Substitution Mechanism of Ni:$LiTaO_3$

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Abstract

A new approach to the intrinsic and extrinsic defect subsystems, considering them as one integrated functional system, is developed for complex oxides. The strong interrelation of these subsystems becomes especially apparent when concentrations of both defect classes are comparable. Experimental results on tantalite lithium $LiTaO_3$ doped with nickel, we will verify the reliability of this results by our theory. We focus our attention on the existence of intrinsic defects in the structure cause variations of physico-chemical materials $LiTaO_3$ to determine precisely the substitution mechanism of these compounds for different levels doping of Ni.

Keywords: Structural materials, lattice defect structure, Lithium vacancy Model, Ni: $LiTaO_3$

Introduction

The fast development of optoelectronics, acousto-electronics and photonics demands new materials with improved characteristics. Sometimes the requested quality or parameters can be successfully achieved from well-known commonly used materials with respective changes to the defect system of the material. However, mainly the lack of knowledge on the rather complicated interrelations between intrinsic and extrinsic defects, their mutual influence and correlation often does not allow us to overcome some drawbacks of the material characteristics in order to make them fit entirely to the specific industrial requirements.

The structure of ferroelectric $LiTaO_3$ (LT) as well as that of $LiNbO_3$ (LN) belong to space group R3c and can be considered as a superstructure of α Al_2O_3 corundum structure, with Li^+ and Ta^{5+} cations along the c-axis [1]. LT and LN are well-known to be narrow-range nonstoichiometric compounds; in LT, the solid solubility range extends from about 46 to 50.4% mol Li_2O at room temperature [2]. The Curie temperature T_C decreases linearly with decreasing Li_2O concentration [3,4]. Different defect models were proposed to account for non stoichiometry. The following lattice imperfections can be considered: antisite defect Nb^{5+}_{Li+}, lithium vacancy v_{Li+}, niobium vacancy v_{Nb5+}, niobium on structural vacancy Nb^{5+}_{v}, lithium on structural vacancy Li^{+}_{v}, oxygen vacancy v_{O2-} and interstitial oxygen O_i. The exact ratios of the relative concentrations of these defects in the crystals have not yet been reliably determined. The oxygen vacancy model was eliminated [5,6] and among the cation site vacancy models, the Li-site vacancy model [5,7,8] seems more probable than the Nb-site vacancy model [9-11]. Different works were published on LN or LT doped with different cations [6,8,12].

Nickel (Ni) in relation with the substitution mechanism when the Ni content increases. In the present paper we propose defect models in order to interpret some observed phenomena such as change of substitution mechanism.

Vacancy Models of Ni-doped lithium tantalate

According to the literature, we found that some authors like Paul [13], Katsumata [14] and Bennani [15] have insisted that the substitution mechanism changes with the concentration of Ni, determining the temperature transition T_c and ionic conductivity of ceramic LT, doped nickel.

The samples used in experimental studies [15] were prepared starting from Li_2CO_3 carbonate, Ta_2O_5 and NiO oxydes. The mentioned reagents weighted and mixed in the required amounts according to the following chemical reaction.

$$(0.49-\mathrm{x}/2)Li_2CO_3+(0.502-x/10)Ta_2O_5+xNiO\rightarrow Li_{0.98-x}Ta_{1.004-x/5}Ni_xO_3+(0.49-x/2)CO_2 \qquad (1)$$

From the table 1 below, given the chemical analysed formulae and proposed. The number of vacancies was calculated by subtraction of the amount of cation sites, considering a main substitution mechanism $5Li^{+}+Ta^{5+}\leftrightarrow 5Ni^{2+}$. The errors in the formulae obtained were estimated to be about 0.8% for Li, 0.1% for Ta, and 0.5% for Ni.

We found that there are two substitution models in this structure doped non-stoichiometric. The first will be valid for the concentrations lower than 3% and the second, for those superior than or equal to 3%.

Table 1: experimental chemical formulas [15] and proposed the LT doped nickel.

