

# Experimental And Theoretical Study Of The Substitution Mechanism In The W6+: Litao3 Correlated With The Ferroelectric Properties

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**Abstract:** The purpose of the present work is to report the latest results of our experimental and theoretical non-stoichiometry investigations of solid solutions isolated close to LiTaO<sub>3</sub> inside the ternary system Li<sub>2</sub>O-Ta<sub>2</sub>O<sub>5</sub>-(WO<sub>3</sub>)<sub>2</sub> correlated with the ferroelectrics transitions. Dielectric measurements performed on ceramic samples have shown that ferro-paraelectric temperatures transitions T<sub>C</sub> varied along the solids solutions, as the stoichiometry deviates from LiTaO<sub>3</sub>. A Safaryan's theory of ferroelectric transition and the various vacancy models in this work reproduce well the experimental results by explaining the substitution nature of Tungsten hexavalent (W<sup>6+</sup>) in LiTaO<sub>3</sub>.

## I. Introduction

Lithium Tantalate (LiTaO<sub>3</sub>, LT) is well known ferroelectric materials which have been the subject of extensive theoretical and practical investigations due to their properties in electro-optic, electro-acoustic and nonlinear-optics, and to their many applications in various fields of modern technology such as optical wave guides, optical memories, information storage by holography and electro-optic devices, it has a high threshold for photorefractive damage, compared to that of LN, [1-4], in the LiTaO<sub>3</sub> the solid solubility range extends from a bout 46 to 50, 4 %mol of Li<sub>2</sub>O at room temperature [5], the structure of ferroelectric LiTaO<sub>3</sub> belongs to the space group R3c, and present a transition of phase at 665° C. A lot of the physical properties of LiTaO<sub>3</sub> were found to be sensitive to the quantity and quality of incorporated impurities within their network and deviated from their original stoichiometry, for example doping with the WO<sub>3</sub>, because its lattice may contain a deficit anionic and cationic excess, we allowed the synthesis of new solid solutions in nonstoichiometric LiTaO<sub>3</sub> neighbourhood inside the ternary diagram Li<sub>2</sub>O-Ta<sub>2</sub>O<sub>5</sub>-(WO<sub>3</sub>)<sub>2</sub> [6]. In this work a new approach was developed to explain the mechanism of substitution the WO<sub>3</sub> in LiTaO<sub>3</sub> for different lines (I, A, B, C, D, E, F, G, H, L, J)[7] in table 1. Using the Curie temperature dependence on the ion mass, charge and distance between them, this approach showed that the considered models gave the best description of the substitution the WO<sub>3</sub> in the LiTaO<sub>3</sub>.

lines	Chemical formula of the synthesis	Formula of the composition limit
-	LiTaO <sub>3</sub>	LiTaO <sub>3</sub>
I	Li <sub>1+x</sub> Ta <sub>1-x/5</sub> O <sub>3</sub>	LiTaO <sub>3</sub> --- Li <sub>2</sub> O
A	Li <sub>1+4x</sub> Ta <sub>1-2x</sub> W <sub>x</sub> O <sub>3</sub>	LiTaO <sub>3</sub> ---Li <sub>6</sub> WO <sub>6</sub>
B	Li <sub>1+7x</sub> Ta <sub>1-5x</sub> W <sub>3x</sub> O <sub>3</sub>	LiTaO <sub>3</sub> ---Li <sub>4</sub> WO <sub>5</sub>
C	Li <sub>1+x</sub> Ta <sub>1-5x</sub> W <sub>4x</sub> O <sub>3</sub>	LiTaO <sub>3</sub> ---Li <sub>6</sub> W <sub>4</sub> O <sub>15</sub>
D	Li <sub>1-x/7</sub> Ta <sub>1-x</sub> W <sub>6x/7</sub> O <sub>3</sub>	LiTaO <sub>3</sub> ---Li <sub>6</sub> W <sub>6</sub> O <sub>21</sub>
E	Li <sub>1-x</sub> Ta <sub>1-x</sub> W <sub>x</sub> O <sub>3</sub>	LiTaO <sub>3</sub> ---WO <sub>3</sub>
F	Li <sub>1-x</sub> Ta <sub>1-17x/23</sub> W <sub>18x/23</sub> O <sub>3</sub>	LiTaO <sub>3</sub> ---Ta <sub>2</sub> W <sub>6</sub> O <sub>23</sub>
G	Li <sup>1-x</sup> Ta <sub>1-4x/7</sub> W <sub>9x/14</sub> O <sub>3</sub>	LiTaO <sub>3</sub> ---Ta <sub>2</sub> W <sub>3</sub> O <sub>14</sub>
H	Li <sub>1-x</sub> Ta <sub>1-5x/11</sub> W <sub>6x/11</sub> O <sub>3</sub>	LiTaO <sub>3</sub> ---Ta <sub>2</sub> W <sub>2</sub> O <sub>11</sub>
L	Li <sub>1-x</sub> Ta W <sub>x/6</sub> O <sub>3</sub>	LiTaO <sub>3</sub> ---Ta <sub>6</sub> WO <sub>18</sub>
J	Li <sub>1-x</sub> Ta <sub>1+x/5</sub> O <sub>3</sub>	LiTaO <sub>3</sub> ---Ta <sub>2</sub> O <sub>5</sub>

