Supplementary Information

Near stoichiometric lithium niobate crystal with dramatically enhanced piezoelectric performance for high temperature acceleration sensing

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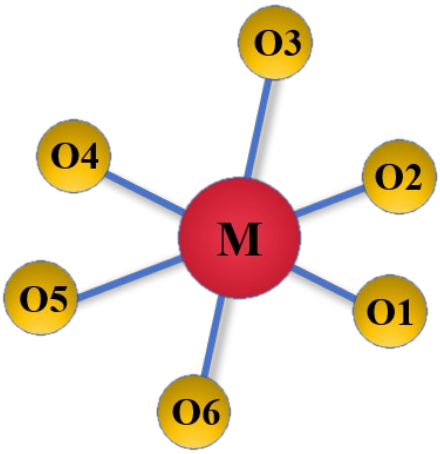

Fig. S1 Distortion model of the MO_6 polyhedron.

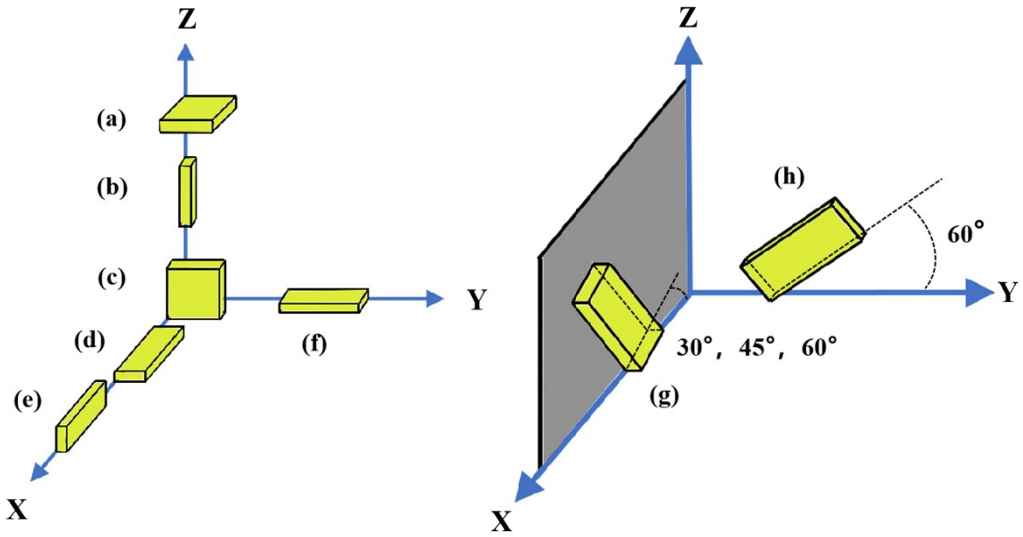

Fig. S2 Crystal cuts for evaluation of the electro-elastic constants [(a) Z-square plate; (b) Z bar; (c) X-square plate; (d) ZX plate; (e) YX plate; (f) ZY plate; (g) YZt/θ (θ= 30°, 45° and 60°); (h) XYt/θ (θ= 60°)]

