

A new analytical description in C^{2+} doped $LiBO_3$ C (Ni, Zn...); B (Nb, Ta)

K Maaider^{1,2*}, A Jennane^{1,2}, A Khalil¹ and N Masaif^{1,2,3}

¹Laboratoire Rayonnement & Matière–Equipe de Recherche Physique de la Matière et Modélisation, Université Hassan 1er, Faculté des Sciences et Techniques, BP 577, Settat, Morocco

²Université Hassan 1er, Ecole Nationale des Sciences Appliquées, BP 77, Khouribga, Morocco

³Département de Physique, Faculté des Sciences, Université Ibn Tofail, BP 133, Kénitra, Morocco

Received: 04 April 2011 / Accepted: 03 May 2012 / Published online: 17 June 2012

Abstract: Defect structure models for C-doped non-stoichiometric lithium niobate and lithium tantalate were generally based on the defect model proposed for undoped crystals i.e. Li-site vacancy or Nb-site vacancy descriptions. The atomic radius of C is $r_C = 135$ pm. This work is an extension of the Safaryan theory. A new analytical description has been proposed. It is based on the vibrations of crystal planes. The substitution mechanism of the doped compositions C in $LiBO_3$ crystal is discussed. The mechanism of phase transition due to thermal expansion of crystal is also described.

Keywords: Lattice defect structure; Vacancy model; C: $LiBO_3$; Curie temperature

PACS Nos.: 61.72.-y; 61.72.jd; 74.62.Dh

1. Introduction

Lithium niobate ($LiNbO_3$) and Lithium tantalate ($LiTaO_3$) are two well known ferroelectric materials which have been the subject of intense studies due to their many applications to the technology of optical, electro-optical, and piezoelectric devices. Since their discovery in 1949 [1], numerous theoretical and experimental papers have been published, and yet the phase transformation mechanism remains unclear [2–6].

The structure of ferroelectric $LiTaO_3$ (LT) as well as that of $LiNbO_3$ (LN) belong to space group $R3c$ and can be considered as a superstructure of α Al_2O_3 corundum structure, with Li^+ and Ta^{5+} cations along the c-axis [7]. LT and LN are well-known to be narrow-range nonstoichiometric compounds; in LT, the solid solubility range extends from about 46 to 50.4 % mol Li_2O at room temperature [8]. The Curie temperature T_C decreases linearly with decreasing Li_2O concentration [9, 10]. Different defect models have been proposed to account for nonstoichiometry. The oxygen vacancy model has been

eliminated [11, 12] and among the cation site vacancy models, the Li-site vacancy model [11, 13, 14] seems more probable than the Nb-site vacancy model [15–17]. Different works have been published on LN or LT doped with different cations [12, 14, 18].

Torii et al. [14] have studied the evolution of T_C , as a function of doping in $(Li_{1-x}M_{x/2})TaO_3$ ($M = Zn, Ni, Mg, Ca$) solid solutions. They have shown that T_C increases with the c/a ratio of the hexagonal cell parameters.

Katsumata et al. [19] have studied the $LiNbO_3$ mesh parameters variation doped with Mg on the elementary volume and its applications on the transition temperature and density. They have found that the transition temperature increases with the increase of doping rate up to 3 % and slightly decreases beyond this value. The calculated value of density increases slightly to 3 % and then it decreases.

Iyi et al. [13] have studied the Mg-doping effect on the structure of LN and Malovichko et al. [20] have studied K and Mg-doped LN. Paul et al. [8] have examined Ni and Co-doped LN and LT. Substitution mechanisms have been the subject of controversy and depend upon the Li/Nb (Li/Ta) ratio of the pure LN or LT, the chosen type of substitution and the nature of the doping cations [8, 11–13, 15].

*Corresponding author, E-mail: maaiderr@gmail.com

Several critical properties of these studied materials depend clearly on the defects in the lattice and the presence of impurities. The problem that persists in using these materials is their susceptibility to optical damage. Doping improves the physical properties of these compounds and serves to minimize damage. The Approach of Safaryan [21] arises in the analysis of the structure defects in LiNbO_3 . This theory has been very important to determine the Curie temperature for some compounds near the stoichiometry. In this article, we have extended the Safaryan theory [21] by making a new theoretical approach to study doped LiBO_3 compounds ($B = \text{Nb}, \text{Ta}$). We have proposed quantitative and qualitative defect models in order to interpret some observed phenomena such as change of the Curie temperature and the substitution mechanism. In addition, we have presented results obtained by applying this new theory in the study of the LiNbO_3 and LiTaO_3 temperature transition doped with nickel and Zinc.

