

NOVEL GROWTH METHODS OF OPTOELECTRONIC CRYSTALS BASED ON ANTIMONIDES

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Abstract

This work contributes to the growth of bulk crystals where crystals are grown from a molten-solution zone (*MSZ*). Our original modifications of *THM* have been used for a crystallization of GaSb and of (Ga.In)Sb – the ternary Solid Solution (*TSS*). The crystallization process has been accelerated with a low frequency and low energy vibrational stirring (*VS*). Lately, the stirring has been combined with the magneto-hydrodynamical stirring (*MHD-S*) and applied on GaSb. The lattice parameter 'a' of *TSS* crystals has been constant throughout the significant part of the ingot length. This approach has permitted the growth of these crystalline ingots with 'a' a priori chosen and calculated – having the deviation from its constancy less than 0.03% (0.2 pm) with a 75 mm length. Crystals can have a mosaic structure at this stage.

Keywords: electrical and magnetic techniques, materials science/engineering, molten-solution zone refining, optical crystals, phases diagrams, semiconductors III-V, solid solutions, temperature gradient methods

Introduction

Today's need for new approaches to the growth of crystals has reflected the fact that the quality of crystals limits parameters of many devices, their wider exploitation, and new potential utilization of advanced materials.

The lower the growth temperature (with some limits), the higher the crystal quality produced. A corresponding approach is a growth from high temperature solutions, and, for bulk crystals, from a molten-solution zone (*MSZ*) [1, 2].

MSZ methods have been originated in an ingenious Pfann's 'Travelling solvent techniques', e.g. [3], which had inspired a creation of many analogical methods [4–8].

The *THM* (Travelling Heater Method) [1, 2], which belongs to the *MSZ* methods, has become up to now the most convenient one, and also has been used in the growth of bulk ternary solid solutions (*TSS*), e.g., [7, 9–12]. Bulk *TSS* crystals possessing adequate quality could significantly minimize a misfit and so could become a more improved substrate material than a binary one [10, 12].

However, *THM* has not allowed, up to now, to grow *TSS* ingots with the lattice parameter 'a' being constant throughout such an ingot length which will be acceptable for a mass production of substrates [9–12]. Moreover, *THM* is, as a rule, 'one-step-operation' method, and, therefore can be hardly used for a reliable purification.

Both disadvantages can be overcome with the combination of 'Crystallization Method Providing Composition Autocontrol in Situ' (*CAM-S*) and 'Calculation Method of Optimal Molten-Solution Composition' (*COM-S*) [6, 7].

Methods

A novel approach to the *TSS* bulk crystal growth inheres in the combination of *CAM-S/COM-S* with a low frequency and low energy vibrational stirring (*VS*). These have been applied on $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ *TSS* [6, 7, 13, 14].

The *CAM-S/COM-S* are *MSZ* methods. They belong to solution growth processes with the common disadvantage – low growth rate [9–12].

This problem has been solved by various techniques of stirring, and forced convection:

- by mechanical forces, e.g., by *VS* [6, 7, 13–17], or by ACRT [18];
- by 'field' forces, e.g., by magneto-hydrodynamical (*MHD*) forces [14, 19]. It is becoming a highly topical problem now [20].

As mentioned above and also in the next paragraph, the stirring effect has produced preliminary results which look highly promising. For *MHD* stirring - *MHD-S*, see particularly [14] and Fig. 4 in [8]. The axial magnetic field which we have used now should be DC or AC with the pulse modulation – see also Refs 13 and 14 in [14]. In future, a rotating magnetic field producing azimuthal swirl in a melt will be used. This also causes magnetic stirring, but we can expect a better impact on the growth process.

The magnetic field \vec{B}_0 induces the electric current density \vec{J} and fluid motion is governed by the electromagnetic force

$$\vec{F} = \vec{J} \times \vec{B}_0 \quad (1)$$

Such a vector product of two harmonically varying quantities contains both static and oscillating components with roughly the same order of magnitudes.

The electromagnetic forces in the melt are much smaller in the amplitude (10^{-3} times) in comparison with the bonding forces in a crystal. Nevertheless, they can favorably influence the solidification process: point defects distribution and, further, the paramagnetic resonance on some kind of crystal formation. Present theory does not exclude the use of *VS* or *MHD-S* for crystal growth, see, e.g., Refs 8 and 46 in [8]. Experimental activity has also supported it [13–17].

