Crystal growth and low coercive field 180° domain switching characteristics of stoichiometric LiTaO₃

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(Received 4 June 1998; accepted for publication 20 September 1998)

We grew LiTaO₃ single crystals with a composition close to stoichiometry by using a double crucible Czochralski method. The switching field required for 180° ferroelectric domain reversal and the internal fields originating from nonstoichiometric point defects were compared for the stoichiometric and conventional commercially available crystals. The switching fields for the domain reversal in the stoichiometric crystal with a Curie temperature of 685 °C was 1.7 kV/mm. This is about one thirteenth of the switching field required for the conventional LiTaO₃ crystals with a Curie temperature near 600 °C. The internal field in the stoichiometric crystal drastically decreased to 0.1 kV/mm.

Lithium tantalate (LiTaO₃) and lithium niobate (LiNbO₃) are of interest for surface acoustic wave (SAW) devices, piezoelectric devices, and in nonlinear optical applications because of their large electro-optic and nonlinear optical coefficients. Among these applications, wavelength conversion by quasiphase matching, which can be calculated from the asymmetry in the Ps versus electric field hysteresis, was decreased to 0.1 kV/mm. © 1998 American Institute of Physics.

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the outer part of the melt by an automatic powder supply system. In this system, the powder supply rate is automatically set from the weight increase of the growing crystal. Details on the supply system are described elsewhere.9,10

By this novel method, stoichiometric LiTaO$_3$ crystals were grown along the Y axis at a pulling rate of 0.5 mm/h. The starting materials were high purity Li$_2$CO$_3$ (> 99.99%) and Ta$_2$O$_5$ (99.99%) powders. Growth was accomplished in an oxygen and nitrogen gas mixture flow with a volume ratio of oxygen to nitrogen 1:100. The seed rotation rate was about 5 rpm, and the crucible was rotated at a rate of 0.05–0.1 rpm in the opposite direction. The grown crystal was colorless, transparent, and crack-free with a size of 45 mm diameter and 80 mm length as shown in Fig. 1. The growing interface shape which can be estimated from the bottom shape of grown crystal when the crystal was detached from the melt at the end of growth was quite flat. No void or striation was observed under an optical microscope. The crystal homogeneity and optical quality were considerably good as it can be understood also from the etched surfaces of Figs. 2 and 3.

The composition of LiTaO$_3$ crystal can be estimated from the Curie temperature measured by differential thermal analysis (DTA). The crystal grown from the Li-rich melt exhibited a Curie temperature of 685 ± 1 °C, while that of the conventional crystal grown from a melt of 48.5 Li$_2$O mol % was 601 ± 2 °C. On the other hand, the powder sintered from a stoichiometric mixture of Li$_2$CO$_3$ and Ta$_2$O$_5$ powders showed a Curie temperature of 690 ± 1 °C. Assuming a linear relationship between the Curie temperature and crystal composition,7,11 the composition of crystal grown from the Li-rich melt can be estimated to be considerably close to stoichiometry. Some impurity concentrations in the stoichiometric LiTaO$_3$ crystal were analyzed by the inductively coupled plasma mass spectrometry (ICP-MS). The iron concentration was 0.9 wt. ppm as Fe. Copper and chromium were contained less than 0.1 and 0.2 wt. ppm, respectively.

Etching experiments using a mixed solution of HF and HNO$_3$ showed that the as-grown crystal grown from the Li-rich melt had a ferroelectric multidomain structure. Figure 2 shows the domain structure on a Z plate surface which was not poled (as grown). The crystal was cut in the shape of a block. The block was first annealed in air at 750 °C and subsequently cooled down at a rate of 2 °C/min to the room temperature applying a dc electric field along the Z direction. The poled block was cut and polished to be Z plate with the size of 10×10×0.5 mm, and the polarization was along the thickness direction. Figure 3 is a microphotograph of an etched +Z surface after poling. Although the sample was almost completely poled by this operation, the figure indicates the existence of microdomains in it.

The 180° ferroelectric domain switching experiments were done at room temperature by applying a dc electric field across the crystal thickness using liquid electrodes (saturated KNO$_3$ solution in water). The voltage was ramped at 15 V/s and the width of the transient current peak during domain reversal was measured to determine the switching field. The first domain reversal of the virgin crystals is called forward poling and the second reversal back to its original state is called reverse poling. The switching fields for forward and reverse poling are denoted $E_f$ and $E_r$, respectively. The asymmetry between the forward and reverse poling fields indicates the presence of internal fields,5 and can be calculated as $E_{int} = (E_f - E_r)/2$.

