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Quantifying the Impact of Disorder on Li-Ion and Na-Ion Transport in Perovskite Titanate Solid Electrolytes for Solid-State Batteries

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SI 1 – Potential Model

The potential model of Pedone et al., was used for all calculations[1], and full details are in the SI. The short-range forces are accounted for by interatomic potentials (Morse / Lennard-Jones type) and the long-range ionic interactions treated using Coulombic terms according to

$$U(r) = \frac{z_i z_j e^2}{r} + D_{ij}\left[\left\{1 - e^{-a_{ij}(r-r_0)}\right\}^2 - 1\right] + \frac{C_{ij}}{r^{12}} \quad (3)$$

where $z_i z_j$ are the charges on atoms i and j, D_{ij} is the depth of the potential energy well, a_{ij} is the a function of the slope of the potential energy well, r is the distance of seperation, r_0 is the equilibrium distance between species i and j, and C_{ij} relates to the potretnial energy well and describes the repulsion at very short distances between species i and j. The parameters for each interaction are listed in Table S1.

Table S1 - Potential model parameters

Ion Pair	D_{ij} (eV)	A_{ij} (Å^{-2})	R_0(Å)	C_{ij}(eV Å^{12})
$Li^{0.6} – O^{-1.2}$	0.00111400	3.429506	2.681360	1.0
$Na^{0.6} – O^{-1.2}$	0.02336300	1.763867	3.006315	5.0
$La^{1.8} – O^{-1.2}$	0.00016219	2.023100	4.400680	3.0
$Ti^{2.4} – O^{-1.2}$	0.02423500	2.254703	2.708943	1.0
$O^{-1.2} – O^{-1.2}$	0.04239500	1.379316	3.618701	22.0

SI 2 – Simulation Cells

Table S2 – Total number of atoms in each simulation cell.

Composition	Ti	O	La	Li	Na	Vacancies
$Li_{0.46}La_{0.51}TiO_3$	768	2304	394	354	N/A	20
$Li_{0.42}La_{0.53}TiO_3$	768	2304	404	324	N/A	40
$Li_{0.38}La_{0.54}TiO_3$	768	2304	414	294	N/A	60
$Li_{0.34}La_{0.55}TiO_3$	768	2304	424	264	N/A	80
$Na_{0.10}La_{0.63}TiO_3$	768	2304	394	N/A	354	20
$Na_{0.27}La_{0.59}TiO_3$	768	2304	404	N/A	324	40
$Na_{0.24}La_{0.58}TiO_3$	768	2304	414	N/A	294	60
$Na_{0.34}La_{0.56}TiO_3$	768	2304	424	N/A	264	80

