# Evaluation of experimental parameters for growth of homogeneous solid solutions ☆

## Hans J. Scheel[a],*, Robert H. Swendsen[b]

[a] Cristallogenèse-IMO, Swiss Federal Institute of Technology, Chemin de Bellerive 34, CH-1007 Lausanne, Switzerland
[b] Physics Department, Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA

## Abstract

In this paper, we discuss the experimental conditions required to grow large two-component crystals from homogeneous solid solutions. Building on the work of Burton, Prim, and Slichter and that of Van Erk, we are able to establish that the concentration fluctuations for diffusion-limited growth are rather insensitive to hydrodynamic fluctuations. This enables a crystal grower to take advantage of forced convection to optimize growth rates without aggravating the striation problem. © 2001 Published by Elsevier Science B.V.

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## 1. Introduction

Mixed crystals or solid solutions are special cases of alloys in which two or more types of atoms or molecules occupy a given type of lattice site in a coherent crystallographic phase.

Solid solutions are playing an increasingly large role in research and technology, both for intrinsic advantages and because they allow physical, chemical, and electrical properties to be optimized for specific purposes by varying the concentration $x$. Some typical examples are

(a) In semiconductors for optoelectronic applications the bandgap can be tuned for the required emission or absorption wavelengths or for optimized mobility, as well as adjusting the lattice constant to match the available substrate material for epitaxial growth. For example, the solid-solution system $Ga_{1-x}In_xAs_{1-y}P_y$ (for injection lasers and detectors in optical communication systems [1]) enables the frequency to be matched to the low-loss windows of glass fibers at 1.3 and 1.55 μm.

(b) Improvement of the resistance of solar cells to radiation and thermal damage has also been demonstrated, based on solid solutions of III–V compounds. This allows up to 1000-fold concentration of the sunlight compared with the low-cost silicon solar cell [2].

(c) In certain cases, specific effects may be obtained in solid solutions, which are not observed in the constituents. The very high dielectric constants near phase transitions can be used for electrooptic, non-linear optic and acoustooptic applications by adjusting $T_c$ to match the temperature at which it is to be used (usually room temperature). In the system $KTa_{1-x}Nb_xO_3$, this can be achieved with $x < 0.35$ for a phase transition slightly below room temperature [3–5].

(d) Solid solutions also exhibit a hardening effect, which can improve the mechanical properties with single-phase material [6].

For these and other applications, the availability of high-quality crystals or crystalline layers of solid solutions is essential. For certain applications (e.g., optical cases (c) above), the requirements on the homogeneity are extreme, whereas for most applications small concentration variations in the crystals are not as critical. Naturally, methods for growing such crystals must deal with all the usual problems encountered in the growth of pure crystals: structural inhomogeneities (such as grain boundaries, domains, dislocations, strain), vacancies, and interstitial defects. However, the production of bulk crystals of solid solutions is considerably more difficult than the production of pure crystals, owing to the necessity of controlling the compositional homogeneity by the growth process itself. In particular, there are two types of compositional inhomogeneity problems that will be dealt with in this paper.

● Bulk concentration gradients produce a variation of the important properties along the growth direction and should be avoided, since their presence restricts the size of useful material that can be obtained. The tolerated limit depends on the material and the application. For example, in $KTa_{1-x}Nb_xO_3$ (KTN), $x$ should be constant within 50 ppm [3] for electrooptic and non-linear-optic applications.

● There is a strong tendency for fluctuations in the growth conditions to produce a fluctuating concentration along the growth direction, known as growth bands or *striations*. The suppression of

striations represents an old problem in crystal-growth technology, and several authors have described striations as an "inherent", "intrinsic" or "unavoidable" phenomenon in crystal growth [7], which has prevented the technological application of otherwise interesting materials [8,9].

The microscopic distribution of the components and the degree of short-range order will not be considered here.

