Electronic Supplementary Information

$Ba_3(BO_3)_2$: the first example of the dynamic disorder in borate crystal

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Computational details

The total energies and forces were calculated by solving the Schrödinger equation based on projector augmented plane-wave implementation of density functional theory within the Vienna Ab initio Simulation Package (VASP) [Kresse and Furthmüller(1996), Kresse and Furthmüller(1996)]. Exchange-correlation effects were treated in the generalized gradient approximation (GGA) with the Perdew–Wang scheme

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[Perdew and Wang(1992)]. Ultrasoft pseudopotentials with s^1 (Ba), s^2p^1 (B), and s^2p^4 (O) electronic configurations have been used.

We performed finite temperature ab initio molecular dynamics (MD) simulations to investigate the evolution of the $Ba_3B_2O_6$ structure with temperature increase at ambient pressure. All MD simulations were performed in the isothermal–isobaric NPT ensemble (N – the number of particles, P – pressure, and T – temperature) using a Langevin thermostat. The integration of the classical Newton's equations of motion uses the Verlet algorithm, and the ground-state search is evaluated within an efficient iterative matrix diagonalization scheme and a Pulay mixer for each step. The time step for the integration was set to 1 fs. Simulations were performed in the temperature range of 300–1700 K for 20–30 ps. The integration of the Brillouin zone was performed using the Γ-point only. The plane-wave cutoff energy was set to 400 eV. The temperature of the simulation and crystallographic properties were derived from time averages taken over at least 15 ps excluding the first 2 ps of the simulation. The structure of $Ba_3B_2O_6$ was approximated by the supercell containing 352 atoms, which are $1 \times 2 \times 1$ supercell of the unit cell considered below.

