# Proton Transport Mechanism and Pathways in the Superprotonic Phase of $M_3H(AO_4)_2$ Solid Acids from Ab Initio Molecular Dynamics Simulations
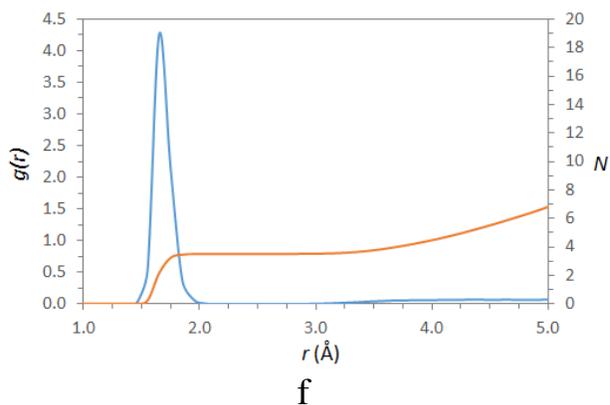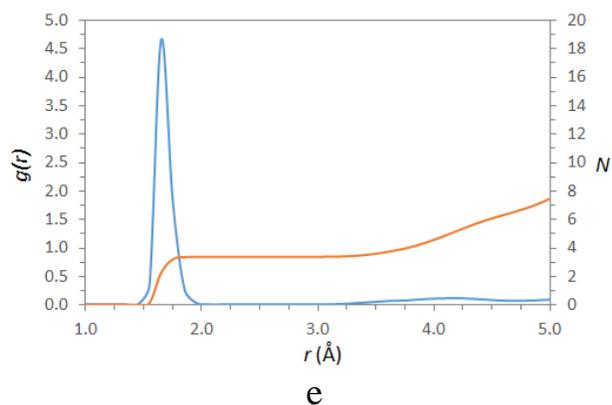
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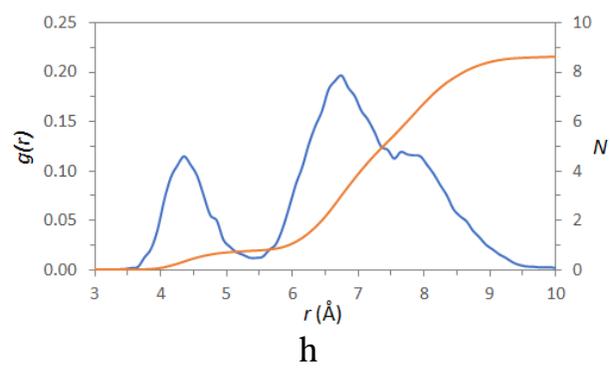
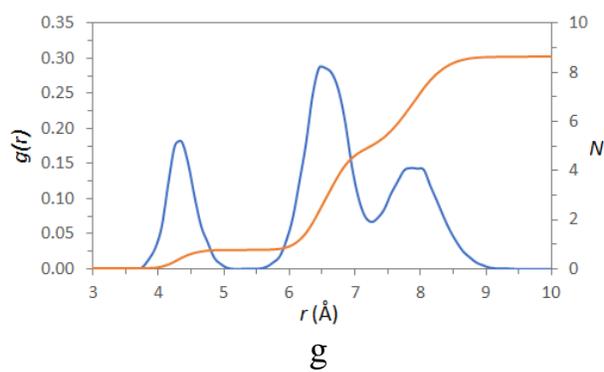[b]Department of Physics of Nanoscale Systems, South Ural State University, 76 Lenin Avenue, Chelyabinsk 454080, Russia
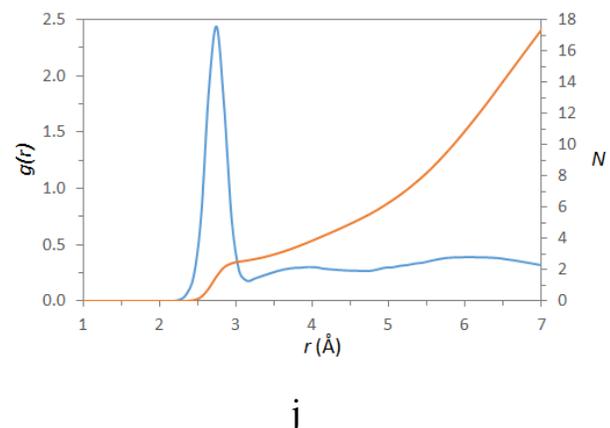
680 K   980 K

