

## Crystallization method providing composition autocontrol in situ (CAM-S)

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### Abstract

A novel approach to crystal growth from a molten solution zone (MSZ) is presented. There are five variants of CAM-S, which is a modification of the travelling heater method (THM), which can solve crystal growth problems as THM does, especially synthesis, repeated creation of the MSZ, zoning operations with vibrational stirring, and perform all these operations in situ. The combination of CAM-S with calculation method of optimal molten-solution composition (COM-S) has been applied to the growth of bulk crystals of the ternary solid solutions  $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ . Extreme constancy of the lattice parameter throughout the crystalline length has been achieved. Both methods are based on the knowledge of phase diagrams.

### INTRODUCTION

This method is a modern modification of the travelling heater method (THM) [1] and is proposed to provide all essential solidification (i.e. not only crystallization) procedures in situ. These procedures include especially the following: synthesis; repeated creation of a molten-solution zone (MSZ); zoning operations with vibrational stirring (VS); consequent crystal growth (if necessary); heat treatment [2–5].

### *Principle of Method*

The CAM-S principle can be explained through its peculiarity as potential variants in forming the MSZ. (The specific phenomena relating to solidification processes, even to a crystal growth, are omitted because they are thoroughly analysed in ref. 1.) This formation depends mainly on the volatility/nonvolatility of components creating the system and on

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reliable knowledge of the phase diagram (PD). Two basic cases are considered. They can be demonstrated, for simplicity, on a hypothetical binary PD in Fig. 1 with a peritectically decomposing component  $A_{1-x}B_x$ . (Note that the appropriate formula indices are recommended for use in the more correct formal determination of the  $A_{1-x}B_x$  compound, but for further consideration the form used here is more convenient.)

(1) First case: one component is volatile. Suppose that it is a B-component (i.e.  $p_B \gg p_A$ ). The solvent is then created by the excess of: (a) a nonvolatile A-component through the evaporation of the B-component—the N–Q path for the A–B system; or (b) a volatile B'-component through its oversaturation in the vapour phase—the N–Q path for the other A'–B' system.

(2) Second case: 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 there 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)  ${}^{\text{ex}}B$  solvent; or (c) by transporting, e.g., the B-component to the zone. (An open system is also possible.)

The formation of the MSZ is presented diagrammatically in Fig. 2: (a) the reaction system arrangement, where F, Z, S and K denote feed, zone, seed and the condensation chamber, respectively; (b) the reaction

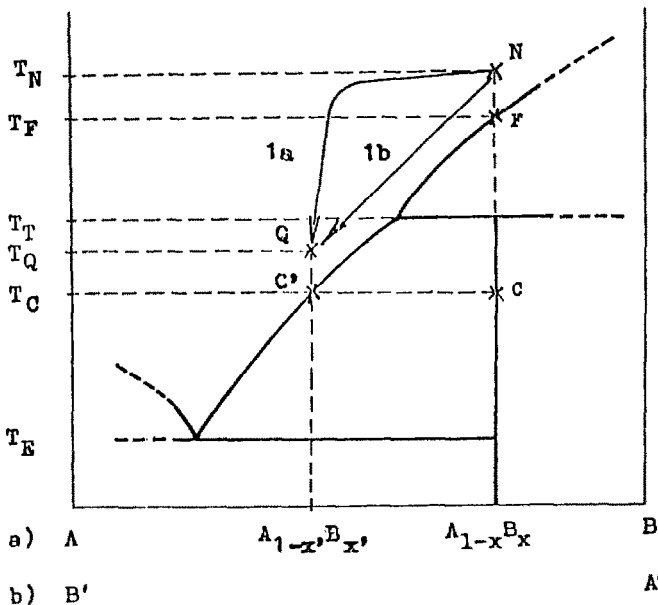


Fig. 1. Hypothetical phase diagram of a binary or quasibinary system with a peritectically decomposing compound  $A_{1-x}B_x$  grown from a MSZ of  $A_{1-x}B_x$ .

