

Bibliographical review on vibration spectroscopy of proton-exchanged LiNbO₃ and LiTaO₃

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ABSTRACT

This article aims to review the majority of papers available in literature where vibration spectroscopy is used for study of proton-exchanged lithium niobate and proton-exchanged lithium tantalate, which are two materials very important for integrated optics. The list of papers on the subject is presented together with some comments on the most important applications and conclusions drawn from the respective studies.

KEYWORDS: proton exchange, optical waveguides, vibration spectroscopy

1. Introduction

Being synthetic ferroelectric crystals with very attractive properties for integrated optics, LiNbO₃ (LN) and LiTaO₃ (LT) are widely used in the field. Both crystals belong to the trigonal crystal system. The unit cell consists of planar sheets of oxygen ions, situated perpendicular to the optical axis *c*. Oxygen ions from adjacent sheets form octahedral interstices which are one-third filled by lithium ions, one-third by niobium/tantalum ions and one-third vacant (V), ordered in the +*c* direction in the sequence: Li-Nb/Ta-V. The large number of vacancies favors the penetration of other ions and their high mobility together with the high mobility of the crystal's own metal ions.

Proton exchange (PE) is one of the most popular contemporary methods for obtaining optical waveguides

in LN and LT by modification of surface layers of these ferroelectrics such as to suit their application in integrated optics.

Going by the scheme:



PE modifies the surface layer (several μm in depth) by Li-H ion exchange at a relatively low temperature (160 ÷ 250 °C) in acidic melts causing a large extraordinary index change Δn_e ($\Delta n_e \cong 0.12\text{-}0.15$ for LN and $\Delta n_e \cong 0.02$ for LT at 0.633 μm). The PE layers show complex phase behavior depending on the hydrogen concentration (the value of *x*) which could be controlled technologically. Up to seven phases exist in proton-exchanged lithium niobate (PELT) and up to five in proton-exchanged lithium tantalate (PELT). Each phase forms its own sub-layer in the protonated region, the one with the highest value of *x* being on the top. Each phase originates as an individual sub-layer undergoing phase jumps with gradual change of *x*. In every single one of them Δn_e is a linear function of proton concentration. Within a phase transition, the value of Δn_e and/or of the deformations perpendicular to the surface change by leaps.

It is widely accepted that the waveguide effect and the increased photorefractive resistance of PE-layers are due to OH group formation when protons interact with oxygen atoms of the crystal lattice [1]. IR absorption or transmission is very sensitive to H concentration in the crystal and is commonly used for the detection and observation of the OH groups present in PE optical waveguides in LN and LT. In principle, OH-stretching vibration spectra allow

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conclusions to be drawn on the proton concentration in the crystal and on the positions of OH defects in the crystal lattice.

The infrared (IR) reflection spectroscopy of PELM provides direct information on the phonon spectrum related to the structure and chemical bonds of the surface crystalline phase. In some respects, this method could be more useful for studying layered structures like multiphase PE-layers than IR absorption spectroscopy. IR reflection spectra show the strong changes caused by PE in the lattice vibration spectrum.

Raman spectroscopy is a powerful tool for studying structural phase transitions in solids. Raman scattering is among the few experimental techniques that can answer questions concerning the phase state and phase transformations, deformations of the crystal lattice, and changes in the atomic configurations. Proton exchange influences both vibration modes in Raman spectra polarized along the Z-axis (A₁(TO)) and polarized along the X- or Y-axis (E(LO)). It causes intensity reduction of some of the bulk lines, appearance of new ones and appearance of lattice disorder-induced broad bands. A₁(TO) type Raman spectra are more expressive. With the development of integrated optics, it has become clear that the waveguide Raman technique is unique in studying the properties of thin waveguide layers [2]. It allows the spectral changes to be followed at different depths of the PE layer where definite modes propagate. Beside waveguide Raman spectroscopy, micro-Raman spectroscopy has been used allowing some comparative and semi-quantitative estimations of the thickness of phase sub-layers to be made.

Since the physical processes which determine the phonons active in Raman and infrared spectra also determine the electro-optical and the non-linear dielectric properties of materials, Raman and infrared spectra provide information for the characterization of the proton-exchanged layers.

2. Vibration spectroscopy of proton-exchanged lithium niobate

2.1. Infrared absorption spectroscopy of PELN

OH groups exist not only in the protonated, but also in the as-grown crystals due to residual water. Their O-H bonds lie in the oxygen planes, perpendicular to the optical (c) axis. The virgin LN crystal

exhibits an absorption peak at 3484 cm⁻¹ polarized perpendicular to the crystal axis [3-8] which could be deconvoluted in at least two peaks separated by about 13 cm⁻¹ with intensities depending on the stoichiometry of the crystal [3-5, 7]. At least two new OH groups with different hydrogen bonding environments are formed after PE, causing two absorption bands with different shapes and polarization dependences: a sharp peak at 3000-3010 cm⁻¹, polarized perpendicular to the optical axis, and a broad unpolarized band peaking at about 3280 cm⁻¹ [9-16]. The asymmetry of the first band suggests more than one type of OH groups lying in the oxygen planes of the crystal lattice [5], while the second band suggests the presence of hydrogen-bonded OH groups [9, 17]. Some authors attribute the second band to a new crystalline structure – HNbO₃ (a cubic phase) [11], which can exist only in LN powders. In the case of monocrystals, where waveguide layers actually are formed, the band centered at 3280 cm⁻¹ indicates substituting hydrogen situated in interstitial sites [10, 18]. PE and post-exchange annealing (APE) affects the intensity of these two bands in different ways depending on the proton source used, the temperature and the duration of both PE and annealing [9, 17, 19].

It has to be noted that the IR absorption studies concerning mobility and incorporation of OH⁻ ions in LN have been performed prior to the emergence of the PE technology. These studies put an emphasis on the reasons for the incorporation of a large amount of OH⁻ ions into the lattice [7]: charge compensation of Li⁺ vacancies and interstitial ions, and almost equal ion radii of OH⁻ and O²⁻.

