Analysis of the correlation between doping with divalent and tetravalent impurities and the stoichiometry of lithium niobate (LiNbO3)

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Abstract- Lithium niobate (LiNbO₃ or LN) has found numerous applications in electro-optics and other fields. We have studied the influence of point defects on the Curie temperature (Tc) of pure LiNbO₃ (LN) and LN doped with impurities of different valencies (divalent and tetravalent) using our newly proposed vacancy model and the theory of ferroelectric phase transition developed by Safaryan. Doping non-stoichiometric LN samples with MgO reduces point defects in the LiNbO₃ crystal, particularly at low magnesium concentrations approaching 3 mol%, bringing the LN closer to stoichiometric composition.

Analyses of the defect composition reveal a decrease in the concentration of Nb_{Li} with divalent doping, which leads to an increase in Tc and confers quasi-stoichiometry on the LN. Conversely, the concentration of Nb_{Li} increases with doping with tetravalent impurities, leading to a reduction in Tc and making the material more non-stoichiometric. These results highlight the impact of doping lithium niobate with divalent and tetravalent impurities on the structure of point defects in LN.

Index Terms-Defect structure; Doping; Lithium niobite; Acousto-optic materials; vacancy model

I. INTRODUCTION

Lithium niobate (LN) is a material used to manufacture a wide range of products, including high-performance surface acoustic wave transducers and delay lines [1], among others. It has both intrinsic and extrinsic point defects [2,3].

$$\ll LiNbO_3 \gg \rightarrow 3Li_2O + 4V'_{Li} + Nb^{4*}_{Li}$$
 (1)
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The presence of a high concentration of vacant Li sites in LiNbO3 congruent was validated by structural analyses [4, 5] and NMR studies [6]. These data support the site vacancy model Li, see equation (1) and [7, 8] in which an antisite Nb is compensated by four V_{Li} . In this model, a congruent LiNbO₃ is described as follows:

$$\{[Li]_{1-5x}[Nb_{Li}]_{x}[V_{Li}]_{4x}\}[Nb_{Nb}]O_{3}$$
(2)

Currently, the Li site vacancy model (2) is widely accepted as relevant and considerations of all defect reconstructions in LiNbO3 are discussed in this area [9, 10]. According to Wilkinson et al [4], the degree of filling of Li sites with Nb ions is random and depends, for example, on growing conditions, so that one can expect the coexistence of the three Nb_{Li} cation stacking defects, V_{Li} and V_{Nb} in low concentration Li crystals as prepared.

Many dopant atoms enter the defect structure of nonstoichiometric crystals and modify it in different ways. On the other hand, certain dopants (Mg, Zn...) are needed to improve resistance to optical damage in non-linear optical devices [11] and reduce non-stoichiometry [12].

Results obtained from LiNbO₃ doped with impurities such as Mg and Zn on defect structures and associated optical measurements show decreasing Nb_{Li} concentrations [13-14]. The presence of the Nb_{Li} antisite in the composition range is important for studying the defect structures of LN doped with impurities of different valencies [15, 16].

The relationship between point defects and Curie temperature (Tc) has been studied. In the case of LN, the Curie temperature varies as a function of the Li/Nb ratio or by impurities [17-18]. The Tc of undoped LN in the solid solution range is described by the following relationship [19]:

 $T_C = 9095.2 - 369.05C + 4.228C^2 (°C)$ (3)

where C is the concentration in units of mol% Li_2O . Impurity concentration varies with LN curie temperature, while the Li/Nb ratio remains constant [20-21]. Vacancy content properties such as Tc are modified by added Mg and the defect structure is strongly dependent on the vacancy content. Each Mg ion incorporated at a Li site also generates a Li vacancy [20]. An increase in Mg concentration leads to a decrease in Nb vacancies, which explains the increase in Curie temperature. Above the Mg concentration, there is no longer any Nb in the Li site, and Mg is incorporated into the Nb sites.

This article focuses on a comparative study between theoretical and experimental values of the Curie temperature (Tc) of various samples of lithium niobate (LiNbO₃ or LN), whether undoped or doped with different divalent (Mg²⁺) and tetravalent (Ce⁴⁺, Ti⁴⁺ and Zr⁴⁺) impurities. We use vacancy models to describe more precisely the structure of point defects in LN, as well as the Safaryan approach to better understand the impact of lithium niobate doping on its properties, with a particular focus on Tc. Our aim is to elucidate the mechanism of substitutions during doping in order to improve the properties of our material and make it more suitable for optimum use in surface acoustic wave (SAW) devices.

