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The growth striations and ferroelectric domain structures in Czochralski-grown $LiNbO_3$ single crystals

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The rotational striations and power striations are studied in $LiNbO_3$ crystals and one-to-one correspondence between the striations and temperature fluctuations is demonstrated. The ferroelectric domain structures related to the rotational striations and the power striations have been observed. The distribution of solute concentration in rotational striations is measured by means of energy dispersive X-ray analysis in the scanning electron microscope, and it has been concluded that the ferroelectric domain structures depend on the solute concentration gradient.

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1. Introduction

It is commonly observed that there are growth striations in most melt-grown single crystals. In order to obtain a crystal with a high degree of homogeneity it is necessary to eliminate growth striations. On the other hand, striations give a useful built-in record of the interface shape at any point within crystal and thus are widely employed in the study of the microscopic growth rate and the morphology of solid–liquid interfaces [1, 2]. Systematic studies of growth striations in melt-grown single crystals have been conducted in semiconductors [3] and, also, many results have been obtained in oxide crystals.

It has been found that the structure of the ferroelectric domain in $LiNbO_3$ single crystals could be changed by doping the crystal with certain solutes [4, 5]. It has been reported by Rauber [6] and Peuzin and Tasson [7] that $LiNbO_3$ single crystals with periodic ferroelectric domain structures have been produced and used as a very efficient hypersonic transducer, and this kind of crystal has also been used to realize quasi-phase matching of second harmonic generation of light by the authors of this paper [8]. In this paper, an account will be given of our experimental results on the growth striations and ferroelectric domain structure investigations in $LiNbO_3$ single crystal.

2. Experimental methods

We intentionally displace the rotational axis of the growing crystal from the symmetry axis of the temperature field by means of a fine screw to adjust the position of the heater relative to the rotation axis. In so doing, periodic fluctuations of temperature, growth rate and solute concentrations within the crystal are produced during Czochralski growth. The interior rotational striations are compositional variations induced by the growth-rate fluctuations, but the surface rotational striations are directly attributed to variation of the radial component of growth velocity. The spacing of the rotational striations may be changed at will by means of adjusting the ratio of pulling rate to rotation rate. The amplitude of both the temperature fluctuations and growth-rate fluctuations can be changed by means of adjusting the displacement of rotation axis from the symmetry axis of the temperature field.

The proportional integral differential (PID) variables in the automatic diameter control system having been so selected, such that the heating power is periodically fluctuated, and power striations are produced in the growing crystal [9]. The microscopic growth rates in forming the power striations are measured by using the periodic rotational striations as time markers, since the time interval forming any two

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adjacent rotational striations is equal to the rotational period at that time. In this way the transient microscopic growth rate at any point of crystal can be measured, providing the pulling rate and rotation rate are known and are constant over the time between the two striations being measured.

In order to reveal the structures of ferroelectric domains with etching, the $LiNbO_3$ specimens with surfaces parallel to $\{0001\}$ or $\{10\bar{1}0\}$ planes have been prepared. After the determination of crystal orientation, the crystal wafers were prepared by usual methods of cutting, grading and polishing, and then the crystal wafers were immersed in a mixture of 1 part HF and 2 parts HNO_3 (by vol) for 10 min at 100° C and etch patterns showing ferroelectric domain structures were thus obtained.

The distribution of solute concentration in the rotational striations was measured by means of energy dispersive X-ray analysis in the scanning electron microscope (Philips, PSEM-500X).

