3\text{H}(\text{SeO}_4)_2$. Red: oxygen, Purple: Rubidium, Blue: hydrogen. The light blue image corresponds to the proton density.