

The impact of the simultaneous presence of Li and Nb(Ta) vacancies in the defect structure of pure LiBO_3 (B=Nb, Ta) on the curie temperature

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Abstract. The lithium niobate (LiNbO_3 , "LN") and lithium tantalate (LiTaO_3 , "LT") crystals are piezoelectric materials that exhibit intrinsic or extrinsic defect structures, which immediately impact their optical and electrical properties. In this study, we examine the influence of point defects on the Curie temperature (T_c) for different samples of pure LN and LT, using three vacancy models: the tantalum (niobium) vacancy model, the lithium vacancy model and the mixed lithium and tantalum (niobium) vacancy model. Based on the Safaryan approach, it was found that the calculated values for the tantalum (niobium) vacancy model did not agree with the experimental data. However, the lithium vacancy model and the mixed vacancy model showed good agreement between experimental and theoretical results. In conclusion, the proposed mixed vacancy model provides the best description of the defect structure in LN and LT materials, and the T_c is influenced by the structural defects present in the LN and LT compounds.

1 Introduction

Crystalline materials such as lithium niobate (LiNbO_3) and lithium tantalate (LiTaO_3) play a crucial role in numerous optoelectronic devices, including acousto-optic devices [1], optical modulators, and waveguides [2]. However, these materials are not free from defects, which can have significant consequences on their physical properties and performance. The intrinsic and extrinsic defects present in LiNbO_3 and LiTaO_3 [3, 4, 5] crystals play a crucial role in determining their optical, electrical, and mechanical characteristics.

Lithium niobate (LN) is a material that does not occur naturally and was first synthesized in Bell laboratories in 1949 [6]. The fabrication techniques for lithium niobate (LiNbO_3) and lithium tantalate (LiTaO_3) include the growth methods of flux melting and solution growth, as well as the Bridgman or Czochralski methods [7]. Additional techniques such as High Temperature Top Seeded Solid Solution Growth (HTTSSG) [8, 9] and Vapor Transport Equilibrium (VTE) [10] are also employed. These techniques allow to produce crystals of varying sizes and purities, as well as thin films on substrates. They are utilized to manufacture materials suitable for a range of optical, electronic, and optoelectronic applications.

The Curie temperature of stoichiometric lithium niobate is $T_C = 1200^\circ\text{C}$ [11], also known as the ferroelectric transition temperature, which is the temperature at which a ferroelectric material loses its spontaneous polarization. The T_C of these materials depends on several factors, such as the exact composition of the material, the presence of impurities, and the manufacturing process [12, 13].

The ferroelectric to paraelectric phase transition temperature (spontaneous polarization) of LiBO_3 occurs at different temperatures depending on the molar ratio $r = [\text{Li}]/[\text{B}]$ of the crystal. The Curie temperature T_c of LiBO_3 varies as a function of the lithium concentration (Li_2O) according to the following relationships:

For lithium niobate LiNbO_3 [14, 15]:

$$T_c = 9095.2 - 369.05C + 4.228C^2 \text{ (}^\circ\text{C)} \quad (1)$$

For lithium tantalate LiTaO_3 [16]:

$$T_c = 11310 - 492.73C + 5.6062C^2 \text{ (}^\circ\text{C)} \quad (2)$$

With C is the concentration of Li_2O in mol%, T_C of LiBO_3 changes as a function of the concentration of impurities at r constant.

Lithium niobate (LN) crystals typically have a congruent composition with a molar ratio of $\text{Li}_2\text{O}/\text{Nb}_2\text{O}_5$ equal to $r = 48.45/51.55$ [17], resulting in a lithium (Li_2O) deficiency. To understand the structure of intrinsic defects caused by this

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Li₂O deficit, several vacancy models have been proposed. Among them, the oxygen vacancy model was suggested by Fay et al. in 1968 [18] with the formula $[\text{Li}_{1-2x}\text{V}_{2x}][\text{Nb}][\text{O}_{3-x}\text{V}_x]$, where V represents vacant sites. The lithium vacancy model, proposed by Lerner et al. in 1968[19], is described by the formula $[\text{Li}_{1-5x}\text{Nb}_x\text{V}_{4x}][\text{Nb}][\text{O}_3]$. The niobium vacancy model, initially proposed by Peterson and Carneval in 1972 [20], is formulated as $[\text{Li}_{1-5x}\text{Nb}_{5x}][\text{Nb}_{1-4x}\text{V}_{4x}][\text{O}_3]$. This model was later adopted and supported by Abrahams and March in 1986[21].

