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

Defect formation and migration in Nasicon $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$

Hamid R. Arjmandi[ab] and Steffen Grieshammer[*abc]

[a] Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen, Germany;

[b] JARA-HPC, Forschungszentrum Jülich, RWTH Aachen University, Germany.

[c] Helmholtz-Institut Münster (IEK-12), Forschungszentrum Jülich GmbH, 48149 Münster, Germany

* E-mail: s.grieshammer@fz-juelich.de

The most stable configurations for $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ with x=0.25 is presented in Figures S1.

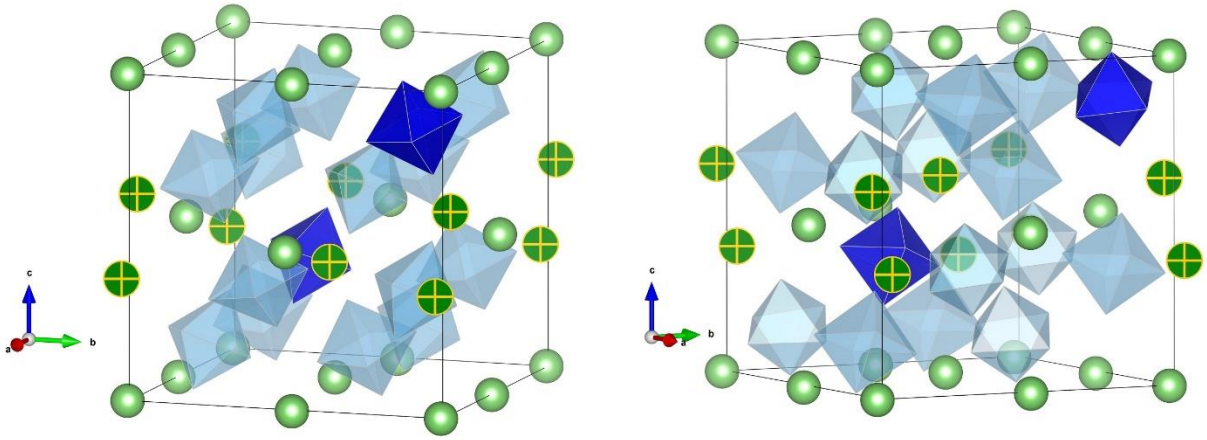

Figure S1 The most stable LATP supercell with Al concentration of 0.25.

The migration pathways of interstitial and vacancy Li, O, Ti/P, Na, and K are shown in Figures S2 to S6.

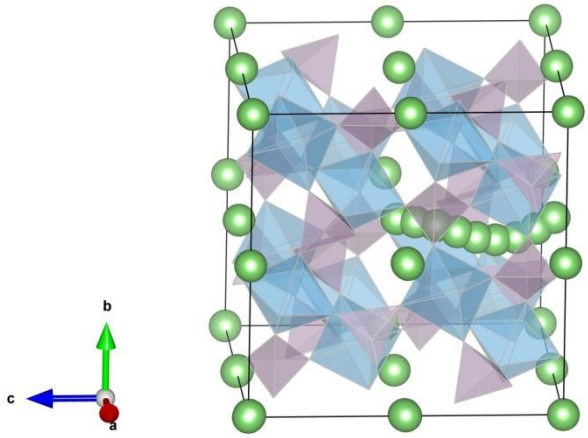

Figure S2 Migration path of lithium vacancy.

