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IR and Raman spectra of poled and unpoled $LiNbO_3$ single crystals

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Abstract

$LiNbO_3$ single crystals were grown by the Czochralski technique in an air atmosphere. The polarized IR and Raman spectra of both poled and unpoled $LiNbO_3$ single crystals were measured and compared. The spectra were recorded at different temperatures between 20 and 300 K. In addition, we discussed the phonon anomalies and anharmonicity in both, IR and Raman spectra.

Keywords: Crystal growth; Anharmonicity; Light absorption and reflection

1. Introduction

Properties and applications of lithium niobate ($LiNbO_3$) have been widely studied, resulted in several thousands of papers on this material. The high level of interest in lithium niobate mainly stems from its outstanding electro-optical and non-linear optical properties [1]. In recent years there has been increasing interest in the use of quasi-phase-matched non-linear crystals for a variety of frequency-conversion applications [2]. Periodically poled lithium niobate (PPLN) has been demonstrated to give efficient second-harmonic generation [3,4] and optical parametric oscillation [5,6] in both the continuous wave (CW) and Q-switched regimes. For these applications, it is of the utmost importance to control ferroelectric domain structures.

Several authors have investigated the optical properties of $LiNbO_3$ single crystals [7–9] in order to study phonon properties and the ferroelectric phase transition. That included a 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 temperatures far 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 $LiNbO_3$ single crystals and suggest possible new applications.

2. Experimental

Single crystals of $LiNbO_3$ were grown by the Czochralski technique using a MSR 2 crystal puller as described previously [10,11]. The pull rates were generally in the range of 5–6 mm h^{-1}, and the best results were obtained with a pull rate of 5 mm h^{-1}. The crystal rotation rate was calculated to be 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 (poling) 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 [12].

A solution of $HF:HNO_3$ in the ratio 2:1 at 338 K was found to be a suitable etching solution. After exposure for 90 min, dark and bright areas due to domain concentration could be clearly seen. Domains could not be seen even after etching for as long as 17 h at room temperature [11].

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

The *c*-axis was perpendicular to the plane of spontaneous cracking and slice was obtained by cutting parallel to the *c*-axis [11].

Structure properties were determined by the XRD powder technique [11]. A Philips 1710 diffractometer with the radiation $\lambda \mathrm{Cu}\ K\alpha_1 = 0.15405$ nm source and the original APD software were used. The samples were pressed into the standard aluminium frames and the measured range for 2θ was from 10° to 60°. The spectra were obtained at the step of 0.02°, with a recording time of 1.25 s for each step. For production identification, the MPDS program and JCPDS (ASTM) card files were used.

Infrared spectra were recorded on a Bomem DA8 Fourier-transform spectrometer. A wide-range hyper-splitter was used for the far infrared region (from 30 to 700 cm^{-1}) and a standard KBr (400–5000 cm^{-1}) one for the mid-infrared region. All the spectra were recorded at a near normal incidence at different temperatures ($T = 75$, 120, 200 and 298 K). The measurements were performed

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using a Janis STDA 100 cryostat, which enabled the precise exchange of the sample and the mirror at the same spot on the cold finger. At lower temperatures, a polyethylene (far IR) and ZnSe (mid-IR) window were used. As a coolant, liquid nitrogen (LN_2) was used. The polarization was $\mathbf{E} \perp c$.

The unpolarized and polarized Raman spectra were recorded on a Jobin-Ivon U1000 spectrometer and excited by the 488 nm line of an Argon ion laser at the average power of 10 mW. The measuring temperatures were 20, 80, 120, 200 and 300 K. The polarisation was $X(YY)\bar{X}$.

3. Results and discussion

When single crystals are grown by the Czochralski technique, two types of convection are usually observed in the melt, the buoyancy driven convection flow due to temperature gradient in the bulk melt and the centrifugal force driven by the rotation of the crystal [13]. These convection are usually described by dimensionless numbers and these measures are, for the driving forces for flows induced by crystal rotation, the Reynolds number (*Re*) and, for buoyancy, the Grashof number (*Gr*). It was presumed, as Carruthers [14] suggested, that there was not a change in kinematic viscosity at the melt/crystal interface during the growth process and there was equilibrium $Gr = Re^2$. There is, in this time, a flat interface melt/crystal with critical rotation rate ω_c and critical diameter d_c. We decided to use the relations derived by Carruthers in calculations for our experimental system. The crucible is considered to be stationary, during the crystal rotation at the constant rate. Tangential stresses generated by surface tension gradients are applied to account for Marangoni flow (described by the dimensionless *Ma* number), while no flow is allowed normal to the melt meniscus. Conduction and convection caused pulling are included in the crystal and rod pull rod. To simplify the current analysis, it was decided to neglect the effects of internal radiation through the crystal. The *Ma* number does 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. In this way, by applying the hydrodynamic forms, the 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^{-1}.