In this article, we investigate a mixed vacancy model that incorporates both lithium and niobium (tantalum) vacancies, providing a better description of the structural defects in lithium tantalate (LT) and lithium niobate (LN) crystals.

2 Theoretical approach

In this section, we consider that our ceramic sample of LT and LN is formed by planes perpendicular to the (c) axis and composed of identical atoms (see Figure 1). The distances between the planes (Li, Ta or Nb, and O at T = 0 K) are as follows [22] for LT and [23] for LN

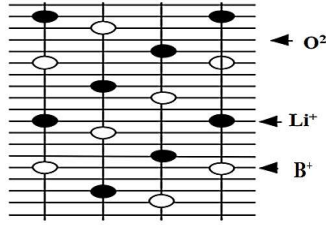


Fig. 1. Different planes in an elementary cell of crystal LiBO₃

In the LiTaO₃ structure, we have $R_{\text{Ta-O}} (R_{10}=0.954\text{\AA})$; $R_{\text{Li-Ti}} (R_{12}=0.745\text{\AA})$; $R_{\text{Li-O}} (R_{20}=0.601\text{\AA})$;

In the LiNbO₃ structure, we have $R_{\text{Nb-O}} (R_{10}=0.883\text{\AA})$; $R_{\text{Li-Nb}} (R_{12}=0.747\text{\AA})$; $R_{\text{Li-O}} (R_{20}=0.68\text{\AA})$;

The ferroelectric phase transition in LBO₃ (B = Nb or Ta) was theoretically investigated by Safaryan [24, 25]. He proposed that the phase transition occurs due to the freezing of one of the two optical mode vibrations on the parallel planes along the polar axis "c" (where the Li⁺, B⁵⁺, and O²⁻ ions are distributed). To calculate the frequencies of these vibrations, a system of differential equations was developed to describe the motion of these planes. In order to do so, it was necessary to initially determine the portion of the potential energy of interaction between the electrically charged planes that is responsible for the restoring force against the relative movement of the planes about their equilibrium positions. Initially, the energy of charged lines was calculated assuming a uniform and continuous distribution of charge along these lines. This result was then extended to the interacting planes. The energy of interaction between two electrically charged lines can be written as follows:

$$W_{ij} = \frac{-e^2 q_i q_j}{b} \ln \left(\frac{2l}{R_{ij}} \right) + \frac{B_{ij}}{R_{ij}^n} \quad (3)$$

Where b, l, R_{ij}, q_i, and $\frac{B_{ij}}{R_{ij}^n}$ are the cell parameter, line length, distance between lines, ion charge, and nonelectrostatic part of the interaction energy, respectively.

The coefficients C_{ij} for the LiBO₃ crystal are determined using the enhanced elastic constants, $C_{ij} = -\frac{e^2 q_i q_j}{b(R_{ij}^0)^2} n$, where R_{ij}⁰ represents the equilibrium distance between the planes.

$$C_{\text{Li-O}} = C_{2-0} = 3 \frac{e^2 q_i q_j}{b(R_{20}^0)^2} n \quad (4)$$

$$C_{\text{B-O}} = C_{1-0} = 3 \frac{e^2 q_i q_j}{b(R_{10}^0)^2} n \quad (5)$$

$$C_{\text{B-Li}} = C_{1-2} = -\frac{e^2 q_i q_j}{b(R_{12}^0)^2} n \quad (6)$$

Here, q₂, q₁, and q₀ represent the electric charges of Li⁺, B⁺, and O²⁻ ions, respectively. For interacting planes, the value of the constant n is attained at n ≈ 1. We reduced the structure of the charged planes to a system of vibrations of a linear lattice to solve the dynamic problem (Figurer 2). V_s(Li⁺), U_s (B⁵⁺), and ξ (3O²⁻). The system is then described by differential equations as follows:

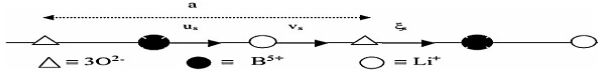


Fig. 2. Displacement of Li^+ , B^{5+} and 3O^{2-} ions in a linear lattice

$$\begin{aligned} M_1 \ddot{U}_s &= C_{12}(V_s - \mu_s) + C_{10}(\xi_{s-1} - \mu_s) \\ M_2 \ddot{V}_s &= C_{20}(\xi_s - \nu_s) + C_{12}(\mu_s - \nu_s) \\ M_0 \ddot{\xi}_s &= C_{20}(V_s - \xi_s) + C_{10}(\mu_{s+1} - \xi_s) \end{aligned} \quad (7)$$

M_1 , M_2 and M_0 are respectively the masses of atoms B, Li and 3O

The choice of solutions in the form of plane waves, $u_s = u e^{i\omega t} e^{i a s k}$ with $U_s = V_s, \mu_s$ ou ξ_s

And k its wave vector, which we choose equals 0.

