ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT

Journal of Crystal Growth 287 (2006) 214–223

JOURNAL OF CRYSTAL GROWTH

www.elsevier.com/locate/jcrysgro

Theoretical and technological solutions of the striation problem

Hans J. Scheel*

Scheel Consulting, Groenstrasse Haus Anatas, 3803 Beatenberg, Switzerland

Abstract

With the increasing demand for solid solutions for numerous applications in micro- and optoelectronics, magneto-optics, and Lasers, the yield in producing extremely homogeneous crystals becomes more and more important. Growth-induced inhomogeneities called *striations* hamper the applications of solid solutions and doped crystals. *Thermal striations* have widely been regarded as inherent problem of crystal growth. They are commonly assumed to be caused by convective instabilities so that reduced convection by microgravity or by damping magnetic fields was and is widely employed to reduce thermal striations. Here it will be shown theoretically that temperature fluctuations at the growth interface cause striations, and that hydrodynamic fluctuations in a quasi-isothermal growth system do not cause striations. The conditions derived from the phase diagram were experimentally established and allowed the growth of striation-free crystals of $KTa_{1-x}Nb_xO_3$ "KTN" solid solutions for the first time. Hydrodynamic variations from the accelerated crucible rotation technique ACRT did not cause striations as long as the growth temperature around 1200 °C was controlled within 0.03°. In the growth of facetted crystals the surface, consisting of regions with different local growth velocities, i.e. macrosteps, may cause the *macrostep-induced striations*. These can be suppressed by controlling the growth mode, by preventing or eliminating macrosteps by the *faceting transition*.

In specific solid-solution systems the striation problem can be circumvented by approaching the effective distribution coefficient $k_{eff} \rightarrow 1$ in growth from melts and from solutions.

The various theoretical aspects and technological solutions of the striation problem will be reviewed and discussed in this paper.

Keywords: A1. Growth from melts; A1. Segregation; A1. Solid solutions; A1. Striations; A2. Accelerated crucible rotation technique; A2. Growth from high-temperature solutions; B2. Nonlinear optic materials

1. Introduction

Solid solutions or mixed crystals are special crystals or alloys in which one or more lattice sites of the structure are occupied by two or more types of atoms, ions, or molecules. The statistical distribution of the species occupying the same site is in many cases random. However, it was theoretically shown by Laves [1] that the distribution can deviate from random in the direction of ordering, leading at full ordering to a superlattice or superstructure, or it can deviate in the direction of clustering leading in the extreme case to unmixing or phase separation. This aspect of site distribution and ways to control or modify it by annealing will not be discussed here, although it has an impact on the physical properties of metallic alloys and of magnetic bubble-domain devices, for example.

In solid solutions the concentration of the constituents can be varied and thus the properties optimized for specific applications, so that mixed crystals play an increasing role in research and technology. One example is III–V semiconductors where the bandgap can be adjusted, along with the lattice constant, to match the available substrates for epitaxial growth for optoelectronic applications. The misfit between substrate and layer is a decisive factor for controlling the epitaxial growth mode and thus the epilayer (device) performance [2]. Another example are III–V compounds for photovoltaic devices where the composition can be adjusted to optimize successive solar-light absorption and thus to maximize solar-cell efficiency as well as radiation and temperature resistance [3]. In certain cases, properties and effects may be obtained in solid solutions which are not observed in the constituents: The

---

*Fax: +41 33 841 2527.
E-mail address: hans.scheel@bluewin.ch.

0022-0248/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2005.10.100

Table 1
Homogeneity requirements for applications of solid solutions

Crystals, substrates, epilayers	$\Delta x/x$
Doped crystals, dependent on function	10^{-2}–10^{-3}
Metals and alloys	10^{-2}–10^{-3}
Magnetic and magneto-optic crystals and layers	10^{-4}–10^{-5}
Semiconductor substrates and layers Ga(As,P), (Ga,In)As, (Ga,In)Sb, (Cd,Hg)Te	10^{-4}–10^{-5}
Dieelectrics: Piezo- and pyroelectrics; electro-optic, nonlinear-optic and Photorefractive crystals; Laser crystals	10^{-5}–10^{-7}

phase transition temperature and the related anomaly of the dielectric constant may be shifted near to the application temperature for electro-optic, nonlinear-optic and acousto-optic applications and thus allows development of highest-efficiency devices [4,5]. The hardening effect of solid solutions is often used to improve the mechanical properties of alloys [6].

In this paper the bulk fluctuations of concentration of the constituents of solid solutions and of dopants will be treated with respect to the application-dependent homogeneity requirements which are shown for the major material classes in Table 1, where the estimated tolerable composition (x) variations (Δx) are listed. Corresponding to these tolerance limits, analytical methods are to be applied or developed in order to assist in the achievement of "striation-free" crystals. In addition to the well-established methods to indicate striations, a colorful optical diffraction method has been developed [7] to visualize striations, and demonstrated with oxide, doped InP, and $Si_{1-x}Ge_x$ crystals. The types of inhomogeneities and their origin, and how inhomogeneities can be reduced or suppressed completely, will also be discussed. Here we define "striation-free" as the degree of homogeneity where the inhomogeneity cannot be detected by analytical methods or where it is less than required for the specific application. An absolute striation-free crystal may neither be achieved nor proven.

There is a strong tendency for fluctuations of the growth conditions causing concentration fluctuations vertical to the growth direction known as growth bands or striations. The suppression of striations is an old problem in crystal growth technology, so that several authors have described striations as an "intrinsic" or "unavoidable" phenomenon in crystal growth [5,8].

Based on the segregation analyses for growth from melts by Burton, Prim and Slichter (BPS 1953 [9]) and for growth from diluted solutions by Van Erk 1982 [10] the role of hydrodynamics and temperature as the relevant growth parameters will be discussed in Section 3, so that the experimental conditions for growth of crystals free of thermal striations can be derived. This theoretical result will be confirmed in Section 4 by the growth of quasi striation-free crystals of solid solutions.

The macrostep-induced striations are caused by locall different growth velocities and can be prevented by contro of the growth mode [2] which requires the adjustment o several growth parameters as briefly discussed in Section 2.

Alternative approaches to reduce or eliminate the striation problem are discussed in Section 5. They are based on achieving an effective distribution coefficient of unity which was shown for growth from melts by Mateika [11] and for growth from high-temperature solutions by Scheel and Swendsen [12]. Finally, in Section 6 novel approaches will be discussed which require further testing.

