Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Accessing Slow Diffusion In Solids Employing Metadynamics Simulation

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Figure S1

The time-evolution of the Cartesian coordinates of a few randomly picked Na^+ ions and some of their respective neighbours from MTD simulation of $Na_4Zr_2(SiO_4)_3$ at 500 K (with the bias factor, γ= 6). The simultaneous changes in the x, y or z –coordinates of different ions indicates correlated hops of neighbouring ions – a few are highlighted.

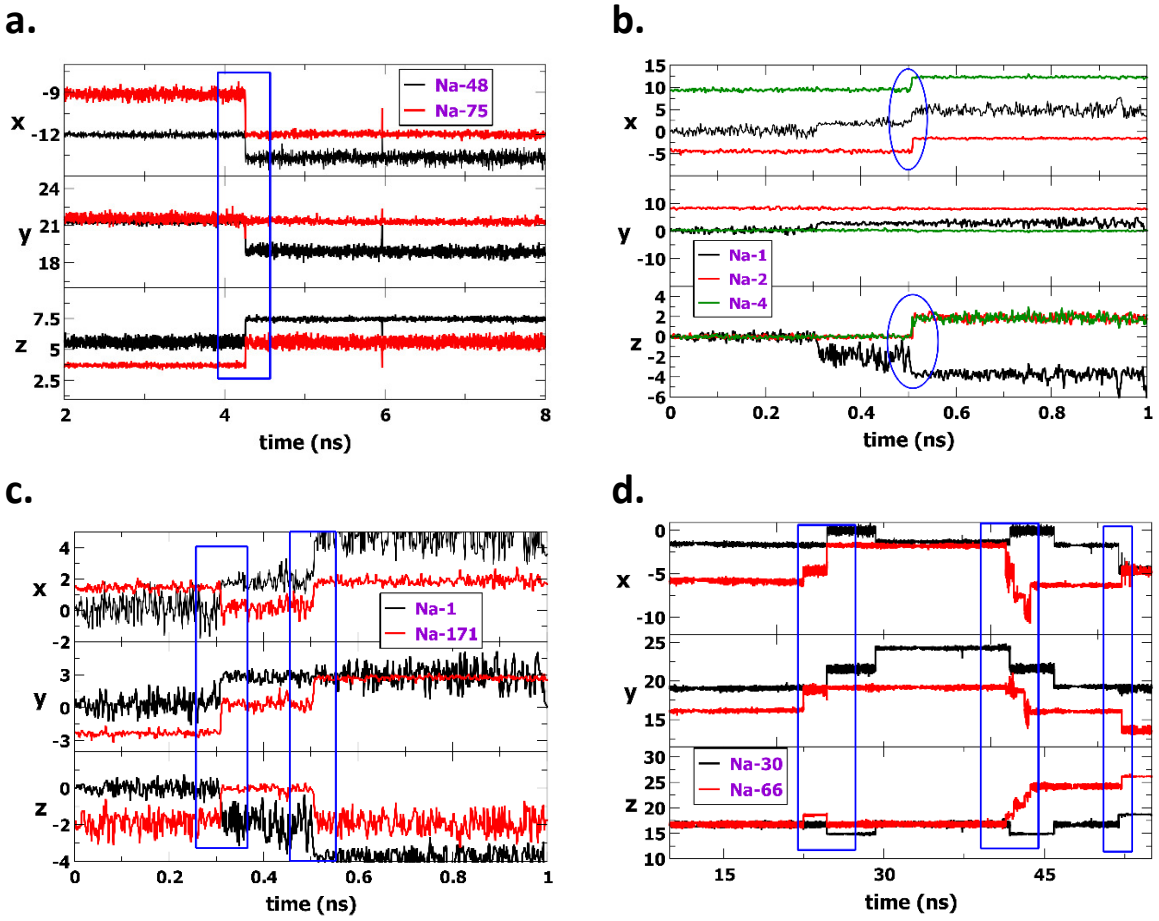

Figure S2:

Statistical distribution of the tagged Na+ ion (panels **a, b**) for $NaZr_2P_3O_{12}$, respectively for γ = 3, and 9, during the 100 *ns* of MTD simulation at 500 K; and (panels **c, d)** for $Na_4Zr_2Si_3O_{12}$, respectively for γ = 3, and 9 during the 200 *ns* MTD simulation at 500 K.