It has been shown [16] that the intensity of the OH IR absorption band and the spatial distribution of the electric charge in the lattice are closely related. That is why protons are considered as the main ions responsible for the lower photorefractivity of LN.

2.2. Applications of IR-absorption spectroscopy for PELN

2.2.1. Stoichiometry studies of the LN

The crystal substrate stoichiometry could be determined [5, 7] since the OH-spectrum band shape and structure depend on the crystal composition. The structure varies from a single broad peak for the lowest Li/Nb ratio to a three-component band for a stoichiometric

crystal. Conclusions about the mechanism of the OH⁻ ion incorporation in the lattice of as-grown and PELN have been made as well [7]. It is difficult to observe any dependence on stoichiometry in the spectra of protonated LiNbO₃ or LiTaO₃ even if it really exists: the intensity of the band of PE crystals is about ten times higher than that of the virgin samples and slight variations in the spectra of untreated samples due to different stoichiometry cannot affect notably the final form of the spectra [20].

2.2.2. Structural study of PELN

The spectra provide information about hydrogen positions and OH bonds orientation in the crystal lattice [4, 9, 10, 18, 21], as well as about the positions and thickness of the sub-layers causing the two bands in the whole PE-layer [11, 17, 22, 23], the most strongly protonated one being on the top [24-26]. The two absorption bands are due to the different lattice positions and bindings of the hydrogen ions present in the exchange layer [10, 20, 27]. Polarization behavior of the 3500 cm⁻¹ band means that the O-H vector is perpendicular to the optical (c) axis and the substituting proton sites lie within hexagonally closest-packed oxygen layers, rather than in metal-like sites between oxygen layers [1, 28]. The authors of [11] consider the 3500 cm⁻¹ band as characteristic for a rhombohedral structure but the 3280 cm⁻¹ one, for cubic lattice. The IR spectrum after deconvolution implies the existence of three OH bands characteristic for the presence of substitute protons [29].

The broad absorption band at 3280 cm⁻¹ results from a very thin surface layer (about 0.1-0.2 μm); the strong band (peak at 3500 cm⁻¹) is due to the protonated layer extending deeper [11, 17, 24]. The layers have different crystal symmetries. The OH groups near the surface are chaotically oriented, indicating a great degree of disorder (amorphous state). The OH groups in the depth of the basic layer are situated in the planes perpendicular to the Z-axis (c) and are connected with stronger hydrogen bonds. The presence of the top film depends on the orientation of the sample, the X- and Y-cut plates being preferable [30]. The thickness of the sub-layer which contains interstitial hydrogen could be determined by stepwise polishing of the surface and recording of the spectrum after each step [24].

The IR spectrum of lightly exchanged LN illustrates the difference between H⁺ and Li⁺ sites suggesting that the O-H vector must lie within the closest-packed oxygen planes in the LN structure, i.e. the proton site must be within the triangular face connecting octahedral Li sites [28]. A model of the occupation sequences of proton sites in the oxygen plane of PELN has been created by analysis of the structure of the OH band at 3500 cm⁻¹ [31]. The narrow absorption band near 3500 cm⁻¹ shifts by up to 20 cm⁻¹ toward higher frequencies at higher hydrogen concentrations [14] and increases in width [32] suggesting substantial change of the lattice structure. Thus protons cause lattice distortion leading to transition to a perovskite structure at higher proton concentrations.

The IR absorption spectra of isotopic-exchanged LN show significant differences between proton and deuterium (D) sites within the crystal lattice [30]. IR spectra of deuterium-exchanged (DE) and PE waveguides show some variations indicating differences in the structure of Li⁺ to ¹H⁺ and Li⁺ to ²H⁺ exchanged LN [30, 33]. Studies on the positions, intensity and polarization of combined libration-vibration OH (OD) bands of PELT have been performed in [34]. These modes are shifted from the stretching vibration near 3500 cm⁻¹ (OH) and 2600 cm⁻¹ (OD) by about 950 cm⁻¹ for ¹H⁺- and about 700 cm⁻¹ for ²H⁺-exchanged samples towards a higher frequency. The intensities of these combined bands are proportional to the intensities of the stretching vibration bands (i.e. to the H/D⁻ concentrations), the polarization being both perpendicular and parallel to the optical axis, reflecting the properties of three-dimensional oscillator.

The IR spectra of isotopic exchange (Li to D and Li to tritium (T) exchange) [32, 35, 36] have shown that proton-, deuterium- and tritium-exchanged LN cannot be regarded as structurally identical.

The effect of MgO doping of LN on the lattice structural changes induced by PE and the subsequent annealing has been studied in [37, 38] by the analysis of the IR absorption peak at 3500 cm⁻¹. It was found that PE causes more serious non-uniformity of the strain in MgO:LN than in undoped LN.

2.2.3. Monitoring of the PE process

The formation of hydroxyl groups in the lattice due to the amount of hydrogen introduced in the

PE layer [39] and of the extent of the PE or DE [33] process has been studied by measuring of the IR absorption peak at about 3500 cm^{-1} and 2600 cm^{-1} , respectively [9, 40]. The OH absorbance increases with exchange time and temperature and indicates the extent of the reaction [41]. Infrared spectra show that the OH absorbance increases with the temperature of the melt [42]. The extent of PE as a function of temperature and time has been studied by using IR spectroscopy also in [40, 43]. It has been found that the dependence of the absorption band area at 3505 cm^{-1} on temperature and time is non-linear [9]. The band area vs. exchange time shows saturation at longer durations [44]. Some authors attribute the non-linearity of the strength of that peak vs. time (being linear for a short period of PE in a fresh melt) to the enrichment of the melt of limited volume with Li^+ acting as melt buffering [45]. When a melt of unlimited volume is used, the areas under the OH-stretched peaks are directly proportional to the time and temperature of PE and to the total quantity of protons in the exchanged layer [41]. The integrated intensity of IR absorption spectra is linearly proportional to the square root of the diffusion time [23, 30, 43]. A linear dependence of band opacity at 3508 cm^{-1} on depth has been observed [46]. The OH absorption increases with the exchange time [47]. It has been found that the relative intensities of the two bands depend on the Li^+ molar fraction in the melt used as a proton source [23]. Infrared absorption spectra also show that the H^+ concentration in the upper layer grows much more quickly in time, i.e. the Li^+-H^+ substitution there is more complete [24, 39].