2. The new theoretical approach formalism of doped LiBO_3 compounds

2.1. Soft mode

The ferroelectric phase transition in LN and LT has been considered theoretically by Safaryan [21], who has assumed that the phase transition is the freezing of the optical vibration branches in parallel planes along the polar axis "c". To calculate the frequency of these vibrations, it is necessary to develop a system of differential equations describing the movement of parallel planes through the energy of their interaction. We proceed to determine the doped structure of perovskite LiBO_3 ferroelectric materials and apply particularly to the experimental results of solid solutions of lithium tantalate doped with nickel. For this we have used the four-atom theory.

In literature there is no real, stable, well-shaped structure of the LiCBO_3 form. We consider that the crystalline structure of these doped samples is formed by a succession of four planes, where each one is formed from the same type of atoms. The dynamic solution of vibration of these planes shows that one of the two branches describes optical soft modes in ferroelectric transition in LiCBO_3 .

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

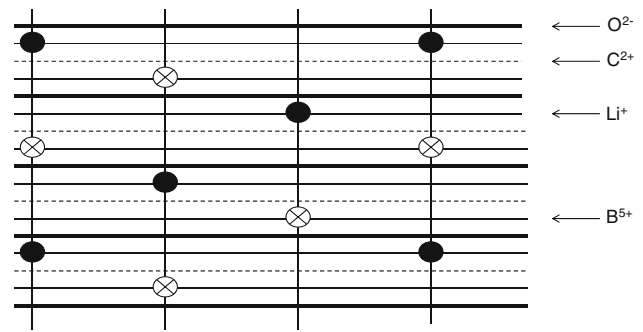
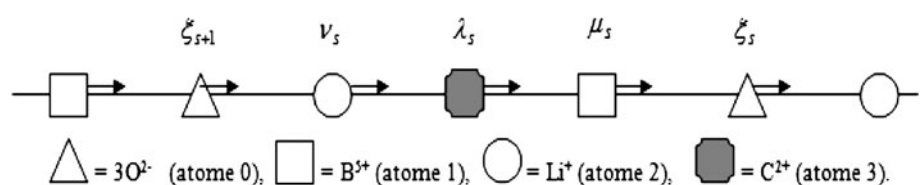


Fig. 1 Different planes in an elementary cell of C^{2+} doped LiBO_3

As the charge and ionic radius of doping elements (C^{2+}) are different from those substituted (Li^+ or B^{5+}), then their location is offset from that of the latter. So the doping element C will also help it with its own plane in the doped structure. In this case, we can assume that the structure is composed of four homogeneous planes, which are arranged as shown in Fig. 1. The N^{2+} doping plane is inserted between the two metal (Li^+ and B^{5+}) planes. So, the plane succession follows a certain ordering depending on the atomic degree of ionization forming these planes, namely in the sequence: Li^+ , C^{2+} and B^{5+} .

The dynamic problem of the composed system vibrations of these loaded planes can be reduced to a problem of a linear lattice vibration of four ions (Li^+ , C^{2+} , B^{5+} and O^{2-}) where each of them is a plane that contains only ions of the same specie.

Projection of Fig. 1 on an axis perpendicular to these planes gives a linear lattice of period a : is the distance between two successive planes of oxygen). Figure 2 shows the arrangement of these ions representative of each plane considered, with v_s (Li^+), λ_s (C^{2+}), u_s (B^{5+}) and ξ_s (O^{2-}) which respectively indicate the ions displacement: Li^+ , C^{2+} and B^{5+} O^{2-} in the unit cell of order s .

The calculation of these vibration frequencies is considered as a system of differential equations describing the linear movement planes in the case of doped solid solutions.

