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ABSTRACT

The temperature dependence of the elastic constants C_{11}^E , C_{12}^E , C_{14}^E , and C_{44}^E as well as the piezoelectrically stiffened constants C_{13}^D and C_{33}^D of lithium niobate (LN) was determined using polarized Brillouin light scattering. The congruent (48.38 mol. % of Li_2O) and nearly stoichiometric (49.5 mol. %) compositions of LN were studied from room temperature up to 800 and 900 °C, respectively. Brillouin measurements were taken on X-, Y-, Z-, and (YXl)/45° LN cuts using temperature-resolved refractive index data and corrected for density variations. At room temperature, the measured elastic constants of congruent LN are generally in agreement with the values previously reported in the literature. Variations of C_{11}^E , C_{12}^E , C_{13}^D , and C_{33}^D with temperature are observed to be approximately linear up to 800 °C. In contrast, shear elastic constants C_{14}^E and C_{44}^E exhibit a strong nonlinear behavior above 400 °C. This coincides with an inversion in the thermal expansion of the c axis lattice parameter. The thermal activation of a shear optical phonon mode, which is estimated to be at 14 THz, may explain these structural and mechanical changes while preserving the trigonal structure. This change is decorrelated from the second-order phase transition driven by spontaneous polarization near the Curie temperature.

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I. INTRODUCTION

Only a few piezoelectric materials have good electromechanical coupling at high temperatures (>400 °C) and commonly used piezoelectric nitrides present chemical stability issues in air at high temperatures. This combination is essential for developing high-temperature ultrasonic transducers. Lead zirconate titanate (PZT) ceramics, for example, are limited by their relatively low Curie temperatures (160–365 °C).¹ Several alternative piezoelectric oxides have been explored, including LiNbO_3 , LiTaO_3 , ZnO , GeO_2 , GaPO_4 , $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{CaBi}_2\text{Nb}_2\text{O}_9$, PbNb_2O_6 , and $\text{ReCa}_4\text{O}(\text{BO}_3)_3$ (Re = Er, Y, Gd, Sm, Nd, Pr, or La).^{2–11} Among these,

LiNbO_3 (LN) exhibits the highest thickness-mode electromechanical coupling coefficient at room temperature [for (YXl)/36° LN, $k_t = 0.48$].²

The LN structure belongs to the trigonal space group $R3c$ (No. 161) at room temperature and undergoes a phase transition to the centro-symmetric $R3c$ group (No. 167) at a Curie temperature (T_c) that is dependent on stoichiometry and, thus, ranges from 1120 to 1200 °C.^{12,13} The rhombohedral lattice of two LiNbO_3 units can be represented by a standard hexagonal cell of six LiNbO_3 units but with threefold symmetry. In this framework, the tensorial representation in terms of an orthogonal matrix is

adopted with the x axis (index “1”) oriented along the a axis which is perpendicular to the mirror plane, the z axis (index “3”) oriented along the c axis of the hexagonal unit cell, and the y axis (index “2”) oriented perpendicular to the x and z axes.

Following the discovery of LN ferroelectricity by Matthias and Remeika,¹⁴ early studies primarily focused on the LN phase transition mechanism at high temperatures. Abraham *et al.*¹⁵ employed x-ray diffraction (XRD) to examine structural changes, and Miller and Savage¹⁶ and Savage¹⁷ examined its optical and pyroelectric properties, respectively. Additionally, Megaw¹⁸ interpreted the structural evolution of LN as a function of temperature in terms of octahedral tilting. It is now widely accepted that the phase transition is of the second order and is driven by the spontaneous polarization along the c axis. This theoretical framework well explains the temperature dependence of the pyroelectric current,¹⁷ the birefringence,¹⁶ and the electro-optic coefficient r_{33} .¹⁹ However, the exact relationship between structural and electronic properties remains unclear.²⁰

LN possesses six independent stiffness constants (C_{11}^E , C_{33}^E , C_{12}^E , C_{13}^E , C_{14}^E , and C_{44}^E) whose values are well known at room temperature.^{21–29} However, only a limited number of studies have reported on the elastic properties of LN at elevated temperatures.^{30–35} A first complete elastic tensor using ultrasonic phase velocity measurements was determined in 1971 up to 110 °C by Smith and Welsh.³⁰ Later, in 1987, elastic constants with the exception of C_{13}^E and C_{14}^E were reported up to 900 °C by Tomeno and Matsumura.³¹ More recently, high-temperature characterization has been performed by two research groups using resonant impedance spectroscopy on plate resonators, with the data analyzed through analytical or finite element models. The complete set of compliance constants (S_{11}^E , S_{33}^E , S_{12}^E , S_{13}^E , S_{14}^E , and S_{44}^E) up to 500 °C has been reported by Chen *et al.*,³⁴ while the measurements of the stiffness constants (C_{11}^E , C_{33}^E , C_{12}^E , C_{13}^E , C_{14}^E , and C_{44}^E) up to 900 °C were performed by De Castilla *et al.*³³ and Bouchy *et al.*³⁵ However, these datasets present highly scattered values and discontinuities. These discrepancies likely arise from the challenges inherent to high-temperature measurement and modeling rather than from the LN properties themselves. These challenges include the influence of multiple coupled parameters, including piezoelectric and dielectric constants, the need for precise mechanical and electrical boundary conditions, the sensitivity of resonant techniques to spurious modes, the size and flatness of the crystal sample, the mass loading of the electrodes, and thermally induced stresses. This indicates that alternative methods should be considered for the reliable characterization of elastic properties at high temperatures.

Alternatively, Brillouin Light Scattering (BLS) is a powerful, non-contact, and electrode-less technique for measuring the elastic properties of materials. The elastic constants of LiTaO_3 at room temperature, which has the same trigonal symmetry as LiNbO_3 , were estimated by Blachowicz *et al.*³⁶ However, they used wrong expressions in calculations of the elastic constants C_{14} and C_{13} (see A1 in the [supplementary material](#) for correct calculations). Both trigonal nonpiezoelectric Al_2O_3 and piezoelectric congruent LN were investigated by Ugarak *et al.* as a function of sample rotation, from which the full elastic and piezoelectric tensors at room

temperature were deduced.²⁹ However, characterization as a function of temperature usually limits sample rotation. Furthermore, the fundamental requirement for accurate elastic constant determination via BLS is the precise knowledge of refractive indices, density, and dielectric and piezoelectric constants as a function of temperature.

The literature reports LN refractive indices as a function of wavelength,^{37–39} temperature,^{16,40,41} and composition.^{38,42} However, there are currently no data for the stoichiometric composition at the wavelength of 532 nm used in our BLS setup as a function of temperature. As for density variation, some reports in the literature point out the influence of nonstoichiometry on thermal expansion.⁴³ Finally, knowledge of LN piezoelectric constants at high temperatures is extremely limited.

In this work, we convert Brillouin frequency shifts associated with acoustic phonons into elastic constants for nearly stoichiometric (NSLN) and congruent LN (CLN) crystals using X-, Y-, Z-, and (YXl)/45° cuts (according to the IEEE convention), from room temperature to 800 °C. We use precise refractive indices (determined by means of the prism deviation method) and density variations (determined by means of x-ray diffraction) as a function of temperature for this conversion. The elastic constants C_{11}^E , C_{12}^E , C_{14}^E , and C_{44}^E (elastic stiffness coefficient at constant electric field) are directly determined. However, the constants C_{13}^D and C_{33}^D (elastic stiffness coefficient at constant electric displacement, which are also called piezoelectrically stiffened elastic constants) remain coupled to the material piezoelectricity due to this piezoelectric stiffening. To isolate the pure elastic components C_{13}^E and C_{33}^E for congruent LN at room temperature, we use the piezoelectric and dielectric tensors reported by Kovacs *et al.*²³ Our experimental results are compared with the values reported in the literature. Finally, we discuss the resulting temperature dependence of refractive indices, lattice parameters, and elastic constants within the framework of the theory on ferroelectricity and thermal activation mode.