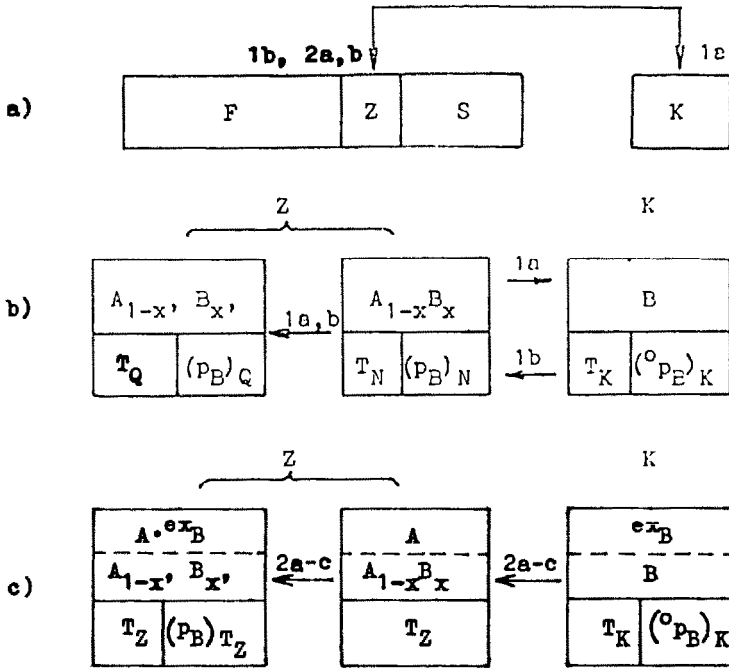


Fig. 2. Diagram of MSZ formation, where F = feed, Z = zone, S = seed, K = source chamber of a B-volatile component or of an “extrinsic” solvent  $^eB$ ,  $p_B$  = actual vapour pressure of a B-component-solvent,  $^o p_B$  = vapour pressure of a pure B-component-solvent: (a) the reaction system arrangement, (b) the reaction diagram for the 1a,b variants. (c) Ditto for 2a-c variants.

diagram for the (1a, b) variants; (c) the reaction diagram for the (2a-c) variants (“A” in the upper part symbolizes any nonvolatile substance, e.g. an element or compound).

EXPERIMENTAL

The discrete steps of the CAM-S procedures mentioned above are shown in Fig. 3: (1) synthesis, (2) creation of an ingot, (3) start of the zone refining from a melt, (4) creation of a MSZ, (5) start of the MSZ refining (which can be repeated—the last passage can enable oriented crystal growth from a MSZ), (6) heat treatment of the solid ingot; alongside is a solid alloy containing after-residues of the passed MSZ. Adequate  $T$  regimes are given in the upper part. A typical arrangement of the growth system is shown in Fig. 4.

The influence of a (partial) vapour pressure  $p_B$ , mainly in variants (1a, b), does not consist in the simple quantitative relationships alone. Its magnitude must be corrected by a coefficient  $\beta$  to include peculiarities of kinetics and stoichiometry, which play a significant role even in the molten solution (MS) growth (see, e.g., refs. 42 and 45 and Fig. 6 in [5], and also

