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S. Margueron, A. Bartasyte, A. M. Glazer, E. Simon, J. Hlinka, I. Gregora, and J. Gleize



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# Resolved E-symmetry zone-centre phonons in LiTaO<sub>3</sub> and LiNbO<sub>3</sub>

S. Margueron,<sup>1</sup> A. Bartaszyte,<sup>2,3</sup> A. M. Glazer,<sup>2</sup> E. Simon,<sup>4</sup> J. Hlinka,<sup>4</sup> I. Gregora,<sup>4</sup> and J. Gleize<sup>5</sup>

<sup>1</sup>Laboratoire Matériaux Optiques, Photonique et Systèmes, EA 4423, Lorraine University and Supélec, 2 rue Edouard Belin, 57070 Metz, France

<sup>2</sup>Department of Physics, Oxford University, Parks Road, Oxford OX1 3PU, United Kingdom

<sup>3</sup>Institut Jean Lamour, CNRS (UMR 7198)-Lorraine University, Parc de Saurupt, CS14234, 54042 Nancy cedex, France

<sup>4</sup>Institute of Physics AS CR, Prague 8, Czech Republic

<sup>5</sup>Institut de Chimie Physique & Matériaux, Lorraine University, 1 Bd Dominique-François Arago, 57078 Metz, France

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E-symmetry optical phonons at the  $\Gamma$  point of LiNbO<sub>3</sub> and LiTaO<sub>3</sub> were experimentally resolved in spectra measured by infrared and Raman spectroscopy. For this purpose, congruent and nearly stoichiometric crystals of LiNbO<sub>3</sub> and LiTaO<sub>3</sub>, and mixed LiNb<sub>1-x</sub>Ta<sub>x</sub>O<sub>3</sub> crystals were studied. The results show that some of the E modes have weak intensities in Raman or infrared spectra. Thus the complete assignment of E-symmetry modes has been achieved by comparing Raman and infrared data. In addition, this assignment has been confirmed by Raman measurements at low temperatures. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4716001>]

## I. INTRODUCTION

Lithium niobate (LN) and lithium tantalate (LT) have been the subject of intense studies because of their applications in electro-optic, nonlinear-optic, photo-refractive, and acoustical devices. Their dynamical properties have also been intensively studied. The optical phonon frequencies, damping parameters, and intensities are of particular interest in studies of phase transitions, symmetry, effect of pressure, stress, composition and heterogeneities in thin films, integrated structures, nano and bulk materials. It is essential to know the frequencies of all zone-centre optical phonons in calculations of dielectric constant (Lyddane-Sachs-Teller relation<sup>1</sup>), oblique modes,<sup>2</sup> and electro-optic coefficients.<sup>3</sup> Both compounds belong to the ferroelectric R3c ( $Z = 2$ ) space group with  $4A_1 + 5A_2 + 9E$  optic modes ( $A_1$  and  $E$  modes being simultaneously infrared (IR) and Raman active). There are numerous reports on optical phonons in LT and LN, studied by Raman<sup>4-7</sup> and IR,<sup>8,9</sup> inelastic neutron scattering<sup>10</sup> spectroscopies, and by theoretical calculations.<sup>11-13</sup> There is good agreement in the reported frequencies of  $A_1$ -symmetry phonons of LN and LT. Nevertheless, over the last 50 years, there has been much discussion in the literature concerning the E-symmetry phonons in LN and LT. Many different assignments with different theoretical and experimental frequencies of LN and LT have been reported.<sup>4,5,7,11,12,14-17,20,21</sup> In Raman spectroscopy, the frequencies of the E modes have been estimated by considering the Raman selection rules and angular dispersion in forward, 90° and backward scattering geometries. Unfortunately, the Raman spectra of LN and LT present several modes whose origins are still under debate as to whether they are first-order, second-order, and defect modes.<sup>7</sup> Moreover, deviation from stoichiometry is typical for the LN-LT family. It has been found that first-order modes in the LN grown from congruent solution (CLN,  $\text{Li}/(\text{Li} + \text{Nb}) = 48.6$

