

Periodic domain formation in LiNbO_3 single crystals during growth

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ABSTRACT

The domain formation phenomena of LiNbO_3 crystals was investigated and the method for the periodic domain formation in LiNbO_3 single crystals during growth was proposed in this study. The stress-induced domain formation mechanism was proposed and explained. The strong piezoelectric effect of LiNbO_3 at elevated temperature, would be the direct driving force for the inversion of the spontaneous polarization direction and form domain walls. It was found that the tensile component of the internal stresses can inverse the original direction of the spontaneous polarization.

1. INTRODUCTION

Quasi-phase matching(QPM) using the ferroelectric domain reversal grating is useful for high-efficiency nonlinear interaction in the wavelength region from short wavelength to far infrared wavelength. The most significant thing among the advantages of the QPM is that any interaction within the transparent range of materials can be noncritically phase matched. So, it is always possible that the largest one among the nonlinear coefficients in the crystal be used for the interacting waves.

Several research teams are carrying out the research on the application of the QPM to the SHG(Second harmonic generation) and also on the formation of the domain reversal grating using the electron beam lithography and the direct electric field application. The second-order harmonic generations of green and blue laser from QPM using bulk LiNbO_3 , and LiNbO_3 waveguide, an LiTaO_3 waveguide and other materials have been reported.

Although low energy threshold of LiNbO_3 crystals restricts the use of the LiNbO_3 single crystals in laser application, large 2nd order nonlinear coefficient($r_{33}=30\text{pm/V}$) makes it be promising materials for QPM application. The large beam size with the large interaction area can reduce the energy density of the optical waves in the crystal and overcome the low energy threshold of LiNbO_3 , if large bulk crystals having domain reversal grating are available.

Ferroelectric domains of LiNbO_3 single crystals were known as frozen and is hard to switch its direction of polarization because of its high phase transition temperature. But there are several reports that the domain reversal gratings can be formed by electron beam lithography and the direct electric field application at room temperature. By these methods because the strength of the electrical field is inversely proportional to the crystal thickness, the crystal thickness is limited to about 0.5mm. And it can not be avoided that the diffuse domain features due to the diffused strength of the electric field inside the crystals.

Many researchers have been interested in the specific domain features of as grown LiNbO₃ single crystals, but the nature of formation ferroelectric domain was not explained completely. The nature of the domain formation of LiNbO₃ single crystals during growth and the method to control the domain formation and to make the periodically poled features during growth will be illustrated by this investigation.

2. EXPERIMENTAL PROCEDURES

The domain structures of the as grown LiNbO₃ single crystals grown by Czochralski method were examined. The ferroelectric domains were observed by optical microscopy on the etched surface of the (0001) or (10 $\bar{1}$ 0) planes. The polarity of the spontaneous polarization, P_s , can be easily distinguished by chemical etching with a boiling solution of 2 parts of HNO₃ and 1 part of HF. The negative P_s end (-c face) shows a deeply etched pattern, while the positive P_s end (+c face) shows a hardly etched pattern. Also, a piezoelectric negative y end, (10 $\bar{1}$ 0) face, shows a deeply etched pattern.

Doped and undoped crystals were grown along the [0001] and [10 $\bar{1}$ 0] directions, with congruently melting composition by Czochralski method. In order to control domain structures by gradient dopant concentration in the crystals during growth, the horizontal temperature gradient was made. The temperature fluctuations due to the crystal rotation with horizontal temperature gradient of the melt, leads to the oscillation of the growth rate and the solute concentrations in the crystals. The amplitude of the temperature fluctuations were adjusted by the temperature gradient which was modified by the furnace structure.

The lattice distortion of the doped LiNbO₃ crystals was estimated by measuring the lattice parameters of the Y₂O₃ doped and undoped crystals by X-ray diffractometry.

3. RESULTS AND DISCUSSIONS

3.1 Back ground for the domain formation in LiNbO₃

The driving force for the formation of ferroelectric domains ins the depolarizing energy. In a perfect and infinite crystal, spontaneous polarization, P_s is constant; but real crystals have surfaces where the spontaneous polarization vanishes, and the change of the spontaneous polarization, $\text{div}P_s$, form the depolarizing field. Ferroelectric domains are formed by minimization of the total free energy, including the depolarizing and domain wall energy.

LiNbO₃ single crystals are expected to have a strong tendency, being single domains, especially at the elevated temperature, just below the phase transition temperature. When the depolarizing field can be compensated by electric conduction, a single domain feature is favored energetically in highly conducting ferroelectric crystals. So, it can be assumed that LiNbO₃ crystals have a single domain features if there is no electrical field when the crystal is grown and cooled below Curie temperature, i.e. all the spontaneous polarizations in the crystal would have the same direction.

The piezoelectric properties of ferroelectric materials are usually stronger than

those of linear piezoelectric materials, that is especially true near the phase transition temperature. Anomalies in piezoelectric properties near the phase transition temperature are a unique property of the piezoelectric effect in ferroelectric materials, which distinguish them from linear dielectric materials[13]. So, at just below the phase transition temperature, it is expected that strong electrical displacement would be formed by internal stresses in the as-grown LiNbO₃ crystals. This strong electric field, which is formed by the piezoelectric effect, is expected to be sufficient to affect the domain structures.

3.2 Domain features of Y₂O₃ doped crystals

As shown in Fig.1, Y₂O₃ doped crystals have the striped features of domains having alternative sign of spontaneous polarizations.

