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THM GROWTH OF MATERIALS FOR ELECTRO-
OPTIC LIGHT MODULATORS

Fritz V. Wald, et al

Tyco Laboratories, Incorporated

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September 1972

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THE GROWTH OF MATERIALS FOR ELECTRO-OPTIC LIGHT MODULATORS

by

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Tyco Laboratories, Inc.
16 Hickory Drive
Waltham, Massachusetts 02154

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FINAL REPORT

15 July 1971 - 14 July 1972

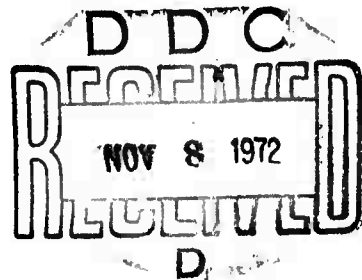
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III a

ABSTRACT

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I. SUMMARY OF OBJECTIVES

The primary goal of this work has been to develop techniques for growing single crystals of promising electrooptic materials by the Traveling Heater Method (THM). In this method, a molten solution zone is moved by an external heater through a solid ingot of the desired compound. Solution growth methods such as THM enable one to grow crystals at temperatures considerably below their melting temperature so as to circumvent difficulties with decomposition, volatilization, and solid state transformation which hinder growth from the melt.

The present contract was preceded by Contract No. F19628-70-C-0288 in which THM experiments on HgS, Ag_3AsS_3 , PbCsCl_3 , and Bi_2S_3 were conducted. Continued investigations of HgS crystal growth and THM experiments on bismuth titanium oxide and II-IV-V₂ compounds were planned for the present contract.

II. SUMMARY OF RESULTS

A few cinnabar (α HgS) crystals were obtained by a modified THM technique utilizing K_2S_4 as solvent. Single crystal boules of proustite (Ag_3AsS_3) were grown by THM from a solvent zone of composition $(Ag_2S)_{.66} (As_2S_3)_{.34}$ and also by directional solidification of a stoichiometric melt. A crystal of $Bi_{12}TiO_{20}$ was grown in one experiment from a Bi_2O_3 solvent zone; other experiments were interrupted by corrosive rupture of the crucible. Platinum suffers less reaction with molten Bi_2O_3 than alumina and may suffice as a container if its temperature is kept below $950^\circ C$.

Considerable effort was devoted to THM growth of $CdSnAs_2$ from Sn and $CdGeAs_2$ from Pb. The thermal stability and gradient in the THM arrangement were significantly improved in the course of this work, but still only coarse grained boules were achieved. Investigations of the phase relationships showed that although each ternary arsenide is the equilibrium phase to crystallize from its solvent zone, another phase (Sn_3As_2 in one case and Ge in the other case) is on the verge of crystallizing. While it was possible to maintain conditions which avoided obvious inclusions, the possibility of multiple nucleation due to very small, infrequent inclusions is not ruled out. From other observations, it was deduced that the $CdSnAs_2$ -Sn system and probably also the $CdGeAs_2$ -Pb system had some constitutional supercooling just ahead of the growth front. Also, it was observed that the twin plane of $CdGeAs_2$ roughly parallels a direction of fast crystal growth from Pb solution so that twin boundaries are abundant in the THM boules.

Consideration of the contrasting results on proustite and the II-IV-V₂ compounds suggests that ordering within the liquid can have a controlling influence on crystal growth.

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III. RESULTS

This section summarizes the work of the first three quarters of this contract period and covers more fully the heretofore unreported work of the final quarter.

A few crystals of cinnabar (α HgS) were achieved by a technique employing K_2S_4 as solvent. In this technique, the powdered HgS feed was maintained at $300^\circ C$ while the K_2S_4 solvent zone was in a region heated to $460^\circ C$. The crystals appeared to be free of inclusions but exhibited relatively low ir transmission. Attempts at hydrothermal growth of cinnabar did not develop crystals larger than 0.1 mm.

Single crystal boules of proustite [$Ag_3AsS_3 = (Ag_2S)_{.75}(As_2S_3)_{.25}$] were grown both by THM with $(Ag_2S)_{.66}(As_2S_3)_{.34}$ as solvent and by directional solidification from stoichiometric melts. The transmission curves of this material exhibit a shallow minimum near $10 \mu m$. Annealing treatments in vacuum, sulfur, and arsenic vapors have no apparent effect on the minimum, indicating that it is probably not caused by native defects.

Attempts to grow bismuth titanium oxides from a Bi_2O_3 solvent zone yielded thin plates of $Bi_4Ti_3O_{12}$ and one crystal ($\sim 150 mm^3$) of $Bi_{12}TiO_{20}$. Repeated efforts to grow more crystals demonstrated the difficulty of containing molten Bi_2O_3 . Table I describes the trials of the final quarter. The crucibles tried were sapphire (single crystal αAl_2O_3), sintered alumina, and platinum. Sapphire tended to crack from thermal stress, and all three crucible materials reacted (sometimes only locally) with the molten bismuth oxide. Platinum is probably still the most promising container if its temperature is kept low, say below $950^\circ C$. Further tests were not possible due to the exhaustion of our stock of platinum crucibles and delayed delivery of a fresh supply.

