

Article

Second-Order Raman Scattering in Ferroelectric Ceramic Solid Solutions $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$

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Abstract: In the second-order Raman spectra of ceramic solid solutions, $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ weak overtone bands of fully symmetric fundamental polar excitations were observed for the first time. The frequencies of the two bands exceeded the value of the overtone frequency corresponding to the fully symmetrical vibration $4A_1(z)$. The possibility of the existence of phonon bound states of the antipolar type in the vibrational spectrum of $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ ceramics is predicted.

Keywords: lithium niobate tantalate; Raman scattering; second order; biphonon; ferroelectric; ceramic solid solution



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1. Introduction

Lithium niobate (LiNbO_3) and tantalate (LiTaO_3) are among the most studied oxide compounds in modern materials science. This interest is due to the wide applications of these materials in functional electronics. The forms in which these materials are used in practice are different—single- or polycrystals, thin films, micro- and nanopowders, and ceramics. Moreover, they can have different chemical compositions—congruent or stoichiometric, and contain various dopants of metal ions. It is obvious that such a variety of forms and applications requires additional research to modify and optimize material properties.

$\text{LiNb}_{1-x}\text{Ta}_x\text{O}_3$ (LNT) solid solutions have recently been studied (see, for example, [1–3]), while they open up prospects for combining the advantages of both materials. In particular, the LNT can be expected to exhibit high piezoelectric coefficients (close to LiNbO_3) and the temperature stability of the LiTaO_3 properties. However, the growth of LNT single crystals is a difficult task due to deviation from stoichiometry inherent in LiNbO_3 and LiTaO_3 crystals, nonhomogeneous distribution of cations caused by fluctuations in the temperature fields in the crystal growth zone and differences in the melting temperatures of both components of the system.

In addition, a LNT complex compound is attractive for both practical applications and fundamental researches, for example, in determining dependence of the $\text{LiNb}_{1-x}\text{Ta}_x\text{O}_3$ structural characteristics on the composition.

The system of ferroelectric solid solutions $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ is a subject of intensive research by different methods because it may be the base of ceramic materials with ferroelectric, superionic, semiconductor properties and cross-effects. The components of the $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ system are phases of variable composition and are characterized by a strongly defective crystal structure of both the cationic and anionic sublattices. The structure of defects largely forms the physical (especially ferroelectric and nonlinear optical) characteristics of materials.

Raman spectroscopy plays a significant role in the study of crystalline systems with a disordered structure and the processes of disordering of their structural units. The Raman spectra are highly sensitive to changes in the interactions between the structural units of a

crystal and, consequently, to various rearrangements of the crystal structure, which occur, in particular, upon changes in its composition and temperature, as well as to anharmonicity effects. In this case, it is important to study simultaneously the Raman spectra of the first and second order, which are especially sensitive to various fine processes of disordering of the crystal structure.

The first-order Raman spectra of single crystals and ceramic solid solutions with the general formula $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ have been studied in a number of works [4–17]. In the article [4], the change in the local composition of the $\text{LiNb}_{1-x}\text{Ta}_x\text{O}_3$ single crystal was analyzed by the Raman spectroscopy. In articles [5–12], the Raman spectra of such crystals were analyzed at various values of the niobium concentration $x = 0\text{--}1$. The concentration dependences of the frequencies of the fundamental modes of $A_1(z)$ - and $E(x,y)$ -symmetries were studied. In [13,14], the temperature dependence of the Raman spectra of a $\text{LiTa}_{0.9}\text{Nb}_{0.1}\text{O}_3$ single crystal was studied. The presence of a second-order ferroelectric–paraelectric phase transition of the order–disorder type was established at temperatures above 900 K. In this case, a "relay" transfer of softness from the fundamental optical phonon of $A_1(z)$ symmetry to a non-fundamental vibration with a frequency of 120 cm^{-1} was observed. The article [15] is devoted to the numerical calculation from first principles (ab initio) of the frequencies of the fundamental modes of the $A_1(z)$ -symmetry of a $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ mixed crystal. The presence of a linear increase in the calculated values of frequencies during the transition from lithium tantalate to lithium niobate is shown. At the same time, the experimental data obtained in [12] reveal a weak nonlinear dependence of the frequencies in the Raman spectra of $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ as a function of x . The Raman spectra of $\text{LiNb}_{0.5}\text{Ta}_{0.5}\text{O}_3:x\text{Pr}$ nanocrystals embedded in a boron-based glass matrix are reported in [16]. An increase in the concentration x of praseodymium from 0 to 0.01 leads to an insignificant frequency shift of the two lines and the appearance of one new Raman line. A study of the concentration dependence of the Raman spectra of $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ nanocrystals 19–45 nm in size introduced into a boron-based glass matrix was performed in [17]. An increase in the niobium concentration led to a shift of some Raman lines to the high-frequency region. Thus, in papers [4–17], the Raman spectra of the first order ($0\text{--}1200\text{ cm}^{-1}$) of ceramic solid solutions of the $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ system were analyzed upon excitation (or relaxation) of single-particle states of polar modes.