The force acting on a melt at the *l-s* interface can be determined by these presumptions: the electric conductivity of a liquid is much higher than that of a solid. So, the maximum of acting force is

$$F_{\text{MAX}} = \frac{I^2}{2} \frac{dL}{dx} \quad (2)$$

where *I* and *L* are the current and inductivity in the coil and *x* is the ingot axis. The real value of the dL/dx is given by a proximity relation

$$\left(\frac{dL}{dx}\right)_{\text{MAX}} \approx \frac{s}{S} \frac{4L}{l} \quad (3)$$

where *s* and *S* are cross sections of an ingot and of a coil and *l* is its length. In this case, for the laboratory apparatus, the acting force F_{max} is approximately 0.02 *N*.

The *CAM-S* principle can be explained by the basic difference between *THM* which results in the possibility of the repeated *MSZ* creation in situ and, therefore also in a zonal purification as the *MSZ* repeatedly passes through the ingot [7].

There reexist 5 variants of a *MSZ* creation in *CAM-S*, and they can be briefly explained for two principle cases on a binary or quasi-binary systems *A-B* [6, 21]:

1) One component is volatile. Suppose that it is a *B*-component (i.e. $p_B \gg p_A$, where p_B , p_A are corresponding vapor pressures). The solvent is then created by the excess of:

(a) a nonvolatile *A*-component through the evaporation of the *B*-component;
or

(b) by a volatile *B*-component through its oversaturation in the vapor phase.

2) No component is volatile, or its volatility can be neglected (the '*l-g*' decomposition is not considered). In such a case one must respect all consequences which could be introduced by an impure element in this process. The solvent then can be created in three ways:

(a) by using an 'extrinsic' volatile solvent $^{\text{ex}}B$;

(b) by using an adequate form of transport process with a (nonvolatile) ^{ex}B solvent; or

(c) by transporting, e.g., the B -component to the zone. (An open system is also possible.)

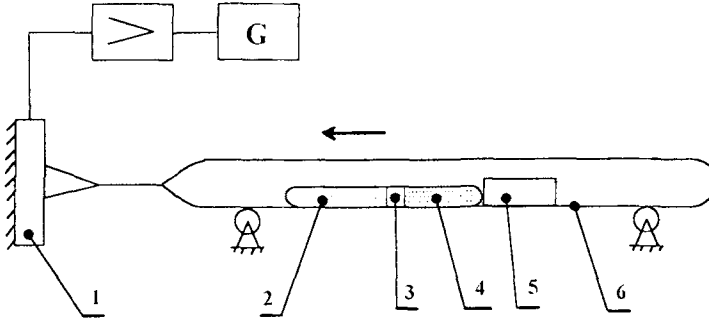


Fig. 1 The arrangement of the growth system; G = low-frequency pulse generator, (1) vibrator, (2) feed, (3) MSZ, (4) crystal, (5) 'pseudo-seed', (6) sealed ampoule. The growth direction follows arrow

The variant '2c' in a horizontal configuration [21] is illustrated by $Ga_xIn_{1-x}Sb$ in the arrangement in Fig. 1. The solvent here is 'In' [6, 7, 13, 22]. It is placed into a separate volume of, e.g., ampoule before it is sealed. The MSZ is then created in the zone. The exact amount of In is calculated by COM-S.

The COM-S principle can be explained on the calculated phase diagram (PD) in Fig. 2 [6, 23]. The excess of the component of variable composition – CVC – $(m')_B$, which is necessary to add for a MSZ creation is easy to calculate [7]. The MSZ composition follows from calculated coordinates of C^* in Fig. 2, e.g., the data in frames for a particular x are $x_{Ga, In, Sb}$ OR $x_{A, B, C}$, respectively. Let denote them x_i , so that

$$x_i = \frac{n_i}{\sum n_i + (n')_B} \quad (4)$$

where n_i mean mole numbers (concentration) of elements A, B, C and $(n')_B$ ditto of the excess of CVC. So, one of three possible equations is

$$(n')_B = v \cdot d \cdot \frac{x - 1 + 2 \cdot x_B}{B(x - 1 + 2 \cdot x_B) + (1 - x_B) \cdot [A \cdot x + B(1 - x) + C]} \quad (5)$$

where v is a volume of MSZ and d its density, A, B, C are molecular masses. Finally, the mass of CVC is

$$(m')_B = B(n')_B \quad (6)$$

Optimal *PD* data were determined on the bases of the Ga–In–Sb ternary *PD*. This *PD* was calculated with the selected values of *TD* (thermodynamic) parameters for liquid and solid phases obtained by the critical evaluation of *TD* and phase equilibrium data for the Ga–Sb [24], In–Sb [25], Ga–In [26, 27] binary and Ga–In–Sb [27] ternary systems.

