



Comments on the Substitution Mechanism of Mg-Doped LiTaO₃ Ceramics

M. Tahiri¹, N. Masaif^{1, 2}, A. Jennane^{1, 2}

¹ Laboratoire Rayonnement & Matière –Equipe de Recherche Physique de la Matière et Modélisation
Département de Physique, Faculté des Sciences et Techniques BP 577 Settat Morocco.
Email : tahisimo@yahoo.fr

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

Received in 26 Apr 2011, Revised 16 Dec 2011, Accepted 16 Dec 2011

*Corresponding author: E-mail: tahisimo@yahoo.fr ;

Abstract

Many properties of LiTaO₃ are influenced by insertion or substitution of the element in this network. We focus our attention on the existence of the defects in the structure of materials LiTaO₃ to determine the substitution mechanism of Mg-doped these compounds for different levels. A new approach based on the variation of the Curie-temperature is introduced and combined with different vacancy models to explain the mechanism of substitution of Mg in LiTaO₃; the calculated values of T_C are close to the experimental data.

Keyword: Ceramics; Defects; Models; Phase transition; LiTaO₃.

1. Introduction

The lithium tantalate has been studied and known recently many applications due to its properties in electro-optics, electro-acoustic and non-linear optics. Recent developments in integrated optics and its applications to signal processing (waveguides for telecommunications, recording technology...) were conducted [1-4]. LiTaO₃ is a ferroelectric material [5], it has a crystal lattice able to accommodate ions through a mechanism of insertion or substitution, each element introduced into the network promotes a perturbation that induces a new ordering of ions from the matrix and therefore the ferroelectric properties are being modified, especially the Curie temperature T_C. The most physical properties of LiTaO₃ and solid solutions derived from it are sensitive to the existence of intrinsic and extrinsic defects appearing in these materials [6-16]. To explain these structural defects we based on the theory of ferroelectric phase transition. The calculation of the T_C which depends on the composition x, shows that T_C increases or decreases as a function on doping with a third cation [17] which allows us to interpret the mechanism of substitution of Mg²⁺ in LiTaO₃ where the solid solution[18](see Fig. 1) are most extensive on the stoichiometric join (LiTaO₃-Mg₄Ta₂O₉) corresponding to substitution mechanism:



But for solid solutions off this join the substitution mechanism is:



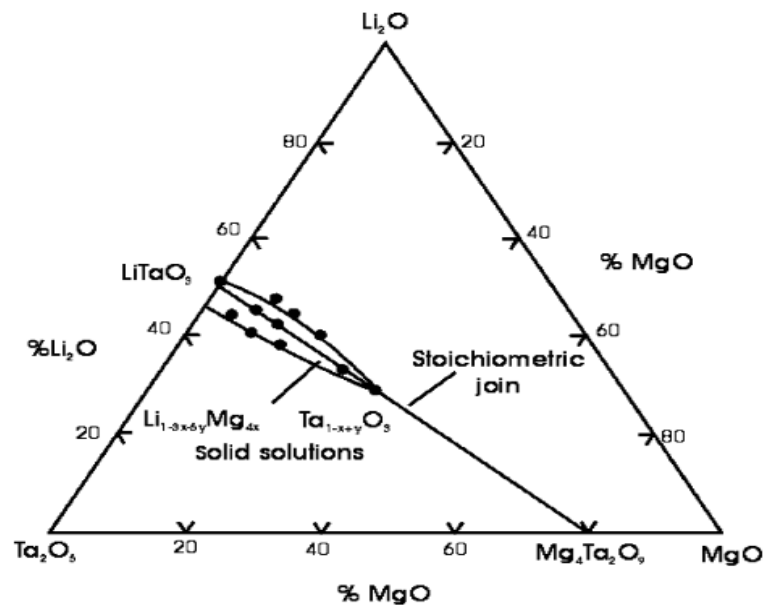


Fig.1. Locus of Mg-doped solid solutions in the system $\text{Li}_2\text{O-MgO-Ta}_2\text{O}_5$

The general experimental formula that represents the solid solutions in the ternary system $\text{Li}_2\text{O-MgO-Ta}_2\text{O}_5$ is: $\text{Li}_{1-3y-5x}\text{Mg}_{4y}\text{Ta}_{1-y+x}\text{O}_3$ [18] where x is the composition and y is the rate of the element Mg^{2+} . All these solid solutions are isolated close to LiTaO_3 inside the ternary system $\text{Li}_2\text{O-MgO-Ta}_2\text{O}_5$. The great objective of our work is to understand the mechanism of substitution of Mg^{2+} in LiTaO_3 on the basis of calculation of the T_c by introducing a new vacancy models.

