In situ Investigation of OH⁻ Absorption in LiNbO₃ and LiNbO₃:MgO Crystals during Reducing/Oxidizing Annealing

Yu. Sugak[a], D. Sugak[a,b,*], Ya. Zhydachevskii[a], I. Solskii[b], O. Buryy[a], S. Ubizskii[a]
and K.-D. Becker[c]

[a]Lviv Polytechnic National University, Lviv, Ukraine

[b]Institute of Materials, SRC "Carat", Lviv, Ukraine

[c]Institute of Physical and Theoretical Chemistry, Technical University Braunschweig, Braunschweig, Germany

The work presents experimental results of an *in situ* investigation of the OH⁻ absorption in pure and MgO-doped LiNbO₃ crystals during reducing (95% Ar + 5% H₂) and oxidizing (O₂) high-temperature treatments in the temperature range from room temperature to 820 K. The absorption spectra measured *in situ* at high temperatures in reducing/oxidizing atmospheres have been analyzed. The origin of the changes in optical absorption caused by heating of the crystal is discussed in terms of the OH-bonds orientation change.

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1. Introduction

In lithium niobate (LiNbO₃) hydrogen can be found in the form of OH⁻ molecular ions, as well as in nearly all ABO₃ compounds. The concentration of OH-groups in nominally undoped LiNbO₃ is about 10^{18}–10^{19} cm⁻³. OH-groups can get to the crystal both together with the raw material and during the crystal growth, since water is always present in air [1, 2].

Role of OH⁻ impurities in LiNbO₃ has been intensively studied because of large number of important applications of this crystal. It is well known that essential role in photorefractive properties of LiNbO₃ is played by hydrogen impurities. In particular, thermal fixing of holograms, recorded in LiNbO₃ crystals is explained by migration of hydrogen ions [3]. On the other hand, fabrication of optical waveguides by the so-called proton exchange method is also connected with the presence of OH⁻ impurities in the crystal. In this case LiNbO₃ crystal plates are heated in water-saturated atmosphere [4].

To investigate the defects, connected with the presence of OH-groups in LiNbO₃ crystal, one can use infrared spectroscopy method, the Raman spectroscopy method, nuclear-magnetic resonance (NMR) etc. The most accessible method for hydrogen impurities investigation is registration of absorption spectra at about 2500 nm, in the range, where vibrations of O–H bonds become apparent [5].

The infrared absorption band, associated with OH⁻ stretching vibrations was firstly reported in 1968 [6]. From that time much work has been done on that topic.

Nevertheless, many aspects related to the OH⁻ absorption spectra, such as site occupation of protons or the components of OH⁻ absorption band are only partly understood [7–10]. The form of the absorption band and its maximum position are dependent on the crystals composition — congruent, stoichiometric, presence of impurities. This fact allowed the authors of Refs. [11, 12] considering the OH⁻ absorption band as an indicator of the crystals composition. As a result a new method of crystals composition determination, by the form and position of the OH⁻ absorption band maximum, was proposed. Nevertheless, despite the huge amount of works devoted to the investigation of OH⁻ impurities in LiNbO₃ crystal, the influence of reduction/oxidation (redox) annealing on the changes in OH⁻ absorption band in LiNbO₃ with different composition as well as the correlation of these changes with changes in visible spectral region are not studied enough.

In Refs. [2, 9] it was shown that incorporation of hydrogen in the crystal can be achieved by means of crystals annealing in vapour-rich atmosphere at about 670 K. In Refs. [2, 3, 9] the experiments of hydrogen removing from the crystal were held during its annealing in vacuum at about 670 K. The authors consider that in this case H⁺-ions leave the crystal in forms of H₂O molecules and, at the same time, crystal reduces and obtains dark color. After that one can make LiNbO₃ crystal transparent and free from hydrogen impurities by annealing it in pure oxygen atmosphere avoiding ingress of moisture.

At the same time NMR investigations of LiNbO₃ crystals, that were previously annealed in vapour-rich atmosphere, have not shown any changes in H⁺ concentrations within the error limits of the experiment [13, 14].

