Supplementary Materials

Intergranular and microstructural evolution regulates mechanical and ion-transport properties of NaSICON-type solid electrolytes

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Supplementary Table 1. Lattice parameters used in and obtained from the Rietveld refinements of pristine NZSP and LN-modified samples

Phase	Parameters	Pristine	1LN	2LN	5LN	10LN
NZSP SG C2/c	V_{UC} (Å^3)	1087.6	1087.8	1089.6	1088.9	1088.1
	a (Å)	15.7421(3)	15.7384(2)	15.7211(3)	15.7284(3)	15.7471(3)
	b (Å)	9.0998(2)	9.1002(1)	9.0936(2)	9.0982(2)	9.1063(2)
	c (Å)	9.1932(2)	9.1945(1)	9.2131(2)	9.2069(2)	9.1956(2)
	β (°)	124.3265(11)	124.3051(8)	124.1845(10)	124.2595(10)	124.3918(11)
$Na_3LaP_2O_8$ SG Pca21	V_{UC} (Å^3)	Not applicable	1411.6*	1411.6*	1422.4	1415.7
	a (Å)	Not applicable	14.083*	14.083*	14.149(3)	14.1029(13)
	b (Å)	Not applicable	5.352*	5.352*	5.389(2)	5.3618(6)
	c (Å)	Not applicable	18.729*	18.729*	18.656(8)	18.7225(18)

ZrO_2 SG P21/c	V_{UC} (Å^3)	140.5*	140.5*	140.5*	140.5*	140.5
	a (Å)	5.144*	5.144*	5.144*	5.144*	5.1466(4)
	b (Å)	5.210*	5.210*	5.210*	5.210*	5.2080(4)
	c (Å)	5.311*	5.311*	5.311*	5.311*	5.3078(5)
	β (°)	99.22*	99.22*	99.22*	99.22*	99.136(5)

Estimated standard deviations (esd) are given in parentheses after the refined values; for example, 15.7421(3) Å corresponds to 15.7421 ± 0.0003 Å. The ICSD crystallographic data were used as initial structural models for Rietveld refinement of the NZSP(38104[1]), $Na_3LaP_2O_8$(430499[2]), and ZrO_2(82543[3]) phases. * Lattice parameters were fixed to the corresponding ICSD values and were not refined because reliable refinement was not possible for the low-content secondary phases owing to strong peak overlap with the main NZSP phase and the limited number of independent reflections. The weighted-profile R-factor (Rwp) values for 1LN, 2LN, 5LN, and 10LN were 6.50%, 6.39%, 5.90%, and 5.54%, respectively, with corresponding goodness-of-fit (GoF) values of 3.33, 3.28, 3.07, and 2.82.

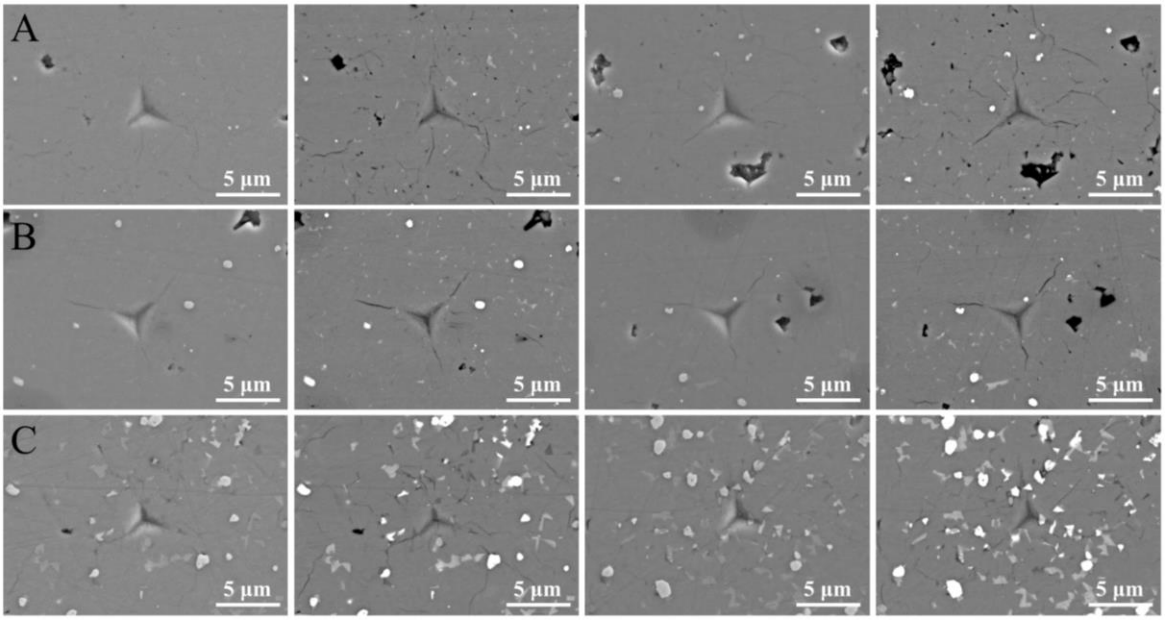
Supplementary Table 2. Comparison of calculated and Rietveld-refined $Na_3LaP_2O_8$ fractions based on La mass balance