2. Theory

In this work, we assume that the ceramic LiTaO_3 is formed by the parallel plans along the polar axis "c", each plan represents the same type of atoms, Fig. 2 represents the linear structure showing the position of each ion, and the latter represents a plan of the same type of ions in the unit cell of order s . The distances between planes (Li, Ta, and O à $T=0^\circ\text{K}$) are: $R_{\text{O-O}}$ ($a=2.30^\circ\text{A}$), $R_{\text{Li-O}}$ ($R_{20}=0.601^\circ\text{A}$), $OR_{\text{Ta-O}}$ ($R_{10}=0.954^\circ\text{A}$), $R_{\text{Li-Ta}}$ ($R_{21}=a-R_{10}-R_{20}$) [19].

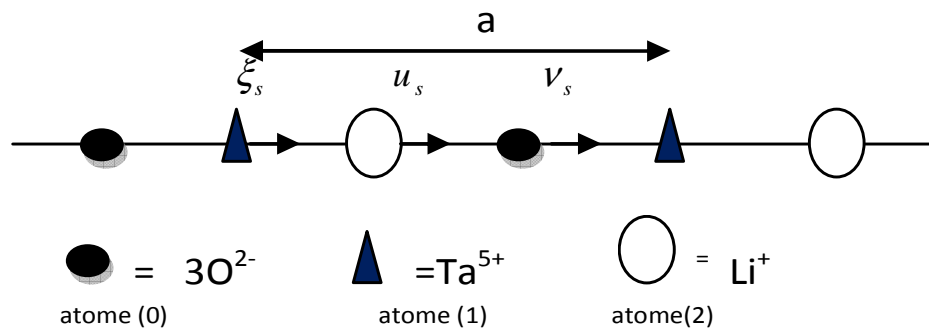


Fig. 2: Linear vibration of ions Li^+ , Ta^{5+} and 3O^{2-}

We avoid the detail of the theory of ferroelectric transition in the LiTaO_3 that is similar to that given in reference [20-23] and we report only the useful expressions in the appendix.

At 0°K, the soft mode frequency ω^2 is proportional to the Curie temperature T_c . We substitute, ω^2 by the expression (A.11) to obtain the following relation that allows calculating the Curie temperature:

$$T_c^* = \frac{\omega_2^{*2}}{\omega_2^2} = \frac{M_0^* + M_1^* + M_2^*}{M_0 + M_1 + M_2} \left(\frac{M_0 M_1 M_2}{M_0^* M_1^* M_2^*} \right) \left(\frac{P_1^*}{P_1} \right) \left(\frac{P_2}{P_2^*} \right) T_C \quad (3)$$

Where X and X* are respectively the stoichiometric and non stoichiometric compositions.

3. Results and discussion

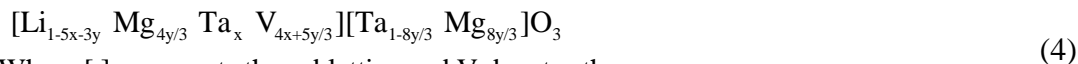
In Table 1 we have presented the different vacancy models and the theoretical values of T_c corresponding to each label (solid solution).

Table 1 Theoretical and experimental temperature of solid solutions studied

Label	Proposed formula	x	y(Mg)	T_{exp} (°C)[18]	T_{the} (°C)
A		-0.024	0.0275	688	661
D	$[Li_{1-5x-3y} Mg_{4y/3} Ta_{x/4} V_{19x/4+5y/3}][Ta_{1+3x/4-8y/3} Mg_{8y/3} V_{-3x/4}]O_3$	-0.0205	0.039	692	683
G		-0.019	0.058	710	712
C		0.019	0.012	688	684
F	$[Li_{1-5x-3y} Mg_{5y/3} Ta_{x/5} V_{24x/5+4y/3}][Ta_{1+4x/5-7y/3} Mg_{7y/3} V_{-4x/5}]O_3$	0.025	0.025	707	698
H		0.018	0.039	695	695
B		0	0.021	696	681
E	$[Li_{1-5x-3y} Mg_{4y/3} Ta_x V_{4x+5y/3}][Ta_{1-8y/3} Mg_{8y/3}]O_3$	0	0.035	718	701
I		0	0.078	733	755
J		0	0.103	765	780

- On the join stoichiometric composition(x=0)

The substitution mechanism of the solid solutions B, E, I and J is represented by the vacancy model:



Where [.] represents the sublattice and V denotes the vacancy

In the sublattice [Li] the excess of Ta^{5+} and Mg^{2+} occupies the vacant sites of Li with creation of the vacancy in this sublattice .

