

Phonon anomalies in optical spectra of LiNbO₃ single crystals

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(Received 29. October, revised 25 December 2003)

Abstract: 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 by equations from the hydrodynamics of the melt. The domain inversion was carried out at 1430 K using a 3.75 V/cm electric field for 10 min. The obtained crystals were cut, polished and etched to determine the presence of dislocations and single domain structures. The optical properties were studied by infrared and Raman spectroscopy as a function of temperature. With decreasing temperature, an atypical behaviour of the phonon modes could be seen in the ferroelectrics LiNbO₃. The obtained results are discussed and compared with published data.

Keywords: lithium niobate, Czochralski technique, single crystal, Raman spectroscopy, infrared spectroscopy, ferroelectrics.

INTRODUCTION

Lithium niobate (LiNbO₃) is an extremely versatile non-linear crystal material. Its electro-optic and non-linear optical coefficients are used for various photonic applications. The growth, chemistry and physics of ferroelectrics lithium niobate LiNbO₃ single crystals have been the subject of extensive studies^{1–3} for more than three decades. These crystals are promising for volume holographic storage. For this reason their photorefractive properties and light-induced charge transport are of special interest.⁴ Application of optical-wafer grade LiNbO₃ in integrated optics include switches, interconnects, multiplexers, waveguide lasers, and non-linear optical wave guides. Available as boules, cut crystals or wafers, LiNbO₃ single crystals possess an attractive combination of piezoelectric and electro-optic properties which enable them to be widely used as frequency doublers, for Q-switches, waveguide substrate, surface acoustic wave (SAW) devices and so on.⁵ A new world of applications of LiNbO₃ sin-

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gle crystals has appeared by using a predetermined order to the domain structure, which can be roughly divided in two classes, opposite domain (ODLN) for acoustic devices⁶ and antiparallel periodic poled (PPLN) for second harmonic generation (SHG) in blue-green laser technology, optical parametric oscillators (OPOS) and recently inhibition of photorefractive damage.^{7–10}

Several authors have investigated the optical properties of LiNbO₃ single crystals^{11–13} in order to study phonon properties and the ferroelectric phase transition. These included symmetry group analysis of the material below and above the critical temperature at 1438 K and soft mode behaviour. Infrared (IR) and Raman spectra were recorded mostly at high temperatures close to T_c . In this study, infrared and Raman spectra were measured at low temperature far removed from the critical temperature looking for possible anomalies or precursors of the phase transition. Soft phonons were found both in IR and Raman spectra, as well as anomalies of the Raman scattering tensor in the range between 100 and 200 K. These results could contribute to a better understanding of the vibrational structure of LiNbO₃ single crystals and suggest possible new applications.

EXPERIMENTAL

Single crystals of LiNbO₃ were grown by the Czochralski technique using a MSR 2 crystal puller as described previously.^{14,15} 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 1430 K, the applied electrical field 3.75 V/cm, and the time of inversion was 10 min.¹⁶

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, dark and bright areas due to domain concentration could be clearly seen. Domains could not be seen after etching for as long as 17 h at room temperature.¹⁵

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

Infrared spectra were recorded on a Bomem DA8 Fourier-transform spectrometer. The newest Bomen's hypersplitter was used for the wider far infrared region (from 30–1000 cm⁻¹) and a standard KBr beamsplitter for the infrared region (400–5000 cm⁻¹). All spectra were obtained using a near normal incidence configuration at different temperatures ($T=75, 120, 200$ and 298 K). The polarisation was $E \perp c$. The c -axis was perpendicular to the plane of spontaneous cracking and slices were obtained by cutting parallel to the c -axis.¹⁴ Structure properties were determined by the XRD powder technique.¹⁵ Unpolarized Raman spectra were recorded on a Jobin–Ivon U1000 spectrometer and excited by the 488 nm line of an Argon ion laser at an average power of 10 mW. The measuring temperatures were 20, 80, 120, 200 and 298 K.

RESULTS AND DISCUSSION

The quality of crystals grown by the Czochralski technique is related to the shape of the liquid–solid interface during the growth process. It is well known that good quality crystals are obtained when the interface is flat, whereas a non-flat interface could be the principal reason for the generation of dislocations and consequently for

many undesirable effects, such as inhomogeneous distribution of impurities, strains, cracks, low-angle grain boundaries, gas bubble entrapment, *etc.*¹⁷ It is known that the hydrodynamics of a melt are governed by buoyancy-driven convection or free convection, by forced convection due to crystal rotation, and by thermo-capillary surface convection. Three dimensionless numbers can describe all these flows: Grashof (Gr), Reynolds (Re) and Marangoni (Ma) numbers. The Ma number does not change significantly if a small temperature gradient exists over the surface of a melt,¹⁸ and so the hydrodynamics are governed mainly by the Re and Gr numbers.