II. EXPERIMENTAL METHODS

Congruent lithium niobate (CLN) and nearly stoichiometric lithium niobate (NSLN) crystals were grown at HUN-REN Wigner Research Centre for Physics using the Czochralski and the high-temperature top-seeded solution growth (HTTSSG)⁴⁴ methods, respectively. The lithium stoichiometry was determined from Raman $E(\text{TO}_1)$ mode damping parameters in the $Z(\text{XY})\bar{Z}$ configuration using a Monovista (S&I, Germany) Raman spectrometer with a 532 nm excitation wavelength. The CLN sample (with a known composition of $\text{Li}_2\text{O} = 48.38 \text{ mol. \%}$ ⁴⁵) exhibited an $E(\text{TO}_1)$ Raman mode linewidth of 11.08 cm^{-1} , identical to that of a commercial wafer supplied by Codex International (France). The NSLN sample showed a narrower $E(\text{TO}_1)$ linewidth of 7.65 cm^{-1} , and our most stoichiometric crystal to date presented a linewidth of 5.5 cm^{-1} .⁴⁶ Assuming a linear dependence of linewidth with stoichiometry, we estimated the Li_2O concentration in the NSLN to be 49.5 mol.%. Both crystal samples were cut into $5 \times 5 \times 2 \text{ mm}^3$ pieces along the X-, Y-, Z- and (YXl)/45° planes. Only one face was polished to eliminate optical backreflections. Crystal orientations were confirmed by XRD. All measurements in

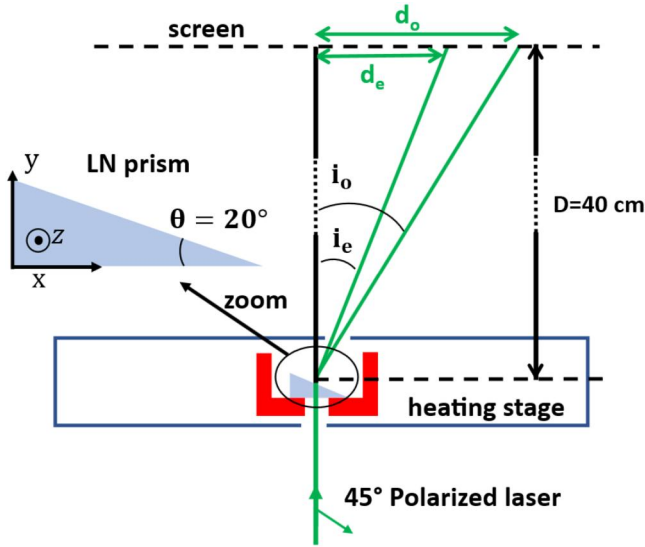


FIG. 1. Experimental setup for high-temperature refractive index measurements. The incident laser beam is polarized at 45° within the ZX plane to simultaneously excite both ordinary and extraordinary refracted beams. The insert indicates the crystallographic orientation of the prism used for deviation measurement. Image not to scale.

this paper were performed in air from room temperature up to 900 °C. The samples were heated and cooled at a rate of less than 10 °C/min, with a 5-min dwell time-off at each step to ensure thermal equilibrium. The absence of hysteresis between heating and cooling cycles indicates that no significant lithium loss occurred during the measurements.

For refractive index measurements, the Z-cut CLN and NSLN single crystals were cut into prisms with a 20° apex angle, as shown in Fig. 1. The prisms were placed on an optical bench at a distance $D = 70$ cm from a flat projection screen. A first precise measurement of the laser beam deviation was performed by stacking the prisms vertically and illuminating them simultaneously with a linearly polarized 45° laser beam at 532 nm. Then, the ordinary (n_o) and extraordinary (n_e) refractive indices were calculated from the lateral distances d_o and d_e of the deviated ordinary and extraordinary beams, respectively, using the following equation:

$$n_{o,e} = \frac{\sin\left(\theta + \tan^{-1}\left(\frac{d_{o,e}}{D}\right)\right)}{\sin(\theta)}. \quad (1)$$

High-temperature refractive index measurements were then conducted in a vertical configuration, as illustrated in Fig. 1. In this setup, the projection screen was placed 40 cm above the sample. Using a ruler with 0.5 mm graduations, the uncertainty in the refractive index was estimated to be better than 0.1%. This configuration enabled the use of the bottom 1 mm entrance port of a LINKAM micro-furnace. To eliminate optical deviations caused by the furnace windows, the top window was removed and

replaced with a metallic cap containing a small aperture. The temperature was increased to 900 °C in air, with measurements taken at 50 °C intervals. The heating rate and stabilization time are the same as the ones used during BLS experiments.

The a and c lattice parameters of the LN crystals were measured using a Bruker D8 Advance diffractometer with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.54056$ Å). The lattice parameters were calculated from the (0006) and (1126) reflections with a precision of 0.0005 Å and the XRD reflections were fitted using pseudo-Voigt profiles. High-temperature measurements were conducted up to 900 °C in air using a Domed Hot Stage (DHS1100) to minimize thermal gradients near the sample,⁴⁷ which allowed to estimate the relative change of lattice parameters as a function of temperature with respect to the room temperature values with precision of ± 0.0001 Å. We further calculated the crystal volume, V , as a function of lattice parameters using the standard formula in the hexagonal cell representation,

$$V = a^2 c \sqrt{\frac{3}{4}}. \quad (2)$$

BLS measurements were performed using the setup described by Ugarak *et al.*²⁹ in a backscattering geometry. Spectra were acquired over a frequency span of 144 GHz using 512 points, corresponding to a frequency step of 0.28 GHz. Assuming a signal-to-noise ratio of 10 and a Brillouin peak linewidth of 3 GHz, the uncertainty in the peak position after Lorentzian fitting is approximately 0.1 GHz. Note that normal incidence was imposed by experimental constraints with the microfurnace. Incident light with a wavevector $\vec{k}_i$ interacts with acoustic phonons of wavevector $\vec{q}$ propagating through the material. The scattered light has a wavevector $\vec{k}_s$, and momentum conservation is given by $\vec{q} = \vec{k}_i - \vec{k}_s$. In the backscattering configuration, the phonon wavenumber $q = \frac{\pi(n_i + n_s)}{\lambda_0}$ and momentum conservation leads to a Brillouin frequency shift $\Delta v_{\vec{q}} = \frac{|\vec{q}|V_{\vec{q}}}{2\pi}$ expressed as

$$\Delta v_{\vec{q}} = \pm \frac{(n_i + n_s) * V_{\vec{q}}}{\lambda_0}, \quad (3)$$

where $V_{\vec{q}}$ is the phase velocity of the phonon; n_i and n_s are the refractive indices for the incident and scattered polarizations, respectively; and $\lambda_0 = 532$ nm is the laser wavelength. The $\pm$ sign corresponds to Stokes or anti-Stokes processes. Using Eq. (3) and the estimated uncertainty in the Brillouin frequency shift, the uncertainty in the acoustic velocity is approximately 24 m/s, corresponding to about 1% for the shear-wave velocity and about 0.5% for the longitudinal-wave velocity. This equation highlights the critical role of the refractive index in determining elastic constants. In the plane wave approximation, the phonon-photon interaction obeys selection rules derived from the modulation of the material dielectric tensor ϵ_{ij} . The scattered power, P , described by Vacher and Courtens,⁴⁸ is given by

$$\frac{dP}{d\Omega} = A k_B T M I_{in}, \quad (4)$$

TABLE I. Summary of BLS configurations used to determine independent elastic constants of LN. (C_{12}^E is determined from $C_{12}^E = C_{11}^E - 2C_{66}^E$.)

