

A SIMS Study on Li Diffusion in Single Crystalline and Amorphous LiNbO₃

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Keywords: Lithium niobate, self-diffusion, isotope hetero-structures, Secondary Ion Mass Spectrometry, ion beam sputter coating

Abstract. We investigated lithium self-diffusion in amorphous and single crystalline lithium niobate at low temperatures of 323, 423 and 623 K. The diffusivity was studied by secondary ion mass spectrometry (SIMS), using ion beam sputtered ⁶LiNbO₃ as a tracer source. Our intention was to get information how structural disorder influences ionic diffusivity, while chemical composition remains unchanged. The results indicate an increase of the Li diffusivity by about eight orders of magnitude in the amorphous state.

Introduction

Lithium niobate (LiNbO₃) does not exist in nature as a stable compound. However, artificial single crystals can be grown from the melt by the Czochralski method. LiNbO₃ is stable over a wide solid solution range from 44 mol% to about 50.5 mol% Li₂O [1]. Czochralski grown single crystals commonly show the congruent composition of about 48.5 mol% Li₂O. In its single crystalline state, lithium niobate is a ferroelectric oxide material of high technological interest because of its piezoelectric, electro-optic and acoustic properties [2-4]. It is also a three-dimensional ion conductor, however, with a relatively low conductivity of $\sim 10^{-12}$ S/cm at 500 K [5] not suitable for technical applications in, e.g., solid electrolytes of secondary Li ion batteries [6]. However, if structural disorder is introduced, ion conductivity is expected to increase significantly [5] due to a higher Li ion mobility. Consequently, this material is an ideal model system to study how structural disorder may modify ionic diffusivity. Structural disorder can be introduced into a system by changing the structural state from single crystalline to amorphous. The aim of the present paper is to show in a first study how the ionic diffusivity differs in amorphous and single crystalline LiNbO₃. Consequently, Li self-diffusion studies were carried out at low temperatures using secondary ion mass spectrometry (SIMS). Such studies do not exist for temperatures below 773 K up to now [7,8].

In order to realize tracer diffusion studies for Li containing solids, stable tracers have to be used. The element has two stable isotopes (⁶Li and ⁷Li) with a natural abundance of 7.5 % and 92.5 %, respectively. Radioactive tracer isotopes with a half-life larger than some seconds, which would be suitable for radio-tracer measurements do not exist. In order to realize tracer deposition a certain amount of stable tracer isotopes have to be positioned in or on top of the material under investigation. In the present study we used isotope enriched ⁶LiNbO₃ as a tracer source (see Fig. 1).

For the study of diffusion in single crystals we deposited by ion beam sputter coating (IBC) a thin layer (30-50 nm) of isotope enriched ⁶LiNbO₃ (enrichment: 95%) as a tracer source on top of a commercially available single crystal with natural isotope abundance (see Fig. 1(a)). The result is a so-called isotope hetero-structure [9,10]. A combination of LiNbO₃ layers with different isotope

enrichment, but the same chemical composition allows one to study pure tracer diffusion without a gradient in chemical potential. The amorphous LiNbO_3 sample was produced by IBC, as well. Here, the arrangement of Fig. 1(b) was used, where first a thick layer (800 nm) of isotope enriched $^7\text{LiNbO}_3$ (enrichment: 99%) is deposited on a sapphire substrate. Afterwards, again a thin layer of isotope enriched $^6\text{LiNbO}_3$ was deposited as a tracer layer. Annealing at elevated temperatures induced isotope interdiffusion, while the ^6Li penetrated deeply into the single crystalline $^{\text{nat}}\text{LiNbO}_3$ or amorphous $^7\text{LiNbO}_3$. From the isotope depth profiles as measured by SIMS, diffusivities can be extracted.