A single crystal (1-cm dia \times 4-cm long) of CdSe was grown by the Bridgman technique in a sealed ampoule. The transmittance of a 1-mm thick sample of the crystal was 66% at $2.5 \mu m$, decreasing steadily with increasing wavelength.

Table I. Growth and Quenching Experiments of the Final Quarter

Run No.	Compound	Experiment ^a	Peak Temperature ^b °C	Results
61	$\text{Bi}_{12}\text{TiO}_{20}$	Zv, Bi_2O_3	1000	Sapphire crucible cracked
63	"	"	1000	Pt crucible leaked $\gamma + \beta \text{Bi}_2\text{O}_3$ regrowth
65	"	"	945	Sapphire cracked
66	"	"	"	Sapphire etched through at one spot
69	"	"	920	Polycrystalline, alumina crucible corroded
72	"	"	945	Pt crucible corroded through at one spot
70	CdSe	DSv	1260	Single crystal
60	CdSnAs_2	Zh, Sn	532	Initial Sn_3As_2 crystal
64	"	"	447	Largest grains 2 x 2 mm
67	"	"	594	Initial Sn_3As_2 crystal
73	"	"	550	Sn_3As_2 crystal at start and at temperature flaw
77	"	", cloth ^c	520	Largest grain 3 x 3 x 2
79	"	"	430	Large Sn_3As_2 inclusions
82	"	"	600	See Fig. 2
87	"	", cloth ^c	455	Large Sn_3As_2 inclusions
59	CdGeAs_2	DSv	750	Largest grain 10 x 2 x 2 mm
62	"	DSh	700	Largest grain 10 x 3 x 2 mm
68	"	Heated in As vapor	625	As enriched layer melted
71	"	Zh, Pb	588	Largest grain 3 x 2 x 2
74	"	Zh, $\text{Pb}_{.8}\text{As}_{.2}$	465	Many Pb inclusions

Table I. (cont.)

No.	<u>Compound</u>	<u>Experiment</u> ^a	<u>Peak Temperature</u> ^b °C	<u>Results</u>
75	CdGeAs ₂	Solubility in Bi	600	15% completely dissolved GeAs + CdGeAs ₂ precipitates
76	"	Zh, Bi	550	Rough interface, GeAs inclusions
78	"	Zh, Pb	600	Ge inclusions
80	"	"	625	See Fig. 5
81	"	"	625	Ge inclusions
83	"	"	480	Rough interface, Pb inclusions
84	"	"	525	No inclusions

- a Z = Zone (THM), solvent as indicated, rate typically 4 mm/day.
 DS = Directionally solidified at 10 mm/day (v) and 60 mm/day (h).
 v = Vertical
 h = Nearly horizontal
- b Estimated peak internal temperature (see text)
- c Regrown within alumina cloth

Most of the effort of the last half of the contract period was devoted to growth of II-IV-V₂ compounds: CdGeAs₂, CdSnAs₂, ZnSnAs₂ and CdGeP₂, with particular emphasis on the first two. Synthesis techniques have been described in our last report.

In general, the crystal growth attempts yielded cracked polycrystalline boules of the intended chalcopyrite structure. We found no clear evidence of any solid state transformation of CdGeAs₂ or CdSnAs₂ which might explain the cracking. Many growth runs utilized carbon films on the inner ampoule wall to avoid stresses in the boule from adherence to the ampoule wall. In addition, two runs were made with an alumina cloth between the boule and ampoule wall. The persistence of the cracks in all these cases indicates that the cracks are caused by internal stresses such as could be caused by anisotropic thermal contraction of the chalcopyrite grains. Such stresses would be avoided if single crystal boules were grown. With this in mind, attention was focussed on improving conditions for single crystal growth.

Recognized deterrents to crystal growth include constitutional supercooling, fluctuations in growth rate from inadequate temperature or motion control, and spurious nucleation at second-phase inclusions or the container walls. During the third quarter of this contract, the THM arrangement was substantially modified to maintain a more constant solvent zone temperature. This was accomplished by effectively extending the length of the ampoule charge about threefold so that both ends could be water cooled throughout a THM run. This change approximately doubled the thermal gradients within test ampoules and substantially reduced the dependence of the zone temperature on ampoule position. In addition, the ampoule was supported nearly horizontally and was slowly rotated about its axis during the run, both to stir the solvent zone and to maintain a more axially symmetric thermal distribution.