SI 3 – Volume change with increasing disorder

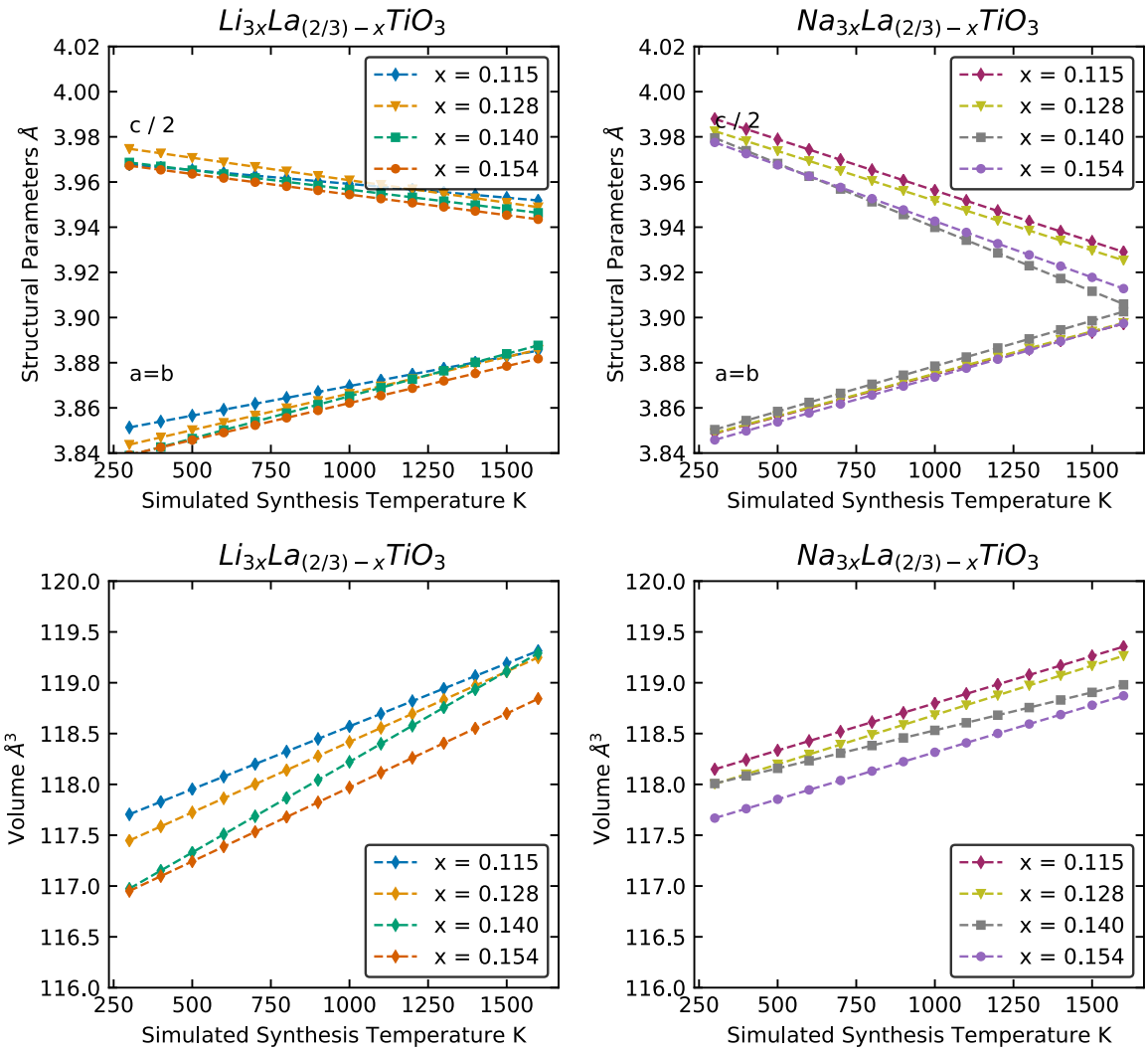

Figure S1 – Calculated volume as a function of temperature for LLTO (A) and NLTO (B) obtained from Monte Carlo. Calculated lattice parameters as a function of temperature for LLTO (C) and NLTO (D) obtained from Monte Carlo.