mol. %) tend to be broader and less resolved than those of nearly stoichiometric LN (SLN,  $\text{Li}/(\text{Li} + \text{Nb}) \approx 50$  mol. %).<sup>21</sup> The effect of Li nonstoichiometry on the Raman modes of LN and LT has been discussed by several groups.<sup>18-21</sup> The importance of measuring stoichiometric specimens has been emphasised.<sup>20,21</sup> The differing assignments of E-modes in LN and LT have been summarized by Hermet *et al.*<sup>11</sup> and Shi *et al.*,<sup>20</sup> respectively. In fact, there is agreement on seven and eight E(TO) mode frequencies in LN and LT, respectively. The reported wavenumbers of these modes are around 152, 237, 265, 322, 368, 431, and 580 cm<sup>-1</sup> for LN and 142, 206, 251, 315, 380, 462, 595, and 660 cm<sup>-1</sup> for LT. Meanwhile, *ab-initio* calculations by Hermet *et al.*<sup>11</sup> suggested that several E modes in LN have very low Raman efficiencies and reasonable oscillator strengths in IR spectroscopy and *vice versa*. Thus, some E modes are very difficult to record in Raman or IR spectra, and this could also explain the disagreement in the literature. In their work, some of the theoretically calculated frequencies of E modes were not proved experimentally, leaving the discussion on the E-mode assignment open.

In this paper, all nine E-symmetry optical phonons at the  $\Gamma$  point of LN and LT are experimentally resolved in IR and Raman spectra for the first time.

## II. EXPERIMENTAL DETAILS

SLN crystals were grown by the top seeded solution growth (TSSG) method using a K<sub>2</sub>O quasiflux (with molar ratio  $\text{K}/\text{Nb} = 0.34$ ).<sup>22,23</sup> Mixed LiNb<sub>1-x</sub>Ta<sub>x</sub>O<sub>3</sub> crystals were grown by Czochralski and TSSG methods.<sup>24</sup> For LiNbO<sub>3</sub> and LiTaO<sub>3</sub> crystals with congruent Li concentration (CLN and CLT, respectively), we used commercially grown and oriented samples (supplied by MTI Corporation). Nearly stoichiometric Y-cut LT crystals (SLT) were obtained by vapour transport equilibration (VTE) using a

double-phase powder (mixture of  $\text{LiTaO}_3$  and  $\text{Li}_3\text{TaO}_4$ ) containing 60%  $\text{Li}_2\text{O}$ . The crystals were equilibrated for 64 h at 1250 °C and then naturally cooled down in the furnace. The equilibrated crystals were polished to an optical finish.

Raman spectra were collected using Jobin-Yvon/Horiba LabRam and Renishaw Raman RM-1000 spectrometers. The experiments were conducted in the micro-Raman mode in backscattering geometry. The 514.5 nm line of an  $\text{Ar}^+$  ion laser was focused to a spot size of about 2  $\mu\text{m}$ . The temperature measurements were carried out from room temperature to 4 K using a commercial Oxford Instruments Microstat cooling stage. Polarized Raman spectra were recorded in several backscattering geometries resumed in Table I (hereafter (X,Y,Z) is an orthogonal reference system where Z is parallel to the *c*-axis and X—to the *a*-axis, which is taken perpendicular to the mirror plane of the  $3m$  point group). The corresponding nonzero (i.e., symmetry-allowed) Raman tensor elements of TO and LO components of  $A_1$  and E-symmetry modes are also shown in Table I. The fitting of the Raman was performed using a procedure “Unifit” (written by I. Gregora) running under the Igor Pro interface.<sup>25</sup> The spectra were reduced by the Bose distribution and fitted using independent damped harmonic oscillator spectral profiles and a constant baseline.

IR reflectivity measurements were performed using an FTIR spectrometer Bruker IFS 113v. Room-temperature spectra were recorded in the range 30–3000  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$ . The unpolarized near-normal reflectivity spectra  $R(\omega)$  were taken from polished surfaces of several mm thick Z-cut crystals at room temperature (RT) so that the measured spectra could be analyzed with the simple Fresnel relation

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2,$$

involving solely the ordinary complex permittivity spectrum  $[\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)]$  defined by E-symmetry modes only. IR reflectivity spectra were fitted assuming the standard factorized form of the oscillator model for the complex permittivity

$$\varepsilon(\omega) = \varepsilon_\infty \prod_{j=1}^n \frac{\omega_{LOj}^2 - \omega^2 + i\omega\gamma_{LOj}}{\omega_{TOj}^2 - \omega^2 + i\omega\gamma_{TOj}},$$

TABLE I. Non-zero Raman tensor elements determining activity of phonon modes of  $3m_x$  symmetry crystal in selected backscattering arrangements given in the standard Porto notation. Primes indicate that the coefficient is modulated by electro-optic interaction. Axes X, Y, Z refer to the orthogonal reference system, where Z is parallel to the *c*-axis and X is perpendicular to the  $m_x$  mirror plane.