Monitoring of the reversed proton exchange (RPE) by IR spectroscopy [48, 49] confirms the complete disappearance of the interstitial protons by the disappearance of the band centered at 3240 cm^{-1} . It has been also shown that further RPE restores the spectrum of pure LN [50]. Monitoring of the process when new PE-techniques have been applied has been done as well [51].

2.2.4. Contribution to the phase model

The IR spectra of samples with different values of x help to estimate the concentration boundaries of the phases (including monoclinic, rhombohedral and cubic ones) [1, 19, 52-55]. For example, the authors of [1] have observed changes in IR spectrum peak positions and spectrum structure when the value

of x crosses the concentration boundaries of different phases. Infrared spectra also show which proton sites are filled first with increasing x .

2.2.5. Phase composition analysis

The phase composition analysis has been performed in [51, 56-60]. According to the phase model, the peak at 3500 cm^{-1} is attributed to the β_1 -phase, while the band at 3240 cm^{-1} – to the β_i phases ($i = 2, 3, 4$) [44, 56, 61]. The spectra show several bands (at 3488 cm^{-1} , 3500 cm^{-1} , 3512 cm^{-1} , $3250\text{-}3280\text{ cm}^{-1}$) which could be attributed to different phases forming the PE layers. Spectra deconvolution when the phase composition is known allows the components to be attributed more precisely to the rest of the phases [58, 59, 62-65], the phase composition of PELN layers obtained by using different proton sources or modified PE technology to be established, and the thickness of each phase sub-layer to be evaluated as well [57].

Infrared absorption spectroscopy has also been used for evaluation of the phase composition of MgO:LN proton-exchanged at different technological regimes (PE, APE and HTPE (high-temperature PE)) [66], for discovery of new phase formation in the PE layer [16, 54] and for recognizing the monoclinic (η) phase ($0.75 < x < 0.77$) obtained in congruent LN by PE [52]. The formation of high-temperature phases, metastable at room temperature, has also been observed by IR absorption spectroscopy [67].

2.2.6. Study of the dynamics of phase formation

The phase formation has been studied by following up the time evolution of the OH absorption band [25]. After spectra deconvolution (usually Gaussian), it is possible to compare the growth rates of each of the phases by following the evolution of the area under each of the components in time [44, 56]. It has been found that Gaussian deconvolution is better for highly protonated samples, but Lorentzian is better for virgin substrates. Theoretically, this different behavior is not surprising since the vibration spectrum of a disordered state, as of the protonated crystal, is closely related to a Gaussian form. After the decomposition, the frequencies and integrated intensities of the bands could be compared. Thereby the evolution of the bands assigned to different phases vs. the variations in the technological parameters could be followed. Thus, the histograms of components intensity show not only the presence of definite

phases, but also how the technological conditions chosen reflect on the thickness of sublayers formed by these phases.

The proton concentration profile and therefore the phase composition has been obtained by measuring the intensity of the band at 3508 cm⁻¹ in the IR OH-stretching vibration spectra after step-like decrease of the layer thickness by polishing and using the relationship between the hydrogen concentration and the absorption coefficient [24]. Calculation of the OH⁻ (proton) concentration in PE layer has also been performed by using the methods described in [13, 55] based on IR transmission spectra. The proton (deuterium, tritium) concentration is estimated as well by using the maximum absorption coefficient for the 3500 cm⁻¹ (2590 cm⁻¹, 2211 cm⁻¹) band [36].

Detection and study of different phases existing in Li_{1-x}H_xNbO₃ as well as investigations of phase transitions between them have been performed [1, 55, 68] since phase transitions affect the OH absorption band. Shift in the OH band frequency due to phase transition is observed in [47, 69]. The evolution of IR spectra at different annealing stages indicates phase transitions from highly protonated phases to the original crystal structure (α -phase).

2.2.7. Evaluation of the waveguide parameters and stability/quality

Correlations between the strength of the OH absorption line and the refractive index change (Δn_e) have been established [55, 70, 71] as well as a way to estimate the thickness of PE waveguides by calculating the area under the IR absorption bands [23, 40, 41, 72].

The PE waveguide stability in time can be followed by IR spectra since it has been found that the behavior of integrated intensity in time is the same as this of Δn_e . Thus, IR spectra can be used for studying the short-term (relaxation) and the long-term (aging) stability of PE waveguide parameters [73]. One of the most significant reasons for PE-layer instability is the migration of the loosely bound hydrogen with time. The lower frequency of the unpolarized OH bonds implies higher mobility of their protons which could deteriorate the waveguide parameters stability. Thus, the presence or absence of the shoulder at 3280 cm⁻¹ in the IR

spectrum could be used as a criterion for waveguide stability [72]. The missing broad band at 3280 cm⁻¹ suggests a good quality and better stability of the waveguide layer parameters. The waveguide stability has been followed up by shoulder relaxation after annealing [55, 59] and after aging [73, 74].

2.2.8. Technology adjustment

The choice of a proton source, temperature and duration of PE and post-exchange annealing: e.g. IR absorption measurements suggest that melt dilution (adding lithium benzoate to benzoic acid) prevents the occurrence of interstitial hydrogen [17, 39, 40]. Control of the thickness of β_1 and β_2 sublayers building the waveguide could be performed by varying the dilution ratio of the mixed melt composition [75]. It has been shown that OH band intensity at 3500 cm⁻¹ increases at a lower extent of melt dilution (i.e. at fast PE) and higher duration of the exchange process [76]. The acid dilution significantly changes the substitute-interstitial proton ratio, influencing the waveguide quality [29]. The effect of proton source dilution on the IR absorption has also been studied [22] showing that monophase (α) waveguides could be obtained by appropriate buffering. The effect of different proton sources on the shape and half-width is studied in [77].

It has been established that the IR spectra of waveguides obtained by high-temperature (above 300 °C) PE have only the polarized OH band, but at lower temperatures the second, unpolarized one also appears. After increasing the temperature of PE up to 350 °C, a strong improvement of the waveguide quality has been observed [78, 79].

