Li Diffusion in (110) Oriented LiNbO₃ Single Crystals

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Abstract. Li diffusion is investigated in Li_2O-deficient, (110) oriented $LiNbO_3$ single crystals in the temperature range between 523 and 673 K by secondary ion mass spectrometry. A thin layer of ion-beam sputtered isotope enriched $^6LiNbO_3$ was used as a tracer source, which allows one to study pure isotope interdiffusion. The diffusivities coincide with those of (001) oriented single crystals and follow the Arrhenius law with an activation enthalpy of 1.33 eV. The results prove the existence of a three-dimensional diffusion mechanism.

Introduction

Lithium niobate ($LiNbO_3$) is a technologically important oxide, with an interesting combination of ferroelectric, piezoelectric, acoustic, optical and ion conducting properties [1-3]. The compound exhibits a wide homogeneity range between 44 mol% and 50.5 mol% Li_2O [4]. Single crystals produced by the Czochralski method generally show the congruent composition of about 48.5 mol% Li_2O. However, by using the vapor transport equilibration (VTE) method the synthesis of near stoichiometric crystals is also possible [5]. The change of composition from the lithium-poor compositions to the stoichiometric composition results in significant changes in the physical properties of the system, including the Curie temperature, the ferroelectric coercive field, and photorefractive properties [1,6]. These changes in physical properties are expected to be the result of point defects and defect clusters occurring for non-stoichiometric samples [2,5,7-11].

Self-diffusion of the constituents in lithium niobate is of importance because formation, stability and dissociation of defect clusters are closely related to the diffusion properties. Furthermore, Li diffusivities are a measure for ionic transport properties and consequently for the ion conductivity. Diffusion studies can determine the dominating ion species that governs conductivity.

In principle, for the investigation of self-diffusion in solids microscopic methods (Nuclear Magnetic Resonance Spectroscopy, Quasi-Elastic Neutron Scattering) and macroscopic tracer methods using radioactive tracers or stable tracers in combination with adequate depth profiling (Secondary Ion Mass Spectrometry, Nuclear Reaction Analysis) can be used [12]. Microscopic methods allow the determination of correlation times, τ_c, or jump rates, τ_c^{-1}, at diffusion lengths in the order of atomic distances. Here, the diffusivity has to be calculated indirectly from the Einstein-Smoluchowski equation. In contrast, using tracer methods it is possible to investigate long range transport processes and directly measure the diffusivity. Tracer methods are especially of large importance if slow diffusion processes are studied, which can be found in single crystals and at low temperature.

Investigations of self-diffusion in Li containing solids were done during the last years almost exclusively by NMR methods [13-17], which allow in generally a characterization of fast ion transport. In addition, conductivity measurements were carried out for an indirect characterization of diffusion [13,18]. In literature, only a small number of experiments done by the radiotracer

method can be found [19,20]. This is mainly due to the absence of suitable radioactive Li tracers. Very elegant experiments done with the short living isotope [8]Li (0.38 s) [19,20] are of limited significance due to the low diffusion times accessible, especially at low temperatures. On the other hand, the natural abundance of the two stable Li isotopes ([6]Li: 7.5 %, [7]Li: 92.5 %) leads to the problem that a high amount of [6]Li is necessary as tracer source, if stable isotopes are used. A small amount of tracer would simply not be detectable due to the high [6]Li isotope background present in the sample. However, the use of high amounts of tracer would lead to chemical inhomogeneities which will give rise to unwanted chemical diffusion if classical tracer deposition methods like ion implantation or a thin Li layer are used. An incorporation of Li via the gas phase is often limited by slow surface exchange processes. Some work done with the stable [6]Li tracer isotope and Secondary Ion Mass Spectrometry or Secondary Neutral Mass Spectrometry can be found in Refs. [21-25].

In the present work, we investigated Li self-diffusion at low temperatures in $LiNbO_3$ single crystals using a thin isotope enriched [6]$LiNbO_3$ layer as a tracer reservoir. The use of these isotope hetero-structures is an extremely reliable method to study self-diffusion processes in solids because pure isotope interdiffusion takes place undisturbed from chemical gradients [26-31].

Reliable data on Li self-diffusion concretely in lithium niobate are rare (for a review see [10,32]). Diffusion experiments are restricted to nuclear magnetic resonance studies and also to impedance spectroscopy [32-37]. Most of the data are limited to the high temperature range above 773 K. Recently, a study on Li self-diffusion on (001) oriented single crystals done by Secondary Ion Mass Spectrometry (SIMS) depth profiling was published for temperatures below 773 K [38]. The results were compared to conductivity measurements on the same type of crystal [38,39]. It is suggested that in the temperature range between 423 and 773 K diffusion of lithium is governed by a single vacancy mechanism with an activation enthalpy of diffusion of 1.33 eV. The results further revealed that Li diffuses at low temperatures via structural vacancies whose concentration is fixed by a frozen-in defect structure that is formed during synthesis of the single crystal. Therefore, the measured activation enthalpy of diffusion essentially consists of the migration enthalpy of single positively charged lithium vacancies. Charge diffusivities derived from conductivity measurements are in good accordance with the tracer diffusivities pointing to a Haven ratio close to one [39]. Recent molecular dynamics calculations suggest the presence of a three dimensional diffusion mechanism of Li [10].