II. THEORETICAL STUDY OF STRUCTURES

To theoretically study the ferroelectric phase transition in magnesium-doped lithium niobate (LiNbO₃:Mg), using the phase

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transition theory developed by Safaryan [9] and maaider et al. [22], which postulates that the ferroelectric-paraelectric transition in LiNbO3 occurs due to the freezing of one of the two optical mode vibrations on planes parallel to the polar axis 'c', where Li⁺, Nb⁵⁺ and O²⁻ ions are distributed. This phase transition is a second-order transition, which implies that it is associated with a discontinuity in the derivative of the order parameter (in this case, polarisation) with respect to temperature. The temperature at which this phase transition occurs is known as the Curie temperature (Tc), and is determined by the frequency of the soft mode (ω_2) associated with the phase transition.

To examine the structure of point defects in non-stoichiometric lithium niobate, Safaryan proposed an equation for determining the soft mode frequency and Curie temperature as a function of parameters such as ionic mass, charge and inter-ionic distances. This equation, known as equation 4, is proving to be a valuable

tool for understanding the ferroelectric phase transition in lithium niobate.

$$T_{C}^{*} = \frac{\omega_{2}^{*2}}{\omega_{2}^{2}} = \frac{M_{0}^{*} + M_{1}^{*} + M_{2}^{*}}{M_{0} + M_{1} + M_{2}} \frac{M_{0}M_{1}M_{2}}{M_{0}^{*}M_{1}^{*}M_{2}^{*}} \frac{P_{2}P_{1}^{*}}{P_{1}P_{2}^{*}} \cdot T_{C}$$
(4)

That's important to note that all physical quantities X (particularly masses and charges) are functions of composition x and the doping parameter y (X*, x, y) since changing from the stoichiometric state considered pure to the doped nonstoichiometric state.

We found in the literature that some authors like Grabmaier and al [20] and N. Iyi and al [17, 23], insisted that the substitution mechanism changed with the concentration of Mg (Table 1). Koyama et al. [24] confirm the similar variation of the Curie temperature Tc of Mg doped LN as a function of magnesium concentration.

Table 1 . Experimental chemical formulae [25] and proposed formula according to (2) models for 1–0.94 (C.L.N) motal fatto.					
Mg%	Experimental formulae analysed [36]	Proposed formulae model (2)			
1% de Mg	$[Li_{0.949}][Nb_{1.007}]Mg_{0.0074}\square_{0.037}O_3$	$[Li_{0.949}][Nb_{1.008}]M_{0.0042}\square_{0.037}O_3$			
3% de Mg	$[Li_{0.924}][Nb_{1.003}]Mg_{0.032}\square_{0.042}O_3$	$[Li_{0.9417}][Nb_{1.001}]M_{0.024}\square_{0.031}O_3$			
5% de Mg	$[Li_{0.896}][Nb_{1.003}]Mg_{0.045}\square_{0.0566}O_{3}$	$[Li_{0.9353}][Nb_{0.995}]Mg_{0.044}\square_{0.024}O_{3}$			

formula according to (2) models for r=0.94 (c I N) molar ratio Table 1. Experimental chemical formulae [23] and propo

We observed that this non-stoichiometric doped structure has two distinct substitution mechanisms. The first one will apply to quantities under 3%, while the second one will apply to values of above or equal to 3%. We proposed model (2) and utilized model (1) given [24] to explain this variation of the experimental results (Table 2).

Dopant	Concentration	Model	
Magnesium (Mg)	3mol%≥[Mg]>0	$[Li_{1-5x-2y}Nb_xMg_y\square_{4x+y}][Nb][O_3]$	[36]
		(Model 1)	
	[Mg] > 3%	$\left[Li_{1-4x-4,25y}Mg_{0,525y-0,5x}\Box_{4,5x+3,725y}\right][Nb_{1+x+0,64y}]$	$\Box_{-(x+0,64y)}][O_3]$
		(Model 2)	
Tetravalent impurity (Ti, Zr, Ce)		$\left[Li_{1-5x+y}Nb_{x}\Box_{4x-y}\right]\left[Nb_{1-y}M'_{y}\right]\left[O_{3}\right]$	[36]
		(Model 3)	

Where M' and \Box are respectively the symbols of tetravalent impurities and vacant site.