Porto notation	$A_1(\text{TO})$	$A_1(\text{LO})$	E(TO)	E(LO)
$Z(\text{XX})\bar{Z}$		$a'$	$c$	
$Z(\text{XY})\bar{Z}$			$c$	
$X(\text{ZZ})\bar{X}$	$b$			
$X(\text{YZ})\bar{X}$ and $Y(\text{XZ})\bar{Y}$			$d$	
$X(\text{YY})\bar{X}$	$a$		$c$	
$Y(\text{XX})\bar{Y}$	$a$			$c'$

TABLE II. Wavenumbers of  $A_1(\text{TO})$  and  $A_1(\text{LO})$  modes of nearly stoichiometric (S) and congruent (C) LN and LT crystals, estimated from Raman spectra.

	1TO	2TO	3TO	4TO	1LO	2LO	3LO	4LO
CLN	253	276	333	632	275	333	418	871
SLN	253	277	334	632	276	334	421	870
SLT	210	259	360	599	259	356	408	863
CLT	207	256	357	598	256	355	405	865

Here,  $\omega_{TOj}$  and  $\omega_{LOj}$  mark the transverse and longitudinal frequencies of the *j*th mode, respectively, and  $\gamma_{TOj}$  and  $\gamma_{LOj}$  denote their corresponding damping constants.

### III. RESULTS

The wavenumbers of  $A_1(\text{TO})$  and  $A_1(\text{LO})$  modes in CLN, SLN, CLT, and SLT (Table II), estimated from  $Z(\text{XX})\bar{Z}$  and  $X(\text{ZZ})\bar{X}$  spectra (given in Figs. 1(a) and 1(b), respectively), are in good accordance with those reported in the literature, and so we shall only discuss the E-modes here. The E(TO) modes of LN and LT crystals were identified from  $Z(\text{XY})\bar{Z}$ ,  $Y(\text{XZ})\bar{Y}$ , and  $X(\text{YZ})\bar{X}$  spectra. The  $X(\text{YZ})\bar{X}$  spectra of congruent and nearly stoichiometric LN and LT crystals, collected at room temperature are given in Fig. 2. The wavenumbers of seven and eight E(TO) modes determined from our room-temperature spectra of SLN and SLT crystals, respectively, are shown in Table III. Our spectra of CLN and CLT crystals show the same number of modes as their SLN and SLT counterparts. There is a wide agreement on these wavenumbers for LN and LT in the literature. However, in disagreement with the reports of Caciuc *et al.*,<sup>12</sup> Ridah *et al.*<sup>21</sup> and Repelin *et al.*,<sup>15</sup> no sign of additional E(TO) modes was observed in the range from 160 to 200  $\text{cm}^{-1}$  in this work. No first-order modes were detected at wavenumbers lower than 140  $\text{cm}^{-1}$ , either.

Crystals of the same origin were studied at room temperature by IR spectroscopy. The experiment revealed eight and seven E(TO) modes in both CLN and CLT crystals,

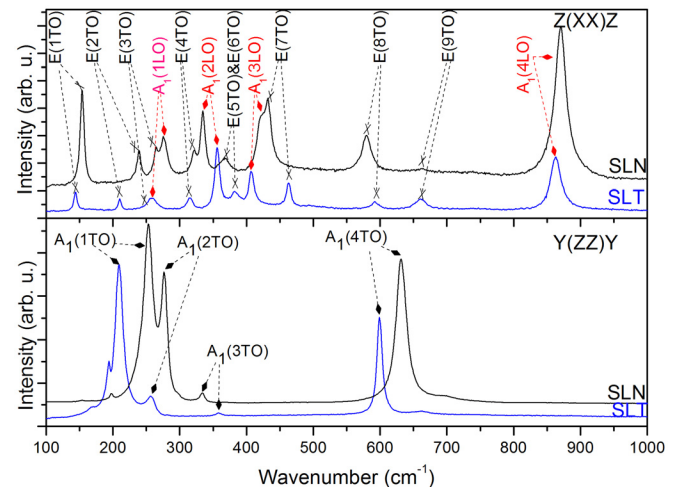


FIG. 1. Raman spectra of nearly stoichiometric LN and LT single crystals measured in  $Z(\text{XX})\bar{Z}$  (a) and  $Y(\text{ZZ})\bar{Y}$  (b) polarization configurations at RT.

