Structural properties and spontaneous polarization behaviour in Cu-doped LiTaO3

M.Tahiri1,2*, A. Jennane2, N. Masaif3 and E.M. Lotfi4

1Laboratory of LBGIM, Physics and chemistry department, University Hassan 2, ENS- Casablanca, Casablanca, Morocco.
2Laboratory of RM&I, Physics department, Faculty of Sciences and Technics, University Hassan 1, 26000 Settat, Morocco.
3Physics department Faculty of Sciences Kenitra, University Ibn Toufail, Kenitra, Morocco.
4Department of Energy and Environment, University Mohammed V, ENSET, B.P: 6207, Rabat Institutes, Morocco.

* m.tahiri@usms.ma

Abstract. In this work, we have study theoretically the effect of cooling modes on the changes of spontaneous polarisation ($P_s$) of non-stoichiometric solid solutions of Cu-doped LiTaO3 in correlation with the defects structure. The changes of spontaneous polarization in rapid and slow cooling modes with the rate of $\%$ Cu$^{2+}$ and with the Curie temperature, allows us to analyse the defect structure of solid solutions synthesized in ternary system $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-(\text{CuO})_2$ in vicinity of LiTaO3. The theoretical results obtained by application of our approach combined with the proposed vacancy models; show that the cooling modes have an effect on the spontaneous polarization, consequently on the defects structure of Cu-doped LiTaO3. In other hand, the proposed vacancy models investigated by our theoretical approach are able to describe the defect structure and the substitution mechanism in each solid solutions of Cu-doped lithium tantalate.

KEYWORDS: Defect Structure; Vacancy Model; Cu; LiTaO3, Spontaneous polarization; Substitution mechanism.

1. Introduction

Generally, a crystal having a spontaneous polarization is composed of positive and negative ions in a certain temperature range. These ions are at in their equilibrium position for which the free energy of a crystal is minimal and no coincidence of the positive and the negative charges center. Knowing that its dielectric properties strongly depend on the crystalline structure of the material, the axis of spontaneous polarization is in general, one of the crystallographic axes of the material. Spontaneous polarization in ferroelectric materials varies with temperature and it is also sensitive to the electric field created in the material. Abrahams et al [1] have been explained the origin of ferroelectricity in LiTaO3 as a results of displacement of Ta$^{5+}$ and Li$^+$ inside their octaedron sites. In paraelectric phase, the spontaneous polarization disappears because the ions Ta$^{5+}$ are in center of the oxygen octahedral and the ions Li$^+$ are in common faces of octahedron along the c-axis (see figure 1.a). In ferroelectric phase, the spontaneous polarization appears when the ions Ta$^{5+}$ and Li$^+$ are in motion along the c-axis (see figure 1.b). Lithium tantalate (LiTaO3) is one of the most used ferroelectric materials and has been the subject of extensive studies, due to their properties in electro-optics, electro-acoustic and nonlinear optics. Their physical properties have influenced by defects (intrinsic or extrinsic) structures [2–7].
Lithium tantalate undergo only one structural phase transition corresponding to a ferroelectric - paraelectric phase transition at temperature \( T_c \) equal to 938K [8]. His ferroelectric structure belongs to the \( R3c \) space group and the atomic arrangement consists of oxygen octaedra sharing faces along the polar trigonal axis. In this work, based on the ferroelectric phase transition theory developed by Safaryan [9], we study the effect of slow and rapid cooling modes on spontaneous polarization in correlation with defects structure of solid solutions synthesized in the vicinity of LiTaO\(_3\) in the ternary system Li\(_2\)O-Ta\(_2\)O\(_5\)-(CuO)\(_2\).

2. Theoretical approach

The structure of the ferroelectric material LiTaO\(_3\) as well as that of LiNbO\(_3\) belongs to space group \( R3c \) and can be considered as a superstructure of the \( \alpha-Al_2O_3 \) corundum structure, with \( Li^+ \) and \( Ta^{5+} \) cations along the c-axis [10]. The formula of spontaneous polarization proposed by Safaryan [9] on ferroelectric phase transition in the crystal LiNbO\(_3\) and investigated by Tahiri et al [6] in LiTaO\(_3\) and LiNbO\(_3\) doped with the nickel is tested also for Cu- LiTaO\(_3\), it can apparently write:

\[
P_0 = \frac{Ne}{V} (q_2 R_{20} + q_1 \left( \frac{a}{2} - R_{10} \right)) \quad [6, 9]
\]

Where \( N \) is the number of Li or Ta ions in the elementary cell of the crystal, \( V \) is the volume of the elementary cell, \( a \) is the distance between two oxygen planes, \( R_{10} \) and \( R_{20} \) are respectively the distances between Ta, Li and O and \( q_1 \) et \( q_2 \) are respectively the charges of Ta and Li.

In this work, while the content of Cu occupy the sites of Li or Ta with the variable rates, we are only three plans and the above formula is applicable successfully in this case of Cu doped LiTaO\(_3\). Than we can write

\[
P_s^* = \frac{Ne}{V^*} (q_2^* R_{20} + q_1^* \left( \frac{a}{2} - R_{10} \right)) \quad [6, 9]
\]

Where \( q_1^* \) and \( q_2^* \) are respectively the charges of Ta and Li ions in nonstoichiometric case. \( V^* \) is the volume of elementary cell which changes with the changes of cell parameters \( a_H \) and \( c_H \) by doping of Cu.

