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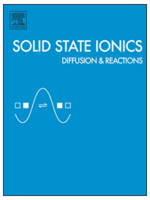

Tantalum and niobium diffusion in single crystalline lithium niobate

P. Fielitz [a],*, G. Borchardt [a], S. Ganschow [b], R. Bertram [b], R.A. Jackson [c], H. Fritze [d], K.-D. Becker [e]

[a] *Technische Universität Clausthal, Institut für Metallurgie, Robert-Koch-Str. 42, D-38678 Clausthal-Zellerfeld, Germany*
[b] *Leibniz-Institut für Kristallzüchtung, Max-Born-Str. 2, D-12489 Berlin, Germany*
[c] *Keele University, School of Physical and Geographical Sciences, Lennard-Jones Laboratories, Keele, Staffordshire ST5 5BG, United Kingdom*
[d] *Technische Universität Clausthal, Institut für Energieforschung und Physikalische Technologien, Am Stollen 19, D-38640 Goslar, Germany*
[e] *Technische Universität Braunschweig, Institut für Physikalische und Theoretische Chemie, Hans-Sommer-Str. 10, D-38106 Braunschweig, Germany*

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ABSTRACT

$LiNbO_3$ and $LiTaO_3$ are isomorphous and Nb and Ta have the same valence electron configuration and the same ionic radii. This suggests the use of Ta as a tracer to probe the self-diffusion of Nb in $LiNbO_3$. The diffusion system consisted of a 20 nm layer of $LiTaO_3$ sputter deposited on top of (i) a congruent $LiNbO_3$ single crystal, i.e. (48.3 ± 0.1) mol% Li_2O, and on top of (ii) a VTE processed $LiNbO_3$ single crystal with nearly stoichiometric composition, i.e. (49.9 ± 0.1) mol% Li_2O. The diffusion anneals ($1000\ ^\circ\mathrm{C} \le T \le 1100\ ^\circ\mathrm{C}$) were performed under a constant oxygen partial pressure of 200 mbar. From the resulting SIMS depth profiles of tantalum a constant diffusivity was extracted which can be assumed to reflect the niobium self-diffusivity in $LiNbO_3$.

For sub-stoichiometric $LiNbO_3$ the joint discussion of this work and of literature data on the basis of the generally accepted defect model, $4[Nb_{Li}^{4\bullet}] = [V_{Li}']$, suggests Nb transport in the Li sublattice. For hyper-stoichiometric $LiNbO_3$ the defect model $5\left[V_{Nb}^{5'}\right] = \left[Li_i^{\bullet}\right]$ is derived from the $Li_3NbO_4/LiNbO_3$ solution reaction of the VTE process designed to obtain Li_2O-rich $LiNbO_3$ in accordance with the $Li_2O–Nb_2O_5$ phase diagram. This model is supported by theoretical calculations of the defect formation energy. Interestingly, the migration enthalpy for the Li vacancy mediated transport of the anti-site defect $Nb_{Li}^{4\bullet}$ in the Li sublattice of congruent, i.e. sub-stoichiometric, $LiNbO_3$ is similar (within a ±10% error) to the one derived for the Nb vacancy mediated transport of Nb in the Nb sublattice of hyper-stoichiometric $LiNbO_3$, i.e. about 3 eV.

The significant discrepancies between our results and some earlier literature data can be consistently rationalised if the experimental procedures of those studies are carefully analysed.

1. Introduction

Lithium niobate, $LiNbO_3$, has attracted substantial scientific and industrial interest in the last decades because of its excellent electro-optical, piezoelectric and acoustic properties [1]. The production of $LiNbO_3$ and $LiTaO_3$ based components as well as the increasing application of lithium niobate at high temperatures require an understanding of the atomic transport of the constituents [2]. Lithium is generally accepted to be the most mobile species [3–8]. For oxygen diffusion in lithium-deficient single crystalline $LiNbO_3$ there are two controversial data sets available [9,10]. The ^{18}O tracer diffusivity data in reference [9] seem, however, to be debatable because the solid–gas exchange method with mass spectrometric monitoring of the $^{18}O_2$ concentration of the gas phase is much less reliable than a state-of-the-art SIMS profiling method [10]. More recently, ^{18}O tracer diffusivity measurements were done using VTE processed single crystalline $LiNbO_3$ [11] and were discussed together with the data of lithium-deficient single crystalline $LiNbO_3$ [10]. Neglecting the older published oxygen diffusion data in reference [9] one can conclude that the lithium diffusivity is about 4–5 orders of magnitude larger than that of oxygen in the temperature range $800\ ^\circ\mathrm{C} \le T \le 1100\ ^\circ\mathrm{C}$.