In [18,19], the manifestation of overtone bands in the Raman spectra of diamond and $\text{LiNbO}_3\text{:Tb}$ crystals was reported for the first time in the spectral range $1300\text{--}2700\text{ cm}^{-1}$. In the second-order Raman spectra studied earlier in a number of crystals [20–23], pairs of phonons with oppositely directed quasi-momenta, corresponding to the boundary or inner region of the Brillouin zone, appeared. Previously, in the second-order Raman spectra of a number of crystals, manifestations of phonon pairs were detected, which were interpreted as anomalies in the density of bound and free two-phonon states.

In this paper, we set the task of studying the full Raman spectrum of polar modes in $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ ceramic solid solutions excited in the backscattering geometry in a wide spectral region, including both the range of fundamental vibrations ($150\text{--}1000\text{ cm}^{-1}$) and the region of the second-order spectrum ($100\text{--}150$ and $1000\text{--}2000\text{ cm}^{-1}$).

2. Materials and Methods

Samples of $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ ceramic solid solutions in the form of pellets up to 10 mm in diameter and 1 mm thick were prepared by standard ceramic technology by high-temperature solid-phase synthesis [12], Figure 1. Table 1 shows the structural characteristics of the crystal lattices of the samples under study.

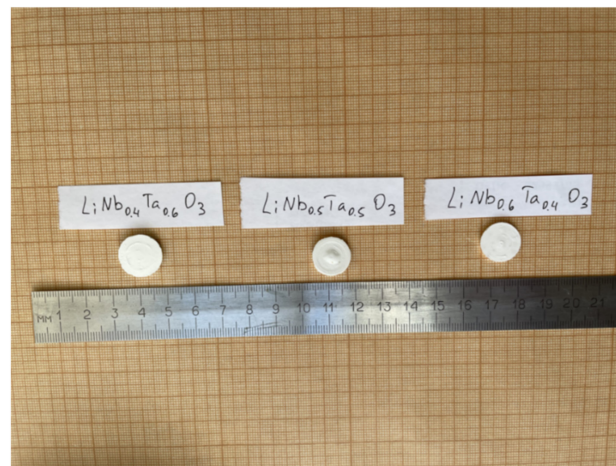


Figure 1. Picture of studied samples.

Table 1. Structural characteristics of the crystal lattices of the studied ceramic solid solutions [8].

Sample	a, Å	c, Å
LiNb _{0.4} Ta _{0.6} O ₃	5.21	13.98
LiNb _{0.5} Ta _{0.5} O ₃	5.15	13.8
LiNb _{0.6} Ta _{0.4} O ₃	5.22	14.04

The setup for recording of Raman spectra at room temperature using a backscattering geometry with BWS465-785H spectrometer was presented in [18,19]. Raman spectra were excited by 785 nm cw semiconductor laser with a 200 mW power. Laser radiation was delivered to the sample surface using one of the channels of a two-wire optical fiber, and the Raman signal was delivered through the second channel to a selective light filter and then to the input of the spectrometer. We used a BWS465-785H spectrometer with a detection range of 50–2850 cm^{-1} .