The total charge in the transient current signal obtained on domain reversal was measured by using an analog integration circuit using a capacitor in series with the sample, thus collecting all the current spikes however short. Upon domain switching, the final voltage across the capacitor gives the total charge $(Q)$, and spontaneous polarization, $P_s = Q/(2A)$ where $A$ is the electrode area. A high input impedance $\Omega$ multimeter was used to read the capacitor voltage.
important observations were made:

- Both stoichiometric and conventional crystals of LiTaO$_3$.
- Neatly revealed in domain switching of LiNbO$_3$.
- Crystal quality may also have some influence on the domain switching.

Table I summarizes the results of $E_f$, $E_s$, and $E_{int}$ for both stoichiometric and conventional crystals of LiTaO$_3$. Figure 4 shows the hysteresis loops between spontaneous polarization ($P_s$) and applied electric field ($E$) for the two crystals. All results bear a close resemblance to those previously revealed in domain switching of LiNbO$_3$. The following important observations were made: (1) Both $E_f$ and $E_s$ greatly decreased with increasing Curie temperature, that is, decreasing nonstoichiometric defect density. The forward poling field for the stoichiometric crystal was 1.7 kV/mm, about one thirteenth of that for the conventional one. This decrease is much larger than that observed in stoichiometric LiNbO$_3$, where the forward poling field decreased from 22 to 4–5 kV/mm. (2) The asymmetry between the forward and reverse poling fields almost disappeared in the stoichiometric crystal.

It has been revealed that the domain switching behavior is directly related with the nonstoichiometric defect density in LiTaO$_3$. The defects which have a similar structure with that generated in LiNbO$_3$ probably play the role of “pinning sites” in domain wall movement. In the same sense, crystal quality may also have some influence on the domain switching. It was postulated earlier that the origin of internal field lay possibly in a combination of nonstoichiometric point defects and/or hydrogen in LiTaO$_3$ and LiNbO$_3$ crystals. However, it turned out that the hydrogen concentration controlled by the thermal annealing in wet gas or dry gas had no influence on the internal fields or switching fields of LiNbO$_3$ crystals. In this study, we therefore did not eliminate the hydrogen in LiTaO$_3$ crystals during growth, which in analogy with LiNbO$_3$ is expected not to play any active role in the domain switching. The origin of the internal field and large changes in switching fields appear largely to be dependent on the [Li]/[Li+Ta] ratio in crystals.

These characteristics in domain switching for stoichiometric crystals are more favorable for fabricating periodically poled grating and other structures such as lenses and prisms for integrated optics in LiTaO$_3$ crystal. Using stoichiometric crystal, one can use thirteen times lower electric fields or thirteen times thicker crystals for domain switching in devices as compared to the conventional commercially available LiTaO$_3$ crystals. This may enable the fabrication of bulk devices (thicker than a few mm) with better mechanical stability and performance, or electro-optic devices that operate at an order of magnitude lower electric fields.

The authors are grateful to Eiji Nagata of Taki Chemical Co. Ltd. for his impurity analysis. This study is partially supported by the special coordination funds of the Science and Technology Agency Japan for promoting science and technology.

### Table I. Comparison in Curie temperature, melt composition, and domain switching properties between conventional and stoichiometric LT crystals.

<table>
<thead>
<tr>
<th></th>
<th>Conventional LT</th>
<th>Stoichiometric LT</th>
</tr>
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<tbody>
<tr>
<td>Curie temperature (°C)</td>
<td>601±2</td>
<td>685±1</td>
</tr>
<tr>
<td>Melt composition (Li$_2$O mol %)</td>
<td>48.5</td>
<td>60.0</td>
</tr>
<tr>
<td>$E_f$ (kV/mm)</td>
<td>20</td>
<td>1.7</td>
</tr>
<tr>
<td>$E_s$ (kV/mm)</td>
<td>12</td>
<td>1.5</td>
</tr>
<tr>
<td>$E_{int}$ (kV/mm)</td>
<td>4</td>
<td>0.1</td>
</tr>
<tr>
<td>$P_s$ (μC/cm$^2$)</td>
<td>60±3</td>
<td>55±3</td>
</tr>
</tbody>
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FIG. 4. Experimental hysteresis loop at room temperature between spontaneous polarization ($P_s$) and applied electric field along Z axis, contrasting the difference between the conventional and stoichiometric LT crystals. The schematics labeled states I and II show the relative orientation of internal field, $E_{int}$ with respect to spontaneous polarization, $P_s$ in the crystal.