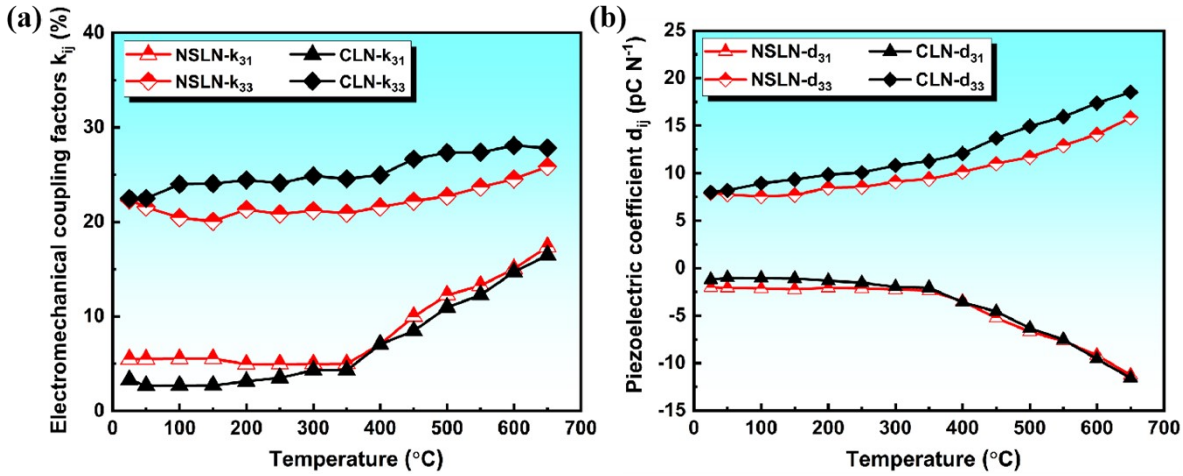

Fig. S3 Variations of (a) electromechanical coupling factors, (b) piezoelectric coefficients as a function of temperatures for NSLN and CLN crystals.

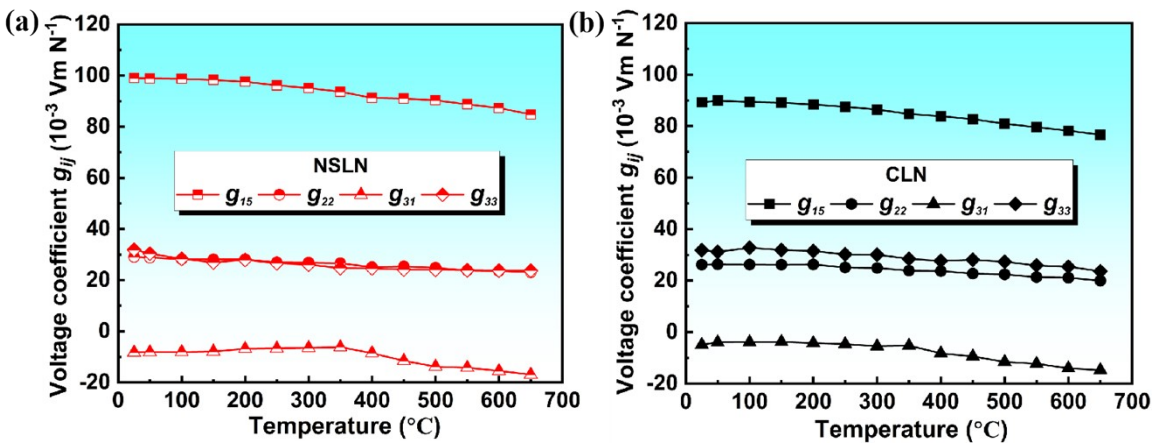

Fig. S4 Variations of piezoelectric voltage coefficients g_{ij} as a function of temperatures for (a) NSLN and (b) CLN crystals.

It was found that the piezoelectric voltage coefficients g_{ij} for NSLN and CLN all showed a decreasing trend with temperature, as shown in Fig. S4. There was a good observation that while the d_{ij} was relatively stable with temperature, the increase in ε_{ij} with temperature leaded to a slight decrease in g_{ij} (since $g_{ij} = d_{ij} / \varepsilon_{ij}$) for NSLN and CLN crystals. Clearly that the g_{15} demonstrated maximum values, which were represented by 98.9×10^{-3} Vm N^{-1} and 89.2×10^{-3} Vm N^{-1} for NSLN and CLN crystals at room temperature.

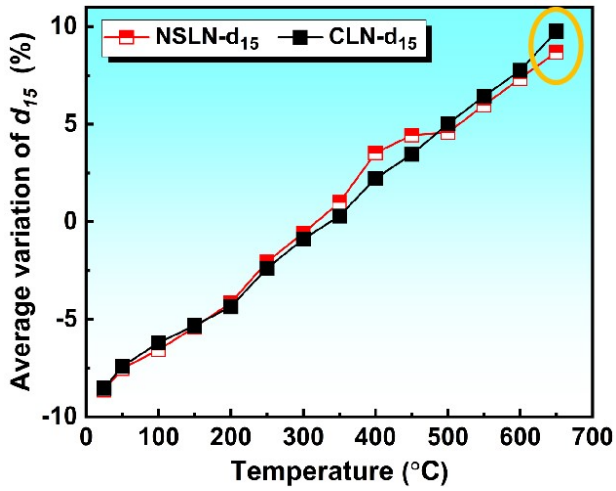

Fig. S5 Average variations of the piezoelectric coefficients d_{15} as a function of temperatures for NSLN and CLN crystals.