The minimal volume (280 ml) of the melt at which its action is not affected by the decrease of H⁺ and the increase of Li⁺ due to the PE itself has been determined [45]. In melts larger than 280 ml, the dependence of OH integrated intensity on time would be linear. Activation energies have been determined from IR spectroscopic measurements [40]. The diffusion coefficient of H⁺ penetrating to the crystal could be calculated from the growth rate of the OH absorption band; it is done for OD in [80].

2.2.9. Study of the proton redistribution during annealing

The redistribution of the diffused protons during thermal treatment of PELN has been performed

by following up the evolution of the two main bands [13, 18, 69, 72, 77, 81, 82]. During post-exchange annealing, a diffusion of interstitial (hydrogen-bonded) OH in the depth of the layer takes place [13, 55]. The IR absorption bands registered at different conditions of annealing and different crystal surface orientations are described in [46]. After long annealing duration, the peak frequency and shape of the IR spectra of PELN tend to those of the untreated crystal [83]. The same is the effect of the strong (high temperature) annealing [35]. Thus, the OH stretching bands can be a sensitive indicator of a progress in a PE-waveguide annealing process.

2.2.10. Following up the changes in the phase composition and H⁺ presence during annealing procedures

Differences in the behavior during post-exchange annealing for X- and Z-cut LN have been reported [84]. It has been established that the higher content of interstitial hydrogen in X-cut LN prevents lithium from free movement during the post-exchange annealing of PELN. After annealing, the intensity of the unpolarized shoulder decreases since protons from out-plane bonds penetrate deeply in the crystal and form new in-plane ones.

The integrated intensity of OH spectra of PE waveguides does not change during annealing procedures, i.e. no loss but only redistribution of hydrogen ions takes place. The IR absorption spectra show that the H⁺ content in the waveguides is not influenced by the annealing procedures and the stoichiometry of the crystal, but only by the parameters of the exchange process [69].

A frequency shift of the polarized band to lower frequencies after strong annealing is observed which means that the crystal restores its structure of untreated LN [83, 85]. The infrared spectra show that after annealing the hydroxyl group with hydrogen situated in oxygen planes is dominant and the hydrogen-bonded OH disappears [69, 86, 87].

2.2.11. Study of the proton-conserving property of SiO₂ cladding over channel PE waveguides

The spectra have shown clearly that SiO₂ cladding keeps protons inside the waveguide and out-diffusion of protons takes place in its absence [88, 89].

2.2.12. Study of the dynamics of a multistep exchange processes including PE as a step

For example when PELN has been Cu-doped, the integrated intensity of the OH band is reduced during Cu incorporation into the PE waveguide, indicating that a replacement of protons by Cu ions takes place. The degree of replacement depends on the duration of treatment and on the Cu content in the melt [90].

2.2.13. Study of the proton-deuterium exchange

It has been shown that both PE and DE waveguides interact with atmospheric water vapor [33, 91]. APELN and soft (in buffered melts) PELN do not react with atmospheric vapor.

2.2.14. Evidence of enrichment of the crystal surface with protons

The comparison of the IR absorption spectra registered before and after mechanical treatment of LN substrate has shown that an effect of enrichment of the crystal surface with protons takes place after cutting and polishing [92]. Such effect is localized to the surface, so no waveguide action is possible because of insufficient thickness of the modified layer.

2.3. IR reflection spectroscopy of PELN

The IR reflection spectroscopy allows the surface phase of multiphase waveguides to be recognized. The information given by the analysis of the IR reflection spectra helps to be much more specific when determining which phases build the waveguide layers investigated. The IR reflection spectra contain new bands within the range 800-1000 cm⁻¹ and each phase has its own reflection spectrum [93, 94]. The characteristic changes are at 975 cm⁻¹ for β_1 -phase, at 980 cm⁻¹ for β_2 and β_3 and at 970 cm⁻¹ for β_4 [93]. Thus, the IR reflection spectra in low-frequency range could determine the top-layer phase status.

It has been established [93] that at 70° angle of light incidence, the spectrum of the surface layer is separated from those of deeper situated layers in multiphase waveguides. This way, only the surface phase contributes to the reflection spectra of multiphase waveguides. When the PE layer's thickness is large (over 12 μm) it is possible to separate the OH spectrum of the PE layer from that of the substrate at any angle of incidence [95].

2.4. Applications of IR reflection spectroscopy of PELN

2.4.1. Information on the structure and chemical bonding of PELN

The estimation of structural disorder in waveguides has been performed in [96, 97]. The attenuation of the 580 to 880 cm⁻¹ band is used as an indication of disorder. For example, it has been established that SPE waveguides demonstrate a less disordered structure than APE ones [97].

2.4.2. Study of the dynamics of multistep exchange processes

IR reflection spectroscopy has been used for studying processes which include PE as a step. For example, when PELN has been Cu-doped, OH vibration frequency decreases, indicating a reduction in the proton concentration in the layer due to the replacement of protons by Cu ions [90].

2.4.3. Studying the surface polaritons

A band in the region of valent OH group vibrations (3600-3400 cm⁻¹) has been discovered [95].

2.4.4. Surface phase detection and phase characterization

PELN layers obtained at different technological conditions have been studied by IR reflection spectroscopy in [62, 93, 96-99]. Since each phase has its own characteristic spectrum, it could be used for phase identification of samples with unknown phase content. The spectra deconvolution [99] allows the dominating band for each phase to be determined.

Recognizing a multiphase or monophasic composition of the PE layer is also possible. Multiphase layers show frequency shift at varying angle of light incidence due to the interfaces between phase sub-layers, while the spectra of monophasic layers do not depend on the angle of incidence [93].

2.4.5. Study of the proton conductivity

Anisotropic proton conductivity in the ferroelectric phases of PELN has been assumed since the spectra show the presence of two energetically non-equivalent OH complexes in these phases [100].