We are limited to interactions between atoms' first nearest neighbors. So we have got a system of linear and homogeneous equations, such as: The system is described by the differential equations as

$$\begin{aligned}
M_1 \ddot{u}_s &= C_{10}(\xi_{s+1} - u_s) + C_{13}(\lambda_s - u_s) \\
M_3 \ddot{\lambda}_s &= C_{13}(u_s - \lambda_s) + C_{23}(v_s - \lambda_s) \\
M_2 \ddot{v}_s &= C_{23}(\lambda_s - v_s) + C_{20}(\xi_s - v_s) \\
M_0 \ddot{\xi}_s &= C_{20}(v_s - \xi_s) + C_{10}(u_{s-1} - \xi_s)
\end{aligned} \tag{1}$$

where M_1 , M_2 , M_3 and M_0 are respectively the masses of the elements B, Li, C and O. The elastic constants C_{ij} , describing the interactions between nearest neighbors planes i and j , are determined in the same way as in Safaryan's article [21]. That is to say:

$$\begin{aligned}
C_{B-O} &\equiv C_{10} = 3 \frac{q_1 \times q_0 \times e^2}{b \times R_{10}^2} \\
C_{Li-O} &\equiv C_{20} = 3 \frac{q_2 \times q_0 \times e^2}{b \times R_{20}^2} \\
C_{Li-O} &\equiv C_{23} = \frac{q_2 \times q_0 \times e^2}{b \times R_{23}^2} \\
C_{Li-O} &\equiv C_{20} = 3 \frac{q_2 \times q_0 \times e^2}{b \times R_{20}^2} \\
C_{B-C} &\equiv C_{13} = \frac{q_1 \times q_3 \times e^2}{b \times R_{13}^2}
\end{aligned} \tag{2}$$

with q_0 , q_1 , q_2 and q_3 are respectively charges of O^{2-} , B^{5+} , Li^+ and C^{2+} ions, and b is the unit cell parameter of equidistant planes perpendicular to the axis c . The parameter R_{ij} denotes the distance between two planes nearest neighbors.

The solutions of this system of equations are functions of plane waves in this form:

$$g_s = g e^{i(\omega t + a s k)} \quad \text{with } g = u, v, \lambda \text{ or } \xi. \tag{3}$$

which lead to a system of linear equations which have a nontrivial solution. In order to obtain the fundamental frequencies of the optical branches, we put $k = 0$ in the determinant equation ($\Delta = 0$). Then, we get the following equation, substituting these expressions in the system (1). We obtain a system of linear algebraic homogeneous equations.

$$\begin{aligned}
(M_1 \omega^2 + C_{13} - C_{10})u_s - C_{13}\lambda_s + C_{1a}\xi_s &= 0 \\
-C_{13}u_s + (C_{13} + C_{23} + M_3 \omega^2)\lambda_s - C_{23}v_s &= 0 \\
-C_{23}\lambda_s + (M_2 \omega^2 + C_{23} - C_{2a})v_s + C_{20}\xi_s &= 0 \\
C_{10}u_s + C_{20}v_s + (M_0 \omega^2 - C_{10} - C_{20})\xi_s &= 0
\end{aligned} \tag{4}$$

The removal of the parameter k in the expression of the determinant leads to getting the fundamental frequencies of optical branches, for the sound becomes zero. The determinant of this system of equations is a polynomial of order four in ω^2 , its detailed expression is complicated, we simplify it by giving the intermediate functions F , S and R as follows:

$$\begin{aligned}
F &= C_{13} \left(\frac{1}{M_1} + \frac{1}{M_3} \right) + C_{23} \left(\frac{1}{M_2} + \frac{1}{M_3} \right) \\
&- C_{10} \left(\frac{1}{M_0} + \frac{1}{M_1} \right) - C_{20} \left(\frac{1}{M_0} + \frac{1}{M_2} \right)
\end{aligned} \tag{5}$$

$$\begin{aligned}
S &= -C_{10}C_{20} \left(\frac{1}{M_0M_1} + \frac{1}{M_0M_2} + \frac{1}{M_1M_2} \right) \\
&+ C_{10}C_{13} \left(\frac{1}{M_0M_1} + \frac{1}{M_0M_3} + \frac{1}{M_1M_3} \right) \\
&+ C_{10}C_{23} \left(\frac{1}{M_0M_2} + \frac{1}{M_0M_3} + \frac{1}{M_1M_2} + \frac{1}{M_1M_3} \right) \\
&+ C_{20}C_{32} \left(\frac{1}{M_0M_2} + \frac{1}{M_0M_3} + \frac{1}{M_2M_3} \right) \\
&+ C_{20}C_{31} \left(\frac{1}{M_0M_1} + \frac{1}{M_0M_3} + \frac{1}{M_1M_2} + \frac{1}{M_2M_3} \right) \\
&- C_{31}C_{32} \left(\frac{1}{M_1M_2} + \frac{1}{M_1M_3} + \frac{1}{M_2M_3} \right).
\end{aligned} \tag{6}$$