In order to confirm the dimensionality of the diffusion mechanism, we investigated Li self-diffusion in L_2O-deficient (110) oriented $LiNbO_3$ single crystals between 523 and 673 K using SIMS. The results are compared to those of (100) oriented single crystals as given in literature [38].

Experimental details

The congruent $LiNbO_3$ single crystals (Li_2O content of about 48.5 mol% [38]) under investigation were supplied by Crystec (Berlin, Germany). 10 x 10 x 0.5 mm[3] [110] oriented polished pieces were used for the experiments. Tracer deposition was carried out by depositing a 20 – 30 nm thin layer of isotope enriched [6]$LiNbO_3$ on the single crystal by ion beam sputtering, using a commercial set-up (IBC 681, Gatan) equipped with two Penning ion sources. Deposition was done at 5 keV and a current of about 200 µA in Argon at an operating pressure of 5 x 10^{-5} mbar. The base vacuum was better than 5 x 10^{-7} mbar. The sputter targets were prepared by solid state syntheses [38]. Coarse Nb_2O_5 from Alfa Aesar (99.95 %) was pestled to a fine powder in an agate mortar and mixed with enriched [6]Li_2CO_3 from Eurisotop (96 % 6Li). In order to account for loss of lithium in the sputtering process, the molar ratio of oxide and carbonate was chosen as 5:6. This results in targets of the composition 90% [6]$LiNbO_3$ + 10% [6]Li_3NbO_4. After subsequent ball milling of the powder mixture in a SPEX 8000M shaker mill, pellets of 2 cm in diameter were pressed and heated to 973 K with a rate of 2 K/min. The reaction step was followed by a sintering process at 1173 K for 12 h, which yielded polycrystalline dense targets. After tracer deposition, the sputtered layer consists of single phase $LiNbO_3$ [40]. Due to the fact that the tracer layer and the single crystal have approximately the same chemical composition pure isotope interdiffusion is expected to be measured during the diffusion experiments.

For the isothermal diffusion experiments the coated samples were placed in a silica glass holder and introduced in the hot zone of a resistance furnace under ambient air conditions. Additional diffusion annealing experiments with short annealing times were carried out in a commercial rapid thermal annealing setup (AO 500, MBE, Germany).

The inward diffusion of the ^{6}Li from the sputter layer into the single crystal was determined by SIMS using a CAMECA IMS-3F machine. An O$^-$ primary ion beam (15 keV, 25 nA) was used in order to prevent electrical charging during the measurement. The sputtered area was about 250 μm x 250 μm, wherefrom 60 μm^2 in the centre were gated for further signal processing. In the depth profiling mode, the secondary ion intensities of ^{6}Li$^+$ and ^{7}Li$^+$ ions were recorded as a function of sputter time. Since the two Li isotopes are chemically identical, for diffusion analysis the intensity of the signals is converted into ^{6}Li atomic fractions c(x, t) according to

$$(1) \qquad c(x,t) = \frac{I(^6Li)}{I(^6Li) + I(^7Li)}$$

Depth calibration was obtained by measuring the crater depth with a mechanical profilometer (Tencor, Alphastep).

Results and discussion

The ^{6}Li atomic fraction as a function of sputter depth is given in Fig. 1 for an as-deposited sample and a sample annealed at 673 K for 5 min. The ^{6}Li tracer penetrates into the single crystal during annealing. Experimentally determined depth profiles broadened after annealing can be described by the following solution of Fick's second law for self-diffusion across an interface [41]

$$(2) \qquad c(x,t) = c_\infty + \frac{(c_0 - c_\infty)}{2}\left[\text{erf}\left(\frac{h+x}{R}\right) + \text{erf}\left(\frac{h-x}{R}\right)\right],$$

where c_∞ is the natural abundance of ^{6}Li in the single crystal and c_0 that in the tracer layer. The original thickness of the as-deposited tracer layer is denoted as h, which ranges between 20 – 50 nm, depending on the sample under investigation. The quantity R, describing the broadening of the tracer profile is treated as a fit parameter. The self-diffusivity D at time t is determined from the difference in R of the diffusion profile and of the starting profile according to $D = (R^2(t) - R^2(0))/4t$. The fits according to Eq. (2) are also given in Fig. 1.