3. Experimental results

3.1. The rotational striations

When the rotation axis of crystal does not coincide with the symmetry axis of temperature field and the measuring junction of a Pt–10% Rh thermocouple rotating with the growing crystal is put into the meniscus, the temperature signal caused by crystal rotation is passed through a rotational slip-ring to a chart-recorder callibrated to record the temperature. Under such a condition, the temperature fluctuations related to crystal rotation [10] were measured. When the rotational rate is suddenly changed in the course of crystal growth, for example, from 4 to 13 rpm, the resulting temperature fluctuations are shown in Fig. 1a. Fig. 1b shows surface growth striations which correspond to the temperature fluctuations, and surface striations can be observed clearly using a metallographic microscope with oblique illumination. In Fig. 1 it is found that crystal rotational rate, frequency of temperature fluctuations and the number of surface growth striations not only quantitatively agree, but also display the same variation when the rotation rate suddenly changes. We also carried out the following procedure: stop crystal rotation, turn 10 revolutions, stop again, turn 40 revolutions and finally stop the crystal rotation altogether. The result of this procedure is shown in Fig. 2. When the crystal is stopped, the striations are eliminated, and when the crystal

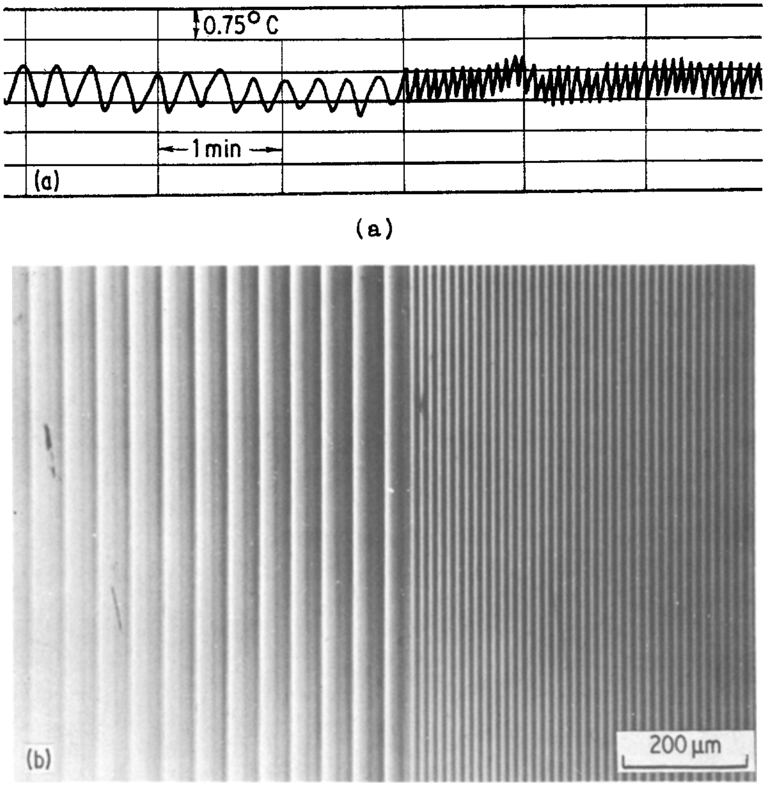

Figure 1 The rotational rate changed suddenly from 4 to 13 rpm. (a) Temperature fluctuation of meniscus and (b) surface growth striations.

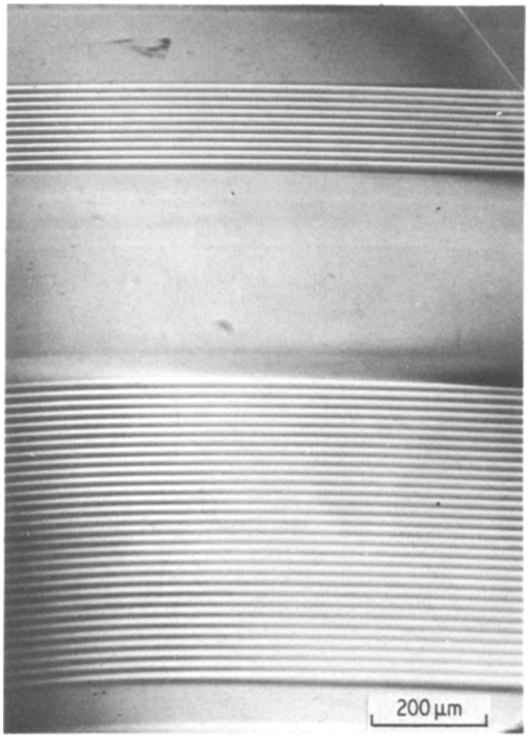

Figure 2 Surface growth striations and crystal revolutions.

begins to rotate, the striations are produced immediately; it can be seen also that the number of striations corresponds completely to the revolutions of crystal. Thus, it is clearly demonstrated that the surface-growth striations are indeed an aspect of the rotational striations themselves.

