

Low-Temperature DC Conductivity of LiNbO_3 Single Crystals

By B. Ruprecht^{1,3,*}, J. Rahn², H. Schmidt^{2,3}, and P. Heitjans^{1,3}

¹ Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, Callinstr. 3-3a, 30167 Hannover, Germany

² Institut für Metallurgie, Thermochemie und Mikrokinetik, Technische Universität Clausthal, Robert-Koch-Str. 42, 38678 Clausthal-Zellerfeld, Germany

³ ZFM – Zentrum für Festkörperchemie und Neue Materialien, Leibniz Universität Hannover, Callinstr. 3-3a, 30167 Hannover, Germany

(Received February 10, 2012; accepted March 15, 2012)

(Published online May 14, 2012)

Lithium Niobate / Self-Diffusion / Ionic Conductivity / Impedance Spectroscopy / Haven Ratio

We report on conductivity measurements of LiNbO_3 single crystals with congruent composition in ambient atmosphere between 449 and 727 K which include the lowest temperatures covered so far. The ionic DC conductivity observed along the *c*-axis at, *e. g.*, 650 K is $6.7 \times 10^{-9} \text{ S/cm}$ and shows an activation energy of 1.33 eV. The corresponding Li^+ diffusion coefficients range between 2.5×10^{-22} and $1.4 \times 10^{-16} \text{ m}^2/\text{s}$. These results are perfectly consistent with our conductivity results in the high-temperature regime as well as SIMS measurements published recently (Rahn *et al.*, Phys. Chem. Chem. Phys. **14** (2012) 2427). From the Li^+ diffusion coefficients obtained here a Haven ratio of 0.7(2) can be deduced.

1. Introduction

Lithium niobate, LiNbO_3 , exists in a composition range between 44 and 50.5 mol% Li_2O [1]. When grown by the Czochralski method the material is non-stoichiometric with a congruent composition of 48.5 mol% Li_2O . LiNbO_3 is known for its ferroelectricity, but also electro-optic, and pyroelectric effects can be observed [2–4]. It has its Curie temperature at about 1200 °C which is close to the melting temperature [5,6]. Over the years several defect models were proposed by different authors; however, the defect chemistry in LiNbO_3 is not yet fully understood [2,7–12]. Since the defect chemistry is directly related to the Li/Nb ratio and the oxygen activity, it is not surprising that also the physical properties, in particular, *e. g.*, the Curie temperature, and the Li diffusivity depend on the composition [10,13–15].

Very recently we published a comparative study of Li diffusion in LiNbO_3 single crystals [16]. There, tracer diffusion coefficients obtained from secondary ion mass

* Corresponding author. E-mail: ruprecht@pci.uni-hannover.de

spectrometry (SIMS) measurements were compared to diffusion coefficients calculated from DC conductivities σ_{DC} . Good agreement was found between diffusion coefficients as well as between activation energies. Hence, a Haven ratio close to unity was deduced. However, the temperature ranges of 423 to 773 K (SIMS) and 694 to 952 K (DC conductivity) covered by the diffusivities obtained by the two methods overlap by only 79 K.

Up to now, the conductivity of LiNbO_3 has been investigated in several studies which have in common that they were focused on the temperature regime above 700 K. Early works of Bergmann [17] and Jorgensen *et al.* [15] elucidated the oxygen partial pressure (p_{O_2}) dependence of the overall conductivity in the high- T regime. Moreover, the authors also found first indications for the conductivity being dependent on the chemical composition. This effect was later confirmed and investigated in more detail by Jundt *et al.* [14].

The conductivity of LiNbO_3 single crystals is barely dependent on the orientation, see Ref. [18]. However, Niitsu *et al.* [19] observed higher dielectric relaxation frequencies in wafers cut perpendicular to the polar axis (Z-cut) than in the samples cut parallel to the c -axis and attributed this to polarization effects.

Furthermore, sintered ceramic LiNbO_3 samples were investigated by Lanfredi *et al.* [20]. They found conductivities comparable to those in single crystals.

Mehta *et al.* [21] reported an activation energy of 1.43 eV for the ionic conductivity of congruent LiNbO_3 in the limited temperature range between 1223 and 1323 K which is close to our findings [16]. However, when the conductivities are extrapolated to higher or lower temperatures, respectively, the absolute values differ by about one order of magnitude.