2. Origin and definitions of striations

Nearly all crystals have inhomogeneities and striations except for line compounds prepared from ultra-pure chemicals. Early observations of striations have been reported for CaF_2 [13] and in semiconductor crystals [14]. Hurle [15] has shown for metal and semiconductor crystals and Cockayne and Gates [16] for Czochralski-grown oxide and fluoride crystals, that striations are caused by temperature fluctuations correlated with convective oscillations when a critical Raleigh number for natural convection is surpassed, or when there is a lack of symmetry in crystal pulling.

Many compounds like GaAs and $LiNbO_3$ are not line compounds, but have an existence range, that is they have a certain degree of solid solubility with one or both of the constituents. This causes a difference between the congruent-melting composition and the stoichiometric composition. Therefore these crystals show composition variations along the growth direction and as striations, depending on the exact growth conditions (melt composition, growth temperature) and their fluctuations. For GaAs and compound semiconductors this is discussed by Wenzl et al. [17].

Melt-grown elements like silicon and line compounds like Al_2O_3 show striations due to impurities or dopants, in the case of silicon oxygen striations from partial dissolution of the SiO_2 crucible. Very pronounced striations are often found in doped crystals (semiconductors, lasers) and especially in crystals of solid solutions.

Various definitions for striations had been suggested. In the following, functional terms are proposed which relate to the origin of the specific striations (instead of type-I, type-II, etc.). Striations are defined as growth-induced inhomogeneities in the crystal which are aligned along the facetted or non-facetted growth surface, or which in the case of facetted growth are caused by step-bunching and thus are related to the traces of macrosteps. These, often periodic, inhomogeneities are caused in the first case by growth rates which fluctuate with time due to temperature fluctuations and are schematically shown in Fig. 1(a). Therefore they could be called *thermal striations*. In Czochralski crystal pulling these striations are frequently linked to the crystal rotation rate, since the crystal feels any lack of symmetry in the crucible-heater-insulation

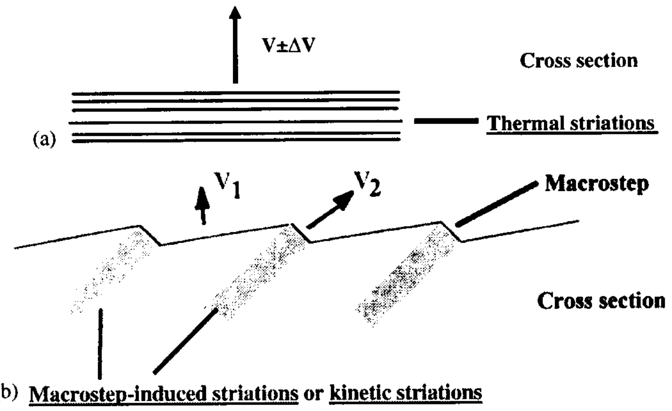

Fig. 1. (a) Striations or growth bands caused by temperature fluctuations leading to growth-rate variations are defined as "thermal striations", (b) Striations caused by macrosteps and corresponding localized (lateral) growth-rate differences are named "macrostep-induce striations" or "kinetic striations".

configuration [18]: these specific thermal striations are called *rotational striations* or in short *rotationals*. It was shown by Witt et al. [19] by using time markers and etching of crystal cross sections, that re-melting may occur followed by fast growth, so that they defined microscopic (instantaneous) and macroscopic (average) growth rates and thus could explain complex striation patterns. The fluctuating temperatures at the growth interface, leading to growth-rate fluctuations in Czochralski growth, are related to convective instabilities [20], due to interactions of several different kinds of flows which will be discussed further below.

The second class of striations is caused by lateral growth rate differences v_1 and v_2 as shown in Fig. 1(b) and are named *macrostep-induced striations* or *kinetic striations* [21]. Facetted growth may be observed in growth from melts in low temperature gradients, and it is practically always observed in growth from aqueous or high-temperature solutions [22].

At high densities of growth steps, i.e. at high supersaturation, the bunching of steps occurs and leads to macrosteps with large multiples of the height of the monostep. Frank [23] and Cabrera and Vermilyea [24] in 1958 applied the kinematic wave theory, which was developed before for the general traffic-flow problem by Lighthill and Whitham [25], for the explanation of *step bunching*. As shown in Fig. 1(b) growth surfaces with macrosteps (also called terrace-riser structure) exhibit different local growth mechanisms and growth rates. The terrace grows by lateral propagation of mono- or double-steps with the facet growth rate v_1, whereas the macrostep with a rough or multistepped surface has the velocity v_2. These growth-rate differences cause corresponding differences in dopant or impurity incorporation and thus lead to striations which mark the traces of the macrosteps. These *macrostep-induced striations* are shown in Fig. 2 with LPE-grown multilayers, where the correspondence of the kinetic striations (visible in the angle-lapped and etched p-GaAs layers) with the marked macrosteps is clearly recognized

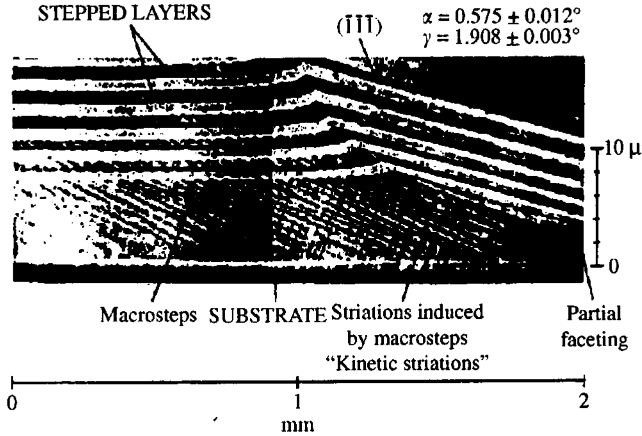

Fig. 2. Angle-lapped (1.9°) and etched composite Nomarski (differential interference contrast) micrograph of an 11-layer p/n-GaAs structure grown by liquid phase epitaxy. A first thick layer grown on the {1 1 1} substrate of 0.58° misorientation shows on the right side the transition to the facet which has a lower growth rate. On the left side the macrosteps and macrostep-induced striations are clearly visible (Scheel [26]).

[26]. In that work the transition of the misoriented macrostep-surface to the facet with continuous step propagation by the Frank-Van der Merwe growth mode is described, a transition which leads to layers (and crystals) with excellent homogeneity, i.e. without striations. Chernov and Scheel [27] analyzed the conditions for achieving such atomically flat surfaces. The flatness was experimentally shown in 1982 by STM by Scheel et al. [28].