Cs −O RDF

a   b

Cs −Cs RDF

c   d

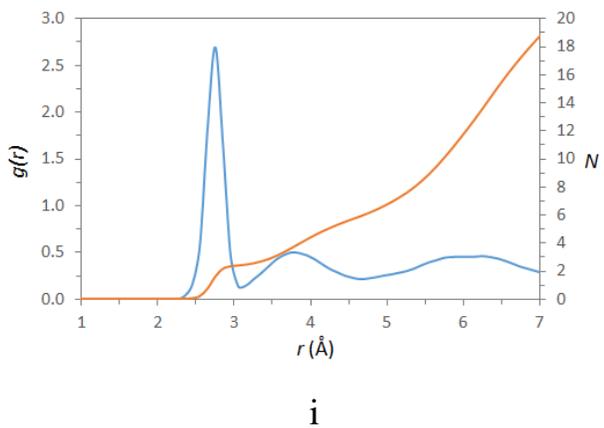## Se – O RDF
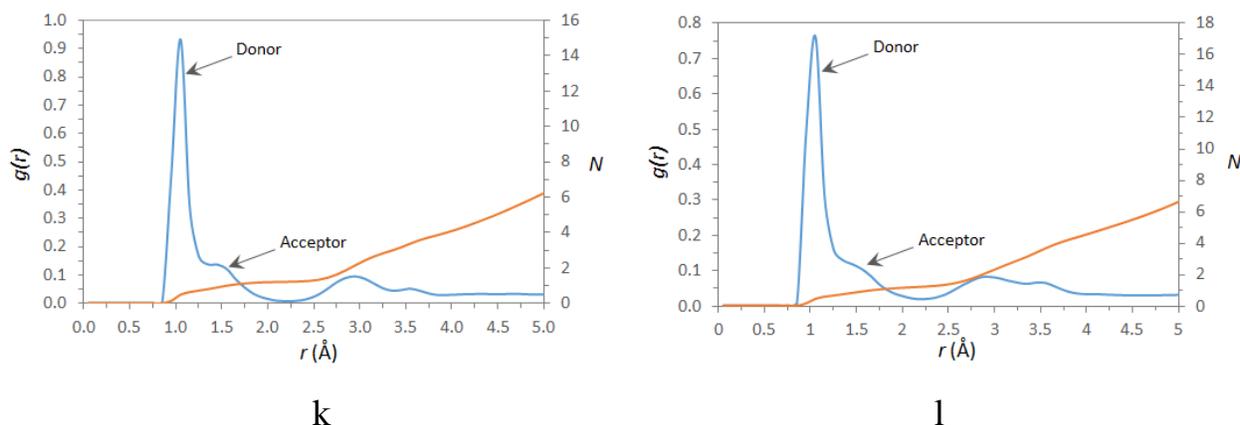