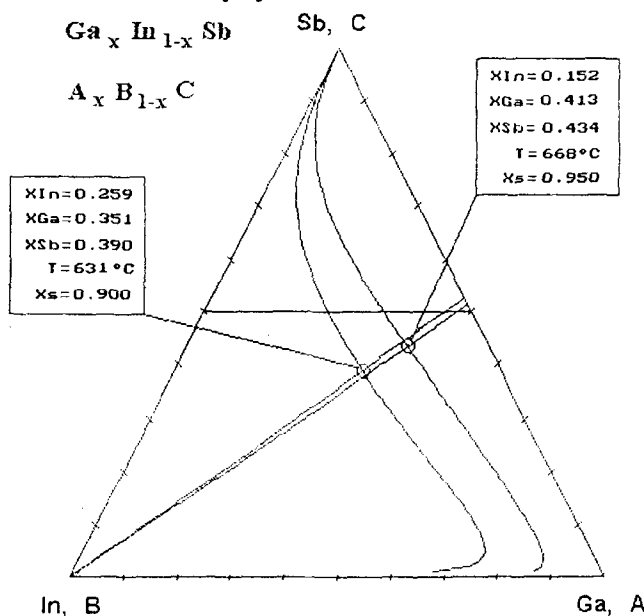


Fig. 2 The calculated *PD* using modified quasi-regular solution model for the crystal growth of $Ga_xIn_{1-x}Sb$ *TSS*. Though the model will be corrected as needed, it reasonably supplements a schematic *PD*. The B–N tie-line marks the constant ratio ($=x$) of the A/C components. Its intersection with the corresponding isoconcentration curve ($x = 0.90$) determines the point C^* . The optimal composition of the *MSZ* for a chosen 'x' is defined by its position. A concentration change of only one component that is B (In), is sufficient to reach this point which corresponds to the adequate *MSZ* composition. The existence of C^* limits the application possibility of *COMS-S*. The B-(In)- component can be called the component of a variable concentration (*CVC*). Crystallization is then reduced to the problem of a binary-like system [6, 19, 20]. The most important liquidus data for a defined *TSS*, i.e. the growth temperature and *MSZ* composition, are given in frames, e.g., for $x = 0.90$; 0.95 and 0.97

Results

The combination of *CAM-S/COM-S* with a low-frequency and low-energy *VS* has been applied to the growth of bulk $Ga_xIn_{1-x}Sb$ crystals. The last three

