

The Growth Rate Difference in Lithium Triborate Single Crystal Along the Polar Direction

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It was observed that the growth rates are different each other in the opposite direction along c-axis due to the crystal polarity. In according to the calculation based on diffusional equations with consideration of the electrical polarization and the surface charge, the difference of growth rates could be explained. Some experiments were compared with this kinetic explanation.

Key word: Crystal growth, Lithium triborate, Crystal polarity

I. Introduction

In general, the morphology of a crystal is related to its structure. If two planes are not crystallographic equivalents, physical properties and growth rates normal to these planes are different though the other conditions for crystal growth are same. Polar crystals such as ZnO and meta-nitroaniline(mNA) show the different growth rates in the opposite direction along the polar axes.^{1,2)} The difference of growth rates between two directions along the polar axis should be regarded as another phenomenon to the anisotropy in the two axes. The latter phenomenon can be explained with PBC(periodic bonding chain) vectors and comes from the edge energy difference principally.³⁾

However, kinetic description is necessary to explain the former development. For examples, in the case of mNA (meta-nitroaniline) crystal, acceptors and donors are arranged along the polar axis so that impurities such as dinitrobenzene absorb the surface in the direction of donors, and the low growth rate is shown. In the case of ZnO crystal, Zn ions are exposed dominantly on one surface, O ions are on opposite surface. This arrangement causes the surface tension difference.

It is observed the growth rate difference along polar axis in the lithium triborate crystal (LiB_3O_5 , LBO) which belongs to space group $\text{Pna}2_1$.⁴⁾ The electrostatic force induced by asymmetric arrangement of ions in this polar crystal would differ the flux of charged growth units and growth rates.

II. Experimental Procedure and Results

Crystals were grown by top seeded solution growth (TSSG) method with excess B_2O_3 , and most of parameters referred the reports⁵⁻⁹⁾ and the repeated experiments to be fixed.

$\text{Li}_2\text{B}_4\text{O}_7$ and H_3BO_3 powder were used as start materials and composition of the solutions was LBO-35.48 mol% B_2O_3

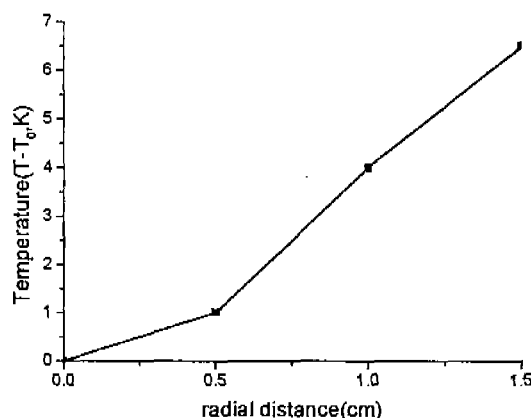


Fig. 1. Radial temperature distribution without seed crystal. T_0 is the temperature at the center of the surface of the undisturbed solution.

(Li/B=1/4.1). The solution occupied 100 g, approximately 70% of the Pt crucible, 50 mm diameter and 50 mm high. $\langle 010 \rangle$ seeds were used to compare growing aspects in opposite direction along polar axis. Crystal rotation rate was 30RPM in unique direction, and horizontal temperature distribution is shown in Fig. 1. Solution cooling rate was 0.48~0.96°C/day. After growing, crystal was separated from the solution and cooled at the rate 25°C/hour to 300°C and at the rate 15°C/hour to the room temperature.

A seed crystal was contacted on the surface of solution, and held for 12 hours, before the solution was cooled if the crystal neither melted nor grew. Because the crystal often did not grow until the solution temperature decreased to 3°C below the starting temperature, the saturation temperature could not be expected precisely, and cooling range was determined after the seed crystal formed the faceted shape.

The $\{110\}$, $\{011\}$ and $\{01\bar{1}\}$ groups of faces are strongly exposed planes out of the crystals obtained with $\langle 010 \rangle$ seeds, and small $\{201\}$ faces are often observed. In the crystals, there