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* corresponding author; e-mail: `sugak@carat.lviv.ua`

As for *in situ* investigations of OH⁻ absorption spectra, we know only one work, where the behaviour of OH⁻ band was studied during crystal heating in air up to 600 K. The crystals were stoichiometric and doped with Mg ions [15].

Thus, one can conclude that, despite the huge amount of publications devoted to investigation of OH⁻ absorption band in LiNbO₃ crystals, its nature and its correlation with crystal defect subsystem are not well explained. This concerns the influence of reducing/oxidizing treatments on crystal's absorption change in the IR region. The aim of present work was investigation of changes in OH⁻ absorption band in LiNbO₃ during heating the crystal from room temperature to 820 K in reducing (gas mixture 95% Ar + 5% H₂) or oxidizing (pure O₂) atmospheres.

2. Experimental details

Samples for investigation were made from congruent LiNbO₃ single crystals grown at SRC "Carat" (Lviv, Ukraine) by the Czochralski technique. The growth technology is described in Refs. [16, 17]. Magnesium oxide was added to the melt of LiNbO₃ to prepare a doped crystal nominally containing 5.63 mol.% of Mg. Such concentration of Mg^{2+} ions in LiNbO₃ exceeds the threshold concentration [17]. The samples were polished and prepared as *Y*-cut and *Z*-cut. Sample dimensions were $5 \times 5 \times 5$ and $5 \times 5 \times 12$ mm³.

The optical *in situ* experiments were performed using a specially designed high-temperature furnace placed in a Perkin–Elmer Lambda 900 spectrophotometer with spectral range 200–3000 nm (50000–3333 cm⁻¹). The furnace allows to heat samples from room temperature up to about 1200 K in various gas atmosphere. A temperature controller ensures a given heating program with the maximal rate of 5 K/min as well as temperature stabilization at desired temperatures. The furnace construction allows for a rapid (≈ 1 min) replacement of gas atmosphere in the furnace and the registration of the subsequent reduction/oxidation (redox) kinetics at a certain wavelength. Mixture of 5% H₂ with 95% Ar was used as reducing atmosphere, whereas pure O₂ — as the oxidizing ones. Details of the optical setup and of the *in situ* experiments were described in Refs. [18, 19]. Experimental quantity obtained is the so-called absorbance $A = \log(I_0/I) = \log(e)\alpha d$. Here, I_0 and I are the intensities of incoming and transmitted light, α is the linear absorption coefficient, and d the thickness of the absorber. The measured optical spectra were corrected to take into account the heat radiation spectrum from the heating system and from the sample at temperatures higher than 673 K, in the same way as in Refs. [18, 19].

3. Results and discussion

The OH⁻ absorption spectra of nominally undoped congruent LiNbO₃ crystal at different temperatures during its heating in oxidizing atmosphere are shown in

Fig. 1. The crystal was oriented in such a way that the light spread along *Z*-axis. As it can bee seen from Fig. 1, at room temperature, the spectrum represents the absorption band caused by OH⁻ stretching vibrations characteristic for congruent LiNbO₃ [2–5, 7–10]. Maximum of the band lies at around 3480 cm⁻¹. As temperature increases, the intensity of the band starts decreasing and its maximum shifts to the low energy region. Thus, at 520 K the intensity of the band is about twice lesser comparing with the starting one at room temperature, and the band maximum is situated at 3475 cm⁻¹. At 820 K the absorption band almost completely disappears and the crystal becomes transparent in this region.
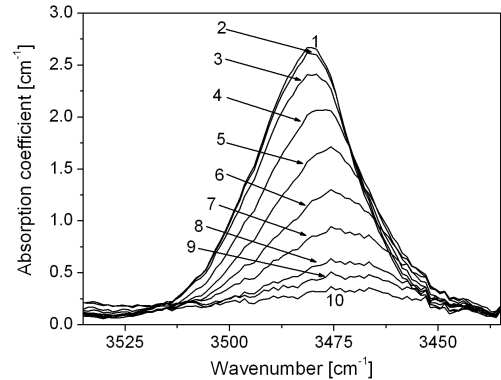

Fig. 1. The OH⁻ absorption spectra of the as-grown undoped LiNbO₃ crystal during its heating in oxidizing atmosphere at different temperatures (light spreads along the Z-axis): 1 — room temperature, 2 — 323 K, 3 — 373 K, 4 — 423 K, 5 — 523 K, 6 — 623 K, 7 — 673 K, 8 — 723 K, 9 — 773 K, 1) — 823 K.

