

Some Theoretical Results of Ferroelectric Transition In The Doped Crystal LiMO_3 ($M = \text{Nb, Ta}$)

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Abstract: This work behaves like an extension of the Safaryan theory. A new analytical description has been proposed based on the vibrations of crystal planes. LiMO_3 is formed by a succession of the plans in the following sequence: Li, M, O_3 , etc. In the N doped LiMO_3 crystal, we supposed that the LiNMO_3 system is formed by a succession of the plans of the sequence: Li, N, M, O, etc. These four crystalline plans vibrate in the direction of trigonal c-axis where each plan consists the ions Li^+ , N^{x+} , M^{5+} or O^{2-} . The dynamic solution of the vibrations of these planes shows that one of two optical branches describes the soft mode at the ferroelectric transition in LiNMO_3 . From dispersion equation, we have show the bond between the soft mode frequency, the Curie temperature, the charges, the masses of ions and the distance between these ions. The substitution mechanism of the doped compositions N in LiMO_3 crystal is discussed. So, the mechanism of phase transition due to thermal expansion of crystal is described.

I. Introduction

Lithium niobate (LiNbO_3) and Lithium tantalite (LiTaO_3) are two well known ferroelectric materials which have been the subject of intense study 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 published, and yet the phase transformation mechanism remains unclear.

The structure of ferroelectric LiTaO_3 (LT) as well as that of LiNbO_3 (LN) belongs 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-axis². 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 temperature³. The Curie temperature T_C decreases linearly with decreasing Li_2O concentration^{4,5}. Different defect models were proposed to account for non stoichiometry. The oxygen vacancy model was eliminated^{6,7} and among the cation site vacancy models, the Li-site vacancy model^{6,8,9} seems more probable than the Nb-site vacancy model¹⁰⁻¹². Different works were published on LN or LT doped with different cations^{7,9,13}.

Torii et al.⁹ studied the evolution of T_C , as a function of doping in $(\text{Li}_{1-x}\text{M}_{x/2})\text{TaO}_3$ ($M = \text{Zn, Ni, Mg, Ca}$) solid solutions. They showed that T_C increases with the c/a ratio of the hexagonal cell parameters.

In 1993, Katsumata al.¹⁴ has studied the variation of parameters of the mesh of LiNbO_3 doped with Mg on the elementary volume and its applications on the

transition temperature and density. They found that the transition temperature increases with the increase of doping up to 3% and slightly decreases past this value. The calculated value of density increases slightly to 3% and then it decreases.

Iyi et al.⁸ contrived the Mg-doping effect on the structure of LN and Malovichko et al.¹⁵ studied K and Mg-doped LN. Paul et al.³ examine 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^{3,6,7,8,10}.

Several critical properties of these studied materials depend clearly the defects in the lattice and the presence of impurities. The problem persists in use this material is their susceptibility to optical damage. Doping improves the physical properties of these compounds and serves to minimize damage.

Approach of safaryan¹⁶, arises in the analysis of the structure defects in LiNbO_3 . This theory has been very important for determining the Curie temperature for some compounds near the stoichiometry. In this present article, we develop a work which consists of an extension of the theory Safaryan¹⁶ by making a new theoretical approach to study compounds LiBO_3 ($B = \text{Nb, Ta}$) doped. We shall present also the results obtained by applying this new theory in the study of the transition temperature of LiNbO_3 and LiTaO_3 doped with nickel.

II. Formalism Of The New Theoretical Near Compounds Doped Libo3

Soft Mode :

The ferroelectric phase transition in LN and LT has been considered theoretically by Safaryan¹⁶, who assumed that the phase transition is the freezing of branches of the optical vibration 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 structure of doped ferroelectric materials of perovskite ABO_3 that we will apply in particular to the experimental results of solid solutions of lithium tantalate doped with nickel. For this we are going to use the theory to four atoms.