Macrosteps can be regarded as a first step towards growth instability and are formed not only at high supersaturation, but also in the presence of certain impurities and on misoriented surfaces [29]. When the thermodynamic driving force is further increased, the impurity built up in front of the growing crystal may reach a critical level and is suddenly incorporated. Crystal growth continues until once again the impurity is incorporated, and so on. This oscillation of growth rate and impurity concentration leading to striations was theoretically analyzed and experimentally proven by Landau [30] and could be named *instability-induced striations.*

3. Segregation phenomena and thermal striations

The concentration of the constituents of a crystallized solid solution generally differs from that in the liquid from which the mixed crystal is grown, a phenomenon known as segregation. In equilibrium or at very low growth rates, the ratio of the concentration of component A in the solid to that in the liquid is defined as equilibrium segregation (or distribution) coefficient

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

k_0 may be derived from the equilibrium phase diagram by the ratio of solidus and liquidus concentrations of A at a given temperature. In a crystallizing system with a limited melt volume, segregation at the growing interface leads to a continuous compositional change of the fluid: $C(A)_L$ decreases for $k_{\text{eff}} > 1$, and $C(A)_L$ increases for $k_{\text{eff}} < 1$, so that the concentration in the solid continuously changes. This causes an ***inherent concentration gradient*** in the crystal for which the concentration at any location of the growth front is given, according to Pfann [31] by

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

where g is the fraction of crystallized material and C_0 the initial concentration. Here it is assumed that k_{eff} does not vary with concentration or temperature changes. This inherent concentration gradient can be made zero by keeping the fluid concentration constant, which can be achieved by growth at constant temperature in combination with transporting feed material from a higher temperature in the gradient-transport technique [32]. Several groups have attempted to grow solid-solution crystals by material transport in temperature gradients [33–35]. However, the large temperature gradients for acceptable growth rates lead to temperature fluctuations so that thermal striations could not be prevented.

In Fig. 3 the phase diagram $KNbO_3$–$KTaO_3$ of Reisman et al. [36] is presented where the gradient–transport technique, using the temperature difference T_3 to T_4, is shown which was used by many groups listed in Ref. [8]. For electro-optic and other optical applications the variation of x must be smaller than 0.00003 [8], see also Table 1, and this requires temperature fluctuations smaller than 0.01 °C as is indicated in Fig. 3. Also shown is the slow-cooling method where a quasi-isothermal solution is slowly cooled from T_1 to T_2. This allows the growth of striation-free crystals. The inherent temperature gradient can be kept within tolerated limits when a single crystal is grown from a large melt. For the KTN system Rytz and Scheel [8] have calculated the mass of melt M which is needed to grow a crystal of volume V with a tolerated inherent concentration difference $x_1 - x_2$. These data and also the temperature cooling range can be read from the nomogram shown in Fig. 4. For example a KTN crystal of 1 cm^3 with $\Delta x < 0.02$ requires a melt of 1000 g which is cooled by 12 °C. The results of growth experiments will be discussed further below.

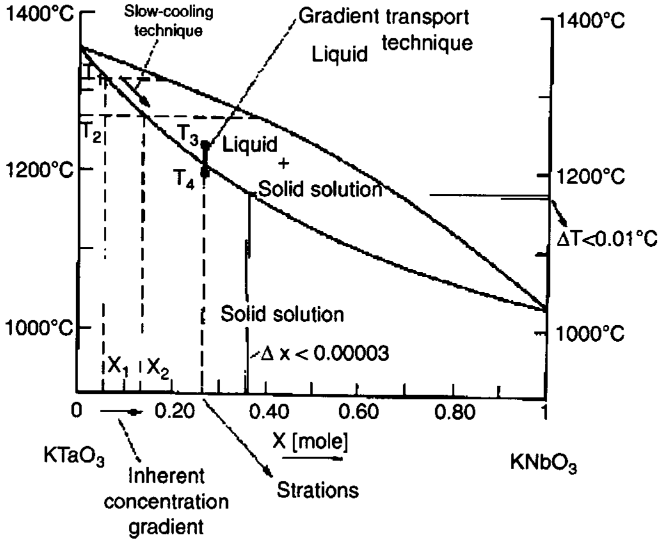

Fig. 3. The composition-temperature phase diagram $KTaO_3$–$KNbO_3$ of Reisman et al. [36] with indicated growth techniques and resulting inhomogeneities, after Rytz and Scheel [7].

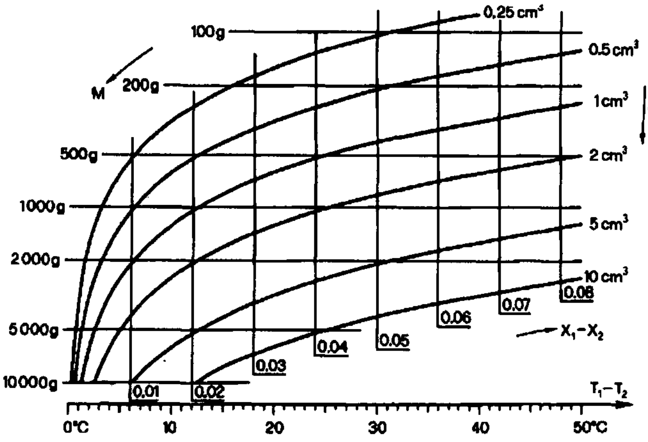

Fig. 4. Nomogram to derive the experimental parameters for the growth of KTN solid-solution crystals of volume V with a specified maximum inhomogeneity $x_1 - x_2$. M is the required mass of melt, $T_1 - T_2$ is the cooling interval [7].

In normal growth we have neither the case of very low growth rates near equilibrium with $k_{\text{eff}} = k_0$, nor the case with very fast growth rate where $k_{\text{eff}} \to 1$. Fig. 5 shows the situation at the crystal–liquid interface for the cases of equilibrium (which could also be achieved by "complete mixing"), for the case of steady-state normal crystal growth, and for very fast diffusion-less solidification. Also shown are the concentrations in the solid and in the liquid with the diffusion boundary layers. In steady-state crystal growth the effective distribution coefficient k_{eff} lies between the equilibrium distribution coefficient k_0 and 1 and is dependent on the diffusion boundary layer δ and the growth rate v as shown in Fig. 5. For the case of