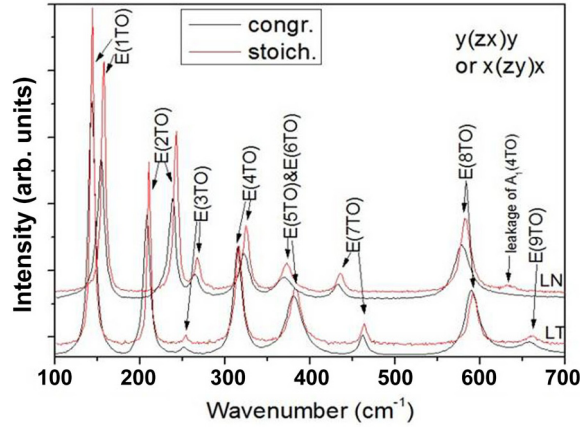


FIG. 2. Raman spectra of congruent and nearly stoichiometric LN and LT single crystals measured in  $Y(XZ)\bar{Y}$  or  $X(YZ)\bar{X}$  polarization configurations measured at RT. The areas of the spectra were normalized.

respectively (wavenumbers obtained by fitting to IR reflectivity spectra shown in Fig. 3 are given in Table III). Six of them match our Raman data well: the difference in estimated wavenumbers from the Raman and IR spectra is less than  $3\text{ cm}^{-1}$ , except for the modes in the  $360\text{--}380\text{ cm}^{-1}$  range. At the same time, the Raman mode denoted E(6TO) in Table III has no clear counterpart in the IR spectra. On the other hand, IR spectra have shown two additional modes for both CLN and CLT, which we naturally identified with the missing E(5TO) and E(9TO) modes.

The damping parameters of modes of our congruent specimens were considerably larger than those of the nearly stoichiometric ones, in agreement with reports in literature.<sup>18,26</sup> For

TABLE III. Wavenumbers of E(TO) and E(LO) modes of congruent (C) and nearly stoichiometric (S) LN and LT crystals, estimated from Raman (RS) and IR spectra, measured at room temperature. The theoretically calculated wavenumbers<sup>11</sup> are given for comparison.

		1TO	2TO	3TO	4TO	5TO	6TO	7TO	8TO	9TO
Theory		155	218	264	330	372	384	428	585	677
SLN	RS	155	240	265	322	364 <sup>a</sup>	370	433	580	...
CLN	RS	154	238	265	322	...	370	433	579	~660 <sup>b</sup>
CLN	IR	152	235	260	322	358	...	432	577	667
CLT	IR	142	...	253	315	373	...	462	592	663
CLT	RS	144	209	253	316	370 <sup>a</sup>	383	464	591	659
SLT	RS	144	210	254	316	374 <sup>a</sup>	383	464	592	660
		1LO	2LO	3LO	4LO	5LO	6LO	7LO	8LO	9LO
Theory		197	224	298	349	384	423	452	675	863
SLN	RS	199	241	298	...	370	425	457 <sup>c,d</sup>	...	879
CLN	RS	194	239	297	...	370	425	457 <sup>d</sup>	...	878
CLN	IR	196	239	294	343	...	426	452	659	876
CLT	IR	194	...	280	344	...	453	475	662	865
CLT	RS	194	211 <sup>e</sup>	280	...	383	454	472 <sup>d</sup>	659	864
SLT	RS	195	211 <sup>e</sup>	282	...	383	454	476	660	864

<sup>a</sup>Determined at 4 K.

<sup>b</sup>Extrapolated from Fig. 4(b).

<sup>c</sup>Determined at 110 K.

<sup>d</sup>Very weak intensity.

<sup>e</sup>Overlaps with  $A_1(1TO)$ .

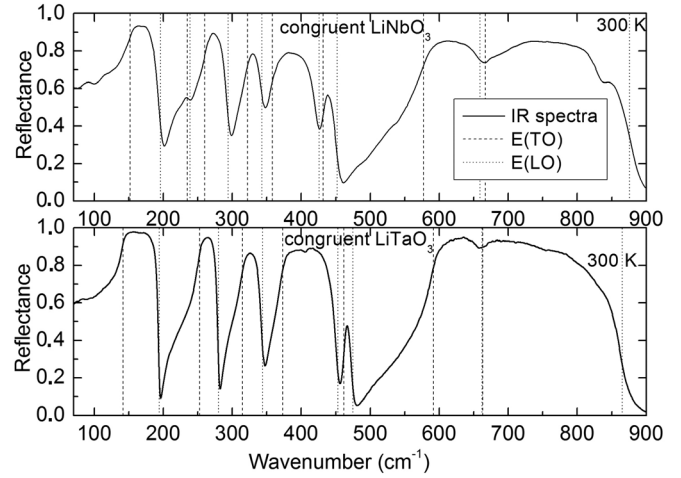


FIG. 3. Unpolarized near-normal reflectivity spectra  $R(\omega)$ , measured at RT, of Z-cut congruent LT and LN crystals.