In literature there is no real structure stable and definite shape LiMNO_3 ($N = \text{Ni}$), we consider that the crystalline structure of these doped samples, is formed by four plans succession where each plan is responsible is the same type of atoms. The dynamic solution of vibration of these plans shows that one of the two branches described optical soft modes in ferroelectric transition in LiMNO_3 . From the dispersion equation, we must show the link between the frequency of soft modes, the Curie temperature, charges, masses of ions and the distance between these ions. The mechanism of alternative compositions N doped LiMO_3 crystal is discussed. So, the mechanism of phase transition due to thermal expansion of the crystal is described. Like the charge and ionic radius of doping elements (N^{2+}) are different from of those substituted (Li^+ or M^{5+}), then their location is offset from that of the latter. So the doping element N will also help him with his own plan in the doped structure. In this case, we can assume that the structure is composed of four planes homogeneous, which are arranged as shown in Figure 1. The plan of doping N^{2+} is inserted between the two plans metal (Li^+) and (B^{5+}). So, the succession plan follows a certain order depending on the degree of ionization of atoms forming the latter, namely in the sequence: Li^+ , N^{2+} and M^{5+} .

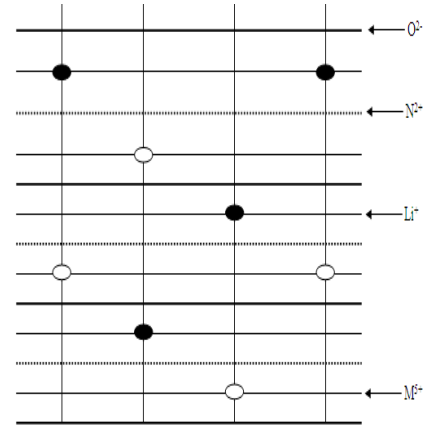


Fig. 1: Different planes in an elementary cell of N^{2+} doped LiMO_3 .

The problem of dynamic vibration system composed of the planes loaded can be reduced to a problem of vibration of a linear lattice of four ions (Li^+ , N^{2+} , M^{5+} and O^{2-}) where each ion is a plan that contains only ions of the same space.

The projected figure 1 about 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 plan considered, with v_s (Li^+), λ_s (N^{2+}), u_s (B^{5+}) and ξ_s (O^{2-}) respectively indicate the movement of ions: Li^+ , N^{2+} and M^{5+} O^{2-} in the unit cell of order s .

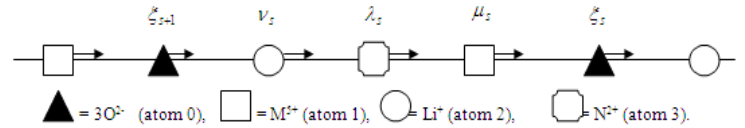


Fig. 2 : Displacement of Li^+ , M^{5+} , N^{2+} and 3O^{2-} ions in a linear lattice

The calculation of frequencies of these vibrations is considering a system of differential equations describing the linear movement plans in the case of solid solutions doped. We are limited to interactions between atoms first nearest neighbors. So we've got a system of linear equations and homogeneous, such as: The displacements of the four ions are indicated by v_s (Li^+), u_s (Ta^{5+}) and ξ_s (O^{2-}). Then, the system is described by the differential equations as

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

where M_1 , M_2 , M_3 et M_0 are respectively the masses of the elements B, Li, N and O.

The elastic constants C_{ij} describing the interactions between nearest neighbors plans i and j , are determined

in the same way as in article of safaryan¹⁶. That is to say:

$$\begin{aligned} C_{Ta-O} &\equiv C_{10} = 3 \frac{q_1 \times q_0 \times e^2}{b \times R_{10}^2} \\ C_{Li-O} &\equiv C_{20} = 3 \frac{q_2 \times q_0 \times e^2}{b \times R_{20}^2} \\ C_{Li-O} &\equiv C_{20} = 3 \frac{q_2 \times q_0 \times e^2}{b \times R_{20}^2} \\ C_{Ta-M} &\equiv C_{13} = \frac{q_1 \times q_3 \times e^2}{b \times R_{13}^2} \\ C_{Li-M} &\equiv C_{23} = \frac{q_2 \times q_3 \times e^2}{b \times R_{23}^2} \end{aligned} \quad (2)$$

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

The choice of solutions in the form of plan waves,

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

leads to a system of linear equations which has 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 equations and homogeneous.