e

f

Se – Se RDF

g

h

O – O RDF

i

j
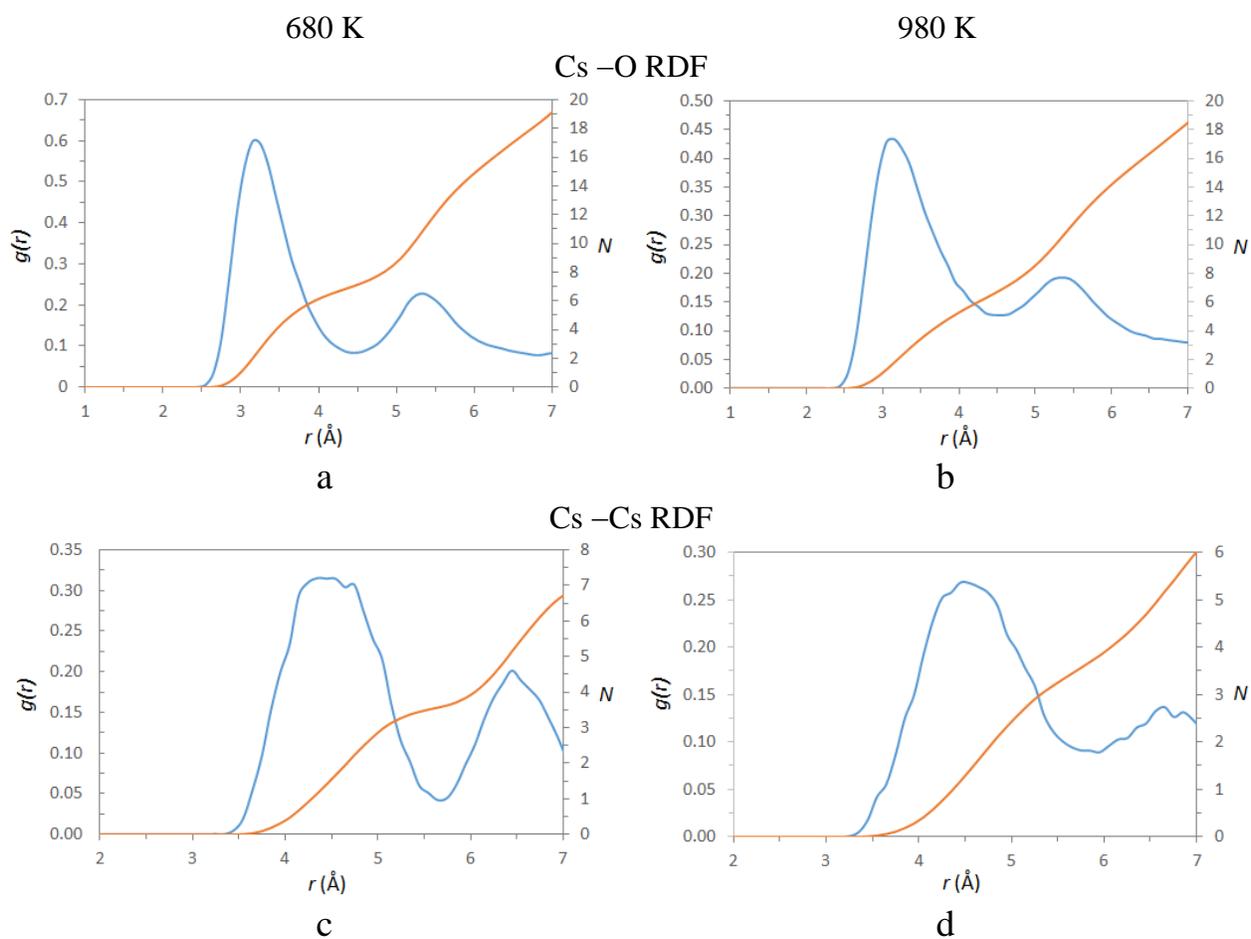
H – O RDF

Figure S1. Pair RDFs (g(r), blue, left axis) and integrated number of bonds (N, orange, right axis) for the $Cs_3H(SeO_4)_2$ superprotonic phase at 680 K (left) and 980 K (right). All cation – anion distances are typical for this group of compounds.