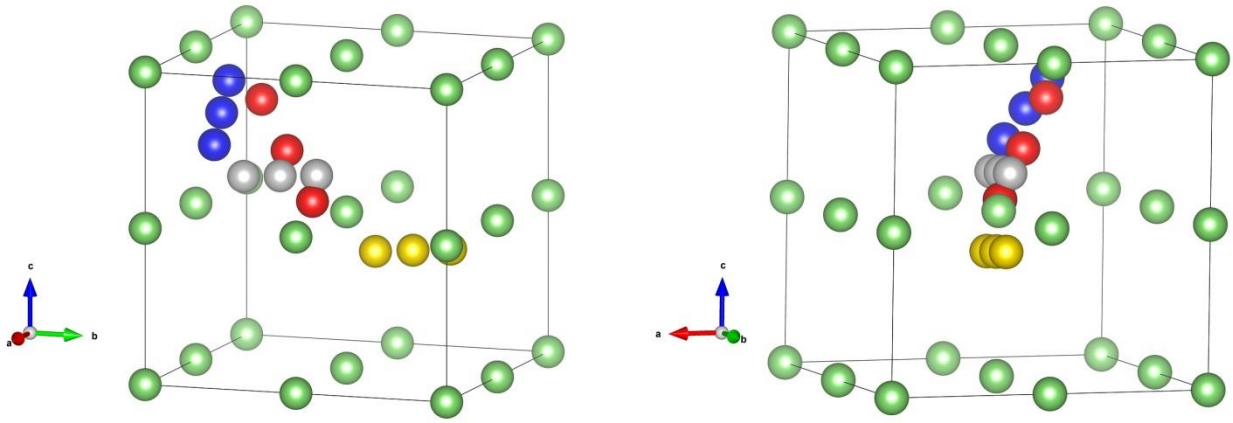

Figure S3 Calculated migration paths for x=0.125 corresponding to Figure 3 in the main text. Path 1 (grey), Path 2 (yellow), Path 3 (blue), Path 4 (red). The aluminum ion is located close to the center of the cell.

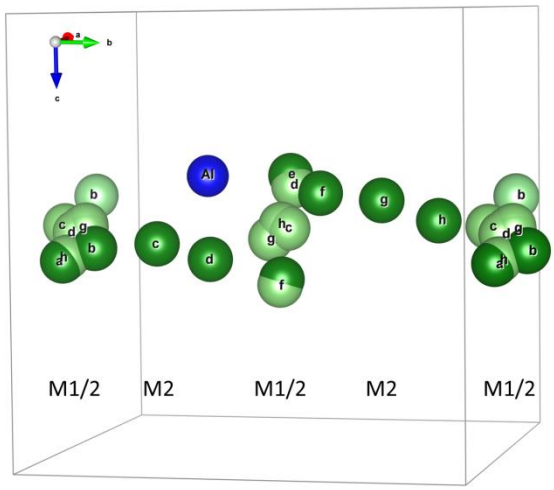

Figure S4 Visualization of Li migration route in LATP with x=0.125. The labels are the same as in Figure 4 in the main text. The migrating ion is shown in dark green and the other Li-ions are represented in light green.

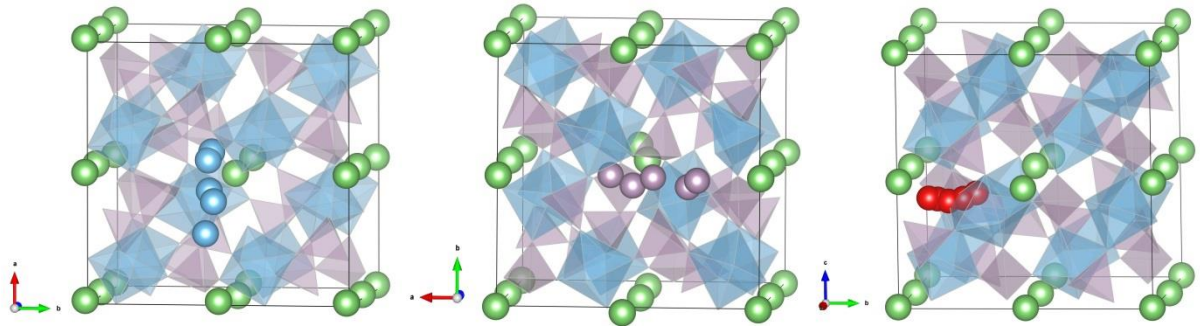

Figure S5 Migration pathway for interstitial titanium, phosphorous and oxygen, respectively.