3. Results and Discussion

Figure 2 shows the Raman spectrum of the LiNb_{0.99}Ta_{0.01}O₃ ceramic solid solution in the frequency range 50–2000 cm^{-1} recorded in the backscattering geometry.

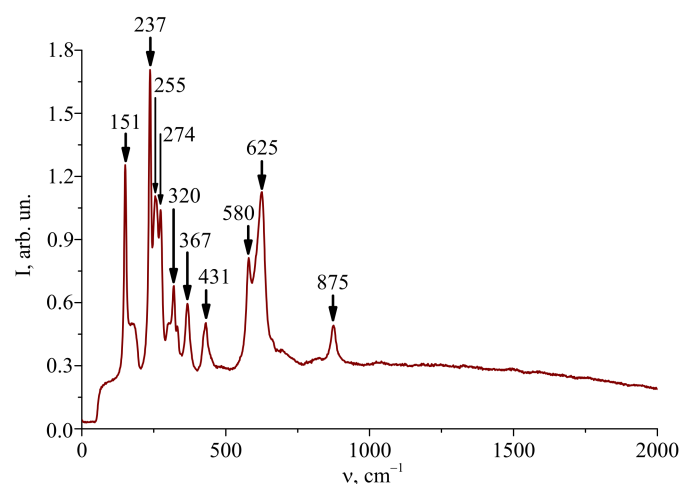


Figure 2. Raman spectrum of the LiNb_{0.99}Ta_{0.01}O₃ ceramic solid solution for the backscattering geometry.

As can be seen from Figure 2, the presented Raman spectrum of a ceramic solid solution with a small addition of Ta contains mainly fundamental modes corresponding to

first-order Raman processes [24–27] in the range of 50–1000 cm^{-1} . It should be noted that in the presented Raman spectrum, as well as in the spectra of a nominally pure stoichiometric or congruent LiNbO_3 crystal [12,24–29], there are no second-order bands in the region above 1000 cm^{-1} .

Figure 3a–c shows the recorded Raman spectra of the three studied samples $\text{LiNb}_{0.4}\text{Ta}_{0.6}\text{O}_3$, $\text{LiNb}_{0.5}\text{Ta}_{0.5}\text{O}_3$ and $\text{LiNb}_{0.6}\text{Ta}_{0.4}\text{O}_3$ obtained at two different points of each sample in the backscattering geometry. In these figures, curves (1) and (2) correspond to different points of the studied samples.

