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# Low temperature elastic constants and piezoelectric coefficients of $LiNbO_3$ and $LiTaO_3$

# $LiNbO_3$ および $LiTaO_3$ 単結晶の低温域における弾性定数と圧電定数

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## 1. Introduction

Recently, one of the authors (R.T.) investivated low temperature elastic constants $C_{ij}$ and piezoelectric coefficients $e_{ij}$ of point group $D_3$ type piezoelectric crystals, $\alpha$-$SiO_2$ ($\alpha$-quartz) and $La_3Ga_5SiO_{14}$ (langasite), by resonant ultrasound spectroscopy (RUS).[1,2] This study revealed that both the $\alpha$-quartz and langasite show unusual elastic softening below ambient temperature and that the softening can be explained from internal displacements caused by thermal contraction. It is also found that piezoelectric coefficients $e_{ij}$ of the crystals depends significantly on temperature. This is due to the internal displacements; $e_{ij}$ are sensitive to the location of ions in unit cell. It is reasonable to suppose that similar phenomena would appear in piezoelectric material which have a different point group symmetry. However, as far as the authors knowledge, a systematic work on the subject has not been conducted yet. The aim of this study is to investigate the complet set of elastic constants $C_{ij}$ and piezoelectric coefficients $e_{ij}$ of $LiNbO_3$ and $LiTaO_3$ single crystals at low temperatures. Since these piezoelectric crystals belong to $C_{3v}$ point group symmetry, temperature dependence of $C_{ij}$ and $e_{ij}$ would be different from those obtained from the $D_3$ type crystals; $\alpha$-quartz and langasite.

## 2. Experimental Procedures

### 2-1. Crystallography of $LiNbO_3$ and $LiTaO_3$

$LiNbO_3$ and $LiTaO_3$ belong to the trigonal class with its point group symmetry of $C_{3v}$ (space group symmetry is *R*3*c*). The independent elastic and piezoelectric components are $C_{11}$, $C_{12}$, $C_{13}$, $C_{14}$, $C_{33}$, $C_{44}$, $e_{15}$, $e_{22}$, $e_{31}$, and $e_{33}$. In matrix notations these are

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ C_{12} & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ C_{14} & -C_{14} & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & C_{14} \\ 0 & 0 & 0 & 0 & C_{14} & C_{66} \end{pmatrix},$$

and

$$e_{ij} = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & -e_{22} \\ -e_{22} & e_{22} & 0 & -e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix}.$$

**Table I** summarizes dimensions and mass-density $\rho$ of the $LiNbO_3$ and $LiTaO_3$ single crystals used in this study. Note that the *z*-axis corresponds to the *c*-axis of the unit cell.

Table I. Dimensions and mass-density of $LiNbO_3$ and $LiTaO_3$ single crystals.

| | *x* (mm) | *y* (mm) | *z* (mm) | $\rho$ ($kg/m^3$) |
|---|---|---|---|---|
| $LiNbO_3$ | 9.97 | 10.03 | 10.01 | 4631.7 |
| $LiTaO_3$ | 10.07 | 10.07 | 10.03 | 7446.1 |

### 2-2. RUS measurement

Low temperature elastic constants $C_{ij}$ and piezoelectric coefficients $e_{ij}$ of $LiNbO_3$ and $LiTaO_3$ single crystals are determined by RUS. A single crystal specimen is mounted on tripod type ultrasound transducers. One transducer excites ultrasound vibration to the specimen and another one detects the vibration amplitude. Free vibration resonance spectrum is obtained by frequency sweep with a step of $\Delta f$ = 10 Hz for $LiNbO_3$ and $\Delta f$ = 6.6 Hz for $LiTaO_3$. Resonance frequencies are determined by least-square fitting of resonance peaks to Lorenz function. Note that the measurement accuracy of resonance frequency is usually better than $10^{-5}$. The RUS unit is set in a cryogenic chamber and which controls the temperature from 4 to 300 K with the accuracy of

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0.1 K. The temperature step is $\Delta T$ = 10 K for $LiNbO_3$ and $\Delta T$ = 5 K for $LiTaO_3$.

## 3. Results and Discussion

### 3-1. Low temperature $C_{ij}$ and $e_{ij}$

**Figures 1** shows low temperature elastic constants $C_{ij}$ and piezoelectric coefficients $e_{ij}$ of LiNbO3 single crystal obtained by RUS measurement. As seen from the figure, all elastic constants show usual monotonic increasing with decreasing in temperature. Piezoelectric coefficients show monotonic increasing too, and hence, there is no unusual temperature behavior in $C_{ij}$ and $e_{ij}$. **Figure 2** shows low temperature $C_{ij}$ and $e_{ij}$ of $LiTaO_3$. Similar to the $LiNbO_3$, we only confirm monotonic increasing of $C_{ij}$ and $e_{ij}$ as temperature approaches to zero.