The characterization of solid solutions in terms of the homogeneity requirements presents formidable problems. The macroscopic variation of the composition across the crystal is relatively easily detected with chemical and physical characterization methods (see Chapter 9 of Ref. [10]). The quantitative evaluation of fluctuating composition and the analysis of both periodic and irregular striations is considerably more difficult, especially when the characteristic width is less than $10 \, \mu m$ and the concentration, or the concentration variation, below 1% (Chapter 9 of Ref. [10]).

In this paper, we discuss the experimental conditions required to grow large two-component crystals of homogeneous solid solutions. In the absence of a general theory for the growth of mixed crystals from all types of solutions or melts, we have considered the situation for the extreme limits growth from melts and from dilute solutions, for which previous authors have discussed certain features of the problem.

We base the analysis of growth from melt on the classic work of Burton, Prim and Slichter (BPS) [11], which attributes the major effect of the growth rate on the distribution coefficient to the transport processes in the melt. Van Erk (VE) [12] published an extensive discussion on the segregation effects in the growth of solid solutions from simple dilute solutions. The BPS and VE analyses have been used to evaluate the experimental parameters for the growth of solid-solution crystals of good homogeneity. Since the results for both limiting cases are qualitatively identical and even remarkably similar quantitatively, there is reason to believe that our conclusions have rather general validity.

After a discussion of the theory of segregation phenomena in Section 2, we establish the

requirements for achieving homogeneous solid solutions. The sensitivity of the concentration fluctuations to fluctuations in the growth parameters is derived on the basis of the work of BPS and VE. As has been known for some time, we show that it is essential for the temperature fluctuations to be minimized to reduce striations. However, we also establish that the concentration fluctuations for diffusion-limited growth are rather insensitive to hydrodynamic fluctuations. This enables the crystal grower to make use of the advantage of forced convection, in contrast to the widespread opinion that convection should be minimized to reduce the striation problem.

In Section 3, the problems of achieving uniform solid solutions by growth from melt are discussed. In Section 4, the steady-state, near-equilibrium approach is described, and in Section 5 the possibilities and advantages of optimizing the solvent composition in growth from solution is discussed.

## 2. Theory of segregation phenomena

The concentration of mixed-crystal components is generally different from those of the fluid from which they are grown, a phenomenon known as segregation. For very slow growth, this is usually described by the equilibrium segregation (or distribution) coefficient $k_0$, which is defined as the ratio of the concentration of a component A in the solid to that in the liquid

$$k(A)_0 = C(A)_S / C(A)_L \qquad (1)$$

and may be derived from the equilibrium phase diagram by the ratio of solidus and liquidus concentrations of A at a given temperature. More generally, segregation depends on the growth rate in an important way and is described by an effective distribution coefficient, $k_{eff}$, which will be discussed later.

Segregation at the crystallizing interface leads to a continuous change of the composition of the fluid: $C(A)_L$ increases for $k_{eff} < 1$, and $C(A)_L$ decreases for $k_{eff} > 1$, so that the concentration $C(A)_S$ in the growing crystal continuously changes. The inherent concentration gradient (ICG) at any location of the growth front is given by

$$C(A) = k_{eff} C_0 (1 - g)^{k_{eff} - 1}, \qquad (2)$$

where $g$ is the fraction of crystallized material and $C_0$ the initial concentration as derived by Pfann [13,14], where it has been assumed that $k_{eff}$ does not change with concentration changes or other growth parameters.

Obviously, the inherent concentration gradient can be made zero by keeping the fluid concentration constant. This is possible by growth at constant temperature in combination with transport of the crystal constituents in a temperature gradient (see Ref. [10, Chapter 7]). However, this method generally involves large temperature gradients, which in turn lead to temperature fluctuations that almost inevitably produce striations.