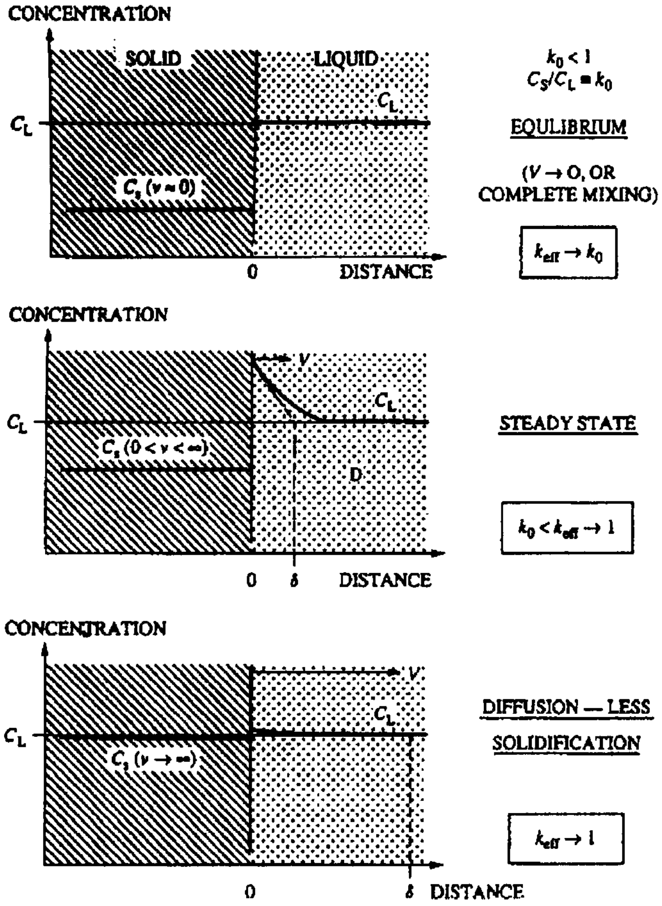

Fig. 5. The concentration relations at the crystal-liquid interface and the effective distribution coefficients for three growth situations: k_{eff} approaches k_0 near equilibrium, that is at very low growth rate or complete mixing; in typical growth situations k_{eff} is between k_0 and 1; and at very fast growth rate k_{eff} approaches unity. The diffusion boundary layer thickness δ depends on the growth rate v and the flow rate u (of melt or solution) according to Eq. (6).

Czochralski growth, the flow analysis of Cochran [37] invoking an infinite rotating disc was applied by Burton et al. [9] in order to derive k_{eff}. It was considered that the solute concentration profile is virtually uniform in the radial direction, i.e. the diffusion boundary layer δ can be regarded as having a constant thickness across the idealized flat growth surface. For moderate growth rates, δ depends essentially on the crystal rotation rate ω (except for the rim which is neglected), the kinematic viscosity v, and on a bulk diffusion coefficient D (which includes solute diffusion and solvent counter-diffusion):

$$\delta = 1.6 D^{1/3} v^{1/6} \omega^{1/2}. \tag{3}$$

BPS derived for the steady-state case the equilibrium distribution coefficient

$$k_{eff} = k_0/[k_0 + (1 - k_0)^{-(vd/D)}] \tag{4}$$

with v the growth rate. This approximation can be utilized since the growth-rate dependence of k_0 is small due to minor variations of the growth rates for growing striation-free crystals. Burton et al. [38] experimentally measured the distribution coefficients of several elements between solid/liquid germanium and correlated them with the tetrahedral covalent radii: the larger the element, the smaller the distribution coefficient. They also measured striations by radioactive tracers and photographic film and pointed out the *importance of forced convection for growth of homogeneous crystals.*

For growth of solid solutions from dilute solutions, Van Erk [10] has considered the complex solute—solvent interactions and has derived the effective distribution coefficient for diffusion-limited growth as

$$\ln k_{eff} = \ln k_0 - (k_{eff} - 1)(v\delta/D). \tag{5}$$

A further discussion of these segregation aspects and a comparison between BPS and van Erk can be found in Scheel and Swendsen [12]. Growth from solutions is normally limited by volume diffusion, and the relatively fast interface kinetics can be neglected. Based on the diffusion-boundary layer concept, Nernst in 1904 [39] derived the growth rate as

$$v = D(n_\infty - n_e)/\rho_c\delta, \tag{6}$$

where n_e and n_∞ are the equilibrium and the effective bulk concentrations of the solute in the solution, and ρ_c is the solute density. The time constant for the effects of temperature fluctuations (and thus on the growth rate v) is on the order of seconds, while that for hydrodynamic fluctuations on δ and v is on the order of minutes. In steady-state growth, within a given range of temperature and time, the D and k_0 in Eqs. (4) and (5) can be taken as constants. Therefore, changes in the effective distribution coefficient k_{eff} are essentially determined by the product ($v\delta$) of the exponent. As a first approximation, this product is constant due to the inverse relation between v and δ in the Nernst equation (6). This means that hydrodynamic variations, which lead to changes of δ, are compensated by growth-rate changes. On the other hand are growth-rate changes caused by temperature fluctuations not compensated and thus lead to changes of k_{eff} and to thermal striations.

It follows from this discussion that for growth of striation-free crystals the temperature fluctuations should be suppressed to less than about 0.01 °C (and thus temperature gradients to less than 1 °C/cm). A compromising requirement is the need to impose a temperature gradient to remove the latent heat at practical growth rates, and to control nucleation.

Homogenizing the melts and solutions facilitates the achievement of above temperature conditions, and it reduces the diffusion problems leading to growth instability and inclusions as discussed in Ch. 6 of Elwell and Scheel [22]. Stirring may be achieved by a continuous flow along the growth interface, by Ekman or Cochran flow towards the rotating growth surface, by periodic flow changes as in reciprocating stirring in growth from aqueous solutions or by accelerated crucible rotation technique ACRT [40] in

Table 2
The role of hydrodynamics

Starting point	Striations connected with convective instabilities [15,20]
General approach	Reduction of Convection by • Baffle (Brice) • Microgravity/Skylab/Space experiments • Magnetic fields ([15], SONY, Fukuda) Disadvantages • Sufficient suppression of convection not achieved • Complexity; large effort • Diffusion/segregation problems • Unstable growth
Alternative approach	Forced convection • Simple technical realization o Stirrer (aqueous solutions) o Rotating substrate/crystal plate [32] o Accelerated crucible rotation technique ACRT [40,45] o Sloshing [43] o Magnetic stirring • Flat interface in Vertical Bridgman/VGF/ACRT o CdTe & solid solutions [41] o GaInSb solid solutions [42] • Reduced diffusion/segregation problems o High (maximum stable) growth rates (Scheel & Elwell, Goernert, Horowitz et al.) o High axial crystal yield Disadvantages: • Requirement of optimized forced convection o Theoretical/numerical simulation approach o Selective growth experiments o Intuition
Optimum approach of combined reduced and forced convection: CRCZ [64]	
Role of dimension-less numbers and of numerical simulation	

growth from high-temperature solutions and in growth by vertical-Bridgman/VGF technique [41,42], or by sloshing proposed by Gunn [43].