%Ni	Experimental formulas analysed	Proposed formulas
0	$Li_{0.977}Ta_{1.005}O_3$	$[Li_{0.977}Ta_{0.005}\nabla_{0.019}][Ta]O_3$
1	$Li_{0.972}Ta_{1.002}Ni_{0.010}O_3$	$[Li_{0.96}Ta_{0.0015}Ni_{0.01}\nabla_{0.0165}][Ta]O_3$
2	$Li_{0.955}Ta_{1.001}Ni_{0.02}O_3$	$[Li_{0.955}Ta_{0.001}Ni_{0.02}\nabla_{0.024}][Ta]O_3$
3	$Li_{0.942}Ta_{0.999}Ni_{0.03}O_3$	$[Li_{0.9420}Ni_{0.029}\nabla_{0.029}][Ta_{0.999}Ni_{0.001}]O_3$
5	$Li_{0.912}Ta_{0.998}Ni_{0.050}O_3$	$[Li_{0.912}Ni_{0.048}\nabla_{0.057}][Ta_{0.998}Ni_{0.002}]O_3$
8	$Li_{0.897}Ta_{0.988}Ni_{0.08}O_3$	$[Li_{0.897}Ni_{0.068}\nabla_{0.035}][Ta_{0.988}Ni_{0.012}]O_3$
15	$Li_{0.836}Ta_{0.973}Ni_{0.15}O_3$	$[Li_{0.836}Ni_{0.123}\nabla_{0.041}][Ta_{0.973}Ni_{0.027}]O_3$
20	$Li_{0.78}Ta_{0.964}Ni_{0.20}O_3$	$[Li_{0.780}Ni_{0.164}\nabla_{0.056}][Ta_{0.964}Ni_{0.036}]O_3$

In Fig. 1, the result of normal Ta site (Ta_{Ta}) measurement is presented. The Ta_{Ta} tends to decrease with Ni doping. The variation of Ta_{Ta}, indicates two Ni-substitution changes found. Below 3 mol. %, that is I region, the Ta remains constant with Ni concentration increase. In region II, the Ta decrease linearly with Ni concentration increase.

We proposed that for Ni doping concentration under 3 mol% (I), the substitution mechanism is:

$$[Li_{1-5x-3y}Ta_{x-y}Ni_{4y}\nabla_{4x}][Ta][O_3] \qquad (2)$$

In region II, we have:

$$[Li_{1+5x-13y}Ni_{(5y-x)}\nabla_{4(2y-x)}][Ta_{1-(x-y)}Ni_{(x-y)}][O_3] \qquad (3)$$

where, ∇ represent the vacancy. We represent these models, described previously, in the following condensed form,

$$[Li_{\alpha 1} Ni_{\alpha 2} \nabla_{\alpha 3} \nabla_{\alpha 4}][Ta_{\beta 1} Ni_{\beta 2} \nabla_{\beta 3} \nabla_{\beta 4}][O_3] \qquad (4)$$

and

$$K^{*} = g\ K$$

With K=M, q and g= α, β. Here α and β allow the two models to be identified as follows:

i) Model (a) corresponds to α_1=1-5x-3y, α_2=4y, β_1=1, β_2=0; and $K_2^* = \alpha_1 K_2 + \alpha_2 K_3$, $K_1^* = \beta_1 K_1 + \beta_2 K_3$ and $K_0^* = K_0$.

ii) Model (b) corresponds to α_1=1+5x-13y, . α_2=5y-x, β_1=1-x+y, β_2=x-y; and $K_2^* = \alpha_1 K_2 + \alpha_2 K_3$, $K_1^* = \beta_1 K_1 + \beta_2 K_3$ and $K_0^* = K_0$.

In this representation α=β=0 signified that ions and vacancies are absent in these nonstoichiometric models.This result reveals the Ni incorporation in $LiTaO_3$, which gives quantitative and qualitative discussion.