SI 4 – Lithium Vacancy Distribution

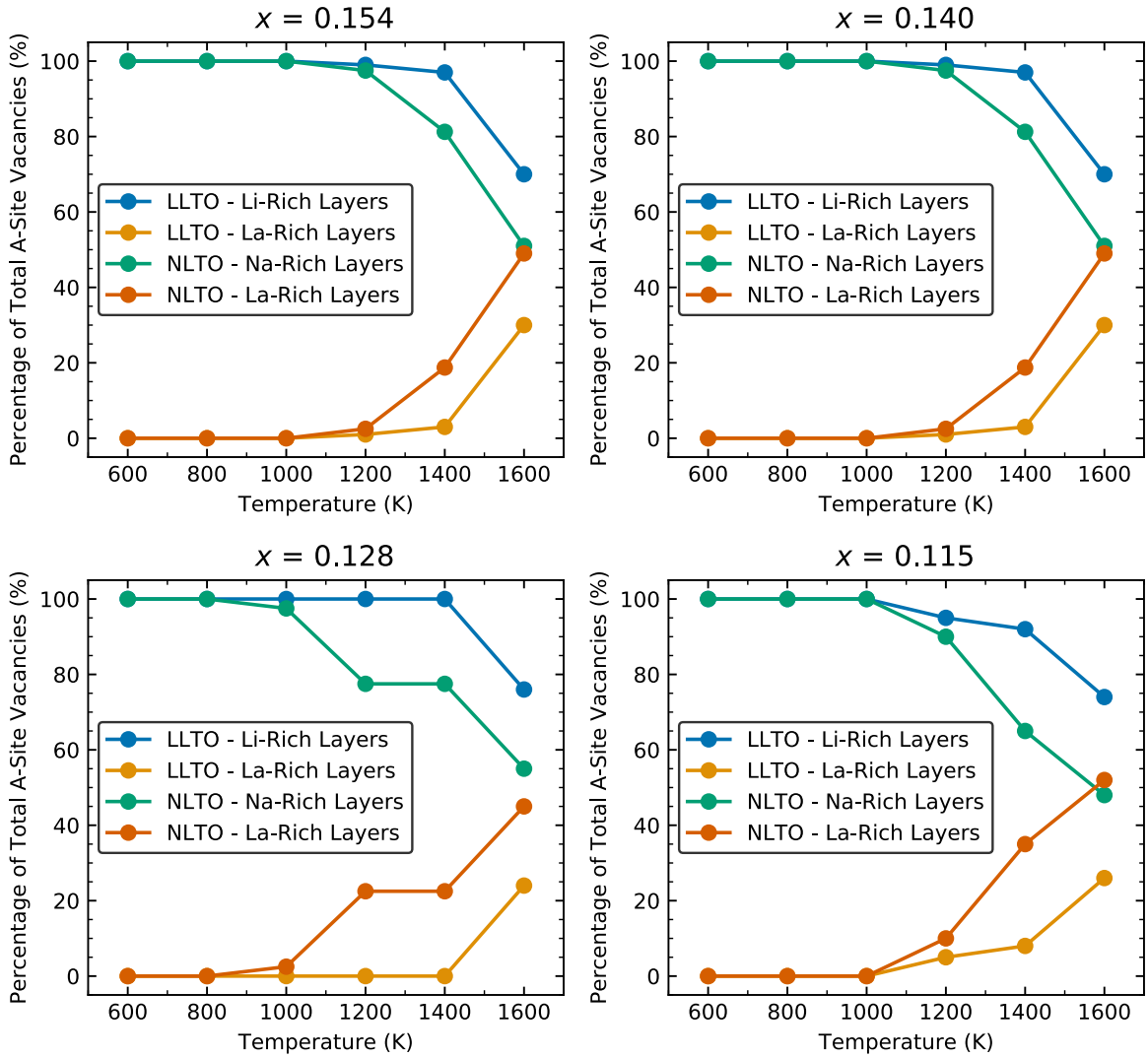

Figure S2 – Percentage of the total number of A-site vacancies in the Li/Na–rich layers for the x=0.115 system. A value of 50% indicates that half of the total A-site vacancies are in the Li/Na-rich layers and half are in the La-rich layers.