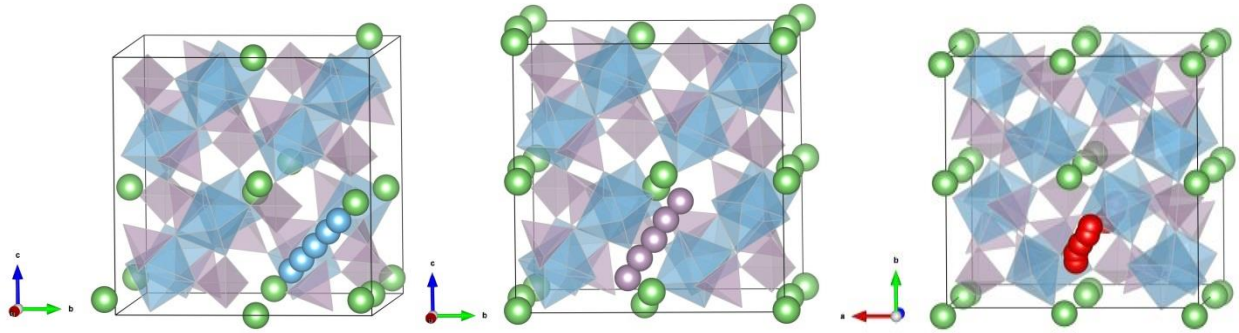

Figure S6 Migration pathway of titanium, phosphorous and oxygen vacancy, respectively.

The migration pathways of Na and K are shown in S7 and S8.

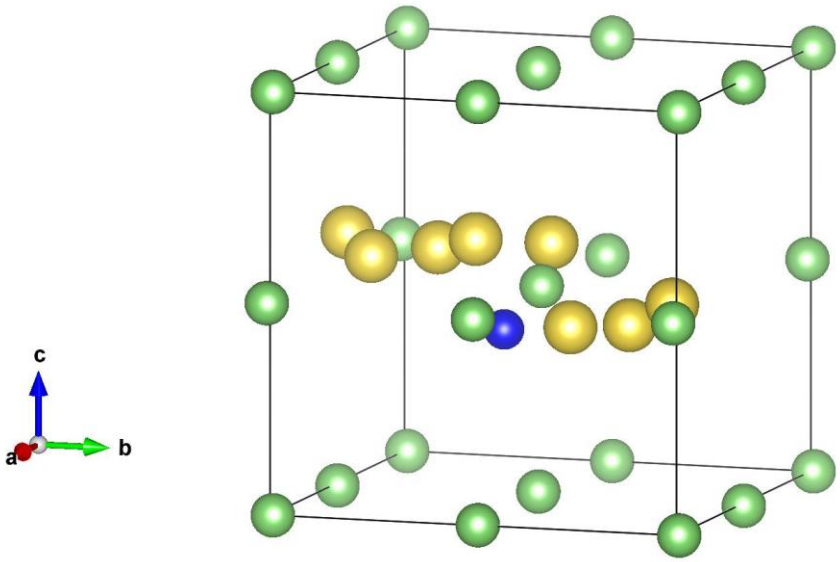

Figure S7 Visualization of migration path for sodium ion, shown in yellow.

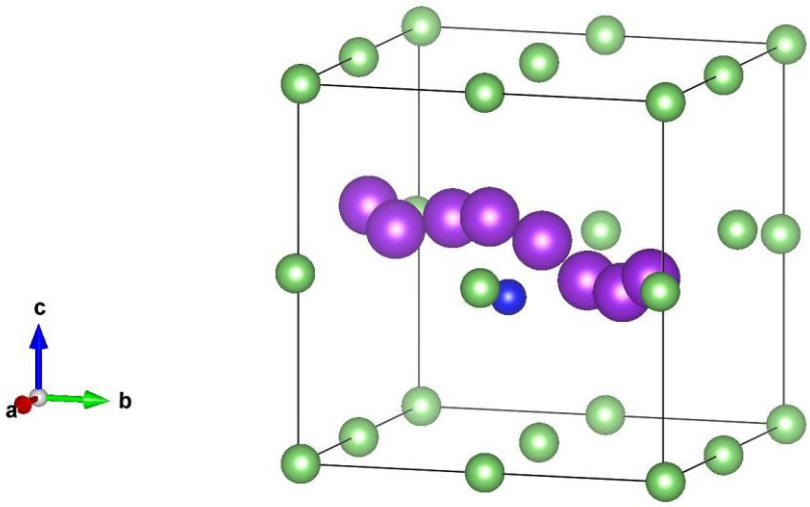

Figure S8 Visualization of migration path for potassium ion, which is shown in purple.