Two other improvements were made during the final quarter: development of a flat interface and better temperature control. The interface shape was controlled simply by adjusting the length of the solvent zone. Fig. 1 illustrates a convex growth interface* for a solvent zone length about half the ampoule diameter, and Fig. 2 shows a planar interface for a zone length about 1.2 times the ampoule diameter.

To improve the temperature control, it was first necessary to eliminate the large ac component of the control couple signal. The heater design of the third quarter

* "Convex" refers to the shape of the solid surface.

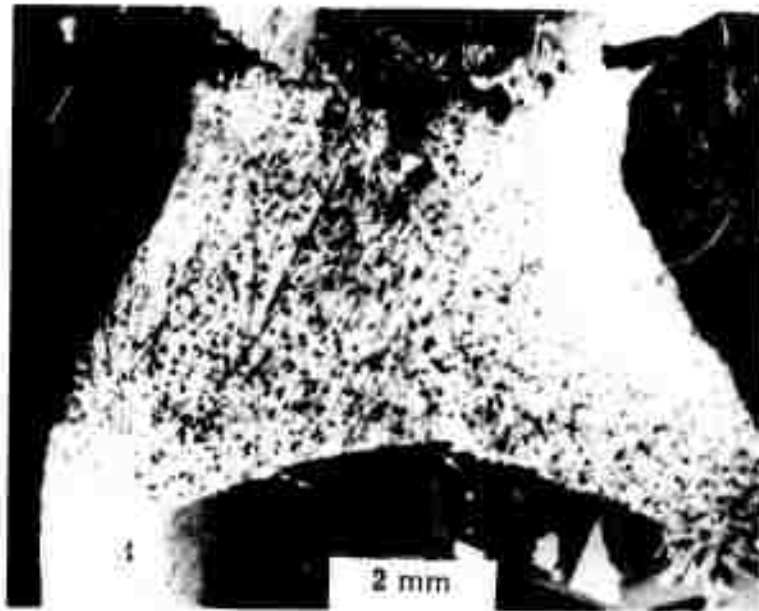
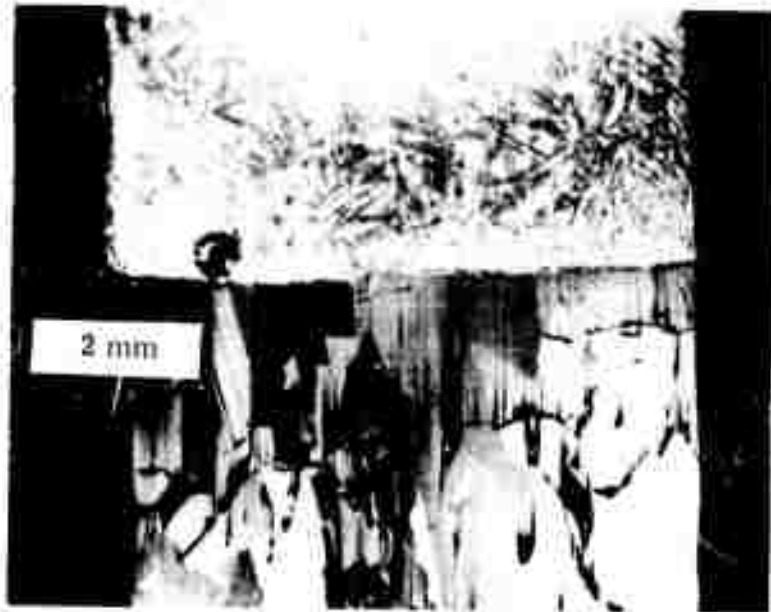


Fig. 1. The quenched solvent zone of Run 58. CdSnAs_2 feed is at the top and regrowth is at the bottom of this figure. The solvent is Sn. Note the convex shape of growth interface



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Fig. 2. Quenched solvent zone of Run 82 showing planar growth interface. Regrown CdSnAs_2 is on the bottom and Sn base solvent zone is at the top

utilized a nickel ring between the ampoule and heating coil. Prior to use, the ring was heated in air to oxidize the surface for electrical insulation. The control couple was imbedded in a hole in the nickel ring. This design had the disadvantage that slight leakage of the NiO insulating film impressed sizable ac signals on the control couple which tended to saturate the deviation amplifier. In the final quarter, a new furnace was constructed without the Ni ring. The control action was adjusted to hold the temperature deviation of a thermocouple near the heater within 0.1°C throughout a THM run.

In spite of these substantial improvements in short and long-term temperature control, temperature gradient, and interface shape, the THM runs (Table I) continued to yield polycrystalline boules. Therefore, in the final weeks of the contract, a few phase equilibrium studies were made to clarify the growth difficulties of CdSnAs_2 and CdGeAs_2 .