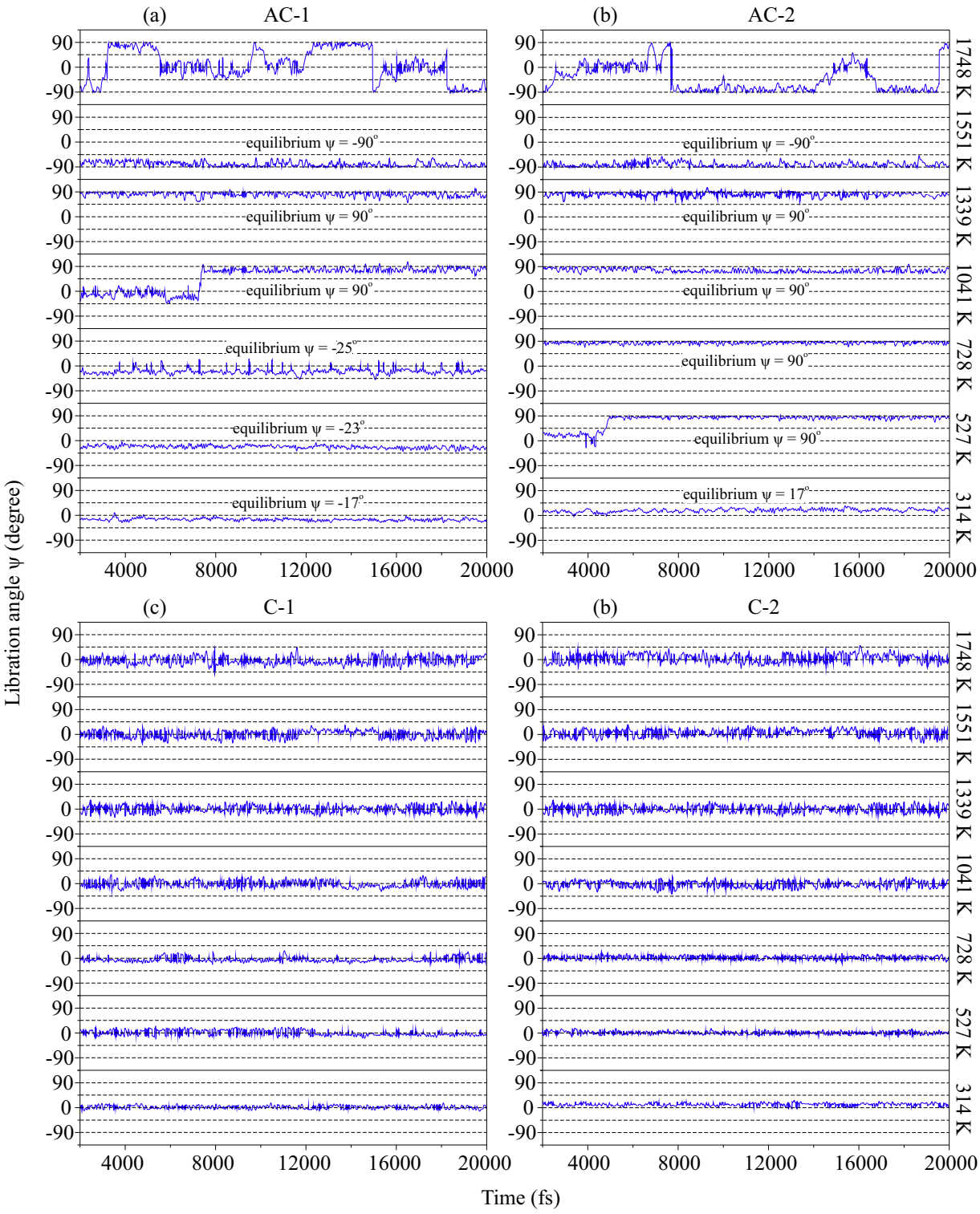

Figure S1: The dependence of libration angle ψ on time for (a) AC-1, (b) AC-2, (c) C-1, and (d) C-2 at 314, 527, 728, 1041, 1339, 1551, and 1748 K.

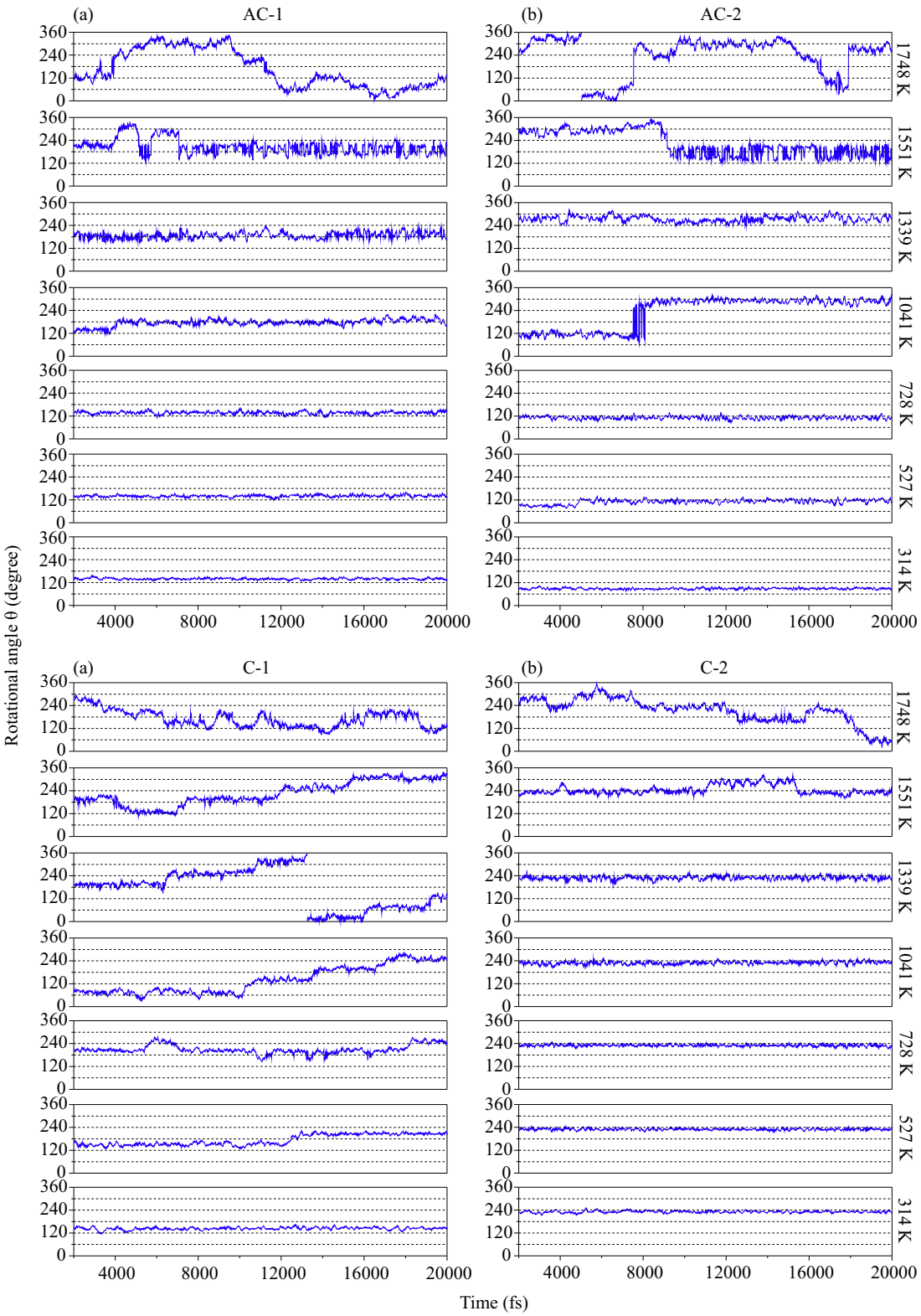

Figure S2: The dependence of rotational angle θ on time for (a) AC-1, (b) AC-2, (c) C-1, and (d) C-2 at 314, 527, 728, 1041, 1339, 1551, and 1748 K.