For many years the favored approach to minimize striations was to reduce convection by growth in a microgravity environment or, in the case of semiconductors, to apply convection-damping magnetic fields, see Table 2. However, the above discussion has shown that forced convection has many advantages to increase the axial yield of crystals and, not at least, to achieve economic growth rates approaching the maximum stable growth rates for inclusion-free crystals.

From above discussion we can also derive the experimental conditions to induce regular striations and superlattice structures by applying a large temperature gradient in combination with periodic hydrodynamic changes (by ACRT) and a constant mean supersaturation.

In the following, the theoretical considerations discussed above will be applied to an example of growing striation-free KTN solid solution crystals. This goal has long eluded experimentalists [8].

4. Growth of striation-free KTN crystals

The solid-solution system $KTa_{1-x}Nb_xO_3$ (KTN) is of special interest due to its very large electro-optic coefficient which can be optimized for specific application temperatures by the choice of x [5]. However, for optical applications the inhomogeneity in refractive index should be less than 10^{-6}, requiring that the crystals and layers be striation-free to this level.

As discussed above, this homogeneity cannot be achieved by the gradient-transport technique, but only by slow-cooling of nearly isothermal solutions. The latter approach was used by Rytz and Scheel [8] and Scheel and Sommerauer [44] who combined ultra-precise temperature control with optimized thermal profile in the furnace and with ACRT [45] to achieve striation-free KTN crystals for the first time. A typical crucible arrangement with bottom cooling to provide a nucleation site is shown in Fig. 6 along with the applied ACRT cycle. In ACRT the crucible with the growth solution is periodically accelerated and decelerated so that by inertia the liquid is moving relative to the crucible wall and forms a spiral when seen from top. This spiral shear flow was analyzed and simulated by Schulz-DuBois [46]. He also analyzed the Ekman layer flow in which, under optimized conditions (flat crucible bottom, time constant), the liquid is always pumped through a thin Ekman layer at the bottom of the crucible. This Ekman-layer flow may be even more effective for mixing than spiral shear flow, and can be seen in a glass of tea with tealeaves which collect in the center bottom when the rotation is stopped. Elwell and Scheel [32] described the derivation of optimized ACRT stirring based on kinematic viscosity of the liquid and on the crucible dimension.

Temperature control with a precision of 0.03 °C at around 1300 °C could be achieved by using a thermopile of 3 to 9 Pt-6%Rh versus Pt-30% Rh thermocouples in series ([47], see also[32] Ch.7).

Unseeded KTN crystals with $x = 0.01$ [8] and $x = 0.25$ [44] and up to $33 \times 33 \times 15\,mm^3$ in size were grown. ACRT stirring and localized cooling controlled nucleation of one to two crystals only. In the best crystals no striations were visible in a Zeiss polarizing microscope with specially selected strain-free lenses, although very faint striations could be revealed by using extremely sensitive methods [5].

5. Homogeneus crystals with $k_{eff} \rightarrow 1$

The segregation and thus the striation problem could be solved when the effective distribution coefficient

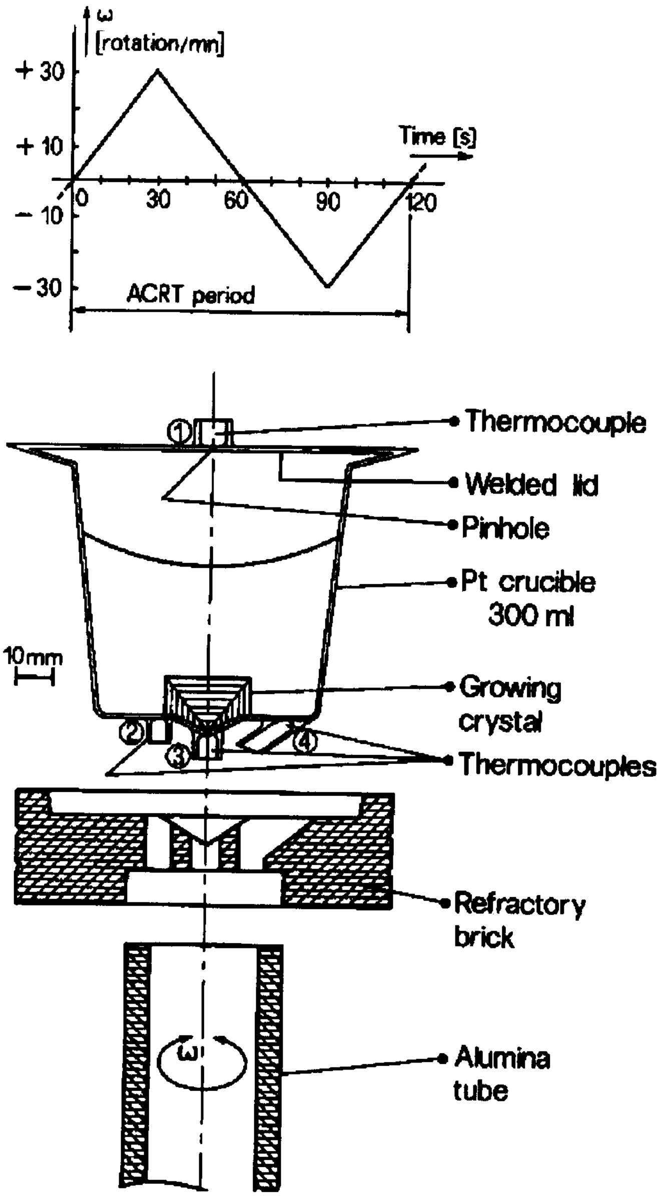

Fig. 6. The typical ACRT cycle is shown at top, and the ACRT-crucible arrangement in the furnace is shown as side view/cross section. The 300 cm^3 platinum crucible with welded lid and slightly cooled spot for nucleation control was used in the experiments for growth of KTN crystals [8].

approaches unity. As discussed above this is possible for the case of very high growth rates which cannot be applied for bulk crystals, but for low-dimensional crystals like plates, surface layers, and fibers. Edge-defined film-fed growth EFG allows the approach of $k_{\mathrm{eff}}{\sim}1$ as was shown theoretically [48] and experimentally [49] and [50] for platelet growth of doped $LiNbO_3$ and $LiTaO_3$. Miyazawa [51] grew relatively homogeneous Te-doped GaSb platelets by "shaped melt lowering", by pulling downwards. A capillary-controlled Czochralski/Stepanov method for growth of shaped crystals of $Sr_xBa_{1-x}Nb_2O_6$ of improved homogeneity was applied by Ivleva et al. [52,53].