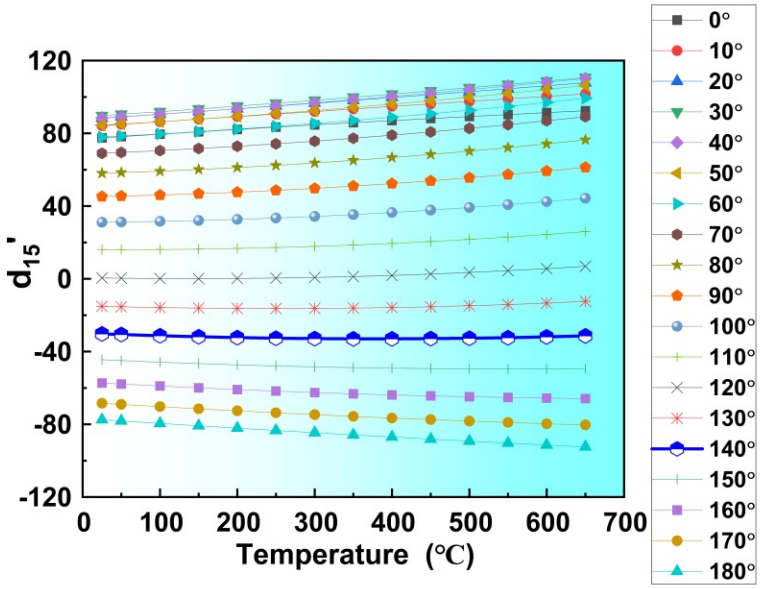

Fig. S6 Variations of the effective piezoelectric coefficients d_{15}' rotated around the X-axis with different angles as a function of temperatures for NSLN crystal.

Table S1 Crystal cuts, vibration modes, material constants and related equations for determination of the electro-elastic constants for NSLN and CLN crystals.

Crystal cuts	Vibration modes	Material constants	Related equations
X plate	/	$\varepsilon_{11}^{T} / \varepsilon_{0}$	$\frac{\varepsilon_{ii}^{T}}{\varepsilon_{0}} = \frac{C \cdot t}{A \cdot \varepsilon_{0}}$
Z plate	/	$\varepsilon_{33}^{T} / \varepsilon_{0}$	
X plate	thickness shear	d_{15}, s_{55}^{E}	$k_{ij}^{2} = \frac{\pi}{2}\frac{f_r}{f_a} tan \frac{\pi}{2}\left(\frac{f_a - f_r}{f_a}\right)$ $s_{ii}^{E} = \frac{1}{4\rho (tf_a)^2 (1 - k_{ij}^{2})}$ $d_{ij} = k_{ij}\sqrt{\varepsilon_{ii}^{T} s_{jj}^{E}}$
Z bar	longitudinal	d_{33}, s_{33}^{E}	$k_{ii}^{2} = \frac{\pi}{2}\frac{f_r}{f_a} tan \frac{\pi}{2}\left(\frac{f_a - f_r}{f_a}\right)$ $s_{ii}^{E} = \frac{1}{4\rho (lf_a)^2 (1 - k_{ii}^{2})}$ $d_{ii} = k_{ii}\sqrt{\varepsilon_{ii}^{T} s_{jj}^{E}}$
YX plate ZX plate	length extension	d_{21}, s_{11}^{E}	$\frac{k_{ij}^{2}}{1 - k_{ij}^{2}} = \frac{\pi}{2}\frac{f_a}{f_r} tan \frac{\pi}{2}\left(\frac{f_a - f_r}{f_a}\right)$
		d_{31}, s_{11}^{E}	$s_{ii}^{E} = \frac{1}{4\rho (lf_r)^2}$ $d_{ij} = k_{ij}\sqrt{\varepsilon_{ii}^{T} s_{jj}^{E}}$
YZ$t/\theta$ XY$t/\theta$		s_{13}^{E} s_{12}^{E}	$s_{33}^{E'}(\theta) = s_{11}^{E} sin^4\theta + s_{33}^{E} cos^4\theta + (2s_{13}^{E} + s_{44}^{E}) sin^2\theta cos^2\theta$
		s_{14}^{E}	$s_{22}^{E'}(\theta) = s_{11}^{E} cos^4\theta + s_{33}^{E} sin^4\theta + (2s_{13}^{E} + s_{44}^{E}) sin^2\theta cos^2\theta - 2s_{14}^{E} sin\theta cos^3\theta$ $s_{11}^{E'}(\theta) = s_{11}^{E} cos^4\theta + s_{11}^{E} sin^4\theta + (2s_{12}^{E} + s_{66}^{E}) sin^2\theta cos^2\theta$

