Composition dependent optical properties of $LiNb_{1-x}Ta_xO_3$ solid solutions

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Introduction

Lithium niobate (LN) and lithium tantalate (LT) are ferroelectric crystals with a wide range of applications, extending from piezoelectric sensors [1] to integrated photonics [2]. Their structural similarities enable the combination of these materials to $LiNb_{1-x}Ta_xO_3$ (LNT) alloys. As the optical absorption edge depends on the stoichiometry, this property can be used to determine the crystal composition non destructively.
Here, we use *special quasi-random structures* (SQS) to simulate LNT crystals with different compositions. These structures mimic an ideal random alloy, even when periodic boundary conditions are employed. Furthermore, we use the Li-vacancy model as well as the Nb-antisite model to simulate congruent LN crystals, as these crystals are commonly used in experiments.
We calculate the first order dielectric tensor of both materials by using *density functional theory* (DFT) and the *indepent particle approximation* (IPA).

Methodology

For all of our calculations we are using DFT as implemented in VASP [3, 4]. The pseudopotentials are given in the PBEsol formulation [5, 6].
Utilizing the orthorhombic $2\times1\times1$ supercell of LN as a starting point for our simulations, we gradually exchange the Nb atoms with Ta atoms. This procedure is carried out such, that the correlation between Ta occupation sites, as defined in Ref. [7], is minimzed. Thus, we obtain 22 SQS of the LNT crystal. Their Ta concentration ranges from 4.2 % to 95.8 %.
For modelling congruent LN, we use cells as large as up to $4\times4\times4$ rhombohedral supercells, removing up to four Li^+ from these structures. This creates Li^+-vacancy concentrations of as low as 0.78 %. Also, we employ the Nb-antisite model as described in Ref. [8]. Additionally, we use a GGA+U scheme for the Nb *d* electrons to correct for the underestimation of the electronic band gap in DFT.
For all of these structures we optimize the ionic positions and the volume, employing the Murnaghan equation of states for the latter. To calculate the dielectric function, we use the IPA as implemented in VASP. The absorption edge is then extracted by a linear fit of the first peak in the imaginary part of the dielectric function.

Results

Our calculations show a clear dependence on the absorption edge with respect to the Nb/Ta ratio of the LNT crystals. The absorption edge increases with increasing Ta concentration. This behaviour holds for all diagonal components of the dielectric tensor and might be explained by the electronic DOS: LT features a higher absorption edge than LN [9], and mainly the states corresponding to Nb and Ta directly above the Fermi-energy change, with the Ta-states featuring slightly higher energies. As the bands near the Fermi-energy are mostly flat throughout the Brillouin-zone and we only consider direct transitions in the IPA, this corresponds to a higher absorption edge in LT than in LN.
For congruent LN, we also observe a non-linear behaviour of the absorption edge with respect to the Li^+-vacancy concentration for all diagonal components of the dielectric function, as has been reported in [8, 10]. Here, the Nb states in the lower valence bands are shifted to smaller energies with increasing Li^+-vacancy concentration.

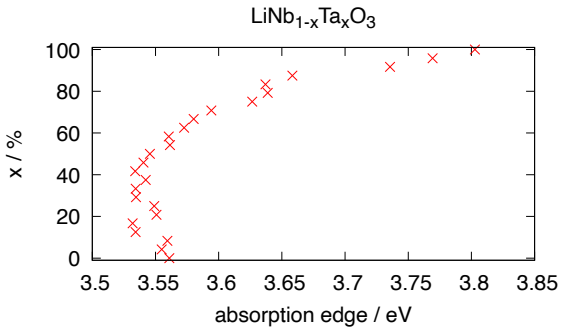

Figure 1: Absorption edge of LNT with respect to Nb/Ta ratio. Only The xx-component of the dielectric tensor has been considered.

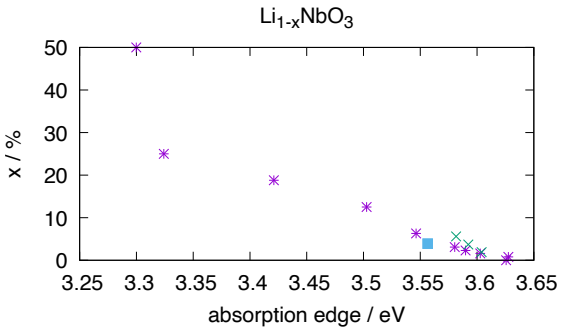

Figure 2: Absorption edge of LN with respect to Li^+-vacancy concentration. Only The xx-component of the dielectric tensor has been considered. The green crosses denote calculation with higher numerical accuracy, whereas the blue cube represents the Nb-antisite model.

Conclusion

The absorption edge of LNT crystals with different Nb/Ta ratios was calculated. We determine a clear trend, that the absorption edge increases with increasing Ta concentration. We also note, that the absorption edge of LN decreases with increasing Li^+-vacancy concentration. These results are in qualitative agreement with experimental measurements.

References

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