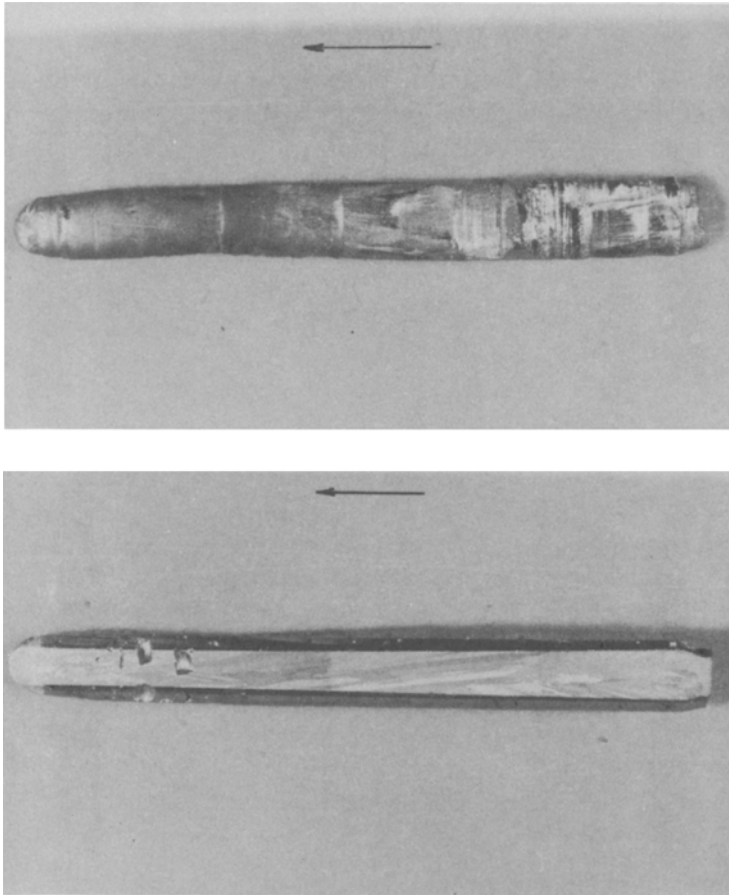


Fig. 3 Photographs of the crystalline ingot grown from a vibrationally stirred MSZ (length 125 mm): a) Ingot as first grown – arrows mark the growth direction; b) ingot after the treatment for a visualization of remarkably long lamellas. However, important control measures of this process could not be fully respected, because the accent was on these methods at this stage

TSS ingots bearing a mosaic structure and having $x \approx 0.95$, were about 125 mm long, with a cross section of 0.43 cm^2 [13] (Fig. 3a,b). The lattice parameter 'a' was measured by the Debye-Scherrer method (accuracy $\pm 0.05 \text{ pm}$) and by the 'Back Scattering Method' (accuracy $\pm 0.1 \text{ pm}$) in 6 places along the all ingots with a period of about 25 mm, which corresponds to 5 parts [6, 13]. The 'a'-values being measured on the first 4 places (corresponding to 75 mm of the ingot length) are in Table 1 and were taken into consideration here [6, 7, 13].

The maximal deviation in the 'a'-values achieved on these 4 places at the first ingot was 0.11%, whereas (after further improvements) the 'a'-values

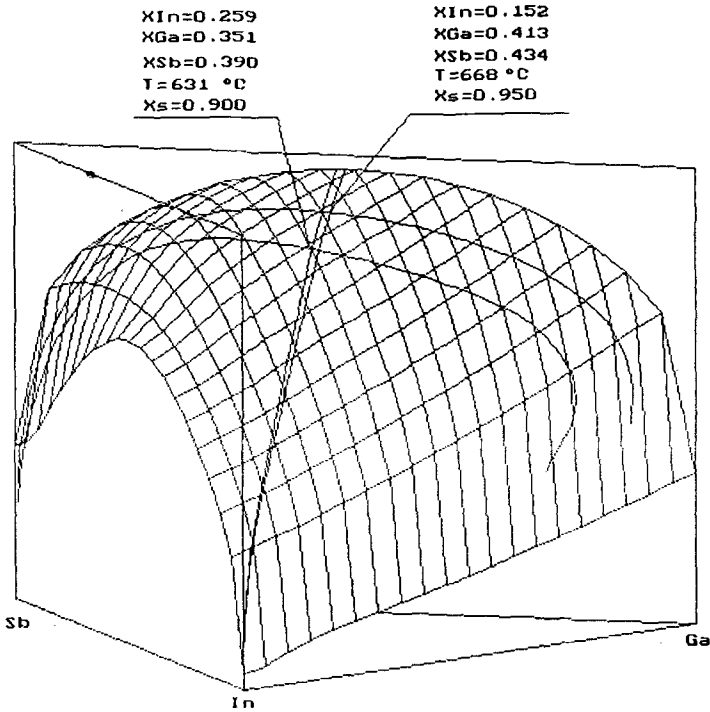


Fig. 4a The calculated PD analogically as in Fig. 2 for the TSS of $Ga_xIn_{1-x}Sb$ in the 3D representation. It illustrates cases for the two x_s composition. The rotation of the figure enables various views as needed

stayed really constant on places 1+2 and 3+4 (25 mm each) at the next two ingots. The deviation of 'a'-values between pairs of these places, i.e. the difference 2 -3 (corresponding to 25 mm), did not exceed at both ingots 0.03% (0.2 pm). (Table 1). All samples of these last two ingots were quite homogeneous.