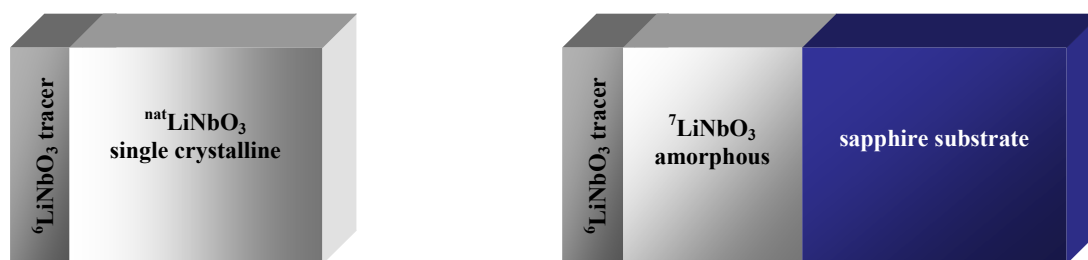


Fig. 1: Arrangement of isotope hetero-structures: (a) $^6\text{LiNbO}_3$ on single crystalline $^{\text{nat}}\text{LiNbO}_3$; (b) $^6\text{LiNbO}_3$ on amorphous $^7\text{LiNbO}_3$.

Experimental

Single crystalline LiNbO_3 with an orientation of (001) from Crystec (Berlin, Germany) was used for the investigation of diffusion in the crystalline state. The single crystal has a chemical composition of 48.6 mol % Li_2O as found by UV absorption spectroscopy according to Ref. [11]. $10 \times 10 \times 0.5 \text{ mm}^3$ polished pieces were used for the experiments. The amorphous samples were produced by IBC on a (001) sapphire substrate from Crystec (Berlin, Germany). No interdiffusion between sapphire and LiNbO_3 took place.

Ion Beam Coating: Sputter deposition was carried out by a commercial ion beam coater of Gatan Inc (IBC 681). Two penning ion guns were in right angular position to each other and were focused on the target material (Fig. 2). Isotope enriched LiNbO_3 powder for the targets was obtained by a chemical reaction of commercially available Nb_2O_5 and $^{6/7}\text{Li}_2\text{CO}_3$. The target material was produced by mechanical pressing of the lithium niobate powder, which was sintered afterwards at 1173 K to a solid body. In order to get a nearly stoichiometric composition after deposition the targets were enriched in Li_2O (+ 10-15%) over the stoichiometric composition. We used two different types of LiNbO_3 targets, one enriched with ^6Li , the other with ^7Li . Both targets could be used as actual sputter targets without breaking the vacuum of (10^{-6} mbar) within the coater. During operation the sputter guns were floated with Ar gas (operating pressure: 5×10^{-5} mbar) and an ion beam with a voltage of 5 keV and a current of about 200 μA was produced which was focused on the target. This process released ions from the target, which formed a homogeneous LiNbO_3 layer on the substrate.

Sputter deposition using an ion beam coater has many advantages over other methods like, e.g., magnetron sputtering. The sputtering targets are comparatively small (20 mm in diameter and 2 mm in thickness). Consequently, the usage of relatively expensive rare stable isotopes becomes possible. Furthermore, the deposition process occurs at room temperatures without significant heating of the target and sharp material interfaces can be produced.

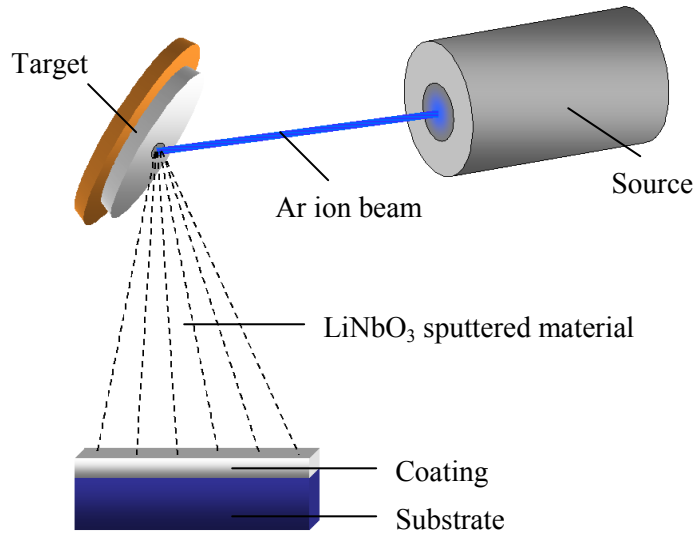


Fig. 2: Schematic view of the sputtering process with an ion beam sputter coater (IBC).