SI 5 – LLTO RDF and Average Bond length

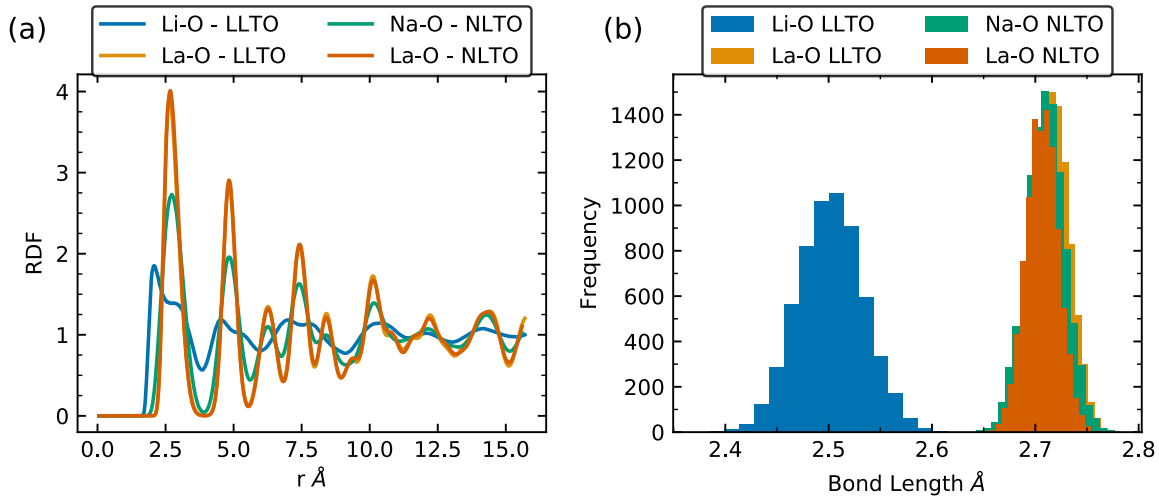

Figure S3– **(a)** Radial distribution function of Li-O (blue) and La-O (orange) in x = 0.115 LLTO and Na-O (green) and La-O (red) in x = 0.115 NLTO at 1600 K. **(b)** Histogram showing the distribution of Li-O (blue) and La-O (orange) bond lengths in x = 0.115 LLTO and Na-O (green) and La-O (red) bond lengths in x = 0.115 NLTO at 1600 K.