The energy profile for migration in NATP and KATP is shown in Figure S9.

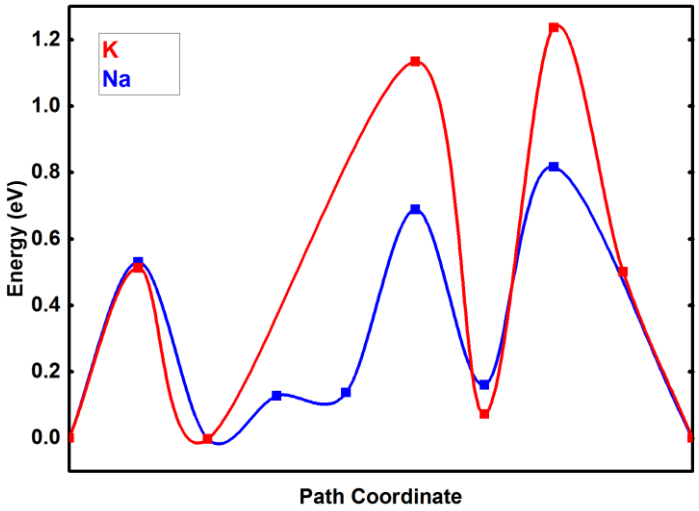

Figure S9 Migration energy profile for Na- and K-ion in NATP and KATP, respectively.

The migration pathway of the proton is shown in Figure S10.

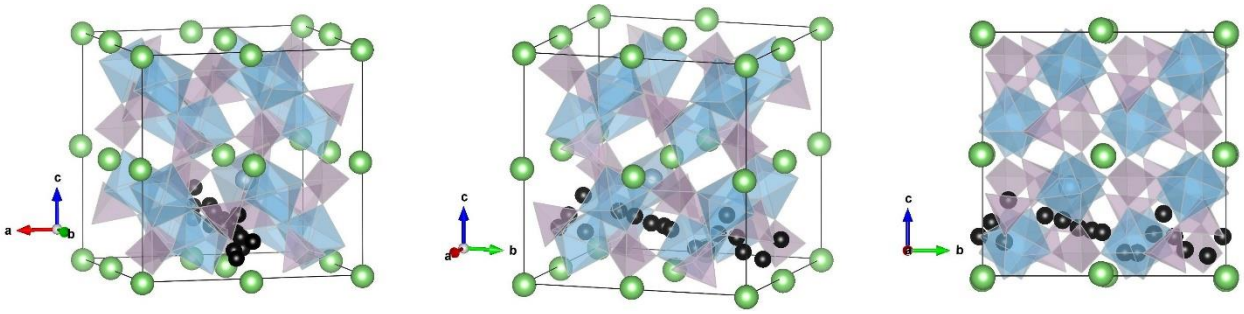

Figure S10 Visualization of migration path for hydrogen ion (black) from different angles.

The following tables contain a more detailed values related to the bottlenecks.

Table S1 Properties of cation or anion bottlenecks for all the pathways at position.

	Average Bond Length in LiO_4 Tetrahedron (Å)	Minimum Bond Length in LiO_4 Tetrahedron (Å)	Minimum distance to the Neighboring Cations (Å)	Li Displacement (Å)	Energy Barrier (eV)
Path 1	2.12	1.96	2.78	6.07	0.26
Path 2	2.25	1.94	2.67	6.14	0.31
Path 3	1.85	1.81	2.30	8.34	1.37
Path 4	1.87	1.86	2.29	10.45	1.52

Table S2 Properties of cation or anion bottlenecks for each step of the most favorable pathway.

	Average Bond Length in LiO_4 Tetrahedron (Å)	Minimum Bond Length in LiO_4 Tetrahedron (Å)	Volume of LiO_4 Tetrahedron (Å3)	Minimum distance to the Neighboring Cations (Å)	Energy Barrier (eV)
Point c	2.19	1.99	5.79	2.73	0.01
Point d	2.21	1.98	6.54	2.74	0.10
Point b	2.25	1.94	6.65	2.67	0.26
Point c	2.19	1.99	5.79	2.73	0.01