Crystal cut (plane) IEEE convention	Backscattering wavevector	Optical configuration $k_i(e_i e_s)k_s$	Phonon polarization	Christoffel eigenvalue
X-cut ($2\bar{1}\bar{1}0$) XZ plate	$\vec{x} = [100]$	$x(zz)\bar{x}$	$\vec{q}_x \parallel \vec{u}_x(\text{LA})$	$C_{11}^E = X_l$
Y-cut ($01\bar{1}0$) YZ plate	$\vec{y} = [010]$	$y(zx)\bar{y}$	$\vec{q}_y \perp \vec{u}_x(\text{TA})$	$C_{66}^E = X_s$
Z-cut (0001) ZY plate	$\vec{z} = [001]$	$z(xx)\bar{z}$	$\vec{q}_z \parallel \vec{u}_z(\text{LA})$	$C_{33}^D = X_l$ $C_{33}^E = X_l - \frac{e_{33}^2}{\epsilon_{33}}$
(YXl)/45°	$\vec{y}' = \left[0 \frac{\sqrt{2}}{2} \frac{\sqrt{2}}{2}\right]$	$y'(xx')\bar{y}'$ $y'(xz')\bar{y}'$	$\vec{q}_y \perp \vec{u}_x(\text{TA})$ $\vec{q}_{y'} \perp \vec{u}_x(\text{Q-TA})$	$C_{44}^E = X_s$ $C_{14}^E = X_s - \frac{1}{2}(C_{66}^E + C_{44}^E)$ X_{qs} : see A1 in the supplementary material for calculation

where Ω is a solid angle, I_{in} is an incident light intensity, and A is a geometric factor related to the scattering volume. The $k_B T$ term (with k_B the Boltzmann constant and T the temperature) arises from the fluctuation–dissipation theorem. This predicts a linear increase in scattering intensity with temperature. M is a wavelength-dependent coupling coefficient proportional to

$$M \propto |e_{(i)m} e_{(s)n} \epsilon_{mi} \epsilon_{nj} p'_{ijkl} u_k q_l|. \quad (5)$$

Here, $p'_{ijkl} = p_{ijkl}^e + p_{ijkl}$ is the effective Pockels tensor, including both electro-optic p_{ijkl}^e and elasto-optic p_{ijkl} effects. The terms $e_{(i)m}$ and $e_{(s)n}$ represent the polarization of the incident and scattered light, respectively. The tensors ϵ_{mi} and ϵ_{nj} are components of the dielectric tensor of the medium. The u_k and q_l are the phonon displacement and wavevector components, respectively.

Furthermore, the phase velocity in Eq. (3) is obtained by solving the Christoffel equation,

$$|\bar{\Gamma}_{il} - \rho V_{q_i}^2 \delta_{il}| = 0, \quad (6)$$

where $\bar{\Gamma}_{il}$ is the second-order Christoffel tensor modified by the piezoelectric effect, given by $\bar{\Gamma}_{il} = c_{ijkl}^E \chi_j \chi_k + \frac{\gamma_i \gamma_l}{\epsilon}$. Here, c_{ijkl}^E are the elastic stiffness constants at constant electric field, and $\chi_j = \frac{q_j}{|q|}$ is the unit vector along the phonon propagation direction. Terms $\gamma_i = e_{kij} \chi_j \chi_k$ and $\epsilon = \epsilon_{ijk} \chi_j \chi_k$ are the effective piezoelectric and dielectric constants, where e_{kij} and ϵ_{ijk} are the piezoelectric and permittivity tensors, respectively. The Christoffel equation is solved as an eigenvalue problem. There are three solutions, which correspond to quasi-longitudinal, shear, and quasi-shear acoustic modes. These solutions are associated with the three eigenvalues X_{ql} , X_s , and X_{qs} . The elastic constants are extracted using the following equation:

$$X(T) = \left(\frac{\lambda_0 \Delta v}{(n_l + n_s)(T)} \right)^2 * \rho(T), \quad (7)$$

where Δv is the average Stokes and anti-Stokes shifts, and $\rho(T)$ is the temperature-dependent density. The refractive index of crystal cuts oriented at an angle θ ($\theta = 0^\circ$ along the z axis) depends on the propagation mode. In a backscattering geometry, the ordinary

propagation mode has a constant refractive index of n_o . For oblique propagation of the extraordinary wave, the effective refractive index is given by $n(\theta) = n_i = n_s = \sqrt{n_e^2 + n_o^2(1 - (n_e/n_o)^2)\sin^2(\theta)}$.

To measure all six independent constants of the elastic tensor by means of BLS under normal incidence, four backscattering configurations are needed, which are attained by using X-, Y-, Z-, and (YXl)/45° cuts of LN (summarized in Table I). Crystal orientations are reported in both the IEEE convention and in the hexagonal crystallographic basis. The backscattering vector defines the propagation direction k_i in an orthogonal xyz basis. The optical configuration $k_i(e_i e_s)k_s$ specifies, in order, the incident wavevector, the incident polarization, the scattered polarization, and the backscattered wavevector ($k_s = -k_i$). Phonon polarizations indicate the displacement direction of the acoustic mode being probed. For both C_{33} and C_{13} , we provide two values: the piezoelectrically stiffened or uncorrected constants (C_{ij}^D), and the corrected constants (C_{ij}^E), which are obtained from the Christoffel equation using the piezoelectric and dielectric constants taken from Kovacs *et al.*²³

III. EXPERIMENTAL RESULTS

The refractive indices n_o and n_e of both CLN and NSLN were measured using the prism setup at a laser wavelength of $\lambda_0 = 532$ nm. At room temperature, we calibrated the distance D in Eq. (1) to reproduce the known refractive index values of CLN, as reported by Nelson and Mikulyak.³⁷ Superposing the CLN and NSLN prisms allowed us to accurately determine the NSLN refractive indices at room temperature. The experimental uncertainty for indices was estimated to be ± 0.005 . Our measurements confirm that NSLN exhibits higher birefringence than CLN, which is consistent with the findings of Schlarb and Betzler³⁸ who observed similar behavior at a laser wavelength of 633 nm. Figure 2 presents the temperature dependence of the ordinary and extraordinary refractive indices of CLN and NSLN up to 900 °C. These results demonstrate that n_e is more sensitive to temperature than n_o . Table II summarizes the refractive index values and provides a polynomial fit of the temperature dependence for both indices.

