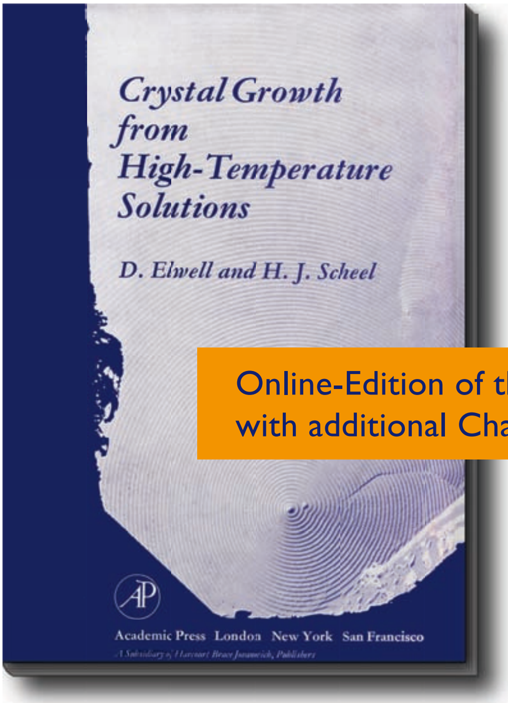

Online-Edition of the original book
with additional Chapter 11 and Appendices A and B

Part 015

Appendix A

Growth of striation-free crystals (see also sections 7.1.3 and 9.2.4)

Striations, or growth bands, have long been regarded as an intrinsic or unavoidable problem of crystal growth. Some otherwise promising materials could not be developed for non-linear optic or electro-optic applications (Scheel and Guenter 1985) or as substrates for optoelectronic devices based on III-V semiconductors (Nakajima 1992) because of the problems of eliminating striations. Numerous other applications of solid solutions could be listed where the lack of homogeneity has hindered their usefulness.

Striations are defined as growth-induced inhomogeneities in the crystal which are aligned along the growth surface, or in the case of faceted growth are related to the traces of macrosteps. These often periodic inhomogeneities are caused by growth rates which fluctuate with time or by lateral growth rate differences along the growth interface, as shown in Fig. A.1.

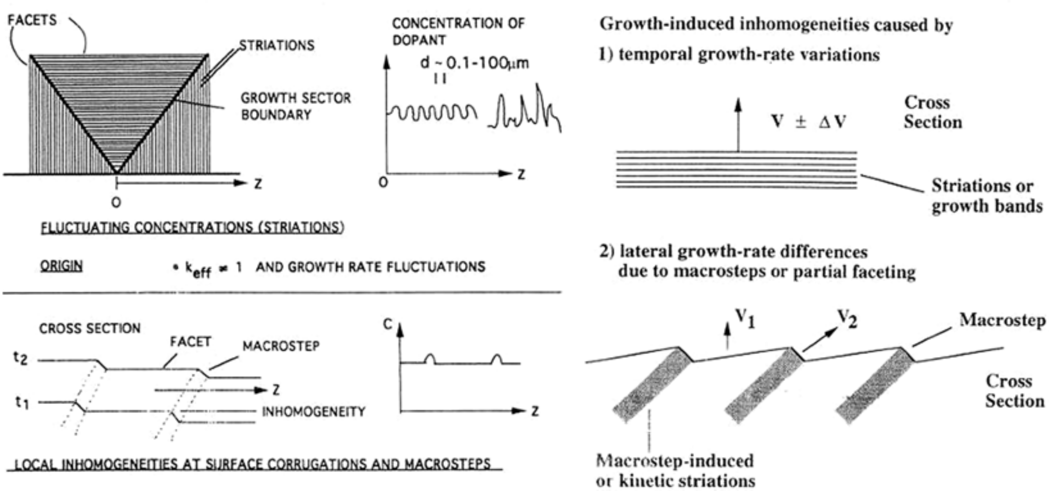

Fig. A1. (a) Striations due to growth rate fluctuations in the growth direction. (b) Striations due to fluctuations in macrostep flow across the growth surface.

