
STUDY OF ELECTRICAL CONDUCTIVITY IN WO₃-DOPED NONSTOICHIOMETRIC LiTaO₃

M. TAHIRI,¹ N. MASAIF,¹ A. JENNANE,^{1,2} E.M. LOTFI³

¹Physics Department, Equipe de Recherche Physique de la Matière et Modélisation, Faculty of Sci. and Techn.

(BP 577, Settat, University Hassan 1st, Morocco; e-mail: tahisimo@yahoo.fr)

²National School of Applied Sciences (ENSA)

(BP 77, Khouribga, University Hassan 1st, Morocco)

³Department of Mechanical Engineering, ENSET

(BP 6207, Rabat Institute, University Mohammed V-Souissi-Rabat, Morocco)

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The results of experimental and analytical studies of the electrical conductivity for different solid solutions synthesized in a vicinity of LiTaO₃ in the ternary system Li₂O-Ta₂O₅-(WO₃)₂ are presented. It is shown that the electrical conductivity increases linearly with the Curie temperature. The experimental conductivity between 200 and 700 °C was measured using an LCR bridge HP4192A on ceramics sintered at 1250 °C. Within the theoretical approach to the defect structure analysis combined with our proposed vacancy models, the theoretical results are in a good agreement with the experimental data.

the mechanism of insertion and/or substitution, giving rise to a wide field of nonstoichiometry.

In any preparation or synthesis, the ratio Li/Ta varies in a wide range. This variation has a great influence on the physico-chemical properties of the material [3, 10] such as the electrical conductivity, the Curie temperature, density, etc.

In works [11–16], the conductivity related to domain walls in ferroelectrics, different conduction mechanisms, and different types of walls was studied.

In the present work, the experimental conductivity between 200 and 700 °C is measured, by using an LCR bridge HP4192A on ceramics sintered at 1250 °C. The plots of the electrical conductivity between 400 and 700 °C have linear variations of the Arrhenius type. We analyze only the electrical conductivity as a function of the temperature for lithium tantalate doped with WO₃ at different compositions x . The experimental models [17] studied in this work are: The line C that has the formula Li_{1+x}Ta_{1-5x}W_{4x}O₃, and the line H where its formula is Li_{1-x}Ta_{15x/11}W_{6x/11}O₃. The calculation of the electrical conductivity allows us to understand and to explain the mechanism of substitution of WO₃ in LiTaO₃. The suggested models are presented in Table 1. The model C which belongs to the cation area excess is represented by the formula [Li_{1+x}][Ta_{1-5x}W_{4x}V_x]O₃, where [.] represents the sublattice and Θ denotes the vacancies. In this model, the sublattice of Li is saturated, while the excess of WO₃ occupies the vacant sites in the sublattice of Ta, with the creation of vacancies

1. Introduction

Lithium tantalate (LT) has been recently considered in a large number of theoretical works and applications in electrooptics, electroacoustics, and nonlinear optics due to its properties. LT does not have the perovskite structure. The structure of ferroelectric LiTaO₃ belongs to the space group $R3c$ and can be considered as a superstructure of the α -Al₂O₃ corundum structure. Within the oxygen cages, the cations appear along a trigonal polar c -axis [1]. This material, which shows a ferroelectric behavior, is well known to be a narrow-range nonstoichiometric compound and is a ferroelectric at room temperature. The material [2] consists of the stacking of oxygen octahedra Ta₂O₆ and Li₂O₆, where two ions Li⁺ and Ta⁵⁺ occupy two thirds of the oxygen octahedra, and the other third is empty. It is likely for host ions by

Table 1. Chemical formula obtained by the analysis, and the proposed formula according to the C, H, and LiTaO₃ models, with the values of activation energy and log(σ_0) for different lines at different compositions x