It was presumed, as Carruthers¹⁹ did, that there was no change in kinematic viscosity at the melt/crystal interface during the growth process and there was equilibrium $Gr = Re^2$. There is, during this time, a flat melt/crystal interface with critical rotation rate ω_c and critical diameter d_c . It was decided to use the relations derived by Carruthers in the calculations for our experimental system. These relations are in a good agreement with the experimental data of many authors^{20,21} and it was assumed that they could also be useful in our case. In this way, 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 found to be 5 mm/h.²²

The crystal structure of LiNbO₃ below the ferroelectric Curie point does not belong to a perovskite type. It has an ABO₃ lattice with oxygen octahedrons²³ with a

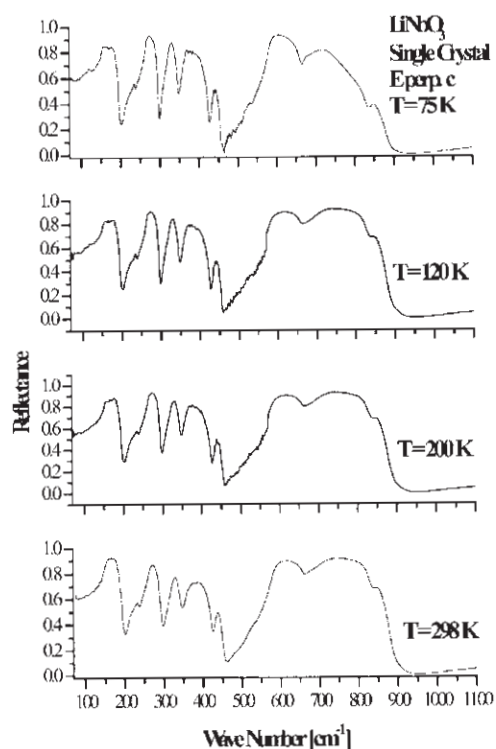


Fig. 1. IR Spectra of LiNbO₃ single crystals at different temperatures for the polarization $E \perp c$.

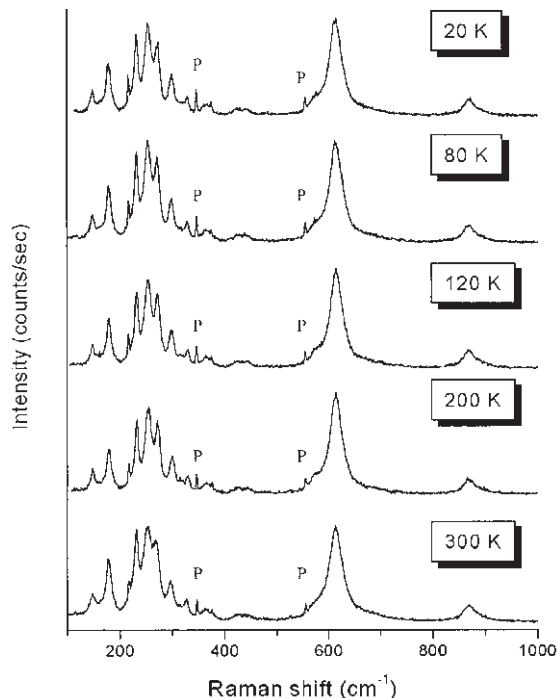


Fig. 2. Unpolarized Raman spectra of LiNbO₃ single crystals at different temperatures. P denotes plasma peaks of the Ar ion laser.

transition metal ion (Nb) in the centre. In the edges of the pseudocubic unit cell, the cations (Li) are to be found.²⁴ Ferroelectricity in this materials results from a slight antiparallel shift of the oxygen octahedra and the centre ions, which leads to a permanent dipole moment. The crystal space group below the T_c is R3c (C_{3v}^6) and the primitive cell contains two formula units. An irreducible representation of C_{3v} consists of 4 A_1 , 5 A_2 and 9E optic modes. For the polarization $E \perp c$ below the Curie temperature, only the 9 E modes are infrared active while Raman involves both 4 A_1 and 9E modes. The A_2 modes are neither IR nor Raman active.²⁵

The infrared reflectance spectra in the region 70–1100 cm^{-1} are presented in Fig. 1.

The spectra were measured at 75, 120, 200 and 298 K. TO and LO modes were calculated by Kramer-Kronig analysis (KKA).²² Attention was focused only on the $E \perp c$ polarization due to the fact that it possesses a mode with a large TO–LO splitting and a strong anharmonicity. An additional reason concerns a previously reported²⁵ phonon softening for this polarization.