Before presenting these results, it is worth reviewing the techniques used to determine the solvent zone temperatures given in Table I. The primary technique was to calibrate each THM furnace with a thermocouple immersed in a Pb or Bi zone between the usual iron rods so as to simulate, as closely as possible, the geometry and the conductivity of a typical THM ampoule. These calibrations were checked on a few occasions by differential thermal analysis (DTA) of quenched solvent zones to determine their solution temperature. Such tests agreed within 10°C with the simulated ampoule calibrations. In view of the crudeness of these measurements, such agreement may be partly fortuitous. An uncertainty of $\pm 20^{\circ}\text{C}$ is perhaps more realistic for the data in Table I.

The following two subsections describe the phase equilibrium studies on the two chalcopyrites of primary focus.

A. CdSnAs_2

Figs. 1 and 2 reveal some long precipitates in the quenched tin solution zone. Fig. 3 shows this structure at higher magnification. By selective etching, some of the long precipitates were removed for X-ray identification. The phase is Sn_3As_2 and occurs as thin sheets, sometimes over 1 mm in width and ~ 0.1 mm thick. In Fig. 3, fine polygonal precipitates of a darker phase are evident on the surface of the Sn_3As_2 plates. These small precipitates are probably Cd_3As_2 , as suggested by their color and the fact that they are softer than CdSnAs_2 . In addition to these two abundant precipitate forms, there are occasional spherical precipitates of fine-grained CdSnAs_2

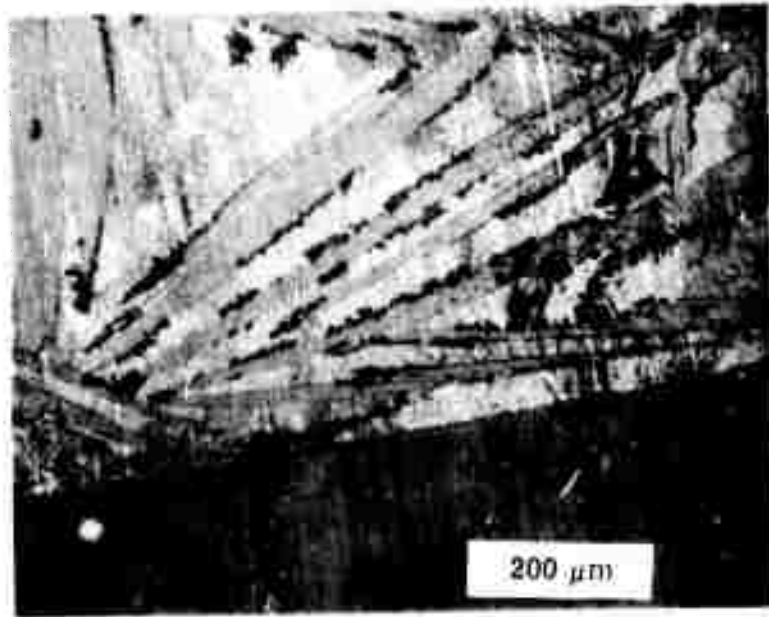


Fig. 3. Enlarged view of growth interface and solvent precipitates of Fig. 2. Regrown CdSnAs_2 is at the bottom of the figure

in quenched solutions such as Fig. 3. The same three phases and morphology have been observed in all quenched THM zones (Runs 79, 82, 87) and in solutions of 10, 15, and 20 mole % CdSnAs_2 in Sn quenched from 510°C . In the three latter cases, primary crystals of CdSnAs_2 were not evident; the Sn_3As_2 plates occupied respectively about 30, 40, and 50% of the volume; and the dark precipitates, tentatively identified as Cd_3As_2 , became progressively larger as the solution became more concentrated. DTA records of a 20 mole % solution of CdSnAs_2 in Sn reveal only one major thermal arrest at about 530°C (cooling rate $2^\circ\text{C}/\text{min}$). Subsequent microscopic examination shows large precipitates of both CdSnAs_2 and Sn_3As_2 , with the former apparently forming first.

These various observations show that the crystallization products of Sn- CdSnAs_2 solutions depend on the cooling rate. At high cooling rates the solution decomposes along tie lines to Sn_3As_2 ; when the liquid composition reaches a eutectic trough in the liquidus surface, the small Cd_3As_2 precipitates also appear. At slow cooling rates (particularly the very slow rate employed in THM), the solution decomposes along tie lines to CdSnAs_2 . The Sn- CdSnAs_2 liquidus passes through 530°C at 20% CdSnAs_2 .

Small inclusions of Sn_3As_2 rarely occur in the CdSnAs_2 boules, but large inclusions occupying the full diameter of the boule frequently occur at the beginning of regrowth* and sometimes also later in the run. In the latter cases, the initiation of the inclusion usually correlated with a known temperature flaw during the run. Interestingly, such inclusions continued to grow several hours after temperature control was restored, which further demonstrates the large kinetic differences between the crystallization processes of Sn_3As_2 and CdSnAs_2 .