The temperature-dependent thermal expansion and density corrections were determined by means of XRD. Figures 3(a)–3(c) show the temperature change of the a and c lattice parameters, as

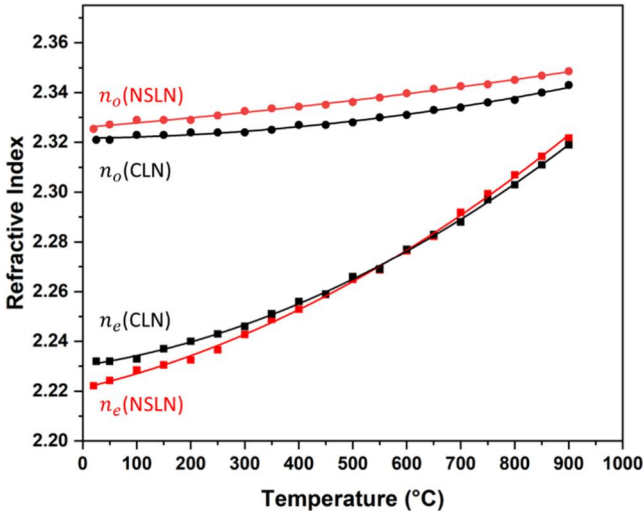


FIG. 2. Temperature dependence of the ordinary (n_o) and extraordinary (n_e) refractive indices of congruent (CLN) and nearly stoichiometric (NSLN) lithium niobate, measured using the prism deviation technique at $\lambda_0 = 532$ nm.

well as the corresponding unit cell volume calculated using Eq. (2) for both CLN and NSLN. The room-temperature lattice parameters $a = 5.1554$ Å and $c = 13.8778$ Å for CLN, and $a = 5.1523$ Å and $c = 13.8673$ Å for NSLN are consistent with those reported by Abrahams and Marsh¹³ $a = 5.1505$ Å and $c = 13.8670$ Å for CLN and $a = 5.1496$ Å and $c = 13.8561$ Å for SLN (stoichiometric LN). A small systematic error may originate from the uncertainties in sample positioning within the XRD setup and uncorrected sample

heights caused by thermal expansion of the heating stage, resulting in errors of ± 0.0005 Å. The thermal expansion coefficients were derived by fitting the lattice parameters with respect to the room-temperature values. The fitted results are summarized in Table II.

Thermal expansion along the a axis is nearly linear, with first-order coefficients $\sim 18 \times 10^{-6}/^\circ\text{C}$ for CLN and $\sim 20.5 \times 10^{-6}/^\circ\text{C}$ for NSLN. These values are slightly larger than those reported by Gallagher and O'bryan⁴³ which are $\sim 16 \times 10^{-6}/^\circ\text{C}$ for both crystals. Along the c axis, thermal expansion is non-monotonic with an inversion point observed at approximately 500 °C for CLN and 600 °C for NSLN. This is consistent with previous observations by Gallagher and O'bryan.⁴³ A third-order polynomial fit is required to accurately capture the nonlinear behavior of thermal expansion along the c axis with temperature. The first-order linear thermal expansion component of the c axis is approximately five times smaller than the corresponding value along the a axis: $2.8 \times 10^{-6}/^\circ\text{C}$ for CLN and $3.3 \times 10^{-6}/^\circ\text{C}$ for NSLN.

Finally, we note that the a and c lattice parameters of CLN are systematically higher than those of NSLN. This results in a unit cell volume of 319.2 Å^3 for CLN and 318.5 Å^3 for NSLN. These values show the same trend as those reported by Abrahams and Marsh¹³ of 318.5 Å^3 for CLN and 318.2 Å^3 for SLN. The temperature dependence of the unit cell volume is nearly linear and varies by 1% from room temperature to 900 °C. This behavior is primarily driven by the thermal expansion of the a axis; in contrast, the c axis change is relatively small over the studied temperature range.

The temperature-dependent density corrections were calculated using the volume expansion method. Assuming no lithium loss (a hypothesis that is consistent with the absence of thermal hysteresis in our measurements) and the absence of a phase transition in the studied temperature range, the change in density with

TABLE II. Polynomial fit of the form $p(x) = \sum p_i x^i$ with p_i are the polynomial coefficients and $x = (T - T_0)/T_0$ ($T_0 = 296.15$ K); applied to experimental lattice parameters, unit cell volume, density, and refractive indices of CLN and NSLN. (*) obtained by fitting results taken from Ref. 43 (N.U. indicates that the coefficient was not used).

	CLN				NSLN			
	p_0	p_1	p_2	p_3	p_0	p_1	p_2	p_3
Lattice parameters (Å)								
a	5.1554	2.914×10^{-2}	1.81×10^{-3}	N.U.	5.1523	3.31×10^{-2}	-1.61×10^{-4}	N.U.
a^*	5.1560	2.602×10^{-2}	2.37×10^{-3}	N.U.	...	...	...	...
c	13.8778	1.213×10^{-2}	4.36×10^{-4}	-1.79×10^{-3}	13.8670	1.47×10^{-2}	1.25×10^{-3}	-1.95×10^{-3}
c^*	13.8657	1.902×10^{-2}	-6.02×10^{-4}	-1.57×10^{-3}	...	...	...	...
Thermal expansion ($10^{-6}/^\circ\text{C}$)								
α_a	N.U.	17.96	0.56	N.U.	N.U.	20.51	-4.99×10^{-2}	N.U.
α_c	N.U.	2.79	-1.14×10^{-2}	-1.3	N.U.	3.35	3.22×10^{-2}	-1.49
Volume cell (Å^3)								
V	319.39	4.09	7.02×10^{-2}	N.U.	318.74	4.66	-17.48×10^{-2}	N.U.
V^*	319.18	3.85	13.27×10^{-2}	N.U.	...	...	...	...
Density (kg/m^3)								
ρ	4628.40	-59.41	-0.19	N.U.	4619.63	-67.25	3.18	N.U.
Refractive index								
n_e	2.231	1.08×10^{-2}	6.50×10^{-3}	N.U.	2.227	1.82×10^{-2}	4.52×10^{-3}	N.U.
n_o	2.321	1.09×10^{-3}	1.98×10^{-3}	N.U.	2.335	9.43×10^{-3}	-1.11×10^{-3}	N.U.