3.2. The power striations

Adjusting the PID variables in the automatic control system in such manner that the heating power periodically fluctuates, produces power striations such as those shown in Fig. 3a. In order to measure the transient microscopic growth rate during the power-striation formation, we have used periodic rotational striations as time markers, and the variation of transient microscopic growth rate within the power striations has been measured. The result is shown in Fig. 3b. The variation of crystal diameter is shown in Fig. 3c. The relative changes of heating power, indicated by the temperature measured using a Pt–10% Rh thermocouple near the heating element, are shown in Fig. 3d. The relationship between the space co-ordinates and time co-ordinates in Fig. 3 can be established because the pulling rate is a known constant. As shown in Fig. 3, it is clear that the power fluctuations, crystal diameter variations and microscopic growth-rate fluctuations correlate quite well and display the same period. By comparing Fig. 3a to d , the adjusting action in the automatic diameter control system may be inferred, i.e., when the crystal diameter increases (or decreases), the error signal is measured by electric weighting and the signal then triggers a "feed-back" into the input command to increase (or decrease) heating power, so the transient microscopic growth rate decreases (or increases) and thus the increase (or the decrease) of crystal diameter is held down, and the crystal diameter could be kept constant. In general, when power striations formed in the automatic diameter control system, the microscopic growth rate decreases as the diameter increases and vice versa. In the case of the rotational striation formation, the situation is reversed, the microscopic growth rate and crystal diameter both increasing within the half-period of low temperature, and decreasing within the half-period of high temperature.

3.3. Growth striations and ferroelectric domain structure

In $LiNbO_3$ single crystal grown from congruent melt composed of 48.6 mol% Li_2O, we have not observed any evidence showing the influence of temperature fluctuations caused by crystal rotations or power fluctuations on the structures of ferroelectric domains. In $LiNbO_3$ single crystals grown from a stoichiometric melt composed of 50 mol% Li_2O, which is equivalent to doping the congruent melt with 2.72 mol% Li_2O, the corresponding ferroelectric domain structures in the power striation within the crystal have been observed, as shown in Fig. 4. Although there is no apparent variation effect of rotational striations on the ferroelectric domain structures, however, in the region where the diameter of crystal increases and the microscopic growth rate decreases, as shown in Fig. 3, a positive domain appears, shown in Fig. 4a. In the region where the diameter of crystal decreases and the microscopic growth rate increases, it is found that domain bands composed of clusters of fine negative domains appear. It is possible to distinguish between positive and negative domains according to their different rates of etching: the etching rate of negative domains is larger than that of positive domains on the (0 0 0 1) plane.