$$\begin{aligned}
R &= (C_{10}C_{20}C_{31} + C_{10}C_{20}C_{32} - C_{10}C_{31}C_{32} - C_{20}C_{31}C_{32}) \\
&\times \frac{(M_0 + M_1 + M_2 + M_3)}{M_0 \times M_1 \times M_2 \times M_3}
\end{aligned} \tag{7}$$

With these expressions, the general expression of the determinant is written:

$$\omega^6 + F \times \omega^4 - S \times \omega^2 + R = 0 \tag{8}$$

The expressions obtained are very long; we simplify them in writing as follows:

$$\begin{aligned}
\omega_1^2 &= \frac{1}{3} \left[-F - \sqrt[3]{2} \frac{L}{P} + \frac{P}{\sqrt[3]{2}} \right] \\
\omega_2^2 &= \frac{1}{3} \left[-F + \frac{1 + i\sqrt{3}LL}{\sqrt[3]{2}^2} \frac{L}{P} - \frac{1 - i\sqrt{3}}{2 \times \sqrt[3]{2}} P \right] \\
\omega_3^2 &= \frac{1}{3} \left[-F - \frac{1 - i\sqrt{3}L}{\sqrt[3]{2}} \frac{L}{P} - \frac{1 + i\sqrt{3}}{2 \times \sqrt[3]{2}} P \right]
\end{aligned} \tag{9}$$

with:

$$\begin{aligned}
L &= -F^2 - 3S \\
M &= \sqrt{4L^3 + (2F^3 + 9F \times S + 27R)^2} \\
P &= \sqrt[3]{(2F^3 + 9F \times S + 27R)^2 + M}.
\end{aligned} \tag{10}$$

2.2. Temperature of transition

The real solution, most probable in the expression (8), is the soft mode of solid non-stoichiometric solutions LiC-BO₃ (C = Ni, Zn) vibrations. The corresponding frequency is given by the following formula:

$$\omega_{sm}^2 = \frac{1}{3} \left[-F - \sqrt[3]{2} \frac{L}{P} + \frac{P}{\sqrt[3]{2}} \right] \tag{11}$$

In the case of non-stoichiometric doped solution, the soft mode frequency is written by analogy:

$$\omega_{sm}^{*2} = \frac{1}{3} \left[-F^* - \sqrt[3]{2} \frac{L^*}{P^*} + \frac{P^*}{\sqrt[3]{2}} \right] \quad (12)$$

with

$$\begin{aligned} L^* &= -F^{*2} - 3S^* \\ M^* &= \sqrt{4L^{*3} + (2F^{*3} + 9F^* \times S^* + 27R^*)^2} \\ P^* &= \sqrt[3]{(2F^{*3} + 9F^* \times S^* + 27R^*)^2 + M^*}. \end{aligned} \quad (13)$$

At $T = 0$ K, the frequencies ω_{sm}^2 and ω_{sm}^{*2} are respectively proportional to the temperature of phase transition corresponding respectively T_c and T_c^* , we can deduce the expression of the transition temperature of non-stoichiometric ceramics doped by:

$$T_c^* = \frac{P}{P^*} \frac{2^{2/3}L^* + 2^{1/3}F^*P^* - P^{*2}}{2^{2/3}L + 2^{1/3}FP - P^2} \times T_c \quad (14)$$

It remains to determine the link between the masses and charges in both systems stoichiometric and non-stoichiometric doped to find expressions of the form in Eq. (12). For this, it suffices to introduce deficient models for this doped non-stoichiometric structure.

3. Deficient models of compounds LN and LT doped with C^{2+}

According to the literature, we found that some authors like Paul [8], Katsumata [19] and Bennani [22, 23] have insisted that the substitution mechanism changes with the

concentration of Ni to determine the temperature transition T_c and ionic conductivity of ceramic LT, doped nickel.