example, the dampings of E(1TO) mode in CLN (CLT) and SLN (SLT) were  $10.6$  ( $8.3$ ) and  $5.5$  ( $5.0$ )  $\text{cm}^{-1}$ , respectively. Such damping parameters are very comparable with the difference between the wavenumbers of the E(5TO) and E(6TO) modes (only about  $10\text{ cm}^{-1}$ ). Since the above room-temperature Raman data revealed only the E(6TO) mode and the IR data only the E(5TO) mode, an additional argument proving that they are distinct E-modes was desirable. For this purpose, low-temperature measurements were performed on SLN, SLT, and CLT crystals. The Raman spectra in the  $330\text{--}410\text{ cm}^{-1}$  range measured in the  $X(YZ)\bar{X}$  or  $Y(XZ)\bar{Y}$  polarization configuration at 4 K, 80 K, and 293 K are given in Fig. 4(a). Under ambient conditions, the profile of the mode at  $370\text{--}380\text{ cm}^{-1}$  can be satisfactorily fitted by one oscillator peak. At 4 K and 80 K, however, both E(5TO) and E(6TO) modes were resolved in this frequency range in all of the three specimens studied. In fact, such a pair of an almost Raman-silent and an almost IR-silent mode in this frequency region was predicted for LN crystal from the theoretical local-density functional study of Refs. 11 and 13. Our experiments confirm fairly well this conjecture for both LN and LT crystals. The mode at lower wavenumbers has 10 (25) times lower intensity than its high-wavenumber neighbour in LT (LN). Low intensity and temperature broadening of the lines explain well the earlier experimental difficulties with E(TO) phonon assignments.

Interestingly, we did not find any direct evidence of an E(9TO) Raman mode in our LN crystals, even though E(9TO) is rather easily observable in Raman spectra of LT crystals. Consequently, to confirm the internal consistency of our assignments, we have also investigated the Raman spectra of  $\text{LiNb}_{1-x}\text{Ta}_x\text{O}_3$  (with  $x = 0, 0.18, 0.30, 0.43, 0.67$ , and  $1.00$ ) mixed crystals. The mode frequencies continuously evolve over the whole solid solution range from LN to LT (to be published elsewhere). In particular,  $Z(XY)\bar{Z}$  and  $X(YZ)\bar{X}$  spectra of  $\text{LiNb}_{1-x}\text{Ta}_x\text{O}_3$  shown in Fig. 4(b) demonstrate that the E(9TO) mode seems to persist at about the same frequency despite the strong reduction of its intensity with increasing Nb content. Our results show that the E(9TO) mode of LT in  $Z(XY)\bar{Z}$  spectra has considerably higher relative intensity than in  $X(YZ)\bar{X}$  spectra (Fig. 4(b)).