In the case of a congruent melt doped with

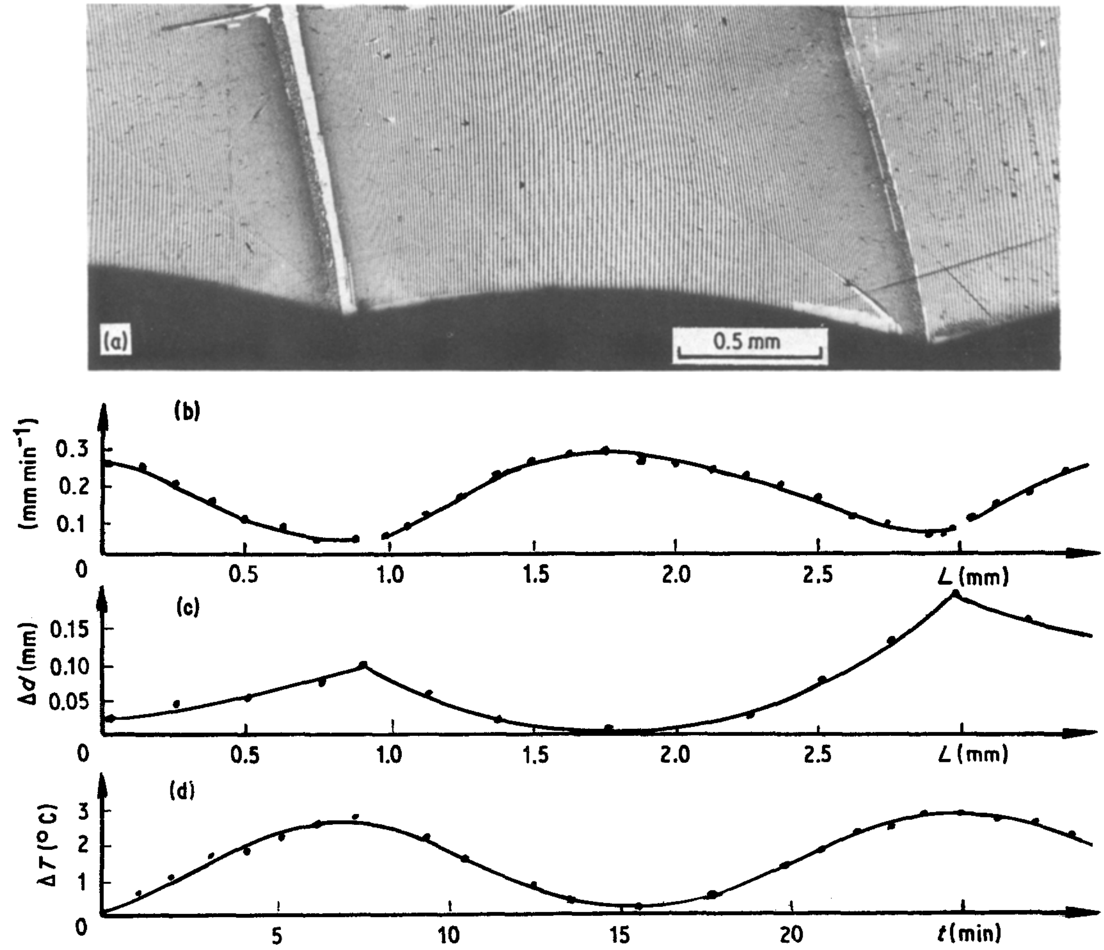

Figure 3 The power striations showing (a) peripheral section of $LiNbO_3$ single crystal, (b) microscopic growth-rate variation of the section depicted in (a), (c) variation of crystal diameter of the section depicted in (a) and (d) relative power fluctuation indicated by the temperature of the heating element.

1 wt% yttrium, the ferroelectric domain structures have been effectively changed such that, within the rotational striations, periodic ferroelectric domain structures have been induced, confirming the results reported by Peuzin and Tasson [7]. The one-to-one correspondence between the rotational striations and the ferroelectric domain structures have been demonstrated with the following procedure: stop crystal rotation, turn 10 revolutions and stop crystal rotation again; the result is shown in Fig. 5. Fig. 5a shows the surface striations and Fig. 5b shows the interior domain structures. Evidently, the surface striations and interior domain structures correspond to each other and to the crystal revolutions. The morphology of the surface striations and interior domain structure having been carefully studied, the surface striation is found to be a spiral winding of 10 turns and the interior periodic laminar domain structure is strictly not composed of parallel lamellae one above the other; rather it is a single lamella in the form of helicoid, or spiral ramp. So Fig. 5a is a cross-section pattern of the helicoid and the end of the helicoid can be clearly seen at the lower left corner in Fig. 5b. Although both the power striations and the rotational striations can change the interior domain structures, the negative region in power striations is a band composed of clusters of fine negative island-like domains (see Fig. 4) and a single lamella negative domain in rotational striation (Fig. 5b). The above observations show that the gradient of yttrium concentration can change the ferroelectric domain structure more efficiently than can that of lithium concentration. Perhaps it is because the concentration gradient in rotational striations is larger than that in power striations as