The structures of the superprotonic phases of solid acids are substantially flexible. This promotes the very high protonic conductivity of these materials. The Cs ions in the superprotonic phase of $Cs_3H(SeO_4)_2$ are located inside very large polyhedra composed of 10 to 12 oxygen atoms.[1] They can shift within these large polyhedra. This leads to the Cs-Cs distances to be distributed over an extended range of distances. That is why the Cs-Cs RDF peaks are broad, the full width at half-maximum values (FWHM) is ~1 Å. It also could lead to the non-zero intensity between the peaks in the Cs-Cs RDF. This effect would be more pronounced at higher temperatures. Lee and Tuckerman[2] performed an AIMD study of another superprotonic solid acid, CsH_2PO_4, and obtained similar results. They found that the RDF for Cs-Cs, P-P and Cs-P possess rather broad peaks with similar FWHM values of roughly 1 Å and concluded that this indicates that the shift of the Cs and PO_4 units is not negligible, and the structure of the superprotonic phase of CsH_2PO_4 is considerably distorted from the perfect CsCl-type structure at any given instant time. They concluded that while the time averaged structure remains cubic, the overall flexibility might provide a better opportunity for each PO_4 group to reorient so as to achieve a favorable hydrogen bond configuration in a given local environment. We obtained very similar results from our simulations.
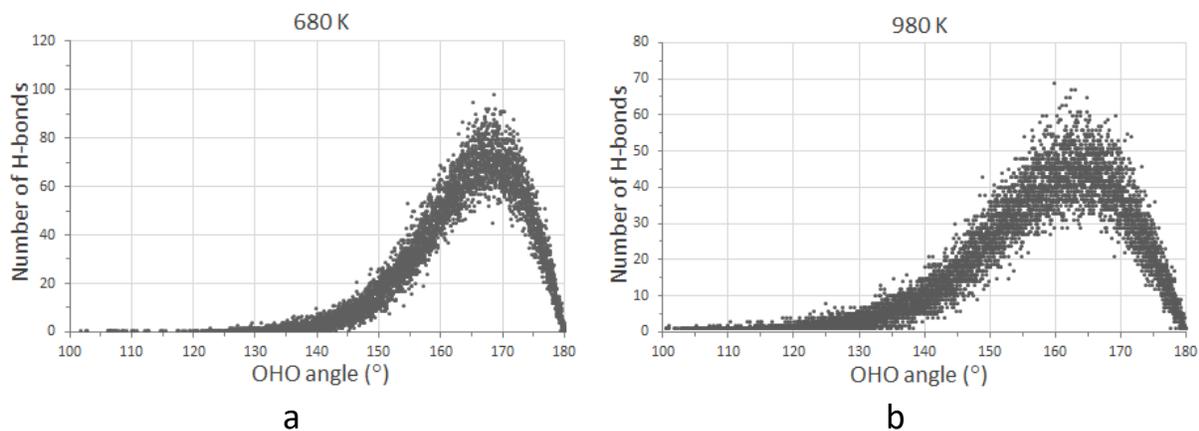
Figure S2. OHO angle distributions of the hydrogen bonds in the $Cs_3H(SeO_4)_2$ superionic phase at 680 K (a) and 980 K (b). The maximum corresponds to approximately 168° and 164° at 680 and 980 K, respectively. These values are typical for normal hydrogen bonds.
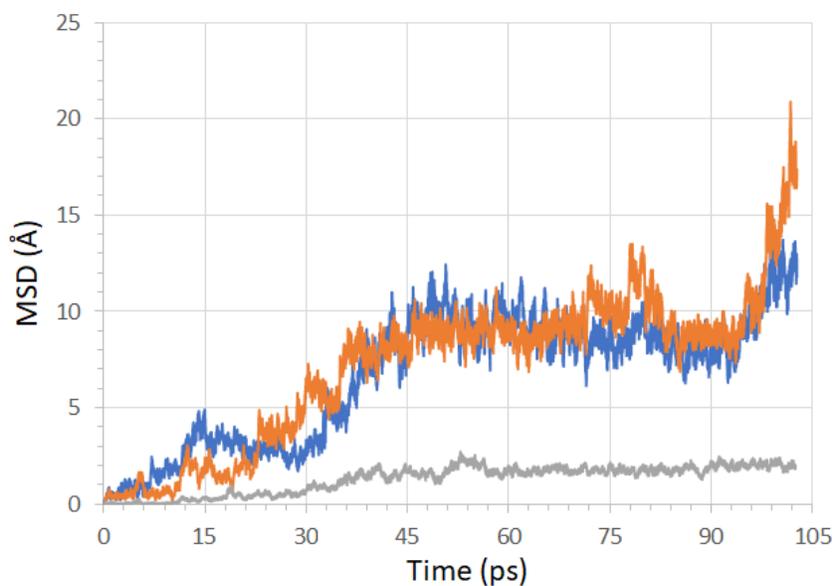