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

Cancel of the parameter k in the expression of the determinant let 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 very long to write, we simplify it by giving the intermediate functions F , S and R following:

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

$$\begin{aligned} S &= -C_{10} C_{20} \left(\frac{1}{M_0 M_1} + \frac{1}{M_0 M_2} + \frac{1}{M_1 M_2} \right) + C_{10} C_{13} \left(\frac{1}{M_0 M_1} + \frac{1}{M_0 M_3} + \frac{1}{M_1 M_3} \right) \\ &+ C_{10} C_{23} \left(\frac{1}{M_0 M_2} + \frac{1}{M_0 M_3} + \frac{1}{M_1 M_2} + \frac{1}{M_1 M_3} \right) + C_{20} C_{32} \left(\frac{1}{M_0 M_2} + \frac{1}{M_0 M_3} + \frac{1}{M_2 M_3} \right) \\ &+ C_{20} C_{31} \left(\frac{1}{M_0 M_1} + \frac{1}{M_0 M_3} + \frac{1}{M_1 M_2} + \frac{1}{M_2 M_3} \right) - C_{31} C_{32} \left(\frac{1}{M_1 M_2} + \frac{1}{M_1 M_3} + \frac{1}{M_2 M_3} \right). \end{aligned} \quad (6)$$

$$R = (C_{10} C_{20} C_{31} + C_{10} C_{20} C_{32} - C_{10} C_{31} C_{32} - C_{20} C_{31} C_{32}) \frac{(M_0 + M_1 + M_2 + M_3)}{(M_0 \times M_1 \times M_2 \times M_3)} \quad (7)$$

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

$$\omega^6 + F \times \omega^4 - S \times \omega^2 + R = 0 \quad (8)$$

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

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

With: $L = -F^2 - 3S$

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

(9)

III. Transition Temperature

The real solution, most probable in the expression (8), is the soft mode vibrations solid solutions LiMNO₃ (M = Ni, Mg) non-stoichiometric. The corresponding frequency is given by the following formula:

$$\omega_{sm}^2 = \frac{1}{3}[-F - \sqrt[3]{2} \frac{L}{P} + \frac{P}{\sqrt[3]{2}}] \quad (11)$$

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

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

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=0K, 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 deduct the expression of the transition temperature of non-stoichiometric ceramics doped by:

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

Knowledge of the Curie temperature has the stoichiometric composition and constants of the formula (10) to determine the temperature of phase transition in the non stoichiometric doped after calculation expressions of L*, M*, and P* the formula (13).

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 (12). For this, it suffices to introduce models deficient for this structure non-doped stoichiometric.

IV. Models deficient compounds doped LN and LT with N2+

According to the literature, we found that some authors like Paul[3], Katsumata[14] and Bennani [18] have insisted that the substitution mechanism changes with the dopant concentration, for determining the temperature transition T_c and ionic conductivity of ceramic LT, doped nickel.

From the table (1, 2) below, give the chemical formulae analyzed [18] and the proposed of lithium tantalate and niobate doped nickel, we found that there are two substitution models in this structure non-doped stoichiometric. The first will be valid for the concentrations lower than 3% and the second, for those superior than or equal to 3%.

Tab. 1: experimental chemical formulas and proposed the LT doped nickel.

