

High Temperature Structure and Properties of Lithium Niobate

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Abstract. High temperature neutron powder diffraction experiments were carried for a thorough detailed study of the structural evolution and phase transition of lithium niobate. Already at low temperatures part of the Li ions enter the hitherto assumed empty octahedra, their amount increasing with temperature. This explains anomalies in the thermal expansion. The phase transition from the ferroelectric to the paraelectric phase proceeds in two steps, complete disordering of Li before Nb reaches its centrosymmetric site within its octahedron. Li is further disordered within the oxygen plane pointing towards relatively strong Li-O bonds. These results settle a number of controversies found in the literature and add new aspects.

Key words: lithium niobate, neutron powder diffraction, structure anomalies, phase transition, disorder.

I. INTRODUCTION

Due to its outstanding electro-optical, acousto-optical and electro-mechanical properties lithium niobate, LiNbO_3 , has attracted enormous interest over almost 50 years. In spite of the huge number of publications, increasing up to the current date, many aspects remain poorly understood and heavily controversial. A proper knowledge of its high temperature crystal structure is fundamental and can help to solve some of these problems.

Lithium niobate melts incongruently, the congruent composition being $\text{Li}_{0.95}\text{Nb}_{1.01}\text{O}_3$. Its properties can be tailored by changing the composition or doping. At low temperatures it is ferroelectric with space group $R3c$ consisting of oxygen octahedra sharing faces along the 3-fold axis. The cations are located on this axis with the sequence Nb- -Li-Nb-..., where denotes a vacant octahedron. In the congruent composition, part of Nb moves onto the Li-site, e.g. [1]. Above about 1450 K (depending on the composition) it becomes paraelectric, space group $R\bar{3}c$. While it is generally accepted that Nb moves into the center of its octahedron, two models are proposed for Li: in the *displacive* model Li becomes triangularly coordinated within the oxygen layer below, in the *order-disorder* model it occupies both sides of this layer with equal probability.

Among others previous temperature dependent structure determinations have been performed on congruent [2] and stoichiometric [3] material, alas only with limited temperature resolution.

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II. EXPERIMENTAL

Measurements were performed at the neutron powder diffractometer SPODI [4]. The (congruent) sample was placed in a Nb can and a Nb resistance vacuum furnace. Data were collected at 50 °C steps up to 1000 C and further up to 1240 C in 15 °C steps. Rietveld analysis was done with standard programs GSAS, FullProf and JANA. The powder suffered from severe extinction effects which can only be handled with GSAS. Only with this the correct composition was obtained and the substitution model confirmed: $[\text{Li}_{0.95}\text{Nb}_{0.01\ 0.04}]_{\text{Li}}[\text{Nb}]\text{O}_3$. FullProf allows rapid sequential refinements of the large amount of data and JANA was used to refine anharmonic terms in the Debye-Waller factor and to produce Fourier maps.

III. RESULTS AND DISCUSSION

A. Refinement strategies

In the polar space group $R3c$ the choice of the origin along z is arbitrary and was fixed such that $z(\text{O}) = 1/12$. Then in the *displacive* model the free parameters are $z(\text{Li})$, $z(\text{Nb})$, $y(\text{O})$ and $x(\text{O})$. In the HT phase the three former ones become $1/4$, 0 and $1/3$, respectively, while the latter one is not critical and the only free parameter in $R\bar{3}c$. In the *order-disorder* model a parameter $z(\text{Li}')$ is introduced for its position in the "empty" octahedron adding two further critical parameters $z(\text{Li})-z(\text{Li}')$ and the occupancies $n(\text{Li}) = 1-n(\text{Li}')$, while $z(\text{Li})$ becomes non-critical.

Since the distribution of Li plays the key role further analyses were performed with (difference) Fourier procedures as well as anharmonic structure refinements.

B. Lattice Constants

The variation of the lattice constants is depicted in Fig. 1. The striking negative thermal expansion along c has been known from the literature. The new data, however, allow a more detailed interpretation. The maximum of c is largely compensated by a retardation of the monotonous increase of a , such that the unit cell volume increases roughly linearly with temperature. Similarly, above the phase transition at $T_c = 1135$ °C, clearly noticeable from this graph, the increase of a is retarded and c increases linearly again, such that there is no volume anomaly at T_c .

C. Order Parameters

In both models $z(\text{Nb})$ goes continuously to zero at T_c roughly following a second order phase transition critical law. There is, however, a marked anomaly around 1000 °C. As expected $x(\text{O})$ shows no anomaly around T_c . In the *displacive* model $z(\text{Li})$ and $y(\text{O})$ slowly decrease roughly linearly up to 1000 °C, followed by a steep drop towards

their HT values, reminiscent of a first order phase transition. In the *order-disorder* model a small occupancy of the Li' site is found already at room temperature. It slowly increases up to 1000 °C, followed by a rapid increase towards equal distribution at T_c . Similar rapid changes in this temperature interval are found for $z(\text{Li})$ and $y(\text{O})$.