Table S2 Distortion Δd of each octahedron contained in the pristine phase and the defect phase.

	Bond	Bond distances (Å)	Bond angle (°)	Δd (Å)
Pristine phase (Nb-O)	Nb_1-O_1	1.90022	165.0362	**0.756**
	Nb_1-O_4	2.14370		
	Nb_1-O_2	1.90022	165.0376	
	Nb_1-O_5	2.14370		
	Nb_1-O_3	1.90021	165.0349	
	Nb_1-O_6	2.14372		
Pristine phase (Li-O)	Li_1-O_1	2.23463	156.0552	**0.671**
	Li_1-O_4	2.03026		
	Li_1-O_2	2.23468	156.0533	
	Li_1-O_5	2.03026		
	Li_1-O_3	2.23461	156.0537	
	Li_1-O_6	2.03025		
V_{Li}^{-} (Nb_1-O)	Nb_1-O_1	1.91450	168.9592	0.591
	Nb_1-O_4	2.10781		
	Nb_1-O_2	1.91439	168.9622	
	Nb_1-O_5	2.10751		
	Nb_1-O_3	1.91426	169.0006	
	Nb_1-O_6	2.10761		
(Nb_2-O)	/	/	/	0.782
(Nb_3-O)	/	/	/	0.713
(Nb_4-O)	/	/	/	0.807
(Nb_5-O)	/	/	/	0.711
(Nb_6-O)	/	/	/	0.807
(Nb_7-O)	/	/	/	0.712
(Nb_8-O)	/	/	/	0.807
	/	/	/	$\overline{\Delta d}$=**0.741**
Nb_{Li}^{4+} (Nb_{Li}-O)	Nb_{Li}-O_1	2.12294	157.1173	**0.629**
	Nb_{Li}-O_4	1.92963		
	Nb_{Li}-O_2	2.12206	157.1548	
	Nb_{Li}-O_5	1.92955		
	Nb_{Li}-O_3	2.12309	157.1493	
	Nb_{Li}-O_6	1.92955		

Table S3 Elastic constants (c_{ij}) and piezoelectric stress constants (e_{ij}) of V_{Li}^{-} and Nb_{Li}^{4+} calculation models.

c_{ij}	c_{11}	c_{12}	c_{13}	c_{14}	c_{33}	c_{44}	c_{66}
V_{Li}^{-}	216	74.6	80.7	8.5	239	59.3	69.9
Nb_{Li}^{4+}	223	78.1	81.6	5.5	238	65.9	72

e_{ij}	e_{15}	e_{22}	e_{31}	e_{33}
V_{Li}^{-}	4.11	2.12	0.45	1.13
Nb_{Li}^{4+}	3.31	1.60	0.58	0.97

Table S4 Concentration of V_{Li}^{-} and Nb_{Li}^{4+} for LN crystal with different [Li]/[Nb] ratios.

Concentration	NSLN (49.83:50.17)	V_{Li}^{-} (48.94:51.06)	CLN (48.65:51.35)	Nb_{Li}^{4+} (47.92:52.08)
V_{Li}^{-} (%)	0.272	1.696	2.160	3.328
Nb_{Li}^{4+} (%)	0.068	0.424	0.540	0.832

Table S5 Bond distances and bond angles for NSLN and CLN crystals. Variations of the distortion Δd of NbO_6 and LiO_6 octahedron for NSLN and CLN crystals.