The unit cell of $LiNbO_3$ was calculated by the least square method using 11 reflections including more $K\alpha_2$ for 5 reflections. All the reflections correspond to $LiNbO_3$ crystal with the parameter of the hexagonal unit cell [15] $a = 0.5148$ nm and $c = 1.3863$ nm. Our calculated results for the lattice parameter are $a = 0.51494$ nm and $c = 1.38620$ nm which are in good agreement with published data [15]. The appearance of splitted $K\alpha_1$ and $K\alpha_2$ showed that the obtained single crystal was highly quality as only crystals with high quality can split Kα radiation.

The crystal structure of $LiNbO_3$ below the ferroelectric Curie point does not belong to a perovskite type. It has an ABO_3 lattice with oxygen octahedrons [16] with a transition metal ion (Nb) in the centre. In the edges of the pseudocubic unit cell one finds the cations (Li) [17]. The stoichiometric $LiNbO_3$ structure can be simply visualized as a stacking of the oxygen octahedra LiO_6, NbO_6, and O_6, where represent a vacant-cation site. The octahedral linking of LiO_6 and NbO_6 can be explained using Pauling's third rule [18] where sharing edges and faces is less favourable than sharing corners. It can be therefore seen that in the former case it is common for cations to shift away from each other as far as possible, i.e. for a formally pure stoichiometric crystal ($R = [Li]/[Nb] = 1$), only two thirds may be occupied by cations (Li^+, Nb^{5+}). The rest of octahedrons are vacant [19]. 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 four A_1, five A_2 and nine E optic modes. In the polarization $\mathbf{E} \perp c$ only the nine E modes are infrared active while the Raman active modes involve both four A_1 and nine E modes [20]. The polarization $\mathbf{E} \parallel c$ does not contain IR active E modes below the Curie temperature, and thus we focused our interest on the phonon anomalies of the E modes in the polarization $\mathbf{E} \perp c$. An additional reason concerns a phonon softening previously reported [20] for this polarization. The infrared reflectance spectra in the region 70–900 cm^{-1} were presented in Fig. 1 at 75 and 298 K. We focused our attention just on the $\mathbf{E} \perp c$ polarization due to the fact that it possesses a mode with a large TO–LO splitting and a strong anharmonicity [21]. Fig. 1 shows enormous TO–LO phonon splitting at 571 cm^{-1}, larger than 300 cm^{-1}. Also, a softening of 320 and 359 cm^{-1} modes were observed [Fig. 2]. There is no single soft mode, but several lines soft around $T \cong 200$ K.

Using the well-known Lyddane–Sachs–Teller relation [22]: $\varepsilon_0 = \varepsilon_\infty \prod_{j=1}^{n} \omega_{LO,j}^2 / \omega_{TO,j}^2$, ε_0 can be calculated from exper-

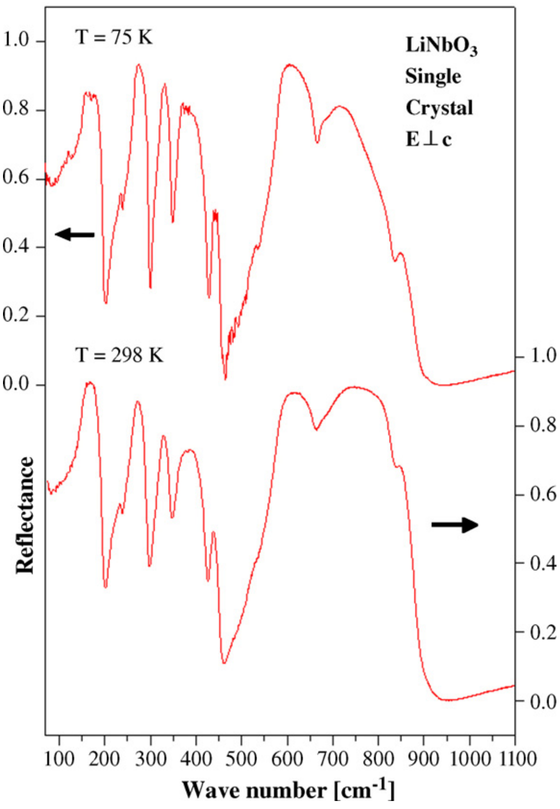

Fig. 1. IR spectra of $LiNbO_3$ single crystals at different temperatures for the polarization $\mathbf{E} \perp c$.