

The crystallization and optical properties of LiNbO₃ single crystals*

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(Received 27 October 1999, revised 21 February 2000)

LiNbO₃ single crystals were grown by the Czochralski technique in an air atmosphere. The critical crystal diameter $D_c = 1.5$ cm and the critical rate of rotation $\omega_c = 35$ rpm were calculated from the dynamic of fluids equations for buoyancy-driven and forced convections under which the shape of the melt/crystal interface changed. The domain inversion was carried out at 1473 K using a 10 min 3.75 V/cm electric field. The obtained crystals were cut, polished and etched to determine the presence of dislocations and single domain structures. The lattice parameters $a = 0.51494$ nm, $c = 1.38620$ nm and $V = 0.3186$ nm³ were determined by X-ray powder diffraction. The optical properties were studied by infrared spectroscopy in the wave number range 20–5000 cm⁻¹. With decreasing temperature, an atypical behaviour of the phonon modes, due to the ferroelectric properties of LiNbO₃ single crystal, could be seen. The optical constants were calculated by Kramers-Kronig analysis and the value of the critical temperature was estimated. The obtained results are discussed and compared with published data.

Keywords: Czochralski technique, lithium niobate, single crystal, optical properties.

INTRODUCTION

The crystal structure of LiNbO₃ is rhombohedral (space group R3c, point group C_{3v}). The lattice constants of the unit cell are $a = 0.5148$ nm and $c = 1.3863$ nm, as determined by Abrahams *et al.*¹ Lithium niobate is insoluble in water and practically inert to acids at room temperature. It has a density of 4.64 g cm⁻³, a molar mass of 147.85, a Mohs hardness of 5, a melting point of 1523 K, a Curie point 1480 K, a thermal expansion coefficient $a_a = 15.4 \times 10^{-6}$ K⁻¹, $a_c = 7.5 \times 10^{-6}$ K⁻¹ and a thermal conductivity of 4.186×10^{-2} J cm⁻¹ s⁻¹ K⁻¹.

The Czochralski technique is widely known for growing single crystals from the melt, and this can be the main reason for using this technique to grow huge amounts of materials, corresponding to about 70 % of the crystals used in practical devices.² Each year a large number of publications appear which are devoted to this

* Dedicated to Professor Slobodan Ribnikar on the occasion of his 70th birthday

technique and applied to a great variety of crystal materials, mainly semiconductors and oxides. Among them, LiNbO₃ has been selected by researchers due to its technological applications.^{3,4}

It is well-known that a flat interface between the liquid and the solid during the complete growth process is the most important criterion for obtaining good crystals.^{5–9} The consequences of a non-flat interface are stresses, cracks, non-homogeneous impurity concentrations, gas-bubble entrapment, *etc.*^{7,8,10} Depending of the hydrodynamics of the melt, a flat interface can be obtained on the set of growth parameters used.

The optical properties of LiNbO₃ single crystals have been investigated by many authors. The aim of the research presented here was, besides studying the experimental conditions to obtain a flat interface, to investigate the behaviour of the optical phonons by infrared spectroscopy at different temperatures and to look for possible soft modes.

EXPERIMENTAL

Single crystals of LiNbO₃ were grown by the Czochralski technique using a MSR 2 crystal puller as described previously.¹² The atmosphere used was air. The platinum crucible (4 cm diameter, 4 cm high) was placed into an alumina vessel surrounded by ZrO wool isolation. Double walls were used to protect the high radiation. To decrease the radial temperature gradient in the melt, silica glass was mounted around all the system. The pull rates were generally in the range 5–6 mm h⁻¹, and the best results were obtained with a pull rate of 5 mm h⁻¹. The crystal rotation rates were between 35 and 45 rpm. The best results were obtained with a crystal rotation of 35 rpm. The crucible was not rotated during the growth. After the growth run, the crystal boule was cooled at a rate of about 50 K/h down to room temperature.

Single domain inversion was carried out in a horizontal cylindrical furnace. The temperature was 1473 K, the applied electrical field 3.75 V/cm, and the time of inversion was 10 min.¹³

A solution of HF : HNO₃ in the ratio 2:1 at 338 K was found to be a suitable etching solution. After exposure for 90 minutes, could be clearly seen dark and bright areas due to domain concentration. Domains could not be seen even after etching for 17 hours at room temperature.¹³

Annealing was performed in a horizontal resistance furnace in an air atmosphere.

The X-ray measurements of the LiNbO₃ powders were recorded with a Philips PW 1170 instrument in the 2θ range from 10° to 60° using the Cu anticathode wavelength $\alpha\text{CuK}\alpha_1 = 0.154051$ nm. The anode load was 40 kV and 33 mA. Recording was in 0.02° steps, and each step was recorded for 1.25 s.