Regarding the niobium diffusion there exist only three data sets published in 1975 and 1976 [12–14]. Unfortunately, the potentially most interesting publication [12], which applied the radioactive tracer ^{95}Nb, does not allow an unambiguous assessment of the ^{95}Nb tracer diffusion data because of an insufficient presentation of the results. Furthermore, the data presented in [12] deviate strongly from the other two data sets [13,14]. From the published information, it was absolutely not clear whether the reasons for the pronounced discrepancies between the diffusion data sets were due to the materials used (purity, etc.) or due to the analytical techniques applied. Therefore, it appeared necessary to design an experimental procedure suitable to exclude potential errors [11]. To avoid a repetition of the experimental details only the most relevant information on the earlier work [11] will be given in Section 2.

The subject of the present work is to study the atomic transport of Nb in $LiNbO_3$. Unfortunately, niobium has only one stable isotope, ^{93}Nb, and two (comparatively) difficult to handle radioactive isotopes,

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* Corresponding author. Tel.: +49 5323 72 2634.
E-mail address: peter.fielitz@tu-clausthal.de (P. Fielitz).

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e.g. ^{91m}Nb and ^{95}Nb. Therefore, we applied Ta as a diffusion tracer in $LiNbO_3$. This choice was motivated by the fact that $LiTaO_3$ is isomorphous to $LiNbO_3$, and that tantalum replaces niobium up to 100% when introduced into the crystal structure of lithium niobate [15]. Further, the ionic radii of Nb^{5+} and Ta^{5+} proposed by Shannon [16] are identical $(r_{Nb^{5+}} = r_{Ta^{5+}} = 64\ pm,\ CN = 6)$ and the atomic mass ratio of the two "isoelectronic" pentavalent ions should impose a diffusivity ratio of about only $\sqrt{2}$. Because of the high oxygen activity $(a_{O_2} = 0.2)$ throughout the different experimental steps no lower valence states than Nb^{5+} or Ta^{5+}, respectively, had to be taken into account [8]. Therefore, a thin $LiTaO_3$ film should be very well suited as a diffusion tracer source for the study of the atomic transport of Nb in $LiNbO_3$.

2. Experimental

For our earlier work [11] in 2011, VTE processed single crystals were produced via the vapour transport equilibration (VTE) technique [17] using a large mass of a lithium-rich two-phase mixture (Li_3NbO_4 and $LiNbO_3$) which acted as a Li_2O source during the VTE process. VTE processed samples from the same batch as used in Ref. [11] were employed for the Ta diffusion measurement of this work so that we refer to Ref. [11] for all experimental details of our VTE procedure. For completeness and better readability, the main parameters of the samples [11] are briefly reviewed: Z-cut $LiNbO_3$ wafers (composition: 49.0 mol% Li_2O, diameter = 50.8 mm, thickness = 0.5 mm) were purchased from Del Mar Photonics. The chemical analysis by ICP-OES spectrometry (after a microwave assisted conversion with a HNO_3/HF mixture into a soluble form) revealed the following impurities (in ppm): Mg (<36), Al (402), Ca (294), Cr (738), Mn (18), Fe (<16), K (<286), Na (<157), and Ti (156). The supplied lithium niobate wafer was cut into two pieces of equal size. One piece was used as reference whereas the other one was used for the VTE process applying a lithium-rich two-phase mixture. Small samples (about $5 \times 5 \times 0.5$ mm^3) were cut from the VTE processed $LiNbO_3$ wafer and cleaned with ethanol in an ultrasonic bath. The Li_2O content in the VTE processed samples was found to be (49.9 ± 0.1) mol% by measuring the absorption edge according to Ref. [18] using a UV–vis–NIR optical spectrometer (Perkin Elmer Lambda 900).

In order to study Ta diffusion in VTE processed, so-called stoichiometric z-cut $LiNbO_3$ as well as in congruent z-cut $LiNbO_3$ (supplied by Del Mar Photonics), we deposited a thin $LiTaO_3$ film on the surface of the samples. The deposition of a 20 nm layer of $LiTaO_3$ at the surface of the $LiNbO_3$ samples was done by 5 keV Ar^+ ion beam sputtering. A commercial ion beam coater of Gatan Inc. (IBC 681) was used with a single crystal of $LiTaO_3$ as sputter target, which allowed the deposition of very smooth $LiTaO_3$ layers. In order to avoid contaminations from the metallic target holder during ion beam sputtering the relatively small single crystal of $LiTaO_3$ (about $10 \times 10 \times 1$ mm^3) was glued on a larger single crystal of $LiNbO_3$ (about $20 \times 20 \times 1$ mm^3).