2.4.6. Estimation of the proton concentration and the value of the electrooptical coefficient r_{33} for different phases

Kramers-Kronig analysis of IR reflection spectra and the value of LO-TO splitting have been used

for evaluation of proton concentration and electro-optical coefficient of different phases existing in PELN [93, 100].

It has also been shown that the change of the band-gap shift in reflection spectra can be used to estimate the values of r_{33} [97].

2.4.7. Study of PE in MgO-doped LN

It has been established that the APE process leads to structural damage of the surface layer, but high-temperature PE and soft PE produce layers whose structure is close to that of the unprotonated crystal (α -phase) [66].

2.4.8. Study of the enrichment of the crystal surface with protons

The IR absorption spectra registered before and after mechanical treatment of LN substrate have shown that an effect of enrichment of the crystal surface with protons takes place after cutting and polishing [101]. It has confirmed the conclusion made in [92] for a random PE at the sample surface due to thermal dissociation of water.

2.4.9. Monitoring of RPE

Following up the decrease in the OH band integrated intensity and the peak frequency shift toward the values characterized for unprotonated LN gives information on the degree of the RPE [101].

2.5. Raman spectroscopy of PELN

Right-angle Ra scattering has been used for investigation of various as-grown and hydrogen-doped LN crystals [102]. As-grown congruent crystals has shown equivalent scattering for (xx) and (yy) geometries, the signal of the (zz) configuration being very low. After electro-assisted H⁺ doping, inequivalent scattering for (xx) and (yy) geometry and increasing scattering efficiency for the off-diagonal component (xy) have been observed, which means that the vibrating hydrogen can no longer be situated in the direction of the O-O bonds and the threefold rotational symmetry is destroyed.

In the Raman scattering geometries commonly used, the phonon spectrum of pure LN consists of four A₁(TO)-phonons (at 254, 275, 332 and 632 cm⁻¹), polarized along the Z-axis, and seven E(TO)-phonons (at 152, 236, 263, 332, 370, 431 and 578 cm⁻¹), polarized along the X- or Y-axis [103]. The main changes introduced by the PE concern the intensity

(considerably reduced) of the main spectral lines, the appearance of new ones and the spectra intensity attenuation compared to those of the substrate. The strong attenuation occurs in samples with the maximal disorder degree [104]. The disorder in crystals causes violation of the selection rules which determine Raman scattering and can also activate new modes forbidden for the regular lattice. Moreover, as vibrations of the material with $k \neq 0$ can take part into the light scattering, the Raman bands are broadened.

The first attempt to study PELN by waveguide Raman spectroscopy has shown that the region $0-900 \text{ cm}^{-1}$ contains the most informative and strong Ra peaks [2, 105]. The PE introduces strong perturbations in the Ra spectrum: it contains narrow lines observed in the spectrum of the bulk but most of them are superimposed on much broader peaks (at about $155, 250, 350$ and 610 cm^{-1}). A new strong band appears at 69 cm^{-1} [2, 69] and another weak peak is observed at 660 cm^{-1} . It has been established that the integrated intensity of the band at 155 cm^{-1} does not change in the depth of the layer and could be used as a reference for the other bands [2].

For quantitative estimations, it is important to obtain Raman scattering by guided modes in order to be sure that the optical power is confined completely into the waveguide layer. When higher-order modes are excited, part of the optical field penetrates more or less into the unprotonated substrate and this should be taken into account.

2.6. Applications of Ra spectroscopy of PELN

2.6.1. Study of the structural changes and structural characterization of PELN waveguides

The micro-Raman scanning has shown that a layer of different structure exists at the very surface of PELN [105-110]. The peaks at 69 cm^{-1} and $600-700 \text{ cm}^{-1}$ are directly related to the formation of Nb-O-H groups into the Nb-O network [111]. These peaks become less pronounced with increasing mode number corresponding to decrease in proton concentration. The broad band at about 650 cm^{-1} appears in the spectrum of HNbO_3 which has centrosymmetric crystal lattice. That band should originate from a paraelectric-like phase [2, 106, 112-114]. Thus, in most cases Ra spectra or PELN represent a combined Ra scattering from coexisting

ferroelectric and paraelectric LN at room temperature with such a phase mixing possible by PE. A strong mixing of the two types of phonons has been observed in the case of highly protonated LN [108, 115, 116]. The calculation shows that most probably this is due to rotation of the optical axis of the exchanged layer resulting from the internal stress and strain, induced by the incorporation of protons.

The authors of [111] consider the Raman peaks appearing in the range of $100-300 \text{ cm}^{-1}$ for $x > 0.56$ as due to a breakdown of the symmetry of the bulk crystal and appearance of new crystalline phases. E(TO) and A1(TO) modes at 580 and 630 cm^{-1} exhibit an intensity transfer indicating that there is a coupling between the two modes arising from the existence of ferroelectric and paraelectric phases in the protonated sample at room temperature [117-119]. The changes of E(TO) Ra spectra originate from the internal strains in the sample as a result of order-disorder distribution of protons, whereas the changes of A1(TO) Ra spectra are due to the displacement of the positive and negative ions. This suggests a strong distortion of the niobium octahedra towards non-polar states and is characteristic for the paraelectric phase of LiNbO_3 [118].

The similarity between Ra spectra of PELN and that of paraelectric LN supports the suggestion that the PE relaxes the distortion of the Nb ions from the centers of the oxygen octahedra [119]. An estimation of structural disorder in waveguides has been made in [96]. Raman scattering confirms the results of IR spectroscopy concerning the structural changes in PE layers: the replacing protons do not occupy exactly the Li^+ positions which causes some lattice deformation [120].

2.6.2. Evaluation of the proton concentration

The estimation of the exchange rate x has been performed by using the intensity of the 650 cm^{-1} peak [121] as well as of the 69 cm^{-1} and the 151 cm^{-1} ones [69, 122]. The most convenient way to determine the exchange ratio $x/1-x$ is to equal it to the ratio of ferroelectric and paraelectric components after deconvolution of the spectrum [82].