After the calculation of the determinant ($\Delta = 0$), Then, we get the following equation:

$$\omega^4 - B\omega^2 + D = 0 \quad (8)$$

Where

$$B = C_{10} \left(\frac{1}{M_1} + \frac{1}{M_0} \right) - C_{12} \left(\frac{1}{M_1} + \frac{1}{M_2} \right) - C_{20} \left(\frac{1}{M_2} + \frac{1}{M_0} \right) \quad (9)$$

$$\text{And } D = (C_{10}C_{20} - C_{10}C_{12} - C_{12}C_{20}) \left(\frac{M_0 + M_1 + M_2}{M_0 M_1 M_2} \right)$$

The solutions of this equation correspond to the two optical modes given by:

$$\omega_{12}^2 = \frac{1}{2} B \pm \left(\frac{1}{4} B^2 - D \right)^{1/2}$$

For small parameter $\left(\frac{4D}{B^2} \ll 1 \right)$, we deduce

$$\omega_2^2 = \frac{D}{B} = \frac{n e^2}{b} \frac{M_0 + M_1 + M_2}{M_0 M_1 M_2} \frac{P_1}{P_2} \quad \text{and} \quad \omega_1^2 = B - \omega_2^2 \quad (10)$$

$$\text{Where } P_1 = 3q_0 R_{12}^2 - q_1 R_{20}^2 - q_2 R_{10}^2$$

$$\text{And } P_2 = \frac{(R_{10} R_{12})^2}{q_1} \left(\frac{1}{M_0} + \frac{1}{M_2} \right) + \frac{(R_{20} R_{12})^2}{q_2} \left(\frac{1}{M_1} + \frac{1}{M_0} \right) - \frac{(R_{10} R_{20})^2}{3q_0} \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \quad (11)$$

The Curie temperature of non-stoichiometric LT and LN is proportional to the Curie temperature T_C , as indicated by the following relationship

$$T_C^* = \frac{\omega_2^2}{\omega_2^2} = \frac{M_0^* + M_1^* + M_2^*}{M_0 + M_1 + M_2} \frac{M_0 M_1 M_2}{M_0^* M_1^* M_2^*} \frac{P_2 P_1^*}{P_1 P_2^*} \cdot T_C \quad (12)$$

The aforementioned relation enables the calculation of Curie temperatures for various vacancy models utilized in this study.

The expression of the quantities X and X^* depends on the composition of the LN (stoichiometric or non-stoichiometric compositions) and the chosen lacunar model.

The values of masses and charges used to calculate the Curie temperature of LiBO_3 are as follows:

$q_{(\text{Nb})} = q_{(\text{Ta})} = q_1 = 5$; $q_{(\text{Li})} = q_2 = 1$; $q_{(\text{O})} = q_0 = 2$; $M_{\text{Nb}} = M_1 = 92.9 \text{ a.u}$ (or $M_{\text{Ta}} = M_1 = 108.95 \text{ a.u}$) ; $M_{\text{Li}} = M_2 = 6.94$; $M_{\text{O}} = M_0 = 48$.

Table 1. The Curie temperature values (Tc) of LN calculated using the mixed vacancy model (a), the lithium vacancy model (b), and the niobium vacancy model (c) are compared to the experimental data from [15]

Composition x	Curie temperature Tc (K)			
	Measured	Model (a)	Model (b)	Model (c)
0.0013	1467	1470.7	1469.4	1376.6
0.0098	1418	1412.90	1404.1	889.4
0.0162	1376	1372.55	1359.1	639
0.0192	1358	1354.49	1338.2	546

Table 2. The Curie temperature values (Tc) of LT calculated using the mixed vacancy model (a), the lithium vacancy model (b), and the niobium vacancy model (c) are compared to the experimental data from [28]

Composition x	Curie temperature Tc (K)			
	Measured	Model (a)	Model (b)	Model (c)
0.0	917	919	919	919
0.004	906	885.77	882.8	704
0.008	861	855.05	849.6	565.4
0.020	783	775.31	764.4	326.9

To calculate the Curie temperatures mentioned in Tables 1 and 2, it is crucial to determine the Curie temperature of the exact stoichiometric compositions. We relied on the average temperature values obtained from the following references: For lithium niobate (LN), the estimated temperatures are 1475 K [26], 1479.5 K [27], and 1483.15 K [12]. Therefore, the average Curie temperature for LN is $T_{cmLN} = 1480$ K. For lithium tantalate (LT), the estimated temperatures are 917 K [28], 928 K [29], and 913 K [30]. The average Curie temperature for LT is $T_{cmLT} = 919$ K.

