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ANALYSIS OF CORRELATION BETWEEN DENSITY VARIATIONS AND DEFECT STRUCTURE OF W^{6+} : $LiTaO_3$

We investigate the defect structure of non-stoichiometric solid solutions of WO_3-doped $LiTaO_3$ in correlation with the evolution of the density within our theoretical approach. The dopant concentration and the mechanism of substitution, which depends of the ionic rays of different cations that exit into the network, have an effect on crystalline parameters and, consequently, on the density. In order to explain the defect structure of solid solutions synthesized in the ternary system Li_2O–Ta_2O_5–$(WO_3)_2$ in a vicinity of $LiTaO_3$,, we have shown a convergence between theoretical and experimental results by the application of our theoretical approach combined with the new proposed vacancy models. We conclude that the new vacancy models are able to describe the defect structure and the substitution mechanism in each solid solutions of WO_3-doped lithium tantalate.

K e y w o r d s: $LiTaO_3$, WO_3, density, vacancy model, stoichiometry.

1. Introduction

The ferroelectric material $LiTaO_3$ (LT) has been extensively studied in recent years in different practical and theoretical works, because of its various applications due to their properties in electro-optics, electroacoustics, and non-linear optics. The structure of ferroelectric $LiTaO_3$, as well as that of $LiNbO_3$, belongs to the space group R3c and can be considered as a superstructure of the a-Al_2O_3 corundum structure with Li^+ and Ta^{5+} cations along the c-axis [1]. $LiTaO_3$ has a nonstoichiometric composition with a high concentration of intrinsic defects. It consists of the stacking of oxygen octahedra, (Ta_2O_6) and (Li_2O_6), where Li^+ and Ta^{5+} ions occupy two thirds of the oxygen octahedra, and one third is empty, which is likely to incorporate impurities such as Ni, Cu, and W added intentionally for a desired application. Consequently, it is easier to modify its physical properties such as the spontaneous polarization, Curie temperature, and density [2–5].

The line B studied in this work is characterized by a weak dissolution of WO_3 in the lattice $LiTaO_3$, the limit of its solubility "x" in the vicinity of $LiTaO_3$ is 0.02, which constitutes the lowest solubility as compared with other lines, as shown in Fig. 1 [6], which represents the range of different solid solutions synthesized in air at 1250 °C in the Li_2O–Ta_2O_5–$(WO_3)_2$.

Analyzed and proposed vacancy models for the solid solution A, where $[\beta]$ defines the sublattice of β, with β =(Li, Ta or O_3)

Solid solution	Experimental model	Proposed vacancy models	Formula of density
B	$Li_{1+7x}Ta_{1-5x}W_{3x}O_3$	$[Li_{1+7x}][Ta_{1-5x}W_{3x}\Delta_{2x}]O_3$	$d^* = \frac{(316.47-408.718x)}{v^*}d$