In the case of the VTE processed $LiNbO_3$ (stoichiometric) crystal, Li_2O loss during diffusion annealing in 200 mbar $^{16}O_2$ gas was avoided by placing the samples in a small platinum box (loosely closed by a platinum lid) which contained two sintered tablets of the lithium-rich two-phase mixture used for the VTE process [11]. The filled platinum box was moved into a furnace tube at room temperature and the furnace tube was subsequently evacuated to about 10^{-3} mbar total pressure for 1 h before filling it with 185 mbar $^{16}O_2$ gas (which resulted in a pressure of about 200 mbar at annealing temperature in the set-up used for the diffusion runs). In the case of congruent $LiNbO_3$, the samples were simply placed on a small Al_2O_3 holder which replaced the platinum box.

In the next step, the furnace was heated with a heating rate of 12 K/min and held for the annealing time, t, at annealing temperature, T. Thereafter the furnace was cooled to room temperature with a cooling rate of 12 K/min. For finite constant heating and cooling rates one can express the diffusion length, L, by $L^2 = 2D(t + \Delta t)$ where D is the diffusion coefficient and Δt is an effective additional annealing time taking into account diffusion during heating and cooling of the furnace (see Ref. [11] for a detailed description of the evaluation of Δt).

Tantalum depth distributions (Fig. 1) were determined by SIMS using a Cameca IMS 3f instrument. Negative 14.5 keV oxygen ions were used as primary beam with 100 nA ion current and a spot size of about 50 μm. The raster-scanned area amounted to 250×250 μm^2 and the diameter of the analysed zone was 60 μm. Positive secondary ions were used for the analysis of the samples. Sample charging was prevented by coating the sample surface with a 50 nm thick carbon film. For depth calibration the SIMS crater depth was measured using a surface profiler (Tencor, Alpha Step 500). The apparently lower background signal of the as-prepared sample is due to the fact that in this case the secondary ion intensity was reduced in order to prolong the life time of the electron multiplier (secondary ion detector). After the diffusion anneal, due to the lower Ta concentration at the surface, a different set of ion optics parameters was used, which led to a higher background signal.

In order to evaluate the diffusion coefficient from the tantalum depth profiles the solution of the diffusion equation for an instantaneous plane tracer source at position $x = 0$ on the surface of an infinite volume was used [19]

$$c(x,t) - c_\infty = \frac{M}{2(\pi D t)^{1/2}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (1)$$

where M is the total amount of diffusing tracer atoms, D is the constant diffusion coefficient, t is the annealing time and c_∞ is the background value for $x \to \infty$. The black solid curve in Fig. 1 shows a least-squares fit of Eq. (1). Also shown in Fig. 1 is the measured tantalum depth distribution of the sample after deposition of a thin $LiTaO_3$ layer (about 20 nm thickness). All measured Ta diffusion coefficients of this work are listed in Table 1. It should be noted that the experimentally determined diffusivity is a constant for a given temperature, which indicates that there is *one* dominant transport mechanism operational in a given material.

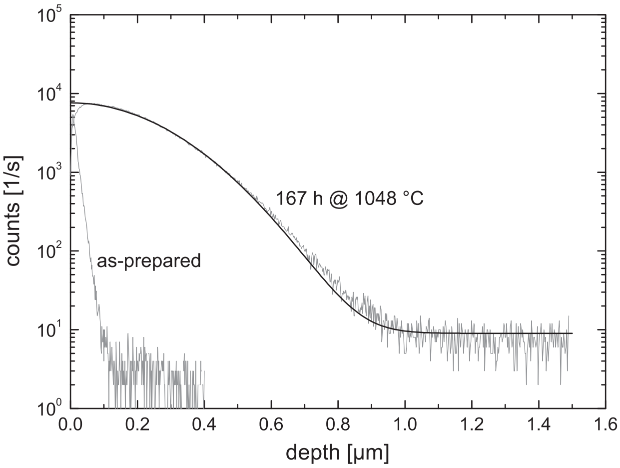

Fig. 1. Typical ^{181}Ta SIMS depth profiles (grey curves) of a VTE processed lithium niobate sample (z-cut). The shallow profile (as-prepared) was measured after the preparation of a 20 nm $LiTaO_3$ film on the sample surface. The deep profile was measured after 167 h of annealing at 1048 °C in 200 mbar $^{16}O_2$ gas.