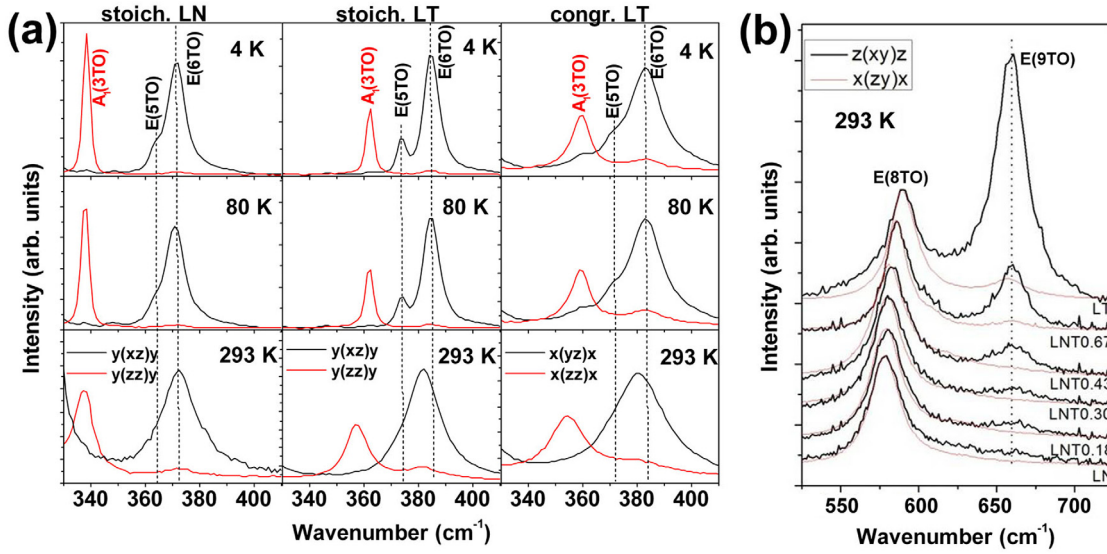


FIG. 4. Raman spectra in the range of 330–410 cm<sup>-1</sup> measured in  $Y(XZ)\bar{Y}$  or  $X(YZ)\bar{X}$  polarization configuration at 4 K, 80 K, and 293 K on stoichiometric LN, stoichiometric LT and congruent LT crystals (a). To represent the possible polarization leakages of  $A_1(\text{TO})$  modes, the  $Y(\text{ZZ})\bar{Y}$  or  $X(\text{ZZ})\bar{X}$  spectra are also shown. Comparison of relative E(8TO) and E(9TO) mode intensities (the amplitudes of E(8TO) modes were normalized) in  $Z(XY)\bar{Z}$  and  $X(YZ)\bar{X}$  spectra of  $\text{LiNb}_{1-x}\text{Ta}_x\text{O}_3$  (LNT<sub>x</sub>, 0 ≤ x ≤ 1) crystals (b).

Still, its intensity decreases drastically when Ta is replaced with Nb. In LNT<sub>0.30</sub>, LNT<sub>0.18</sub>, and LN, the E(9TO) mode has too low an intensity to be identified. Nevertheless, the extrapolated frequency agrees well with the IR experiment as well as with *ab-initio* calculations<sup>10</sup> for LN crystal (both reported in Table III).

In backscattering geometry, the E(LO) modes can be observed together with  $A_1(\text{TO})$  modes in the  $Y(\text{XX})\bar{Y}$  polarization configuration. However, some of the E(LO) modes present very low Raman intensities. Thus, the identification can be confusing as a result of the high number of modes present in the  $Y(\text{XX})\bar{Y}$  spectra:  $A_1(\text{TO})$  modes and polarization leakage of E(TO) modes (Figs. 5 and 6). To overcome this problem,  $X(\text{YY})\bar{X}$  spectra, consisting of  $A_1(\text{TO})$  and E(TO) modes, were measured under the same experimental conditions. In both  $X(\text{YY})\bar{X}$  and  $Y(\text{XX})\bar{Y}$  spectra, the inten-

sities of  $A_1(\text{TO})$  modes are represented by the same coefficients  $a$ . Thus, the intensities and damping parameters of the  $A_1(\text{TO})$  modes in the fitting procedure for  $Y(\text{XX})\bar{Y}$  spectra were fixed to those observed in the  $X(\text{YY})\bar{X}$  spectra. The damping parameters and relative intensities of E(TO) modes were fixed to those observed in the  $X(\text{YY})\bar{X}$  spectra. The intensity of leakage of E(2TO)–E(9TO) modes was estimated from the intensity of the E(1TO) mode, which is isolated from the other modes. The seven and eight E(LO) modes of LN and LT were identified from the  $Y(\text{XX})\bar{Y}$  Raman spectra as illustrated in Figs. 5 and 6. Their wavenumbers are compared with those estimated from IR spectra in Table III. Despite the complexity of  $Y(\text{XX})\bar{Y}$  Raman spectra, the agreement in wavenumbers estimated by Raman and IR spectroscopies was better than 3 cm<sup>-1</sup>. E(5LO) of LN and LT and E(2LO) of LT have low oscillator strengths, while