2.6.3. Monitoring of the distribution of proton concentration in the depth of the PE layer

The change in proton concentration in the depth of the PELN-layer has been monitored by

micro-Raman profiling [106]. The results described show that a layer of lower OH concentration closest to the surface is present in as-exchanged PELN-waveguides obtained in melt of strong acidity (e.g. pyrophosphoric acid). This layer disappears upon annealing.

2.6.4. Study of non-linear optical properties of PELN

A correlation between the changes in Ra modes and changes in non-linear optical properties has been established. The bands of highest importance for the estimation of the electro-optical properties of LN are those at 254 and 630 cm⁻¹ (A1(TO)-phonons). The decrease of their intensities after PE serves as an indication of loss of non-linear optical properties [27, 106, 123].

2.6.5. Study of Ra intensity kinetics of photorefractive PELN

The LN crystal doped with Cu after PE [90] has been studied by analysis of photoinduced light scattering. The results show an exponential-like decrease in the intensity of the Ra spectrum in the Stokes region with the exposure time due to photorefractive. A shifting of the Stokes region by 152 cm⁻¹ depending on Cu diffusion duration is also observed.

2.6.6. Monitoring of the PE process

The Ra spectra of waveguides obtained at different acidity of the proton source [124, 125] and different durations of PE [104, 116, 126] has been recorded. The intensities of A1(TO) modes at 254 and 632 cm⁻¹ as well as of E(TO) modes at 152 and 236 cm⁻¹ vs. PE time have been studied, showing very strong attenuation with PE duration [115]. An increase of E(TO) mode intensities with PE duration has been observed in [116], which the authors attribute to the internal strains resulting from the order-disorder distribution of protons in the as-exchanged layers which causes the displacements of positive and negative ions. Observations on the E(TO)/A1(TO) intensity ratio vs. PE duration show maxima and minima [120]. The authors of [104] observe anomalous intensity attenuation of Ra scattering after longer proton diffusion durations and attribute this anomalous attenuation to phonon localization-related effects, resulting from the strongly disordered distribution of protons in the highly protonated samples.

The influence of the proton source acidity on the structure of PELN waveguides has been studied

by the change of intensity of the band at 650 cm⁻¹ [29, 124, 125]. The effect of proton source dilution on the phase composition has been studied in [29]. No substantial effect of acid dilution on Ra scattering has been observed.

2.6.7. Estimation of change in spontaneous polarization (ΔP_s) caused by the PE

The PELN-waveguides demonstrate a drastic decrease of the spontaneous polarization [97]. The attenuation of the intensity of the LO-phonon band at 870 cm⁻¹ could serve as an indicator for decrease of the spontaneous polarization [97]. The Ra spectra analysis have shown that ΔP_s in PELN is much larger than in PELT since PELT has less lattice distortion. That is the main reason for the higher index change in PELN than in PELT [120].

2.6.8. Phase identification and phase composition analysis

The most notable changes after PE are observed in band intensities in the 200-500 cm⁻¹ region. They show a bulk spectra intensity attenuation and, most importantly, an appearance of a broad band in the 520-750 cm⁻¹ range [118] peaking at 630 cm⁻¹ (E(TO)-mode) and at 690 cm⁻¹ (A1(TO)-mode). This new band could be due to a second-order Raman scattering which is a combined Ra scattering from coexisting ferroelectric (α) and paraelectric (β_i , $i = 1-3$) LiNbO₃. That way the Ra spectra give some evidence of the presence of α -phase in the PE layer as the IR absorption spectra do. Since the relative intensity of this band is not high, it could be concluded that the paraelectric layer is thin and is present at the top of the waveguide layer. As it is known, in a strained crystal some coupling between E(TO) and A1(TO) modes is possible. Thus, the presence of such large band is an evidence of the existence of phases having the highest value of x as β_4 for Z-cut samples, β_3 for X-cut or β_1 for Y-cut samples [58, 60, 73]. The set of narrow peaks in the Ra spectrum and the new one which appears at 69 cm⁻¹ also indicate high value of x and the presence of β_i phases ($i = 1-3$) [118].

Micro-Raman depth profiling [63, 106] allows the spectra of phase sublayers to be distinguished as attributed to α , β_1 , and κ_1/κ_2 , the latter being spectroscopically indistinguishable.

The presence and absence of some Raman lines at 127, 194 and 214 cm⁻¹ and the intensity dependence

of the proton-induced phonon band at 69 cm^{-1} have enabled the degree of $\text{Li}^+\text{-H}^+$ substitution in the PE layers to be determined. The results indicate that the phase diagram presented for proton-exchanged powders may also be applicable [119] at least for Z-cut PELN waveguides. Monitoring of the formation of various phases is also performed in [96, 127].

2.6.9. Study of the structural changes caused by post-exchange annealing

Raman scattering has been used to determine the kinetics of phase transitions in proton-exchanged LN waveguide layers subjected to thermal treatment [119]. The results concern intermediate phase states including the β_1 - and the $(\alpha + \beta_1)$ -phases, as well as room-temperature equilibrium and quenched states in the high H^+ concentration phases. It has been shown that annealing leads to either evolution within a given phase or appearance of phase transition [119].

The micro-Raman profiling of the PE layer provides information about structural changes caused by PE and annealing as a function of the depth [106, 107]. The effect of cooling rate on the phase formation is studied in [124, 128] and shows that the metastable phase (β_1) is obtained at quick cooling to room temperature after PE is performed, and the equilibrium β_2/β_1 combination is present in the slow-cooled samples. A definite crystal transformation was observed between the β_i ($i = 2, 3, 4$) and the β_1 phases [129].

It has been established by micro-Raman profiling that the SPE process causes less degree of structural disorder and better quality of the waveguides than APE [97].

3. Vibration spectroscopy of proton-exchanged lithium tantalate

3.1. Infrared absorption spectroscopy of PELT

In general, the vibrational spectroscopic behavior of pure and proton-exchanged LN is very similar to that of the pure and proton-exchanged LT. A systematic study of PELT waveguides obtained in melts of different acidity [129-132] has shown that the IR spectra, as in the case of PELT, consist of a sharp polarized band at about 3500 cm^{-1} and a wide depolarized shoulder peaking at about 3240 cm^{-1} .