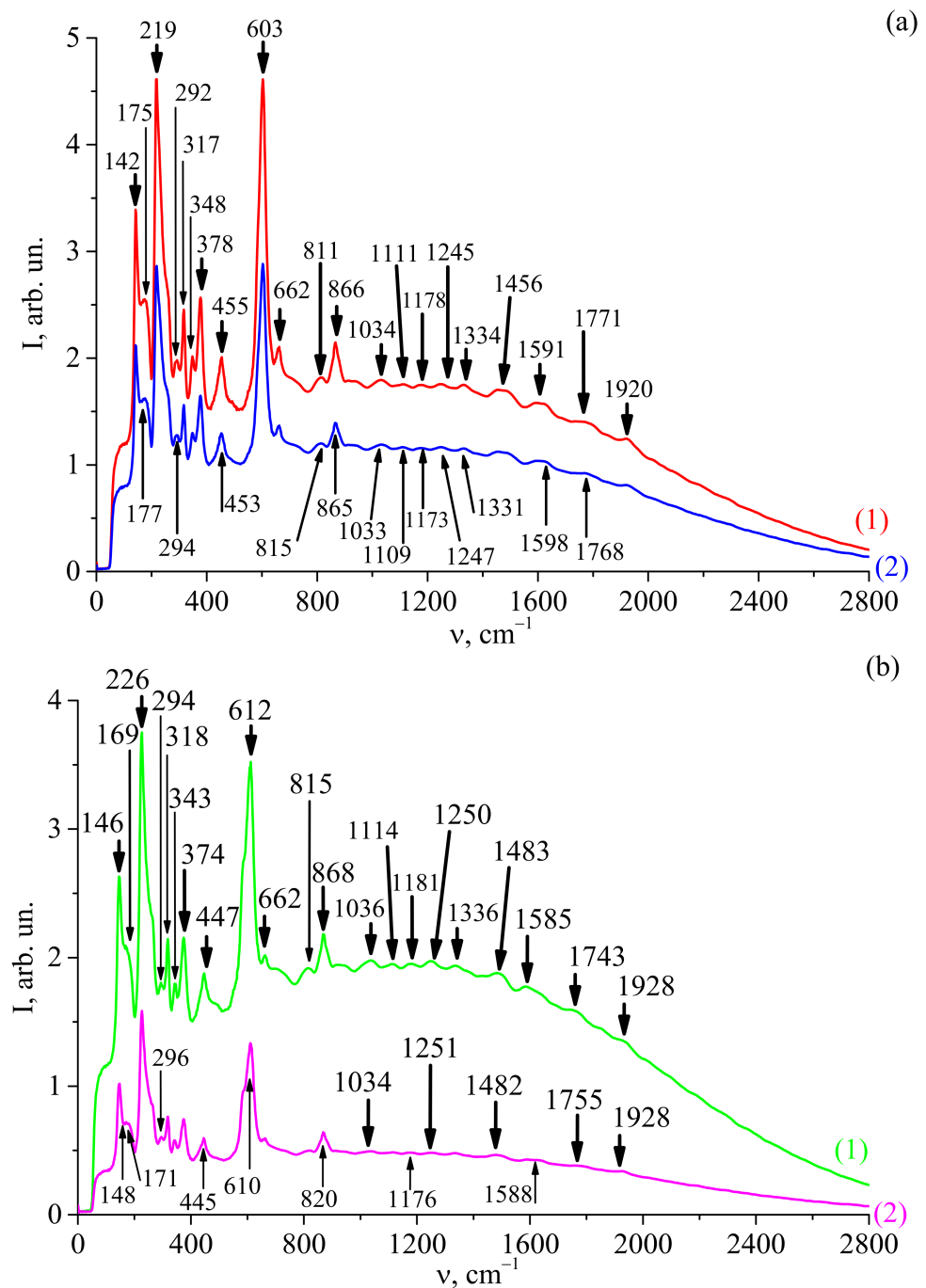


Figure 3. Cont.