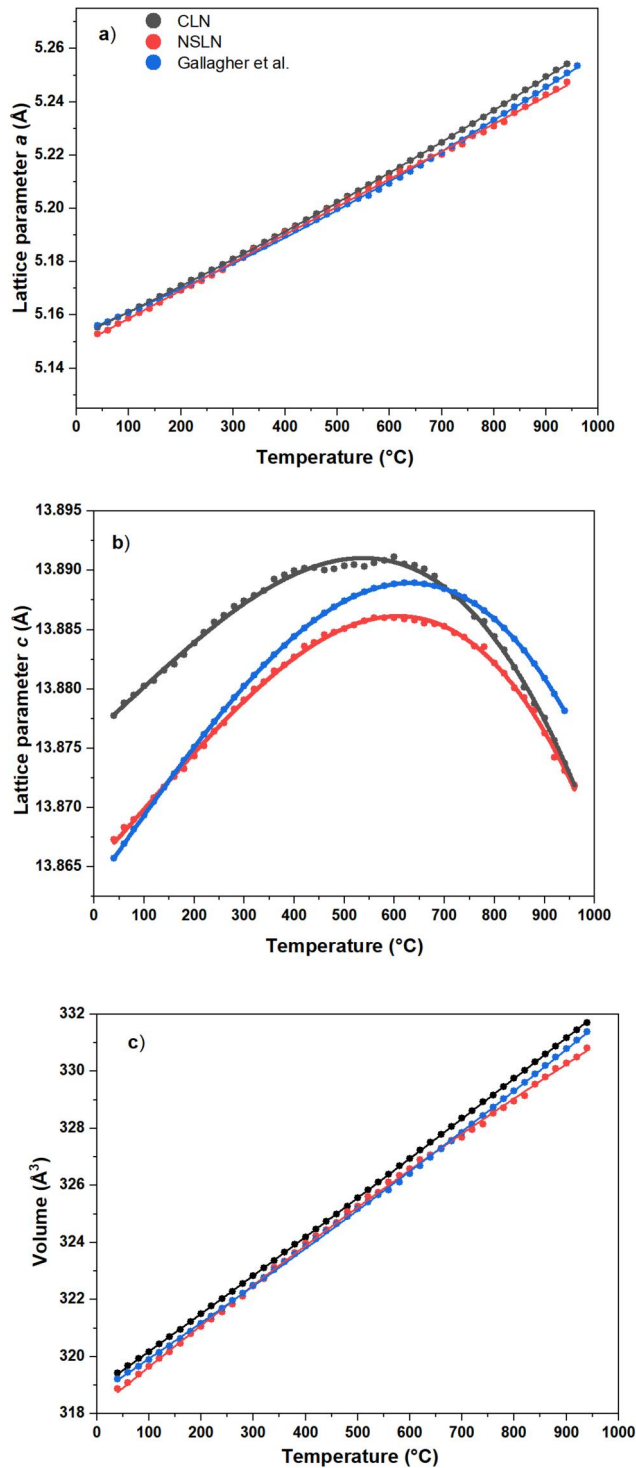


FIG. 3. Temperature dependence of the a (a) and c (b) lattice parameters, and the calculated unit cell volume (c) for CLN and NSLN. A comparison is provided with the reference values from Gallagher and O'bryan.⁴³

temperature is given by

$$\rho(T) = \rho_0 \frac{V_0}{V(T)}, \quad (8)$$

where ρ_0 is the density at room temperature, and V_0 and $V(T)$ are the unit cell volumes determined at room temperature and at temperature T , respectively.

All these parameters are composition-dependent. The value of ρ_0 is critical for determining elastic constants from the Christoffel equation [see Eq. (6)], as it directly influences the calculated phonon velocity. For defect-free, stoichiometric lithium niobate, the expected room-temperature density is given by

$$\rho_0 = \frac{MZ}{N_A V_0}, \quad (9)$$

where M is the molecular weight, $Z = 6$ is the number of formula weights per unit hexagonal cell, $N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$ is Avogadro's number, and V_0 is the unit cell volume. The molar mass, M , of LiNbO_3 was calculated as the sum of the atomic weights of lithium, niobium, and three oxygen atoms, considering the natural isotopic abundances of ^7Li (92.5%), ^6Li (7.5%), ^{16}O (99.8%), and monoisotopic ^{93}Nb . Based on the measured unit cell volume at room temperature, the calculated density of defect-free (stoichiometric) LN is $\rho_0 = 4617.6 \text{ kg/m}^3$. This value is consistent with the 4620 kg/m^3 reported for stoichiometric LN by Etschmann *et al.*⁴⁹ but lower than the 4635 kg/m^3 reported for stoichiometric samples by Abrahams and Marsh.¹³ It is worth noting that absolute density measurements with such precision are extremely challenging using gravimetric methods. For congruent LN compositions, the density values reported in the literature vary significantly: 4628 ,^{23,28} 4642 ,^{25,50,51} or 4648 kg/m^3 .¹³ These values are systematically higher than those for stoichiometric compositions. This difference is attributed to the presence of intrinsic defects in CLN, primarily Nb^{5+} ions occupying Li^+ sites and forming Nb_{Li} anti-sites.¹³ Charge compensation occurs through lithium vacancies, as described by the defect model: $(\text{Li}_{\text{Li}})_{1-5x}(\text{Nb}_{\text{Li}})_x(\text{V}'_{\text{Li}})_{4x}(\text{Nb}_{\text{Nb}})\text{O}_3$.⁵² Consequently, CLN has a higher density than NSLN. The measurements of LN density with different Li_2O compositions around the congruent point by Kushibiki *et al.*⁵⁰ gave a gradient of $+6.94 \text{ kg/m}^3$ per mol. % lithium deficiency. This corresponds to an increase of approximately 10 kg/m^3 in CLN compared to SLN. Following these authors and keeping the frequently cited values of Kovacs *et al.*,²³ we adopt reference densities of 4628 and 4618 kg/m^3 for CLN and NSLN, respectively, at room temperature. It should be noted that the absolute uncertainty in the density of LN is less than 0.1% and, therefore, has only a negligible influence on the determination of the elastic constants, according to Eq. (6). Table II summarizes our findings from Figs. 2 and 3. All temperature-dependent properties were fitted using a polynomial of $x = \frac{T-T_0}{T_0}$, where $T_0 = 296.15 \text{ K}$. The polynomial degree was chosen to ensure a coefficient of determination $R^2 = 0.99$. Unnecessary higher-order terms were, thus, excluded.

To validate the elastic constants of CLN and NSLN measured by means of BLS at room temperature and estimated by using the

previously discussed density values, we compared the derived elastic constants with the literature, as summarized in Table III. A comparison with the results from Kushibiki *et al.*⁵⁰ confirms that transition from CLN to NSLN results in slightly stiffened C_{11}^E and softened C_{44}^E . Notably, the measured value for uncorrected C_{33}^D remains unchanged between the two compositions within limits of errors. The BLS results for CLN are in good agreement with those of Ugarak *et al.*,²⁹ showing a difference of only 1%–2% for all elastic constants (corrected from the piezoelectric effect for C_{13}^E and C_{33}^E). The reference values from Kovacs *et al.*²³ have notable discrepancies with our data only for C_{12}^E , which is 9% lower. The uncertainties in our BLS values reported in Table III reflect the combined propagation of two primary error sources: a statistical error attributed to the fitting of the Brillouin spectral peaks and an uncertainty derived from cumulative errors.

The high-temperature Brillouin shifts were converted into elastic constants using Eq. (7), which incorporates temperature-dependent corrections for density and refractive index, as indicated in Table II. The different relative elastic constants, normalized to their value at room temperature (given in Table III), are presented as a function of temperature in Figs. 4(a)–4(f) and reported in A3 in the supplementary material. C_{66}^E is given in A4 in the supplementary material as it is not independent of C_{11}^E and C_{12}^E . Polynomial fits of the temperature-depend elastic constants are provided in A5 in the supplementary material. The six elastic constants in Fig. 4 can be grouped into two categories based on their temperature behavior.

The first group, Figs. 4(a)–4(d), shows mostly linear variations and includes C_{11}^E , C_{33}^D , C_{12}^E , and C_{13}^D . Both C_{11}^E and C_{33}^D exhibit a thermal softening of 10%, while C_{12}^E shows a more pronounced decrease of about 30% from room temperature to 800 °C. However, C_{13}^D exhibits 5% hardening for NSLN and 1% hardening for CLN with an increase in temperature to 800 °C. This coefficient is subject to significant uncertainty due to its dependence on other coefficients (see A2 in the supplementary material). The softening of C_{11}^E , C_{33}^D , and C_{12}^E with an increase in temperature was also reported in the literature and the hardening of C_{13}^D was also observed by Bouchy *et al.*³⁵ and Chen *et al.* to some degree, but the quality of their data is questionable.

The second group, Figs. 4(e) and 4(f), consists of elastic constants C_{44}^E and C_{14}^E which vary nonlinearly from room temperature to 800 °C. Clearly, C_{44}^E and C_{14}^E exhibit a nonlinear variation that becomes dominant above 400 °C. Above 500–600 °C, C_{44}^E shows a hardening consistent with the results of Bouchy *et al.*³⁵ No consistent and reliable data on temperature dependence of C_{14}^E are available in the literature: reported data by all authors are highly scattered. Our measured C_{14}^E in contrast displays continuous nonlinear softening with increasing temperature [Fig. 4(f)].