When the crystal is cooled from 820 K to room temperature, the OH⁻ absorption starts increasing and at 273 K one can observe the absorption band with the same form and intensity as in the as-grown crystal. It should be noted that changing of the annealing atmosphere from oxidizing to reducing one and vice versa does not produce any changes in OH⁻ absorption spectra. The band increases and disappears depending on the temperature but irrespectively of the annealing atmosphere.

The behaviour of OH⁻ absorption band in *Z*-cut LiNbO₃:MgO sample during its heating/cooling in different atmospheres is similar to behaviour of the OH⁻ absorption band in nominally undoped LiNbO₃, except for the fact that the maximum of the band for LiNbO₃:MgO is situated at 3488 cm⁻¹ that correlates with the data in Refs. [1, 8]. The dependences of absorption decrease with the temperature in band maxima for undoped LiNbO₃ (3480 cm⁻¹) and for LiNbO₃:MgO (3488 cm⁻¹) are shown in Fig. 2. As it is seen from the figure, the dependences have linear character unlike to changes in visible and near IR spectral region, where arising/bleaching of the absorption during redox annealing is described by an exponential law [18, 19].
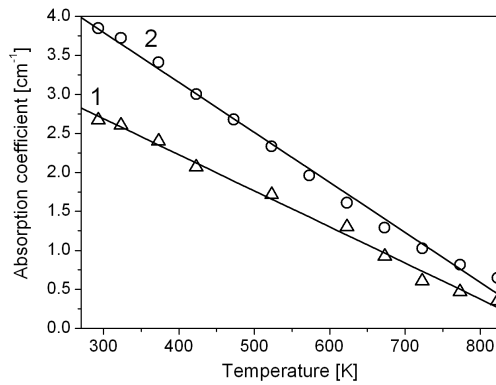
Fig. 2. Temperature dependence of the absorption change for undoped LiNbO$_3$ 1 and for LiNbO$_3$:MgO 2 in the OH$^-$ band maxima.

Different situation is observed for OH$^-$ spectra when both undoped LiNbO$_3$ and LiNbO$_3$:MgO are oriented in such a way that the light spread along Y-axis. As it is seen from Fig. 3, the intensity of the band is much lesser at room temperature comparing with the Z-cut sample. Heating the crystal does not change the intensity, only band maximum shifts to the low energy spectral region. Change of the annealing atmosphere from oxidizing to reducing one and vice versa does not produce changes in OH$^-$ absorption band behaviour just as for Z-cut samples.

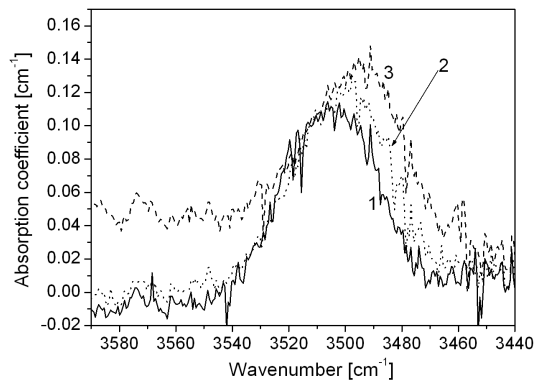Fig. 3. The OH$^-$ absorption spectra of the as-grown undoped LiNbO$_3$ crystal during its heating in oxidizing atmosphere at different temperatures (light spreads along the Y-axis): 1 — at room temperature, 2 — 473 K, 3 — 573 K.

It can be assumed that the observed linear decrease of the OH$^-$ absorption band during heating of undoped LiNbO$_3$ and LiNbO$_3$:MgO when the light is spread along the Z crystal direction, and conservation of the band when the light is spread along the Y crystal direction, are connected with orientation change of O–H bonds with the temperature. The fact that O–H dipole orientation in lithium niobate crystals is sensitive to the influence of external fields was proven in [20]. In this work the

authors observed decrease of OH$^-$ absorption band under the influence of electric field applied transversely to the Z crystal direction.