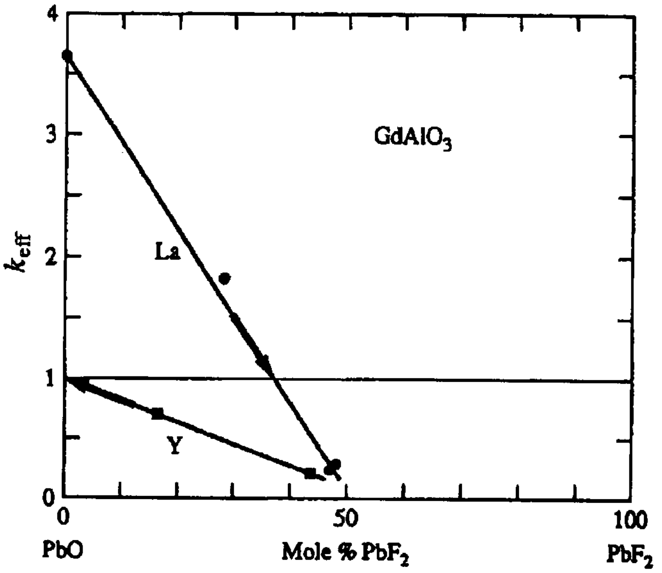

Fig. 7. The dependence of the effective distribution coefficient on the solvent composition in growth of Y- and La- doped gadolinium aluminate, after Scheel and Swendsen [12].

A quite different approach to achieve $k_{\mathrm{eff}} = 1$ was demonstrated by Mateika [11] who prepared complex garnet compositions, by using ionic radii and optimized replacements on the tetrahedral, octahedral and dodecahedral sites in the complex garnet structure, which resulted in $k_{\mathrm{eff}} = 1$. Two examples of preparing substrate crystals for liquid phase epitaxy LPE of magneto-optic layers, with specific lattice constants, are

1. $Gd_3Sc_xGa_{5-x}O_{12}$ with $x = 1.6$ approaches $k_{\mathrm{eff}}(\mathrm{Sc}){\sim}1$ with $a = 12.543$ Å, and
2. $Gd_{3-x}Ca_xGa_{5-x-2y}Mg_yZr_{x+y}O_{12}$ with $0.31<x<0.45$; $0<y<0.37$; $0.45<(x+y)<0.68$ approaches k_{eff} (Ca, Mg, Zr)$\sim$1 with $a = 12.453$–12.507 Å.

An effective distribution coefficient of unity could also be achieved in crystal growth from high-temperature solutions by optimized solvent mixtures as shown by Scheel and Swendsen [12], since the distribution coefficient depends on solvent-solute interactions. Systematic experiments have shown that different solvents and solvent mixtures may cause $k_{\mathrm{eff}}<1$ and $k_{\mathrm{eff}}>1$. By proper mixing of the solvent composition it is then possible to obtain $k = 1$ and thus eliminate the segregation problem. Two examples for perovskite solid solutions ($Gd_{1-x}Y_xAlO_3$ and $Gd_{1-x}La_xAlO_3$) are shown in Fig. 7. A systematic investigation would help to understand these approaches to achieve $k_{\mathrm{eff}} = 1$ and to establish rules for general applicability.

6. Alternative approaches to reduce thermal striations

In Table 2 a number of approaches to overcome the striation problem have been listed. In the following specific attempts, which got wider interest or found application in crystal production, will be briefly discussed. Ostrogorsky and Mueller [54] proposed a submerged-heater method for vertical Bridgman growth, where the combined effect of thin melt layer and stabilizing temperature gradient should minimize striations, but the complexity has hampered technological application so far. This is in contrast to the application of ACRT in VGF and vertical Bridgman production of CdTe and GaInSb solid solution crystals by Capper et al. [41] and Dutta [42]. A modified Czochralski process has been described by Goriletsky et al. and by Eidelman et al. [55] for pulling huge halide scintillation crystals (up to 700 mm diameter and 550 kg weight) from small melt volumes. In this case there is a combined effect of small melt volume and forced convection due to counter-rotation of crystal and crucible. In practical fabrication of semiconductor crystals it was recognized that microgravity would not be applicable for various reasons, so that magnetic fields of various configuration were introduced to increase viscosity and damp convection, first by SONY 1980 for silicon followed by Terashima and Fukuda [56] for GaAs. The sloshing of Gunn [43] was mentioned earlier and was re-introduced as special vibration technique [57]. Kirgintsev and Avvakumov [58] compared several stirring techniques including vibrators and found the latter not very effective. Recently several authors [59–61] revived the interest in vibration stirring although it has not found application in commercial crystal production.

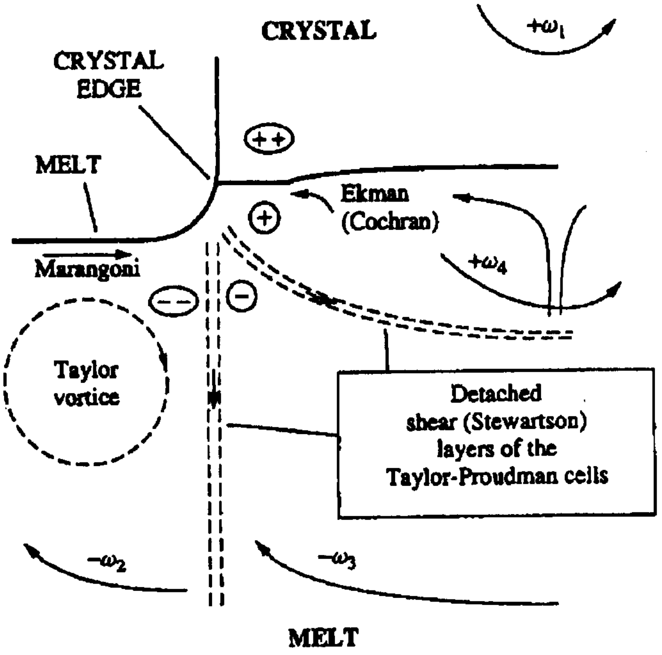

Fig. 8. Below the edge of a Czochralski-growing crystal there are more than six types of flow which differ in direction and/or velocity, for the case of crystal rotation $+\omega_1$ and crucible counter-rotation $-\omega_2$ above the critical Rossby number, after Scheel and Sielawa [63].