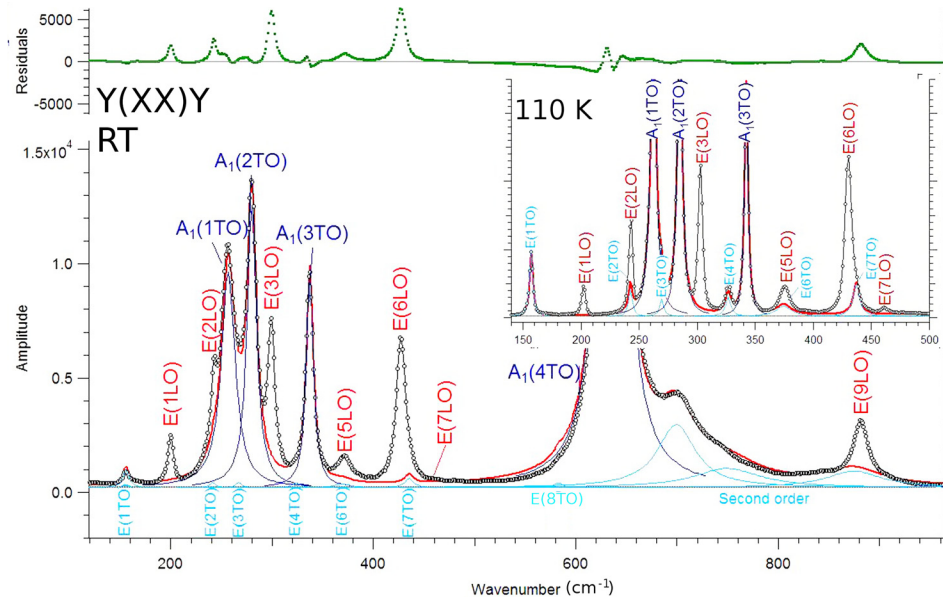


FIG. 5. Comparison of  $Y(\text{XX})\bar{Y}$  spectra of nearly stoichiometric LN crystals, measured at RT, and reconstructed spectra from calibrated intensities and damping parameters of  $A_1(\text{TO})$  modes and the possible polarization leakages of E(TO) modes from  $X(\text{YY})\bar{X}$  spectra (for more details, see the text). The difference between the reconstructed and  $Y(\text{XX})\bar{Y}$  spectra (residuals) represents E(LO) modes, expected in this polarization configuration. The  $Y(\text{XX})\bar{Y}$  spectrum of nearly stoichiometric LN measured at 110 K is given in the inset.

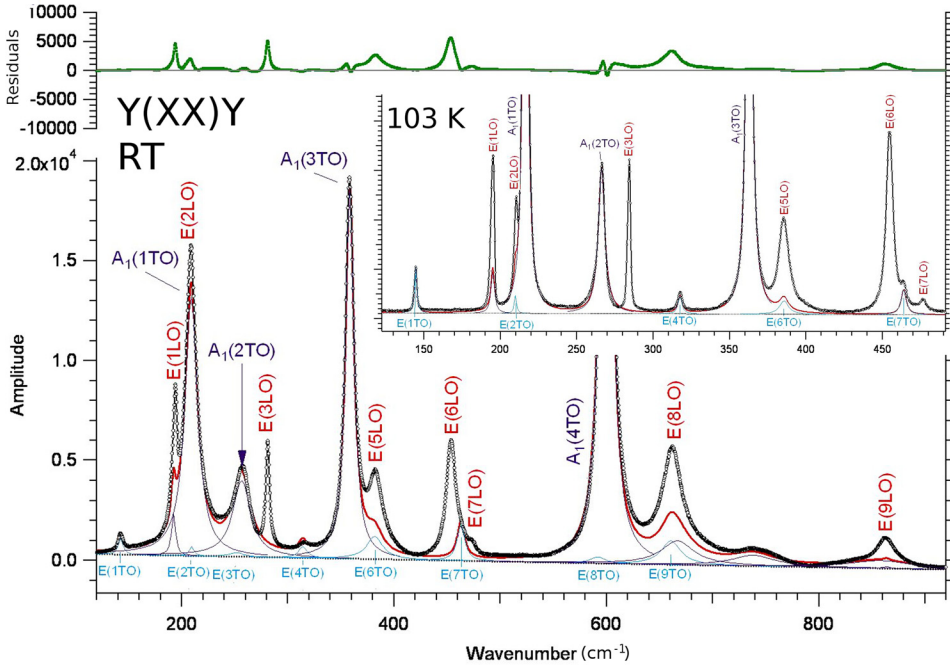


FIG. 6. Comparison of  $Y(XX)\bar{Y}$  spectra of nearly stoichiometric LT crystals, measured at RT, and reconstructed spectra from calibrated intensities and damping parameters of  $A_1(\text{TO})$  modes and the possible polarization leakages of  $E(\text{TO})$  modes from  $X(\bar{Y}\bar{Y})\bar{X}$  spectra (for more details, see the text). The difference between the reconstructed and  $Y(XX)\bar{Y}$  spectra (residuals) represents  $E(\text{LO})$  modes, expected in this polarization configuration. The  $Y(XX)\bar{Y}$  spectrum of nearly stoichiometric LT measured at 103 K is given in the inset.

$E(4\text{LO})$  of LT and LN and  $E(8\text{LO})$  of LN have low Raman efficiencies. The experimental frequencies of LN are close to the theoretical values as well. Contrary to the experimental data reported in the literature, no  $E(\text{LO})$  modes of LN and LT were observed at wavenumbers lower than  $190\text{ cm}^{-1}$ .

#### IV. DISCUSSION

From the point of view of the electronic structure, LN and LT have been reported to be very similar systems. Moreover, LN and LT are isostructural. In this work, the experimental identification of the E-modes in LN and LT was based on the theory for LN as reported by Ghosez *et al.*<sup>11,13</sup> and on the similarity between LN and LT. Experimental results show that the Raman and IR spectra of LN and LT are very similar and the E modes of both materials can be identified by using the same reasoning. The comparison and

combination of results obtained by Raman and IR spectroscopies have allowed for the first time a complete assignment of the E-modes in LT and LN.