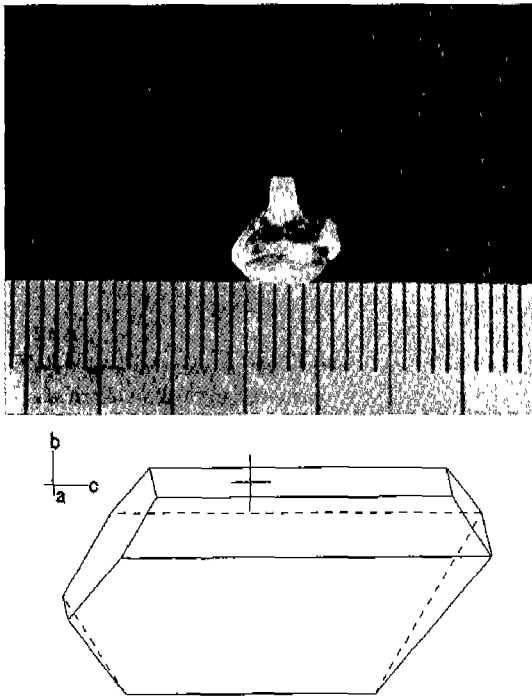


Fig. 2. LBO crystal grown for 0.9°C cooling since the faceted shape was constructed. Seed crystal direction is $\langle 010 \rangle$. The scale indicates 1 mm.

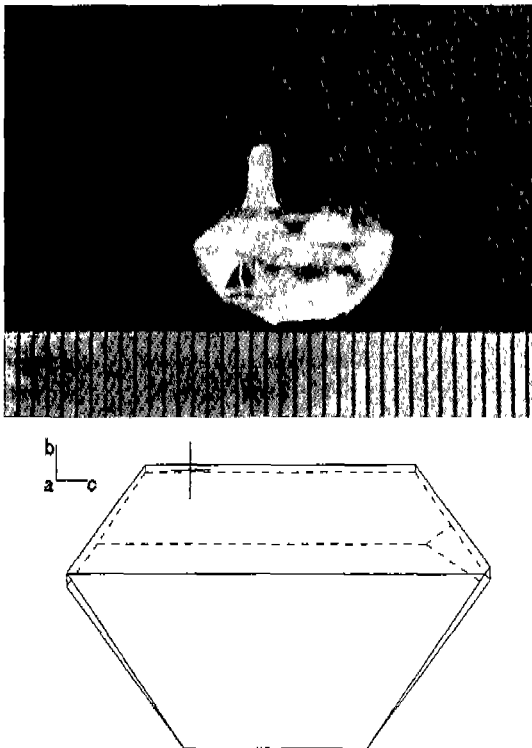


Fig. 3. LBO crystal grown for 2.6°C cooling since the faceted shape was constructed. Seed crystal direction is $\langle 010 \rangle$. The scale indicates 1 mm.

are inclusions under seed crystal along rotation axis. A little of solution stuck to the bottom of the grown crystal shrank in cooling process to result in crack to seed crystal.

Fig. 2. shows the LBO crystal grown within 0.9°C cooling range at 0.72°C/day and Fig. 3. is grown within 2.6°C range. After the faceted shape was constructed, crystal started to grow rapidly in one direction along c-axis, but slowly in another direction. $\{011\}$ and $\{01\bar{1}\}$ groups of faces cover the c-axis, growth rates of these directions are relative to those of these faces.

The crystal that grew within 4.0°C range is shown in Fig. 4. The crystal orientations in Fig. 2. and Fig. 3. are same, but this is in the opposite direction. This crystal grew very anisotropically in the early stage similar to Fig. 2. and Fig. 3., but the growth rate of the faces that had migrated very slowly got increased, anisotropy lessened along the polar axis, and finally the lengths of grown crystal were reversed to be longer.

In our investigation, over than 10 growth runs were made, and observed the growth aspects likely to the crystal shown Fig. 4., but it was rare that growth length grown slowly at initial stage exceeded that of the opposite direction.

III. Discussion

1. Spontaneous polarization and surface charge

Polar crystals such as LBO has piezoelectricity¹⁰⁾ and pyroelectricity due to the non-vanishing dipole moment resulted from asymmetric arrangement of ions. However these crystals do not generate electric field out of them unless the