3.2. Applications of the IR absorption spectroscopy of PELT

3.2.1. Determining the crystal substrate stoichiometry

The stoichiometry of the unprotonated LT has been obtained by following up the positions and intensities (which depend on Li/Ta ratio) of the IR absorption spectrum after deconvolution [133].

3.2.2. Structural study

IR absorption spectra are used for determination of the OH bond orientation in the proton-exchanged layer (in or out of the oxygen planes) and therefore, of the diffused proton sites and lattice deformations introduced by the PE. The polarization study shows that, as in the case of H:LiNbO_3 , the main narrow band (at about 3500 cm^{-1}) lies in the oxygen planes perpendicular to the optical axis (Z) while the OH bonds corresponding to the wide band (at about 3240 cm^{-1}) are distributed both in and out of this planes (hydrogen-bonded OH) [133, 134]. The unpolarized band indicates the presence of hydrogen in interstitial positions out of the oxygen planes, which usually means a higher level of doping. The IR spectra of waveguides obtained at a low level of doping do not contain the band at 3240 cm^{-1} . A possible reason for that band is that higher proton concentrations cause a displacement of Ta ions from their equilibrium positions, which permits incorporation of interstitial protons [131]. It has been established that the absorption band centered at 3240 cm^{-1} is due to a very thin surface layer while the 3500 cm^{-1} band is related to the proton-exchanged layer extending much deeper in the crystal [129, 132]. The thickness of the surface layer ($0.1 \div 0.2\ \mu\text{m}$) which contains interstitial hydrogen is determined by stepwise polishing of the surface and following up the decrease of shoulder intensity after each step [132].

3.2.3. Monitoring the exchange process

The monitoring has been performed by following up the changes in the two bands after annealing [129, 134, 135-137] or on varying the PE conditions (melt acidity, temperature and duration) [18, 134]. It has been established [19] that when the PE is performed in a slightly acidic melt, the absorption by OH groups around 3240 cm^{-1} and 3480 cm^{-1} increases with doping time and both peaks show linear increase with the square root of the exchange time,

demonstrating a behavior characteristic for diffusion processes [132, 138, 139].

The infrared intensity at 3500 cm⁻¹ has been used as a criterion for the existence of PE [140] when, for example, more than one diffusion/exchange process takes place in obtaining the waveguide layer [141]. Comparison of different proton sources and technological conditions is performed in [62, 142]. It has been shown that the addition of Cu₂O to the benzoic acid melt acts in a similar way as lithium benzoate does [142].

The band at 3240 cm⁻¹ completely disappears after annealing while the intensity of the polarized one increases [139]. This suggests that the hydrogen from hydrogen-bonded OH groups diffuses into the more slightly protonated regions and forms OH groups oriented in the oxygen planes [121, 135].

3.2.4. Study of the anomalous increase in refractive index

A remarkably stronger band at 3500 cm⁻¹ and a quenched band at 3240 cm⁻¹ have been observed after annealing [87, 130, 135-137] which indicates that a larger number of protons contribute to refractive index increase, in spite of the decrease in the proton concentration. This has led to a very important conclusion: the refractive index increase in general is not proportional to the proton concentration [137]. As it is explained by the phase model, the proportionality is valid only in the concentration range of each separate phase building the PE layer.

Since the displacement of protons results in a change of polarization, the refractive index should be affected towards increase at the early stage of annealing when movement of protons to the stable positions in a unit cell takes place [136, 137]. Further annealing has relaxed the polarized peak and the refractive index changes back to its initial (prior annealing) value [137, 138]. The latter has been suggested to be due to structural changes in the lattice altering the OH oscillator strength [138].

3.2.5. Study of the dynamics of more complicated exchange processes

IR spectra allow three stages of the PE to be distinguished when simultaneous two-step PE is performed [135]. It has been established, for example, that when non-isovalent ion exchange is performed simultaneously with PE, increased duration of the

process makes Ni²⁺/Zn²⁺ ions preferably replace protons occupying Li⁺ sites (as a result of the PE) rather than Li⁺ ions themselves.

3.2.6. Study of the combined libration-vibration OH (OD) bands of PELT

These modes are shifted from the stretching vibration near 3500 cm⁻¹ (OH) and 2600 cm⁻¹ (OD) by about 950 cm⁻¹ for H⁺ and about 700 cm⁻¹ for D⁺ exchanged samples towards higher frequency. The intensity of these combined bands is proportional to the H⁺/D⁺ concentration, the polarization being both perpendicular and parallel to the optical axis reflecting the properties of the three-dimensional oscillator [34].

3.2.7. Detection and study of different phases existing in Li_{1-x}H_xTaO₃ and phase transitions between them

Quantitative descriptions of IR spectra of different phases which are present in PELT are shown in [68, 143]. The IR spectra measurements have been used for characterization of a high-temperature phase frozen by quick cooling from melt to room temperature and the process of its relaxation was observed as a quenching of the OH absorption band [144]. The formation of high-temperature phases, metastable at room temperature, has also been observed by IR absorption spectroscopy [67, 144-146].

The main peak shape and frequency allow estimation of the phase composition of the PE layer [147]. A spectra deconvolution, when the phase composition is known, allows the components to be attributed to the different phases [62, 64, 138, 148]. Thus, the phase composition analysis of waveguides obtained by using different sources of protons (melts or vapors of different acidic compounds) or by modifying the PE technological conditions could be performed [62, 99, 148, 149]. Investigations supporting the phase model in single PELT crystal have also been performed in [19]. The disappearance of the 3240 cm⁻¹ peak (attributed to monoclinic Li_{1-x}H_xTaO₃) under annealing suggests that a phase transformation from monoclinic to rhombohedral Li_{1-x}H_xTaO₃ takes place [137].

3.2.8. Evaluation of the hydrogen content in waveguides

The IR absorption spectra have been used for evaluation of the hydrogen content in the PELT waveguides since the frequency and shape of the band at 3500 cm⁻¹ depend on x [134, 137, 138, 147].

3.2.9. Monitoring of PE and RPE in LT powders

IR transmission spectra have been used for monitoring the process of obtaining high-purity LT by RPE [50].