To our knowledge, ion conductivity studies of LiNbO_3 in the low-temperature regime below 700 K are quite rare. In a comparative study of nanocrystalline and amorphous LiNbO_3 by Masoud *et al.* [22], single crystals were investigated in N_2 atmosphere in the narrow temperature regime between 470 and 512 K for reference purposes. An investigation in the range from 323 to 573 K by Franke [23], using Li electrodes, lacked comparative measurements with blocking electrodes in air, and therefore the surprisingly small activation energy values, reported to be between 0.5 eV and 0.7 eV, are questionable.

In the present study, our goal was to extend our conductivity measurements to considerably lower temperatures and thus to examine the Arrhenius behaviour of the conductivity over a larger range as well as to provide a much larger overlap with the temperature regime of the SIMS measurements so that the consistency of the different data sets could be checked in more detail.

2. Experimental

C -axis oriented LiNbO_3 single crystal wafers from CrysTec (Berlin, Germany) were polished on both sides to a thickness of 0.35–0.40 mm. Note that the measurements were done on the same sample material as discussed in Ref. [16]. Silver conductive adhesive paste from Alfa Aesar was used to apply plane-parallel electrodes of about 5 mm in diameter on both sides of the cleaned samples. After a first drying step Pt sheets

were glued on both sides with a small amount of Ag paste. In a final preparation step the samples were kept at $T > 700$ K in air for several days.

The frequency dependent complex conductivity $\sigma(\omega)$ was measured using a home-built cell with four-point Pt wiring and spot-welded Pt contacts. Good electric contact between the sample and the jig was achieved by using a spring mechanism. For temperature variation the cell was placed in a LOBA tube furnace from HTM Reetz (Berlin, Germany) and the temperature was measured within ± 2 K accuracy using a type K thermocouple attached close to the sample and read out by a Eurotherm controller. Before a measurement was started, the temperature was allowed to stabilize for at least one hour.

The cell was connected to an Alpha-A impedance analyzer and a ZG4 impedance interface, both from Novocontrol (Hundsangen, Germany). $\sigma(\omega)$ was probed between 449 and 727 K with an alternating voltage of 100 mV applied. In order to accurately record the DC plateau values, data were taken down to low frequencies of 10 mHz. The program WinDETA (Novocontrol) was used for analyzer control and data acquisition. All measurements were performed in ambient atmosphere.

The Li/Nb ratio of the material was determined by UV/Vis spectroscopy of the wafers and yielded the congruent composition of 48.5(1) mol% Li₂O. The polar crystal orientation specified by CrysTec was confirmed in XRD measurements.

3. Results and discussion

The temperature dependent conductivities of LiNbO₃ single crystals were measured in two runs with positive and negative temperature stepping. In the first run T was increased from 474 to 704 K while in the second run the sample was heated to 727 K and subsequently stepwise cooled down to 449 K. The two runs gave consistent results, *i. e.* no hysteresis showed up. In the regime of low frequencies distinct DC plateaus of $\sigma'(\omega)$ were observed. The plateau values between 10 and 100 mHz were used for further processing. Such $\sigma_{\text{DC}}(\omega \neq 0)$ values taken from AC measurements are strictly speaking not identical to $\sigma'(0)$, the real part of $\sigma(\omega)$ for $\omega = 0$, which can only be probed in DC measurements. However, the methods usually yield the same value, *i. e.* $\sigma_{\text{DC}}(\omega \neq 0) = \sigma'(0)$ is commonly observed.

In our previous study we compared DC conductivity values to diffusion coefficients measured by SIMS [16]. Since the latter diffusion anneals were done in ambient air, we applied also oxidizing atmosphere in the conductivity spectroscopy studies. Thus, it was not possible to use lithium electrodes and DC currents to probe $\sigma'(0)$. DC conductivity measurements with Li electrodes done by Franke showed a significant drop of $\sigma'(0)$, when air was allowed to flow into the cell evacuated beforehand [23]. Fortunately, in our case the low-frequency plateaus were not disturbed by significant blocking effects of the passive Ag electrodes. There is also no indication for a dispersive behaviour of $\sigma'(\omega)$ below 100 mHz. Hence, we identified the values $\sigma'(10 \text{ mHz} - 100 \text{ mHz})$ with the DC conductivity σ_{DC} .