Figure S3. MSD values of H atoms *vs.* simulation time along the *a* (blue), *b* (orange) and *c* (gray) directions in the $Cs_3H(SeO_4)_2$ superprotonic phase at 680 K which indicate the anisotropy of the proton diffusion in this phase. The proton diffusion is much faster along the *a* and *b* directions compared to that along the *c* direction.
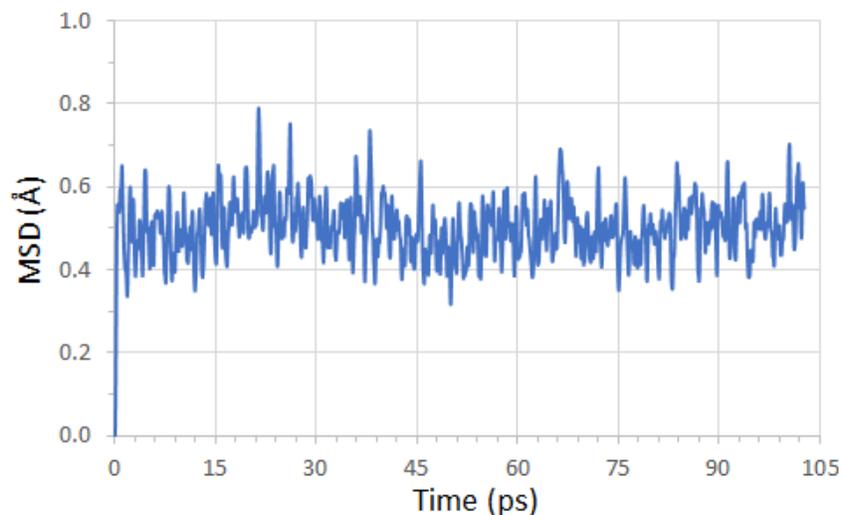
Figure S4. MSD values of Cs atoms *vs.* simulation time in the $Cs_3H(SeO_4)_2$ superprotonic phase at 680 K which indicate that there is no Cs diffusion in this phase.
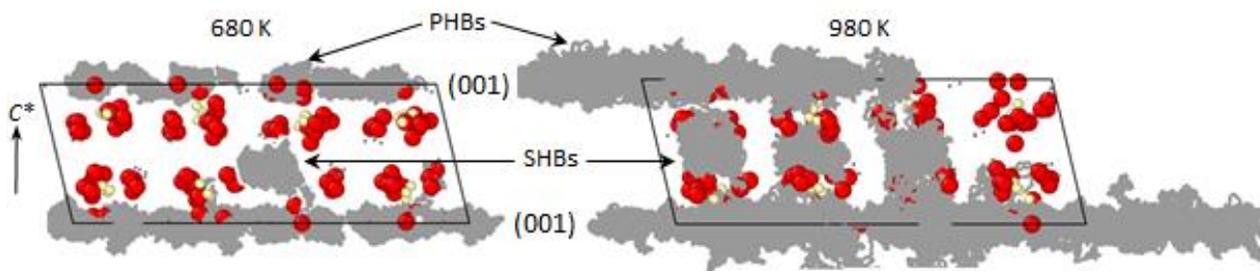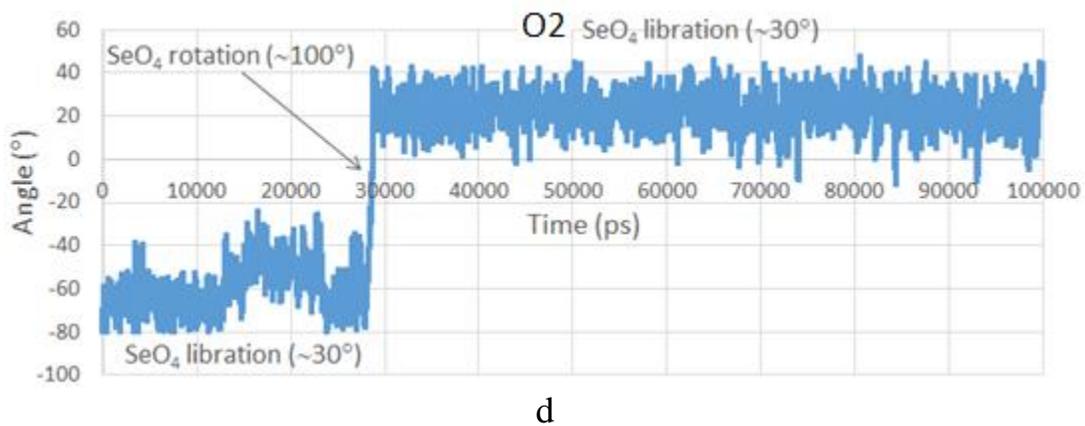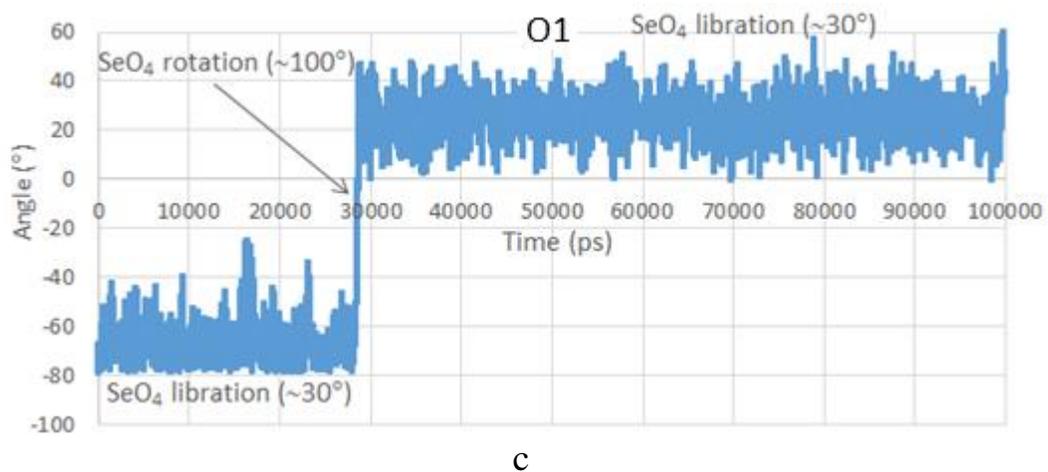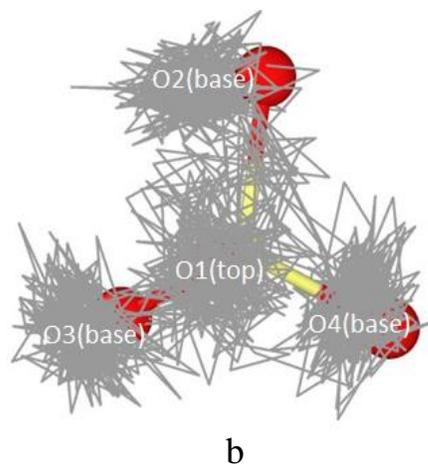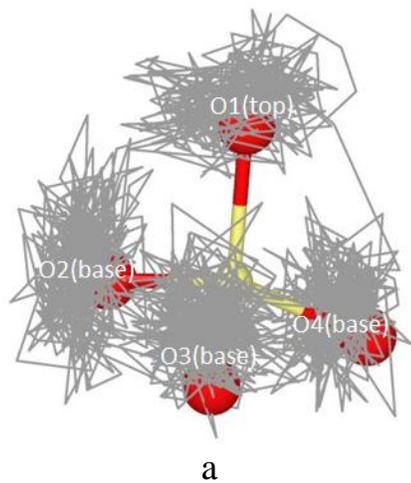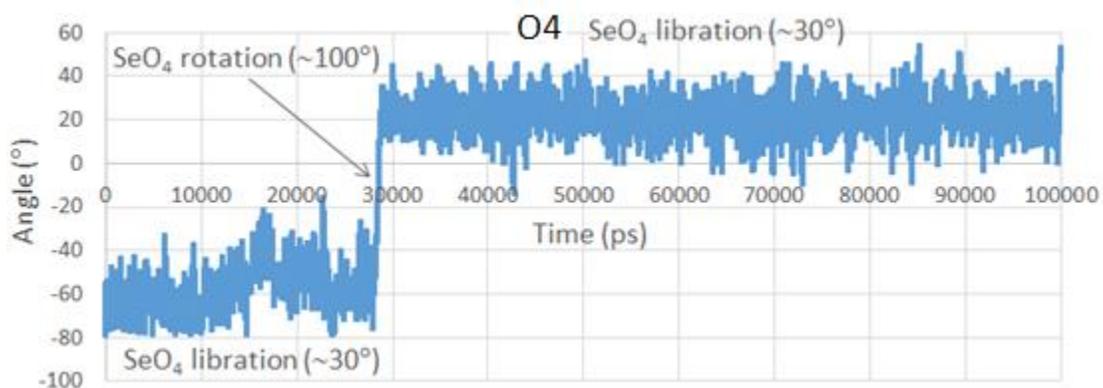

Figure S5. Hydrogen atom trajectories at 680 K (a) and 980 K (b). In addition to principal hydrogen bonds (PHBs) in (001) planes, supplementary hydrogen bonds (SHBs) were formed between (001) planes.

a

b

c

d

e

f

Figure S6. An example of a SeO$_4$-tetrahedron libration: trajectories of the corresponding O atoms (a) a view perpendicular to the *z*-direction and (b) along the *z*-direction, (c-d) libration angles over simulation time for O1, O2, O3, and O4, respectively, at 680 K. The SeO$_4$-tetrahedron rotation by ~100° occurred around the Se−O3 bond at approximately 29 ps so that the top O1 atom occupied the base O2 site, the base O2 and O4 atoms moved to the base O4 and top O1 sites, respectively. The libration and rotation angles are in good agreement with earlier obtained experimental and computational results.[1,3,4]

References

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