If slow-cooling is required for other reasons, a large ratio of fluid to crystal might be sufficient to keep the ICG within acceptable limits, which has been discussed in more detail elsewhere [15]. Under the assumption that the growth process is dominated by a diffusion layer, $\delta$, beyond which stirring in the bulk of the fluid assures a uniform bulk concentration, BPS derived the equation

$$k_{eff} = k_0 / (k_0 + (1 - k_0)e^{-\Delta}), \qquad (3)$$

where

$$\Delta = v\delta / D \qquad (4)$$

with $v$ representing the growth velocity, and $D$ the diffusion constant. Eq. (3) is plotted in Fig. 1 for various values of the equilibrium distribution coefficient, $k_0$.

Another possible representation of the BPS equation arises from rewriting Eq. (3) as

$$e^{-\Delta} = (k_{eff}^{-1} - 1)/(k_0^{-1} - 1). \qquad (5)$$

This way of writing the BPS equation allows all values of $k_0$ and $\Delta$ to be represented by a single exponential curve.

In Fig. 1, we have chosen to use a linear plot, rather than following the logarithmic representation in the original BPS paper, because we believe it gives a clearer picture of the physical consequences. The logarithmic plot makes it appear as if fluctuations in the growth parameters have no effect on the distribution coefficient for small
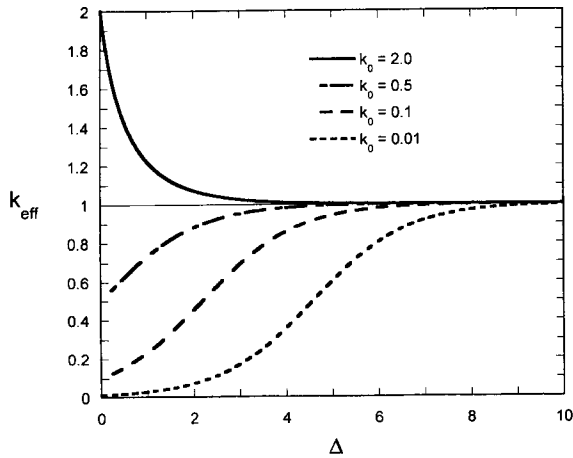
Fig. 1. Effective distribution coefficient as a function of $\Delta$ from the Burton–Prim–Slichter theory for melt growth (Eq. (3)).

growth rates. If this were true, slow growth could be used to produce uniform crystals, without the necessity of carefully controlling the growth parameters. Unfortunately, this is not the case.

From the BPS analysis, it is clear that a given concentration in the solid solution can be obtained in different ways by varying the concentration in the liquid and the effective distribution constant in such a way that

$$C_S = k_{eff}C_\ell, \tag{6}$$

where $C_\ell$ is the concentration in the bulk liquid.

The fluctuations in the grown crystal are then related to the fluctuations in the effective distribution coefficient by

$$\delta C_S / C_S = \delta k_{eff} / k_{eff}. \tag{7}$$

Since the BPS equation gives the derivative of $k_{eff}$ with respect to $\Delta$ as

$$\frac{\partial k_{eff}}{\partial \Delta} = k_{eff}(1 - k_{eff}) \tag{8}$$

we see that fluctuations in $\Delta$ give rise to fluctuations in the concentration in the solid as

$$\delta C_S = C_S(1 - k_{eff})\delta\Delta. \tag{9}$$

Since the accuracy to which $k_{eff}$ can be kept constant usually depends weakly on the magnitude of $\Delta$ for a given growth technique and apparatus, Eq. (9) predicts that the effects described by the

BPS equation are *most* sensitive to fluctuations in the crystal-growth parameters for *small k* values. This is just opposite of what one might expect by looking at a logarithmic plot of the BPS equation.

To investigate the extent to which these qualitative features are more generally valid, we have considered the opposite extreme of growth from a dilute solution. Since Van Erk [12] has presented an excellent analysis of growth of a mixed crystal from an ideal dilute solution, we need only discuss the consequence of the equations he has derived.