This assignment of E- and  $A_1$ -symmetry modes has been used to calculate the ordinary and extraordinary clamped relative permittivity (above piezoresonance),  $\epsilon_0^o$  and  $\epsilon_0^e$ , of LN and LT using the Lyddane-Sachs-Teller relation (LST).<sup>1</sup> This equation is valid for multi-mode and anharmonic crystals.<sup>27</sup> In our calculation, the optical dielectric constants of LN and LT were taken from Refs. 6 and 8 and considered to be weakly dependent on stoichiometry ( $2 \times 10^{-2}$  in LN from Ref. 28). The obtained relative permittivity values for both materials are given and compared with the literature values in Table IV. Previously, the clamped relative permittivity was estimated by fitting the oscillator strengths of IR spectra and by using a three parameter dielectric function.<sup>3,6,8</sup> This method does not require a complete assignment of all modes but takes into account the strongest contributions of modes; therefore, it provides correct values while the LST approach calls for a complete mode assignment. There is good agreement between the values of  $\epsilon_0^o$  and  $\epsilon_0^e$  of LN and LT calculated from our attributed mode wavenumbers and those obtained from oscillator strengths in the IR spectra. Similar values of ordinary and extraordinary dielectric constants were measured by terahertz time domain spectroscopy (THz-TDS, Table IV).<sup>29–31</sup> Minor discrepancy remains because of the dispersion in the THz regime resulting from the proximity of low-frequency modes, particularly for the ordinary axis. For comparison,  $\epsilon_0^o$  and  $\epsilon_0^e$  were calculated from mode wavenumbers reported by Kaminow *et al.*,<sup>3</sup> Barker *et al.*<sup>6,8</sup> and Ridah *et al.*<sup>21</sup> (Table IV). One can see that there is a significant difference between the  $\epsilon_0^o$  values obtained from oscillator strengths in IR spectra and those from erroneously assigned mode wavenumbers, using the LST relation. For example, the wrong assignment of two  $E(\text{TO})$  and two  $E(\text{LO})$  modes by Ridah *et al.* resulted in a

TABLE IV. Ordinary and extraordinary clamped relative permittivities,  $\epsilon_0^o$  and  $\epsilon_0^e$ , of congruent LT and LN, calculated from our IR and Raman data and compared with the reported values. (IR osc. str.—estimated by fitting the oscillator strengths of IR spectra and by using the three parameter dielectric function).

References	Method	LN		LT	
		$\epsilon_0^o$	$\epsilon_0^e$	$\epsilon_0^o$	$\epsilon_0^e$
Kaminow <i>et al.</i> <sup>3</sup>	IR osc. str.	41	24	41	36.4
	LST	67.5	24	38.4	33
Barker <i>et al.</i> <sup>6,8</sup>	IR osc. str.	41.5	26	41.5	37.6
	LST	...	...	38.0	30.1
Ridah <i>et al.</i> <sup>21</sup>	LST	47.5	24	...	...
This study	LST	40.2	23.7	39.6	35.9
THz-TDS					
Wong <sup>29</sup>	9 GHz	42.5	26	...	...
Sakai <sup>30</sup>	300 GHz	44	25.9	...	...
Fujii <i>et al.</i> <sup>31</sup>	200 GHz	...	...	42	40

15% error compared with values obtained from IR data. However, very close values were obtained for  $\varepsilon_0^c$  of LN, where the  $A_1$ -modes were correctly assigned. Once again, this illustrates the importance of attributing the correct wave-numbers to all optical phonons.

## V. CONCLUDING REMARKS

Nearly stoichiometric and congruent LN, LT, and  $\text{LNT}_x$  single crystals have been studied by Raman and IR spectroscopies. The E(5TO) mode has been identified in Raman spectra collected at low temperature (80 K and 4 K) and has been confirmed by IR spectroscopy. The E(9TO) mode of LN, which shows a low Raman efficiency, was found by analysis of  $\text{LNT}_x$  mixed crystal spectra and was in good agreement with that observed in IR spectra. The wavenumbers of the E-modes, estimated experimentally, were close to those calculated theoretically for LN. In agreement with predictions from *ab initio* calculations, the E(6TO) mode has a low oscillator strength. The clamped relative ordinary and extraordinary permittivities of LN and LT were calculated using LST relation with good agreement with Terahertz Time Domain spectroscopy.

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