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ELECTRO-OPTIC LIGHT MODULATOR MATERIAL BY THM

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I. SUMMARY OF OBJECTIVES

Due to some encouraging results in growing cinnabar by THM, some effort will be continued in this area. It was found that a modified THM-vapor transport method has produced a light-transparent crystal ~1.5 cm long and 0.5 cm in cross section. Based on this result, another run is under way to see if this technique is reproducible. The hydrothermal growth of cinnabar has been started and will be continued for 2-3 months depending on how well the pressure vessel holds up.

The synthesis and THM growth of the $A^{II} B^{IV} C_2^{V}$ compounds will be continued. So far, initial experiments have indicated the possibility of growing $CdGeAs_2$ by THM using Sn/Ge mixtures and particularly Pb as solvents. Experiments with $ZnSiP_2$ have had little success so far. Presently attempts to synthesize $CdGeP_2$ are underway. A concentrated effort will be maintained toward perfecting the THM growth of $CdGeAs_2$ and synthesizing $CdGeP_2$. Once the synthesizing methods have been developed, growth by THM will follow.

Work on the growth of $Bi_4Ti_3O_{12}$ is going on presently. It is hoped that a solution to the problems of growing this material by THM will be found. The present difficulties are of an experimental nature, namely:

1. To obtain a durable furnace which can run at a sustained temperature of from 1100°C - 1150°C for 2 weeks without failure.

2. Find a substitute crucible to replace the expensive Pt crucibles which have been used.

Experiments indicate that sapphire tubes, produced at the Saphikon Division of Tyco Laboratories, make suitable molds to precast the mixed Bi_2O_3 and TiO_2 powders into solid rods of feed material and may also be able to serve as crucibles for crystal growth.

II. SUMMARY OF SCIENTIFIC WORK*

During this second quarter, some work was continued on HgS (cinnabar) and a moderate effort was made towards $Bi_4Ti_3O_{12}$. Very little time was spent on proustite (Ag_3AsS_3), and most of the effort was on the synthesis and THM growth of the II IV V_2 compounds, in particular, $CdGeAs_2$, $ZnSiP_2$ and $CdGeP_2$.

A modified THM method was employed in the regrowth of HgS. It is a combination of THM and vapor transport. A two-zone furnace was used instead of the usual single-zone arrangement normally used in THM. The method will be discussed further in Section IV. The results were the best we have yet obtained. A transparent crystal ~1.5 cm long with 0.5 cm cross section was one of a cluster of three obtained. Further work will determine the reproducibility of this method.

An experiment has been started employing the hydrothermal method to grow HgS using a new stainless steel pressure vessel internally coated with Teflon. The experiment has been running for several weeks so far without any leakage developing. It will be continued for at least 2 months. The vessel has a capacity of ~500 cc. A Teflon support for the seed extends from the bottom of the vessel almost to the top. The three seeds (two HgS and one CdS) are held in the upper third of the vessel by holes drilled into the Teflon rod (see Fig. 1). At the base of the seed support, ~20 g (three vapor grown rods) of HgS are placed to serve as feed material. A gradient of ~50 °C has been obtained by heating only the lower third of the outside of the vessel. The average temperature in the vessel is ~ 200 °C. Temperatures much higher than 200 °C tend to degenerate the Teflon lining.

Further attempts were made to grow $Bi_2Ti_3O_{12}$ by THM but without satisfactory success. Only very polycrystalline material was produced. A problem with the solvent vaporizing out of the crucible and reacting with the exposed heating

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*All crystal growth runs are summarized in Table I.