4. Conclusions

The results of investigations showed that the character of the OH$^-$ absorption does not depend on the annealing atmosphere (oxidizing or reducing). It was shown that, when the light is spread along the Y axis, the intensity of the OH$^-$ absorption band does not depend on the temperature, while, when the light is spread along the Z axis, the absorption intensity decreases with the temperature growth (at 520 K the intensity of the band is about twice lesser comparing with the starting one, and at 820 K the absorption almost completely disappears). It can be assumed that this fact is connected with orientation change of O–H bonds with the temperature, which correlates with the results of [20].

Acknowledgments

References

[1] M. Woehelcke, L. Kovacs, *Crit. Rev. Solid Cryst. Mater. Sci.* **26**, 1 (2001).

[2] J.M. Cabrera, J. Olivares, M. Carrascosa, J. Rams, S. Mueller, E. Dieguez, *Adv. Phys.* **45**, 349 (1996).

[3] E.M. de Miguel-Sanz, M. Carrascosa, L. Arizmendi, *Phys. Rev. B* **65**, 165101 (2002).

[4] P. Nekvindova, J. Spirkova, J. Cervena, M. Budnar, A. Razpet, B. Zorko, P. Pelicon, *Opt. Mater.* **19**, 245 (2002).

[5] T. Volk, M. Wöhlecke, *Lithium Niobate: Defects, Photorefraction and Ferroelectric Switching*, Springer, Berlin 2009.

[6] R.G. Smith, D.B. Fraser, R.T. Denton, T.C. Rich, *J. Appl. Phys.* **39**, 4600 (1968).

[7] Y. Kong, W. Zhang, X. Chen, J. Xu, G. Zhang, *J. Phys., Condens. Matter* **11**, 2139 (1999).

[8] X.Q. Feng, Y.B. Tang, *J. Phys., Condens. Matter* **5**, 2423 (1993).

[9] W. Bollmann, H.J. Stoehr, *Phys. Status Solidi A* **39**, 477 (1977).

[10] T.B. Wang, S.L. Guo, L. Chen, L. Cao, H. Li, Z.G. Liu, C.Z. Tan, *Optik* **118**, 604 (2007).

[11] L. Kovacs, V. Szalay, R. Capaletti, *Solid State Commun.* **52**, 1029 (1984).

[12] G. Dravecz, L. Kovacz, *Appl. Phys. B* **88**, 305 (2007).

[13] A. V. Yatsenko, *Ukr. J. Phys.* **44**, 381 (1999) (in Russian).

[14] S.V. Evdokimov, A.V. Yatsenko, *Crystallography* **48**, 594 (2003) (in Russian).

[15] K. Lengyel, L. Kovács, Á. Péter, K. Polgar, G. Corradi, *Technical Digest of the International Workshop Lithium Niobate from Material to Device, from Device to System*, 2005, p. 97.

[16] I. Solskii, D. Sugak, V. Gaba, *Techn. Des. Electron. Dev.* **5**, 51 (2005) (in Russian).

[17] D. Sugak, A. Matkovskii, I. Solskii, B. Kopko, V. Olijnyk, I. Stefanskii, V. Gaba, V. Grabovskii, I. Zaritskii, L. Rakitina, *Cryst. Res. Technol.* **32**, 805 (1997).

[18] D. Sugak, Ya. Zhydachevskii, Yu. Sugak, O. Buryy, S. Ubizskii, I. Solskii, M. Schrader, K.-D. Becker, *J. Phys., Condens. Matter* **19**, 086211 (2007).

[19] D. Sugak, Ya. Zhydachevskii, Yu. Sugak, O. Buryy, S. Ubizskii, I. Solskii, A. Boerger, K.-D. Becker, *Phys. Chem. Chem. Phys.* **11**, 3138 (2009).

[20] U. Heinemeyer, M.C. Wengler, K. Buse, *Appl. Phys. Lett.* **89**, 112910 (2006).