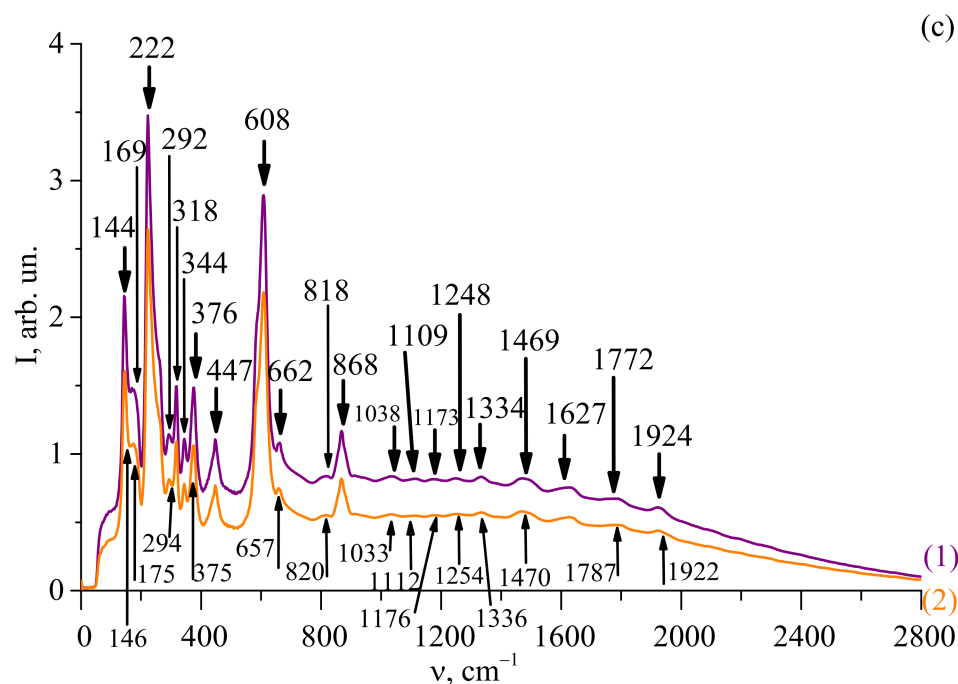


Figure 3. Raman spectra at the backscattering geometry in the region of fundamental and overtone vibrations of $\text{LiNb}_{0.4}\text{Ta}_{0.6}\text{O}_3$ (a), $\text{LiNb}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (b) and $\text{LiNb}_{0.6}\text{Ta}_{0.4}\text{O}_3$ (c) ceramic samples. Curves (1) and (2) correspond to two different points of the corresponding sample.

As can be seen from Figure 3, in the region of the Raman spectra ($100\text{--}1000\text{ cm}^{-1}$), where fundamental vibrations of the crystal lattice are manifested, a number of lines of different intensity are observed. It can be seen from this figure that in the Raman spectra of ceramic solid solutions $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ at approximately the same concentration of Nb and Ta ($x \approx 0.5$) in the overtone region of the Raman spectra ($1000\text{--}2000\text{ cm}^{-1}$) several second-order bands are present. The frequencies of the two bands are significantly higher than the value of the overtone (1736 cm^{-1}) corresponding to the fully symmetrical vibration of 868 cm^{-1} . In this case, the relative intensity of the two highest frequency bands (in the region of $1700\text{--}2000\text{ cm}^{-1}$) is the lowest for the $\text{LiNb}_{0.5}\text{Ta}_{0.5}\text{O}_3$ sample (Figure 3b). It should be noted that exactly in this concentration range ($0.2 < y < 0.8$), according to the data of [12], a strong disordering of the solid solution structure (maximum at $y \approx 0.5$) and a nonlinear dependence of the main characteristics (frequency, width, intensity and shape parameter) of the spectral lines takes place. The observed nonlinearity in the behavior of the main parameters of the spectral lines allows us to conclude that the transformation of the structure of LiNbO_3 ceramics into the structure of LiTaO_3 ceramics in the system of solid solutions $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ with decreasing x occurs continuously through the region of increased structural disorder ($0.2 < y < 0.8$) with the maximum value of the unit cell deformation at $y \approx 0.5$. No structural phase transition is observed in this case.

Table 2 shows the assignment of the Raman lines recorded in this work by symmetry types based on polarization measurements [7,28–32] performed for single-crystal samples.

Table 2. Frequencies of polar modes of LNT ceramic solid solutions registered in this work and their assignment taking into account the results of [7,28–32].

ν, cm^{-1}			Assignment
$\text{LiNb}_{0.4}\text{Ta}_{0.6}\text{O}_3$	$\text{LiNb}_{0.5}\text{Ta}_{0.5}\text{O}_3$	$\text{LiNb}_{0.6}\text{Ta}_{0.4}\text{O}_3$	
142	146 (148)	144 (146)	$1E(x,y)$
175 (177)	169 (171)	169 (175)	$2E(x,y)$ [28–31]
219	226	222	$1A_1(z)$

Table 2. Cont.

ν, cm^{-1}			Assignment
$\text{LiNb}_{0.4}\text{Ta}_{0.6}\text{O}_3$	$\text{LiNb}_{0.5}\text{Ta}_{0.5}\text{O}_3$	$\text{LiNb}_{0.6}\text{Ta}_{0.4}\text{O}_3$	
292 (294)	294 (296)	292 (294)	3E(x,y)
317	318	318	4E(x,y)
348	343	344	2A ₁ (z); 3A ₁ (z)
378	374	375 (376)	6E(x,y)
453 (455)	445 (447)	447	7E(x,y)
603	610 (612)	608	4A ₁ (z)
662	662	657 (662)	8E(x,y); 9E(x,y)
811 (815)	815 (820)	818 (820)	Li ₃ NbO ₄ phase [32]
865 (866)	868	868	4A ₁ (z)