Brillouin spectra exhibit changes in both broadening and intensity as a function of temperature, as described by Eq. (4) and presented in A6 in the supplementary material. The broadening of the Brillouin peaks reflects the damping of acoustic modes and shows a systematic increase of a few percent. However, this broadening approaches the resolution limit of our setup and our measurements exhibit significant fluctuations (see A7 in the supplementary material). Therefore, we focused instead on the variation of the integrated area of the Brillouin modes and the

TABLE III. Mass density and elastic constants of CLN and NSLN obtained by means of BLS measurements at room temperature and their comparison with literature values. (C_{33}^E and C_{13}^E for CLN are corrected using Kovacs' piezoelectric coefficients.) A more complete review is given in A2 of the supplementary material.

Elastic constants (GPa)									
Method	Density	C_{11}^E	C_{12}^E	C_{13}^E	C_{14}^E	C_{33}^E	C_{44}^E	C_{66}^E	Reference
BLS (48.45%)	4628	202.6 ± 1	55.8 ± 2	$63.6 \pm 1(C_{13}^D)$ $67.9(C_{13}^E)$	8.1 ± 0.3	$254.8 \pm 1(C_{33}^D)$ $239.6(C_{33}^E)$	61.1 ± 0.3	73.4 ± 0.3	Our CLN uncorrected
BLS (49.5%)	4618	205.7 ± 1	59.7 ± 2	$71.6(C_{13}^D)$	8.5 ± 0.3	$254.26(C_{33}^D)$	58.8 ± 0.3	72.9 ± 0.3	Our NSLN uncorrected
BLS	4628	200.24	49.75	67.98	7.98	234.24	62.20	75.24	Ugarak <i>et al.</i> (2023) ²⁹
BLS (48.41%)	4642.8	198.83	54.63	68.11	7.79	234.31	59.86	75.24	Kushibiki <i>et al.</i> (2002) ⁵⁰
SAW velocity	4628	198.39	54.72	65.13	7.88	227.9	59.65	71.83	Kovacs <i>et al.</i> (1990) ²³
Ultrasonic phase velocity (47.1%)	N.C.	198.1	55.02	N.C.	N.C.	242.5	59.3	71.56	Tomeno and Matsumura (1987) ³¹
Impedance + FEM	N.C.	194	42.8	52.2	8.4	223	61.5	75.6	Chen <i>et al.</i> (2019) ³⁴
Impedance + analytical model	4640	192	54.7	75.1	8.6	231	59.5	68.65	Bouchy <i>et al.</i> (2002) ³⁵

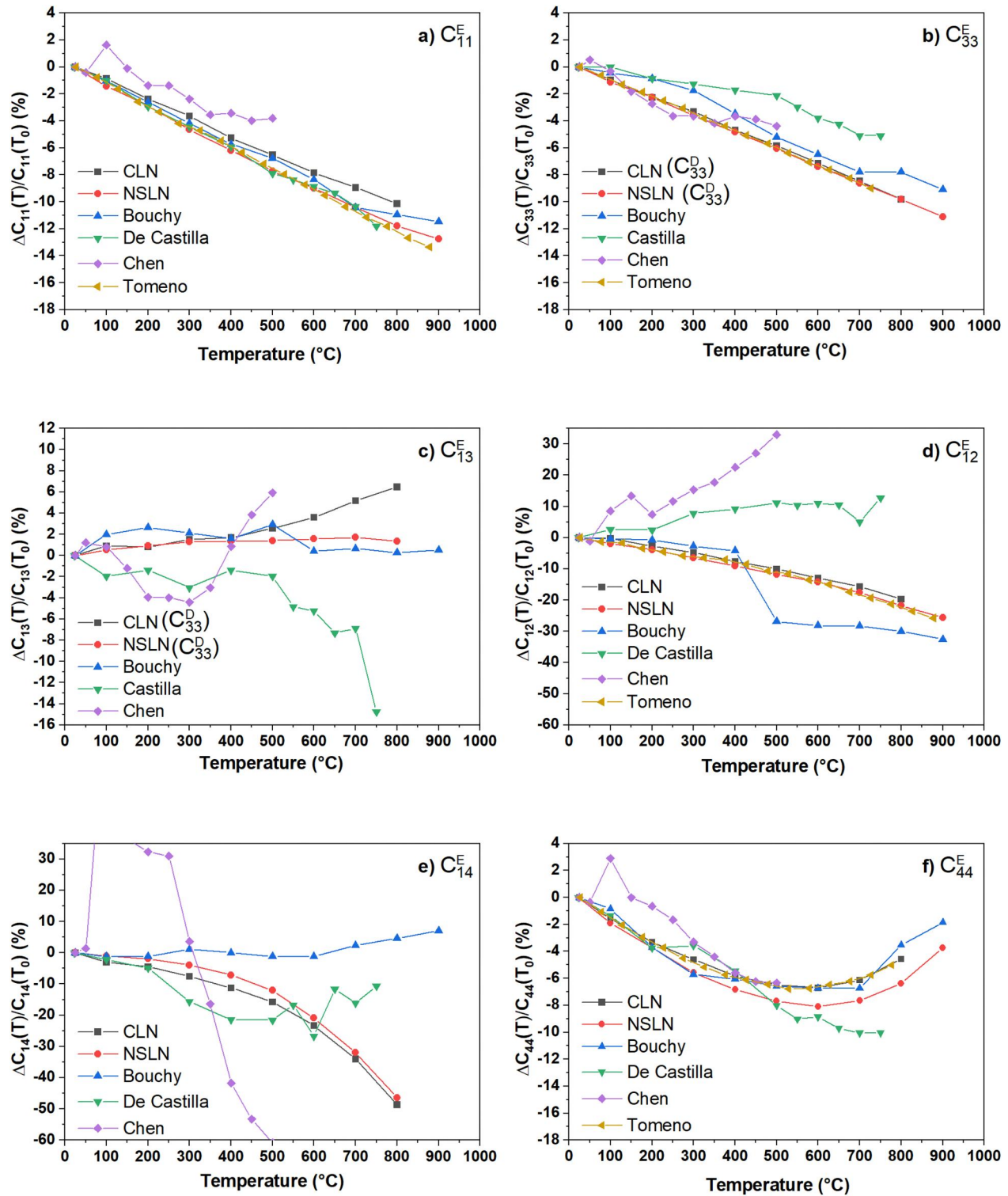


FIG. 4. Temperature variation (in %) of elastic constants C_{11}^E (a), C_{33}^E (b), C_{13}^E (c), C_{12}^E (d), C_{14}^E (e), and C_{44}^E (f) for NSLN and CLN, normalized to room temperature T_0 , where $\Delta C_{ij}(T) = C_{ij}(T) - C_{ij}(T_0)$. For C_{33}^E (b) and C_{13}^E (c), our data C_{33}^D and C_{13}^D are reported. Results are compared with literature data C_{ij}^E from Refs. 31 and 33–35.

