Electronic Supplementary Information for

**Cation ordering in A-site-deficient Li-ion conducting perovskites La\(_{1-x}/3\)Li\(_x\)NbO\(_3\)**

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**Fig. S1** Powder XRD patterns obtained from single-crystalline LNO and LLNO4 samples. Splitting of the (200) peaks shown in the insets indicates an orthorhombic crystal symmetry (space group C\(_{mmm}\)) for both compounds. Calculation revealed their lattice parameters of LNO (\(a = 7.8129\) Å, \(b = 7.8437\) Å, \(c = 7.9364\) Å) and LLNO4 (\(a = 7.7888\) Å, \(b = 7.8252\) Å, \(c = 7.9164\) Å).

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**Fig. S2** Simulated (a) [001]\(_p\) and (b) [110]\(_p\) SAED patterns from the average crystal structure model of La\(_{0.32}\)Li\(_{0.06}\)NbO\(_3\) (\(x = 0.06\)) which has the same crystal symmetry (orthorhombic) and a similar Li content compared to LLNO4 (\(x = 0.04\)).
Fig. S3 SAED patterns taken from (a) LNO and (b) LLNO4 along their [110]<sub>p</sub> zone axes. (c) Intensity-scan profiles taken from the marked regions in (a) and (b) to reveal the positions of weak reflections, i.e. (π<sub>1</sub>, π<sub>2</sub>) of LNO and (π<sub>1</sub>', π<sub>2</sub>' and ω) of LLNO4, along the [1-10]<sub>p</sub> direction.

Fig. S4 [001]<sub>p</sub> zone-axis HAADF/ABF imaging. (a) HAADF and (b) ABF micrographs of LNO. (c) HAADF and (d) ABF micrographs of LLNO4. Overlaid structure models indicate the positions of O (red), Nb+O (blue) and La+vacancy (green) columns.