Reexamination of the final boule of the previous quarter (Run 58) established (by hardness measurements) that what was originally thought to be a large grain of CdSnAs_2 is, in fact, a grain of Sn_3As_2 . This leaves the maximum crystal dimension of CdSnAs_2 achieved by THM as only about 3 mm.

Detailed examination of the growth interfaces of the quenched THM runs (e.g., Fig. 3) reveals a boundary layer about $25\ \mu\text{m}$ thick separating the CdSnAs_2 front from the Sn_3As_2 precipitates. Evidently the arsenic concentration in this region is below that for equilibrium with Sn_3As_2 but still at or above the concentration in equilibrium

* Sn_3As_2 adheres to the iron, whereas CdSnAs_2 does not adhere. This difference may cause the initial preference for Sn_3As_2 nucleation.

with CdSnAs_2 . This conclusion is consistent, with CdSnAs_2 being the more thermodynamically stable phase in equilibrium with the tin solution. Taking $25 \mu\text{m}$ as the width of the diffusion zone ahead of the growth front and an arsenic diffusivity in liquid tin of the order of $10^{-5} \text{ cm}^2/\text{sec}$, we compute that an arsenic concentration difference across this zone of ~ 0.006 mole % will provide the flux necessary for the imposed growth rate. (In comparison, the volume fraction of Sn_3As_2 in the quenched solvent zone indicates that the total arsenic concentration initially in solution is perhaps ~ 14 mole %.)

Knowledge of the concentration and temperature gradients in the diffusion zone permits an estimate of the possibility of constitutional supercooling. The above figures indicate an arsenic concentration gradient of ~ 0.2 mole fraction/cm and corresponding gradient of CdSnAs_2 content $\partial c/\partial z \sim 0.3$ mole fraction/cm. The temperature profile measured with the simulated ampoule determines a gradient $\partial T/\partial z \sim 65^\circ/\text{cm}$ at a position corresponding to the growth interface. To avoid supercooling conditions, one therefore must operate the THM growth in a c, T regime where the slope of the liquidus $\partial T/\partial c < 220^\circ/\text{mole fraction CdSnAs}_2$. The detailed shape of the liquidus of the Sn - CdSnAs_2 pseudobinary section has not been determined; but assuming a reasonable shape (comparable to that of the Sn-ZnSnAs₂ liquidus¹), we expect the avoidance of constitutional supercooling for solutions more concentrated than $\sim 40\%$ CdSnAs_2 . Only the highest temperature THM runs on this compound may approach this condition. However, since there was no apparent improvement in these runs, it is plausible that they also were limited by constitutional supercooling. Still higher temperatures and slower growth speeds are necessary to clearly assess the importance of constitutional supercooling in such solution growth experiments on CdSnAs_2 .

The growth difficulty also may be related to the metastable decomposition along Sn_3As_2 tie lines. It is difficult to rule out the possibility that very small and infrequent precipitates of Sn_3As_2 do indeed form and help to nucleate new grains of CdSnAs_2 at the growth front. In seeking solvents which may avoid such difficulty, one must consider all the competing compounds in the system. The following table shows the close proximity of the reported "melting points" of the various compounds in the Cd-Sn-As system.

<u>Compound</u>	<u>CdSnAs_2</u>	<u>Cd_3As_2</u>	<u>CdAs_2</u>	<u>Sn_3As_2</u>	<u>SnAs</u>
"Melting Point" ($^\circ\text{C}$)	595	721	621	578-596	588-605

Any solvent which is to avoid decomposition ambiguities must effectively depress the virtual liquidus* surfaces of all the binary arsenides relative to that of the desired ternary arsenide.

B. CdGeAs₂

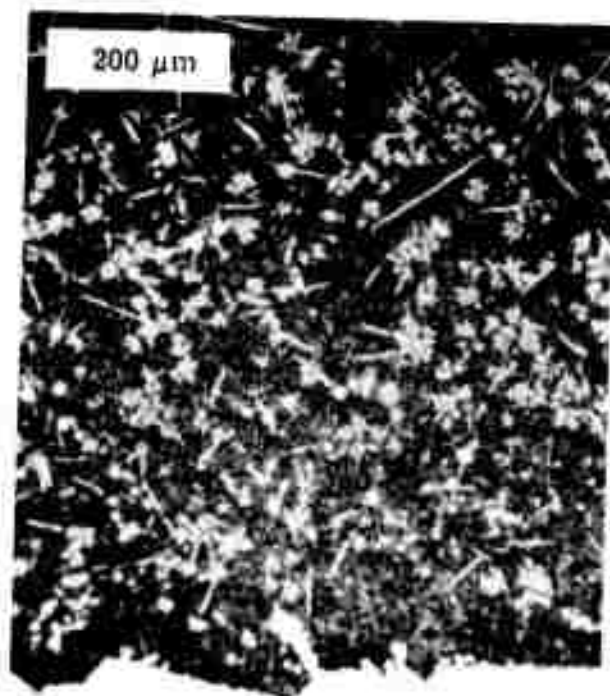
The THM boules of CdGeAs₂ were generally free of inclusions, except for those grown at $\geq 600^\circ\text{C}$ where Ge inclusions appeared. Fig. 5 shows the microstructure of Run 80 quenched from growth at $\sim 625^\circ\text{C}$. The finger-like grains protruding into the solvent zone from the regrown CdGeAs₂ are identified by microprobe analysis as Ge. Microhardness measurements have identified occasional Ge grains in the other high temperature THM runs. At somewhat lower temperatures, the quenched solvent zone contains Ge precipitates whose surfaces are covered by small grains of CdGeAs₂. At still lower zone temperatures, the non-active (non-CdGeAs₂) precipitates (the globular precipitates of Fig. 4) were not specifically identified, but their morphology suggests that they also were Ge.