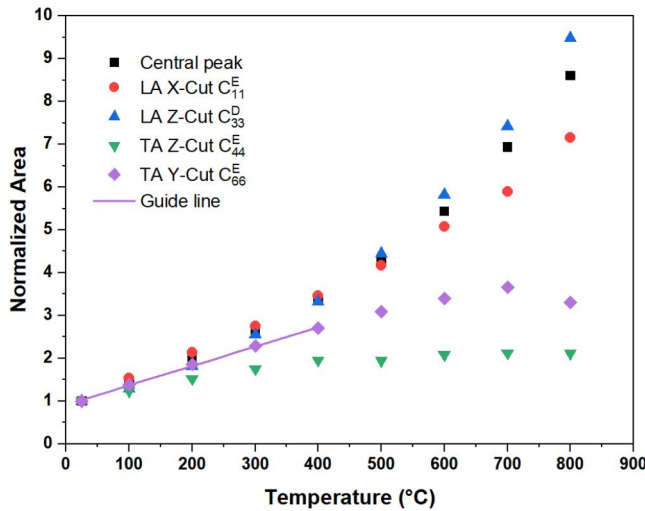


FIG. 5. Relative variation of the integrated area of Brillouin modes and of the central peak as a function of temperature (normalized to the room temperature value).

central peak [with the baseline taken near the laser line in the X (ZZ)X configuration]. Figure 5 shows the integrated area of the modes, normalized to the room-temperature value. Consistent with Eq. (4), we observe an initial linear increase in area with temperature, which is consistent with the fluctuation–dissipation factor $k_B T$. Another observation that occurs simultaneously above 400 °C is a plateau for the transverse acoustic (TA) mode and a nonlinear increase for the longitudinal acoustic (LA) modes, as well as for the central peak. Assuming that the temperature dependence of the geometric factor in Eq. (4) is weak, the nonlinear variations of the LA mode and the central peak above 400 °C appear to originate from a quadratic effect that is not included in the model.

IV. DISCUSSION

To gain insight into experimental data and since the temperature range is below the Curie temperature, we compared optical measurements as a function of temperature with second-order phase transition theory. The results were then correlated with the structural variation of the c axis lattice parameter before attempting to explain the nonlinear behavior of the elastic coefficients C_{44} and C_{14} .

The refractive indices shown in Fig. 2 exhibit a well-defined sensitivity to temperature. Wemple *et al.*¹⁹ derived a relation between static birefringence and spontaneous polarization P_{spont} , expressed as

$$\Delta n(T) = \Delta n_{\text{para}} - \frac{1}{2} n^3 \left(\frac{g_{44}}{\zeta^3} \right) P_{\text{spont}}^2, \quad (10)$$

where Δn_{para} is the birefringence in the paraelectric phase, n is the average refractive index [$1/3 (n_e + 2n_o)$], g_{44} is a quadratic electro-optic coefficient and, ζ is the octahedral packing density. All these

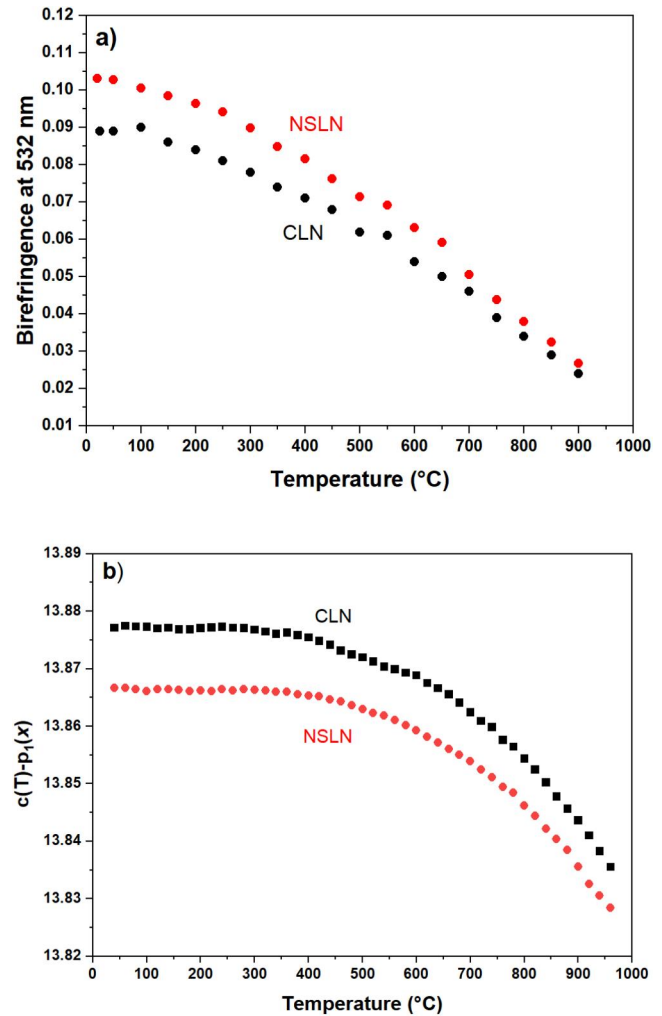


FIG. 6. Temperature dependence of the birefringence at 532 nm (a) and the variation of the c axis corrected by the linear thermal expansion (b).

parameters are supposed to depend smoothly on temperature. According to second-order phase transition theory, $P_{\text{spont}} \propto \sqrt{T_c - T}$ below the Curie temperature. Substituting this into Eq. (10) yields a predicted linear decrease in birefringence $\Delta n(T)$ up to T_c . Figure 6(a) shows the experimental birefringence as a function of temperature. NSLN exhibits higher birefringence than CLN, likely due to its higher Curie temperature ($T_c = 1195$ °C for NSLN and $T_c = 1122$ °C for CLN).¹³ Near T_c , the birefringence is approximately linear, and saturation occurs when approaching room temperature, which is consistent with observations in several other ferroelectrics.⁵³ Overall, second-order phase transition theory well explains the observed trends in birefringence.

Next, we consider thermal expansion. The temperature-dependent inversion of the c axis occurs well before the Curie temperature. This raises the question of whether it is governed by

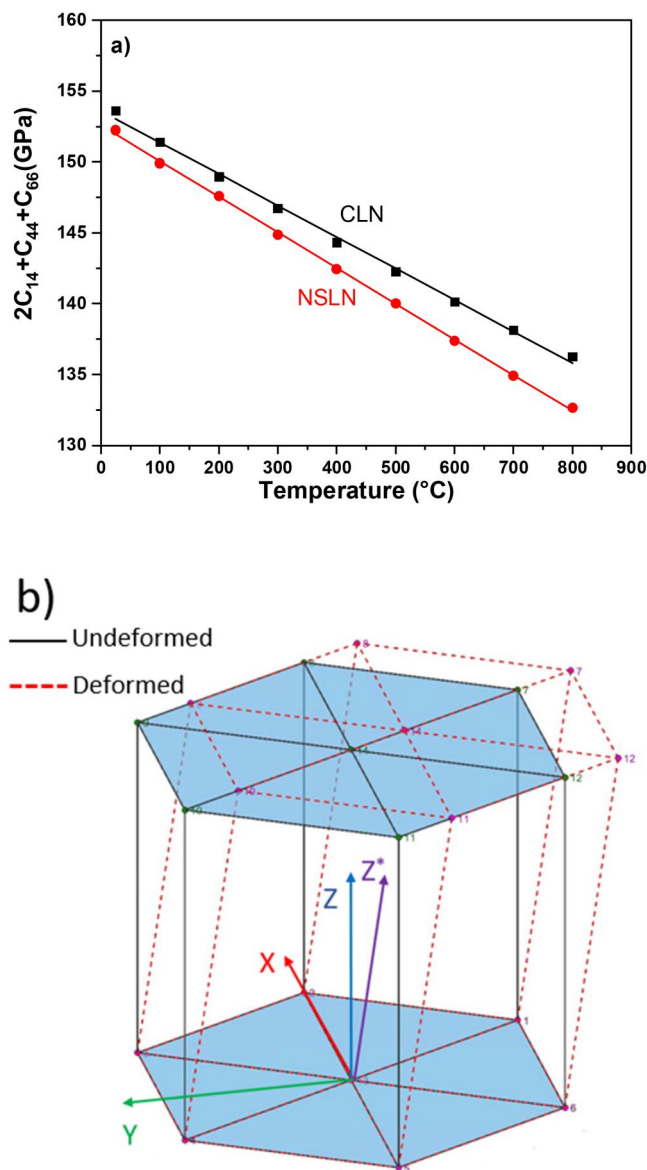


FIG. 7. The quantity $2C_{14} + C_{44} + C_{66}$ as a function of temperature (a) and a schematic illustration of shear strain $\epsilon_4 = 2\epsilon_{yz}$ showing the tilting of the polar axis of a hexagonal unit cell like that of lithium niobate (b).