Secondary Ion Mass Spectrometry: SIMS was done using a Cameca IMS 3f/4f machine. An O⁻ primary ion beam (15 keV, 50 nA) was used in order to prevent electrical charging during the measurement. The sputtered area was about 250 μm x 250 μm from which 20 % in the centre were gated for further signal processing in a double focused mass spectrometer. Measurements were made in the depth profile mode. The resulting sputter crater was evaluated afterwards by a mechanical profilometer. This allowed one to transform sputter time into depth. The secondary ion intensities of ${}^6\text{Li}^+$ and ${}^7\text{Li}^+$ 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 ${}^6\text{Li}$ atomic fractions $c(x, t)$ according to

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

Annealing: For the 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. The annealing time was between 2.5 h and 35 days. Additional diffusion annealing experiments were carried out in a commercial rapid thermal annealing setup (AO 500, MBE, Germany) in Argon. Here, extremely high heating rates are possible which allow one to apply annealing times down to several seconds.

X-Ray Diffraction: The investigations with X-ray diffractometry were carried out with a Bruker D5000/Kristalloflex diffractometer in the grazing incidence mode using $\text{CoK}\alpha$ radiation (40 kV, 40 mA) and an incidence angle of 3° . Phase analysis was carried out using the Rietveld program named POWDERCELL for WINDOWS 2.3.

Results and Discussion

As shown in Fig. 3 the LiNbO_3 layers deposited by IBC were X-ray amorphous. The amorphous state was retained for annealing in Argon up to 673 K. Annealing at a higher temperature of 773 K lead to crystallization and the formation of nearly single phase polycrystalline LiNbO_3 (Fig. 3). This was checked for sputtered layers of each target material. The excess Li_2O present in the targets vanished during the sputtering processes.

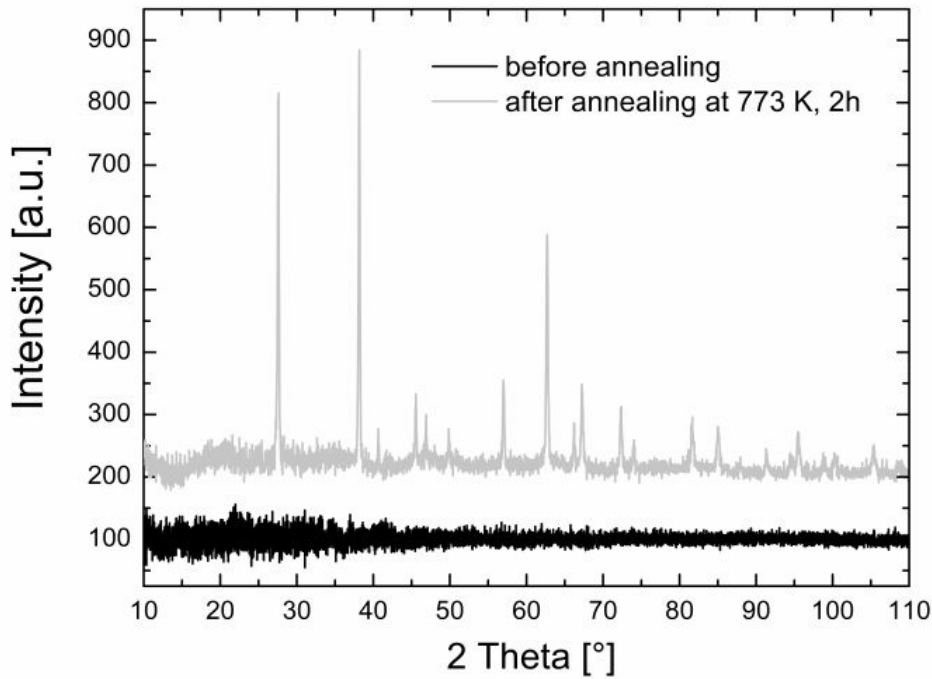


Fig. 3: X-ray diffraction patterns of a LiNbO₃ sputter layer in the as-deposited state and after annealing at 773 K. All Bragg peaks correspond to the LiNbO₃ phase (space group R3c) [4].