The samples used in the experimental studies were described elsewhere [21, 22].

Tables 1 and 2 give the analyzed chemical formulae. The number of vacancies was calculated by subtraction of the cation sites amount, considering a main substitution mechanism $5Li^+ + B^{5+} \leftrightarrow 5Ni^{2+}$. The errors in the obtained formulae were estimated to be about 0.8 % for Li, 0.1 % for Ta, and 0.5 % for Ni. We found that there are two substitution models in this doped non-stoichiometric structure. The first is valid for the concentrations lower than 3 % and the second, for those superior or equal to 3 %.

From the experimental results presented in Tables 1 and 2, we found that there are two alternative models in this doped non-stoichiometric structure. The first will be valid for Ni concentrations below 3 % (α) and the second for those greater or equal than 3 % (β).

3.1. Substitution model of dopant $C < 3$ %

In both tables, a change in the mechanism of substitution is observed at $y = 3$ mol% C. We proposed a vacancy model that is based on that of lithium [21, 22] to describe the structure of non-stoichiometric substitution where Ta cations are in excess, which occurs in the sublattice of lithium (Li). This model (α) is given by:



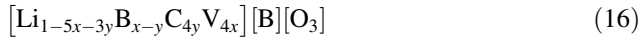
whose expression is modified by considering the various sub-lattices of the structure and showing up the vacancy (V) which permits compensation of the charge, where:

Table 1 Experimental chemical formulas and proposed the LT doped nickel

%Ni	Experimental formulas analysed	Proposed formulas
0	$Li_{0.977}Ta_{1.005}O_3$	$[Li_{0.977}Ta_{0.005}V_{0.019}][Ta]O_3$
1	$Li_{0.972}Ta_{1.002}Ni_{0.010}O_3$	$[Li_{0.96}Ta_{0.0015}Ni_{0.01}V_{0.0165}][Ta]O_3$
2	$Li_{0.955}Ta_{1.001}Ni_{0.02}O_3$	$[Li_{0.955}Ta_{0.001}Ni_{0.02}V_{0.024}][Ta]O_3$
3	$Li_{0.942}Ta_{0.999}Ni_{0.03}O_3$	$[Li_{0.942}Ni_{0.029}V_{0.029}][Ta_{0.999}Ni_{0.001}]O_3$
5	$Li_{0.912}Ta_{0.998}Ni_{0.050}O_3$	$[Li_{0.912}Ni_{0.048}V_{0.057}][Ta_{0.998}Ni_{0.002}]O_3$
8	$Li_{0.897}Ta_{0.988}Ni_{0.08}O_3$	$[Li_{0.897}Ni_{0.068}V_{0.035}][Ta_{0.988}Ni_{0.012}]O_3$
15	$Li_{0.836}Ta_{0.973}Ni_{0.15}O_3$	$[Li_{0.836}Ni_{0.123}V_{0.041}][Ta_{0.973}Ni_{0.027}]O_3$
20	$Li_{0.78}Ta_{0.964}Ni_{0.20}O_3$	$[Li_{0.78}Ni_{0.164}V_{0.056}][Ta_{0.964}Ni_{0.036}]O_3$

Table 2 Experimental chemical formulas and proposed the LN doped nickel

%Ni	Experimental formulas analysed	Proposed formulas
0	$Li_{0.976}Nb_{1.005}O_3$	$[Li_{0.976}Nb_{0.005}V_{0.019}][Nb]O_3$
1	$Li_{0.960}Nb_{1.0038}Ni_{0.010}O_3$	$[Li_{0.96}Nb_{0.0038}Ni_{0.01}V_{0.026}][Nb]O_3$
3	$Li_{0.939}Nb_1Ni_{0.03}O_3$	$[Li_{0.939}Ni_{0.03}V_{0.031}][Nb]O_3$
5	$Li_{0.92}Nb_{0.9958}Ni_{0.04975}O_3$	$[Li_{0.92}Ni_{0.046}V_{0.034}][Nb_{0.996}Ni_{0.004}]O_3$
8	$Li_{0.869}Nb_{0.9941}Ni_{0.08}O_3$	$[Li_{0.869}Ni_{0.074}V_{0.057}][Nb_{0.9941}Ni_{0.006}]O_3$
10	$Li_{0.867}Nb_{0.988}Ni_{0.098}O_3$	$[Li_{0.867}Ni_{0.086}V_{0.0047}][Nb_{0.988}Ni_{0.012}]O_3$