To further define the phase relations, a series of Pb-based solutions containing 5, 10, 15, and 20% CdGeAs₂ were used for DTA and solubility tests. The DTA cooling curve of the 20% solution clearly indicates two primary processes at about 598 and 573°C (cooling rate 4°/min). The 15% solution shows a broad unresolved peak initiated at about 580°C and, similarly, the 10% solution shows one at 563°C. Fig. 6 shows the primary crystals in the 15% solution after solution treating at 620°C, soaking 24 hr at 512°C and quenching. The large central grain in each precipitate is Ge and the peripheral grains are CdGeAs₂. Similar crystals occurred in the 10 and 20% solutions, whereas primary crystals were not seen in the 5% solution.

These results suggest a situation somewhat similar to that encountered with CdSnAs₂-Sn. Germanium nucleates more readily than CdGeAs₂ from Pb solution and has a virtual liquidus approaching that of CdGeAs₂ at $\sim 625^\circ\text{C}$. Fig. 7 suggests a possible phase diagram. Regardless of the details it is certain that at the very slow cooling rates of the THM runs, the solutions predominantly decomposed along tie lines to CdGeAs₂.

There is no indication of the diffusion boundary layer in the quenched THM zones of this system. Nevertheless we expect properties similar to those of CdSnAs₂

* The "virtual liquidus" is simply the solubility limit of the designated crystalline phase in supercooled liquid.




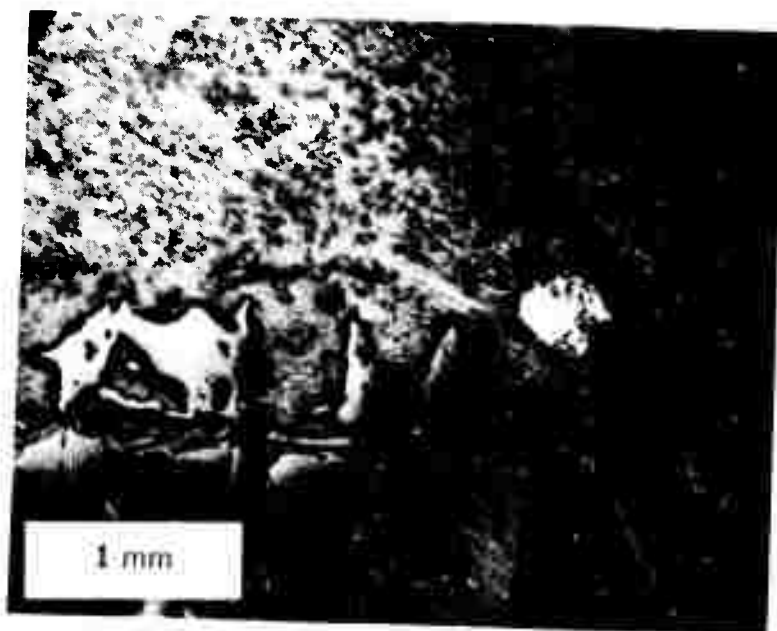
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Fig. 4. Quenched solvent zone of Run 81 (CdGeAs_2 - Pb). Note rough growth front and precipitates in solvent zone