NSLN					
Bond distances (Å)		Bond angles (°)		Δd (Å)	Total Δd (Å)
Nb-O_1	2.1354	$\angle O_1-Nb-O_4$	165.588	0.2812	**0.8448**
Nb-O_4	1.8631				
Nb-O_2	1.8629	$\angle O_2-Nb-O_5$	165.593	0.2815	
Nb-O_5	2.1356				
Nb-O_3	2.1358	$\angle O_3-Nb-O_6$	165.604	0.2821	
Nb-O_6	1.8626				

NSLN					
Bond distances (Å)		Bond angles (°)		Δd (Å)	Total Δd (Å)
Li-O_1	2.2566	$\angle O_1-Li-O_4$	153.616	0.2272	**0.6800**
Li-O_4	2.0531				
Li-O_2	2.0534	$\angle O_2-Li-O_5$	153.604	0.2266	

Li-O_5	2.2564				
Li-O_3	2.2562	$\angle O_3-Li-O_6$	153.602	0.0062	
Li-O_6	2.0536				

CLN					
Bond distances (Å)		Bond angles (°)		Δd (Å)	Total Δd (Å)
Nb-O_1	2.1277	$\angle O_1-Nb-O_4$	165.681	0.2628	
Nb-O_4	1.8731				
Nb-O_2	1.8731	$\angle O_2-Nb-O_5$	165.681	0.2628	**0.7884**
Nb-O_5	2.1277				
Nb-O_3	2.1277	$\angle O_3-Nb-O_6$	165.681	0.2628	
Nb-O_6	1.8731				

CLN					
Bond distances (Å)		Bond angles (°)		Δd (Å)	Total Δd (Å)
Li-O_1	2.2696	$\angle O_1-Li-O_4$	152.464	0.2479	
Li-O_4	2.0497				
Li-O_2	2.0497	$\angle O_2-Li-O_5$	152.464	0.2479	**0.7437**
Li-O_5	2.2696				
Li-O_3	2.2696	$\angle O_3-Li-O_6$	152.464	0.2479	
Li-O_6	2.0497				

Table S6 Cell parameters for NSLN and CLN crystals.

	NSLN	CLN
Crystal system	Trigonal	Trigonal
Space group	3m	3m
Unit cell dimension (Å)	*a*=5.1380(6), *c*=13.8300(2)	*a*=5.1417(6), *c*=13.8520(2)
c/a	2.6917	2.6941
Unit cell volume (Å^3)	316.18	317.14

Table S7 Atomic coordinates for NSLN and CLN crystals.

NSLN			
Atom	x	y	z
Nb_1	0.66667	0.33333	0.46880
O_1	0.99192	0.37193	0.36503
O_2	0.96140	0.67467	0.53165
O_3	0.62803	0.62004	0.36503

O_4	0.32529	0.28667	0.53165
O_5	0.37992	0.00804	0.36503
O_6	0.71329	0.03856	0.53165

NSLN			
Atom	x	y	z
Li_1	0.33333	0.66667	0.58200
O_1	0.65864	0.70527	0.69838
O_2	0.71333	1.03859	0.53169
O_3	0.29475	0.95338	0.69838
O_4	-0.03856	0.67469	0.53169
O_5	0.04664	0.34138	0.69838
O_6	0.32533	0.28669	0.53169

CLN			
Atom	x	y	z
Nb_1	0.66667	0.33333	0.53210
O_1	0.95213	0.29514	0.63539
O_2	1.00969	0.62846	0.46870
O_3	0.70482	0.65696	0.63539
O_4	0.37151	0.38120	0.46870
O_5	0.34300	0.04783	0.63539
O_6	0.61876	-0.00973	0.46870

CLN			
Atom	x	y	z
Li_1	0	0	0.42000
O_1	0.28547	-0.03813	0.30204
O_2	0.37153	0.38125	0.46866
O_3	0.03815	0.32363	0.30204
O_4	-0.38122	-0.00968	0.46866
O_5	-0.32360	-0.28544	0.30204
O_6	0.00971	-0.37150	0.46866