The infrared spectra were recorded on a Bomem DA8 Fourier-transform spectrometer. A new hyper splitter was used for the far infrared region (from 20–700 cm⁻¹) and a standard KBr (400–5000 cm⁻¹) beamsplitter for the infrared region. All the spectra were obtained for a near normal incidence configuration at different temperatures ($T = 75$ K, and 298 K). A Globar (SiC) source was used in both regions of the infrared spectra. All measurements were performed using a Janis STDA 100 cryostat, which enabled the precise exchange of the sample and the mirror in the same position of the cold finger. At the lower temperature, a polyethylene (far IR) and ZnSe (mid IR) window were used. Liquid nitrogen (LN₂) we used as the coolant. The temperatures below 77 K were obtained through an additional pumping-out of N₂. A Lake Shore 330 temperature controller provided a temperature error within 0.1 K. The polarization was E||a. The size of the polished sample was several millimetres (3 mm) which enabled very good signal-to-noise ratios of the measured infrared spectra.

RESULTS AND DISCUSSION

The hydrodynamics of a melt are governed by the buoyancy-driven convection or free convection, by the forced convection due to crystal rotation, and by the thermocapillary surface convection. All these flows can be described by three dimensionless numbers: Grashof (Gr), Reynolds (Re) and Marangoni (Ma) numbers. It can be said that the depth of the melt influences the Grashof number, the rotation rate of the crystal modifies the Reynolds number, and the temperature gradients over the surface of the melt acts on the Marangoni number.² Several growth parameters can be modified simultaneously to obtain a change in the hydrodynamics of the melt.

As has been pointed out by different authors,^{14,15} the crystal rotation rate and the axial temperature distribution are two very important parameters which affect the shape of the interface. Both of them are critical parameters which drastically modify the Re and Gr numbers, respectively. Therefore, these two growth parameters must be taken into account in order to understand the shape of the interface. The Ma number will not change significantly if a small temperature gradient exists over the surface of the melt, and so the hydrodynamics will be governed mainly by the Re and Gr numbers. This was the situation in our case and by applying the hydrodynamic forms values for the critical rate of rotation $\omega_c = 35$ rpm, and the critical diameter $d_c = 15$ mm were obtained. The rate of crystal growth was experimentally obtained to be 5 mm/h.

The structure properties were obtained using X-ray analysis of powdered samples. A PW 1710 diffractometer was used in the 2θ range from 10° to 60° . The unit cell of LiNbO₃ was calculated by the least square method using all 11 reflections including more $K\alpha_2$ for 5 reflections. Many of the reflections correspond to LiNbO₃ crystals with the parameter of the hexagonal unit cell $a = 0.5148$ nm and $c = 1.3863$ nm.¹ Some divergence from the compared results can be explained by the fact that X-ray powder diffraction analysis gives a statistical result. Our calculated results for the lattice parameters are $a = 0.51494$ nm, $c = 1.38620$ nm and $V = 0.3186$ nm³, which are in good agreement with published data.^{1,15}

The c -axis is perpendicular to the plane of the spontaneous cracking and we obtained slices by cutting parallel to the c -axis. The mechanically damaged surface layers were etched off in a hot mixture of two parts HF and one part HNO₃ for about 2 min.¹² The [210] or a -axis direction is perpendicular to the direction of the spontaneous polarization, *i.e.*, the [001] direction. All spectra were recorded by polarization E|| a and confirmation for this was the spectrum recorded at room temperature,¹² which is almost identical with the published spectrum.¹¹

The infrared reflectance spectra in the region 50–1500 cm⁻¹ are presented in Fig. 1.

The spectra were measured at 75 and 298 K. We concentrated just on the E|| a polarization due to the fact that it possesses a mode with a large TO-LO splitting