3 Models of intrinsic defects in LiBO3 (B = Ta or Nb) crystal

3.1 Previous models

Several models of intrinsic defects have been proposed in the literature to describe the congruent LiBO₃ crystal [31, 32]. Due to the close ionic radii of Li and B ions, the relative deficiency of Li in the lattice results in the displacement of B ions to Li sites (referred to as Nb antistes). Fay et al. introduced the first model, called the oxygen vacancy model, with the formula $[Li_{1-2x}□_{2x}][Nb][O_{3-x}□_x]$ [18], to describe these defects. They assumed that the ceramic sample of LiBO₃ consists of lithium and oxygen vacancies. However, this initial model was discarded as it proved incompatible with the measurement of LiNbO₃ density, which increases with increasing lithium deficiency.

Lerner and al. later proposed another model called the lithium vacancy model, with the chemical formula $[Li_{1-5x}Nb_xV_{4x}][Nb][O_3]$ [19]. Typically, congruent LiBO₃ samples exhibit a deficiency of lithium (Li₂O) to balance the charge difference resulting from Nb ions occupying Li sites. For each Nb_{Li} antisite, there are four lithium vacancies (□_{Li}). Several references have supported the idea that this model provides a better description of the intrinsic defect structure in LiBO₃.

Peterson and Carnevale proposed the defective structure model of niobium, with the formula $[Li_{1-5x}Nb_{5x}][Nb_{1-4x}V_{4x}][O_3]$ [20], to explain the defects in non-stoichiometric lithium niobate. This model was introduced in their scientific article published in 1972, where they employed electron paramagnetic resonance (EPR) spectroscopy techniques to investigate the defect structure of lithium niobate.

In their study, they observed an EPR signal associated with defects in non-stoichiometric lithium niobate. However, the intensity of this signal was much weaker than expected for the lithium defect model, which assumes that the defects are lithium vacancies.

Consequently, Peterson and Carnevale proposed a new model, known as the niobium vacancy model, suggesting that the defects are niobium vacancies. This model better explains the observed intensity of the EPR signal associated with defects in non-stoichiometric lithium niobate. The niobium vacancy model has received support from other scientific references, including Abrahams and Marsh in 1986 and Donnerberg et al. in 1989.

3.2 Our model

In the literature [33-25], it has been observed that pure LiNbO3 and LiTaO3 materials exhibit a coexistence of lithium (Li) and niobium (Nb) vacancies within their structures. This coexistence significantly affects the physical properties of the materials, particularly their electro-optical properties [34]. To provide a more comprehensive description of the defect structure in non-stoichiometric LT (LiTaO₃) and LN (LiNbO₃) crystals, we have proposed a mixed vacancy model for each crystal (model a) . In order to validate this model

and understand its impact on material properties, including the Curie temperature (T_c), we have conducted experimental studies and computer simulations of Tc. According to our model, there is a simultaneous appearance of lithium and niobium vacancies in the crystal structure as shown in Tables 1 and 2. These voids may be due to compositional imbalances, where there is an excess of lithium or niobium compared with the ideal stoichiometry.

Table 3. Chemical formula obtained by analysis [28] and proposed formula according to (a) models for different Li/Nb ratios

Specimen	Li/Nb	x	Experimental formulae analysed	Proposed formulae
ST	1	0	$LiNbO_3$	$LiNbO_3$
NST	0.992	0.0013	$Li_{0.994}Nb_{0.0013}\square_{0.004}O_3$	$[Li_{0.994}Nb_{0.0013}\square_{0.0054}][Nb_{1.0001}\square_{-0.00001}][O_3]$
CG	0.944	0.0094	$Li_{0.951}Nb_{0.0098}\square_{0.0039}O_3$	$[Li_{0.951}Nb_{0.009}\square_{0.038}][Nb_{1.0005}\square_{-0.0005}][O_3]$
MN	0.904	0.0162	$Li_{0.919}Nb_{0.0098}\square_{0.0039}O_3$	$[Li_{0.919}Nb_{0.015}\square_{0.066}][Nb_{1.001}\square_{-0.001}][O_3]$
HN	0.886	0.0194	$Li_{0.904}Nb_{0.0192}\square_{0.077}O_3$	$[Li_{0.903}Nb_{0.0184}\square_{0.0784}][Nb_{1.001}\square_{-0.001}][O_3]$