It is known that some of the properties of LiNbO₃ are dependent on stoichiometric defects.²⁶ When defects are present a phonon can be missing or be quite small. The quality of the obtained LiNbO₃ single crystal was checked by the XRD powder technique. The appearance of splitted $K\alpha_1$ and $K\alpha_2$ showed that the obtained single crystal was of high quality as only crystals with high quality can split $K\alpha$ radiation.²²

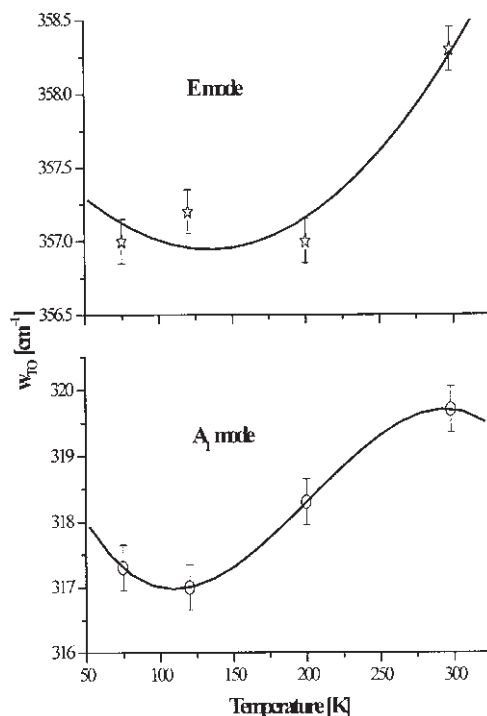


Fig. 3. Anomalous behaviour of two IR active modes in LiNbO₃ single crystals. The line denotes a polynomial fit.

Hence, all active modes could be observed. In this study interest was focused on phonon anomalies of the E modes. For this reason E||C IR spectra were not considered as they do not contain active E modes below the Curie temperature.²⁵

The unpolarized Raman spectra in the region 120–1000 cm⁻¹ and direction E⊥C are presented in Fig. 2, which shows all 13 Raman active modes (9 E modes and 4A₁ modes) below T_c as functions of temperature. P in Fig. 2 denotes the plasma peaks of the Ar ion laser. All theoretically predicted modes in the literature were obtained,^{25,27,28} the Raman spectra reported by Okamoto *et al.*¹¹ seem to be of lower quality and the peaks less resolved than our spectra, as is the case for the A₁ (TO) mode at 332 cm⁻¹. The peaks at 571 and 680 cm⁻¹ probably represent anharmonic two-phonon modes, as was previously proposed in the literature.^{13,22,25,28} The peak at 871 cm⁻¹ is assigned to a vibrational LO mode of Nb–O in isolated groups such as, NbO₆, and the peak at 614 cm⁻¹ is probably associated with another TO mode in the same octahedra. The peaks at 253, 271, 326 and 614 cm⁻¹ belong to A₁ (TO) modes, and those at 148 and 231 cm⁻¹ to E (TO+LO) modes.¹³ Two smaller softening modes at 320 and 359 cm⁻¹, previously seen in IR spectra,²² were also obtained and they are presented separately in Fig. 3.

Anomalous behaviour of these phonon modes can be clearly seen from Fig. 3. The Raman scattering spectra were analysed by convolution of a Lorentzian and a

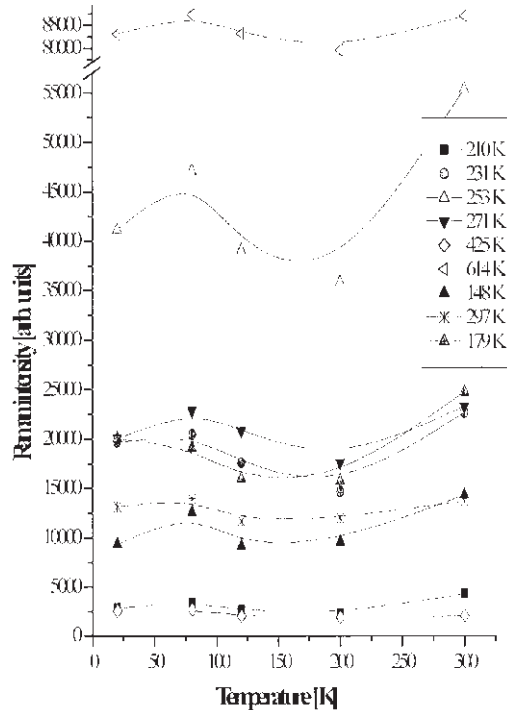


Fig. 4. Function $I = f(T)$ for Raman active modes in LiNbO_3 single crystals.

Gaussian curve. Relations $I = f(T)$ for the 13 obtained modes are presented in Fig. 4. The insert denotes phonon energies in cm^{-1} at room temperature.

