CRYSTAL CHEMISTRY AND NON-STOICHIOMETRY APPROACH OF THE PHASE TRANSITIONS IN DISPLACIVE FERROELECTRICS: PART I.- $LiNbO_3$ and $LiTaO_3$ based Systems.

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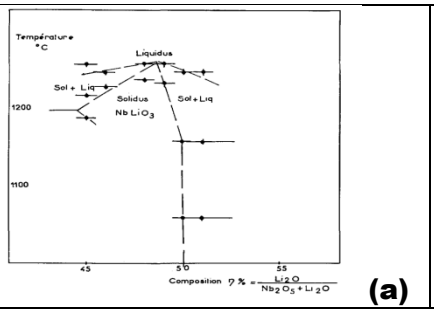
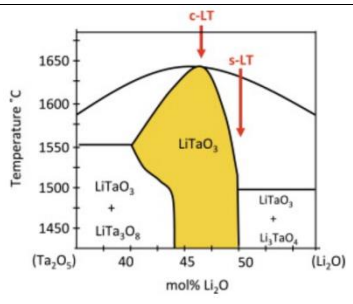
欢迎各位老师和同学参加！

Lithium niobate $LiNbO_3$ (LN) and lithium tantalate $LiTaO_3$ (LT) are key ferroelectric materials with displacive character. Like perovskite oxides $BaTiO_3$, PMN-PT systems, they are widely used in various fields of electronic and optoelectronic high-tech applications. The early studies of LN and LT compounds get rise to a confusing ferroelectric behaviour between their stoichiometric and congruent forms. The ambiguity has been overcome only after the determination of the phase diagrams Li_2O-Nb_2O_5 and Li_2O-Ta_2O_5; which evidenced a clear non-stoichiometry (Fig.1) affecting deeply their physical properties: i) ferroelectric T_C values, ii) electrooptical properties, iii) photorefractive behaviour, iv) etc. As a matter of fact, the 1st diagram of Reisman et al. (**J. Am. Chem. Soc. 80 (1958) 6503**) giving stoichiometric $LiTaO_3$ needed to be updated (Fig.1).



(a)



(b)

Fig.1 Phase diagrams
(a) Li_2O-Nb_2O_5 - ref: P. Lerner et al. J. Cryst. Growth 3-4 (1968) 231

(b) Li_2O-Ta_2O_5 – ref : S. Fujii et al. J. Cryst. Growth 383 (2013) 63

Different Authors have proposed various approaches of the non-stoichiometry and tempted to explain the observed change in the physical properties versus: i) chemical doping, ii) thermal treatments, iii) state of the sample: single crystal, ceramic, thin film, iv) etc. In the case of the ferroelectric behaviour for example, most of Authors have correlated the evolution of the Curie temperature to the lattice deformation and notably to the lattice parameters ratio c_H/a_H as the structure is hexagonal with the polar space group R3c.

We have conducted investigations on the crystal chemistry and related ferroelectric properties of $Li(Nb,Ta)O_3$ solid solutions within various ternary systems (Li_2O-M_2O_5-M'_nO_p) with M=Nb, Ta and M'= various transition element cations of different oxidations degrees like Cu^{2+}, Fe^{3+}, Ti^{4+}, Zr^{4+}, W^{6+}, etc.

Considering the basic structure of $Li(Nb,Ta)O_3$ with corundom type $\square M_2O_3$ ($\square$=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:

A1.- Same Stoichiometry as $LiMO_3$ (M=Nb, Ta): $\square M_2O_3$ **(Eq.1)**
A2.- Cationic excess with the general formula : $\square_{1-x}M_{2+x}O_3$ **(Eq.2)**
A2.- Cationic deficit with the general formula : $\square_{1+x}M_{2-x}O_3$ **(Eq.3)**

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

B1.- Anionic deficit alone with the general formula: $\square M_2O_{3-y}\Delta_y$ **(Eq.4)**
B2.- Anionic deficit & cationic excess with the general formula: $\square_{1-x}M_{2+x}O_{3-y}\Delta_y$ **(Eq.5)**
B2.- Anionic deficit & cationic deficit with the general formula : $\square_{1+x}M_{2-x}O_{3-y}\Delta_y$ **(Eq.6)**

where $\square$ **and** Δ represent cationic and anionic defects, respectively.

Eqs 1-6 allow to predict the point defects in the lattice while the key point to explain the ferroelectric behaviour is to determine the cationic distribution over the unit cell which will allow to know how the dipoles are arranged. From the atomic arrangement it was possible for us to follow the ferroelectric deformation versus the chemical composition. In our lecture, we will give our updated key results for :

i) $LiTaO_3$ solid solutions along the binary system Li_2O-Ta_2O_5 ;
ii) $LiTaO_3$ solid solutions along two lines within the ternary diagram Li_2O-Ta_2O_5-TiO_2;
iii) $LiTaO_3$ solid solutions within the ternary diagram Li_2O-Ta_2O_5-WO_3;

Dr Brahim ELOUADI
University Professor in France & Morocco

A.- ACADEMIC ACTIVITIES IN MOROCCO

- **Maître de Conférence (Associate Professor) at Université Mohammed-5 de Rabat - Morocco**
- **Professeur de l'Enseignement Supérieur (Full Professor) at Université Mohammed-5 de Rabat -Morocco**
- **Initiator & Director of Laboratoire de Chimie du Solide Appliquée (LCSA) at Faculté des Sciences de Rabat, l'Université Mohammed-5 de Rabat, Morocco**
- **Co-Creator of the Moroccan Series of International Conferences on Materials Science named ReMCES (Rencontres Marocaines sur la Chimie de l'État Solide). We are organizing ReMCES-XIII to celebrate the 40th Anniversary of ReMCES activities (https://remces-13.sciencesconf.org/resource/page/id/15)**

B.- INTERNATIONAL PROFESSIONAL ACTIVITY

- **PIFI Invited Professor SICCAS, Shanghai, China**
- **One Year Visiting Professor at Oklahoma State University (OSU), Stillwater, OK-USA**
- **Invited Professor in various Universities in France (Angers, Bordeaux, Dijon, Lille, Mulhouse) for teaching and Research (for periods of 03 Month to 12 Months)**
- **Over 100 Invited Lectures in International Conferences (Morocco, UK, US, Europe, China, Japan, Korea, etc.)**
- **About 200 Publications.**

C.- ACADEMIC CAREER AT UNIVERSITÉ DE LA ROCHELLE, FRANCE

- **Professeur des Universités (Full Professor for Education & Research activities)**
- **Co-creator of the Series CFSAM-(Chinese French Symposium on Advanced Materials), with Academician Professor YAO Xi (Member of the Chinese Academy of Science) and Professor Luo Haosu (Group Leader in SICCAS)**
- **With continuous support of our French Embassy in China (Ambassade de France en Chine), we alternatively organize CFSAM in China and in France. The next CFSAM-6 will be organized in SICCAS in October 2024, under the label of 60th Anniversary of Diplomatic Relations between China and France.**

E.- RESEARCH TOPICS

- **Ferroelectric and Non-linear Materials.**
- **Crystal Chemistry and the correlation between the Chemical Composition, the Crystal Structure and Physical Properties (Ferroelectrics, Laser Spectroscopy, etc.)**