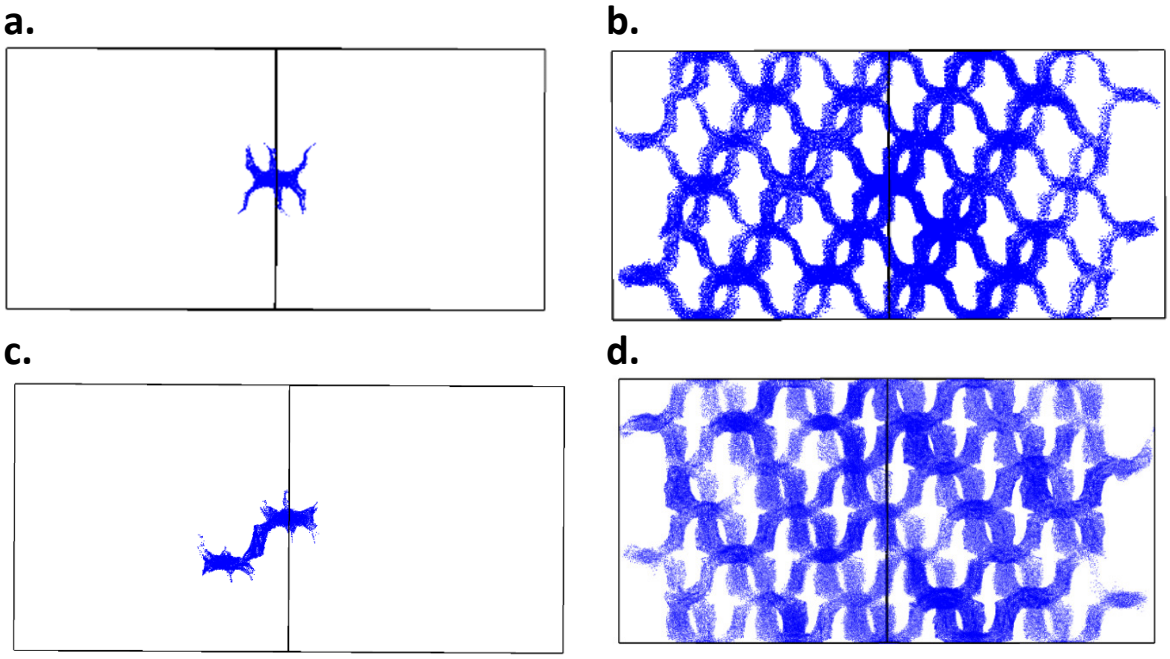

Figure S3:

Distance of the tagged 'Na^{+}' from its initial location as a function of the time elapsed (panel a) for $NaZr_2(PO4)_3$, and (panel b) for $Na_4Zr_2(SiO_4)_3$ from MTD simulations at 500 K, for bias factor γ= 6. In panels c) and d) an enlarged view of the short time behaviour of Na^+ ions are shown respectively for $NaZr_2(PO4)_3$ and $Na_4Zr_2(SiO_4)_3$ systems. It shall be noted in Fig. S3 c) that the tagged ion makes several unsuccessful hops to its neighbours at 6.4 A within about 1.6 ns before hoping off from the initial Na1 site. Fig.S3 d) also shows several attempts by the tagged Na^+ to reach the neighbouring Na2 site (~3.4 A) before it succeeds. The motion of the ion in its newer sites also follow this pattern. In Fig.S3 a) and b) there are instances when the tagged ion after diffusing off to distance sites returns *close* to the original site, respectively after durations of 80 ns and 60 ns. Thus, the ion explores the local minima quite extensively before diffusing off, thus ensuring the quality of the sampling.