The striations due to lateral growth-rate differences can be eliminated in the majority of cases by control of the interface shape, either by adjusting a continuous curvature or by a flat interface achieved by a transition to faceting (see Scheel 1980 and Chernov and Scheel 1995). The key is to prevent macrostep formation and lateral growth rate differences.

A third cause of striations was described by Landau (1958), who showed that for conditions close to the maximum stable growth rate, an oscillation of the growth rate may occur by alternating build-up and capture of impurities at the interface. This leads to inclusion bands or to striations parallel to the growth interface.

Here we suggest that the term "striation-free" be used for crystals in which periodic inhomogeneities cannot be detected by analytical techniques, and in which any residual trace inhomogeneities are not harmful for the specific application. Absolutely striation-free crystals may be difficult to achieve and verify.

In this Appendix we discuss the origin of "thermal striations" due to temporal growth rate fluctuations, and their relation to the temperature distribution and hydrodynamic conditions within the growth system. The critical parameters in designing growth processes for striation-free crystals will be discussed and demonstrated with respect to$KTa_{1-x}Nb_xO_3$ (KTN) solid solutions.

The concentrations of the components of a solid solution generally differ from those of the liquid from which they are grown, a phenomenon known as segregation. In equilibrium or at very slow growth rates the ratio of the concentration of a component A in the solid to that in the liquid is defined as the equilibrium (or phase diagram) segregation coefficient k_0. Thus

$$k_0(A) = n_s\,(A) \,/\, n_L\,(A) \qquad \text{(A1)}$$

where the n's are concentrations of A in the solid and liquid phase respectively. Under practical growth conditions segregation is described by an effective segregation coefficient

$$k_{eff} = k_0 \,/\, [k_0 + (1 - k_0)\exp - (v\delta \,/\, D)] \qquad \text{(A2)}$$

with the growth rate v, diffusion boundary layer thickness δ, and D the diffusion coefficient. This approximation was derived by Burton, Prim and Slichter (1953) for the case of Cochran (or Ekman) flow towards a crystallizing rotating disc for the case where the growth process is dominated by a diffusion boundary layer.

For growth of mixed crystals from dilute solutions, van Erk (1982) has derived the effective segregation coefficient for diffusion-limited growth by

$$ln\, k_{eff} = ln\, k_0 - (\, k_{eff} - 1\,)\,(\, v\delta \,/\, D). \qquad \text{(A3)}$$

Plotted solutions using eqs. A2 and A3 are similar, but the sensitivity to fluctuations in the growth parameters is different (Scheel and Swendsen 2001).

Growth from solution is normally limited by volume diffusion, and the relatively fast interface kinetics can be neglected. Following the diffusion boundary layer concept of Nernst (1904), the growth rate can be expressed by

$$v = D\,(n - n_e)/\rho_c\,\delta. \qquad \text{(A4)}$$

Here n and n_e are the equilibrium and effective bulk concentrations of the solute in the solution, and the solute has the density ρ_c. The time constant for the effects of temperature fluctuations (and those of n_e and v) is on the order of seconds, while that for the effect of hydrodynamic fluctuations on δ and v is on the order of minutes. In steady-state crystal growth, within a given time and temperature range, D and k_0 in eqs. A2 and A3 change only slowly, and can be taken to be constants. Therefore changes in the effective segregation coefficient k_{eff} are essentially determined by the product (vδ). This product is approximately constant due to the inverse relation between v and δ of eq. A4. This means that hydrodynamic changes which lead to changes in δ are compensated by growth rate changes. On the other hand, growth rate changes caused by temperature changes are not compensated, and so lead to changes in k_{eff} and to striations.

For the growth of homogeneous crystals free from striations, it follows from the above discussion that temperature gradients should be minimized (less than about 1 degree/cm) and temperature fluctuations suppressed to less than about 0.01°C. These requirements must be reconciled with the requirement that the growing crystal must be cooled in order to control nucleation and to remove the latent heat due to the desirable high growth rates.