In Fig. 4 the ⁶Li atomic fractions, as determined by SIMS, are plotted versus depth for diffusion in the single crystal at 423 K (a) and 623 K (b), respectively.

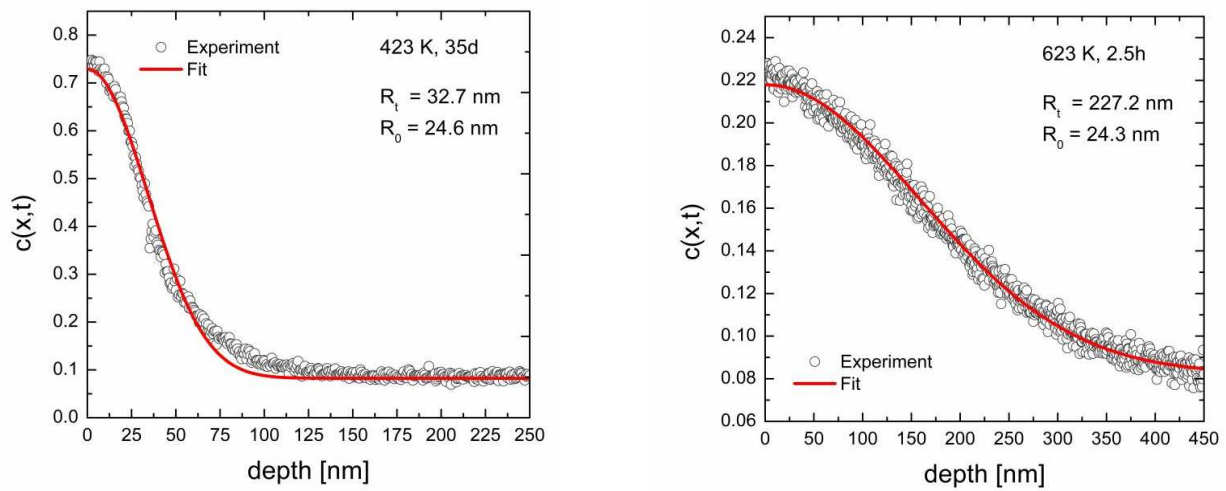


Fig. 4: ⁶Li fraction as a function of depth for the single crystalline samples annealed at (a) 423 K and (b) 623 K. The straight lines correspond to fits according to Eq. 2.

The experimentally determined depth profiles, which broadened after annealing, can be described by the following solution of Fick's second law for self-diffusion across an interface [12]

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

where c_∞ is the natural abundance of ^6Li in the single crystal ($c_\infty = 0.075$) or in the amorphous layer ($c_\infty = 0.01$) and $c_0 = 0.99$ that in the tracer layer. The original thickness of the as-deposited tracer layer is denoted as h , which was determined by SIMS to range between 20 – 50 nm, depending on the sample under investigation. In order to get the diffusivity, D , the quantity R , describing the broadening of the tracer profile was treated as a fit parameter and we obtained the self-diffusivity at time t from the difference in R of the diffusion profile and of the starting profile according to $D = (R_t^2 - R_0^2)/4t$. The values of R_t and R_0 are indicated in Fig. 5 and the determined diffusivities are listed in Table 1. At room temperature, no diffusion takes place within several month of storing the samples in air.