the same order parameter as the refractive index. Table II shows that thermal expansion is slightly larger along the a and c axes in NSLN than in CLN. This difference may result from variations in vibrational anharmonicity or density because denser materials generally exhibit reduced thermal expansion.⁵⁴ The quasi-linear expansion of the a axis over the full temperature range [Fig. 3(a)] can be explained by lattice anharmonicity. This is because the measurement range is primarily above the Debye temperature, which indicates little involvement of the order parameter. In

contrast, the linear dependence of thermal expansion along the c axis is an order of magnitude smaller (see Table II), which is consistent with a flatter lattice potential in the z -direction dominated by electrostatic ferroelectric forces. Figure 6(b) shows the temperature deviation $c(T) - p_1(T - T_0)$, where $c(T)$ is the c axis lattice parameter and p_1 is the first-order thermal expansion from Table II, to isolate the nonlinear thermal expansion of the c axis. The change in slope Fig. 6(b) occurs concurrently with anomalies in the temperature variation of elastic constants C_{44} and C_{14} above 400 °C [Figs. 4(e) and 4(f)]. Notably, the linear to nonlinear transition occurs at a higher temperature than the transition observed in the birefringence data [Fig. 6(a)].

Previously, we observed that four out of six independent elastic constants exhibit mostly linear temperature dependence. The nonlinear hardening of C_{44} and the softening of C_{14} were fitted using a second-order polynomial (as detailed in A5 in the supplementary material). Interestingly, the sum $2 \times C_{14} + C_{44} + C_{66}$ is linear with temperature, as illustrated in Fig. 7(a). This indicates that the two quadratic nonlinearities of Figs. 4(e) and 4(f) cancel each other out. This quantity could be interpreted as part of the elastic energy associated with the system's shear strain ϵ_5 (see A8 in the supplementary material). It is also noteworthy that shear strains ϵ_4 and ϵ_5 are the only strain components that generate a tilt of the polar (Z) axis compared to other strain tensor elements. This shear effect is clearly visible in Fig. 7(b), where the shear stresses $\epsilon_4 = \epsilon_{yz}$ break the hexagonal cell to a monoclinic one, which would tilt the spontaneous polarization P_{spn} .⁵⁵ The same effect should occur with $\epsilon_5 = \epsilon_{xz}$ but is not represented. As the symmetry breaking and tilt of spontaneous polarization is not observed, these results suggest that two distinct phenomena could coexist. While the optical index is directly driven by the electronic polarization (Fig. 5), the nonlinear change of elastic constants is related to another independent mechanism involving lattice octahedral tilting.¹⁸ We hypothesize that a thermally activated lattice mode, excited above 400 °C, could account for this mechanism. This phonon mode compensates the tendency of symmetry breaking under shear strain by the octahedral tilting. This distortion induces the shrinking of the c axis lattice parameter [Fig. 3(b)], which indicates that the mode should be most likely a shear mode that brings atoms closer together along c axis, as observed in many crystals presenting a negative thermal expansion.⁵⁶ Moreover, the distortion of the lattice induced an apparent nonlinear dependence of shear elastic properties (Fig. 4), whereas the total elastic energy remains linear with temperature [Fig. 7(a)]. The energy of this phonon mode is higher than the Debye temperature, driving the linear thermal expansion of the a axis above room temperature. Assuming the shear mode becomes thermally populated around 400 °C (673 K), it should correspond to an optical phonon greater than 460 cm^{-1} (14 THz), that could be either E(TO7) or E(TO8).⁴⁶ However, this hypothesis certainly requires further theoretical investigation.

V. CONCLUSION

The elastic stiffness constants C_{11}^E , C_{12}^E , C_{14}^E , C_{44}^E , C_{13}^D , and C_{33}^D of lithium niobate crystals were measured as a function of temperature using Brillouin light scattering to support the design of high-

temperature transducers. The results provide reliable elastic constants for congruent lithium niobate and, for the first time, for the nearly stoichiometric crystal up to 800 °C. This considers the temperature dependence of refractive indices and density. The BLS technique is a non-contact, electrode-free method that produces significantly less scattered data than other techniques. It yields room-temperature results that are in good agreement with literature data. However, additional measurements are required to determine C_{13}^E and C_{33}^E constants in order to isolate the effect of piezoelectricity and dielectric constant in C_{13}^D and C_{33}^D . A detailed analysis revealed a temperature inversion of the c axis lattice parameter and the nonlinear temperature dependence of elastic constants C_{14}^E and C_{44}^E above 400 °C. Both CLN and NSLN exhibit this behavior, which differs from the temperature dependence of birefringence associated with spontaneous polarization (the order parameter). We propose a mechanism involving the thermal activation of an optical shear mode that is not directly linked to the phase transition. Further theoretical studies are needed to validate the proposed mechanism.

SUPPLEMENTARY MATERIAL

The [supplementary material](#) contains eight sections. A1 presents the expression of the C_{13}^D and C_{13}^E elastic constants derived from the eigenvalues of Christoffel equation for the (YXl)/45 cut, correcting the expressions reported by Blachowicz *et al.* A2 provides an extensive comparison of elastic constants reported in the literature for congruent crystals with those listed in [Table III](#). A3 compiles the elastic coefficients obtained from room temperature to 800 °C obtained in the present paper and presented in [Fig. 4](#). A4 presents the temperature dependence of the normalized C_{66}^E elastic constant measured by cross polarization of Y-cut crystals, which was used to determine $C_{12}^E = C_{11}^E - 2C_{66}^E$ and A5 provides the polynomial fits of elastic constants as a function of temperature corresponding to [Fig. 4](#). A6 presents representative raw Brillouin spectra recorded as a function of temperature, while A7 reports the fitted temperature dependence of the Lorentzian linewidth. Finally, A8 provides the expression for the shear elastic energy expression used to justify the linear behavior of $2 \times C_{14}^E + C_{44}^E + C_{66}^E$.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Hatim Bakhtaoui: Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Visualization (equal);

Writing – original draft (equal). **Quentin Micard:** Investigation (equal); Methodology (equal); Visualization (equal). **Alexis Mosset:** Conceptualization (equal); Methodology (equal). **Vincent Laude:** Formal analysis (equal); Methodology (equal); Software (equal); Writing – review & editing (equal). **Krisztian Lengyel:** Resources (equal). **Gabriella Dravecz:** Resources (equal). **Pascal Boulet:** Resources (equal); Software (equal). **Fabrice Sthal:** Supervision (equal); Validation (equal); Writing – review & editing (equal). **Gael Chevallier:** Supervision (equal); Validation (equal); Writing – review & editing (equal). **Ausrine Bartaszyte:** Funding acquisition (equal); Project administration (equal); Validation (equal); Writing – review & editing (equal). **Samuel Margueron:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Methodology (equal); Project administration (equal); Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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