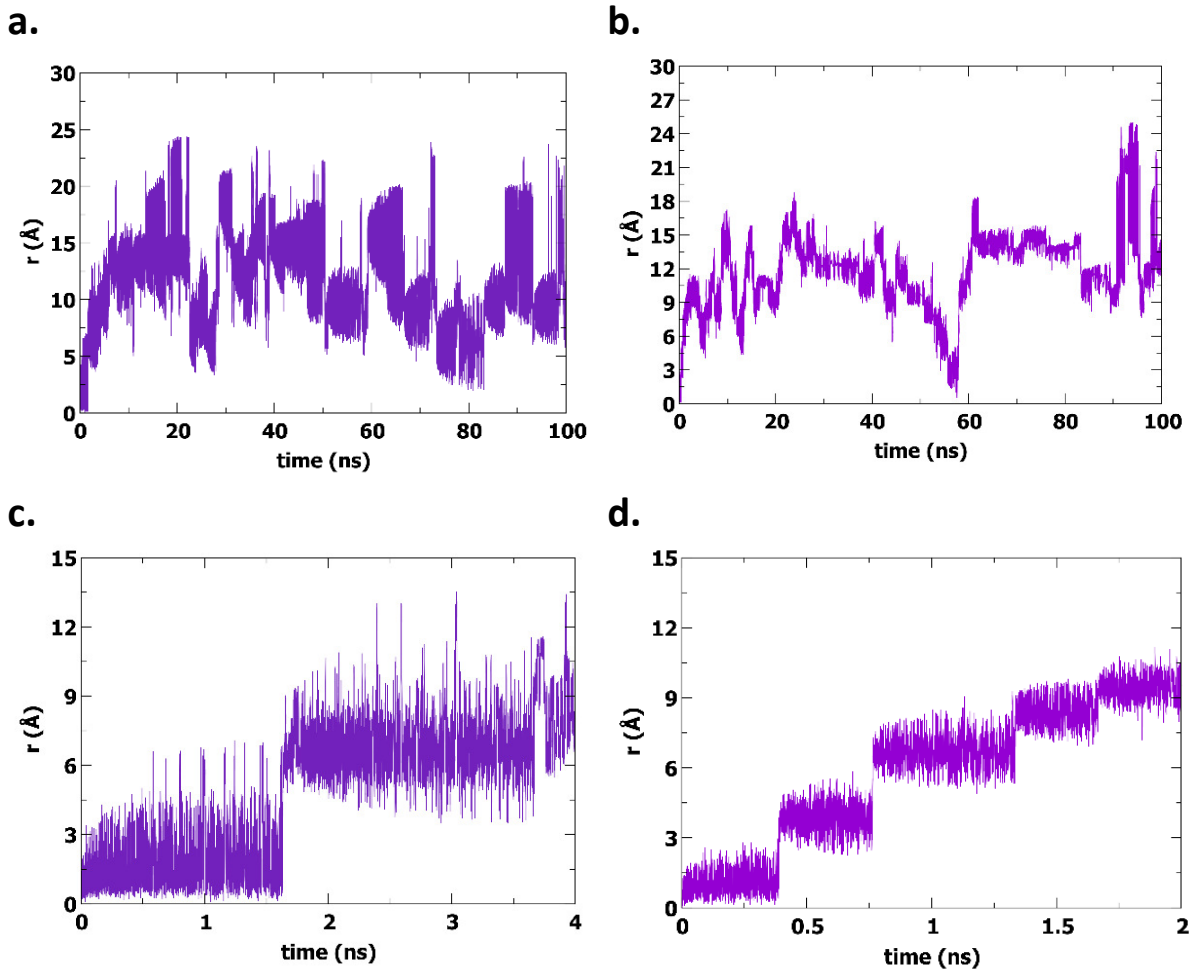

Figure S4:

Free energy profiles for γ= 6 and 9, for $NaZr_2P_3O_{12}$ (left), and $Na_4Zr_2Si_3O_{12}$ (right) from MTD simulations at 500 K.