The analysis by Van Erk shows the effect of many possible variations in material and growth parameters. To clarify the discussion, we shall make a number of simplifying assumptions and refer the reader to Van Erk's paper for a more complete analysis.

We shall consider the case of strong dilution for a system in which the diffusion and the rate constants of the two components are essentially equal. This corresponds to what Van Erk denotes as case (a). If we make the further assumption that the growth process is predominantly diffusion limited, so that the Nusselt number is large, we can rewrite Eqs. (61) and (62) in Van Erk's paper [12] in terms of the same parameter $\Delta$ [see Eq. (4)] that enters the BPS equations:

$$\ln k_{eff} = \ln k_0 - (k_{eff} - 1)\Delta. \tag{10}$$

Solutions of this equation are plotted in Fig. 2. Although Eq. (10) looks very different from the BPS Eq. (3), it is clear from a comparison with Fig. 1 that their solutions are quite similar. For small values of the growth rate (small $\Delta$), they even agree numerically. As the growth rate is increased, they both approach $k = 1$, although Eq. (10) for solution growth does so more slowly.

It is straightforward to repeat the analysis of the sensitivity of the final concentration in the solid to fluctuations in the growth parameters through $\Delta$ for dilute-solution growth. The result is

$$\delta C_S = C_S(1 - k_{eff})(1 + \Delta k_{eff})^{-1}\delta\Delta. \tag{11}$$

Eq. (11) is remarkably similar to the corresponding Eq. (9) for the BPS analysis. Again, it decreases monotonically as $k$ goes to unity, but
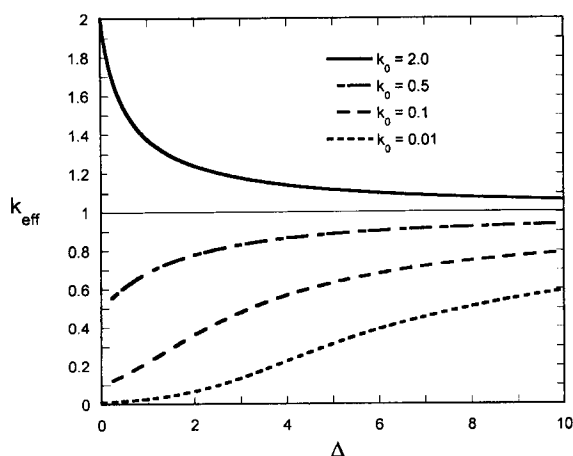
Fig. 2. Effective distribution coefficient as a function of $\Delta$ from the Van Erk theory for simple dilute solution growth (Eq. (10)).

the sensitivity is further decreased by the factor $1/(1 + \Delta k_{eff})$.

It is necessary to note that the violation of assumptions we have made above in considering Van Erk's case (a) might have important consequences. As Van Erk has shown, it is possible to have fewer symmetric parameters than we have assumed and still produce $k = 1$ for a particular growth rate. If this were the case, the conclusion that the concentration in the solid becomes insensitive to fluctuations in the growth parameters when $k = 1$ would no longer be completely true. We refer the reader to Van Erk's work [12] for details.

It is clear from Eqs. (3) and (11) that $k_{eff}$ depends essentially on the product $(v\delta)$ since $k_0$ and $D$ can be taken as constant within a given time or temperature interval of the growth process. This relation is also shown in Fig. 1 where the BPS equation is plotted for various $k_0$ values, and where typical parameters for crystal growth from melts and from solutions are given.

Thus, the first consequence is that experimentally one has to achieve *steady-state conditions*. Hydrodynamic oscillations can be suppressed by proper geometry, small temperature gradients, and control of the hydrodynamic flows by either forced convection ($\delta \Rightarrow 0$), or by pure diffusion, suppression of convection ($\delta \Rightarrow \infty$). The temperature

must be regulated very carefully to suppress growth-rate fluctuations.