Figure 5 shows the anomalous behaviour of the modes at 326 and 359 cm^{-1} in the Raman spectrum.

It was found that beside the well known soft mode in ferroelectric LiNbO_3 there are several modes that show softening or anomalous behaviour in the range 100 to 300 K as is presented in Figs. 3 and 5, which show phonon softening in the IR spectra (a few wave numbers)²² and anomalies of the Raman intensity and half-widths, respectively. Phonon softening were not observed in the Raman spectra, probably due to insufficient accuracy of the monochromator which could not resolve the small phonon energy shifts of the order of $1\text{--}2 \text{ cm}^{-1}$. These anomalies could have different causes. Regarding the Raman anomalies, a spontaneous polarization effect has to be excluded. Namely, the intensity of Raman (Stokes) scattering I for modes that are Raman inactive above T_c could be given to a first approximation as a function of the spontaneous polarization²⁸ $I \approx \text{const} \cdot |\alpha_{ij}|^2 \approx \text{const} \cdot P_s^2 \approx \text{const} \cdot (T_c - T)$, where α_{ij} is the Raman tensor and P_s the spontaneous polarization. Unfortunately, the temperature dependence does not match the experimental findings. The other possibilities concern strain effects, anharmonic effects²⁹ or small A_1 -E coupling that could arise from grown-in imperfections.²⁸ A possibility that the observed anomalies, found in both the IR and Raman spectra, represent precursors of the phase transition seems

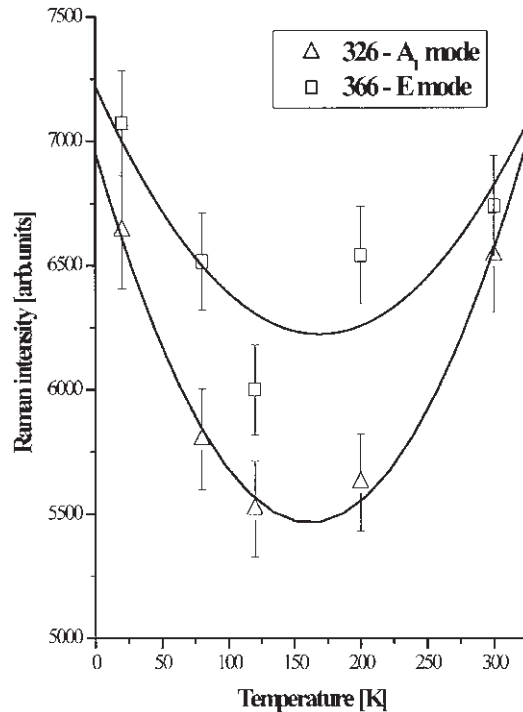


Fig. 5. Anomalous behaviour of two Raman active modes in LiNbO₃ single crystals. The line denotes a polynomial fit.

to be unlikely as the measured temperatures are far removed from T_c . Further investigations are necessary to resolve this issue.

CONCLUSION

The conditions for growing LiNbO₃ single crystals were calculated by using a combination of Reynolds and Grashof numbers.

The unpolarized Raman and IR spectra of LiNbO₃ for the $E \perp c$ at different temperatures were recorded. All 13 Raman active E modes were found. The presence of small softening modes at 320 and 359 cm⁻¹, which observed previously in our work on the IR spectra of LiNbO₃ single crystals, were confirmed. As well as in the IR spectra, phonon anomalies both in the intensities and half-widths were found in the Raman spectra in the range 100–300 K. Below 100 K, the phonons start to harden as is to be expected.

Acknowledgement: This work was supported by the Serbian Ministry of Science, Technology and Development under Projects 1469 and 1481. Radoš Gajić would like to acknowledge support by the Austrian project FWF 15513.

ИЗВОД

АНОМАЛИЈЕ ФОНОНА У ОПТИЧКИМ СПЕКТРИМА МОНОКРИСТАЛА LiNbO₃

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Монокристали LiNbO₃ су добијени методом раста по Чохралском на ваздуху. Вредности критичног пречника кристала $D_c = 1,5$ cm и вредност критичне брзине ротације $\omega_c = 35$ o/min су одређене помоћу једначина динамике флуида. Монодоминанција је обављена на температури од 1430 K, при електричном пољу од 3,75 V/cm у трајању од 10 минута. Добијени кристали су сечени, полирани и нагризани да би се одредило присуство дислокација и добијање монодоменске структуре. Оптичке особине су проучаване инфрацрвеном и Рамановом спектроскопијом у функцији температуре. Са опадањем температуре може да се види у фероелектричном LiNbO₃ атипично понашање фононских модова. Добијени резултати су дискутовани и упоређивани са подацима из литературе.

(Примљено 29. октобра, ревидирано 25. децембра 2003)

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