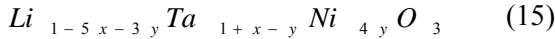
%Ni	compounds	Proposed formulae
0	Li _{0.977} Ta _{1.005} O ₃	[Li _{0.977} Ta _{0.005} V _{0.019}][Ta]O ₃
1	Li _{0.972} Ta _{1.002} Ni _{0.010} O ₃	[Li _{0.96} Ta _{0.0015} Ni _{0.01} V _{0.0165}][Ta]O ₃
2	Li _{0.955} Ta _{1.001} Ni _{0.02} O ₃	[Li _{0.955} Ta _{0.001} Ni _{0.02} V _{0.024}][Ta]O ₃
3	Li _{0.942} Ta _{0.999} Ni _{0.03} O ₃	[Li _{0.9420} 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 _{0.780} Ni _{0.164} V _{0.056}][Ta _{0.964} Ni _{0.036}]O ₃

Tab. 2: experimental chemical formulas [19] and proposed the LN doped nickel.

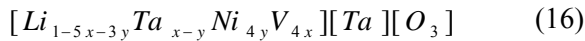
%Ni	compounds	Proposed formules
0	$\text{Li}_{0.976}\text{Nb}_{1.005}\text{O}_3$	$[\text{Li}_{0.976}\text{Nb}_{0.005}\text{V}_{0.019}][\text{Nb}]\text{O}_3$
1	$\text{Li}_{0.960}\text{Nb}_{1.0038}\text{Ni}_{0.010}\text{O}_3$	$[\text{Li}_{0.96}\text{Nb}_{0.0038}\text{Ni}_{0.01}\text{V}_{0.026}][\text{Nb}]\text{O}_3$
3	$\text{Li}_{0.939}\text{Nb}_1\text{Ni}_{0.03}\text{O}_3$	$[\text{Li}_{0.939}\text{Ni}_{0.03}\text{V}_{0.031}][\text{Nb}]\text{O}_3$
5	$\text{Li}_{0.92}\text{Nb}_{0.9958}\text{Ni}_{0.04975}\text{O}_3$	$[\text{Li}_{0.92}\text{Ni}_{0.046}\text{V}_{0.034}][\text{Nb}_{0.996}\text{Ni}_{0.004}]\text{O}_3$
8	$\text{Li}_{0.869}\text{Nb}_{0.9941}\text{Ni}_{0.08}\text{O}_3$	$[\text{Li}_{0.869}\text{Ni}_{0.074}\text{V}_{0.057}][\text{Nb}_{0.9941}\text{Ni}_{0.006}]\text{O}_3$
10	$\text{Li}_{0.867}\text{Nb}_{0.988}\text{Ni}_{0.098}\text{O}_3$	$[\text{Li}_{0.867}\text{Ni}_{0.086}\text{V}_{0.0047}][\text{Nb}_{0.988}\text{Ni}_{0.012}]\text{O}_3$

From the experimental results presented in Table 1 and 2, we found that there are two alternative models in this structure non-doped stoichiometric. The first will be valid for Ni concentrations below 3% (a) and the second for those greater than or equal to 3% (b). Substitution model of dopant Ni <3% :

From the above table, a change in the mechanism of substitution is observed to $y = 3$ mol% Ni. We proposed a vacancy model that is based on that of lithium^{16,17}, to describe the structure of non-stoichiometric substitution where Ta cations are in excess, is in the sublattice of lithium (Li). This model (α) is given by:

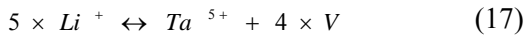


whose expression is modified by considering the various sublattice of the structure and showing up the vacancy (V) which permit compensation of the charge, where:

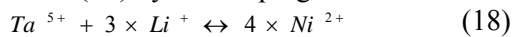


It is defined by two phenomenons that take place at the sublattice [Li], while the other two sublattice ([Ta] and [O]) remain intact:

A substitution the five atoms of lithium by a metal atom Ta, is to say:



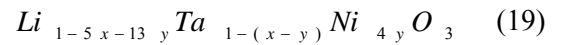
Next, a substitution of three cations lithium and a metal cation (Ta) by four doping divalent cations:



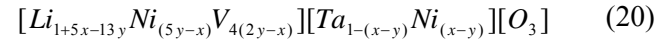
- substitution model of dopant Ni $\geq 3\%$.