Subsequently, the proposed model for each crystal is

- The proposed model of $LiNbO_3$. Model (a)
$$[Li_{1-5x}Nb_{\frac{19}{20}x}\square_{\frac{81}{20}x}][Nb_{1+\frac{1}{20}x}\square_{-\frac{1}{20}x}][O_3]$$

- The proposed model of $LiTaO_3$. Model (a)
$$[Li_{1-5x}Ta_{\frac{4}{5}x}\square_{\frac{21}{5}x}][Ta_{1+\frac{1}{5}x}\square_{-\frac{1}{5}x}][O_3]$$

Table 4. Experimental chemical formulae [23] and proposed formula according to (a) models for different Li/Ta ratios

Li/Ta	x	Experimental formulae	Proposed formulae
1	0	$LiTaO_3$	$LiTaO_3$
0.976	0.004	$Li_{0.98}Ta_{1.004}O_3$	$[Li_{0.98}Ta_{0.0032}\square_{0.017}][Ta_{1.0008}\square_{-0.0008}][O_3]$
0.95	0.0084	$Li_{0.958}Ta_{1.008}O_3$	$[Li_{0.958}Ta_{0.007}\square_{0.035}][Ta_{1.002}\square_{-0.002}][O_3]$
0.88	0.0204	$Li_{0.90}Ta_{1.02}O_3$	$[Li_{0.90}Ta_{0.016}\square_{0.086}][Ta_{1.004}\square_{-0.004}][O_3]$

3.3 Analysis of Curie temperature in LiBO3 through Different Vacancy Models

The general formula for the vacancy modules of $LiBO_3$ is expressed by the following equation.

$$[Li_{\lambda_1}B_{\lambda_2}\square_{\lambda_3}][B_{\mu_1}\square_{\mu_2}][O_3]$$

The occupancy rates on the lithium site Li_{Li} , Nb_{Li}, and Li vacancies ($\square_{Li}$) are represented by λ_1 , λ_2 , and λ_3 respectively. Similarly, the occupancy rates on the niobium site Nb_{Nb} and Nb vacancies ($\square_{Nb}$) are represented by μ_1 and μ_2 .

The occupancy rates must satisfy the following conditions:

$$\lambda_1 + \lambda_2 + \lambda_3 = 1$$

$$\mu_1 + \mu_2 = 1$$

The electronic neutrality of charges requires that $\lambda_1 + 5\lambda_2 + 5\mu_1 = 6$

Using the vacancy models (a), (b) and (c), we determined the expression for the Curie temperature as a function of the composition x of $LiBO_3$. Substituting the values of the masses and charges in the non-stoichiometric state with $M_1^* = \mu_1 M_1$, $M_2^* = \lambda_1 M_2 + \lambda_2 M_1$, $M_0^* = M_0$ and $q_1^* = \mu_1 q_1$, $q_2^* = \lambda_1 q_2 + \lambda_2 q_1$, $q_0^* = q_0$ respectively into the previously mentioned Curie temperature expression (equation 1), we obtain the following expressions.

- For tantalum or Niobium vacancy model (c) $[Li_{1-5x}B_{5x}][B_{1-4x}\square_{4x}][O_3]$

In this case
$$T_{C,LT}^* = \frac{(1-17.88)(1+1.62x)(1+20x)}{(1+78.01)}T_{c,mLT} \quad (19) \text{ and } T_{C,LN}^* = \frac{(1-24.75)(1+0.39x)(1+20x)}{(1+52.37x)}T_{c,mLN} \quad (20)$$

- For Lithium vacancy model (b) $[Li_{1-5x}B_x\square_{4x}][B][O_3]$

In this case
$$T_{C,LN}^* = \frac{(1+0.62x)}{(1+10.86x)}T_{c,mLN} \quad (21) \text{ and } T_{C,LT}^* = \frac{(1+0.39x)}{(1+5.95x)}T_{c,mLT} \quad (22)$$