## 3. Steady-state growth from melts

A large and important fraction of bulk crystals is grown by solidification from melts. These processes occur far from equilibrium with high crystallization rates (1–10 cm/h), large temperature gradients at the fluid crystal interface (50–500°C/cm), and by non-equilibrium interface shapes ("boules" with little or no facets).

Under these conditions, growth-rate fluctuations are induced by temperature oscillations coupled to oscillatory convection [16]. Witt and Gatos [17], Witt et al., [18] and others have shown by time markers and etching studies that significant differences between the microscopic (instantaneous) and macroscopic (average) growth rates occur in Czochralski growth of semiconductors. The resultant striations may or may not be correlated with the crystal rotation rate (rotational striations), and Carruthers and Nassau [19] have demonstrated various complex convection patterns due to interference between forced and natural convection.

Since the temperature fluctuations at the growth interface were related to convective instabilities [16], most efforts were devoted to suppressing all convection. Buoyancy-driven convection was reduced by baffles [20], shallow melts [16], convection-free cells [21], or reduction of the temperature gradients [16]. Crystal-growth programs were also initiated under reduced gravitation: Skylab, Apollo-Soyouz Test Program (ASTF), Texus, and in the future Spacelab. However, it was soon realized that experiments in space provided only microgravity (not zero gravity). "g-jitter" was present and the important role of Marangoni convection in space as well as on earth was recognized.

The requirement of minimum temperature gradients in combination with the reduced-convection approach presents severe problems. Material transport is slow and the melt is not homogenized. Interfacial stability requires a slow growth rate because of the lack of a stabilizing

temperature gradient and the need to remove the evolved latent heat of crystallization.

Forced convection has been proposed as an alternative to minimize the effects of oscillatory convection [22–24]. It would have the advantages of homogenizing the melts, enhancing material and heat transport, and increasing interface stability. A specific proposal involving the accelerated crucible rotation technique (ACRT) in Czochralski growth [25] has been supported by numerical simulation studies [26,27] as well as experiments on Czochralski-grown silicon. The main difficulty is the necessary temperature control ($\pm 0.01°C$ in KTN). This requires a reduced temperature gradient and correspondingly reduced growth rate at the expense of improved crystal homogeneity with this approach.

## 4. Steady-state growth near equilibrium

A reduction of the growth rate in melt growth, generally at high temperatures, would be impractical with respect to experimental duration, energy consumption, crucible corrosion, etc. and would require enormous efforts on the control of all growth parameters; a reduction of the steady-state growth rate by say three orders of magnitude would require an improvement of temperature control by the same factor! A specific problem is the moving growth front, which must be maintained constant to within about 0.01–0.1°C depending on the required homogeneity of the solid solution, and on the slope of the solidus in the phase diagram. The required spatial uniformity and temperature stability demand a constant heat flux through the crystal and through the fluid, and a constant growth velocity.

Whereas a constant heat flux through the crystal can be achieved with most crystal-growth techniques, the other requirements present severe problems. A constant growth velocity can only be obtained if there is a single growth mechanism. There must either be growth on a facet with (nearly) monomolecular steps [28,29], growth on a surface with constant curvature, or growth on a rough surface at a high deposition rate.

The difficulty of maintaining steady-state conditions at the moving solid–liquid boundary increases with increasing growth rate, and Landau [30] has shown that for critical parameters (growth rate, segregation coefficient), near the morphological stability limit, an oscillation of the growth rate may occur leading to striations or to inclusion bands parallel to the growth interface.

These problems can be reduced by utilizing near-equilibrium conditions, and by diluting the system with a solvent so that the concentration of the crystal components typically lies between 5% and 30%. This allows a lowering of the growth temperature $T$ (growth) to $\sim 0.5\,T$ (melting), with small temperature gradients at the interface. Equilibrium surfaces (facets) are formed, which may be extremely flat if sufficiently small supersaturations are used [28,29,31] (see also Chapters 4–6 for Ref. [10]).

