

CRYSTAL CHEMISTRY AND NON-STOICHIOMETRY APPROACH OF THE PHASE TRANSITIONS IN DISPLACIVE FERROELECTRICS: PART II.- Differentiation between LiNbO₃ & LiTaO₃ Ferroelectric Behaviour

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欢迎各位老师和同学参加!

In our last presentation (SICCAS -- Wednesday 10th April 2024) we focused on the cationic effect on the phase transition evolution along various solid solutions in the vicinity of LiTaO₃ within various ternary systems. The reasonable interpretation we have given was mainly based on the localization of Li(I) cations inside the vacant tetrahedral sites. These tetrahedral sites are filled as cluster of related ilmenite structure for tantalates but not for niobates.

In this new lecture we will explain the difference in the ferroelectric behaviour of the same solid solutions having the same global chemical composition as well as the same type of non-stoichiometry (Annexe-1) with the only difference is that Ta(V) ions are replaced totally by Nb(V) cations. For example:

- i) Li_{1+5x}Nb_{1-x}O₃ to be compared with the system Li_{1+5x}Ta_{1-x}O₃
- ii) Li_{1+x}Nb_{1-x}Ti_xO₃ to be compared with the system Li_{1+x}Ta_{1-x}Ti_xO₃
- iii) Li_{1+x}Nb_{1-x}Zr_xO₃ to be compared with the system Li_{1+x}Ta_{1-x}Zr_xO₃
- iv) etc.

Indeed, the basic network of these solid solutions is the same as could be deduced from Annexe-I, but the localization of Li cations is different in the Nb and Ta based systems, although Nb⁵⁺ and Ta⁵⁺ have the same ionic radii, but the chemical nature of Nb and Ta plays here a key role as their effective charge is different. In the case of Ti(IV) and Zr(IV) inserted in Nb and Ta compounds, we have evidenced the behaviour difference from the cationic size of Ti⁴⁺ and Zr⁴⁺.

The effective local charges of Nb(V) and Ta(V), as well as the size effect on mechanical deformation of the lattice have shown the decrease of the cluster's stability of niobates, compared to the tantalates of the same composition.

Annexe-1

Type of Non-Stoichiometry of Li(Ta, Nb)O₃

Considering the basic structure of Li(Nb,Ta)O₃ with corundum type □M₂O₃ (with □=cationic deficit, M= Al, etc) our studies have concluded to the possibility of only six types of non-stoichiometry represented hereafter by Eq 1 to Eq 6 and corresponding the following classes A and B:

A.- Structural defects located only on the cationic sites:

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| A1.- Same Stoichiometry as LiMO₃ (M=Nb, Ta): | □M ₂ O ₃ | (Eq.1) |
| A2.- Cationic excess with the general formula : | □ _{1-x} M _{2+x} O ₃ | (Eq.2) |
| A2.- Cationic deficit with the general formula : | □ _{1+x} M _{2-x} O ₃ | (Eq.3) |

B.- Structural defects located on both anionic and cationic sites:

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|---|---|--------|
| B1.- Anionic deficit alone with the general formula: | □M ₂ O _{3-y} Δ _y | (Eq.4) |
| B2.- Anionic deficit & cationic excess with the general formula: | □ _{1-x} M _{2+x} O _{3-y} Δ _y | (Eq.5) |
| B2.- Anionic deficit & cationic deficit with the general formula : | □ _{1+x} M _{2-x} O _{3-y} Δ _y | (Eq.6) |