It is defined by two phenomena that take place at the sub-lattice [Li], while the other two sub-lattices ([B] and [O]) remain intact:

A substitution of the five atoms of lithium by a metal atom Ta:



Next, a substitution of three lithium cations and a metal cation (B) by four doping divalent cations:

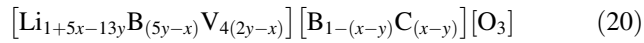


3.2. Substitution model of dopant $C \geq 3 \%$

From Tables 1 and 2 we see that from the concentration of 3 mol% of C, sub-lattice of tantalate begins to be affected by the substitution of nickel. While the mechanism of the impurity incorporation changes, we have tried to find a comprehensive and simplified formula that will generate all the compositions analyzed with the dopant concentration which is above 3 mol% of C. That is to say:

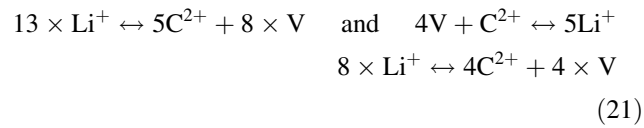


As in the previous case, the various sub-lattices of the structure are considered in showing the vacancies concentration (V) allowing compensation to balance the global charge:

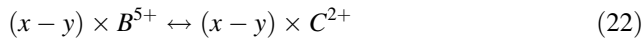


The model (β) given by Eq. (19) is defined by two types of substitutions:

– In the sub-lattice [Li]:



– In the sub-lattice [B]:



What characterized this last model from the first (α) is that the metal sub-lattices [Li] and [B] are both concerned with the substitution, which involves replacing the cations of lithium Li^+ by that of nickel C^{2+} and B^{5+} cations.

On the contrary, in the model (α), the site [Ta] is completely filled with its own cations B^{5+} , and in the site [Li] any substitution could take place. This is summed up

in a replacement of some atoms by Li Ta atoms which are in excess in the non-stoichiometric composition. They will be substituted in their laps with other atoms by the Li doping elements C [Eqs. (17) and (18)].

As the number of seats that can be occupied by Ta atoms in the sites [Li] is limited by the non-stoichiometric field, it makes sense to have a saturation of the substitution at some doping rate which corresponds to 3 mol% C for C-doped $LiBO_3$.

4. New formulations of vacancy models

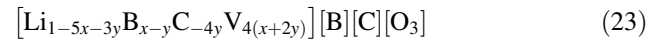
It is worthy to note that in passing from the stoichiometric state considered pure to the doped non stoichiometric state, all the physical quantities X (in particular the masses and the charges) become functions of the composition x and the parameter doping y ($X^*(x, y)$).

Therefore, ω_{sm}^* and T_C^* respectively designate the frequency of soft mode and the Curie temperature in the doped non-stoichiometric case. The evaluation of T_C^* , from Eq. (14), requires a combination of the new theory based on a simplified structure to four planes, and the new models incomplete (α) and (β) of the other part.

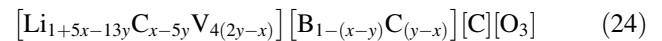
The knowledge of the Curie temperature in the pure stoichiometric case, and the frequency ω_{sm}^* and ω_{sm}^* allows to determine the Curie temperature in the doped non-stoichiometric considered case.

Then, we need to determine the frequency ω_{sm}^* . For this, we must determine the masses M_i^* and q_i^* the charges corresponding to the various sub-lattices of the doped structure. As the percentage (4y) of foreign elements in the structure is very limited (without considering the structures to side effects), we assume that the fourth plane is formed (1-4y). With these assumptions, we have tried to rewrite the models (α) and (β) in such a way to show a fourth sub-lattice which corresponds to the doping elements. We then propose the following expressions:

The new version of the vacancy model (α) is:



The new version of the vacancy model (β) is:



For pure stoichiometric, we have $x = y = 0$ which corresponds to a structure with four atoms or four sub-lattices that are [Li] [B], [C] and [O]. We will use the models Eqs. (23) and (24) to determine the masses and charges of each type of atoms contributing to the doped non-stoichiometric considered structure, then we have:

For the vacancy model (α)

$$\begin{aligned} M_0^* &= M_0; M_1^* = M_1; M_3^* = M_3 & q_0^* - q_0; q_1^* &= q_1; q_3^* &= q_3 \\ M_2^* &= (1 - 5x - 13y)M_2 + (x - y)M_1 - 2y \times M_3 & q_2^* &= (1 - 5x - 3y)q_2 + (x - y)q_1 - 2y \times q_3 \end{aligned} \quad (25)$$

For the vacancy model (β)

$$\begin{aligned} M_0^* &= M_0; M_1^* = (1 - (x - y))M_1 + \left(\frac{y-x}{2}\right)M_3 & q_0^* - q_0; q_1^* &= (1 - (x - y))q_1 + \left(\frac{y-x}{2}\right)q_3 \\ M_2^* &= (1 + 5x - 13y)M_2 + \left(\frac{x-5y}{2}\right)M_3; M_3^* = M_3 & q_2^* &= (1 + 5x - 13y)q_2 + \left(\frac{x-5y}{2}\right)q_3; q_3^* = q_3 \end{aligned} \quad (26)$$

Therefore, it can determine the elastic constants which describe the interactions between the atoms' closest neighbors i and j in the non-doped stoichiometric case, and also the functions F and S which appear in the expression (13) of the Curie temperature in the doped non stoichiometric case.

Accordingly, we can calculate theoretically the transition temperature of the ferroelectric phase to the paraelectric phase compositions for non-stoichiometric LiBO_3 doped with solid solutions whose parameters x and y are determined.

5. Results

In principle, one could test these models by comparing the experimental results with the calculated values according to the theoretical approach previously mentioned.

To make the comparison between the two models (α) and (β), we have used the experimental data of the Curie temperatures and the crystal parameters measured by Bennani [23] and Shuangquan Fang et al. [24].

To calculate the Curie temperatures suggested in Eq. (14), we need to know the Curie temperature of the exact stoichiometry compositions. So, we used the following estimations of the Curie temperatures in the stoichiometry lithium tantalate 928 K [25], 917 K [23] and 913 K [26] and in the stoichiometry lithium niobate 1475 K [27], 1479.5 K [28]. The average values of these estimations are $T_{\text{CTa}} = 919$ K and $T_{\text{CNb}} = 1480$ K.

The calculated and experimental values of T_{CTa}^* for different Ni-doped LT are illustrated in Fig. 3. We note that the temperature increases while increasing ratio Ni. Comparing the measured Curie temperature for doped nonstoichiometric LiTaO_3 with the two vacancy models

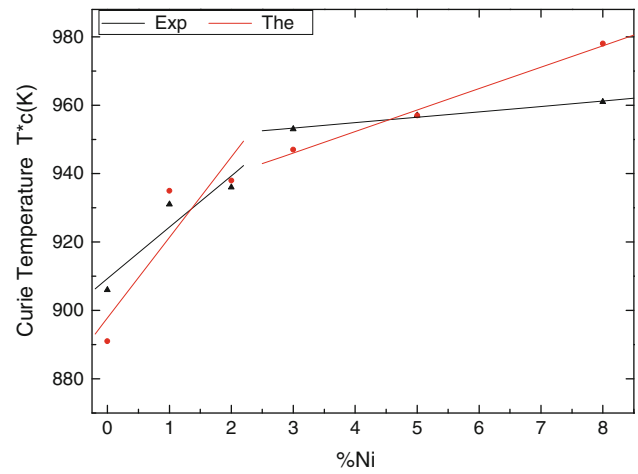


Fig. 3 Comparison experimental [18] and theoretical Curie temperature T_c^* as function of Ni content in the LiTaO_3

(model (α) and model (β)), the results demonstrate clearly that the calculated values are in a good agreement with the data obtained by the experiment.

To illustrate the nonstoichiometric LiNbO_3 structure doped with Ni, we report in Fig. 4 the Curie temperature, T_{CNb}^* as a function of the ratio Ni. In this figure, we presented only the theoretical results calculated from the vacancy models (α) and (β). As LiNbO_3 is isomorphous with LiTaO_3 we can employ the experimental results for Curie temperature calculated from the LiTaO_3 .