Line	Experimental formula	Proposed formula	Compositi on (x)	Ea _{exp.} (eV)	Log(σ_0)($\Omega^{-1} \text{ cm}^{-1}$)
LiTaO ₃		–	–	0.84	–1.5
C	Li _{1+x} Ta _{1-5x} W _{4x} O ₃	[Li _{1+x}][Ta _{1-5x} W _{4x} Θ _x]O ₃	0.0125 0.01 0.0375	0.79 1.32 0.87	–0.4 8.6 2.9
H	Li _{1x} Ta _{15x/11} W _{6x/1} O ₃	[Li _{1-x} W _{x/11} Θ _{10x/11}][Ta _{15x/11} W _{5x/11}]O ₃	0.10 0.20	1.28 0.59	3.4 –3.6

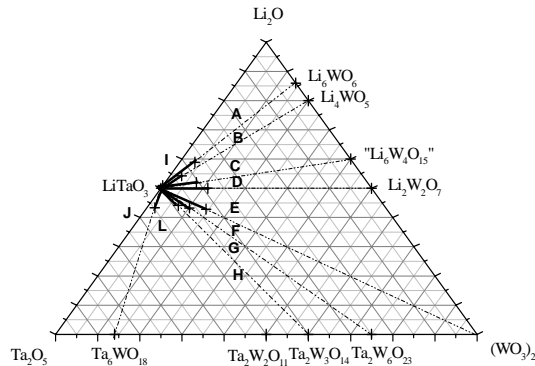


Fig. 1. Extent of different solid solutions synthesized in the ternary diagram Li₂O – Ta₂O₅ – (WO₃)₂

in this network. The other model H, which belongs to the cation area deficiency, is described by the formula $[\text{Li}_{1-x}\text{W}_{x/11}\Theta_{10x/11}][\text{Ta}_{1-5x/11}\text{W}_{5x/11}]\text{O}_3$. In this vacancy model, the excess of W⁶⁺ occupies the vacant sites of Li and Ta with variable rates. The calculated values and the experimental data of the conductivity of models C and H and the pure LiTaO₃ are in good agreement.

2. Experimental Part

The experimental technique and the preparation of the solid solutions have been described in [17]. The measurements of conductivity were made between 200 and 720 °C with the use of an LCR bridge HP4192A on ceramics sintered at 1250 °C. E.M. Lotfi [17] showed experimentally that the conductivity $\sigma(1/T)$ between 200 and 700 °C for some solid solutions, which are located in the ternary system Li₂O–Ta₂O₅–(WO₃)₂ and represent the areas of excess cationic and cationic deficits (see Fig. 1), increases with the temperature, but there are the points of inflection near temperatures of 300–400 °C.

We will focus only on the values of conductivity measured between 400 °C and 720 °C. Figure 2 represents the logarithmical conductivities measured at different compositions x as a function of the reciprocal temper-

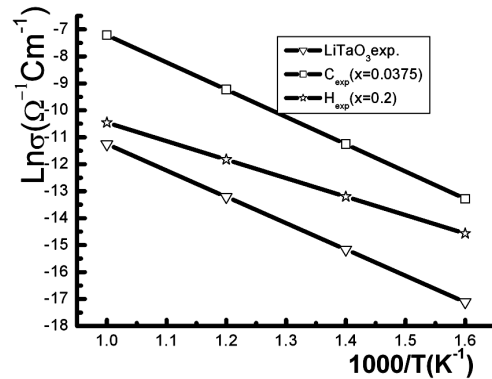


Fig. 2. Thermal evolution of the experimental values of conductivity as a function of $10^3/T$ measured between 400 and 720 °C, at 10 KHz for solid solutions of composition limits of the system Li₂O–Ta₂O₅–(WO₃)₂

ature, where the plots of conductivity reveal the linear Arrhenius type. In what follows, we consider only lines C and H and the nonstoichiometric line LiTaO₃.