Using vacancy models for each dopant and the molar ratio r =[Li]/[Nb], we determined the concentration of non-stoichiometry x (Nb_{Li}) in each sample of MgO-doped and tetravalent impuritydoped LN. As indicated in Table 3, the concentration of x may be represented as a function of the impurity concentration (y) and molar ratio r. Furthermore, in Fig 3, we depicted the development of the non-stoichiometric composition in doped lithium niobate (d-LN) as a function of impurity concentration.

The charge and mass values of the LiNbO3 compound doped with magnesium and tetravalent impurities are presented below:

 $q_{(Nb)} = q_1 = 5; q_{(Li)} = q_2 = 1; q_{(O)} = q_0 = 2; q_{(Mg)} = 2; q_{(Ti)} = q_{(Zr)} = q_{(Ce)}$ =q_5 = 4; $M_{Nb} = M_1 = 92.9 \ a.u$; $M_{Li} = M_2 = 6.94$; $M_O = M_0 = 48$ $M_{Mg}=24.305$; $M_{Ti}=47.86$; $M_{Zr}=91.224$; $M_{Ce}=140.116$

Fig 1 shows the separations between the planes (Li, Nb, and O to T = 0K) [9]. $R_{Nb-0}(R_{10} = 0.883A^{\circ})$, $R_{Li-0}(R_{20} = 0.68A^{\circ})$ and $R_{Li-Nb}(R_{12} = 0.747A^{\circ})$ [26]



Fig 1: Different planes in an elementary cell of crystal LiNbO3

Based on Safaryan theory and using the vacancy model (1). T_c of non-doped lithium niobate non-doped is written:

$$T_C^* = \frac{1+0.39x}{1+5.95x} T_0 \tag{5}$$

 $T_0 = 1210^{\circ}C$ [19] represents the Curie temperature for a material with an exactly stoichiometric composition, while T_{C}^{*} corresponds to the Curie temperature for a non-stoichiometric composition. Tc of doped congruent lithium niobate (c.LN) changes as a function of the nonstoichiometric composition x according to the following relationship [24].

$$T_C(x) = 1186.6 - 49.47x + 3.7827x^2 \quad (^{\circ}C) \tag{6}$$

III. RESULTS AND DISCUSSION

A. Impact of Point Defects on Tc in LN Doped with MgO

In this study, thermally induced point defects were not considered as defect structures. The dominant defects in LN were considered to be Nb_{Li} and V_{Li} , which can be present at levels up to several mole percent.

We depend on the previous vacancy models via comparing the experimental results with the values calculated consistent with the theoretical method. To provide an explanation for the effect of doping at the Curie temperature, we used experimental values of Curie temperature [24]. Fig 2 suggests that the Curie temperature Tc of each series A and B will increase with the concentration of MgO as much as values of 3 mol% and 5 mol%, respectively, before reducing.



Fig 2: Comparison experimental [24] and theoretical Curie temperatures (Tc) of MgO-doped lithium niobate samples (series A and B) as a function of MgO concentration,

As Tc decreases with a decrease in the concentration of Li₂O in our material [25, 26], we observe that Tc of c.LN (series A) is higher than Tc of series B at y=0, which can be explained by way of the fact that series A is wealthier in lithium than series B ([Li]_A = $48,38 > [Li]_B = 47,38$).

The increase in Tc with MgO concentration can be interpreted as the substitution of excess Nb⁵⁺ ions that occupy lithium sites (Nb_{Li}) in LN by means of Mg²⁺ ions, which transition LN from a non-stoichiometric to a quasi-stoichiometric state. This explains why the Tc of series A and series B boom respectively up to 3% and 5% mole MgO awareness (Figure 4) [29]. The decrease in Tc after the critical point for each series is due to the coexistence of Mg²⁺ ions in the lithium and niobium sites, as indicated in Table 2 [25, 27]. Based on our examine, there's a correspondence between theoretical and experimental results (fig 2). Fig 3 shows that the concentration of Nb_{Li} (x) in series A is decease than that of series B, due to a better molar ratio of ([Li]/[Nb]) in series A (48.38/51.62) than in series B (47.38/52.62). The increase of MgO concentration (y) in each series leads to a decrease in Nb_{Li}, as Mg ions replace Nb_{Li} sites. This reduces intrinsic defects and modifies the properties of LN. However, doping of lithium niobate with tetravalent impurities increases intrinsic defects (table 3).