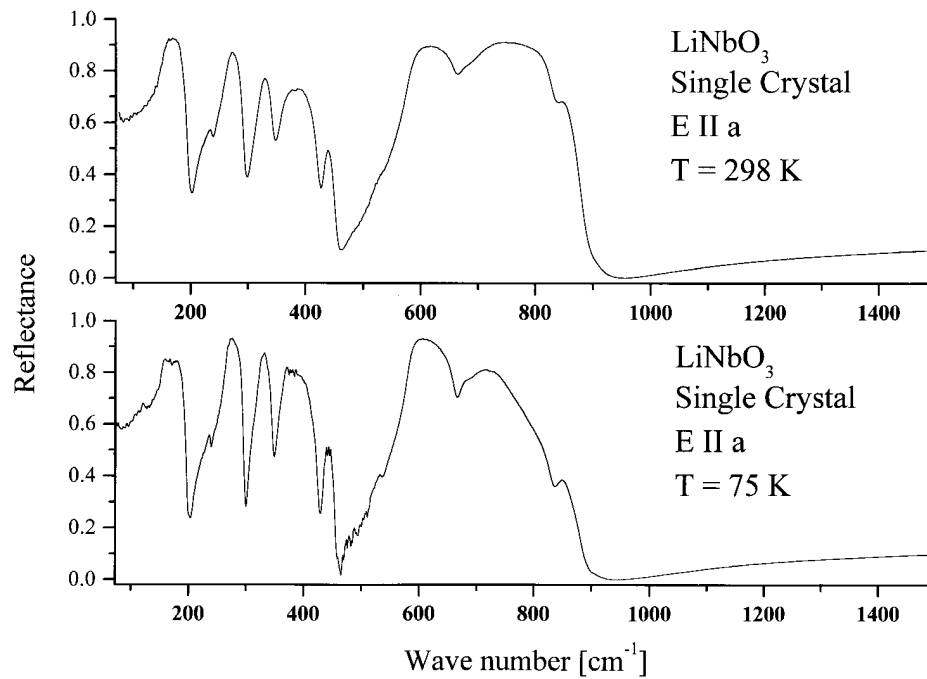


Fig. 1. Reflectance spectra of LiNbO₃ single crystals at 77 K and 298 K. Polarization E||a.

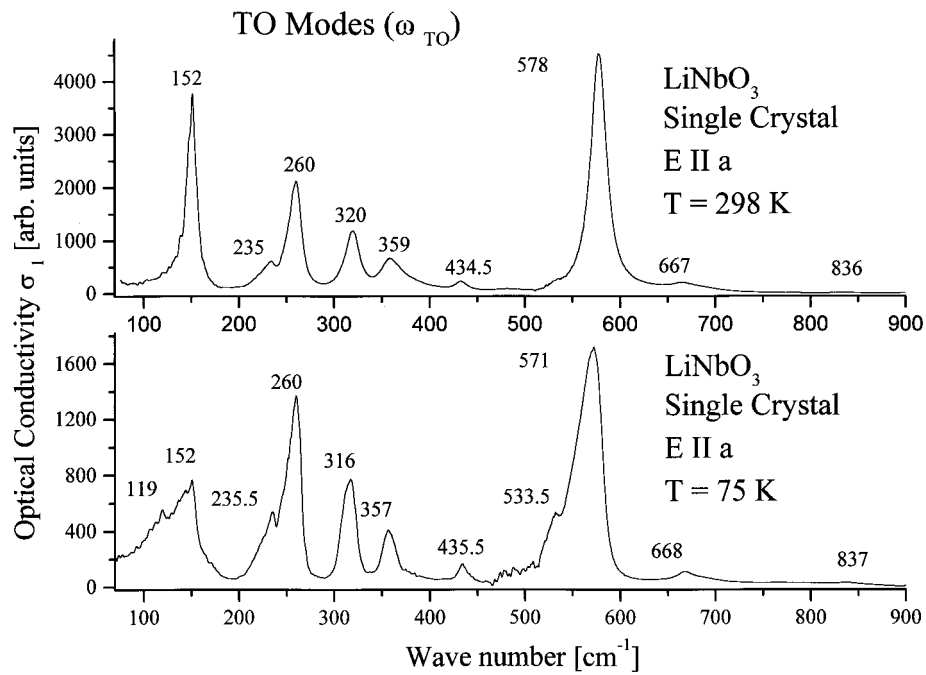


Fig. 2. TO modes (ω_{TO}) of LiNbO₃ single crystals at 75 K and 298 K. Polarization E||a.