The application of forced convection is recommended for efficient crystal growth. Stirring may be achieved by continuous flow along the growth surface, by Ekman flow towards the rotating growth surface, by periodic changes as in reciprocating stirring in growth from aqueous solutions, or by accelerated crucible rotation as stressed in various chapters of this book. Forced convection within a specific range of Reynolds numbers assists with homogenization of the solution with respect to temperature and concentration. Stirring is also beneficial in reducing the thickness of the diffusion boundary layer and so increasing the maximum stable growth rate, as discussed in Ch. 6. It may also be noted that periodic hydrodynamic fluctuations, as in ACRT in the presence of large temperature gradients can be utilized to induce regular striations, forming a superlattice which may be suitable for specific applications. Reduced convection and convection-free growth systems have been proposed as a remedy against striations, but should be applied only if large temperature gradients cannot be avoided.

The occurrence of striations was for long regarded as an unavoidable or "intrinsic" problem of crystal growth, as expressed for example by Byer (1974), Räuber (1978) and Reiche et al (1980). The foregoing discussion has shown that the striation problem can be solved in principle if temperature fluctuations at the growth interface are minimized, and preferably when forced convection is applied. This will be demonstrated with a practical example.

The solid solution system $KTa_{1-x}Nb_xO_3$ (KTN) is of interest on account of its very large electro-optic coefficient which can be optimized for specific application temperatures by the choice of x. The composition with x=0.35 is used for room temperature applications, because the ferroelectric transition temperature is then 10°C and the very large dielectric constant and electro-optic coefficient are observed just above this transition. However the inhomogeneity in refractive index should be less than 10^{-6} for optical applications, requiring that the crystals be striation-free to this level. From the phase diagram $KTaO_3$-$KNbO_3$ (Reisman

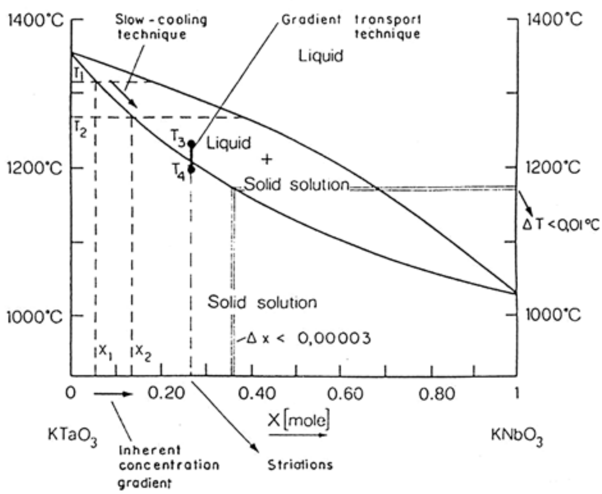

Fig. A.2. Phase diagram for KTaO3-KNbO3 (after Reisman et al 1955).

et al 1955) shown in Fig. A.2, the temperature fluctuations at the growth interface should be less than 0.01°C. This condition cannot be achieved in growth by gradient transport combined with top-seeding (TSSG- see Ch. 7) which was the most popular method reported in the review of Rytz and Scheel (1982). In this technique the solute material is dissolved in the hotter zone of the solution and transported by free convection to a cooler zone where the growing crystal is located. This method allows a constant concentration to be achieved, but always with striations caused by temperature fluctuations as shown in the example of Fig. 7.23.

A simple approach to minimize temperature fluctuations at the growth interface, by a homogenized and nearly isothermal solution, is the slow-cooling technique. This results in an *inherent concentration gradient* within the crystal, with a higher Ta concentration at the onset of growth, slowly reducing as growth proceeds, following the solidus line of Fig. A.2. However this inherent variation can be reduced by the use of a solution volume which is large compared with that of the crystal. Fig. A.3 shows a nomogram derived by Rytz and Scheel (1982) which gives the relationship between the inhomogeneity $x_1 - x_2$ of a crystal and the solution volume V, solution mass M, and the cooling interval $T_1 - T_2$ for KTN in the concentration range 0x0.04. For example, with M=1000 kg (requiring a platinum crucible of 300 to 500 cm^3) and $T_1 - T_2 = 20°C$, the crystal grown is of 1.6 cm^3 in size and has inhomogeneity $\Delta x = 0.033$. For KTN crystals with x=0.35, the mass of melt must be doubled because of the smaller slope of the solidus line.