From Tables (1, 2), we certify that from the concentration of 3 mol% of Ni, sublattice of tantalate beginning to be affected by the substitution of nickel. While the mechanism of incorporation of the impurity

changes, we have tried to find a comprehensive and simplified formula that will generate all the compositions analyzed with the dopant concentration is ≥ 3 mol% of Ni, which is such that:

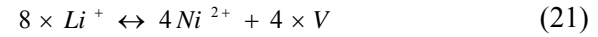
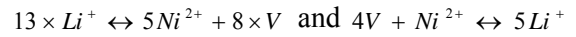


As in the previous case, the various sublattice of the structure are considered in showing the concentration of vacancies (V) allowing compensation to equilibrium the global charge:

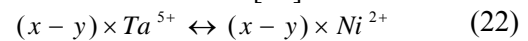


The model (β) given by (19) is defined by two types of substitutions:

❖ In the sublattice [Li]



❖ In the sublattice [Ta]:



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

By contrast, in the model (α), the site [Ta] is completely filled by its own cations Ta^{5+} and is the site [Li] that any substitution takes place. This is summed up in a replacement of some atoms by Li Ta atoms are in excess in the composition non-stoichiometric, they will be substituted in their laps with other atoms by Li doping elements Ni (17 and 18).

As the number of seats that can be occupied by Ta atoms in the sites [Li] is limited by the field of non-stoichiometric, so it makes sense to have a saturation

of the substitution at some rate doping which corresponds to 3 mol% N for N-doped LiMO₃.

V. New Formulations of Vacancy Models

We remember that in passing of the state stoichiometric considered pure the state non stoichiometric doped, all the physical quantities X (in particular the masses and the charges) are becoming 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 case non stoichiometric doped.

The evaluation of T_c^* from equation (IV-21) requires a combination of the new theory based on a simplified structure to four plans, and the new models incomplete (α) and (β) of the other part.

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

Then, we need to determine the frequency ω_{sm}^* . For this, it must determine the masses M_i^* and the charges

q_i^* corresponding to the various sublattice of the doped structure. As the percentage (4y) dopants elements in the structure is very limited (without considering the structures to side effects), we assume that the fourth plan is formed of (1-4y) with these assumptions, we have tried to rewrite the models (α) and (β), in such a way to show a fourth sublattice which corresponds to the doping elements. We then propose the following expressions:

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

$$[Li_{1-5x-3y} B_{x-y} Ni_{-4y} V_{4(x+2y)}][B][Ni][O_3] \quad (23)$$

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

$$[Li_{1+5x-13y} Ni_{x-5y} V_{4(2y-x)}][B_{1-(x-y)} Ni_{(y-x)}][Ni][O_3] \quad (24)$$

For pure stoichiometric, then x = y = 0 which corresponds to a structure with four atoms or four sublattices that are [Li] [B], [Ni] and [O].

We will use models (23) and (24) for determination the masses and charges of each type of atoms contributing to the structure non- stoichiometric doped considered, then we have:

❖ For the vacancy model (α)

$$M_0^* = M_0; M_1^* = M_1; M_3^* = M_3$$

$$M_2^* = (1-5x-3y)M_2 + (x-y)M_1 - 2y \times M_3$$

$$q_0^* = q_0; q_1^* = q_1; q_3^* = q_3 \quad (25)$$

$$q_2^* = (1-5x-3y)q_2 + (x-y)q_1 - 2y \times q_3$$

❖ For the vacancy model (β)

$$M_0^* = M_0; M_1^* = (1-(x-y))M_1 + (\frac{y-x}{2})M_3$$

$$M_2^* = (1+5x-13y)M_2 + (\frac{x-5y}{2})M_3; M_3^* = M_3$$

$$q_0^* = q_0; q_1^* = (1-(x-y))q_1 + (\frac{y-x}{2})q_3 \quad (26)$$

$$q_2^* = (1+5x-13y)q_2 + (\frac{x-5y}{2})q_3; q_3^* = q_3$$

Therefore, it may determine the elastic constants which describe the interactions between atoms closest neighbors i and j in the case none doped stoichiometric and to determine the functions F and S which appear in the expression (IV-12) of the Curie temperature in the case non stoichiometric doped.