Fig 3: Nb_{Li} concentrations (x) in each impurity-doped as a function of the impurity concentration (y) divalent (Mg) and tetravalent for different LN samples (series A and B). the lines were obtained from Equations 2 and 4.

Table 3: The existing relationship between the nonstoichiometric
composition x (Nb _{Li}) and the impurity concentration (y)

Model	Nonstoichiometric composition x		
1	$x = \frac{1-r}{r+5} - y\frac{2}{r+5} \qquad (2)$		
2	$x = \frac{1-r}{r+4} - y \frac{(4,25+0,64r)}{r+4} (3)$		
3	$x = \frac{1-r}{r+5} + y\frac{1+r}{r+5} \tag{4}$		

B. The Impact of Point Defects on Tc in c.LN Doped with Various Tetravalent Impurities

According to Fig 4, the Curie temperature (Tc) of congruent lithium niobate (c-LN) doped with tetravalent impurities decreases continuously with increasing impurity concentration. This decrease can be explained by the fact that the tetravalent impurities promote an increase in the non-stoichiometry composition x (Nb_{Li}) in the material, as they simultaneously penetrate the lithium and niobium sites (table 4), as shown in Fig 3. Consequently, lithium niobate becomes more non-stoichiometric, and it has been demonstrated that the Tc of LN decreases with increasing non-stoichiometry x (Nb_{Li}) of LN, as shown in Fig 5 [9, 21, 24]. These calculations show that Tc is mainly determined by the concentration of Nb_{Li} in the MgO-doped LN.

Tetravalent impurities M'%	Х	Model (3)
0%	0.0106	$[\text{Li}_{0.9471}][\text{Nb}_{1.0105}]\Box_{0.0422}O_3$
1%	0.0138	$[Li_{0.9408}][Nb_{1.0038}]M'_{0.01}\square_{0.0453}O_3$
3%	0.0203	$[Li_{0.9281}][Nb_{0.9903}]M'_{0.03}\square_{0.0514}O_3$
5%	0.0268	$[Li_{0.9155}][Nb_{0.9768}]M'_{0.05}\square_{0.0575}O_3$
8%	0.0366	$[Li_{0.8966}][Nb_{0.9566}]M'_{0.08}\square_{0.0666}O_3$

Table 4: the chemical formula of congruent lithium niobate (r=0.9372) for different concentrations of the tetravalent impurity (y)

To determine the Curie temperature of doped lithium niobate (LN) as a function of composition x and impurity concentration y, we need to know the Curie temperature of the exact stoichiometric composition, which is around $1207^{\circ}C$.



Fig 4: Shows the variation of the temperature Tc as a function of the concentration of different tetravalent impurities for congruent lithium Niobate c.LN (series A)

C. Influence of Point Defects on the Curie temperature in Doped and Undoped cLN

Tc calculation and defect structure analyses of Mg-doped LN show that Tc depends on the concentration of Nb_{Li}. The Tc of the LN doped with divalent impurities increased with the impurity concentration up to about 3 mol%. In contrast, the Tc of LN doped with tetravalent impurities decreased continuously with increasing impurity concentration. This difference was then analysed as a function of Nb_{Li} concentration.

Fig 8 shows the Tc values for each impurity-doped cLN as a function of Nb_{Li} concentration, obtained by converting the impurity concentrations in Fig 2 and 4. This graph confirms that the Tc values of the impurity-doped and undoped LNs vary with Nb_{Li} concentration.





Note that the lines calculated in this figure are relatively close to each other, which leads to the conclusion that Tc is mainly determined by the amount of Nb_{Li} , regardless of whether the LN has been doped with an impurity or not. The slope of the decrease in Tc is higher for non-stoichiometric lithium niobate (series B) than for congruent lithium niobate (series A). These results can be explained by the difference in the initial lithium concentration of each sample [22] and by an increase in the non-stoichiometry x in the material.