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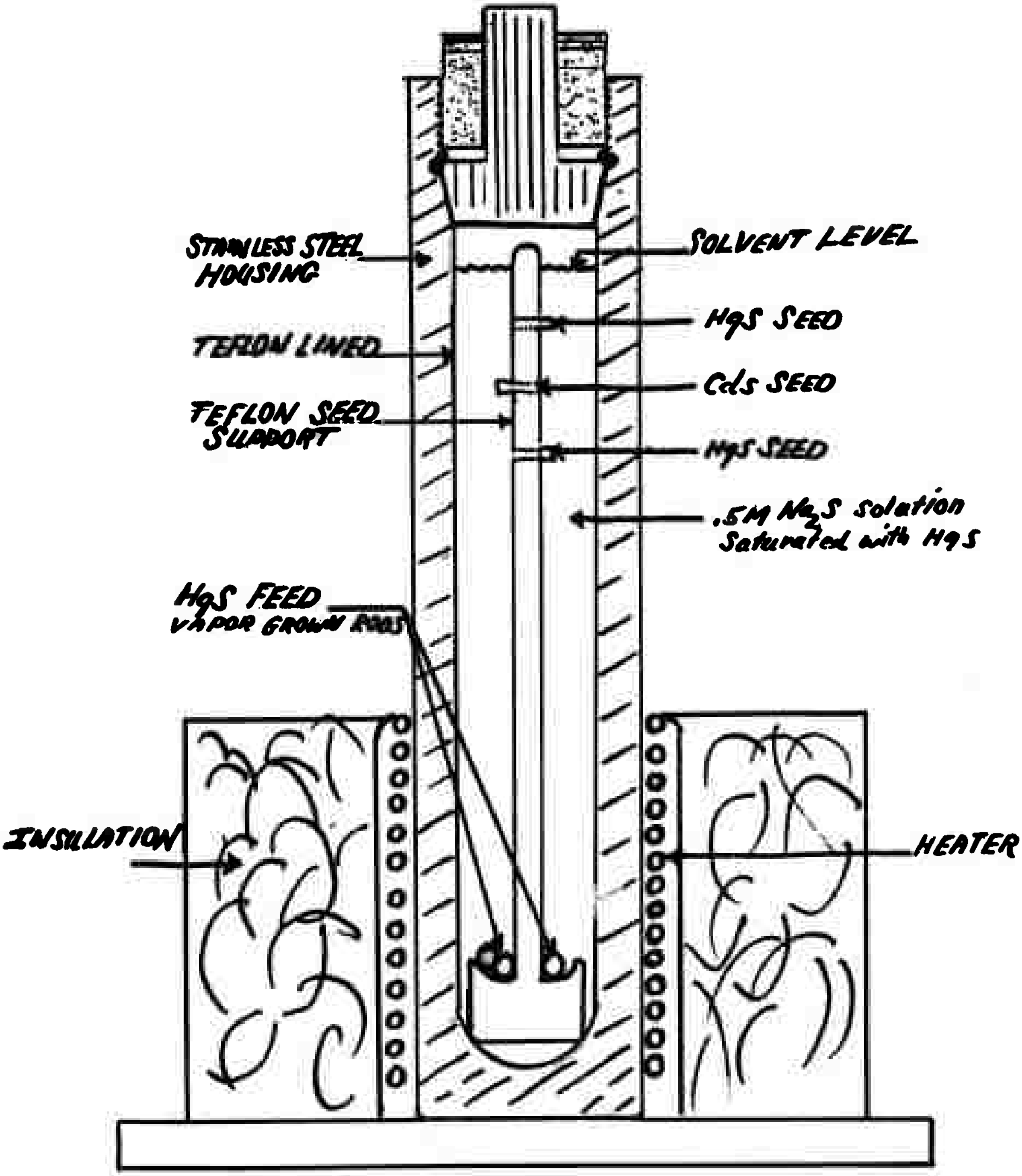

Fig. 1. Hydrothermal growth setup (1/3 actual size)

Table 1. Crystal Growth Runs by THM (Second Quarter)