The proposed and simplified vacancy models of solid solutions described the defects structure of Cu doped LiTaO\(_3\) in the cases of slow and rapid cooling modes are in Table 1.

| Table 1: Analytical formulae of lines B and D in cases of slow and rapid cooling modes |
|---|---|---|
| Lines | Analysed models | Proposed and simplified models |

\( P_0 \) and \( P_s^* \) represent the spontaneous polarization in ferroelectric and paraelectric phases, respectively.
Our approach combined with the above vacancy models allows us the calculation of spontaneous polarization as a function of % Cu. For each vacancy model, we substitute the charges with her expressions in non-stoichiometric case, for example:

Line B:
\[ q_1^* = (1-x)q_1 + \frac{3x}{2} q_{Cu} \] et \[ q_2^* = (1-x)q_2 + \frac{3x}{2} q_{Cu} \]

Line D:
\[ q_1^* = (1-\frac{x}{3})q_1 + \frac{2x}{3} q_{Cu} \] et \[ q_2^* = (1-x)q_2 + \frac{2x}{3} q_{Cu} \]

The injection of those quantities in the formula of spontaneous polarization gives the analytical formulae situated in table 2.

Table 2: Analytical formulae of lines B and D in cases of slow and rapid cooling modes, where: \( V_{Sc} \) and \( V_{Rc} \) are respectively the volume of unit cell of B and D in slow and rapid cooling modes.

| Lines | Proposed and simplified models | Analytical formulae |
|-------|--------------------------------|---------------------|
| Line B | \([\text{Li}_{1-x}\text{Cu}_{3x/2}][\text{Ta}_{1-x}\text{Cu}_{3x/2}]\text{O}_3\) | \( P_s(B) = 1.52 + 0.78x \) \( V_{Sc}(B) \) |
| Line D | \([\text{Li}_{1-x}\text{Cu}_{2x/3}][\text{Ta}_{1-x/3}\text{Cu}_{2x/3}]\text{O}_3\) | \( P_s(D) = 1.52 + 0.13x \) \( V_{Sc}(D) \) |

3. Results and discussion

Our approach, which combines a ferroelectric phase transition theory and the above vacancy models allow us to calculate and to analyse the behaviour of the spontaneous polarization of Cu doped LiTaO₃. The analytical formulae corresponding of each vacancy model in two cases of cooling modes are in table 2. Generally, in the two cases of slow and rapid cooling modes, the theoretical results obtained by our approach show that the spontaneous polarization depends strongly of the quantity of dopant for the two lines B and D with some difference.

**Figure 2.** Variation of spontaneous polarization for Cu-doped LiTaO₃ as a function of % Cu in rapid and slow cooling modes
The figure 2 represents the spontaneous polarization of lines B and D in cases of slow and rapid cooling modes, we see that the spontaneous polarization increases with the rate of Cu, this result is similar to that of LiNbO₃ and LiTaO₃ doped by the nickel [6]. This phenomenon may be explained by the substitution of the vacant sites of Li and Ta with the variable rate of Cu. In this work we choose to study the case where 50 percentage of Cu occupy the site of Li and other rate occupy the sites of Ta. According to this results we assume that the spontaneous polarization increases when Cu occupy totally the site of Li, because this latest become big than the opening of triangle oxygen and is not able to pass through it. Consequently, the Li occupy both sites above and below the oxygen triangle with equal rates and the Ta ions occupies the center of its octahedron of oxygen, this result is similar to that concluded by Safaryan when, He analysed LiNbO₃ based on TC. We have confirmed our proposition by study of the spontaneous polarization as function of the Curie temperature in two cases of cooling modes; the results are gathered in figure 3. It shows that the spontaneous polarization increases with decreasing of Curie temperature.

This result is logical because generally, at low temperatures and sometimes at temperatures below of Tc, LiTaO₃ is ferroelectric material.

4. Conclusion
In this paper, we have study and analyze in the cases of rapid and slow cooling modes the defect structure of non-stoichiometric solid solutions of Cu doped LiTaO₃, in correlation with the changes of the spontaneous polarization at different rates of Cu content and as a function of Tc. The results shows the proportionality between the increasing of Ps with increasing of Cu content in Li site and allows us to predict and to propose the suitable vacancy models that describing this defect in the structure of Cu doped LiTaO₃. In other hand, this study shows that the Ps increases when Tc decreases.

References
[1] Abrahams S C and Bernstein J L 1967 J. Phys. Chem. Solids 28 1685
[2] Dash B N, Dash P, Rath H, Mullick P, Biswal R, Kuliya P K, and Mishra N C 2010 Indian J. Phys. 84 1315
[3] Sanyal P, Tarat S and P Majumdar 2010 Indian J. Phys. 84, 1379
[4] Modi K B, Pathak T K, Vasoya N H, Lakhani V N, Balidha G J and Jha P K 2011 Indian J. Phys. 85 411
[5] Tahiri M, Jennane A, Masaif N and. Lotfi E. M 2019 Ferroelectrics 540 222-226, DOI: 10.1080/00150193.2019.1611098
[6] Tahiri M, Masaif N and. Jennane A 2015 Ferroelectrics, 481 189–195 DOI: 10.1080/00150193.2015.1051931
[7] Tahiri M, Jennane A, Masaif N, Lemdek E.M and Lotfi E M 2018 Ukr. J. Phys. 63 347
[8] Razbirin B. S 1964 Sov. Phys. Solid State 6 254
[9] Safaryan F. P 1999 Phys. Lett. A 255 191
[10] Abrahams S C and Bernstein L J 1967 Phys. Chem. Solids 28 1685