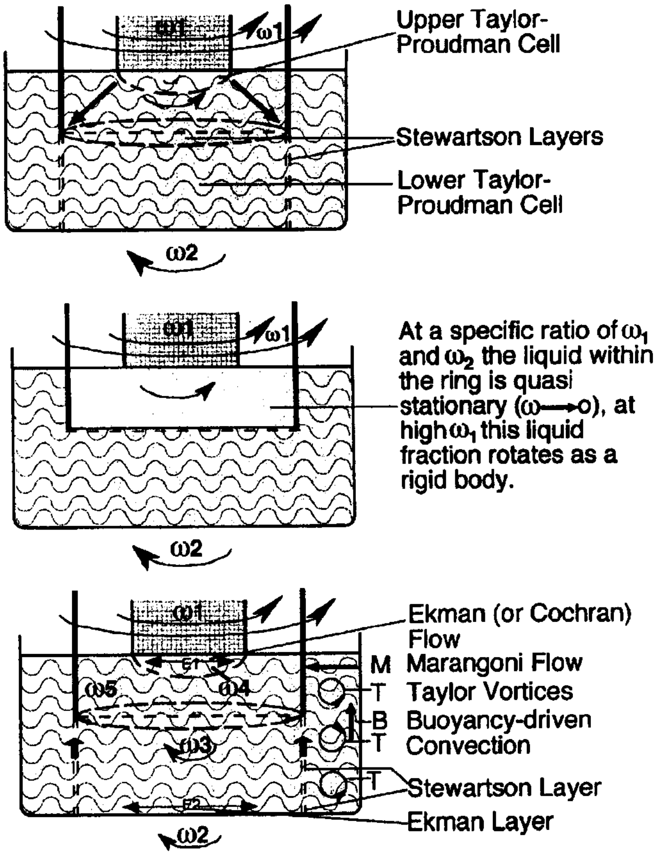

Fig. 9. Schematic presentation of the CRCZ where the complex flow region of Fig. 8 is transferred deeper into the melt by the ring and where the liquid fraction within the ring can be separated from bulk melt flow at optimum parameters [64]. A quasi convection-free liquid zone can be achieved at optimum setting of $+\omega_1$ and $-\omega_2$.

For growth from melts by Czochralski crystal pulling there are six or more different kinds of flows below the rim of the crystal as shown in Fig. 8. A special problem arises with Taylor–Proudman cells [62] and with Taylor vortices [63]. Double crucibles will help somewhat to simplify the flow pattern and to increase axial yield and therefore are used in certain production lines of GaAs and of stoichiometric $LiNbO_3$, but have practical disadvantages in the growth process.

A technologically simpler approach consists of a solid ring co-axial with the crystal and rotating with same direction and velocity with the crystal. This ring, introduced into the melt, separates the melt fraction inside the ring from the well-mixed bulk melt (see Fig. 9). In simulation experiments it was shown that at optimized setting of rotation rate of crystal and ring, and counter-rotation of the crucible, the melt fraction can be quasi stationary with only minor Ekman-layer flow. This co-rotating ring Czochralski (CRCZ) approach [64] has the positive double-crucible effects (for increased axial crystal yield and reduced striations) without the disadvantages of double crucibles. Numerical simulations have started, but the growth technology has yet to be developed.

7. Discussion and Summary

Several experimental and theoretical solutions were presented to overcome the intrinsic pervasive problem of striations:

1. k_0, D, v, $\delta =$ constant: very difficult ; chance with submerged heater or with CRCZ.
2. k_0, D, v = constant; δ may vary: Rytz and Scheel [8], Scheel and Sommerauer [44], Scheel and Swendsen [12], Capper et al. [41], Dutta [42].
3. $k_{\text{eff}} = 1$ for growth from melts: Mateika [11], for growth from solutions: Scheel and Swendsen [12].

Further conditions are

(a) Continuous flat or smooth (isothermal) growth surface: Scheel [26–28], Capper et al. [41], Dutta [42].
(b) Homogeneous melt or solution with $\Delta n/n < 10^{-5}$ and $\Delta T/T < 10^{-5}$ by forced convection leading to constant growth rate with $\Delta v/v < 10^{-5}$.

These indicated tolerances are typical values and depend on the individual system and on the tolerated inhomogeneity of the crystal. Therefore it is advisable to first analyze theoretically a new growth system and the phase relations so that the technological parameters can be established. With respect to optimized hydrodynamics, simulation experiments with a liquid of similar kinematic viscosity are very useful in the early phase and may be complemented by numerical simulation for process optimization. In certain cases, dimension-less numbers may be helpful to get a feeling for the convection regime.

In conclusion one can say that the striation problem is solvable (on earth) but requires a certain theoretical and technological effort. Hydrodynamic fluctuations are not harmful as long as the fluid is sufficiently isothermal, as long as the transport of fluid of different temperature to the growth interface is suppressed. Forced convection is essential for economic growth of solid -solution crystals as it increases yield and assists to establish the conditions for growth of inclusion-free and striation-free crystals.

