

Stress induced domain formation in LiNbO₃ single crystals

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The domain formation phenomenon of LiNbO₃ crystals was investigated in this study. A stress induced domain formation mechanism was proposed, and domain formation of the as-grown crystals and domain inversion of substrate crystals were explained. The strong piezoelectric effect of LiNbO₃ at elevated temperature, could be the direct driving force for inversion of the spontaneous polarization direction and could 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

The ferroelectricity of LiNbO₃ is known as “frozen” at room temperature, i.e. the ferroelectric domains will not switch under the application of an electric field in the conventional manner [1]. On the other hand, at elevated temperatures the material becomes switchable easily. So the domain structure of the as-grown LiNbO₃ crystal must be strongly affected by the thermal history and other factors at elevated temperature and it cannot be changed at room temperature. LiNbO₃ has 180° domains, because it belongs to the 3*m* point group [2].

Since LiNbO₃ belongs to wide band ferroelectric semiconductors, the depolarizing field can be compensated for by electrical conduction during growth. So, a single domain crystal will be favoured energetically [3], due to the lack of depolarizing energy, which is the driving force for formation of a ferroelectric domain wall.

It has been reported that the domain patterns of the as-grown LiNbO₃ crystals show characteristic features according to the growth directions [4, 5]. Miyazawa [6] and Thaniyavarn *et al.* [7] reported that domain inversion occurred as a result of titanium diffusion on the LiNbO₃ substrates during the process of the Ti-diffused waveguides. And Nakamura *et al.* [8] also reported domain inversion occurring only by heat treatment and cooling of LiNbO₃ substrates. But, the domain formation mechanism of the crystals and inversion phenomena have not been understood fully yet.

In this study, a stress induced domain formation model was proposed and explained by the piezoelectric property. The domain features of the as-grown crystals and the domain inversion phenomena which are already reported can be explained by this model. In order to support this model, the domain structures of doped and undoped LiNbO₃ crystals were investigated.

2. Experimental procedure

LiNbO₃ crystals were grown by the Czochralski method and the shape of the ferroelectric domains were examined. Y₂O₃ doped and undoped crystals were grown along the [0001] and [10 $\bar{1}$ 0] directions, with congruently melting compositions. During growth of the Y₂O₃ doped crystals, the symmetry axis of the temperature field was intentionally displaced from the rotational axis by modification of the furnace structure [9]. By periodic fluctuations of temperature during growth, crystal rotation, growth rate and solute concentrations in the crystals were oscillated. The amplitude of both the temperature and the growth rate fluctuations can be adjusted by the furnace structure. Also, the spacing of rotational striations due to growth rate fluctuations can be changed by controlling the pulling and rotating speed.

In order to estimate lattice distortion by doping of Y₂O₃ in the LiNbO₃ crystal, the lattice parameters of Y₂O₃ doped and undoped LiNbO₃ were measured by X-ray diffractometry.

The ferroelectric domains were observed by optical microscopy on the etched surface of the (0001) and (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 2HNO₃ + 1HF [10]. 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.

3. Results

3.1. Domain structures of the Y₂O₃ doped crystals

Domain structures of the Y₂O₃ doped crystals were 1:1 corresponding with the rotational striations