- For mixed vacancy (a) model $[Li_{1-5x}Nb_{\frac{19}{20}x}\square_{\frac{81}{20}x}][Nb_{1+\frac{1}{20}x}\square_{-\frac{1}{20}x}][O_3]$ for LN and $[Li_{1-5x}Ta_{\frac{4}{5}x}\square_{\frac{21}{5}x}][Ta_{1+\frac{1}{5}x}\square_{-\frac{1}{5}x}][O_3]$ for LT

In this case

$$T_{C,LN}^* = \frac{(0.25x-1)(1+0.393x)(1+0.31x)}{(9.4910^{-4}x-1)(1+5.32x)} T_{C,mLN} \quad (23) \text{ for LN} \quad T_{C,LT}^* = \frac{(0.5x-1)(1+1.24x)(1+0.62x)}{(0.037x-1)(1+10.30)} T_{C,mLT} \quad (24) \text{ for LT}$$

4 Results and discussion

We rely on previous vacancy models by comparing experimental results with values calculated using the theoretical approach mentioned above .To determine the variation of the Curie temperature as a function of non-stoichiometric composition x , we used experimental values of the Curie temperature [28] for LN and [15] for LT.

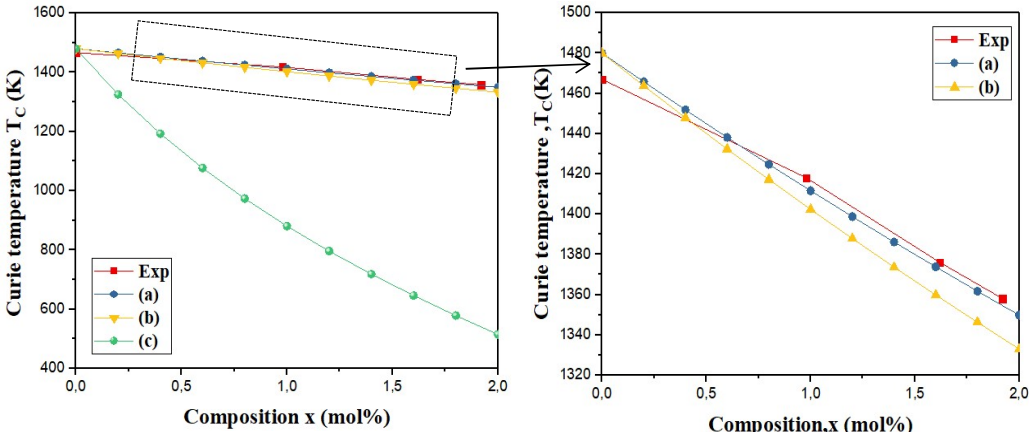


Fig. 3. Variation of the Curie temperature T_c ;LN versus nonstoichiometric composition x . The calculated values according to the (a),(b) and (c) vacancy models are compared to the experimental data of [15]

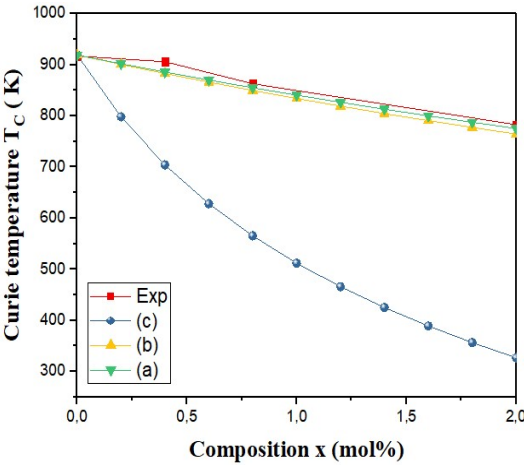


Fig. 4. Variation of the Curie temperature T_c ; LT versus nonstoichiometric composition x . The calculated values according to the (a),(b) and (c) vacancy models are compared to the experimental data of [28]

Variations in Curie temperature (T_c) as a function of non-stoichiometric composition (x) are shown in Figures 3 and 4 for lithium niobate (LN) and lithium tantalate (LT) respectively. It can be seen that T_c decreases for LN and LT as the concentration of the non-stoichiometric composition (x) increases. In other words, as the materials become less stoichiometric, T_c increases for LN and LT (T_c for stoichiometric LN and LT is higher than for less stoichiometric LN and LT). This result can be explained by the decrease in Li_2O concentration in LN and LT as the non-stoichiometric composition (x) increases (Figure 5 and Table 5), as well as by the fact that excess B^{5+} ions (B_{Li}) simultaneously occupy Li_{Li} sites (normal Li site) and B_B sites ($B = Ta, Nb$), as shown in Tables 3 and 4. Comparing the results of the three vacancy models with the experimental data, there is good agreement between the measured temperatures and the values

of the mixed vacancy model. Therefore, we can conclude that the mixed vacancy model effectively describes the intrinsic defect structure in our materials.