3. Theoretical Approach

Here, we consider that the solid solution LiTaO₃ consists of a single crystal. On the basis of its structure, Safaryan's new approach to the ferroelectric transition in the crystal LiNbO₃ was tested recently in order to explain the mechanism of substitution of WO₃ in LiTaO₃ for different lines. The details of the theory of the ferroelectric transition are similar to those in [18, 20]. In this work, we report only on the useful expressions. Below, the elements X and X^* are related to exactly stoichiometric and nonstoichiometric compositions, respectively. At $T = 0$ °K, the soft mode frequency ω_2^2 is proportional to the Curie temperature. So, relation (1) allows us to calculate the Curie temperature, and Table 2 regroups the formula for T_c^* :

$$T_c^* = \frac{\omega_2^{*2}}{\omega_2^2} = \frac{M_0^* + M_1^* + M_2^*}{M_0 + M_1 + M_2} \times$$

Table 2. Curie temperature T^* as a function of the nonstoichiometric composition x , for C and H vacancy models

Line	Proposed Formulae	$T_c^* = g(x)T_c$
C	$[Li_{1+x}][Ta_{1-5x}W_{4x}V_x]O_3$	$T_c^* = \frac{(1 - 0.89x)(1 - 0.69x)(1 - 0.2x)}{(1 - 0.91x)(1 + 0.21x)}T_c$
H	$[Li_{1-x}W_{x/11}V_{10x/11}][Ta_{1-5x/11}W_{5x/11}]O_3$	$T_c^* = \frac{(1 - 0.454x)(1 + 0.047x)(1 + 0.09x)(1 + 0.406x)}{(1 - 0.027x)(1 + 0.461x)}T_c$

Table 3. Equations of theoretical conductivity and the values of nonstoichiometric functions of different lines for different compositions x

Line	$\text{Log } \sigma^* = \text{Log } \sigma_a - Bz$	Composition (x)	$g(x)$	$E_{a\text{exp.}}$	$E_{a\text{the.}}$ (eV)	$\text{Log } (\sigma_0)$ ($\Omega^{-1} \text{cm}^{-1}$)
LiTaO ₃	$-1.5 - 9.76z$	-	0	0.84	0.83	-1.5
C	$-1.4 - 9.56z$	0.0125	0.98	0.79	0.8	-0.4
	$8.6 - 15.98z$	0.01	0.99	1.32	1.36	8.6
	$2.9 - 10.53z$	0.0375	0.96	0.87	0.86	2.9
	$3.4 - 16z$	0.10	0.96	1.28	1.32	3.4
H	$-3.6 - 7.37z$	0.20	0.93	0.59	0.58	-3.6

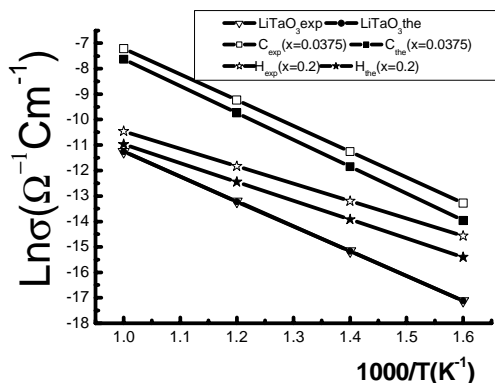


Fig. 3. Experimental and theoretical conductivities as a function of $10^3/T$ for solid solutions of the composition of the system $Li_2O-Ta_2O_5-(WO_3)_2$

$$\times \left(\frac{M_0 M_1 M_2}{M_0^* M_1^* M_2^*} \right) \left(\frac{P_1^*}{P_1} \right) \left(\frac{P_2}{P_2^*} \right) T_c. \tag{1}$$

The electrical conductivity can be described by the Arrhenius law

$$\sigma = \sigma_0 e^{-\frac{E_a}{K_B T_c}} \tag{2}$$

where σ_0 is the pre-exponential factor, E_a is the activation energy, K_B is the Boltzmann constant, and T_c is the Curie temperature (K). Note that the presence of nonstoichiometry in the form of lattice vacancies influences the physical properties of $LiTaO_3$ such as the electrical conductivity. In this case, we must redefine the Arrhenius law, by taking this effect into account. We introduce the conductivity σ^* to explain the role of the defect structure in nonstoichiometric lithium tantalate

doped with WO_3 :

$$\sigma^* = \sigma_0 e^{-\frac{E_a}{K_B T_c^*}} \tag{3}$$

Then we can write Eq. (3) in the following form:

$$\text{Log } \sigma^* = \text{Log } \sigma_0 - \frac{E_a}{K_B g(x) 10^3 T_c^*} \tag{4}$$

The function $g(x)$ characterizes the defects of the structure. Assuming that

$$z = \frac{10^3}{T}, \quad B = \frac{E_a}{K_B g(x) 10^3},$$

we can write

$$\text{Log } \sigma^* = \text{Log } \sigma_0 - Bz \tag{5}$$

The results of calculations are represented in Table 3.