In the temperature range from 449 to 727 K we obtained DC conductivities σ_{DC} from 1.9×10^{-13} to 6.7×10^{-8} S/cm. Compared to the HP 4192A analyzer used for the measurements published in Ref. [16] the Alpha-A can detect conductivities which are

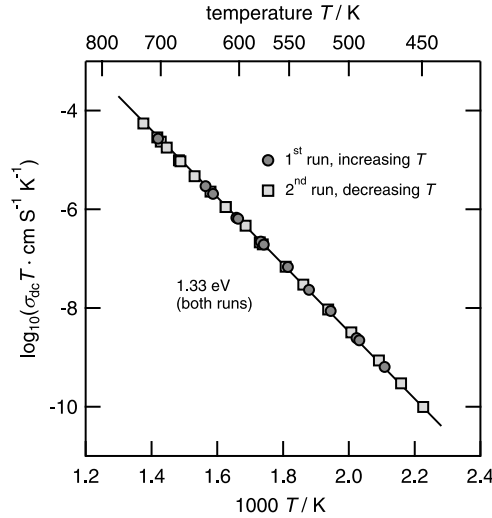


Fig. 1. DC conductivity σ_{DC} of LiNbO_3 single crystals measured between 449 and 727 K in two separate runs. $\sigma_{\text{DC}}T$ shows Arrhenius behaviour over the temperature range covered. The corresponding activation energy found is 1.33 eV.

lower by up to seven orders of magnitude. Thus, we could extend the range in which the LiNbO_3 single crystals have been probed significantly.

In Fig. 1 the DC conductivities multiplied by the annealing temperature are plotted against the inverse temperature. Data of both runs show Arrhenius behaviour according to

$$\sigma_{\text{DC}}(T)T = A \exp\left(-\frac{E_a}{k_B T}\right), \quad (1)$$

where k_B is Boltzmann's constant and A is a pre-exponential factor. The activation energy turned out to be $E_a = 1.33$ eV. This result was found for a joint fit of data from the two runs as well as the separate fits of the first and second run, respectively.

The results of the measurements shown here are perfectly consistent with the data from our studies at higher temperatures presented earlier [16]. There we reported on Li conductivity measurements between 694 and 952 K with conductivities ranging between 2.8×10^{-8} and 1.3×10^{-5} S/cm. The corresponding activation energy of 1.42 eV is slightly higher than in the present measurements at low temperatures.

For a direct comparison of σ_{DC} in the high- T and low- T regions, the data are plotted together in Fig. 2. In terms of absolute $\sigma_{\text{DC}}T$ values both data sets show excellent agreement at common temperatures close to 700 K. Moreover, $\sigma_{\text{DC}}T$ can be fitted between 449 and 952 with a single Arrhenius line, *i. e.* there is no visible change in the conduction mechanism between 449 and 952 K. As expected, the corresponding activation energy of 1.35 eV is just between the values of 1.33 and 1.42 eV of low- T and high- T data fitted separately.

In an early publication Bergmann [17] reported a $p_{\text{O}_2}^{-1/4}$ dependence of σ for O_2 partial pressures well below one atmosphere and for high temperatures up to 1400 K.

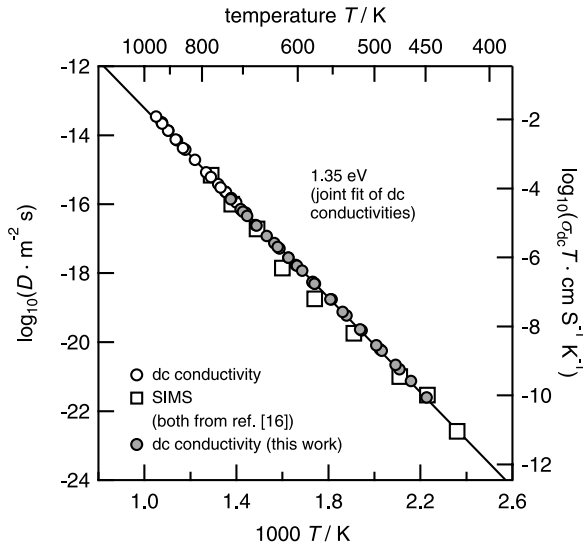


Fig. 2. Li diffusion coefficients in LiNbO₃ single crystals. Nernst–Einstein diffusion coefficients D^{NE} from low- T (this work) and high- T (Ref. [16]) conductivity data (right-hand scale) are compared to tracer diffusion coefficients obtained by SIMS [16].