In Fig. 5, the Curie temperature NSLN was plotted as a function of ZnO content in the melt. In LiNbO_3 crystals, the Curie temperature reflected the Nb concentration of crystal, which increased with the decrease of NbLi (anti-site Nb, Nb in Li site) concentration or the increase of NbNb (normal Nb site) [29].

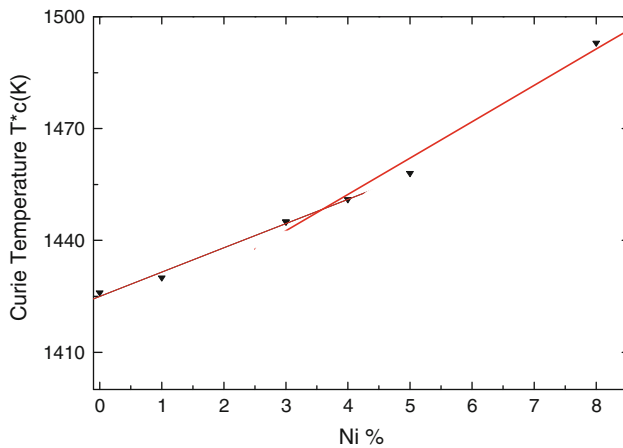


Fig. 4 Calculated Curie temperature as function of Ni content in the LiNbO_3

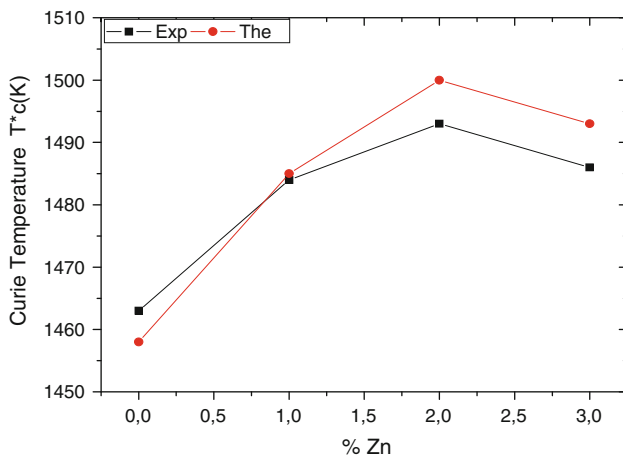


Fig. 5 Curie temperature experimental [19] and theoretical as a function of ZnO content

6. Discussion

The results of our theory indicate that the mechanism of change effect of the LiBO_3 occurs in the range 2.0–3.0 mol% of C. This effect may be caused by the lattice defect or by the substitution of C in both sub-lattice sites.

According to Figs. 3 and 4 representing the variation of the Curie temperature depending on the concentration of $\text{Ni}:\text{LiBO}_3$, the evolution of temperature as a function of (% Ni) shows a change of slope when the concentration exceeds 2.5 Ni mol% [22]. This change may be related to the fact that we have a change of mechanism of substitution Ni in the lattice. For the vacancy model (α) (% Ni < 3), the growth of temperature may be due to the decrease of atoms Nb (Ta) and Li in the sub-lattice [Li] which is obviously accompanied by an increase of Ni atoms. For higher Ni contents (model β), Ni ions occupy simultaneously the vacant Li and Nb (Ta) ions sites.

The Curie temperature (Fig. 5) reached a maximum value when ZnO doped concentration was between 2 and 3 mol% in near-stoichiometric samples. At this doping level, all Nb_{Li} ions were completely replaced by Zn ions, and this doping level of ZnO was called as the ‘threshold concentration’. When ZnO dopant concentration was lower than ‘threshold’, Nb_{Li} ions were gradually replaced by Zn ions, thus the curie temperature would increase; otherwise, when ZnO dopant concentration was higher than ‘threshold’, all Nb_{Li} ions were replaced and Zn ions began to occupy Li_{Li} site (normal Li site) and Nb_{Nb} site simultaneously, which made Nb_{Nb} ions decrease. So the Curie temperature would decrease.

7. Conclusions

Measured and calculated results show that the substitution mechanism of $\text{C}:\text{LiBO}_3$ is between 2 and 3 mol%. We can conclude that the new theory based on the simplified structure with four planes, combined with new theoretical vacancy models (α) and (β), is a successful means to describe the doped non-stoichiometric LiBO_3 structure.

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