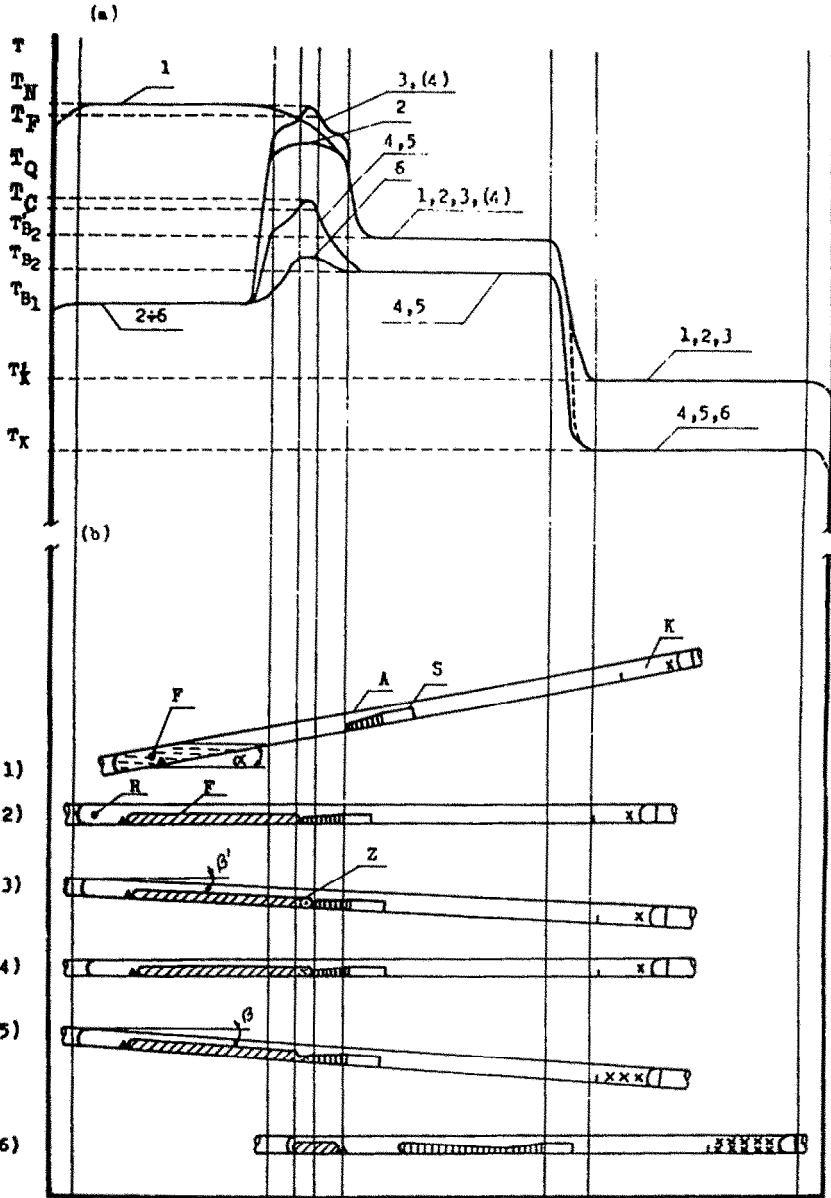


Fig. 3. The “step” diagram of CAM-S procedures: (a) the temperature profiles corresponding to discrete steps; (b) operations: 1, synthesis; 2, creation of an ingot; 3, start of the zone refining from a melt; 4, creation of a MSZ; 5, start of the MSZ refining; 6, heat treatment.

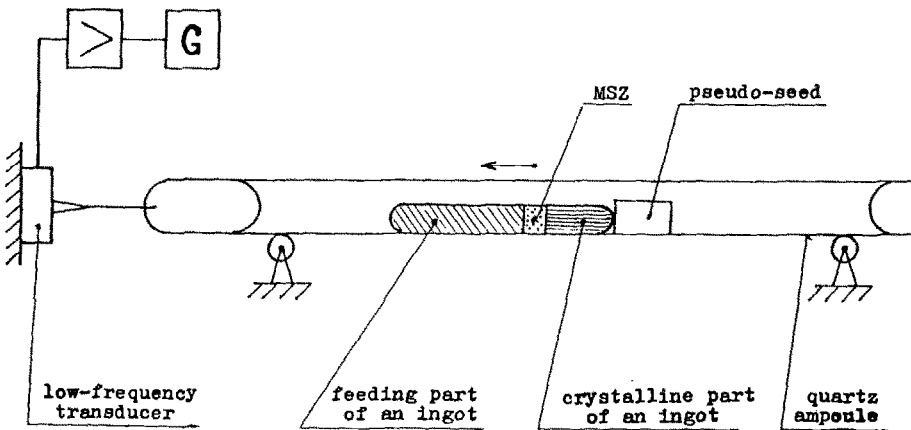


Fig. 4. The arrangement of the growth system; G = low-frequency generator.

eqns. (1)–(3) in [2]). This can be expressed as

$$[(p_B)_T]_{Q,x'} = \beta [({}_0p_B)_T]_{Q,x'} = [({}^0p_B)_T]_K$$

and  $\beta$ , given by

$$(T_Q/T_K)^{1/2} \leq \beta \leq {}_{st}p_B / {}_0p_B$$

can reach several orders of magnitude [2, 5], where  ${}_{st}p_B$ ,  ${}_0p_B$ , and  ${}^0p_B$ , denote the “stoichiometric”, equilibrium and pure element vapour pressure, respectively.