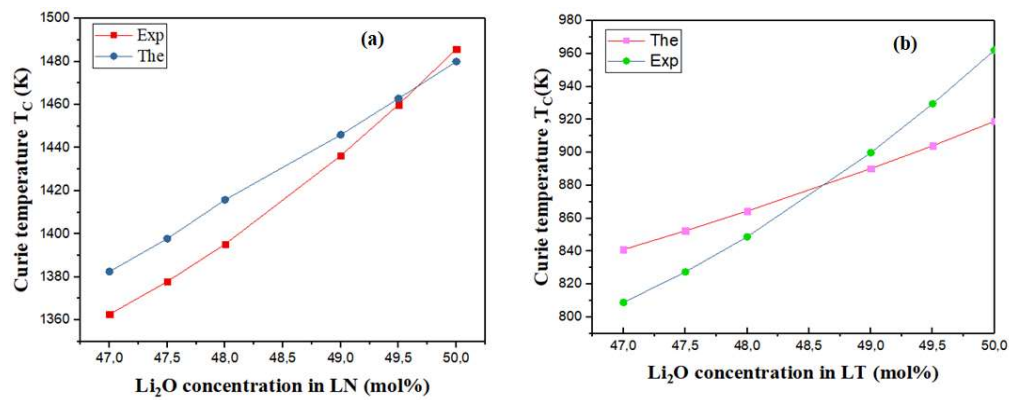


Fig. 5. (a) Variation of the theoretical Curie temperature (calculated according to model (a)) and experimental Curie temperature [35] as a function of the Li_2O concentration in LN, and (b) Theoretical Curie temperature of LT as a function of Li_2O , with the experimental T_c obtained from equation (2).

The variation of the Curie temperature, T_c , of LiBO_3 with respect to the Li_2O concentration is depicted in Figure 5. It is evident that T_c increases with an increase in the Li_2O concentration. In other words, the transition temperature, T_c , for Li-rich compositions in LiBO_3 is higher compared to compositions with lower lithium content. When comparing the theoretical and experimental trends of T_c as a function of lithium concentration, we observe a good agreement between the measured temperatures and the values predicted by the mixed vacancy model (model (a)).

Based on the data presented in Tables 1, 2, and 5, as well as Figures 3, 4, and 5, it is evident that the theoretical approach of Safaryan using the vacancy model (a) for non-stoichiometric LT and LN compounds yields results closer to the experimental ones compared to the vacancy models (b) and (c).

Table 5. The Curie temperature values calculated using the mixed model (a) for lithium niobate (LN) and lithium tantalate (LT) are compared to the experimental values reported in references [35] for LN and [16] for LT.

Composition (mol% Li_2O)	$\frac{[\text{Li}]}{[\text{B}]}$	Curie temperature			
		LN		LT	
		Model (a)	Measured	Model (a)	Measured
47	0.8867	1382.51	1362.65	841.083	808.93
47.5	0.9047	1397.81	1377.9	852.4892	827.46
48	0.923	1415.85	1395.262	864.435	848.795
49	0.9607	1446	1436.32	890.236	899.87
49.5	0.980	1462.84	1460.03	904.1	929.6
50	1	1480	1485.85	919	962.15

5 Conclusion

This work is devoted to the study of intrinsic defects in non-stoichiometric lithium niobate (LiNbO_3) and lithium tantalate (LiTaO_3) crystals. To do this, we use three vacancy models (model (a), model (b), and model (c)), as well as the Safaryan approach. The results of computer simulations of the Curie temperature T_c convincingly demonstrate that the proposed mixed vacancy model shows excellent agreement with the other models in terms of the match between theoretical and experimental results. In conclusion, we can state that the mixed vacancy model, which incorporates the coexistence of lithium and tantalum (or niobium) vacancies, adequately describes the intrinsic structural defects in LiNbO_3 and LiTaO_3 crystals.