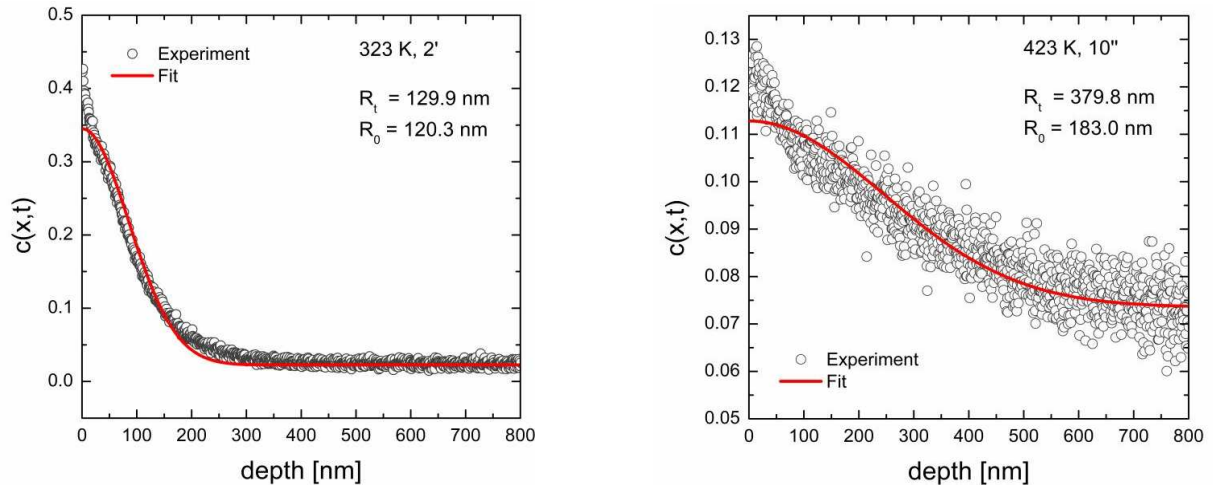


Fig. 5: ^6Li fraction as a function of depth for the amorphous samples annealed at (a) 323 K and (b) 423 K. The straight lines correspond to fits according to Eq. 2.

Fig. 5 shows the ^6Li fraction as function of depth for the amorphous samples at 323 K (a) and 423 K (b), respectively. In order to fit these data we use again Eq. 2. It has to be mentioned that considerable diffusion takes place in the amorphous state at room temperature on the time scale of several hours. In order to eliminate or at least minimize this effect, the $^6\text{LiNbO}_3$ tracer layer was deposited on two identical samples in a single sputter run. Afterwards one sample was measured by SIMS immediately after deposition. The R value determined serves as starting state $R = R_0$, in order to determine the diffusivity of the second sample, which was immediately annealed and measured by SIMS after deposition. The diffusivities are shown in Table 1.

Table 1: Comparison of diffusivities, D , in amorphous and single crystalline lithium niobate at different temperatures.

	323 K	423 K	623 K
Amorphous	$5.0 \cdot 10^{-18} \text{ m}^2/\text{s}$	$2.8 \cdot 10^{-15} \text{ m}^2/\text{s}$	-
Single crystal	-	$3.8 \cdot 10^{-23} \text{ m}^2/\text{s}$	$1.4 \cdot 10^{-18} \text{ m}^2/\text{s}$

If we compare the method. In contrast, in amorphous samples fast diffusion on the length scale of several tens of nanometer occurs within minutes. At 623 K approximately the same diffusivity is measured for the single crystals as for the amorphous sample at 323 K. At 623 K diffusivity in the amorphous state is too fast to be measured by the present arrangement. At 423 K a direct comparison of diffusivities in both states is possible. Diffusion in amorphous lithium niobate is faster by about eight orders of magnitude, which is tremendous. In other materials like *e.g.* silicon nitride, where a direct comparison of diffusivity in the amorphous and crystalline states was done, this fac-

tor is much lower (about one to two orders of magnitude) [10,13]. An explanation for this high Li ionic mobility in amorphous lithium niobate is that in the amorphous state the atoms are more loosely packed than in the crystalline state. Consequently, the activation enthalpy of Li migration is expected to be smaller than in the crystalline state. Detailed temperature dependent measurements, which will clarify this point, are in progress.

Conclusion

We used secondary ion mass spectrometry (SIMS) and isotope hetero-structures to investigate Li self-diffusion in single crystalline and amorphous lithium niobate at 323, 423 and 623 K. We showed that Li diffusion is much faster in the amorphous state, about eight orders of magnitude at 423 K. A very loosely packed structure of the amorphous state should be present in order to explain this result.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft (DFG) in the framework of the research unit 1277 molife (SCHM1569/17-1) is gratefully acknowledged. Thanks are due to H. Shi (TU Braunschweig) for the determination of the Li_2O content of the single crystal.

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Diffusion in Materials - DIMAT 2011
10.4028/www.scientific.net/DDF.323-325

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10.4028/www.scientific.net/DDF.323-325.69