Accordingly, we can calculate theoretically the transition temperature of the ferroelectric phase to the para-electric phase compositions for non-stoichiometric doped LiMO₃ solid solutions with x and y parameters are determined.

VI. 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 [18].

To calculate the Curie temperatures suggested in equation 14, we have needed to know the Curie temperature of the exact stoichiometry compositions. So, we have used the following estimations of the Curie temperatures in the stoichiometry lithium tantalate 928 K [20], 917 K [18] and 913 K [21] and in the stoichiometry lithium niobate 1475 K [22], 1479.5 K [23] and 1485.7 K [19]. The average values of these estimations are $T_{cTa} = 919$ K and $T_{cTa} = 1480$ K.

The calculated and experimental values of T_{cTa}^* for different Ni-doped LT are illustrated in Figure 3. We note that the temperature increases with increasing ratio Ni. Comparing the measured Curie temperature for nonstoichiometric doped LiTaO₃ with the two vacancy models (model (α) and model (β)); the results

demonstrate clearly that the calculated values are in a good agreement with the data obtained by the experimental study.

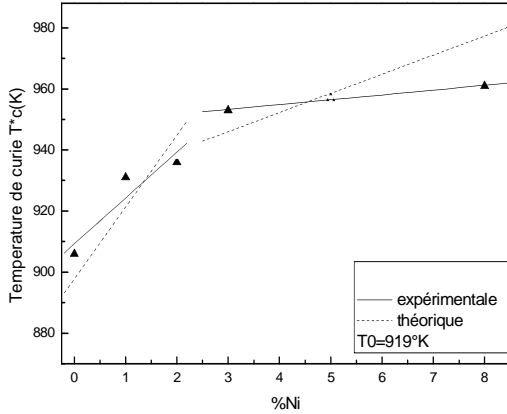


Fig. 3: Comparison of experimental [18] and theoretical Curie temperature T_c^* as function of Ni content in the LiTaO₃.

To illustrate the structure doped of Ni the nonstoichiometric LiNbO₃, we report in Figure 4 the Curie temperature, $T_{c_{Nb}}^*$ as a function of the ratio Ni. In this figure, we presented only the results theoretical calculated from the vacancy models (α) and (β). As LiNbO₃ is isomorphous with LiTaO₃ we can employ the results experimental Curie temperature calculated from the LiTaO₃.

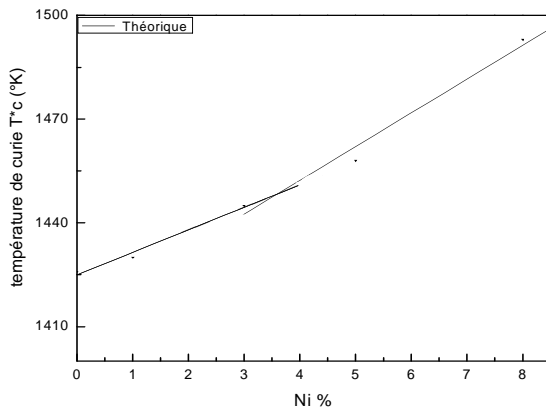


Fig. 4: calculated Curie temperature T_c^* as function of Ni content in the LiNbO₃.