Reference

1. D. Kip , Appl. Phys. B **67** , 131–150 (1998)
2. P. Gunter, J.P. Huignard, Topics in applied physics **61**, (1988).
3. K.Maaider, N. Masaif, A .Khalil, Indian J Phys **95**, 275-280 (2021)
4. S. Kar, R.K. Choubey, P. Sen, G. Bhagavannarayana, K.S , Bartwal , Physica B **393**, 37–42 (2007)
5. G. Malovichko, V. Grachev, O. Schirmer, AIP Conf. Proc **677**, 196-203 (2003).
6. B.T.Matthias ,J.P. Remeika , Phys. Rev **76** ,1886-1887(1949)
7. P.E.Tomaszewski, Journal of crystal growth **236**,1-4(2002)
8. K. Polgar, L. Kovacs , G. Corradi, Z. Szaller, A. Peter, J. Cryst. Growth **177**, 211–216 (1997).
9. K. Polgar, A. Peter, Foldvari , J. Opt. Mat **19**, 7–11(2002).
10. C.C Wu, W.T. Hsu, Z.B. Chen, R.K . Choubey ,C.W. Lan , J. Cryst. Growth **318**, 649–652 (2011)
11. J. R. Carruthers , G.E. Peterson, M. Grasso, J. Appl. Phys **42**, 1846 (1971)
12. C. Koyama, J. Nozawa, K. Fujiwara,S. Uda , Journal of the American Ceramic Society **100**, 1118-1124(2017)
13. F. Abdi, M. Fontana , M. Aillerie, P.Bourson , Appl. Phys. A **83** , 3-427 (2006)
14. J.R .Carruthers, G.E .Peterson, M .Grasso, P.M. Bridenbaugh, J Appl Phys **42**, 1846–1851(1971).
15. H.M .O'Bryan, P.K .Gallagher, C.D. Brandle, J. Am. Ceram. Soc **68**, 493–496(1985).
16. X .Xiao,J. Si,S. Liang,Q. Xu,H. Zhang, L. Ma, C.Yang, X, Zhang, Crystals **13**,1031(2023).
17. B.C. Grabmaier, W. Wersing, N. Koestler, J. Cryst. Growth **110**, 339-347 (1991).
18. H.Fay, W.J Alford ,H.M .Dess , App. Phys. Letters **12**, 89-92(1968).
19. P. Lerner, C. Legras ,P.J. Duman , J. Cryst. Growth **3**, 231–235(1968).
20. G.E. Peterson, A. Carneval , J. Chem Phys **56** , 4848-4851(1972).
21. S.C. Abrahams , P. March, Acta. Crystallogr. B **42**, 61–68(1986).
22. M.E. Lines, A.M. Glass, Principles and Application of Ferroelectrics and Related Materials (Oxford: Clarendon Press) (1977)
23. N.Iyi, K.Kitamura, F. Izumi, J.K .Yamamoto, T. Hayashi, H. Asano, S. Kimura, J. Solid. State. Chem **101**, 340–352 (1992)
24. F.P. Safaryan, Phys. Lett. A **255**, 191-200 (1999)
25. K. Maaider ,A. Jennane ,N. Masaif, A, Khalil , *Journal of Modern Physics* **9** , 7155(2011)
26. H. Donnerberg, S. M. Tomlinson, C. R. A. Catlow , O.F Schirmer , Phys. Rev. B **40**, 11909 (1989)
27. M. Wohlecke and G. Gorradi and K Betzler Appl. Phys. B **63**, 323-330 (1996)
28. F. Bennani, E. Husson, J. Eur. Ceram. Soc **21**, 847-854 (2001)
29. S. C. Abrahams , J.M .Reddy , J.L. Bernstein, J. Phys. Chem. Solids **27**, 997–1012 (1966)
30. A. Huanosta and A. R. West, J. Appl. Phys **61**, 5386-5391 (1987)
31. Y.L. Chen, J.P. Wen, Y.F. Kong, S.L .Chen, W.L. Zhang, J.J. Xu,G.Y. Zhang, Journal of crystal growth **242**, 400-404(2002)
32. S.C. Abrahams, P. Marsh, Acta Cryst. B **42**, 61-68 (1986)
33. F. Abdi, M. Fontana , M. Aillerie, P. Bourson , Appl. Phys. A **83**, 427-434 (2006)
34. F. Jermann, M. Simon, E. Krätzig, J. Opt. Soc. Am. B **12**, 2066-2070 (1995)
35. O'BRYAN, M. Henry, K. Patrick. Gallagher, C. D. Brandle, J.Ame. Cer. Soc **68**, 493-496 (1985).