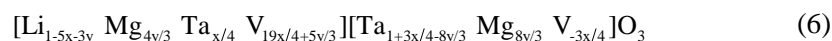
In the sublattice [Ta] we have:



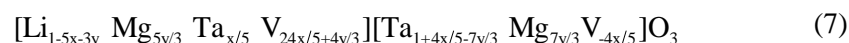
On doping $LiTaO_3$ with Mg^{2+} , we see that Mg^{2+} occupies the vacant sites of Li and Ta with different rates and the T_c increases with increasing %MgO.

- Off the join stoichiometric composition

- When “x” takes the negative values, the substitution mechanism of solid solution A,D and G is described by the vacant model :



- When “x” takes the positive values, the substitution mechanism of solid solution C,F and H is described by the vacant model :



For those last models the Mg^{2+} and Ta^{5+} occupy the vacant sites of [Li], and Mg^{2+} occupies the vacant site in the sublattice [Ta], with creation of vacancy in sublattices [Li] and [Ta].

Conclusion

The application of the theory of ferroelectric phase transition for solid solutions studied in the ternary system $\text{Li}_2\text{O-MgO-Ta}_2\text{O}_5$ [18] in the vicinity of LiTaO_3 gives a good description of experimental results. A comparative study between theoretical and experimental results of T_C shows that our proposed new vacancy models are able to describe substitutional mechanism in Mg-doped lithium tantalate.

References

1. Verber C. M., Hortman N. F., Glass A. M.; *Appl. Phys. Lett.* 3 (1977) 272
2. Kostritskii S. M., Kip D.; *Phys. Status Solidi a- Appl. Res.*; 16 (1998) 171
3. Kip D., *Appl. Phys. B- lasers and optic*, 6 (1998) 131
4. Revue Electronique, n°156(Mars 2005)
5. VLADIMIR YA. SHUR, *Journal of Materials Science* 41 (2006) 199–210
6. Nassau, K., Lines, E. M., *Journal of Appl. Phys.* 41(2) (1970).
7. Kovacs, L., Polgar, K., *Cryst. Res. Technol.* 21, (6) (1986) 101-104
8. Iyi, N., Kitamura, K., Izumi, F., Yamamoto, J.K., Hayashi, T., Asano, H., Kimura, S., *J. Solid State Chem.*, 101 (1992) 340.
9. Wilkinson A.P., Cheetham, A. K., Jarman R.H., *J. Appl. Phys.* 74 (1993) 3080-3083
10. Watanabe, T., Sota, Suzuki, K., Iyi, N., Kitamura, K., Kimura, S., *J. Phys.: Condens. Mater* 7(1995) 3627-3635
11. Boysen, Altorfer, F., *Acta. Cryst.*, B50 (1994) 405-414
12. Yatsenko, A. V., Ivanova, E. M., *Phys. Solid State*, 37(8) (1995)
13. Thomson, J. B., Small, C., Lightfoot, P., Bruce, P., *J. Mater. Chem.* 5 (7) (1995) 1039-1040
14. Yatsenko, A.V., Ivanova, E.N., Sergeev, N. A., *Physica , B* (240) (1997) 254-262
15. Paul, M., Tabuchi, M., West, A.R., *Chem. Mater*, 9 (1997) 3206-3214.
16. Kaczmarek, S. M., Swirkowicz, M., Jablonski, R., Lukasiewicz ,T., Kwasny, M., *J.of. Alloys and Compounds* (2000) 300-301; 322-32
17. Huanosta, A., West, A.R., *J. Appl. Phys.* 61 (1987) 5386.
18. Huanosta, A., Alvarez, E., Villafuerte-Castréjon, M.E., West, A.R, *Materials Research Bulletin* 39 (2004) 2229.
19. Lines, M. E., Glass, A. M., Principles and Application of ferroelectrics and related materials, (Clarendon Press, Oxford, 1977).
20. Safaryan, F. P. *Physics Letters A*, 255 (1999) 191-200.
21. Safaryan, F. P., Feigelson R. S., Petrosyan, A. M., *J. Appl. Phys.*, 85, 8079 (1999) 648.
22. Masaif, N., Jebbari, S., Bennani, F., Hafid, M., Jennane, A. *Phys. Stat. Solidi (b)*, 240 (2003) 640.
23. Tahiri, M., Masaif, N., Lotfi, E. M., Jennane, A., *M. J. Condensed Matter*, 12 (2010) 166.

APPENDIX

The energy of the electrostatic interaction of two charged long lines is,

$$W=e^2\delta_i\delta_jb^2\ln\frac{2l}{R_{ij}}$$

(A.1)

Where $\delta_i = \frac{N_i q_i}{lb}$ with b, l, R_{ij} , q_i and N_i is the cell parameter, the line length, the distance between the lines, the charge of ions and their number respectively. We deduce the full energy of interaction of planes such as:

$$U_{ij} = -\frac{e^2 q_i q_j}{b} \ln \frac{2l}{R_{ij}} + \frac{B_{ij}}{R_{ij}^n} \quad (\text{A.2})$$

Where $B_{ij} = \frac{e^2 q_i q_j}{bn} (R_{ij}^0)^n$ with R_{ij}^0 is the equilibrium distance between planes and n is the index of non electrostatic repulsion for interacting planes.