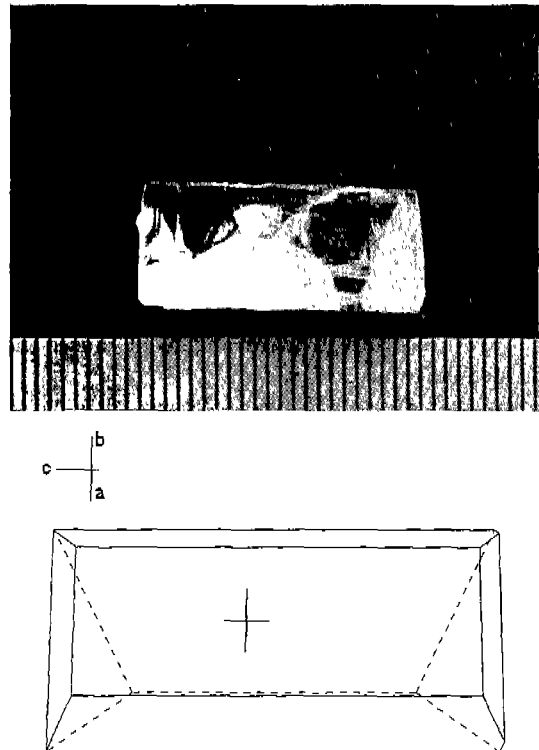


Fig. 4. LBO crystal grown for 4.0°C cooling since the faceted shape was constructed. Seed crystal direction is $\langle 010 \rangle$. The crystal was cracked in the cooling process. The arrow marks the seed position and the each scale is 1 mm

temperature or pressure change. Polar crystals growing in the solution have the surface charges absorbed from the solution and it would vanish net dipole moment of the whole crystal.

Electric dipoles in the crystal and surface charge form electric potential gradient near the crystal surfaces.¹¹⁾

$$\begin{aligned} \phi(r) &= \frac{1}{4\pi\epsilon} \left[\sum_i \frac{p \cdot (r - r_i)}{|r - r_i|^3} V_c + \oint \frac{\rho_s(r') dS'}{|r - r'|} \right] \\ &= \frac{1}{4\pi\epsilon} \oint \frac{P_c \cdot n' + \rho_s(r')}{|r - r'|} dS' \end{aligned} \quad (1)$$

where ϕ is the electric potential in any position r out of the crystal, ϵ is dielectric constant, and r' the one position in the crystal. p represents the electric dipole moment of an unit cell, V_c is the volume of an unit cell, S' the surface area on the crystal, $P_c (=p/V_c)$ means spontaneous electric polarization, and ρ_s is the surface charge density.

The solution is an ionic conducting material due to complex ions so that there is no electric field in the region sufficiently far from crystal solution interface.

$$P_c \cdot n + \rho_s(r') = 0 \quad (2)$$

To calculate P_c , there must be no ion that forms imperfect unit cell on the crystal surface. Otherwise P_c cannot be unique and its physical meaning would be lost.

Because the surface structure of growing crystal are altered regularly, the spontaneous polarization can be replaced with mean value. For an example, there is a mirror symmetry, the surface charge and spontaneous polarization will not appear.

We calculated the mean values of the spontaneous polarizations and surface charge densities for the {011} faces of LBO single crystal. There are two types of surface structure a face, and the mean values of the charge densities are $\pm 0.041C/m^2$.

It can be obtained the distribution of charge and electric field by the spontaneous polarization with solving the diffusional equations.

$$D_e \frac{d^2 \rho_e}{dz^2} + R \frac{d\rho_e}{dz} - \frac{\sigma \rho_e}{\epsilon} = 0 \quad (3)$$

$$\rho_e = \frac{\rho_s}{\zeta} \exp\left(-\frac{z}{\zeta}\right) \quad (4)$$

$$\phi(z) = -\frac{\rho_s \zeta}{\epsilon} \exp\left(-\frac{z}{\zeta}\right) \quad (5)$$

$$\frac{1}{\zeta} = \frac{R}{2D_e} \left(1 + \sqrt{1 + \frac{4D_e \sigma}{\epsilon R^2}} \right) \doteq \sqrt{\frac{\sigma}{\epsilon D_e}} \quad (6)$$

where D_e is mean value of diffusion coefficient of charges in the solution, R is migration rate of the surface, ρ_e is volume charge density, σ conductivity of the solution, and z is distance from the surface of crystal.

The polarization has an effect on the complex ions included charged growth units and impurities in the very nar-

row region compared with concentrational boundary layer.

2. Effect of spontaneous polarization on the charged solute transportation

Growth units are in thermal motion, and net flux is measured if the fluxes toward the opposite directions lose the balance. From the diffusional equation, the flux density toward one direction may be approximated. Net flux is composed of flows by thermal energy and electrostatic force.

$$\begin{aligned} J &= -D \frac{dN}{dz} - MN_q \frac{d\phi}{dz} \\ &\approx -D \frac{N_2}{\Delta z} + D \frac{N_1}{\Delta z} - MN_q \frac{d\phi}{dz} \\ &= J_T^{2 \rightarrow 1} + T_T^{1 \rightarrow 2} + J_E \end{aligned} \quad (7)$$

where J is net flux density, J_T is flux density by thermal activation, J_E is by the electrostatic force. D is the diffusion coefficient of growth units in the solution, and M is the mobility (=velocity/force). q is mean charge of growth units considered, N is the solute concentration, and Δz is mean distance that solutes can jump at a time.