Table 1 Lattice parameters of $Ga_xIn_{1-x}Sb$; 300K, $x \approx 0.95$

Sample number (distance) / mm	Debye-Scherrer a / nm	Back Scattering method a / nm
1D (0)	0.6113	0.6117
2D (25)	0.6113	0.6116
3D (50)	0.6111	0.6112
4D (75)	0.6111	0.6112
5D (100)	0.6107	0.6110
6D (125)	0.6120	0.6125

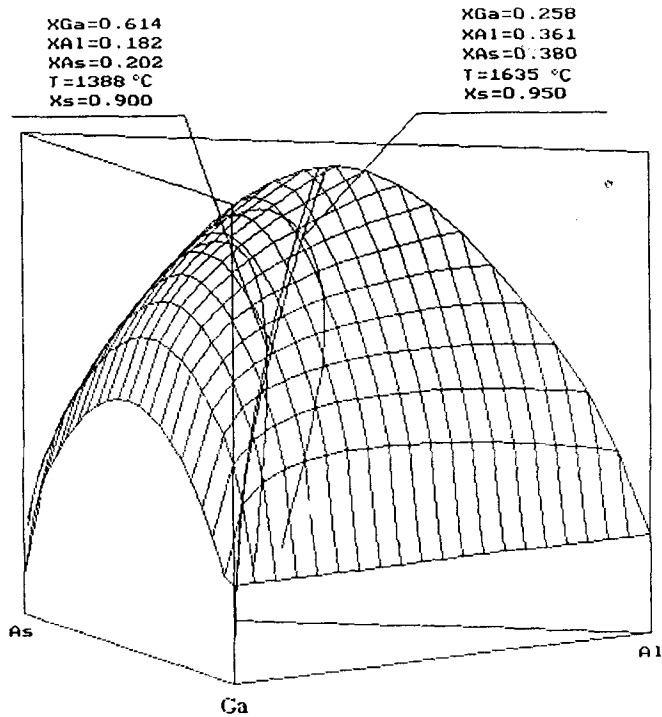


Fig. 4b 3D representation of the Al-Ga-As system for an analogical purpose as in Fig. 4a

The GaSb ingot grown by the *CAM-S* method combined with the *VS/MHD-S* can be seen in Fig. 5a,b in [8].

Discussion

The whole process was accelerated by a low-frequency and low-energy *VS*. The growth rate was 1–2 mm/h. (Macroscopic inclusions were not observed owing to specially introduced vibrations.) Though the single-crystal wasn't grown, the preliminary results are as follows: At 300K/78K: $p = 10^{22}/10^{21} \text{ m}^{-3}$; $\mu_p = 0.49/1.8 \text{ m}^2/\text{Vs}$.

These results, compared, e.g., with [9, 28], look highly promising and mark novel approach to better crystal growth.

The *CAM-S/COM-S* principle can be applied more widely, to another ternary systems, to a non-crystalline state, etc. The knowledge of a *ID* model of *PD* and the existence of C^* are necessary [6, 11, 21].

Potential application possibilities of *CAM-S/COM-S* are illustrated in Fig. 4a–d on 3D and on 2D ternary phase diagrams of several III–V and of

other systems. The $\text{Pb}_x\text{Sn}_{1-x}\text{Te}$ for $0.2 < x < 0.8$ is of particular interest, too [29]. Also those organic crystals which have been grown from solutions, and where their high purity is demanded, can be successfully treated with the *CAM-S/COM-S* techniques.

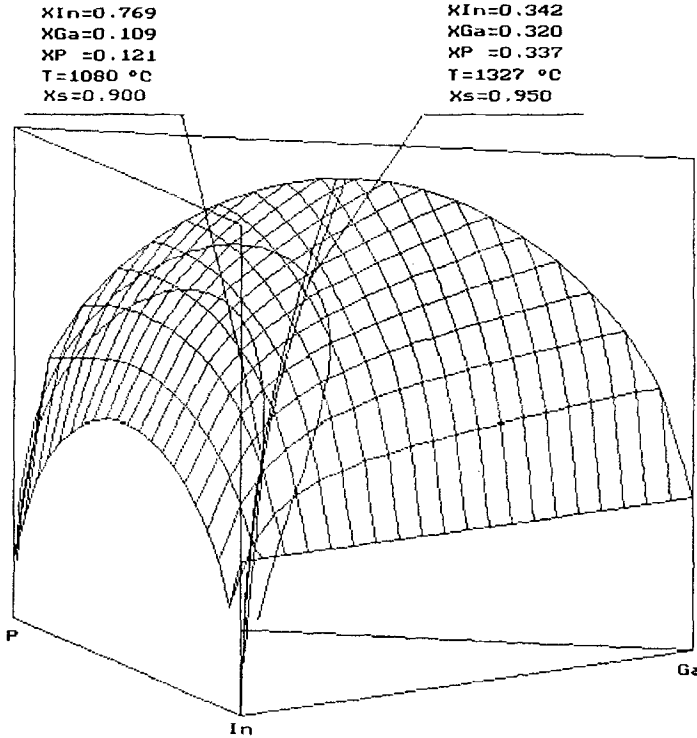


Fig. 4c 3D representation of the Ga-In-P system for an analogical purpose as in Fig. 4a