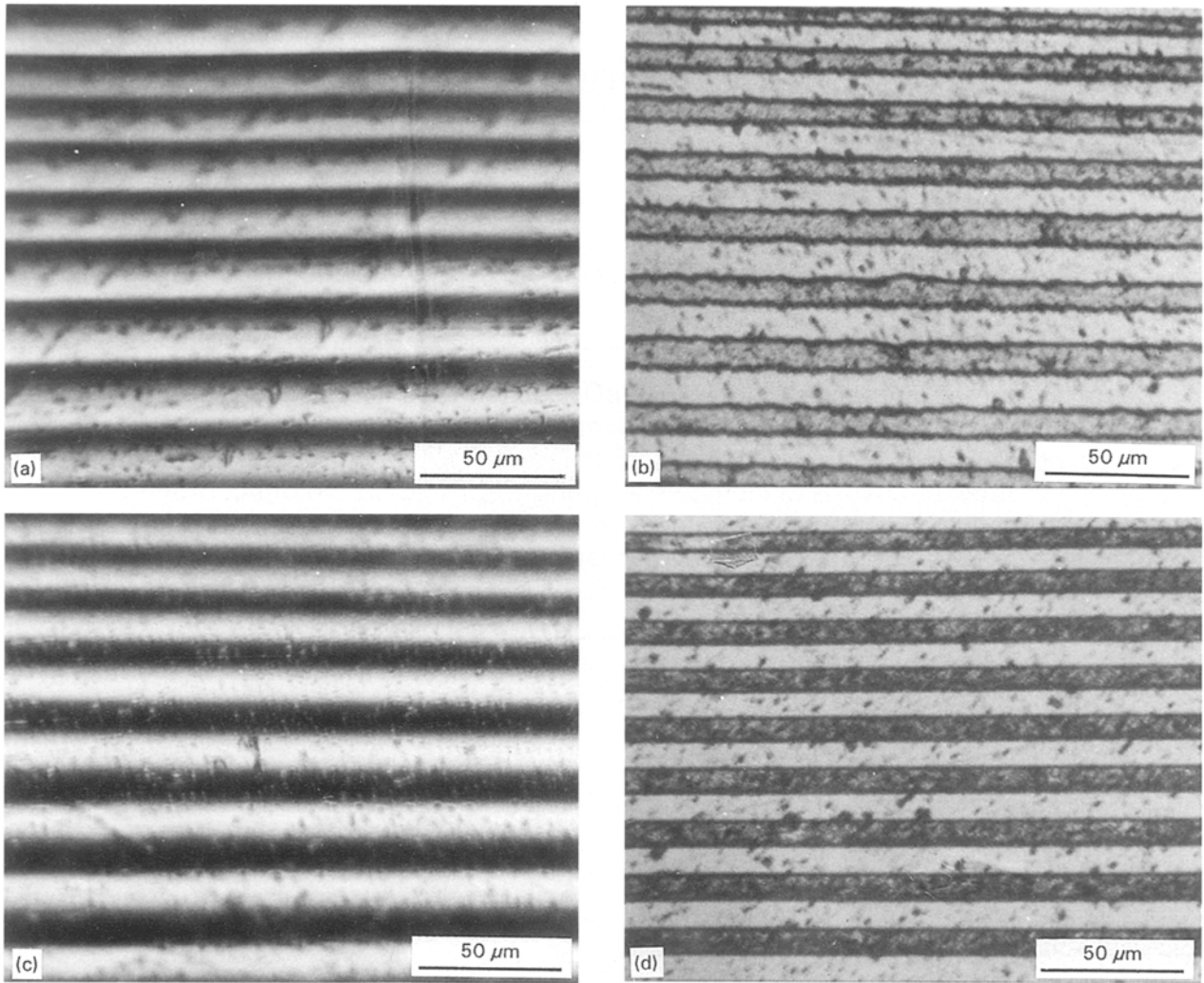


Figure 1 Domain structures corresponding to the rotational striations of the Y_2O_3 doped crystals: (a) growth striation of $[000\ 1]$ grown crystal (surface), (b) domain structure of $[000\ 1]$ grown crystal $[(10\ \bar{1}\ 0)$ plane], (c) growth striation of $[10\ \bar{1}\ 0]$ grown crystal (surface), and (d) domain structure of $[10\ \bar{1}\ 0]$ grown crystal $[(000\ 1)$ plane].

formed by the intentionally induced asymmetrical temperature field. As shown in Fig. 1, the $[000\ 1]$ and $[10\ \bar{1}\ 0]$ grown crystals have the same domain structures, and show periodic inversion of the polarity. The pulling rate was $2\text{--}3\ \text{mm h}^{-1}$ and the rotation speed was 5 r.p.m.

This result is coincident with the result of Ming *et al.* [9]. They investigated the domain structure of a c -axis grown crystal only and concluded that the space charge which is formed by concentration fluctuations of Y_2O_3 makes crystals having domain. But the author's have found that the domain structures of the $[000\ 1]$ and $[10\ \bar{1}\ 0]$ axis grown crystals were the same.

The lattice parameters of the undoped and Y_2O_3 doped crystals were measured as shown in Table I. There was significant lattice distortion by doping. So, it is expected that internal stress was formed by the concentration fluctuation of Y_2O_3 , which was caused by growth rate oscillation. The variation of concentration of the solute atom by the change of growth rate was explained by the BPS model, which introduced the effective segregation coefficient and was proposed by Burton, Prim and Slichter [12].