From the equation (5) and (6),

$$\left. \frac{d\phi}{dz} \right|_{z=0} = -\frac{\rho_s}{\epsilon} \quad (8)$$

$$J_T = \frac{D}{\Delta z} N, \quad J_E = -MN_q \frac{d\phi}{dz} = -\frac{MN_q \rho_s}{\epsilon} \quad (9)$$

In the case that charged growth units move toward the direction of the electrostatic force, the flow contain those not only by thermal motion but also by the electrostatic force, but in the other case only transportation by thermal motion has to be considered.

3. Growth rate difference

LBO crystals are grown in the high temperature solution with excess borates which is so viscous⁷⁾ as transportation of the growth units are restricted, and its {011} planes are microscopically smooth.⁹⁾ Therefore the crystal is able to grow normal to these planes by 2 dimensional nucleation growth mechanism or along the screw dislocations. For general approach, first mechanism was considered.

In this point of view, the growth rate is represented as exponential function of supercooling or driving force.³⁾

$$\begin{aligned} R &\propto \exp\left(-\frac{\Delta G^*}{kT}\right) \\ &= \exp\left(-\frac{\beta}{\Delta T(T_s - \Delta T)}\right) \end{aligned} \quad (10)$$

where ΔG^* is the activation energy for a critical nucleus, T_s is saturation temperature, ΔT is the supercooling ($=T_s - T$), k is Boltzmann's constant, and $\beta (= \Delta G^* \Delta T / k)$ represents a constant.

In the solution, borates exists in the various molecular configuration.⁹⁾ However Li is inclined to be dissociated to Li^+ , borates would form the complex anions, and crystal is consisted of infinite chains of B_3O_7 .^{9,12)} Therefore it is thought

Table 1. The Sites of the Ions^{4,13)} in the LBO Crystal and Electric Polarizations. Two Types of the Surface Structure for (011) Face can be Considered, and on Growing the Crystal, the Surface Structure Would Alternate by Turns

	x	y	z	charge		1/2+x	1/2-y	z	
O	0.161	0.873	0.637	-0.34	O	0.661	-0.373	0.637	-0.34
	0.237	0.591	0.827	-0.2		0.737	-0.091	0.827	-0.2
	0.058	0.797	1.03	-0.13		0.558	-0.297	1.03	-0.13
	0.087	0.505	1.216	-0.23		0.587	-0.005	1.216	-0.23
	-0.115	0.703	1.365	-0.22		0.385	-0.203	1.365	-0.22
B	0.008	0.662	1.205	0.42	B	0.508	-0.162	1.205	0.42
	0.194	0.444	1.001	0.26		0.694	0.056	1.001	0.26
	0.157	0.749	0.826	0.38		0.657	-0.249	0.826	0.38
Li	0.588	0.433	1.065	0.06	Li	1.088	0.067	1.065	0.06
	1/2-x	1/2+y	1/2+z			-x	-y	1/2+z	
O	0.339	1.373	1.137	-0.34	O	-0.161	-0.873	1.137	-0.34
	0.263	1.091	1.327	-0.2		-0.237	-0.591	1.327	-0.2
	0.442	1.297	1.53	-0.13		-0.058	-0.797	1.53	-0.13
	0.413	1.005	1.716	-0.23		-0.087	-0.505	1.716	-0.23
	0.615	1.203	1.865	-0.22		0.115	-0.703	1.865	-0.22
B	0.492	1.162	1.705	0.42	B	-0.008	-0.662	1.705	0.42
	0.306	0.944	1.501	0.26		-0.194	-0.444	1.501	0.26
	0.343	1.249	1.326	0.38		-0.157	-0.749	1.326	0.38
Li	-0.088	0.933	1.565	0.06	Li	-0.588	-0.433	1.565	0.06
P _c	0	-0.126	0.0496	(C/m ²)	P _c	0	0.126	0.0496	(C/m ²)
ρ _S ^A		0.0313		(C/m ²)	ρ _S ^A		-0.113		(C/m ²)

that the transportation and incorporation of borates are more limiting factors than those of Li ions.