By diluting the components with a solvent, the growth process becomes limited by mass transport: coupled diffusion of crystal constituents towards the interface and of solvent away from the crystal. Compared to melt growth, the growth rate is reduced by 3–4 orders of magnitude, to values between 50 and 5000 Å/s. According to the diffusion-boundary-layer concept of Nernst [32], the growth rate $v$ is then given by

$$v = \frac{(n_\infty - n_e)D}{\rho_c \delta} \tag{12}$$

for the diffusion-limited regime, neglecting the comparatively fast interface kinetics. Here $n_e$ and $n_\infty$ are the equilibrium and the effective bulk concentrations of the solute (of density $\rho_c$) in the solution, respectively.

Changes of $k_{eff}$ are determined essentially by the product $(v\delta)$, and $k_0$ and $D$ are practically constant. Since the growth rate $v$ is inversely proportional to $\delta$, the product $(v\delta)$ also remains practically constant when $\delta$, or the hydrodynamic flow rate $u$, changes. Hydrodynamic fluctuations are thus compensated by corresponding growth-rate changes. However, growth-rate changes caused by temperature oscillations are not compensated and thus lead to change of $k_{eff}$ and to striations. Temperature gradients have to be minimized so that forced convection is sufficient

to provide the constant temperature required at the growth interface. Even periodic changes of the stirring action (as in reciprocating stirring of seed crystals in aqueous-solution growth and as in ACRT in high-temperature solution growth) will not induce striations as long as the temperature gradients are sufficiently small. Accordingly, the assumption that hydrodynamic oscillations automatically lead to inhomogeneities is only valid for crystal growth at large temperature gradients ($G \geqslant 1°C/cm$). Hydrodynamic oscillations do not cause striations by themselves.

## 5. Growth with $k = 1$

A constant effective distribution coefficient of unity would clearly solve the striation problem in melt growth. However, except for special cases, $k_0$ is not unity and $k_{eff} = 1$ can only be obtained by extremely fast solidification rates. High growth rates might be acceptable for one-dimensional crystals (whiskers or rods) or in two-dimensional crystals (plates or epitaxial layers), but for the growth of bulk crystals, much slower growth rates are needed.

The use of solutions provides an additional degree of freedom, since the effective distribution coefficient is also dependent on the properties of the solvent and the solvent–solute interactions. Systematic experiments with oxide solid solutions, using different solvents and mixtures of solvents have shown that both $k_{eff} > 1$ and $k_{eff} < 1$ are possible for a given oxide solid solution. By proper mixing, it is then possible to "tune" the solvent mixture to obtain $k = 1$ and thus eliminate the segregation problem. An example is given by the perovskite solid solutions $Gd_{1-x}La_xAlO_3$ and $Gd_{1-x}Y_xAlO_3$, which are grown from solvent mixtures with the major components PbO, and $Bi_2O_3$ and $PbF_2$. The effects of the minor components of the solvent mixtures (excess $Al_2O_3$, $B_2O_3$, and $PbF_2$. The effects of the minor components of the solvent mixtures (excess $Al_2O_3$, $B_2O_3$, $V_2O_5$) have not yet been studied.

In Fig. 3, the measured effective distribution coefficients of the La and Y dopants in $GdAlO_3$ are shown as a function of the oxide–fluoride
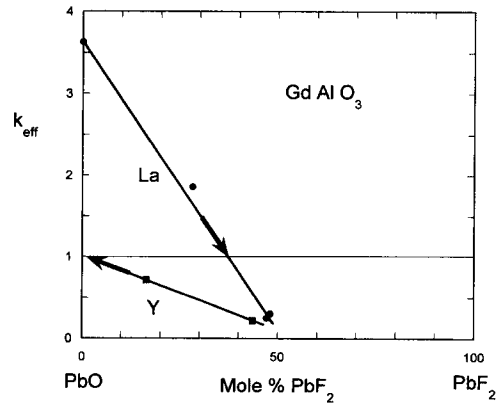