TABLE I Lattice parameters of the $LiNbO_3$ crystals

Chemical composition	a (nm)	c (nm)
$0.486Li_2O \cdot 0.514Nb_2O_5$	0.515148	1.385919
$0.486Li_2O \cdot 0.514Nb_2O_5 \cdot 0.01Y_2O_3$	0.516768	1.385513

3.2. Domain structures of the undoped crystals

Domain structures of the undoped crystals changed with the growth directions. As shown in Fig. 2, the domain structure of the $[000\ 1]$ grown crystal has almost the same feature with growth striations. The overall domain boundary is coincident with the shape of solid-liquid interface; and there are many isolated domains. The domain shapes of the upper part of the crystal, which was grown at the initial stage, show convex shapes to the melt; while those of the lower part of the crystal, which was grown during the body growing process, show concave shapes. The change of the interface shape of the oxide crystals during growth

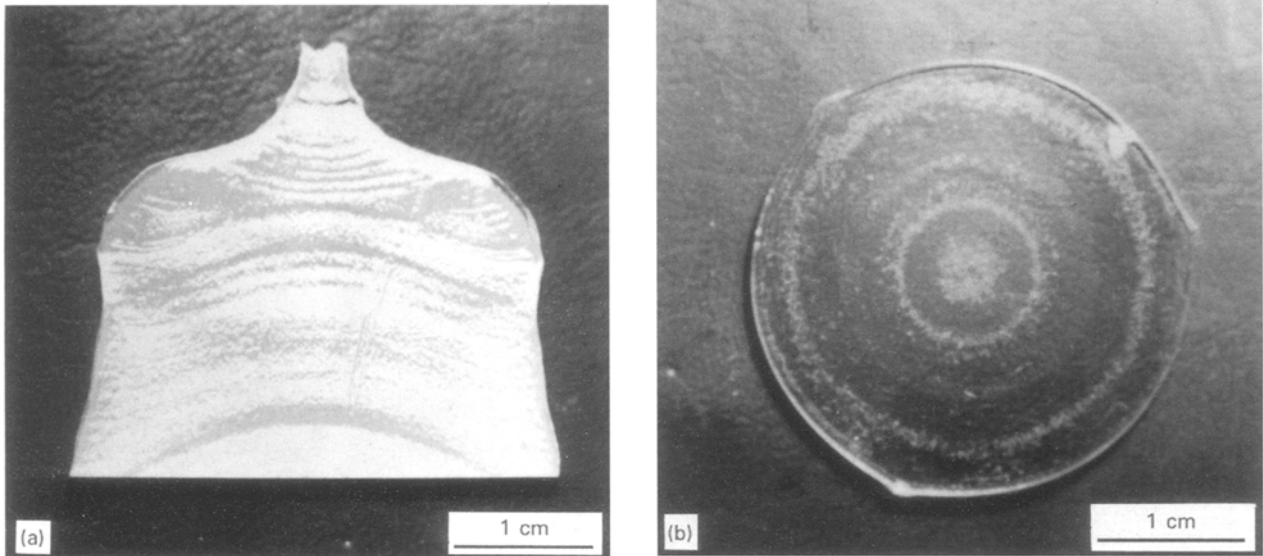


Figure 2 Domain structure of the undoped $[000\ 1]$ grown crystal: (a) $(10\bar{1}\ 0)$ plane, parallel to the growth direction; and (b) $(000\ 1)$ plane, perpendicular to the growth direction.