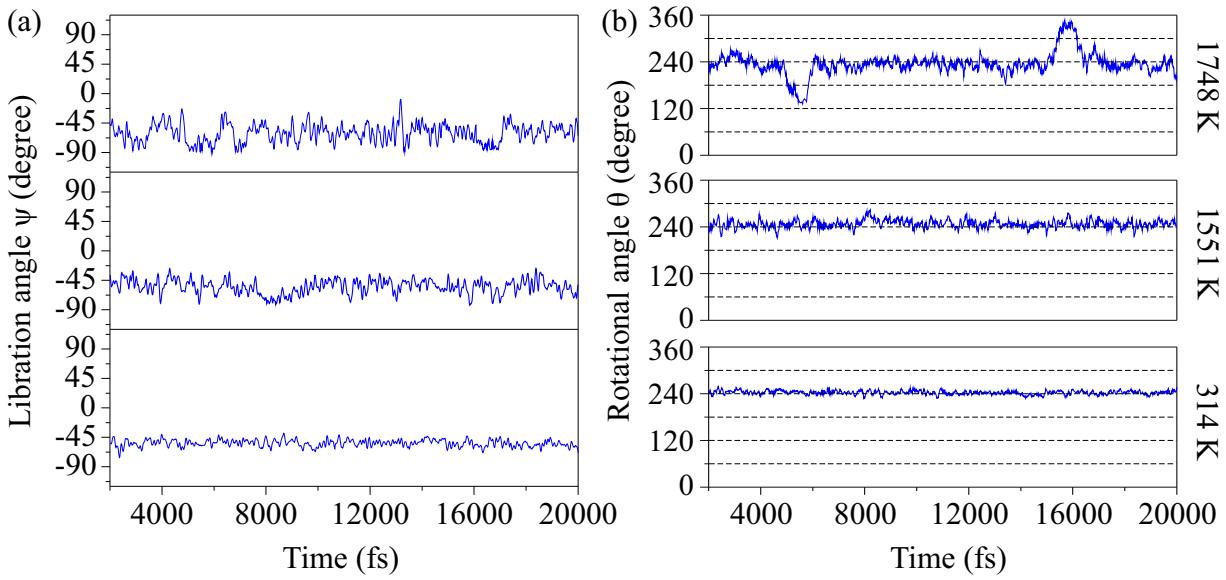

Figure S3: The dependence of (a) libration ψ and (b) rotational angle θ on time for BO_3 triangle located out of ab-plane at 314, 1551, and 1748 K.