Fig. 3. Dependence of the effective distribution coefficient on solvent composition for growth of La-doped and Y-doped $GaAlO_3$.
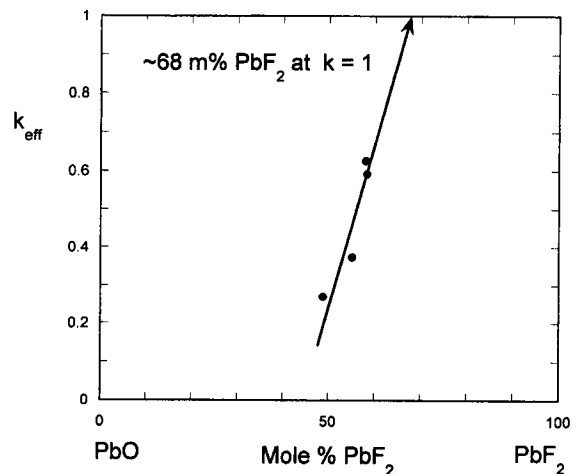


Fig. 4. Dependence of $k_{eff}$ on solvent composition for growth of Cr-doped $Y_3Fe_5O_{12}$ using experimental data of Krishnan [33].

solvent composition. For a pure oxide flux, $k_{eff}$ for La in $GdAlO_3$ is nearly four, whereas for equal concentrations of oxide and fluoride, $k_{eff}$ is smaller than 0.5. At a composition of about $37 mol\%$ $PbF_2$, $k_{eff} = 1$ is obtained. In the case of Y-doped $GdAlO_3$, a nearly fluoride-free solvent is required to obtain $k_{eff} = 1$.

An example of garnet solid solutions grown from PbO–$PbF_2$ mixtures is shown in Fig. 4, using data published by Krishnan [33]. Here $k_{eff}$ for Cr

in yttrium-iron garnet increases with increasing $PbF_2$ concentration; about 32 mol% PbO should give $k_{eff} = 1$.

Further measurements are naturally necessary to determine how widely this approach is applicable, but it is clear from these examples that it is very promising.

## 6. Conclusions

Crystal growth of solid solutions has been a well-recognized problem for many years. Since homogeneous crystals can only be expected from a steady-state growth process, the steady-state approaches to the segregation phenomena can be applied to derive the critical technological parameters for the experimental crystal grower. The Burton–Prim–Slichter analysis of growth from melts, and the Van Erk analysis of growth from diluted solutions are quite similar and show only quantitative differences; the diffusion barrier in growth from solutions leads to a smoother dependence of $k_{eff}$ on growth parameters compared to growth from melts.

The temperature at the growth interface (or of the fluid in front of it) is the crucial parameter and must be controlled with a precision that is difficult to achieve in growth from melts. It is easier to achieve by using solutions. Temperature gradients can be reduced so that application of forced convection in combination with extremely precise temperature control gives the temperature stability required at the interface.

The most important feature is that hydrodynamic fluctuations are not necessarily harmful. Their effects are largely compensated by growth-rate changes so that the exponent in the BPS equation remains practically constant. Hydrodynamic fluctuations are only harmful when large temperature gradients in the fluid lead to (oscillatory) transport of fluid parts with different temperature to the growth interface thereby causing striations.

In crystal growth from high-temperature solutions, the type of supersaturation determines whether the crystals have minimum striations (slow-cooling technique) or a minimum inherent

concentration gradient (gradient-transport technique).

One important aspect has been discussed very briefly in this paper; namely, the role of the interface morphology and of the growth mechanisms on the homogeneity as this was published earlier [28]. Thus, it has been shown in this paper that small temperature gradients, forced convection (or alternating flow), and high-precision temperature control are the main requirements for the growth of bulk crystals of homogeneous solid solutions.

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