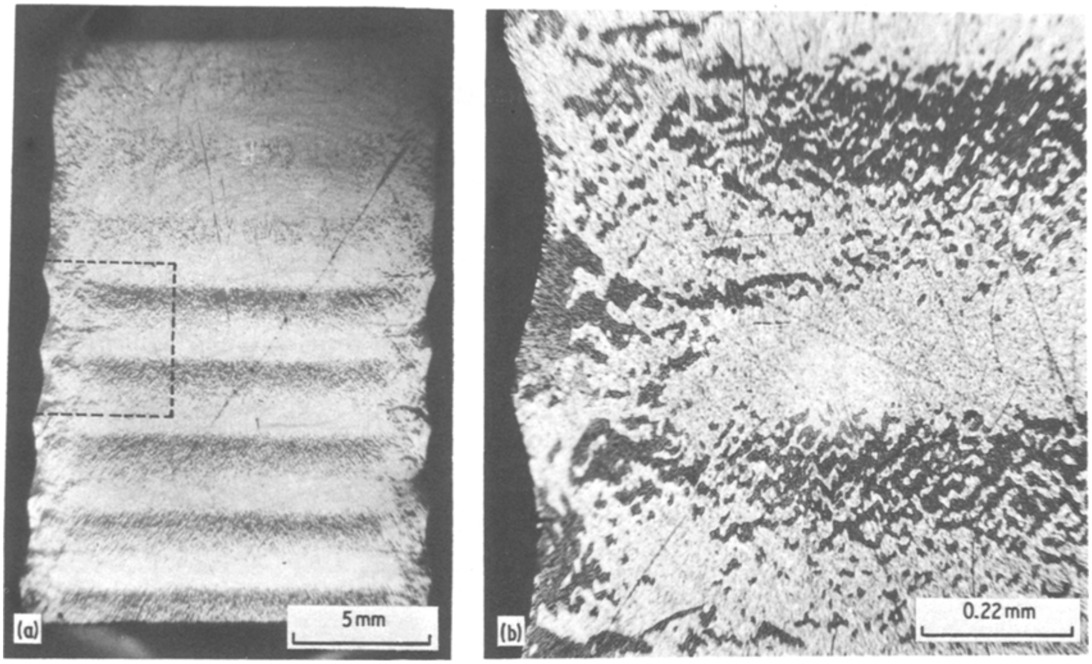

Figure 4 The power striations and ferroelectric domain structures. The area outlined with a broken line in (a) is shown at higher magnification in (b).

the period of the rotational striation is shorter and the valence of the yttrium ion is larger than that of the lithium ion.

In order to unravel the relationship between solute concentration distribution and the ferroelectric domain structures, we have used energy dispersive X-ray analysis in the scanning electron microscope to measure the solute concentration distribution in the rotational striations and to study the relationship between the solute distribution and the domain structures. The intensity of the $L\alpha$ spectral line of yttrium has been measured, at distances, d, point by point, along a line normal to the domain boundaries and it has been found to be proportional to the mean solute concentration of a selected region. The diameter of the selected region being measured is 0.125 μm. The result is shown in Fig. 6, in which the curve represents the distribution of yttrium concentration and the shaded area represents the positive domain. Domain boundaries are found near the maxima and minima of the curve and, in the positive domain area, the concentration decreases and its gradient is negative; in the negative domain area, however, the concentration increases and its gradient is positive. This directly confirms that the gradient of the solute concentrations determines the structures of the ferroelectric domains, which