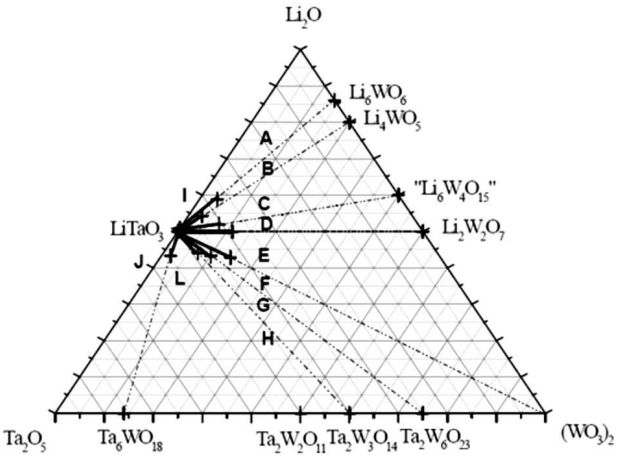

Fig. 1. Solid solutions synthesized in the Li_2O–Ta_2O_5–$(WO_3)_2$ diagram

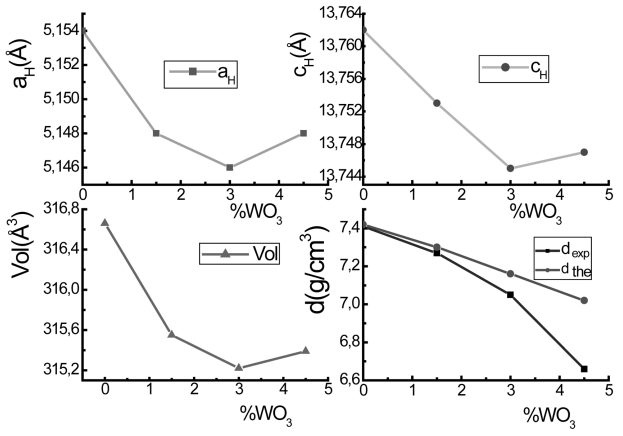

Fig. 2. Evolution of the volume, crystalline parameters a_H and c_H, and density of line B with $\%WO_3$

Our interest is to study the effect of the W content on the structure and to evaluate the behavior of the density at different concentrations of W in $LiTaO_3$ in order to get information about the mechanism of substitution and to find a suitable vacancy model that will explain the defect structure.

2. Theoretical Approach

The density is defined by the following relation:

$$d = \frac{ZM}{VN_A}. \tag{1}$$

By analogy in the non-stoichiometric case, we can write

$$d^* = \frac{ZM^*}{V^*N_A}. \tag{2}$$

Finally in the non-stoichiometric case, the density is given by the relation

$$d^* = \frac{VM^*}{V^*M}d. \tag{3}$$

N_A is the Avogadro number, M and V are the molecular weight and the volume of a unit cell of the stoichiometric material, respectively, and V^* and M^* are the measured volume and the molecular weight of the non-stoichiometric compound.

The proposed and simplified vacancy model describes the defect structure in terms of the dopant concentration x of the solid solution named B represented in Table.

3. Results and Discussions

In this paper, in order to explain the defect structure of WO_3 doped with $LiTaO_3$ in correlation with the evolution of the density, we have established a relation for the density, by developing our theoretical approach combined with the proposed vacancy model concerning the solid solution B. The result is summarized in Table.

From the application of our analytical approach, we can calculate different values of the density of the solid solutions of tungsten doped with lithium tantalate for different tungsten concentrations x. The calculated and measured values of the density are illustrated in Fig. 2.

We observe from the experimental and theoretical results that the density decreases with the concentration of WO_3. We see also that the crystalline parameters and the volume decrease also with $\%WO_3$. On the other hand, the decrease of the parameters a_H, c_H, and V may be due to the proximity of the ionic rays of all engaged cations in octahedral sites ($r_{Li^+} = 0.78$ Å, $r_{Ta^{5+}} = 0.68$ Å, $r_{W^{6+}} = 0.58$ Å) [7]. Indeed, a substitution of Ta^{5+} ions by W^{+6} seems very probable, because the latter have a low affinity for the L^+ sites. Hence our study reveals that the tungsten substitutes only tantalum sites in the [Ta] sublattice.

4. Conclusion

The results of studies within our approach have shown that the density of lithium tantalate doped with tungsten decreases with the increase in the doping rate of WO_3. However, the proposed vacancy model $[Li_{1+7x}][Ta_{1-5x}W_{3x}\Delta_{2x}]O_3$ can be conveniently used to describe the substitution mechanism and the defect structure ofthe solid solution B that is synthesized in the vicinity of $LiTaO_3$ in the ternary system Li_2O–Ta_2O_5–$(WO_3)_2$.

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АНАЛІЗ КОРЕЛЯЦІЇ
МІЖ ЗМІНАМИ ЩІЛЬНОСТІ
І СТРУКТУРОЮ ДЕФЕКТІВ У W^{6+} : $LiTaO_3$

Р е з ю м е

Ми досліджували кореляцію структури дефектів у нестехіометричних твердих розчинах $LiTaO_3$, легованих WO_3 зі змінами щільності в запропонованому нами теоретичному підході. Концентрація домішки і механізм заміщення, який залежить від траєкторій катіонів, що входять в решітку, впливають на параметри кристала і, отже, на щільність. Для опису структури дефектів твердих розчинів, синтезованих у тернарній системі Li_2O–Ta_2O_5–$(WO_3)_2$ поблизу $LiTaO_3$, ми застосували наш підхід разом з новими моделями вакансій. Досягнуто згоди теоретичних і експериментальних результатів.