Conclusions

Both methods exhibit a wide degree of possible utility. They cover all application options of *THM*. Furthermore, they bring the possibilities of: 'in situ' operations coupled with the repeated *MSZ* creation. Moreover, all these processes can be accelerated with *VS/MHD-S*. They bring the following advantages:

- The purification process realized by the passes of the *MSZ* can be very effective, as a *MS*-segregation coefficient drops down by several orders of magnitude;
- stoichiometry control;
- stable growth of some *TSS*.

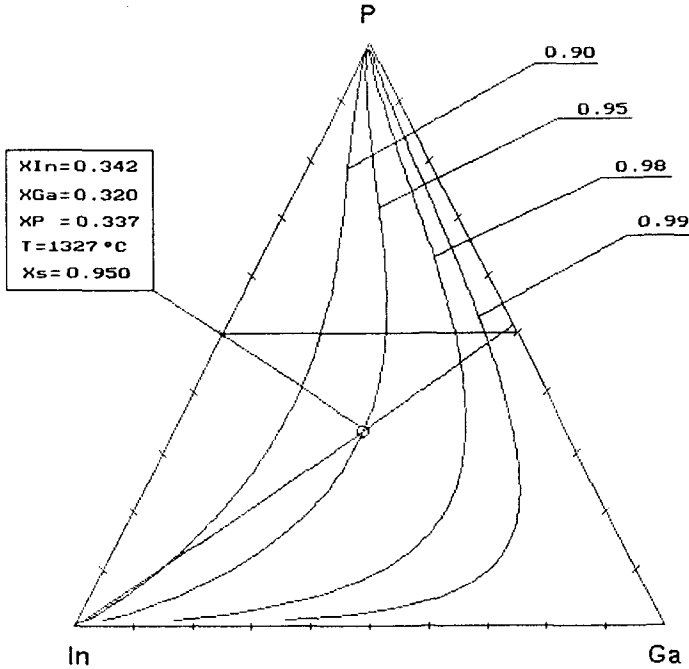


Fig. 4d 2D representation of ditto as in Fig. 4c

Though ingots can possess a mosaic structure at this stage and their characterization is modest, the remarkable constancy of 'a' having been reached is, at least on this type of *TSS*, optimum. It is caused by *TD* peculiarities of the *CAM-S/COM-S* combination.

It seems this work has contributed to one of the most successful method in crystal growth using *MSZ*:

- for a preparation/production of homogeneous bulk *TSS* crystals (of some materials with the apriori chosen and calculated composition kept constant throughout the prevailing part of the whole crystalline ingot);
- as well as for a binary one – inorganic or organic.

However, further study and improvements are required.

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Zusammenfassung — Vorliegende Arbeit ist ein Beitrag zur Züchtung von Vollkristallen, wobei die Kristalle aus einer Schmelzen-Lösungszone (MSZ) gezüchtet werden. Unsere ursprünglichen

Modifikationen von *THM* wurden zur Kristallisation von GaSb und der ternären festen Lösung (TSS) von (Ba.In)Sb benutzt. Der Kristallisationsprozeß wurde durch Vibrationsrühren niedriger Frequenz und Energie (*VS*) beschleunigt. In letzter Zeit wurde dieses Rühren mit magneto-hydrodynamischem Rühren (*MHD-S*) kombiniert und an GaSb angewendet. Der Gitterparameter 'a' des TSS-Kristalles war über den signifikanten Teil der Blocklänge konstant. Diese Methode ermöglichte die Züchtung dieser Kristallblöcke mit vorgegebenem bzw. vorberechnetem 'a' mit einer Abweichung von weniger als 0.03 % (0.2 pm) von seiner Konstanz über die Länge von 75 mm. Kristalle in diesem Stadium können eine Mosaikstruktur besitzen.