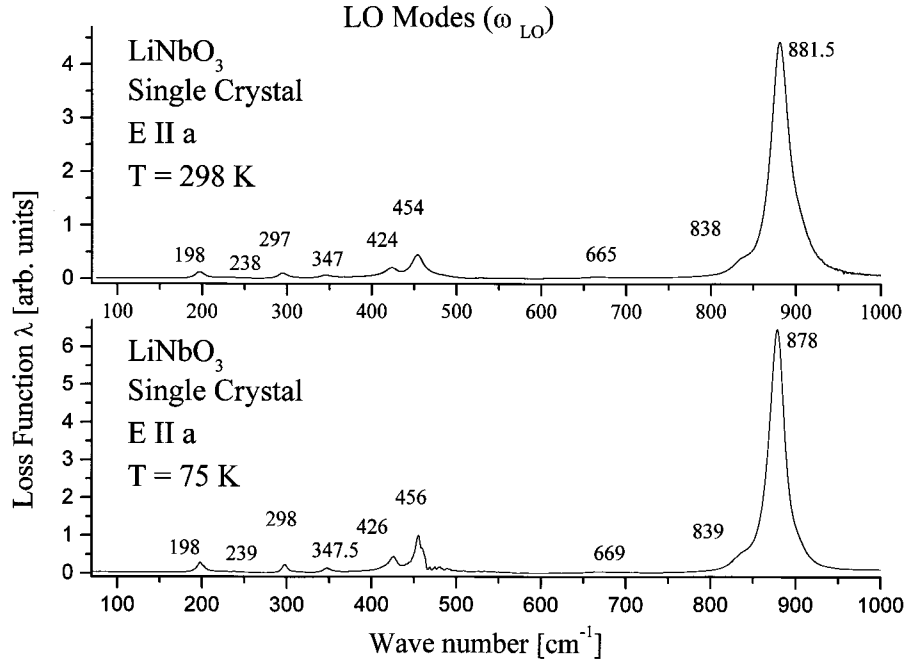


Fig. 3. LO modes (ω_{LO}) of LiNbO₃ single crystals at 75 K and 298 K. Polarization E||a.

and a strong anharmonicity. An additional reason concerns a phonon softening previously reported¹¹ for this polarization. The crystal structure of LiNbO₃ below the ferroelectric Curie point does not belong to a perovskite type. It has an ABO₃ lattice with oxygen octahedrons.¹⁶ The crystal space group is R3c (C_{3v})⁶ and the primitive cell contains two formula units below the T_c . Irreducible representations of C_{3v} consists of 4 A_1 , 5 A_2 and 9 E optic modes. With E||a polarization, only the 9 E modes are infrared and Raman active. At the low temperature, all 9 modes were observed as shown in Fig. 1. Their TO and LO frequencies were obtained by the Kramers-Kronig analysis (Figs. 2 and 3).

The lines at 668 and 837 cm^{-1} in Fig. 2 for 75 K probably represent anharmonic two-phonon modes.

Using the Lyddane-Sachs-Teller relation:

$$\frac{\epsilon_0}{\epsilon_\infty} = \prod_{j=1}^n \frac{\omega_{LO,j}^2}{\omega_{TO,j}^2} \quad (1)$$

the ratio $\epsilon_0/\epsilon_\infty$ were calculated for both temperatures. In order to obtain the static dielectric constant ϵ_0 , ϵ_∞ was determined from measurements of the reflectance at high wave numbers (R_∞) and the following relation:

$$\epsilon_{\infty} = \left(\frac{1 + \sqrt{R_{\infty}}}{1 - \sqrt{R_{\infty}}} \right)^2 \quad (2)$$

The obtained values were $\epsilon_{\infty}(75 \text{ K}) = 5.1$ and $\epsilon_{\infty}(298 \text{ K}) = 6.6$. This gave $\epsilon_0(75 \text{ K}) = 52.3$ and $\epsilon_0(298 \text{ K}) = 62.4$. Applying the relation:¹⁷

$$\frac{1}{\epsilon_0} = \text{const} (T_c - T)^{\gamma} \quad (3)$$

the Curie critical temperature T_c was estimated. We assumed the critical exponent $\gamma = 1$ and obtained $T_c = 1453 \text{ K}$. This value is in a excellent agreement (within 2 %) with the well established value of 1480 K. In this way we confirmed that the transition in LiNbO_3 is very close to the second order phase transition ($\gamma = 1$).

For most of modes, except three of them, no significant phonon shifts due to temperature changes were observed. This is in agreement with the formula¹⁷ for the soft mode in ferroelectrics:

$$\omega_{\text{TO}}^2(T \leq T_c) = \text{const} \cdot (T_c - T) \quad (4)$$

In our case the ratio: $\omega_{\text{TO}}(75 \text{ K})/\omega_{\text{TO}}(298 \text{ K}) = 1.087$. This means that the phonons shift slightly with temperature. The surprising result concerns the large phonon softening of the 571 cm^{-1} (75 K) mode (7 cm^{-1}), which has, to the best of our knowledge, not been reported so far. Also, the modes at 320 and 359 cm^{-1} (298 K) soften 4 and 2 cm^{-1} , respectively. The phonon at 571 cm^{-1} shows enormous TO-LO splitting, larger than 300 cm^{-1} . Also, it has a strong anharmonic behaviour according to its shape (Fig. 1). This could be important due to the fact that anharmonicity plays a crucial role in stabilising a ferroelectric phase transition. In addition, the softening of these modes could points to a second phase transition below T_c .