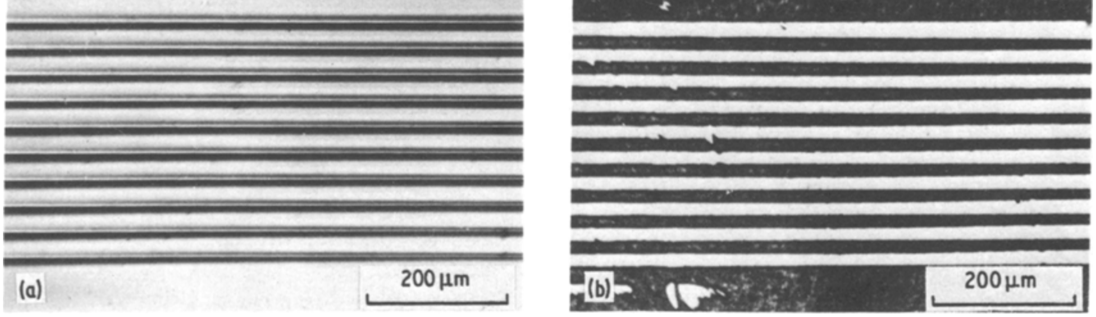

Figure 5 The rotational striations and ferroelectric domain structures. (a) Surface rotational striations and (b) interior ferroelectric domain structures.

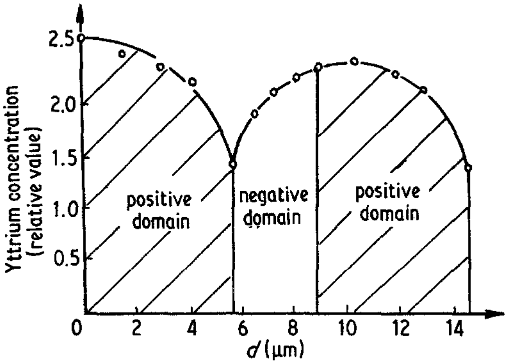

Figure 6 The yttrium concentration distribution and ferroelectric domain structures in rotational striations measured at distances, d, point by point, along a line normal to the domain boundaries.

conforms with the conclusion of Tasson *et al.* [11, 12]. It is worth noting that there are two types of sign inversion of concentration gradient, i.e., at the minima the change of gradient takes place abruptly; at the maxima, the change of gradient takes place gradually. The difference is also shown in the morphology of the domain boundaries observed with the scanning electron microscope (see Fig. 7). An abrupt change of concentration gradient corresponds to a smooth boundary in Fig. 7, while a gradual change of concentration gradient corresponds to a rough boundary in Fig. 7, while a gradual change of concentration gradient corresponds to a rough boundary in Fig. 7. This effect on domain boundary morphology have also been displayed in the power striations, shown in Fig. 4. There are also two kinds of boundaries of the domain bands composed of clusters of fine negative domains, the diffuse boundaries at the maxima of solute concentration distribution, and the sharp boundaries at its minima.

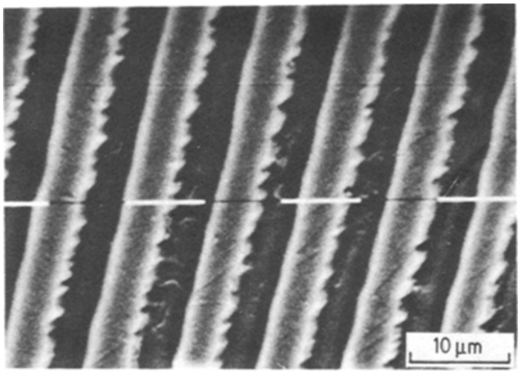

Figure 7 Morphology of ferroelectric domain boundaries.

4. Discussion

4.1. The production of $LiNbO_3$ single crystal with periodic laminar domain structures

We have established the correspondence between temperature fluctuations, growth-rate fluctuations, solute concentration fluctuations and the ferroelectric domain structure, and reached the conclusion that the ferroelectric domain structures are determined by the gradient of the solute concentration. Therefore, if it is desired to change the domain structure in ferroelectrics, besides varying the applied electric field, we can also use the inhomogeneous solute concentration distribution in the crystal. We have already intentionally produced a crystal with rotational striations and obtained a periodic concentration distribution in the crystal, producing $LiNbO_3$ single crystals with periodic laminar domain structure. The layer thickness of laminar domain structures can be adjusted by changing the ratio of pulling rate to rotation rate.