As can be seen from this table, the assignment was not performed for all registered first-order Raman lines. In particular, in one of the first works on Raman scattering in a single-domain lithium niobate crystal, the 175 cm^{-1} line was assigned to the mixed mode [27]. Moreover, in [28,29], this line refers to the fundamental 2E(x,y) mode of stoichiometric lithium niobate. In [30], this line is also assigned to the fundamental 2E(x,y) mode based on theoretical calculations and experimental results [31] for stoichiometric $^7\text{LiNbO}_3$ and $^6\text{LiNbO}_3$ single crystals. The lines near 820 cm^{-1} , which appear in the region of oxygen carcass vibrations, apparently correspond to the Li₃NbO₄ phase. Such a phase can manifest itself due to the decomposition of a phase with a variable composition of lithium metaniobate [32].

Figure 4 shows the concentration dependences of the observed second-order Raman lines of LNT ceramic solid solutions. As can be seen from this figure, the change in the frequencies of the second-order Raman lines has a multidirectional character.

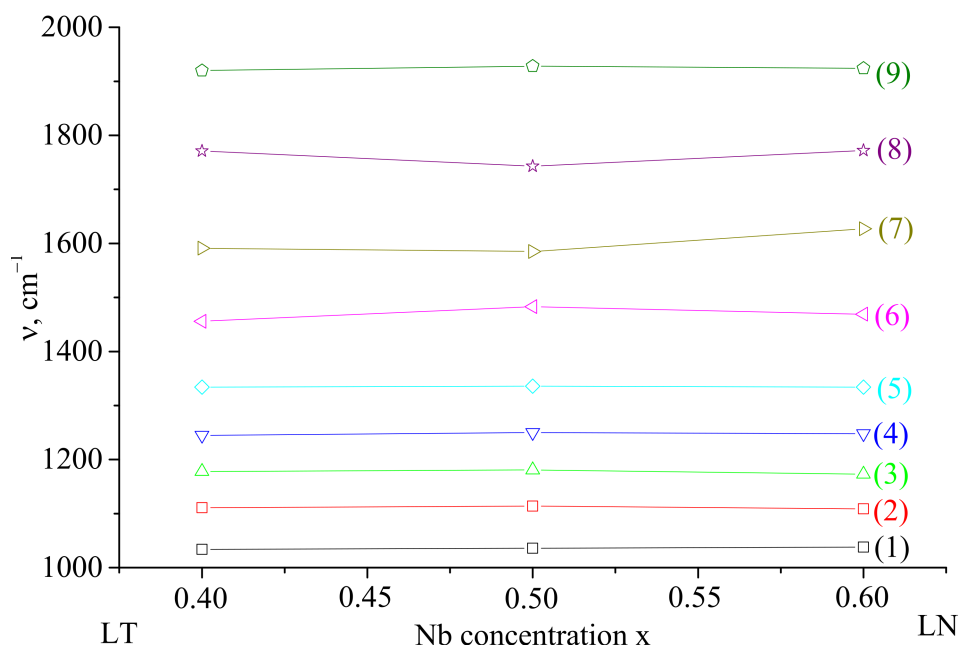


Figure 4. Dependence of second-order Raman lines frequency on the composition of LNT ceramic solid solutions. Lines (1–9) correspond to the frequencies of Raman lines marked in Figure 3a–c in the region of $1000\text{--}2000 \text{ cm}^{-1}$: (1)–1034, (2)–1111, (3)–1178, (4)–1245, (5)–1334, (6)–1456, (7)–1591, (8)–1771 and (9)–1920 cm^{-1} .