In contrast, for high p_{O_2} and $T < 1200$ K the conductivity was independent of p_{O_2} . Furthermore, for high oxygen partial pressures $\sigma(T)$ showed Arrhenius behaviour with activation energies of 1.5 and 2.15 eV for temperatures lower and higher than about 1200 K, respectively. A similar investigation by Jorgensen *et al.* [15] also revealed the $p_{\text{O}_2}^{-1/4}$ dependence of the conductivity in LiNbO₃. In good accordance with Bergmann [17] the authors found an activation energy of 2.12 eV at low p_{O_2} and high T . This is half of the formation energy of a singly charged oxygen vacancy and a free electron [15,17]. Hence, the corresponding conduction mechanism is electronic in nature. However, the low-temperature activation energy is between about 1.7 eV (see Fig. 3 in Ref. [15]) and 1.89 eV which is higher than the value of 1.5 eV found by Bergmann [17].

In summary, this discussion means for our measurements in ambient atmosphere, *i. e.* at high oxygen partial pressures p_{O_2} , and at temperatures well below 1200 K that the conductivity probed is ionic. Thus, ionic diffusion coefficients D^{NE} can be calculated from the conductivities σ_{DC} , using the Nernst–Einstein relation

$$\sigma_{\text{DC}} = \frac{ne^2 D^{\text{NE}}}{k_{\text{B}} T}, \quad (2)$$

where e is the elementary charge and n is the number density of mobile charge carriers. The latter can be estimated as follows. Since the LiNbO₃ single crystals were prepared from a congruent melt with 48.5 mol% Li, a significant amount of Li vacancies has to be expected enabling the Li⁺ ions to contribute to the conduction process. Considering the small diffusion coefficients of oxygen and niobium in LiNbO₃, it

is appropriate to regard Li^+ ions as the only mobile ion species at the temperatures under investigation [15,18,24,25]. Since an electronic contribution to conductivity was ruled out (see above) we attributed the overall conductivity to the transport of Li^+ and used the number N of Li^+ ions per unit cell volume V as the charge carrier density $n = N/V = 6/(0.318 \text{ nm}^3)$.

The diffusion coefficients calculated from high- T conductivity measurements and the tracer diffusion coefficients determined by SIMS showed excellent agreement, *i. e.* a Haven ratio

$$H = D/D^{\text{NE}} \quad (3)$$

close to unity was obtained [16]. Correspondingly, also the results from the present work are highly consistent with the SIMS data, as can clearly be seen from Fig. 2. From tracer diffusion measurements based on SIMS experiments between 423 and 773 K the activation energy of Li diffusion was found to be 1.33 eV which is in perfect agreement with the present low- T results. Let us emphasize that the temperature range covered in the two experiments is very similar. In terms of absolute diffusion coefficients there is only a minor deviation between the two experiments, and correspondingly a Haven ratio of $H = 0.7 \pm 0.2$ can be estimated. This confirms that under the present conditions Li is the only mobile species contributing to conductivity and that strong correlation effects in the Li jump process are absent.

Finally, our results are also in accordance with those reported in literature. In terms of absolute conductivities the values of the present work compared to those from Refs. [19,20] are less than half an order of magnitude smaller. Furthermore, when our data are extrapolated to higher temperatures, very good agreement with the low- T results from Refs. [15,17] is observed. Additionally, the corresponding activation energies found for non-stoichiometric single crystals range from 1.24(2) to about 1.7 eV and are therefore fully compatible with our results [15,19].