Table 1: Formula and limits of the different solid solutions within the ternary diagram Li<sub>2</sub>O-Ta<sub>2</sub>O<sub>5</sub>-(WO<sub>3</sub>)<sub>2</sub>

## II. Curie temperature of lithium tantalate

In this paper, we consider that the solid solution LiTaO<sub>3</sub> consist of a single crystal on the basis of their structure. The figure 1 represents a dispositions of crystal planes in unit cell of crystal LN. Safaryan's new approach on the ferroelectric transition in the crystal LiNbO<sub>3</sub> is tested another time in order to explain the mechanism of substitution the WO<sub>3</sub> in the LiTaO<sub>3</sub> for different lines [7]. Having the energy of interaction per ion [8], the problem of dynamic vibration is reduced to linear vibration in figure 2. The detail of the theory of ferroelectric transition is similar to that of reference [9]. Show that at T<sub>c</sub>=0°K the

distances between planes (Li, Ta and O) are denoted:  
 $R_{O-O}$  ( $a = 2.30^\circ \text{A}$ ),  $R_{Li-O}$  ( $R_{20} = 0.601^\circ \text{A}$ ),  $R_{Ta-O}$  ( $R_{10} = 0.954^\circ \text{A}$ ),  $R_{Li-Ta}$  ( $R_{21} = a - R_{10} - R_{20}$ ) [10].

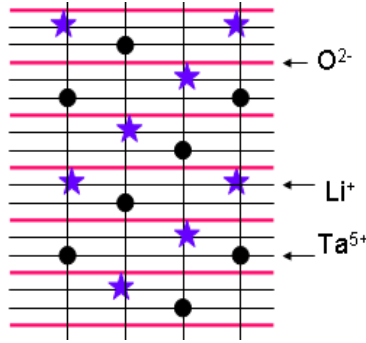


Figure 1: Different planes in an elementary cell of LiTaO<sub>3</sub>

The interactions between planes  $i$  and  $j$  are described by

$$C_{ij} = \frac{e^2 q_i q_j}{b (R_{ij}^0)^2} n, \text{ so we can write finally for}$$

LiTaO<sub>3</sub>,  $C_{ij}$  coefficients are:

$$\begin{aligned} C_{Li-O} &\equiv C_{20} = 3 \frac{q_0 q_2 e^2}{b R_{20}^2} n \\ C_{Ta-O} &\equiv C_{10} = 3 \frac{q_1 q_0 e^2}{b R_{10}^2} n \\ C_{Li-Ta} &\equiv C_{21} = - \frac{q_1 q_2 e^2}{b R_{21}^2} n \end{aligned} \quad (1)$$

Where:  $q_1$ ,  $q_2$  and  $q_0$  are the electric charge of  $Ta^{5+}$ ,  $Li^+$  and  $O^{2-}$ , respectively. The displacements of the