Run No.	Feed Material	Solvent Material Plus Zone Length	Temperature of Furnace (Peak)	Drop Rate, mm/day	Comments
24B	two pellets $Bi_4Ti_3O_{12}$, sintered at 900 °C, ~7.2 g	1-cm Bi_2O_3 cast by torch 5 g	1050 °C	5	Zone separated growth stopped early in run; remaining feed microcrystalline.
25B	Proustite	1-cm eutectic no. 1, $Ag_{1.4}As_{0.6}S_{1.6}$	485 °C	Stationary	Special run to profile temperature conditions during run using special ampoule with center tube
26B	three HgS pellets, ~8-mm dia., 3 cm long	K_2S_4, ~2-mm dia., 2.5 cm long	Lower heater - 3-mm long, 460 °C; Upper heater - 10 cm long, 300 °C	~2	Best regrowth so far; several large transparent crystals nearly single; see photos; transmission poor
28B	~3 cm of $CdGeAs_2$, cast from synthesis run no. 27B	Sn, 1-cm dia., 1 cm long	600 °C	~3	Passed through feed-polycrystalline regrowth (confirmed by X-ray), ampoule cracked after 2-cm regrowth
30B	$CdGeAs_2$ (from 27B)	Sn, 1-cm dia., 1 cm long	580 °C	~3	Sn requires equilibrium condition with Ge solvent should contain ~20% Ge in solution initially
32B	$CdGeAs_2$ (29B), cast	Bi, 1 cm long, 1-cm dia.	600 °C	~3	Solubility too low for THM at desired temperature of less than 650 °C
33B	$Bi_4Ti_3O_{12}$ sintered pellets, two pellets ~1 cm long	Bi_2O_3 cast in Pt ampoule, 1 cm long, 1-cm dia.	1080 °C	~3	Some very polycrystalline regrowth at bottom; solvent appeared to bubble up from bottom and prevent further growth
34B	$ZnSiP_2$ pellets	Sn, 1 cm long, 8-mm dia.	730 °C	3	Temperature too low, zone remained at bottom; pellets contained Zn_3P_2 + Si
35B	HgS packed powder	K_2S_4	Lower heater - 3 mm long, 460 °C; top heater-5 cm long, 300 °C	~2	In progress, repeat of 26B, larger dia. ampoule 1-cm; regrowth occurred; method reproducible
36B	HgS 3 cm vapor grown plug	K_2S_4	470 °C bottom heater; 300 °C top heater	~2	Regrowth occurred but very poly and mixed with metacinnabar
37B	$CdGeAs_2$ cast	Cd 1 cm long, 1 cm dia.	600 °C	~2	Solubility too low at this temperature
38B	Bi_2O_3-TiO_2(20:1) sintered pellets	Bi_2O_3 1 cm long	1075 °C	3	~1-cm regrowth, amber color ~60% transmission - X-ray
40B	$CdGeAs_2$ cast	Pb	600 °C	2	Very polycrystalline, but regrowth all $CdGeAs_2$, no transmission

element caused degeneration and subsequent burnout of the heater. The loss of some of the solvent may have been the cause of the limited success.

The only work done on proustite was to determine the operating temperature profile. This was achieved by using an ampoule which had a thin Pyrex tube passing completely through the middle of it. Through this tube, one could pass a very small thermocouple and thus by having the ampoule clamped in position in the furnace, a profile was easily measured. The ampoule was loaded such that ~ 2 cm of proustite was cast into place at the bottom, followed by 1 cm of solvent ($Ag_{1.6}As_{0.6}S_{1.4}$) and this was followed by ~ 3 cm of proustite cast on top of the solvent so that the system represented closely a normal THM run. The experiment showed that very little change occurred in the profile when the ampoule was empty or loaded. This is believed to be due to the low thermal conductivity of the materials used. In the case where a material has a higher thermal conductivity, a greater flattening and broadening of the profile occurs.

During this quarter, we were successful in synthesizing $CdGeAs_2$ consistently. THM regrowth of the quenched castings has also been successful using Sn or Pb as solvent. However, the Sn solvent was found to react with $CdGeAs_2$ to form $CdGeAs_2$-$CdSnAs_2$ solution. X-ray analysis showed that the material which grew first had a deficiency of Ge and this was apparently substituted for by Sn. A second sample taken ~ 2 cm from the bottom of the ingot showed a trace of Sn which means that, once the solution reaches equilibrium, it is useful as a solvent. Thus, a Sn-Ge mixture could be a proper solvent in this case but the phase equilibrium here needs far more elaboration to confirm this conclusion. Lead is a far better solvent, since a lead zone passed completely through the solid cast of $CdGeAs_2$ and the X-ray analysis showed no measurable Pb in the regrown sample. So far, only polycrystalline boules have been regrown and optical measurements have shown no transmittance which is probably due to the large number of grain boundaries and/or impurities.