The variant (2c) can be used for the solidification (i.e. not only for crystal growth) of the ternary solid solutions (TSS). It is very profitable, for this purpose, to modify CAM-S by the calculation method of optimal molten solution composition (COM-S) [5].

The COM-S principle can be explained on the T–X–X' PD in Fig. 5 for the crystal growth of  $A_xB_{1-x}C$  TSS. (This relates to III–V semiconductors.) The optimal composition of the MSZ is defined by the position of the point  $C^*$ , the existence of which limits the application of COM-S.  $C^*$  is determined by the intersection of the isoconcentration curve and the tie-line which connects the triangle vertex with the point corresponding to “ $x_1$ ”. This tie-line marks the constant ratio ( $x_1$ ) of the A/C components. The actuality of the point  $C^*$  means that a concentration change of only one component (B) is sufficient to reach this point, which corresponds to the adequate MS composition. The B-component can be called the component of variable concentration (CVC). Crystallization is then reduced to the problem of a pseudo-binary system [4, 5].

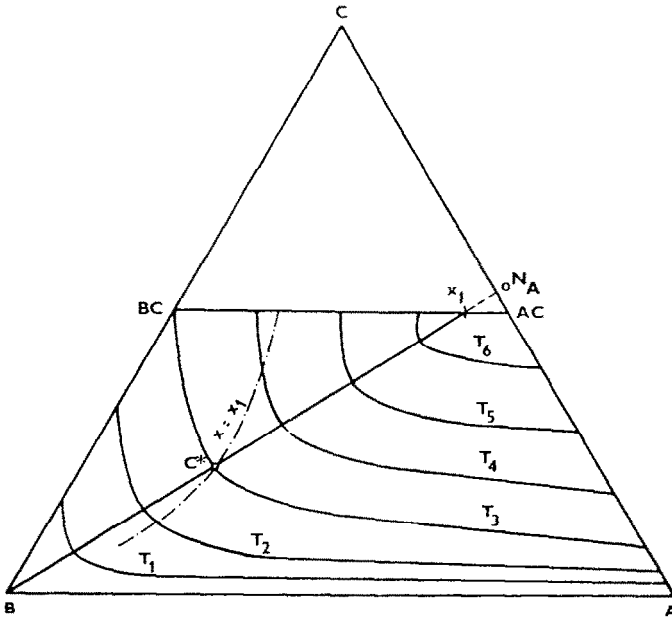


Fig. 5. Schematic concentration triangle for the ternary systems with two binary compounds as the III–V semiconductors. The tie-line marks the constant ratio ( $\approx x_1$ ) of the A/C components and intersects the isoconcentration curve at the point  $C^*$ , which can be reached by a concentration change of the B-component only.

## DISCUSSION

The COM-S principle can be applied more widely, to other ternary systems, to a non-crystalline state and so on. The knowledge of a TD (thermodynamic) model of PD and the existence of  $C^*$  are necessary [6–8].

The combination of CAM-S with COM-S and with low-frequency vibrational stirring (VS) has been applied to the growth of bulk TSS crystals of (Ga, In)Sb (see Fig. 4) [9, 10]. An extreme stability of the growth process has been reached. The lattice parameter “ $a$ ” was constant throughout the significant part of the ingot length. The deviation from constancy of “ $a$ ”, being chosen and calculated a priori, was less than 0.033% (0.2 pm) on a length of 75 mm [11–12].

These results, when compared e.g. with [13–15], look highly promising. The application of VS to crystal growth remains attractive [16, 17] because of its evident, although only potential, advantages. An attractive application of these methods can also be performed in the growth of “tunable” optoelectronic materials [18–21].

## CONCLUSION

Both methods possess a relatively large range of possible utility. They cover all application options of THM plus the possibilities of “in situ” operations coupled with repeated MSZ creation, i.e. highly effective MSZ refining (the MS segregation coefficient drops by several orders of magnitude), stoichiometry control, stable growth of some TSS, etc.

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