3.3. IR reflection spectroscopy

The main changes in the reflection spectra introduced by proton exchange in LiTaO_3 occur in the range of $850\text{-}1050\text{ cm}^{-1}$ and are most visible when the incident light is polarized parallel to the optical axis [94].

3.4. Applications of the IR reflection spectroscopy of PELT

3.4.1. Surface phase detection

It has been observed that each phase has its own characteristic IR reflection spectrum [62, 94, 98]. Correlations between the lattice deformations and the reflection minima have been made in order to assign the spectral changes to a definite phase. According to [94], for example, the changes observed at 899 , 952 and 985 cm^{-1} in the IR reflection spectra could be assigned to the β -phase, and the change at about 1000 cm^{-1} - to the δ -phase.

3.4.2. Determining the electro-optical coefficients

The electro-optical coefficients have been obtained on the basis of the existing correlations between vibration bands and electro-optical properties of PELT [94].

3.4.3. Phase model confirmation and determination of concentration boundaries of the phases

The IR reflection spectra of waveguides obtained at different conditions and thus having different phase composition have shown that the dependence of the OH libration mode on proton concentration is non-monotonous and demonstrates discontinuity at the phase boundaries [94].

3.4.4. Study of structural changes

The β and κ phases cause a high degree of disorder manifested in noticeable attenuation of the maximum reflectivity in the IR spectra [94].

3.5. Raman spectroscopy

The Ra spectrum of PELT consists of A1(TO) bands at 190 , 356 , and 596 cm^{-1} and E(TO) bands at 144 , 208 , 316 , 382 , 460 and 656 cm^{-1} [118].

3.6. Applications of Raman spectroscopy of PELT

3.6.1. Observation of the structural changes in PELT and APELT waveguide layers

The paraelectric behavior at room temperature demonstrated by the Raman spectra can be explained by lowering of the Curie point after PE [150, 151]. The β and κ phases cause a high degree of disordering expressed in a strong broadening of Ra lines [95]. The existence of an energy transfer between A1(TO) and E(TO) modes (596 and 656 cm^{-1} ; 356 and 382 cm^{-1}) is explained as due to the coexistence of paraelectric and ferroelectric phases in the PE samples [113]. The appearance of the peak at 190 cm^{-1} is due to the PE and is caused by the internal strain introduced by it. The changes in the proton concentration reflect on the intensity of that peak. A considerable violation of the selection rules in the Ra spectra of PELT has been found [151].

3.6.2. Monitoring of the PE process

The Ra spectra of waveguides obtained at different durations of PE have been recorded in [104, 118, 126]. The intensities of the E(TO) modes at 144 and 208 cm^{-1} show very strong attenuation with PE duration due to phonon localization-related effects, resulting from the strongly disordered distribution of protons in the highly protonated samples. The A1(TO) modes exhibit a dependence on the PE process duration as well.

It has been shown that annealing leads to either evolution within a given phase or appearance of phase transition [151, 152]. Proton exchange causes intensity reduction of all bands and appearance of a new peak at 63 cm^{-1} which dominates in the spectrum of PE samples at high values of x together with a wide band at $600\text{-}700\text{ cm}^{-1}$ [151].

3.6.3. Estimating the change in spontaneous polarization (ΔP_s)

The reason for the index change after PE in LN and LT is the change in spontaneous polarization caused by the lattice deformations. The Ra spectra analysis shows that PELT has less lattice distortion than PELN suggesting lower index change [94, 118, 120].

3.6.4. Evaluation of the electro-optical coefficients of PELT

Each optical mode polarized along the Z-axis produces an individual contribution to the electro-optical

coefficient r_{33} , which is proportional to the product of the Ra-scattering efficiency and IR-oscillator strength. So, the data on phonon frequencies and Ra-scattering efficiencies could be used to estimate the electro-optical coefficients and spontaneous polarization in PELT samples [94].

3.6.5. Monitoring of the formation of various phases and analysis of the phase composition

A contribution to the phase model has been made by establishing the correlations between the Ra scattering of different phases and their refractive index change [94, 127, 150-153]. The micro-Raman depth profiling [151] has confirmed the substantial structural changes and the phase-sublayer structure.

3.6.6. Study of the kinetics of phase transitions in PELT

Phase transitions could take place when waveguide layers are subjected to thermal treatment. The effect of a post-exchange annealing on the Ra-spectrum of PELT has been studied in [152, 154].

3.6.7. Comparison between phonon properties of PELN and PELT

The difference of phonon properties and spectral behavior of these two materials suggests their microstructural difference [120].

4. Supplement

Several books and reviews on PE exist where the vibration spectra of LN and LT have been discussed [32, 149, 155, 156].

Many of the findings on OH spectra of PELN are summarized in the review [155].

A review of methods of studying optical waveguides in LN and LT including vibration spectroscopy is included in [157].

The spectroscopic properties (IR and Raman) of OH stretching vibrations in PELN and PELT are reviewed in [158].

The review does not include the PhD theses on the subject.

5. Conclusion

The above-covered studies on the vibration spectroscopy of PELN and PELT contribute to a better understanding of the mechanisms of the PE

process, the structure and properties of PE waveguides and further development of the technology for their production and application.

The review presented would support researchers working in the area of proton exchanged optical waveguides in their studies on material research and methods for characterization of PELN and PELT.

CONFLICT OF INTEREST STATEMENT

The author declares no conflict of interest.

ABBREVIATIONS

APE	–	annealed proton-exchanged
APELT	–	annealed proton-exchanged lithium tantalate
APELN	–	annealed proton-exchanged lithium niobate
DE	–	deuterium exchange
HTPE	–	high temperature proton exchange
IR	–	infrared
LN	–	lithium niobate
LT	–	lithium tantalate
PE	–	proton exchange/proton-exchanged
PELM	–	proton-exchanged lithium niobate/tantalate
PELN	–	proton-exchanged lithium niobate
PELT	–	proton-exchanged lithium tantalate
Ra	–	Raman
RPE	–	reversed proton exchange
SPE	–	soft proton exchange
TE	–	tritium exchange

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