VII. Discussion

According to Figure (3, 4) representing the variation of the Curie temperature depending on the concentration of Ni:LiMO₃ (M=Nb or Ta), we can draw the following certifications:

For both theoretical and experimental Curie temperature, increases linearly with the increase of doping (% Ni²⁺), with a break before 3 mol% of Ni. Contrary to what happens with other cations as well as valence Ni²⁺ such as Zn²⁺ or Ca²⁺ [37].

The evolution of T_c^* as a function of (% Ni) shows a change of slope when the concentration exceeds 2.5 Ni mol%, 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), growth of T_c^* may be due to the decrease of atoms Nb (Ta) and Li in the sublattice [Li] 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,

VIII. Conclusion

We can conclude that the new theory based on the simplified structure with four plans, combined with new theoretical vacancy models (α) and (β) is a successful means for describing the structure of ceramic non-stoichiometric LiMO₃ doped.

IX. References

1. B. T. Matthias and J. P. Remika, Phys. Rev., **76**, 1886 (1949)
2. Abrahams S.C. and Bernstein L.J., Phys. Chem. Solids **28**, 1685 (1967)
3. Paul M., Tabuchi M. and West A.R., Chem. Mater. **9**, 3206 (1997).
4. Ballman A.A., Levinstein H.J., Capio C.D. and Brown H., J. Amer. Ceram. Soc., **50**, 657 (1967).
5. Fujino Y., Tsuya H. and Sugibuchi K., Ferroelectrics, **2**, 113 (1971).
6. Iyi N., Kitamura K., Izumi F., Yamamoto J.K., Hayashi T., Asano H. and Kimura S., J. of Solid State Chem. **101**, 340 (1992).
7. Allemann J.A., Xia Y., Morriss R.E., Wilkinson A.P., Eckert H., Speck J.S., Levi C.G., Lange F.F., Anderson S., J. Mater. Res. **11**, 2376 (1996).
8. Iyi N., Kitamura K., Yajima Y. and Kimura S., Furukawa Y. and Sato M., J. of Solid State Chem., **118**, 148 (1995).
9. Torii Y., Sekiya T. and Yamamoto T., Koyabachi K. and Abe Y., Mater. Res. Bull. **18**, 1569 (1983).
10. Abrahams S.C. and Marsh P., Acta Cryst. **B42**, 61 (1986).
11. Schirmer O.F., Thiemann O. and Wöhlecke M., J. Phys. Chem. Solids, **52**, 185 (1991).
12. Donnerberg H., J. of Solid State Chem. **123**, 208 (1996).

13. Joo G.T., Ravez J. and Hagenmuller P.,
Revue de Chimie Minérale, **22** 8 (1985).
14. T. Katsumata, K. Shibata and H. Imagawa,
Materials research bulletin, Vol. 29, N°5,
pp. 559-566 (1994)
15. Malovichko G., Cercelie O., Estienne J.,
Grachev V., J. Phys. Chem. Solids, **56**, 1285
(1995).
16. F.P. Safaryan, Physics Letters A, 255, pp.
191- 200 (1999).
17. F. Bennani and E. Husson Journal of the
European ceramic society, Vol. 21, 7, pp.
847- 854 (2001).
18. F. Bennani, Thèse d'état, Université Ibn
Tofail, Faculté des sciences, Kenitra, Maroc.
19. N. Masaif, 1, S. Jebbari1, 2, F. Bennani3, M.
Hafid3, and A. Jennane, Phys. Stat. Solidi
(b), Vol. 240, N°3, (2003) 640 – 648.
20. H. D. Megaw. Acta. Crystallogr., 7, 187,
(1954).
21. A. Huanosta and R. West J. Appl. Phys.,
Vol.61, No. 12, 5386-5391(1987)
22. H. Donnerberg, S. M. Tomlinson, C. R. A.
Catlow and O. F. Schirmer., Phys. Rev. B,
40, 909 (1989).
23. D. M. Smyth, "Proceedings of the Sixth IEEE
International Symposium on the Application of
Ferroelectrics." June 1986.