4.2. The solute distribution in rotational striation

The measured solute (Y) distribution (Fig. 6) in the rotational striation of the $LiNbO_3$ single crystal resembles the curve of antimony concentration in the rotational striation of silicon crystal measured by Muargai *et al.* [13], and also similar to the theoretical curve obtained recently by Wilson [14] in the improved version of the Burton–Prim–Slichter theory [15]. It should be noticed that the temperature fluctuation with sinusoidal form caused by the crystal rotation has been measured under our experimental condition [10], but the solute distribution resulting from this form of the temperature fluctuation, deviates from the sinusoidal form as shown in Fig. 6. This phenomenon can be explained as follows. In general, assuming the growth kinetics of a non-facetted interface is linear, the sinusoidal temperature fluctuation will cause a sinusoidal growth rate fluctuation; as a result, a thicker layer of crystal is grown within the half-period of the growth rate larger than the average rate and a thinner layer of crystal is grown within the half-period of growth rate smaller than the average rate. Therefore, the solute distribution in the crystal (space distribution) is distorted from a sine curve. Using the measured value of the average growth rate, the period of rotation and the amplitude of the growth-rate

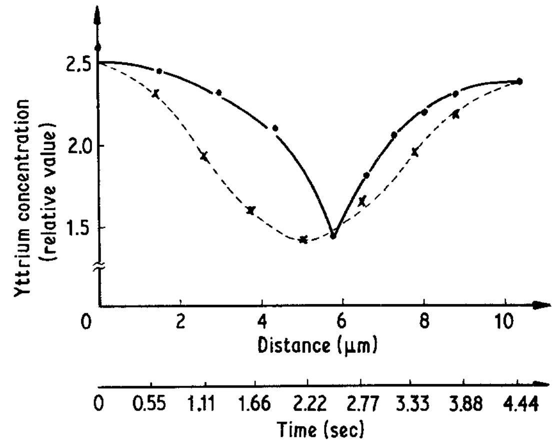

Figure 8 Solute distribution plotted against distance (dotted line) and time (solid line).

fluctuation, the space solute distribution against distance relation (solid line in Fig. 8) can be transformed into a space solute distribution against time plot (dotted line in Fig. 8). Obviously, the solute distribution against time plot is approximately a sine curve. So far it has been assumed that the validity of the theory of segregation is based on the assumption that the growth interface is at equilibrium, and so the solute concentration of solidifying crystal, C_s, is given by

$$C_s = kC_L, \tag{1}$$

where k is the equilibrium segregation coefficient and C_L is the concentration of the bulk liquid. Consequently, the dotted curve in Fig. 8 also represents a plot of the variation of solute concentration of liquid at the growth interface against time, caused by crystal rotation, which roughly agrees with the theoretical curve estimated by Wilson [14].

4.3. The mechanism of polarization and the non-uniform distribution of solute

The fact that the non-uniform distribution of solutes can change the ferroelectric domain structures may be explained as follows. The solutes in a crystal are generally ionized but not completely shielded, especially when the temperature is decreasing and passing through the ferroelectric phase transition; thus, the non-uniform solute distribution is equivalent to the non-uniform space-charge distribution in the crystal and a non-uniform internal field is produced in it. Although the field is comparatively small, it can induce the ions of lithium and niobium within the lattice to displace preferentially at a temperature close to the Curie point. If we express the solute distribution, related to the periodic rotational striation shown in Fig. 6, as an approximate sine function, the internal field within the crystal can be derived as the same function with a phase difference of $\pi/2$. Thus, it can be clearly seen that the domain structures and the solute distribution have the same period and it is the gradient of the solute concentration which determines the domain structure.

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