4. Results and Discussion

The effect of the incorporation of WO_3 in $LiTaO_3$ on the conductivity is studied on the basis of our proposed models. Those models have been tested by comparing the experimental data with the calculated values of conductivities within this theoretical approach. We note that the plots which represent the calculated and experimental conductivities are parallel. The resemblance of these results allows us to think that our proposed models explain the mechanism of substitution in $LiTaO_3$. Figures 2 and 3 represent the plots of the conductivity as a function of $10^3/T$. The conductivity increases

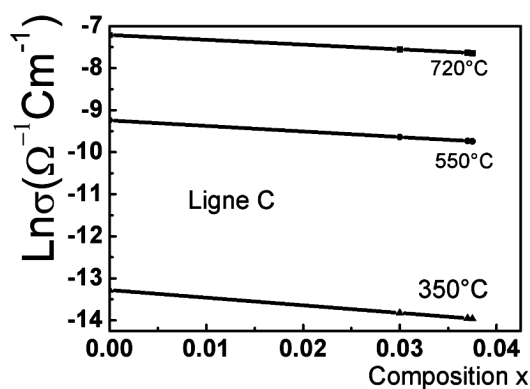


Fig. 4. Variation of the conductivity as a function of the composition x for three values of T_C

with the temperature, so the solid solutions belonging to the cationic excess area are more conductive than those in the cationic deficit area. In Fig. 4, the plots of line C show that the conductivity decreases slightly with increasing the composition x . This phenomenon may be due to the blockage of ions Li^+ responsible for the conduction by the excess of tungsten. In the case of nonstoichiometric undoped LiTaO_3 , Masaif *et al.* [21] have shown that the increase of the conductivity with the composition x results from an increasing Ta density and a decreasing Li density.

5. Conclusion

In the present work, we have studied, within our approach, the conductivity as a function of the temperature and composition x in LiTaO_3 ceramics doped with WO_3 . The theory of ferroelectric phase transition combined with our proposed vacancy models gives a good agreement with the experimental results. The comparison of our vacancy models and the experimental values of conductivities shows that the proposed models can be used to describe the defects and the mechanism of substitution in the structure of LiTaO_3 doped with tungsten.

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ДОСЛІДЖЕННЯ ЕЛЕКТРОПРОВІДНОСТІ НЕСТЕХІОМЕТРИЧНОГО LiTaO_3 З ДОМІШКОЮ WO_3

М. Тахірі, Н. Масаїф, А. Джєннан, Е.М. Лотфі

Резюме

Представлено результати експериментальних і аналітичних досліджень електропровідності різних твердих розчинів, синтезованих поблизу LiTaO_3 у трикомпонентній системі $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$. Показано, що електропровідність зростає лінійно зі зростанням температури Кюрі. Виміри зроблено LCR-містком типу HP4192A на кераміці, відпаленій при 1250°C . Запропоновані вакансійні моделі спільно з відомим методом аналізу дефектних структур добре узгоджуються з даними експерименту.

ИССЛЕДОВАНИЕ ЭЛЕКТРОПРОВОДНОСТИ
НЕСТЕХИОМЕТРИЧЕСКОГО LiTaO_3 С ПРИМЕСЬЮ WO_3

М. Тахири, Н. Масаиф, А. Дженнан, Е.М. Лотфи

Р е з ю м е

Представлены результаты экспериментальных и аналитических исследований электропроводности различных твердых

растворов, синтезированных вблизи LiTaO_3 в трехкомпонентной системе $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$. Показано, что электропроводность растет линейно с ростом температуры Кюри. Измерения сделаны LCR-мостиком типа HP4192A на керамике, отожженной при 1250°C . Предложенные вакансионные модели совместно с известным методом анализа дефектных структур хорошо согласуются с данными эксперимента.