References

[1] F. Laves, Die Chemie 57 (1944) 30, translated reprint Z. Kristall. 151 (1980) 21.
[2] H.J. Scheel, in: H.J. Scheel, T. Fukuda (Eds.), Crystal Growth Technology, Wiley, Chichester, UK, 2003/2004, p. 623 (Chapter 28).
[3] R. Loo, G.S. Kamath, R.C. Knechtli, in: Fourteenth IEEE Photovoltaics Spealists Conference, 1980.
[4] F.S. Chen, J.E. Geusic, S.K. Kurtz, J.C. Skinner, S.H. Wemple, J. Appl. Phys. 37 (1966) 388.
[5] H.J. Scheel, P. Guenter, in: E. Kaldis (Ed.), Crystal Growth of Electronic Materials, Elsevier, Amsterdam, 1985, p. 149 (Chapter 12).
[6] F.R.N. Nabarro, in: P.B. Hirsh (Ed.), Solution and Precipitation Hardening. The Physics of Metals, Part 2. Defects, Cambridge University Press, Cambridge, 1975, p. 152.
[7] J. Donecker, B. Lux, P. Reiche, J. Crystal Growth 166 (1996) 303.
[8] D. Rytz, H.J. Scheel, J. Crystal Growth 59 (1982) 468.
[9] J.A. Burton, R.C. Prim, W.P. Slichter, J. Chem. Phys. 21 (1953) 1987.
[10] W. Van Erk, J. Crystal Growth 57 (1982) 71.
[11] D. Mateika, in: E. Kaldis (Ed.), Current Topics in Materials Science, North-Holland/Elsevier, Amsterdam, 1984 (Chapter 12).
[12] H.J. Scheel, R.H. Swendsen, J. Crystal Growth 233 (2001) 609.
[13] W.R. Wilcox, L.D. Fullmer, J. Appl. Phys. 36 (1965) 2201.
[14] A.J. Goss, K.E. Benson, W.G. Pfann, Acta Met. 4 (1956) 332.
[15] W. Bardsley, J.S. Boulton, D.T.J. Hurle, Sol. State Electron. 5 (1962) 365.
[16] B. Cockayne, M.P. Gates, J. Mater. Sci. 2 (1967) 118.
[17] H. Wenzl, W.A. Oates, K. Mita, in: D.T.J. Hurle (Ed.), Handbook of Crystal Growth, vol. 1, Elsevier, Amsterdam 1993, p. 103 (Chapter 3).
[18] P.R. Camp, J. Appl. Phys. 25 (1954) 459.
[19] A.F. Witt, M. Lichtensteiger, H.C. Gatos, J. Electrochem. Soc. 120 (1973) 1119; 121 (1974) 787.
[20] D.T.J. Hurle, in: H.S. Peiser (Ed.), Crystal Growth, Pergamon, Oxford, 1967, p. 659.
[21] H.J. Scheel, in: H.J. Scheel, T. Fukuda (Eds.), Crystal Growth Technology, Wiley, Chichester, p. 69 (Chapter 4).
[22] D. Elwell, H.J. Scheel, Crystal Growth from High-Temperature Solutions, Academic Press, London, New York (Chapters 4, 5, 6).
[23] F.C. Frank, in: R.H. Doremus, B.W. Roberts, D. Turnbull (Eds.), Growth and Perfection of Crystals, Wiley, Chapman and Hall, New York, London, 1958, p. 411.
[24] N. Cabrera, D.A. Vermilyea, in: R.H. Doremus, B.W. Roberts, D. Turnbull (Eds.), Growth and Perfection of Crystals, Wiley, Chapman and Hall, New York, London, 1958, p. 393.
[25] M.J. Lighthill, G.B. Whitham, Proc. Roy. Soc. 229 (1955) 281.
[26] H.J. Scheel, Appl. Phys. Lett. 37 (1980) 70.
[27] A.A. Chernov, H.J. Scheel, J. Crystal Growth 149 (1995) 187.
[28] H.J. Scheel, G. Binnig, H. Rohrer, J. Crystal Growth 60 (1982) 199.
[29] A.A. Chernov, J. Crystal Growth 118 (1992) 333.
[30] A.I. Landau, Fiz. Metall. Metall. 6 (1958) 148 [193 (Russ.)].
[31] W.G. Pfann, Trans. AIME 194 (1952) 861.
[32] D. Elwell, H.J. Scheel, Crystal Growth from High-Temperature Solutions, Academic Press, London, New York, 1975 (Ch. 7).
[33] K. Nakajima, J. Crystal Growth 125 (1992) 127.
[34] T. Kusonoki, C. Takenaka, K. Nakajima, J. Crystal Growth 115 (1991) 723.
[35] W.A. Bonner, Crystallod Inc. , 25 Fourth Street, Somerville NJ 08876, USA.
[36] A. Reisman, S. Triebwasser, F. Holtzberg, J. Am. Chem. Soc. 77 (1955) 4228.
[37] W.G. Cochran, Proc. Cambridge Philos. Soc. 30 (1934) 365.
[38] J.A. Burton, E.D. Kolb, W.P. Slichter, J.D. Struthers, J. Chem. Phys. 21 (1953) 1991.
[39] W. Nernst, Z. Phys. Chem. 47 (1904) 52.
[40] H.J. Scheel, E.O. Schulz-DuBois, J. Crystal Growth 8 (1971) 304.
[41] P. Capper, C. Maxey, C. Butler, M. Grist, J. Price, Proceeding of ICCGE-14 (August 9-13, 2004), J. Crystal Growth 275 (2005); J. Crystal Growth 46 (1979) 623; 70 (1984) 356; 83 (1987) 69; 94 (1989) 959; 102 (1990) 848.
[42] P. Dutta, J. Crystal Growth 275 (2005) 106.
[43] J.B. Gunn, IBM Techn. Disc. Bull. 15 (1972) 1050.
[44] H.J. Scheel, J. Sommerauer, J. Crystal Growth 629 (1983) 291.
[45] H.J. Scheel, J. Crystal Growth 13/14 (1972) 560.
[46] E.O. Schulz-DuBois, J. Crystal Growth 12 (1972) 81.
[47] H.J. Scheel, C.H. West, J. Phys. E: Sci. Instrum. 6 (1973) 1178.
[48] J.P. Kalejs, J. Crystal Growth 44 (1978) 329.
[49] T. Fukuda, H. Hirano, J. Crystal Growth 35 (1976) 127.
[50] S. Matsumura, T. Fukuda, J. Crystal Growth 34 (1976) 350.
[51] S. Miyazawa, J. Crystal Growth 60 (1982) 331.
[52] L.I. Ivleva, Y. Kuz'minov, V.V. Osiko, N.M. Polozkov, J. Crystal Growth 82 (1987) 168.
[53] L.I. Ivleva, N.V. Bogodaev, N.M. Polozkov, V.V. Osiko, Opt. Mater. 4 (1995) 168.

[54] A.G. Ostrogorsky, G. Mueller, J. Crystal Growth 137 (1994) 64.

[55] [a] L.G. Eidelman, V.I. Goriletsky, V.A. Nemenov, V.G. Protsenko, A.V. Radkevich, Crystal Res. Technol. 20 (1985) 167.

[56] K. Terashima, T. Fukuda, J. Crystal Growth 63 (1983) 423.

[57] W.-S. Liu, M.F. Wolf, D. Elwell, R.S. Feigelson, J. Crystal Growth 82 (1987) 589.

[58] A.N. Kirgintsev, E.G. Avvakumov, Sov. Phys. Cryst. 10 (1965) 375.

[59] Y. Hayakawa, M. Kumagawa, Cryst. Res. Technol. 20 (1985) 3.

[60] G.N. Kozhemyakin, J. Crystal Growth 149 (1995) 266.

[61] N.A. Verezub, E.V. Zharikov, S.P. Kalitin, S.V. Lavrshchev, A.Z. Myaldun, Y.M. Papin, A.I. Prostomolotov, N.R. Storozhev, Crystal. Rep. 41 (1996) 1056.

[62] J.R. Carruthers, K. Nassau, J. Appl. Phys. 39 (1968) 5205.

[63] H.J. Scheel, J.T. Sielawa, in: Proceedings of International Symposium High-Purity Materials, Dresden GDR, 6–10 May 1985, p. 232.

[64] H.J. Scheel, US patent 5,471,943 (December 5, 1995).