CONCLUSION

The conditions for growing LiNbO_3 single crystals were calculated by using a combination of Reynolds and Grashof numbers.

The infrared spectra of LiNbO_3 for the E||a polarisation at different temperatures were recorded. From the obtained experimental data, the static relative permittivity were determined and the Curie temperature estimated. Also, for the first time, a large phonon softening of the anharmonic mode at 571 cm^{-1} (ω_{TO}) ($T = 75 \text{ K}$) and smaller softening of modes at 320 and 359 cm^{-1} ($T = 298 \text{ K}$) were found, which suggested a new phase transition below T_c .

ИЗВОД

КРИСТАЛИЗАЦИЈА И ОПТИЧКЕ ОСОБИНЕ МОНОКРИСТАЛА LiNbO₃

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Монокристали LiNbO₃ су добијени методом раста кристала по Чохралском на ваздуху. Из једначина динамике флуида за термичку и форсирану конвекцију израчунати су критични пречник кристала $D_c = 1,5$ cm и вредност критичне брзине ротације $\omega_c = 35$ o/мин при којима долази до промене облика фронта кристализације. Монодоменизација је обављена на температури од 1473 K, при електричном пољу од 3,75 V/cm у трајању од 10 минута. Добијени кристали су сечени, полирани и нагрзани да би се одредило присуство дислокација и добијање монодоменске структуре. Рендгенском дифракцијом праха одређени су параметри јединичне ћелије $a = 0,51494$ nm, $c = 1,38620$ nm и запремина $V = 0,3186$ nm³. Оптичке особине су проучаване у инфрацрвеној области спектра у опсегу таласних бројева од 20–5000 cm⁻¹. Рефлексионски спектри су снимани на различитим температурама да би се посматрао положај фононских модова. Са опадањем температуре може да се види атипично понашање фононских модова што се приписује фероелектричним особинама монокристалног LiNbO₃. Оптичке константе монокристалног LiNbO₃ су добијене коришћењем Крамерс-Крониг анализе и процењена је вредност критичне температуре. Добијени резултати су дискутовани и упоређивани са подацима из литературе.

(Примљено 27. октобра 1999, ревидирано 21. фебруара 2000)

REFERENCES

1. S. C. Abrahams, J. M. Reddy, J. L. Bernstein, *J. Phys. Chem. Solids* **27** (1966) 997
2. M. T. Santos, J. C. Rojo, L. Arizmendi, E. Dieguez, *J. Crystal Growth* **142** (1994) 103
3. K. Kawasaki, Y. Okano, S. Kan, M. Sakamoto, K. Hoshikawa, T. Fukuda, *J. Crystal Growth* **119** (1992) 317
4. M. Simon, St. Wevering, K. Buse, E. Krätzig, *J. Phys. D: Appl. Phys.* **30** (1997) 144
5. J. R. Carruthers, *J. Crystal Growth* **36** (1976) 212
6. A. R. Tanguay, Jr., S. Mroczkowski, R. C. Barker, *J. Crystal Growth* **42** (1977) 431
7. S. Miyazawa, *J. Crystal Growth* **49** (1980) 515
8. V. Nikolov, K. Iliev, P. Peshev, *J. Crystal Growth* **89** (1988) 313
9. J. Trauth, B. C. Grabmaier, *J. Crystal Growth* **112** (1991) 451
10. V. Nikolov, K. Iliev, P. Peshev, *J. Crystal Growth* **89** (1988) 324
11. A. S. Barker, Jr., R. Loudon, *Phys. Rev.* **158** (1967) 433
12. A. Golubović, R. Gajić, A. Valčić, *J. Serb. Chem. Soc.* **63** (1998) 863
13. A. Golubović, S. Nikolić, R. Gajić, S. Đurić, A. Valčić, *Tehnika: Novi materijali* **8** (1999) 5
14. A. Golubović, S. Nikolić, R. Gajić, S. Đurić, A. Valčić, *J. Serb. Chem. Soc.* **64** (1999) 637
15. JCPDS 20-631
16. M. Lains, A. Glass, *Segnetoelektriki i rodstvennie im materialy*, Mir, Moskva, 1981, p. 302
17. P. Bruesch, *Phonons: Theory and Experiments III*, Springer-Verlag, Berlin, Heidelberg, 1991, pp. 44 - 51.