In accordance to the previous considerations, the flow of borates toward positively polarized surface is aided by the electrostatic force.

$$J_- = \frac{D}{\Delta z} N$$

$$J_+ = \frac{D}{\Delta z} N \left(1 + \frac{M|q|\rho_S \Delta z}{\epsilon D} \right) \quad (11)$$

where + and - mean the sign of the spontaneous polarization of the crystal.

Equation (10) and (11) are combined to :

$$R \propto \frac{N_n^*}{N_n^0}, R \propto J$$

$$R_- = \alpha \exp\left(-\frac{\beta}{\Delta T(T_S - \Delta T)}\right) \quad (12)$$

$$R_+ = \alpha \left(1 + \frac{M|q|\rho_S^N \Delta z}{\epsilon D} \right) \times \exp\left(-\frac{\beta}{\Delta T(T_S - \Delta T)}\right) \quad (13)$$

where α is a proportional constant.

4. Effects of the temperature gradient and calculation of lengths of grown crystal

In our experiment, we observed the growing aspects along the polar axis using <010> seeds, and considered the radial

temperature distribution. The radial temperature gradient at the center of the crucible is nearly zero but the temperature is relatively high so that the supercooling and the driving force for growth get decreased as the crystal grows. We fitted the temperature distribution as a function in proportion to square of the radial distance from the center.

Therefore the growth rates and lengths of growing crystal is not functions of the temperature but of the growing time. We calculated the values of them with the elapsed time and show the variation in Fig. 5. α , β and other parameters are fitted from the data reported in some references,^{7,9)} and spontaneous polarization and the electric field at the crystal surface are calculated macroscopically.^{4,11,13)} We compared the calculated with experiments. In the early stage after the faceted shapes are constructed, the crystal grows by the 2 dimensional nucleation mechanism in the region without temperature gradient, and the growth rate difference between the opposite directions comes from the flow rate difference due to the interaction of the charged growth units and the polarization of crystal. However 2 dimensional nucleation rate are slowed down to constrain the growth rate normal to in the high temperature region considerably.

IV. Conclusions

It is general that the spontaneous polarization due to the asymmetric configuration of ions in the crystal does not generate the electric field out of the crystal without the changes of the temperature or the pressure. However, the polar crys-

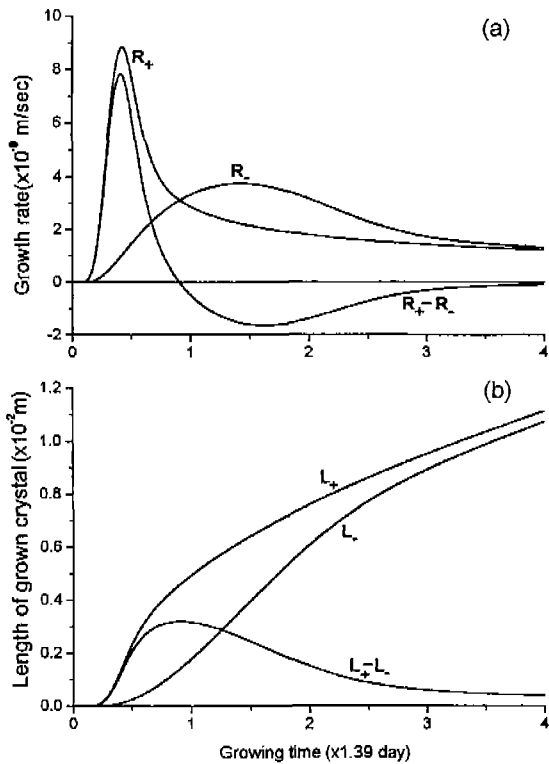


Fig. 5. Calculated growth rates and lengths of grown crystal in the direction normal to the $\{011\}$ faces. (a) The R_{\pm} mean the growth rates in the spontaneously polarized crystal faces signed (\pm), (b) L_{\pm} are the lengths of grown crystal. R_+ is very larger than R_- in the initial stage, but decreases rapidly to get smaller.

tal interact on the growth units in the narrow region, and the growth rate difference is due to this interaction.

It is advantageous using $\langle 001 \rangle$ or $\langle 110 \rangle$ seeds⁹⁾ to obtain a large single crystal and apply to the optical devices with a linear temperature gradient. In this case, there is no decrease of difference between the length of grown crystal due to the temperature gradient, and the seed orientation may be a very important parameter along the polar axis.

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