Equation (3) has two optical modes, in the following we take a soft mode that corresponding to a bass frequency  $\omega_2^2$ .

$$\omega_{12}^2 = \frac{1}{2} (F \pm \sqrt{F^2 - 4H}) \quad (4)$$

For small parameter  $((4H/F^2) \ll 1)$

we deduce

$$\begin{aligned} \omega_1^2 &= F - \omega_2^2 \\ \omega_2^2 &= \frac{H}{F} = \frac{ne^2 (M_0 + M_1 + M_2) P_1}{b (M_0 M_1 M_2) P_2} \end{aligned} \quad (5)$$

three ions are denoted by  $u_s (Ta^{5+})$ ,  $v_s (Li^+)$  and  $\xi_s (O^{2-})$

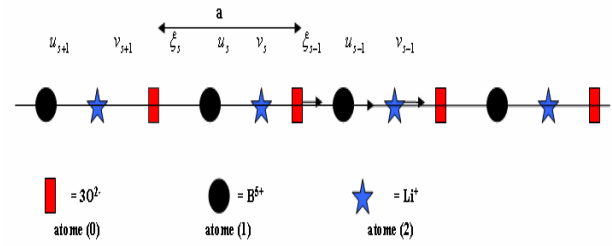


Figure 2 : Linear vibration of ions  $Li^+$ ,  $Ta^{5+}$  et  $3O^{2-}$   
then, the system differential equations of vibration is:

$$\begin{aligned} M_1 \ddot{u}_s &= C_{10} (\xi_{s+1} - u_s) + C_{21} (v_s - u_s) \\ M_2 \ddot{v}_s &= C_{21} (u_s - v_s) + C_{20} (\xi_s - v_s) \\ M_0 \ddot{\xi}_s &= C_{20} (v_s - \xi_s) + C_{10} (u_{s-1} - \xi_s) \end{aligned} \quad (2)$$

Where:  $M_1$ ,  $M_2$  and  $M_0$  are the masses of Ta, Li and O respectively. We show the solutions in the form of plan waves:  $h_s = h e^{i(\omega t + a s k)}$  with  $h = u, v$  or  $\xi$

A system (2) has a nontrivial solution. We put  $k=0$  (the acoustic solution equal to zero) in the determinant equation  $\Delta = 0$ , in order to obtain the fundamental frequencies of optical branches. Then we obtain the equation (3).

$$\text{Where} \quad \omega^4 - F \omega^2 + H = 0 \quad (3)$$

$$\begin{aligned} H &= C_{10} C_{12} \left( \frac{1}{M_0 M_1} + \frac{1}{M_1 M_2} + \frac{1}{M_0 M_2} \right) + \\ &C_{10} C_{20} \left( \frac{1}{M_0 M_1} + \frac{1}{M_0 M_2} + \frac{1}{M_1 M_2} \right) + \\ &C_{12} C_{20} \left( \frac{1}{M_0 M_2} + \frac{1}{M_1 M_2} + \frac{1}{M_0 M_1} \right) \end{aligned}$$

$$F = C_{10} \left( \frac{1}{M_0} + \frac{1}{M_1} \right) + C_{20} \left( \frac{1}{M_0} + \frac{1}{M_2} \right) + C_{12} \left( \frac{1}{M_1} + \frac{1}{M_2} \right)$$

With

$$\begin{aligned} P_1 &= 3q_0 R_{21}^2 - q_1 R_{20}^2 - q_2 R_{10}^2 \\ p_2 &= \frac{(R_{10} R_{21})^2}{q_1} \left( \frac{1}{M_2} + \frac{1}{M_0} \right) - \frac{(R_{10} R_{20})^2}{3q_0} \left( \frac{1}{M_2} + \frac{1}{M_1} \right) \\ &- \frac{(R_{21} R_{20})^2}{q_2} \left( \frac{1}{M_1} + \frac{1}{M_0} \right) \end{aligned} \quad (6)$$

The element  $X$  represents the exact stoichiometric composition and  $X^*$  is the nonstoichiometric composition.