In Fig. 2 the determined tracer diffusivities are plotted as a function of reciprocal temperature together with the diffusivities of (001) axis oriented single crystals as given in Ref. [19]. As obvious, the diffusivities are identical within error limits for both orientations. A common fit to the Arrhenius law

$$(3) \qquad D = D_0 \, \exp\left(-\Delta H/k_B T\right)$$

gives an activation enthalpy of $\Delta H = (1.33 \pm 0.03)$ eV and a pre-exponential factor of $D_0 = 1.7$ x 10^{-7} m²/s (error: ln D_0/m²/s = ± 0.66) in the temperature range between 423 and 773 K. As pointed out in Ref. [38], this activation enthalpy corresponds to the migration enthalpy of a single positively charged Li vacancy.
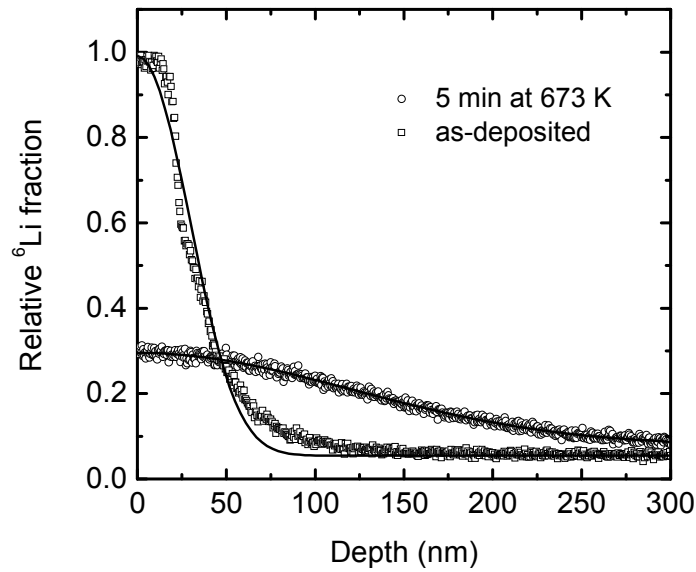
Figure 1 Atomic fraction of [6]Li as a function of depth for an as-deposited sample and a sample annealed at 673 K for 5 min. Also shown are fits according to Eq. (2).
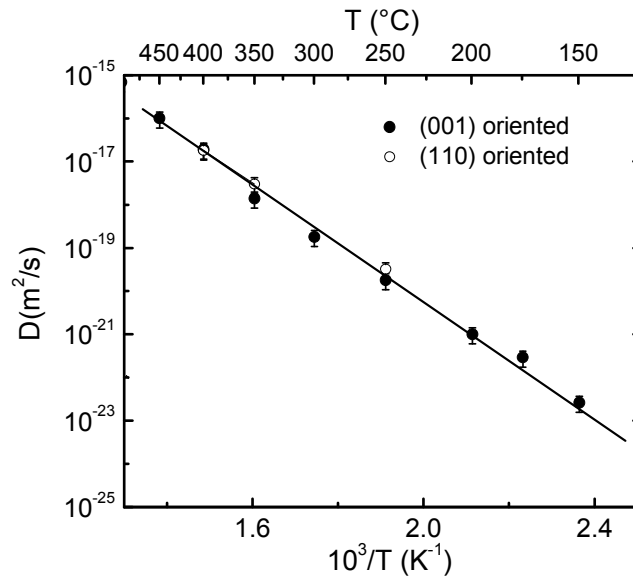

Figure 2 Diffusivities of Li in LiNbO$_3$ single crystals as a function of reciprocal temperature.

The main result of the present paper is that the Li diffusivity in lithium niobate single crystals does not depend on the crystallographic orientation ((001) or (110)) of the crystal. This result confirms the presence of a three dimensional diffusion mechanism in the hexagonal crystal. In Ref. [10] calculations of diffusion barriers based on the nudged elastic bands (NEB) method were carried out and the most favourable diffusion path was determined. Diffusion occurs as a compromise between two possible paths. (i) The first one is the diffusion of a lithium vacancy directly to its first Li nearest neighbor in the Li sublattice at a distance of 3.771 Å. This corresponds to a jump direction along (2-21) or equivalent sites [10]. (ii) The second one describes diffusion through the neighboring vacant site and then to its first nearest neighbour in the Li sublattice. For example, the lithium vacancy first move towards (1-10) then to (001) to reach (2-21). Consequently a curved diffusion path is most plausible according to these calculations. As the diffusion directions maintain the three-fold symmetry, for both the plane above and below, the overall effect leads to an isotropic diffusion mechanism [10] in accordance with the present measurements.

Conclusion

We carried out Li tracer diffusivity measurements in Li_2O-deficient, (110) oriented $LiNbO_3$ single crystals at low temperatures using SIMS depth profiling. The diffusivities are found to be identical to those of (001) oriented single crystals. This result demonstrates that a three dimensional diffusion mechanism is present.

Acknowledgements

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