IV. CONCLUSION

This study is devoted to exploring the doping of lithium niobate (LiNbO₃ or LN) with magnesium (Mg) and tetravalent impurities (Ti⁴⁺, Zr⁴⁺, Ce⁴⁺), which have a significant impact on its chemical composition and properties. Using Safaryan's approach and proposing a new vacancy model that provides a more accurate description of point defects in magnesium-doped LN, we have succeeded in aligning theoretical and experimental results for the Curie temperature (Tc).The addition of Mg makes LN almost stoichiometric and increases the Tc when the Mg concentration is low, reaching up to 3% for the A series and 4.8% for the B series. Conversely, tetravalent impurities increase the non-stoichiometry of LN and decrease its Tc.

Stoichiometric LN has advantages in electromechanical applications due to its more regular and ordered crystalline structure. This results in a more robust piezoelectric response, making it better suited to surface acoustic wave (SAW) applications. Therefore, for high-temperature SAW applications, it is preferable to use LN samples doped with low concentrations of magnesium rather than tetravalent impurities.

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REFERENCES

[1] J H Collins, H M Gerard and H J Shaw Appl. Phys. Lett. 13, 312 (1968)

[2] G Malovichko, V Grachev and O Schirmer *AIP Conf. Proc.* **677**, 196 (2003)

[3] V Grachev, G Malovichko and O Schirmir J. Phys. 49, 438 (2004)

[4] A P Wilkinson, A K Cheetham and R H Jarman J. Appl. Phys. 74, 3080 (1993)

[5] N Zotov, H Boysen, F Frey, T Metzger and E Born J. Phys. Chem. Solids. 55, 145 (1994)

[6] J Blumel, E Born and T Metzger J. Phys. Chem. Solids. 55, 589 (1994)

[7] N Iyi, K Kitamura, F Izumi, J K Yamamoto, T Hayashi, H Asano *et al J. Solid State Chem.* **101**, 340 (1992)

[8] P Lerner, C Legras and J P Dumas J. Cryst. Growth. 3, 231 (1968)

[9] F P Safaryan *Physics Letters*. A 255, 191 (1999)

[10] K Maaider, A Jennane, N Masaif and A Khalil *Journal of Modern Physics.* **2**, 7155 (2011)

[11] M Soljacic and J D Joannopoulos Nat. Mater. 3, 211 (2004)

[12] R Bhatt, I Bhaumik, S Ganesamoorthy, R Bright, M Soharab, A Kumar Karnal *et al Crystals.* **7**, 23 (2017)

[13] Xu Y Amsterdam: Elsevier (1991)

[14] DA Bryan, R Gerson and HE Tomaschk Appl Phys Lett 44, 847 (1984)

[15] S Enomoto and S Ashihara J Appl Phys. 110, 063111 (2011)

[16] T Volk, N Rubinina and M Wöhlecke Opt Soc Am B. 11, 1681 (1994)

[17] N Iyi, K Kitamura, Y Yajima, S Kimura, Y Furukawa and M Sato J Solid State Chem **118**, 148 (1995)

[18] T Volk, B Maximov, T Chernaya, N Rubinina, M Wöhlecke and V Simonov *Appl Phys B* **72**, 647 (2001)

[19] O'BRYAN HM, GALLAGHER PK and BRANDLE CD 1985 J Am Ceram Soc. 68 493

[20] Grabmaier BC, Wersing W and Koestler W 1991 *J Cryst Growth.* **110** 339

[21] Gallagher PK and O'Bryan HM 1988 J Am Ceram Soc. 71 56

[22] K Maaider, A Jennane, A Khalil, N Masaif Indian J Phys 86, 575 (2012)

[23] lyi N, Kitavura K, Izumi F, Yamamoto LK, Hayashi T, Asano H 1992 J. Sol. State Chem. **101** 340

[24] C Koyama, J Nozawa, K Fujiwara and S Uda Journal de l'American Ceramic Society **100**, 1118 (2017)

 $\left[25\right]$ Beriniz M , El bouayadi $\,$ O, El barbri N , Maaider k and Khalil A ,

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[26] J Streque, T Aubert, N Kokanyan, F Bartoli, A Taguett, V

Polewczyk, E Kokanyan IEEE Sensors Letters 3, 1 (2019)

[27] PF Bordui, RG Norwood, DH Jundt, MM Fejer *Journal of Applied Physics*. **71**, 875 (1992)

[28]Carruthers JR, Peterson GE, Grasso M and Bridenbaugh PM 1971 J Appl Phys. **42** 1846

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