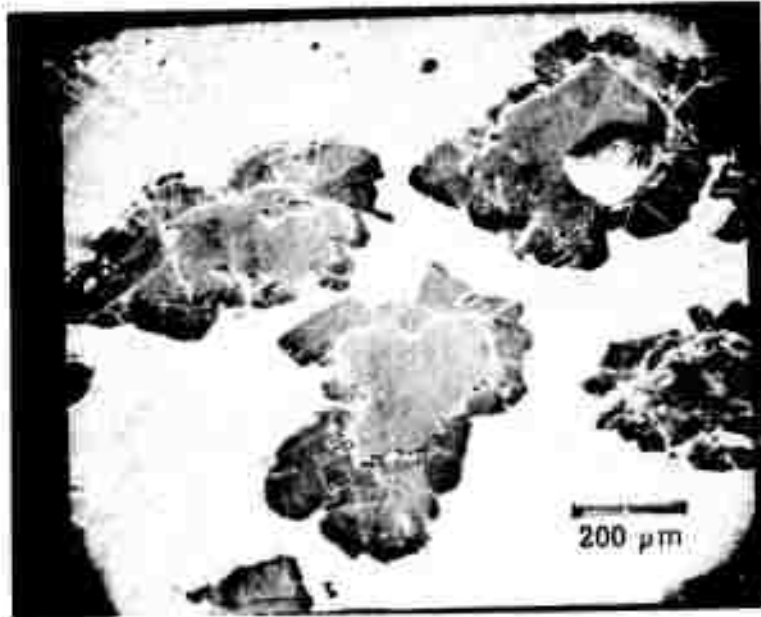
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Fig. 5. Quenched growth interface of Run 80 (CdGeAs_2 - Pb). The crystals protruding into the solvent from the CdGeAs_2 growth front were identified by electron microprobe as essentially pure germanium



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Fig. 6. Primary crystals in a mixture of 15 mole % CdGeAs_2 in Pb soaked 24 hr at 512°C . The central grain of each cluster is Ge and the peripheral grains are CdGeAs_2

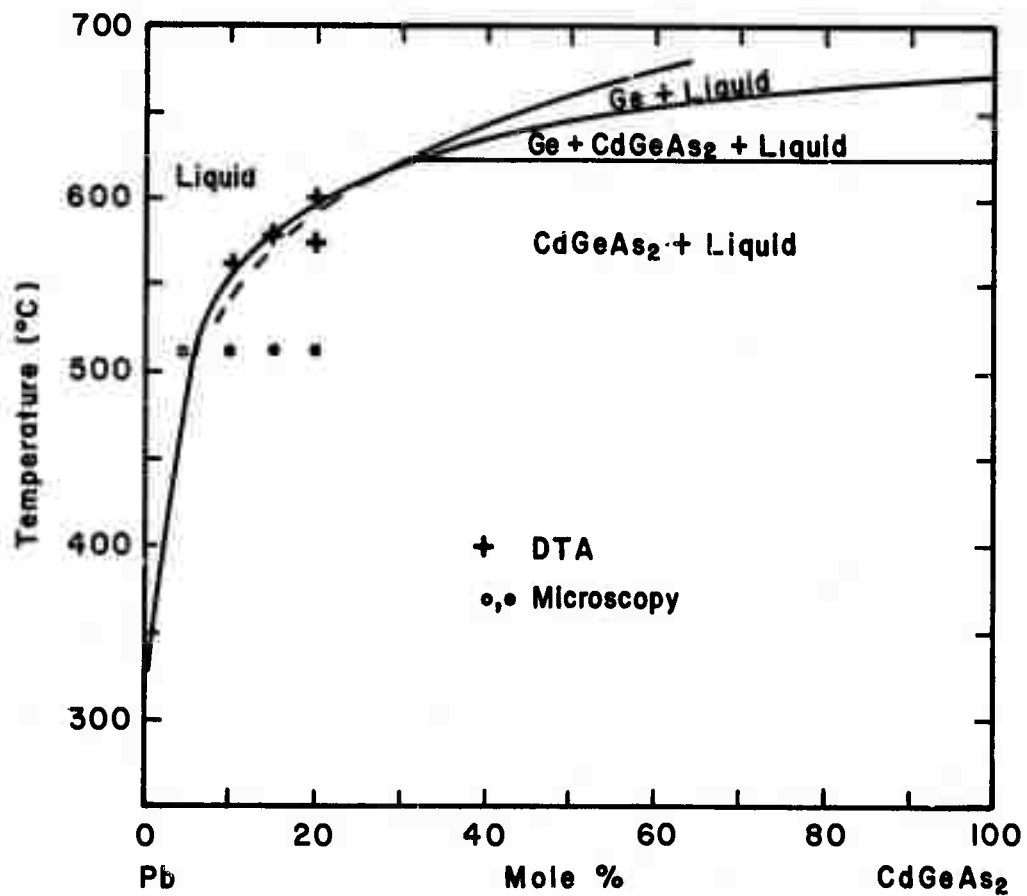


Fig. 7. Section of the quaternary phase diagram as suggested by our few DTA, quenching, and THM studies

so that constitutional supercooling also seems likely for CdGeAs_2 . The intrusion of Ge crystallization precludes attempts to avoid supercooling by higher temperature THM.

Other solvents have not been extensively investigated. With Bi we find GeAs inclusions in a THM growth at 550°C . One run with CdAs_2 as solvent gave polycrystalline regrowth similar to that of the Pb runs. Sn is not a suitable solvent because it substitutes for Ge in the compound. Gallium fails to have sufficient solubility for THM of CdGeAs_2 . A eutectic solution of Au and Ge might be worth investigating as a solvent because it at least should avoid the difficulty of Ge precipitation.