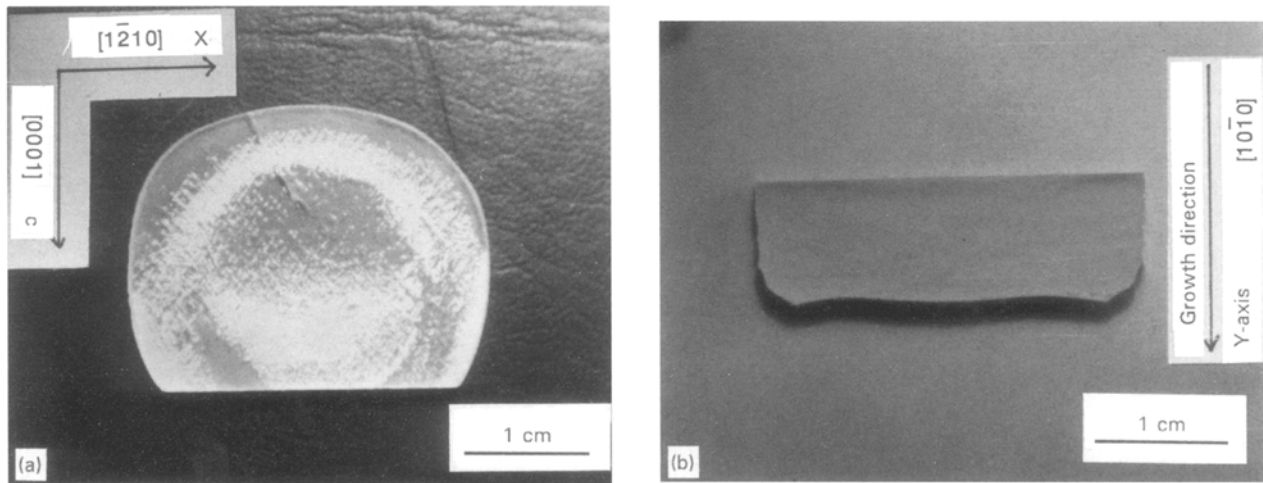


Figure 3 Domain structure and the solid-liquid interface shape of the undoped $[1\ 0\bar{1}\ 0]$ grown LiNbO_3 crystal: (a) domain structure, and (b) solid-liquid interface shape.

by the Czochralski method had been reported by Carruthers [11].

The $[1\ 0\bar{1}\ 0]$ grown crystal shows split type domain structure, as shown in Fig. 3. Luh *et al.* [5] also reported a split domain structure in the $[1\bar{2}\ 1\ 0]$ grown LiNbO_3 fibre crystal. But the domain structure shown in Fig. 3 has inversion regions at which the solid-liquid interface shape is concave and there are many isolated domains like the $(000\ 1)$ as-grown crystal.

4. Discussion

4.1. Background to stress induced domain formation

The driving force for the formation of ferroelectric domains is 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

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.

LiNbO_3 crystals are expected to have a strong tendency, being single domains, especially at elevated temperature, just below the phase transition temperature. When the depolarizing field can be compensated for by electrical conduction, a single domain feature is favoured energetically in highly conducting ferroelectric crystals. It can be assumed that LiNbO_3 crystals have a single domain feature if there is no electrical field when the crystal is grown and cooled below the 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

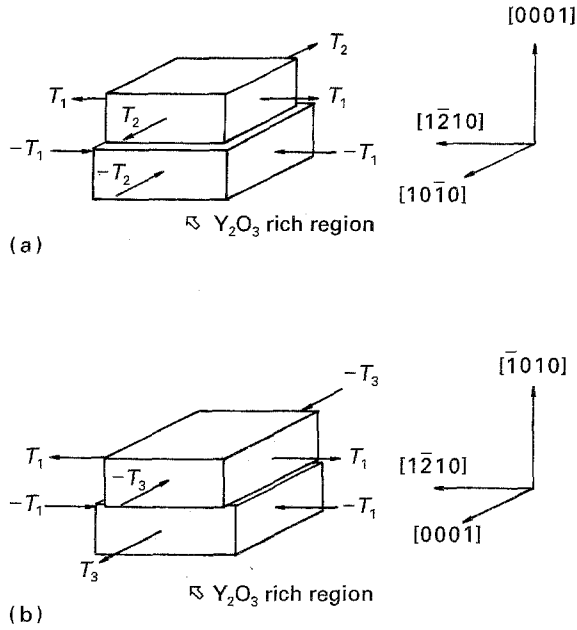


Figure 4 Schematic diagram of the internal stresses produced by lattice mismatch due to inhomogeneous distributions of Y_2O_3 in $LiNbO_3$ crystals. Internal stress feature of (a) the $[0001]$ grown crystal, and (b) the $[1010]$ grown crystal.

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 $LiNbO_3$ crystals. This strong electrical field, which is formed by the piezoelectric effect, is expected to be sufficient to affect the domain structures.

4.2. Domain structures of Y_2O_3 doped crystals

As shown in Fig. 1, Y_2O_3 doped crystals have the striped features of domains having alternative sign of spontaneous polarizations. The intentionally induced concentration fluctuations of Y_2O_3 in the crystals produced internal stresses. Fig. 4 shows a schematic diagram of internal stresses which were formed by lattice mismatch. The Y_2O_3 rich regions have a tendency to contract along the c -axis and expand along the a -axis, while the Y_2O_3 poor regions have the opposite behaviour.