$$X(M, q, T, \omega_2^2, p_1, p_2) \rightarrow X^*(M^*, q^*, T^*, \omega_2^{*2}, p_1^*, p_2^*)$$

At  $T=0^\circ\text{K}$  the soft mode  $\omega_2^2$  is proportional to a Curie temperature, and then the following relation of temperature is:

$$\frac{T_c^*}{T_c} = \frac{\omega_2^2}{\omega_2^2} = \frac{M_0^* + M_1^* + M_2^*}{M_0^* + M_1^* + M_2^*} \left( \frac{M_0^* M_1^* M_2^*}{M_0^* M_1^* M_2^*} \right) \left( \frac{P_1^*}{P_1} \right) \left( \frac{P_2^*}{P_2} \right) \quad (7)$$

This formula allows us to calculate the Curie temperature  $T_c$  of different lines in order to compare with those measured experimentally.

### III: Application of the proposed lacunars models

To explain the mechanism of substitution the  $\text{W}^{6+}$  in  $\text{LiTaO}_3$  based on the Curie temperature, we have proposed in the table 2, the experimental [7] and the proposed formula of different lines, which  $\Theta$  denotes a gap. We put each expression of  $M_0^*$ ,  $M_1^*$ ,  $M_2^*$ ,  $q_0^*$ ,  $q_1^*$  and  $q_2^*$  in equation (7) for different lines, we obtain the expression of Curie temperatures depending on the composition  $x$ , the results are grouped in the table 3. To can represent the variation of the Curie temperature you must calculate the  $\gamma = \text{number}$  of cations - 2, for each line.

Table 2: Experimental and proposed model for different lines.

lines	Chemical formula of the synthesis	Proposed models
-	$\text{LiTaO}_3$	$[\text{Li}][\text{Ta}][\text{O}_3]$
I	$\text{Li}_{1+x}\text{Ta}_{1-x/5}\text{O}_3$	$[\text{Li}_{1+x/5}][\text{Ta}_{1-x/5}\text{Li}_{x/5}]\text{O}_3$
A	$\text{Li}_{1+4x}\text{Ta}_{1-2x}\text{W}_x\text{O}_3$	$[\text{Li}_{1+4x}][\text{Ta}_{1-2x}\text{W}_x\Theta_x]\text{O}_3$
B	$\text{Li}_{1+7x}\text{Ta}_{1-5x}\text{W}_{3x}\text{O}_3$	$[\text{Li}_{1+7x}][\text{Ta}_{1-5x}\text{W}_{3x}\Theta_{2x}]\text{O}_3$
C	$\text{Li}_{1+x}\text{Ta}_{1-5x}\text{W}_{4x}\text{O}_3$	$[\text{Li}_{1+x}][\text{Ta}_{1-5x}\text{W}_{4x}\Theta_x]\text{O}_3$
D	$\text{Li}_{1-x/7}\text{Ta}_{1-x}\text{W}_{6x/7}\text{O}_3$	$[\text{Li}_{1-x/7}\text{W}_{x/7}][\text{Ta}_{1-x}\text{W}_{5x/7}\Theta_{2x/7}]\text{O}_3$
E	$\text{Li}_{1-x}\text{Ta}_{1-x}\text{W}_x\text{O}_3$	$[\text{Li}_{1-x}\text{W}_{x/10}\Theta_{9x/10}][\text{Ta}_{1-x}\text{W}_{9x/10}\Theta_{x/10}]\text{O}_3$
F	$\text{Li}_{1-x}\text{Ta}_{1-17x/23}\text{W}_{18x/23}\text{O}_3$	$[\text{Li}_{1-x}\text{Ta}_{-17x/23}\text{W}_{18x/23}\Theta_{22x/23}][\text{Ta}]\text{O}_3$
G	$\text{Li}_{1-x}\text{Ta}_{1-4x/7}\text{W}_{9x/14}\text{O}_3$	$[\text{Li}_{1-x}\text{Ta}_{-4x/7}\text{W}_{9x/14}\Theta_{13x/14}][\text{Ta}]\text{O}_3$
H	$\text{Li}_{1-x}\text{Ta}_{1-5x/11}\text{W}_{6x/11}\text{O}_3$	$[\text{Li}_{1-x}\text{W}_{x/11}\Theta_{10x/11}][\text{Ta}_{1-5x/11}\text{W}_{5x/11}]\text{O}_3$
L	$\text{Li}_{1-x}\text{Ta}\text{W}_{x/6}\text{O}_3$	$[\text{Li}_{1-x}\text{W}_{x/6}\Theta_{5x/6}][\text{Ta}]\text{O}_3$
J	$\text{Li}_{1-x}\text{Ta}_{1+x/5}\text{O}_3$	$[\text{Li}_{1-x}\text{Ta}_{x/5}\Theta_{4x/5}][\text{Ta}]\text{O}_3$