The twinning tendency and growth habit also contribute to the difficulty of single crystal growth of CdGeAs_2 . From studies of the reflected colors under crossed polarizers, we conclude that the twin boundaries are symmetric twist boundaries. The twist axis appears to be normal to the crystalline optic axis and the twin plane is at some angle between 36 and 48° from the optic axis. The lowest index plane fitting these observations is, of course, (110) . Precipitates of CdGeAs_2 formed in quenched solutions consist of crystallites growing radially from a common nucleating point (spherulitic growth). Often the radial arms have central twin boundaries. This twinned growth habit accounts for the abundance of twin boundaries in the THM boules. The precipitates also show greater twinning and faceting the lower the quenching temperature. Whether this results from temperature or growth rate dependence of the morphology is not established.

To summarize, we have identified various impediments to solution growth of CdGeAs_2 crystals: constitutional supercooling, lack of a solvent with a pseudobinary phase relationship, and twinned growth habit. The ease of cracking this material practically eliminates hope of cutting useful-sized crystals from polycrystalline boules. Since the chalcopyrite phase of CdGeAs_2 seems to crystallize directly from the melt, melt growth experiments are worth pursuing. In addition, the observation that the growth anisotropy may increase with decreasing growth temperature encourages further efforts on solution growth of specific orientations.

IV. CONCLUDING REMARKS ON CRYSTAL GROWTH

It is instructive to compare the contrasting experience in crystal growth of proustite and the II-IV-V₂ compounds. Both materials are ternary, covalently-bonded compounds containing volatile components for which one might expect similar growth difficulties, morphologies, and processes at the liquid solid interface. Proustite crystals are easily grown, whereas crystals of the II-IV-V₂ compounds which we have studied are difficult to grow.

Two points seem worth making in this comparison. First, for THM growth, knowledge of the phase diagram is almost a prerequisite to choice of solvent and successful growth. Prior to our work on proustite, Wehmeier, et al.² had published information on the Ag₂S-As₂S₃ join (which includes proustite) and Roland and Seidensticker³ had shown all the phase relations in the vicinity of proustite in the ternary Ag-As-S system. In particular, the latter work showed that a slight excess of sulfur results in co-precipitation of Ag₇AsS₆ with proustite (Ag₃AsS₃) during crystal growth. Earlier work of Bardsley and Jones⁴ determined limits on temperature gradient, growth speed, and deviation from stoichiometry which separated cellular from single crystal growth. For instance, they found that for a temperature gradient of 60°/cm and growth rate of 4 mm/day, single crystal growth could be achieved from melts deviating from the (Ag₂S)_{.75}(As₂S₃)_{.25} stoichiometry of proustite by ±7 mole percent As₂S₃. Our successful THM growths with the same growth rate, about half the temperature gradient, and +9 mole percent deviation of the stoichiometry extend, somewhat, the limits suggested by Bardsley and Jones. In any case, it is clear that considerable information on phase relations and growth limitations was available to us for planning the THM experiments.

In comparison, the THM experiments on CdSnAs₂ and CdGeAs₂ were considerably hampered by lack of phase diagram information. The liquidus surface of the Cd-Sn-As system to our knowledge has not been determined. The liquidus of the Cd-Ge-As system has been published,⁵ but information on the quaternaries of these

elements with Pb, Bi, or Sn was completely unknown prior to the THM experiments. Perhaps the lesson here to the crystal growers is that one should either attempt solution growth within known ternary systems or plan to determine the necessary phase diagram information prior to solution growth experiments.

The other point to be made in comparing crystal growth experiences on proustite and the II-IV-V₂ compounds derives from the fact that only the former could be grown by the Bridgman technique. Comparing the curvatures of the liquidus surfaces^{2, 3, 5} of Ag₃AsS₃ and CdGeAs₂, we find distinctly greater curvatures for the former compound. This signifies more negative deviation from ideality, i.e., more molecularly bonded solution, for molten proustite than for molten CdGeAs₂ in qualitative accord with their relative growth difficulties.

For solution growth, a strongly curved liquidus causes high liquidus slopes $\partial T/\partial c$ which would seem to make constitutional supercooling more of a problem. On the other hand, the molecular clustering presumably accompanying such curvature may limit supercooling. Certainly, if our growth conditions for CdSnAs₂-Sn allowed constitutional supercooling as the experiments have suggested, supercooling would be even more prevalent in the proustite experiments (less gradient, greater $\partial T/\partial c$). Since, in fact, the THM growth of proustite was evidently not hindered by constitutional supercooling, some factor like clustering in the liquid must have had a controlling influence on the growth process. Further cataloguing of supercooling conditions, liquidus curvatures, and crystal yields in other systems would help to define the interplay between clustering and supercooling effects during solidification.

V. REFERENCES

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