4. Conclusion

We probed the conductivity of LiNbO_3 single crystals along the polar c -axis ([0001]-direction) in the regime of low temperatures between 449 and 727 K in air. Taking into account the known effects of an oxidizing atmosphere and high temperatures it is clear that the conductivity measured is ionic in this regime. The DC conductivity can be attributed to the motion of Li ions and described by a single Arrhenius law with an activation energy of 1.33 eV in the whole temperature range investigated. The results fit well to those from studies in the literature and, in particular, to the results obtained in the high-temperature regime on the same sample material in our previous study [16]. Consequently, there is no indication for a change in the Li conduction mechanism in LiNbO_3 for temperatures between 449 and 952 K. Moreover, the results are supported by SIMS based tracer diffusion measurements in the same temperature regime, which allowed us to determine a Haven ratio of 0.7(2).

Acknowledgement

Financial support from the Deutsche Forschungsgemeinschaft (DFG) in the framework of the research unit FOR 1277 ('molife') is gratefully acknowledged. We thank Prof. M. Wilkening for access to the impedance analyzer system Concept 80 as well as Dr. I. Hanzu and Dr. E. Hüger for helpful discussions.

References

1. P. Lerner, C. Legras, and J. P. Dumas, *J. Cryst. Growth* **3** (1968) 231.
2. B. T. Matthias and J. P. Remeika, *Phys. Rev.* **82** (1951) 727.
3. K. Nassau, H. J. Levinstein, and G. M. Loiacono, *J. Phys. Chem. Solids* **27** (1966) 983.
4. G. E. Peterson, A. A. Ballman, P. V. Lenzo, and P. M. Bridenbaugh, *Appl. Phys. Lett.* **5** (1964) 62.
5. K. Nassau, H. J. Levinstein, and G. M. Loiacono, *Appl. Phys. Lett.* **6** (1965) 228.
6. G. A. Smolenskii, N. N. Krainik, N. P. Khuchua, V. V. Zhdanova, and I. E. Mylnikova, *Phys. Status Solidi (b)* **13** (1966) 309.
7. H. Fay, W. J. Alford, and H. M. Dess, *Appl. Phys. Lett.* **12** (1968) 89.
8. G. E. Peterson and A. Carnevale, *J. Chem. Phys.* **56** (1972) 4848.
9. S. C. Abrahams and P. Marsh, *Acta Crystallogr. B* **42** (1986) 61.
10. D. P. Birnie and P. F. Bordui, *J. Appl. Phys.* **76** (1994) 3422.
11. H. Xu, D. Lee, S. B. Sinnott, V. Dierolf, V. Gopalan, and S. R. Phillpot, *J. Phys. Condens. Matter* **22** (2010) 135002.
12. J. Shi, H. Fritze, G. Borchardt, and K.-D. Becker, *Phys. Chem. Chem. Phys.* **13** (2011) 6925.
13. J. R. Carruthers, G. E. Peterson, M. Grasso, and P. M. Bridenbaugh, *J. Appl. Phys.* **42** (1971) 1846.
14. D. H. Jundt, M. M. Fejer, R. G. Norwood, and P. F. Bordui, *J. Appl. Phys.* **72** (1992) 3468.
15. P. J. Jorgensen and R. W. Bartlett, *J. Phys. Chem. Solids* **30** (1969) 2639.
16. J. Rahn, E. Hüger, L. Dörrer, B. Ruprecht, P. Heitjans, and H. Schmidt, *Phys. Chem. Chem. Phys.* **14** (2012) 2427.
17. G. Bergmann, *Solid State Commun.* **6** (1968) 77.
18. D. P. Birnie, *J. Mater. Sci.* **28** (1993) 302.
19. G. T. Niitsu, H. Nagata, and A. C. M. Rodrigues, *J. Appl. Phys.* **95** (2004) 3116.
20. S. Lanfredi and A. C. M. Rodrigues, *J. Appl. Phys.* **86** (1999) 2215.
21. A. Mehta, E. K. Chang, and D. M. Smyth, *J. Mater. Res.* **6** (1991) 851.
22. M. Masoud and P. Heitjans, *Defect Diffus. Forum* **1016** (2005) 237.
23. H. Franke, *Phys. Status Solidi (a)* **83** (1984) K73.
24. P. Fielitz, G. Borchardt, R. A. De Souza, M. Martin, M. Masoud, and P. Heitjans, *Solid State Sci.* **10** (2008) 746.
25. P. Fielitz, O. Schneider, G. Borchardt, A. Weidenfelder, H. Fritze, J. Shi, K. D. Becker, S. Ganschow, and R. Bertram, *Solid State Ion.* **189** (2011) 1.