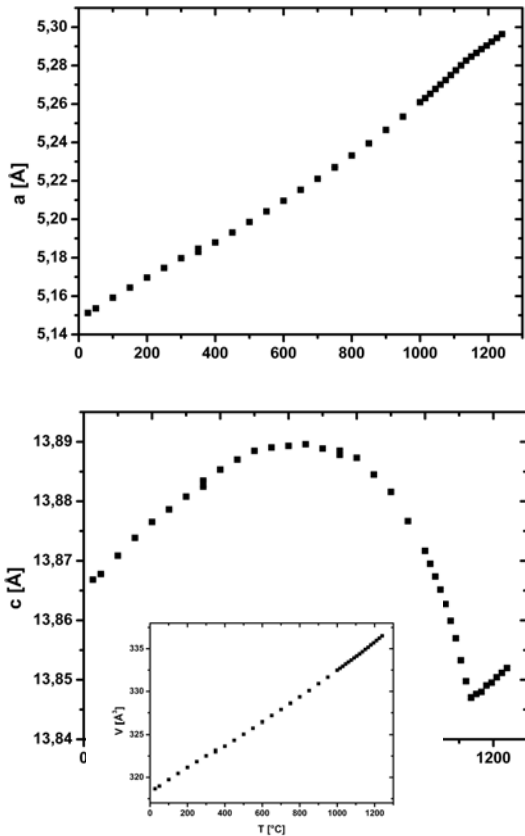


Fig. 1. Temperature dependence of the lattice constants a (top), c (bottom) and the unit cell volume (inset).

D. Atomic Displacement Parameters

Analysis of the temperature dependence of the (anisotropic) atomic displacement parameters shows that in no case there is any appreciable static disorder apart from the Li distribution within both octahedral, i.e. the disorder discussed in the next section is predominantly dynamic.

E. Disorder

It has to be admitted that the fit quality is rather similar for both models, although there is a very slight preference for the *order-disorder* model. A clear decision for this model can, however, be made on the basis of Fourier maps and anharmonic refinements. As an example Fig. 2 presents difference Fourier maps below and above T_c . The Li density is described by the dashed lines (negative scattering density) in the centers, the refined positions by light green circles. Red circles are O, dark green one Nb. Far below T_c the majority of Li is within the upper O-octahedron, but appreciable density is found within the “empty” octahedron and at the middle of the O-triangle. In fact there is a shoulder near this point. Clearly, this cannot adequately be described by *one* single second Li position. Moreover, there is a pronounced threefold anisotropy in the lateral direction with lobes towards the neighboring oxygens. Above T_c the Li

density is largely extended symmetrically into both octahedra, again with (slight) shoulders on each side.

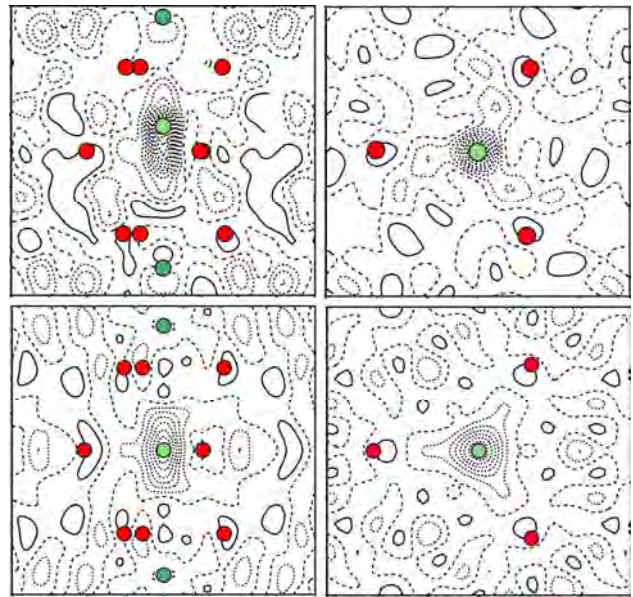


Fig. 2. Difference Fourier maps showing Li density at 650 °C (top) and 1225 °C (bottom) parallel (left) and perpendicular (right) to c -axis.

IV. CONCLUSIONS

The phase transition in lithium niobate proceeds in two steps, first a disordering of Li connected with disordering of O (distortion of octahedra) in an abrupt way at about 1000 °C, followed by a smooth disappearance of the off-center positions of Nb at T_c . The Li disorder is 6-fold, above and below the oxygen plane, attached to each of the neighboring oxygen ions. This emphasizes the role of the Li-O bonds.

Further results concerning the distortion and rotation of the oxygen octahedra, the variation of the bond lengths, a proper interpretation of the thermal expansion anomalies and the phase transition by coupled order parameters and a comparison with stoichiometric lithium niobate [3] will be presented at the conference and published in a forthcoming paper. Credit to other relevant publications will be given too.

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