The first experiments to grow striation-free crystals of KTN solid solutions were reported by Rytz and Scheel (1982) and by Scheel and Sommerauer (1983). A Pt-6%Rh vs. Pt-30%Rh thermopile (see Section 7.2.2) allowed temperature control with a precision of 0.03°C at temperatures around 1300°C. Nucleation control was achieved by localized cooling and the solution was stirred by the accelerated crucible rotation technique described in Section 7.2.7. KTN crystals

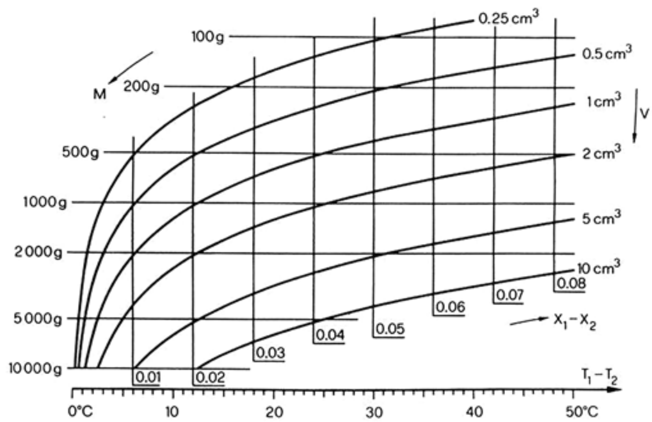

Fig. A.3. Nomogram for estimation of inhomogeneity in KTN crystals grown by slow cooling (Rytz and Scheel 1982).

with x ≈ 0.26 and up to 33x33x15 mm^3 in size, weighing 131g, were grown under optimized conditions by slow cooling (KTN3- see Fig. A.4) and by slow cooling with minimized thermal gradient (F 556 AII). The first crystal showed faint striations in crossed polarizers and a small, statistically significant variation in Nb and Ta concentration as measured by electron microprobe. The crystal grown by slow cooling under optimized conditions had no striations visible in a polarizing microscope, although very faint striations could be revealed using very sensitive methods (Scheel and Guenter 1985).

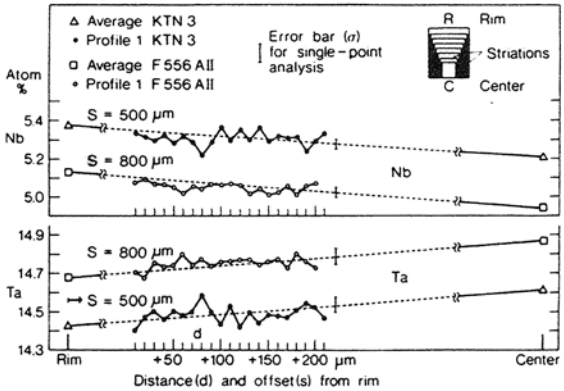

Fig. A.4. Electron microprobe analyses of KTN crystals with x=0.26 grown by slow cooling in a small temperature gradient (sample KTN3) and by slow cooling in a minimized thermal gradient (sample F 556 AII) (Scheel and Sommerauer 1983).

In growth of solid-solution crystals from solutions exists an additional degree of freedom, since the effective distribution coefficient is dependent on the solvent and the solute-solvent interactions. Different solvents may have distribution coefficients $k<1$ and $k>1$, so that by proper mixing a composite solvent with $k=1$ may be found. In the growth of oxide solid solutions of garnet and perovskite structure, homogeneous and striation-free crystals could be obtained by this solvent-mixing approach (Scheel and Swendsen 2001).

Striations can no longer be considered an intrinsic problem of crystal growth, since the methods described above allow their elimination. For growth of homogeneous crystals of doped materials and solid solutions it is recommended to analyze the specific case theoretically and then to try to establish the appropriate experimental conditions. This approach should permit, for example, the economic growth of other solid solution crystals for optical applications and of III-V mixed crystal substrates for optoelectronics..

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