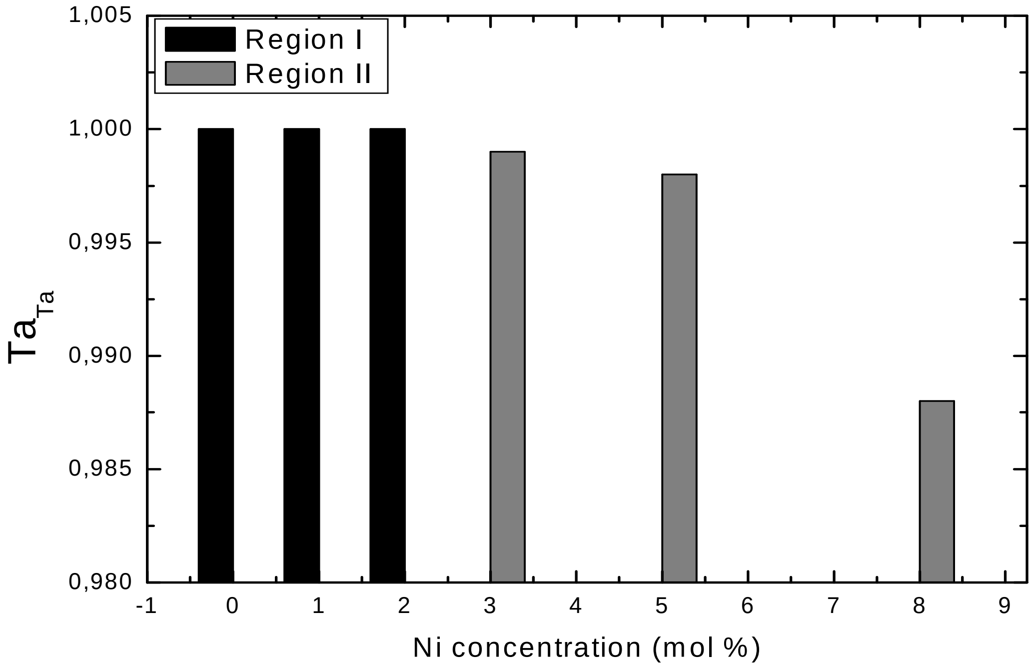

Figure 1: Plot of normal Ta site (Ta_{Ta}) as function of Ni doping concentration.

Results and discussion

- *Substitution model of Ni <3%*

From the above table, a change in the substitution mechanism is observed to y = 3 mol% Ni. We proposed a vacancy model that is based on that of lithium [15,16], to describe the structure of non-stoichiometric substitution where Ta cations who are in excess takes place in the sublattice of lithium (Li).This model (a) is given by:

$$Li_{1-5x-3y} M_{1+x-y} Ni_{4y} O_3 \qquad (5)$$

whose expression is modified by considering the various sublattice of the structure and showing up the vacancy (∇) which permit compensation of the charge, where:

$$[Li_{1-5x-3y}M_{x-y}Ni_{4y}\nabla_{4x}][M][O_3] \tag{6}$$

It is defined by two phenomena that take place at the sublattice [Li], while the other two sublattice ([Ta] and [O]) remain intact:

Substitution of the five atoms of lithium by a metal atom Ta is to say:

$$5\times Li^{+} \leftrightarrow Ta^{5+} + 4\times\nabla \tag{7}$$

Next, a substitution of three cations lithium and a metal cation (Ta) by four doping divalent cations:

$$Ta^{5+} + 3\times Li^{+} \leftrightarrow 4\times Ni^{2+} \tag{8}$$

- Substitution model of Ni ≥ 3%

From the formulae given in Table 1, it is seen that this is obtained for a Ni content comprised between 2 and 3%. For higher Ni contents, Ni cations should be located on both Li and Ta sites, which is such that:

$$Li_{1-5x-13y}M_{1-(x-y)}Ni_{4y}O_3 \tag{9}$$

As in the previous case, the various sublattice of the structure are considered in showing the concentration of vacancies (∇) allowing compensation to equilibrium the global charge:

$$[Li_{1+5x-13y}Ni_{(5y-x)}V_{4(2y-x)}][M_{1-(x-y)}Ni_{(x-y)}][O_3] \tag{10}$$

The model (b) given by (9) is defined by two types of substitutions:

- In the sublattice [Li]

$$13\times Li^{+} \leftrightarrow 5Ni^{2+} + 8\times\nabla \text{ and } 4\nabla + Ni^{2+} \leftrightarrow 5Li^{+}$$

$$8\times Li^{+} \leftrightarrow 4Ni^{2+} + 4\times\nabla \tag{11}$$

- In the sublattice [Ta]:

$$(x-y)\times Ta^{5+} \leftrightarrow (x-y)\times Ni^{2+} \tag{12}$$

What characterized this last model from the first (b) is that the metal Sublattices [Li] and [Ta] are both concerned with the substitution, which involves replacing the cations of lithium Li^{+} by Such as nickel Ni^{2+} and Ta^{5+} cations.

In contrast, in the model (a), the site [Ta] is completely filled by its own cations Ta^{5+} and it's the site [Li] where any substitution takes place. This is summed up in a replacement of some atoms Li by atoms Ta who are in excess in the composition non-stoichiometric, they will be substituted in their laps with other atoms by Li doping elements Ni (7 and 8).

As the number of seats that can be occupied by Ta atoms in the sites [Li] is limited by the field of non-stoichiometric, so it makes sense to have a saturation of the substitution at some rate doping which corresponds to 3 mol% N for Ni-doped $LiTaO_3$.

Conclusion

We have proposed the new vacancy models which are able to describe substitutional mechanism in Ni-doped lithium tantalite. When Ni cations are inserted in the lattice (%Ni<3%), it is thus probable that they are preferentially located on the lithium sites and replace the tantalum atoms. Beyond 3%, Ni cations should be located on both Li and Ta sites.

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