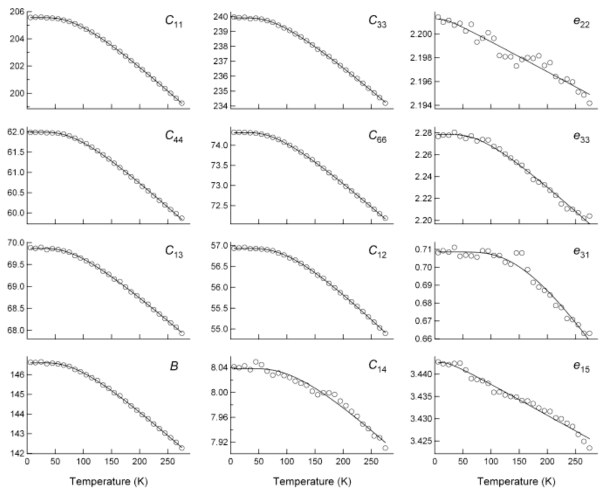


Figure 1. Low temperature elastic constants $C_{ij}$ and piezoelectric coefficients $e_{ij}$ of $LiNbO_3$.

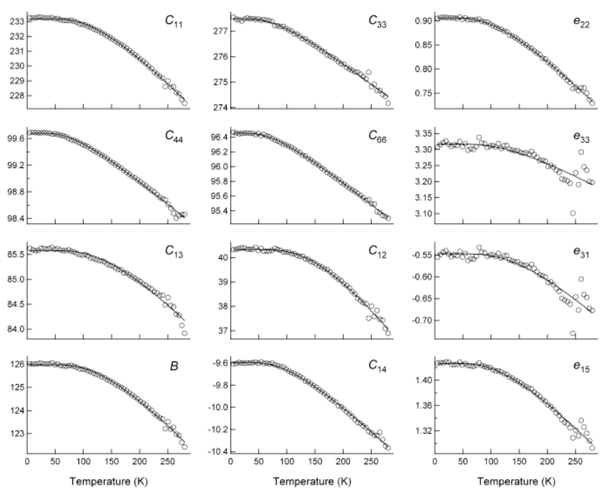


Figure 2. Low temperature elastic constants $C_{ij}$ and piezoelectric coefficients $e_{ij}$ of $LiTaO_3$.

### 3-2. Einstein temperature

Temperature dependence of elastic constants of Einstein type lattice vibration model can be written in the following form

$$C_{ij}(T) = C_{ij}(0) - \frac{s}{\mathrm{Exp}(\theta_E - T)}$$

This is called Varshni's function. Here $C_{ij}(0)$, $s$ and $\Theta_E$ represent zero-temperature elastic constant, lattice anharmonicity parameter and Einstein temperature, respectively. Solid curves in Figs. 1 and 2 show least square fitting of the function to the experimental results. Estimated Einstein temperatures $\Theta_E$ as well as $\Theta_E/\Theta_D$ ratios are summarized in **Table II**. Here, the $\Theta_E/\Theta_D$ ratio of $LiNbO_3$ varies in a small range, 0.44 to 0.63, and slightly lower than the theoretical value 0.79. On the other hand, that of $LiTaO_3$ varies in much wide range, 0.5 to 1.18, and some of them exceed 0.79. This result implies that in $LiTaO_3$ crystal phonon frequency depends significantly on vibration mode.

Table II. Einstein temperature $\Theta_E$ and $\Theta_E/\Theta_D$ ratio. Here $\Theta_D$ denotes acoustic Debye temperature estimated from low temperature $C_{ij}$: $\Theta_D$ = 580.4 K for $LiNbO_3$ and $\Theta_D$ = 454.0 K for $LiTaO_3$.

| | $LiNbO_3$ | | $LiTaO_3$ | |
|---|---|---|---|---|
| $C_{ij}$ | $\Theta_E$ | $\Theta_E/\Theta_D$ | $\Theta_E$ | $\Theta_E/\Theta_D$ |
| $C_{11}$ | 276.2 | 0.48 | 394.9 | 0.88 |
| $C_{12}$ | 328.8 | 0.57 | 530.5 | 1.18 |
| $C_{13}$ | 261.0 | 0.45 | 499.9 | 1.11 |
| $C_{14}$ | 367.0 | 0.63 | 304.9 | 0.68 |
| $C_{33}$ | 252.8 | 0.44 | 241.4 | 0.54 |
| $C_{44}$ | 267.9 | 0.46 | 257.4 | 0.57 |
| $C_{66}$ | 253.3 | 0.44 | 226.2 | 0.50 |

## 4. Conclusions

In summary, complete set of elastic constants $C_{ij}$ and piezoelectric coefficients $e_{ij}$ of $LiNbO_3$ and $LiTaO_3$ single crystals are determined by low temperature RUS experiments. Unlike previous studies to $\alpha$-quartz and langasite, both the $LiNbO_3$ and $LiTaO_3$ crystals show usual elastic stiffening upon cooling and no unusual behavior has been confirmed. Einstein temperatures estimated from the $C_{ij}(T)$ curves suggest that phonon frequency is uniform in $LiNbO_3$ while that of $LiTaO_3$ depends significantly on vibration mode.

## References


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