If we put: $x_{ij} = R_{ij} - R_{ij}^0$, then the energy writes:

$$U_{ij} = \frac{e^2 q_i q_j}{b} \left(\frac{1}{n} - \ln \frac{2l}{R_{ij}^0} \right) + \frac{e^2 q_i q_j n}{b (R_{ij}^0)^2} \frac{x_{ij}^2}{2} \quad (A.3)$$

The coefficient $C_{ij} = \frac{e^2 q_i q_j}{b (R_{ij}^0)^2} n$ describing the interaction between Li and O planes (as well as for Ta and O)

are obtained by differentiating (A.3) from x_{ij}

However, the interaction between Li and Ta will deduce from the total energy:

$$U_{ij} = \frac{e^2 q_i q_j}{b} \ln \frac{2l}{R_{ij}^0} - \frac{B_{ij}}{R_{ij}} \quad (A.4)$$

The C_{ij} coefficients are

$$\begin{aligned} C_{Li-O} &\equiv C_{20} = -3 \frac{q_0 q_2 e^2}{b R_{20}^2} n \\ C_{Ta-O} &\equiv C_{10} = -3 \frac{q_0 q_1 e^2}{b R_{10}^2} n \\ C_{Li-Ta} &\equiv C_{21} = \frac{q_1 q_2 e^2}{b R_{21}^2} n \end{aligned} \quad (A.5)$$

q_1 , q_2 and q_0 are respectively the electric charges of Ta^{5+} , Li^+ and O^{2-} ions. To solve the dynamic problem, we reduced the structure of the charged planes to a system of vibration of linear lattice (Fig. 1). The displacements of the three ions are indicated by $v_s(Li^+)$, $u_s(Ta^{5+})$ us and $\xi_s(O^{2-})$. Then, the system is described by the differential equations as:

$$\begin{aligned} M_1 \ddot{u}_s &= C_{10} (\xi_{s+1} - u_s) + C_{21} (v_s - u_s) \\ M_2 \ddot{v}_s &= C_{21} (u_s - v_s) + C_{20} (\xi_s - u_s) \\ M_0 \ddot{\xi}_s &= C_{20} (v_s - \xi_s) + C_{10} (v_{s-1} - \xi_s) \end{aligned} \quad (A.6)$$

M_1 , M_2 , M_0 are respectively the masses of the elements Ta, Li and 3O. The choice of solutions in the form of plan waves:

$$f_s = f e^{i(\omega t + a s k)} \quad \text{With} \quad f = u, v \text{ or } \xi \quad (A.7)$$

leads to a system, of linear equations, which has a nontrivial solution. In order $f_s = f e^{i(\omega t + a s k)}$ 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:

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

Where

$$B = C_{10} \left(\frac{1}{M_1} + \frac{1}{M_0} \right) + C_{21} \left(\frac{1}{M_1} + \frac{1}{M_2} \right) + C_{20} \left(\frac{1}{M_2} + \frac{1}{M_0} \right)$$

and

$$D = \frac{M_1 + M_2 + M_0}{M_1 M_2 M_0} (C_{10} C_{20} + C_{10} C_{21} + C_{21} C_{20}) \quad (A.9)$$

The two optical modes are given by:

$$\omega_{12}^2 = \frac{1}{2}B \pm \left(\frac{1}{4}B^2 - D\right)^{1/2} \quad (\text{A.10})$$

For small parameter $((4D/B^2) \ll 1)$ we deduce:

$$\omega_2^2 = \frac{D}{B} = \frac{ne^2}{b} \frac{M_1 + M_2 + M_0}{M_1 M_2 M_0} \frac{P_1}{P_2}, \quad \omega_1^2 = B - \omega_2^2$$

Where:

$$P_1 = 3q_0 R_{21}^2 - q_1 R_{20}^2 - q_2 R_{10}^2$$

And

$$P_2 = \frac{(R_{20} R_{21})^2}{q_2} \left(\frac{1}{M_1} + \frac{1}{M_0}\right) + \frac{(R_{10} R_{21})^2}{q_1} \left(\frac{1}{M_2} + \frac{1}{M_0}\right) - \frac{(R_{10} R_{20})^2}{3q_0} \left(\frac{1}{M_1} + \frac{1}{M_2}\right) \quad (\text{A.11})$$

(2012) www.jmaterenvirosnci.com