The scheme for the formation of bound states of phonons in crystals was considered in theoretical works [18,19,33–35]. In accordance with these works, the density of two-

phonon states $\rho_2(\omega)$ is calculated using one-phonon Green's functions $D_1(k, \omega)$ according to Formulas (1)–(5):

$$D_1(\vec{k}, \omega) = \frac{\omega(\vec{k})}{2} \left[\frac{1}{\omega - \omega(\vec{k}) + \frac{1}{2}i\Gamma} - \frac{1}{\omega + \omega(\vec{k}) - \frac{1}{2}i\Gamma} \right] \quad (1)$$

$$F(\omega) = \frac{i}{(2\pi)^4} \int d^3\vec{k} \int D_1(\vec{k}, \omega - \omega_1) D_1(-\vec{k}, \omega_1) d\omega_1. \quad (2)$$

Here, $\vec{k}$ -phonon wave vector, ω -frequency in rad/s, $\omega(\vec{k})$ -dispersion dependence of the optical phonon frequency on the wave vector, i -imaginary unit, Γ -phonon damping constant and ω_1 is the integration variable.

The density of single-phonon states $\rho_1(\omega_1)$ in the parabolic approximation of the optical phonon dispersion law near the center of the Brillouin zone $\omega \approx \omega_0$ has the form:

$$\rho_1(\omega_1) = b\sqrt{\omega_0 - \omega_1} \quad (3)$$

In this expression, the frequencies ω_1 of phonons of the optical branch of the $4A_1(z)$ -phonon can take values from $\omega_1 = \omega_0 - \Delta$ to $\omega_1 = \omega_0$; b is normalizations coefficient and Δ is the integration range of ω_1 taken into account in Equation (2). For the function $F(\omega)$, we get:

$$F(\omega) = \frac{1}{4}\omega_0^2 b \int_0^\Delta \frac{\sqrt{x}}{\omega - 2(\omega_0 - x) + i\Gamma} dx \quad (4)$$

The second-order Raman intensity is proportional to the density of two-phonon states $\rho_2(\omega)$:

$$\rho_2(\omega) = -\frac{1}{\pi\omega_0^2} \text{Im} \left[\frac{2F(\omega)}{1 - \Lambda_4 F(\omega)} \right] \quad (5)$$

here Λ_4 is the fourth-order anharmonicity parameter of the crystal lattice.

Let us introduce a dimensionless variable u :

$$u = (\omega_0 - \omega_1)/\omega_0 \quad (6)$$

For definiteness, we require the fulfillment of the normalization condition:

$$\int_0^d \rho_1(u) du = 1 \quad (7)$$

From here, taking into account (3), with the relative width of the integration range $d = \Delta/\omega_0$, we obtain

$$b = \frac{3}{2\sqrt{d^3}} \quad (8)$$

Let us introduce dimensionless function $f(\omega)$ taking into account (4, 6–8):

$$f(\omega) = b \int_0^d \frac{\sqrt{u}}{2u + a} du = \frac{3}{2\sqrt{d^3}} \left(\sqrt{d} - \sqrt{\frac{a}{2}} \arctg \sqrt{\frac{2d}{a}} \right) \quad (9)$$

here $a = (\omega - 2\omega_0 + i\Gamma)/\omega_0$, $\gamma = \Gamma/\omega_0$ -phonon damping coefficient. Accordingly, relation (5) up to a constant factor takes the form:

$$\rho_2(\omega) = -\text{Im} \left[\frac{2f(\omega)}{1 - \lambda_4 f(\omega)} \right] \quad (10)$$

where λ_4 is the dimensionless anharmonicity parameter.

Let us consider, for definiteness, the overtone state of the fully symmetric mode $4A_1(z)$ with the frequency $\nu_0 = 868 \text{ cm}^{-1}$ ($\omega_0 = 2\pi c\nu_0 = 1.64 \times 10^{14} \text{ rad/s}$). The results of a comparison between the calculated Raman spectrum in the overtone region $2\nu_0 = 1736 \text{ cm}^{-1}$ and the experimentally observed one for the $\text{LiNb}_{0.6}\text{Ta}_{0.4}\text{O}_3$ ceramic solid solution are shown in Figure 5. The choice of this sample is due to the highest observed relative intensity of the second-order Raman scattering. The dashed arrow in this figure indicates the exact position of the $2\nu_0$ overtone.