From the schematic diagram of the stress features in the crystal (Fig. 4), the electrical displacement which was produced by the piezoelectric effect can be calculated as follows

- For the (0001) grown crystal
 Y_2O_3 rich region: $D_1 = D_2 = 0$,
 $D_3 = -d_{31}(T_1 + T_2)$
 Y_2O_3 poor region: $D_1 = D_2 = 0$,
 $D_3 = d_{31}(T_1 + T_2)$
- For the $(10\bar{1}0)$ grown crystal
 Y_2O_3 rich region: $D_1 = 0$, $D_2 = -d_{21}T_1$,
 $D_3 = -d_{31}T_1 + d_{33}T_3$
 Y_2O_3 poor region: $D_1 = 0$, $D_2 = d_{21}T_1$,
 $D_3 = d_{31}T_1 - d_{33}T_3$

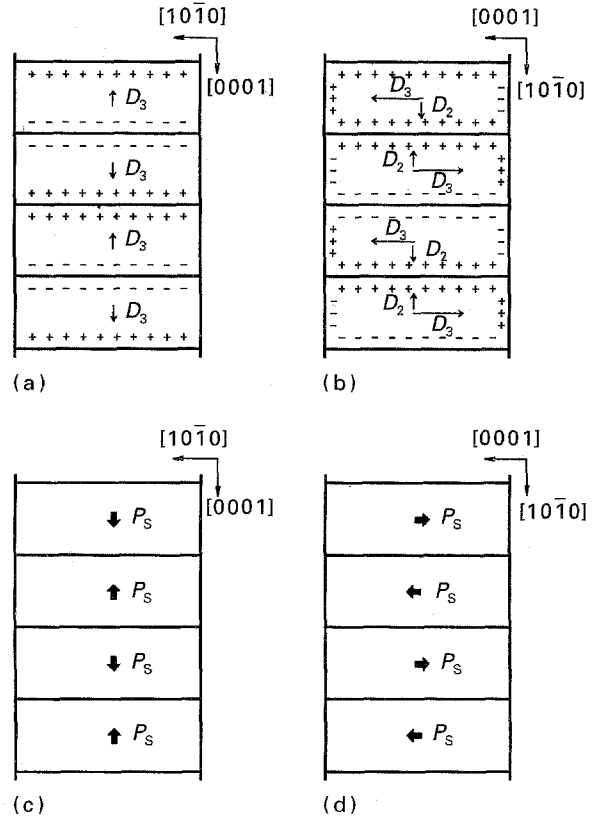


Figure 5 Schematic diagram of the electrical displacement produced by the internal stresses and expected domain structures in Y_2O_3 doped $LiNbO_3$ crystals. Electrical displacement feature of (a) the $[0001]$ grown crystal, (b) the $[10\bar{1}0]$ grown crystal. Expected domain structure of (c) the $[0001]$ grown crystal, and (d) the $[10\bar{1}0]$ grown crystal.

where D = electrical displacement tensor; d = piezoelectric constant (tensor form) and T = stress in the crystal (tensor form).

The electrical displacement calculated above is shown in Fig. 5a, and the domain structures can be expected as shown in Fig. 5b. Due to the strong piezoelectric effect just below the transition temperature, the single domain feature of the as-grown crystal would be an unstable state. The strong electrical field seems to be sufficient to inverse the direction of spontaneous polarization; and the formation of a layered domain structure can reduce the localized electrical field, and become energetically stable.

The orientation of the spontaneous polarization should be opposite to the electrical displacement, i.e. it will be reversed in regions under tensile stress. The fact that the Ti-doped $LiNbO_3$ 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.

4.3. Domain structures of the undoped crystals

The domain structures of the undoped crystals (Figs 2 and 3) show island type small domains, located near the domain boundary. This means that the driving force for domain formation was weak compared to the doped crystals, as shown in Fig. 1.

If there was no significant change of temperature profile in the crystal during cooling under the phase transition temperature, strong internal stresses would not be formed by differences in the thermal contractions. So, domain formation of the *c*-axis grown crystal seems to be due to the relatively weak internal stresses, which are formed by irregular segregation of impurities. The small island type domains seems to be produced by localized stresses which were formed by defects such as dislocations or inclusions. It is expected that the electrical field, which is produced by the pyroelectric effect having a direction coincident with the temperature gradient, seems to be too weak to form a single domain crystal.

The domain structure of the [1010] grown crystal shows a split type domain feature. The electrical field of the pyroelectric effect seems to create LiNbO₃ crystals mainly with split type domain structures because of the radial temperature gradient. The half ring type domains seem to be formed by internal stress which formed during cooling from the concave solid-liquid interface. The concave region of the crystal would have a tensile stress during cooling, while other regions of the crystal would exhibit a compressive stress. As mentioned above, the tensile component of the stress can inverse the domain from the original orientation.

5. Conclusions

A stress induced domain formation model was proposed and the domain structures of the as-grown

LiNbO₃ crystals was explained. Domain inversion phenomena during Ti-diffusion or heat treatment, could be explained by this model. The tensile component of internal stresses can reverse the orientation of spontaneous polarization from the original direction.

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