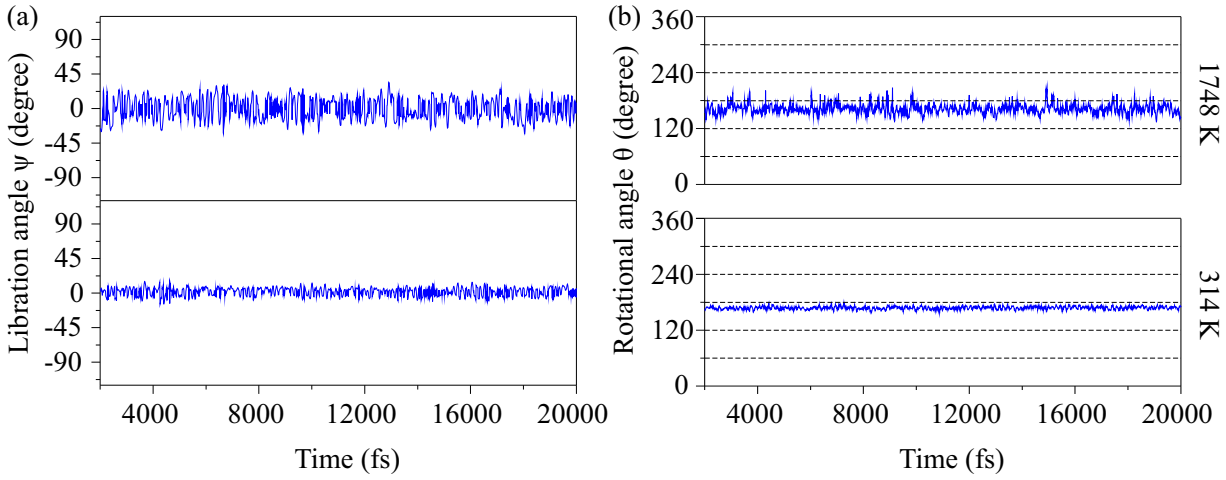

Figure S4: The dependence of (a) libration ψ and (b) rotational angle θ on time for BO_3 triangle located parallel to ab-plane at 314 and 1748 K.

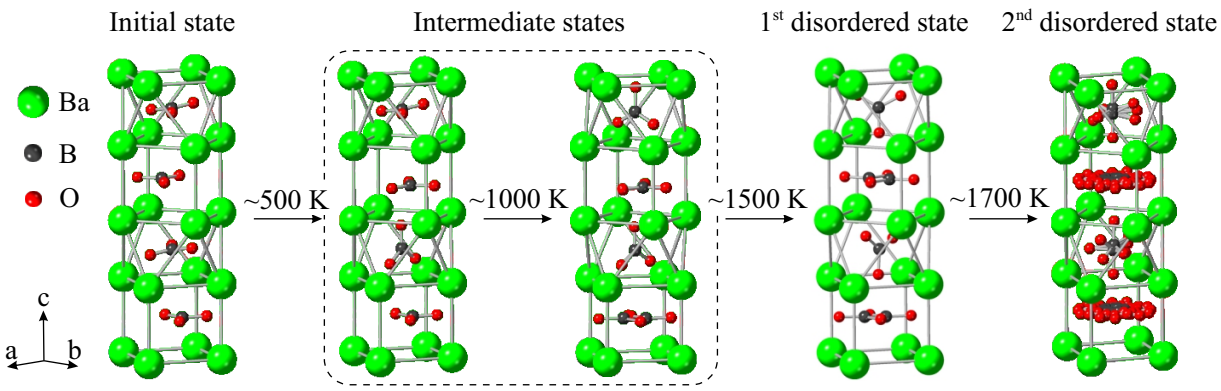

Figure S5: The behavior of BO_3 groups with temperature increase.

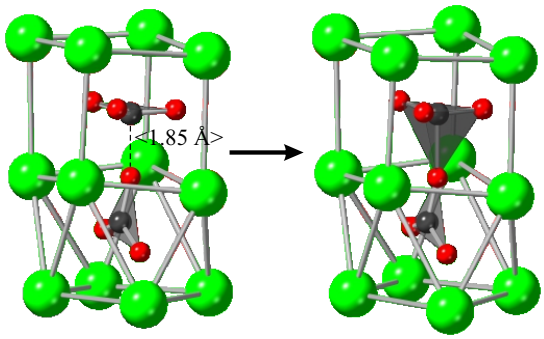

Figure S6: Observed BO_3–BO_4 dynamical conversion

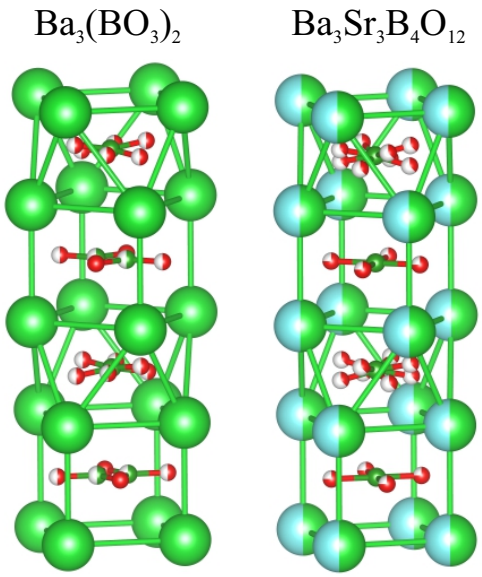

Figure S7: Comparison of static disordering of BO_3 groups in $Ba_3(BO_3)_2$ and $Ba_3Sr_3B_4O_{12}$.

References

[Kresse and Furthmüller(1996)] G. Kresse and J. Furthmüller, *Physical Review B*, 1996, **54**, 11169–11186.

[Kresse and Furthmüller(1996)] G. Kresse and J. Furthmüller, *Computational Materials Science*, 1996, **6**, 15–50.

[Perdew and Wang(1992)] J. P. Perdew and Y. Wang, *Physical Review B*, 1992, **45**, 13244.