Table.3: Proposed formula with her expression of Curie temperature.

lines	Proposed formula	Expression of $T_c$ temperature
I	$[\text{Li}_{1+x/5}][\text{Ta}_{1-x/5}\text{Li}_{x/5}]\text{O}_3$	$T_c^* = \frac{(1-0.188x)(1-0.16x)(1+0.511x)}{(1-0.191x)(1+0.070x)(1+0.2x)} T_c$
A	$[\text{Li}_{1+4x}][\text{Ta}_{1-2x}\text{W}_x\Theta_x]\text{O}_3$	$T_c^* = \frac{(1-3.57x)(1-0.8x)(1-0.63x)}{(1-0.98x)(1+0.75x)} T_c$
B	$[\text{Li}_{1+7x}][\text{Ta}_{1-5x}\text{W}_{3x}\Theta_{2x}]\text{O}_3$	$T_c^* = \frac{(1-6.26x)(1-1.4x)(1-1.3x)}{(1-1.96x)(1+1.33x)} T_c$
C	$[\text{Li}_{1+x}][\text{Ta}_{1-5x}\text{W}_{4x}\Theta_x]\text{O}_3$	$T_c^* = \frac{(1-0.89x)(1-0.69x)(1-0.2x)}{(1-0.91x)(1+0.21x)} T_c$
D	$[\text{Li}_{1-x/7}\text{W}_{x/7}][\text{Ta}_{1-x}\text{W}_{5x/7}\Theta_{2x/7}]\text{O}_3$	$T_c^* = \frac{(1-0.64x)(1-0.14x)(1-0.10x)(1+0.71x)}{(1-0.27x)(1+0.12x)(1+2.24x)} T_c$
E	$\text{Li}_{1-x}\text{W}_{x/10}\Theta_{9x/10}][\text{Ta}_{1-x}\text{W}_{9x/10}\Theta_{x/10}]\text{O}_3$	$T_c^* = \frac{(1-0.4x)(1-0.017x)(1+0.08x)(1+0.35x)}{1+0.5x} T_c$
F	$[\text{Li}_{1-x}\text{Ta}_{-17x/23}\text{W}_{18x/23}\Theta_{22x/23}][\text{Ta}]\text{O}_3$	$T_c^* = \frac{1+0.013x}{1+0.24x} T_c$
G	$[\text{Li}_{1-x}\text{Ta}_{-4x/7}\text{W}_{9x/14}\Theta_{13x/14}][\text{Ta}]\text{O}_3$	$T_c^* = \frac{(1+0.033x)}{1+0.582x} T_c$
H	$[\text{Li}_{1-x}\text{W}_{x/11}\Theta_{10x/11}][\text{Ta}_{1-5x/11}\text{W}_{5x/11}]\text{O}_3$	$T_c^* = \frac{(1-0.45x)(1+0.047x)(1+0.09x)(1+0.406x)}{(1-0.027x)(1+0.461x)} T_c$
L	$[\text{Li}_{1-x}\text{W}_{x/6}\Theta_{5x/6}][\text{Ta}]\text{O}_3$	$T_c^* = \frac{1+0.100x}{1+1.760x} T_c$
J	$[\text{Li}_{1-x}\text{Ta}_{x/5}\Theta_{4x/5}][\text{Ta}]\text{O}_3$	$T_c^* = \frac{1+0.124x}{1+2.17x} T_c$

## IV- Results

Table 4: Comparison of Curie temperatures measured and calculated.