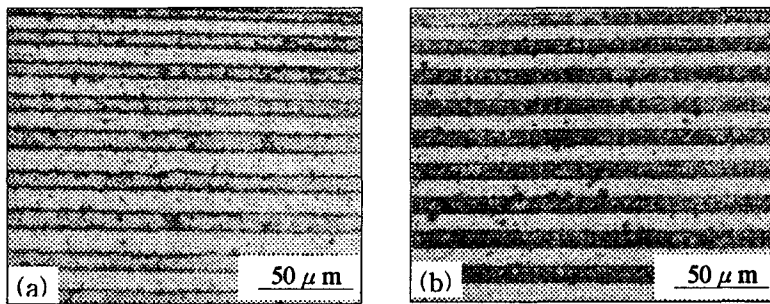


Fig.1 Domain features of Y₂O₃ doped crystals grown along (a) [0001] and (b) [10 $\bar{1}$ 0] directions.

Y₂O₃ rich regions have the opposite behavior. From the stress features in the crystal (Fig.2), the electrical displacement which was produced by the piezoelectric effect can be calculated as followings:

1. [0001] grown crystal
 Y₂O₃ rich region: $D_1=D_2=0, D_3=-d_{31}(T_1+T_2)$
 Y₂O₃ poor region: $D_1=D_2=0, D_3=d_{31}(T_1+T_2)$
2. [10 $\bar{1}$ 0] grown crystal
 Y₂O₃ rich region: $D_1=0, D_2=-d_{21}T_1, D_3=-d_{31}T_1+d_{33}T_3$
 Y₂O₃ poor region: $D_1=0, D_2=d_{21}T_1, D_3=d_{31}T_1-d_{33}T_3$

The electrical displacement calculated above, is shown Fig.3(a,b) and the domain structures can be expected as shown in Fig.3(c,d). Because of the strong piezoelectric effect just below the transition temperature, the single domain feature of the as grown crystal would be the unstable state. The strong electrical field seems to be sufficient to inverse the direction of the spontaneous polarization. And the formation of the layered domain structure can reduce the localized electrical field, and become energetically stable.

The orientation of the spontaneous polarization

The intentionally induced concentration fluctuations of dopants should have produced the internal stresses in the crystals. Fig.2 shows a schematic diagram of internal stresses which were formed by lattice mismatch. The Y₂O₃ rich regions have a tendency to contract along the c-axis and expand along the a-axis, while the

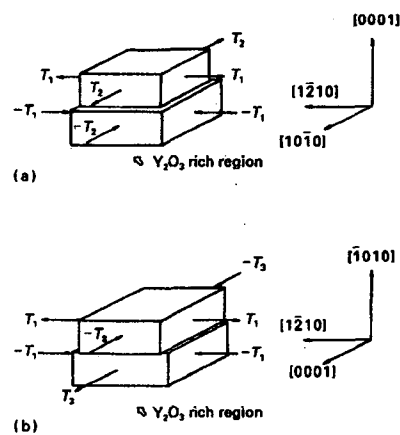
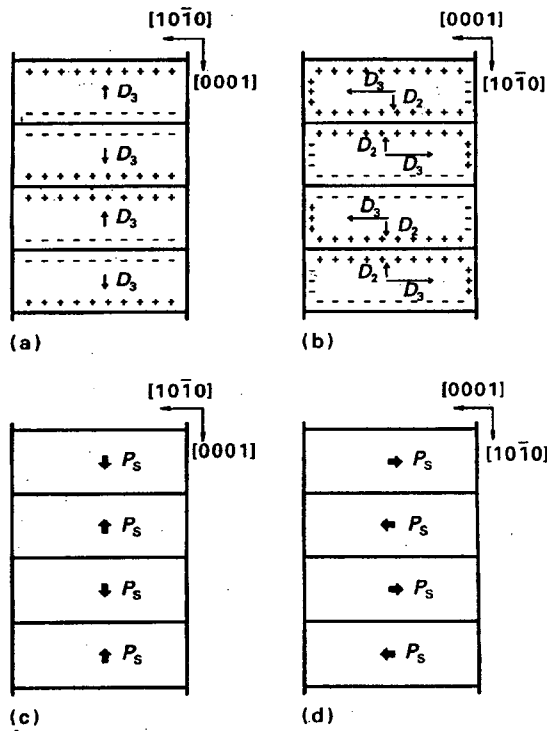


Fig. 2 Schematic diagram of internal stresses produced by the lattice mismatch due to the inhomogeneous distribution of Y₂O₃ in LiNbO₃ single crystals. (a) [0001] grown crystal (b) [10 $\bar{1}$ 0] grown crystal



should be opposite to the electrical displacement, i.e. it will be reversed at the regions under the tensile stress. The fact that the Ti-doped LiNbO₃ substrate was not inverted on the -c face, while it was inverted on the +c face, which was reported by Miyazawa [6], could be understood by this model.

Fig.3 Schematic diagram of the electrical displacement produced by the internal stresses and the expected domain structures in the Y₂O₃ doped LiNbO₃ crystals.

- (a) Electrical displacement feature of the [0001] grown crystal.
 (b) Electrical displacement feature of the [10 T 0] grown crystal.
 (c) Expected domain structure of the [0001] grown crystal.
 (d) Expected domain structure of the [10 T 0] grown crystal.

4. CONCLUSION

The stress-induced domain formation model was proposed and the domain structures of the as grown crystals of LiNbO₃ was explained. The method for the periodic domain formation in LiNbO₃ single crystals during growth were proposed and explained by this model. The tensile component of internal stresses can reverse the orientation of the spontaneous polarization from the original direction.

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