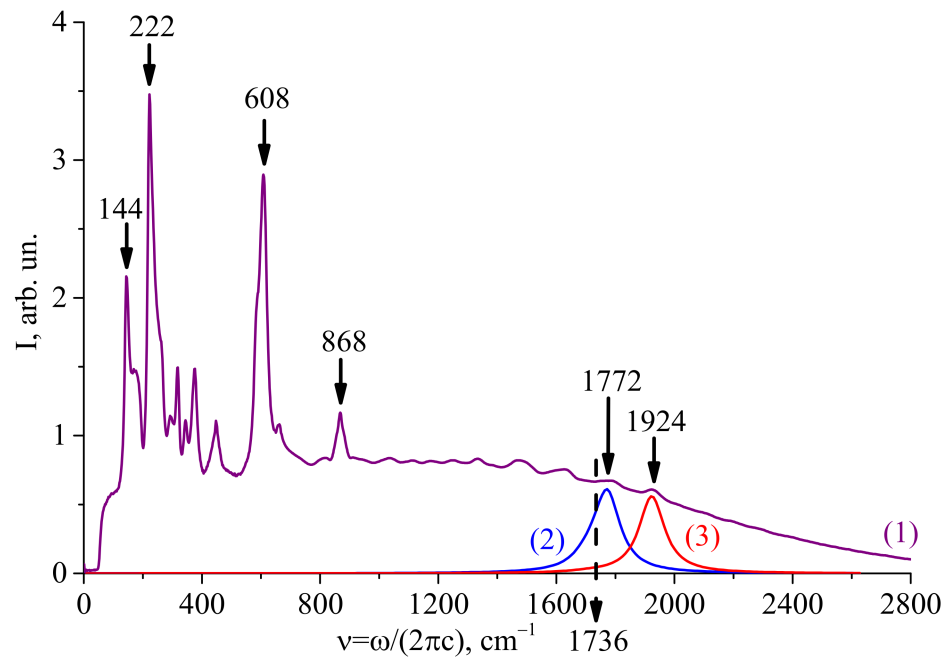


Figure 5. Comparison of the spectral Raman intensity of the $\text{LiNb}_{0.6}\text{Ta}_{0.4}\text{O}_3$ ceramic solid solution (curve 1) in the overtone region with the calculated $\rho_2(\nu)$ dependences (2) and (3).

We can see from this figure, that the band at 1772 cm^{-1} (curve 2 in Figure 5), is well approximated by the bound state of the polar mode $4A_1(z)$ at $\nu_0 = 868 \text{ cm}^{-1}$ with the following parameters: $d = 0.05$, $\gamma = 0.03$ and $\lambda_4 = 0.07$. For the 1924 cm^{-1} band (curve 3 in Figure 5), satisfactory agreement is achieved at $d = 0.05$, $\gamma = 0.03$ and $\lambda_4 = 0.25$. The integration region d in Formula (9) is chosen in accordance with the frequency range occupied by the $4A_1(z)$ branch on the phonon dispersion curve $\omega(k)$.

4. Conclusions

It was found for the first time that in the Raman spectra of ferroelectric ceramic solid solutions of lithium niobate-tantalate with different $[\text{Nb}]/[\text{Ta}]$ concentrations, there are second-order bands in the overtone region ($1000\text{--}2000 \text{ cm}^{-1}$) of fundamental polar modes, whereas the Raman spectrum of the $\text{LiNb}_{0.99}\text{Ta}_{0.01}\text{O}_3$ ceramic solid solution in the range of $1000\text{--}2000 \text{ cm}^{-1}$ contains only a weak continuous background for all recorded modes. We have found two bands with frequencies that exceed the exact value of the overtone ($868 \times 2 = 1736 \text{ cm}^{-1}$) of the $4A_1(z)$ mode. Theoretical modeling performed testifies that these bands are due to biphonons. Further studies of biphonons are of interest for establishing the conditions for the generation of entangled and bound states of two phonons in spontaneous and stimulated Raman scattering in ferroelectric and piezoelectric crystals and ceramics.

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Data Availability Statement: The raw data required to reproduce these findings are available from corresponding author N.S. on a reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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