SI 6 – LLTO Mean Squared Displacement

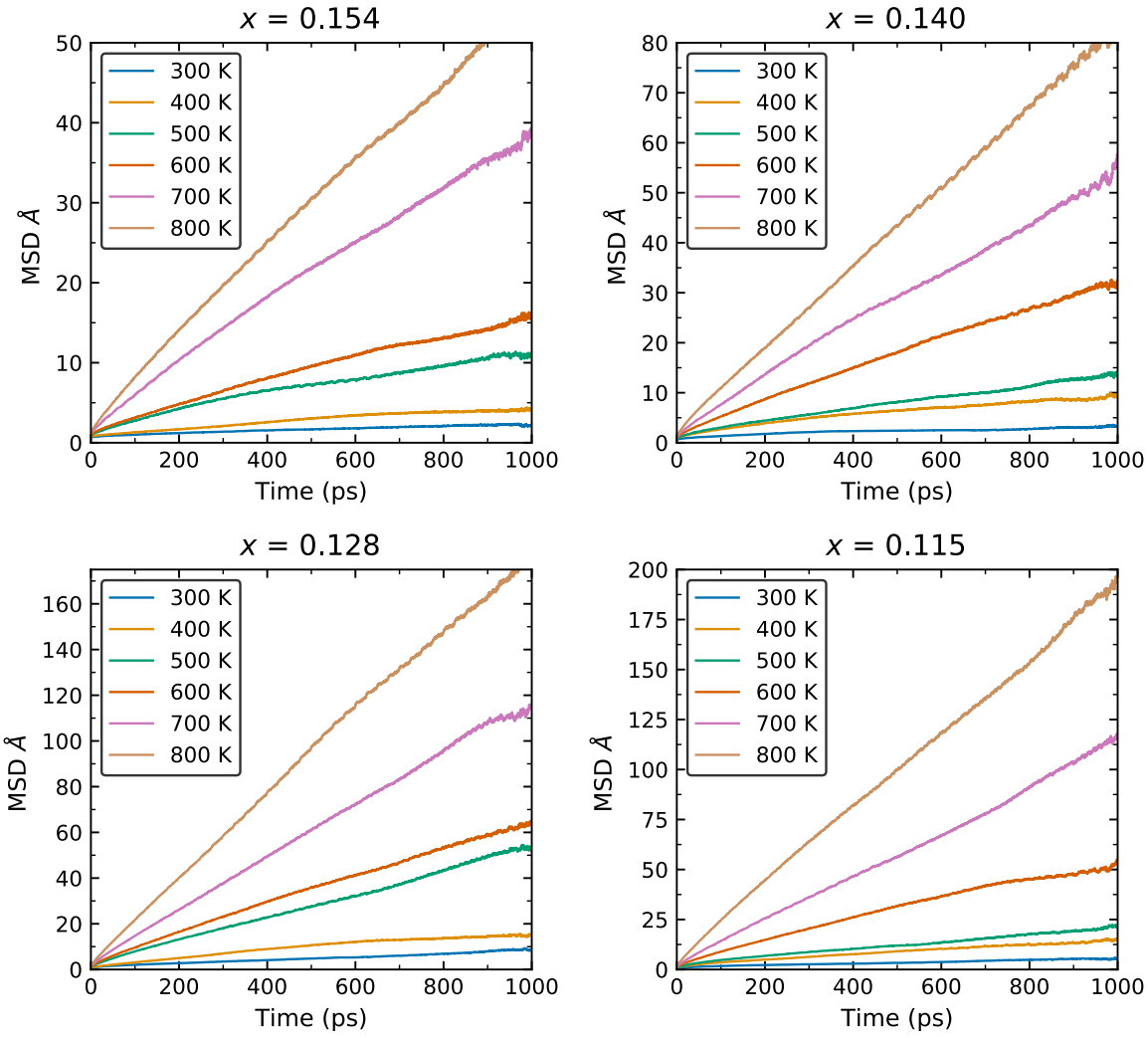

Figure S4 – MSD plots for each LLTO system at within a temperature range of 300 – 800 K.

SI 7 – Order Parameter

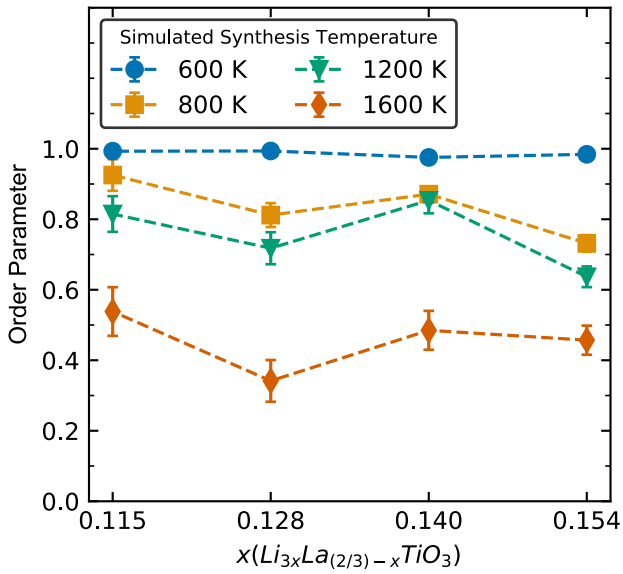

Figure S5 – Order parameter for the x = 0.115, 0.128, 0.140 and 0.154 LLTO configurations for simulated synthesis temperatures of 400 K (blue), 800 K (orange), 1200 K (green) and 1600 K (red).

SI 8 – Comparison of conductivity and activation energy with other work.

Table S3 – Li-ion conductivities $\sigma_{Bulk}(Scm^{-1})$ and activation energies for different compositions.

Composition	$\sigma_{Bulk}(Scm^{-1})$	E_a(eV)	Reference
$Li_{0.46}La_{0.51}TiO_3$	6.2 x 10^{-5}	0.19	This work
$Li_{0.42}La_{0.53}TiO_3$	4.2 x 10^{-4}	0.21	This work
$Li_{0.38}La_{0.54}TiO_3$	6.1 x 10^{-4}	0.19	This work
$Li_{0.34}La_{0.55}TiO_3$	1.0 x 10^{-3}	0.23	This work
$Li_{0.10}La_{0.63}TiO_3$	7.9 x 10^{-5}	0.36	2
$Li_{0.27}La_{0.59}TiO_3$	6.8 x 10^{-4}	0.36	3
$Li_{0.24}La_{0.58}TiO_3$	3.9 x 10^{-4}	0.37	4
$Li_{0.34}La_{0.56}TiO_3$	6.9 x 10^{-4}	0.35	5

References

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