Sample	x	Calculated $Na_3LaP_2O_8$ (wt%)	Refined $Na_3LaP_2O_8$ (wt%)
1LN	0.01	0.7	0.7
2LN	0.02	1.5	1.3
5LN	0.05	3.6	3.7
10LN	0.10	7.0	6.0

For the LN-modified compositions, x mol of nominal $LaNbO_4$ was added per mole of pristine NZSP with x = 0.01, 0.02, 0.05, and 0.10 for 1LN, 2LN, 5LN, and 10LN, respectively. Assuming that the added La is incorporated into $Na_3LaP_2O_8$, the corresponding nominal $Na_3LaP_2O_8$ fraction was calculated from the La balance. Using the molar masses, *M*, of NZSP (538.6 g mol^{-1}), $LaNbO_4$ (295.8 g mol^{-1}), and $Na_3LaP_2O_8$ (397.8 g mol^{-1}), the nominal $Na_3LaP_2O_8$ weight fraction is calculated as:

$$w_{Na_3LaP_2O_8} = \frac{397.8x}{538.6 + 295.8x} \times 100\%$$

The calculated $Na_3LaP_2O_8$ weight fractions are in reasonable agreement with the Rietveld-refined values, supporting the quantitative consistency between $Na_3LaP_2O_8$ formation and the nominal $LaNbO_4$ addition.



Supplementary Figure 1. SEM images of imprints after nano indentation. (A) 1LN; (B) 2LN; (C) 10LN. 10LN sample has more ZrO_2 particles (white) with indents on or nearby.

The 10LN sample contains a higher amount of ZrO_2 (bright particles). Compared with 1LN, more indents in 10LN are located near or on the ZrO_2 particles, resulting in a slightly higher measured hardness. In addition, both 1LN and 10LN exhibit more microcracks than 2LN, leading to correspondingly lower elastic modulus and hardness.

Supplementary Table 3. Parameters used for fracture toughness calculations

Sample	Pillar radius, R (μm)	E/H	Critical load of failure, P_c (mN)	Fracture toughness, K_{IC} (MPa·m$^{0.5}$)
Pristine	2.58 ± 0.08	14.7 ± 0.1	8.6 ± 1.3	0.60 ± 0.10
1LN	2.63 ± 0.10	13.1 ± 0.1	15.2 ± 1.9	0.97 ± 0.12
2LN	2.57 ± 0.07	12.5 ± 0.1	17.7 ± 1.9	1.09 ± 0.12
5LN	2.62 ± 0.09	12.3 ± 0.1	17.8 ± 3.0	1.08 ± 0.18
10LN	2.59 ± 0.13	12.4 ± 0.1	12.8 ± 2.3	0.78 ± 0.14

The Elastic modulus (E) and hardness (H) were taken from measurements within the critical load range.

Supplementary Table 4. Individual ring-on-ring fracture-strength measurements of pristine and LN-modified NZSP samples

Sample	Individual fracture strength values (MPa)	n	Range (MPa)
Pristine	56, 64, 64, 67, 68, 72, 74, 75, 79, 83, 85, 86, 87, 87, 88, 89, 101, 104	18	56-104
1LN	85, 90, 64, 102, 94	5	64-102
2LN	97, 88, 90, 72, 85, 93	6	72-97
5LN	68, 81, 117, 99, 80	5	68-117
10LN	99, 108, 82, 97, 94	5	82-108

Statistical differences in fracture strength among the LN-modified samples were evaluated using Welch's one-way ANOVA, which does not assume equal variances and is suitable for groups with unequal variances and slightly different sample sizes. Statistical significance was defined as $P < 0.05$. The analysis showed no statistically significant difference among the LN-modified groups [$F(3, 8.76) = 0.797$, $P = 0.527$].

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