Line	X limite	$T_c \text{ exp}(^\circ\text{C}) \pm 10^\circ\text{C}$	$T_c \text{ th}(^\circ\text{C})$
I	0.10	640	651
A	0.06	380	472
B	0.02	370	542
C	0.0375	540	620
D	0.25	435	401
E	0.25	600	571
F	0.23	607	614
G	0.20	538	582
H	0.20	605	601
L	0.21	515	482
J	0.12	485	520

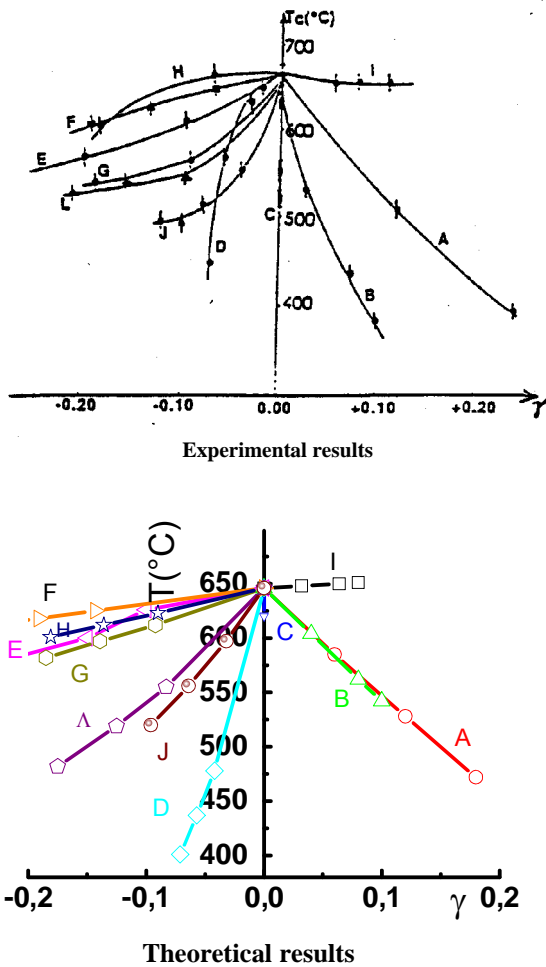


Figure 4: Variation of Curie temperature with  $\gamma$  for studied solid solutions.

## V. Discussion

Only available octahedral sites are at stake, the tetrahedral sites are not affected, assumptions take into account considerations related the symmetry and size of ions involved. For lines A, B and C, they are in the area of excess cationic, the number of  $\text{Li}^+$  ions is much larger than  $\text{Ta}^{5+}$ ,  $\text{W}^{6+}$  appear to preferentially occupy the sites vacated Ta While, for line D, it lies in the area of cationic deficit, the number of  $\text{Li}^+$  cations is relatively larger than  $\text{Ta}^{5+}$ , there is a lack of ions and it is likely that the  $\text{W}^{6+}$  ions occupy the sites vacated of Li and Ta with variable rates. Regarding the lines: E, F, G, H and L the number of ions of  $\text{Ta}^{5+}$

is larger than that of  $\text{Li}^+$ , so the excess  $\text{Ta}^{5+}$  and  $\text{W}^{6+}$  appear to occupy vacant sites of Li, except for line H, where  $\text{W}^{6+}$  probably occupies the vacant sites of Li and Ta with variable rates. Finally for line J the excess Ta seems occupy vacant sites of Li, with creation of gaps in the network of Li.

## VI. Conclusion

The application of the theory of ferroelectric's phase transition of solid solutions studied in the vicinity of  $\text{LiTaO}_3$  gives a good description of the experimental results. A comparative study between the experimental and theoretical results of temperature shows that our proposed models explain well the mechanism of substitution in  $\text{LiTaO}_3$ .

## VII. References

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