We have managed to partially synthesize $ZnSiP_2$ through a long time-low temperature procedure at ~ 450°C. This material is not completely reacted but we plan to remove it from its heavy walled ampoule and regrow it using Sn as a solvent if it is usable as regrowth material.

Along with the other II IV V_2 compounds, we have been trying to synthesize $CdGeP_2$ using a two-zone furnace. Again not until we know exactly how to synthesize the material safely and efficiently will be able to regrow this material by THM. Here some mention must be made about the difficulties of synthesizing high melting phosphides in general and phosphides which contain also a group II metal in particular. Any attempts at direct synthesis from the elements have the substantial danger of an explosion associated with them. This is due to the somewhat unpredictable behavior of red phosphorous on heating and the unpredictability of the reaction rates for the highly exothermic group IIb phosphides. If any sudden heating due to reaction occurs at a time when free phosphorous and free Cd or Zn are still around, the vapor pressure usually exceeds the pressure capabilities of quartz ampoules and a fiery explosion is the result. Only autoclaving or very slow reaction via slow and preferably directional heating is successful. Alternatively, chemical exchange reactions of some type could be sought but this is a lengthy and cumbersome search. Thus, the severe difficulties of simply preparing large amounts of such phosphides must be recognized here.

III. PLANS FOR THE NEXT THREE MONTHS

The work planned for the next 3 months will consist of the following:

1. Synthesizing $CdGeAs_2$ and improving the quality of the THM grown material as well as attempting to find solvents other than Pb.

2. Synthesizing $CdGeP_2$ which so far we have not been able to do. If we are able to form the compound, we will then attempt THM regrowth.

3. Possibly synthesizing and growing by THM other selected II IV V_2 compounds.

4. Continuing the hydrothermal growth of cinnabar and the THM-vapor transport regrowth as time permits.

5. Initiating growth experiments and other materials of electrooptic interest such as CdSe.

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IV. DESCRIPTION OF EXPERIMENTAL AND THEORETICAL RESULTS

A. Crystal Growth Section

1. Cinnabar

a. Vapor growth: The vapor growth of HgS was halted during this period having produced an adequate supply of feed material for any THM or hydrothermal growth planned for the near future.

The procedure here is to pack an 8-mm-i.d. quartz ampoule with HgS powder or pressed pellets (pellets allows more material per unit length where a larger ingot is needed). After evacuation, the ampoule is placed in a moveable horizontal furnace with the temperature set at 600 °C. By holding the ampoule in a stationary position and moving the furnace back, the HgS vapor crystallizes on the cooler end of the ampoule thus forming a polycrystalline plug of cubic metacinnabar which in time converts to very polycrystalline trigonal cinnabar.

An attempt was made to anneal a section of this polycrystalline vapor grown material in vacuo at 300 °C to produce larger grain size and hopefully see possibilities of using this method for improving crystal quality. After 4 weeks of this treatment, very little improvement was noticeable - except that the material was a more definite vermillion color.

b. Hydrothermal growth: An experiment was started during this period using a new, smaller stainless steel autoclave which is completely lined with Teflon. This run will be continued for 2-3 months, if no problems develop (Fig. 1). The autoclave capacity is ~ 500 ml when nearly filled to the top with 0.5M Na_2S, seed holder, and feed material. There is only ~ 20 cc of air space above the solution level.

The basic method used is essentially that discussed by Y. Toudic and R. Aumont[4] and also S.D. Scott and H.L. Barnes.[5] The procedure used was as

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follows: The autoclave (made by Autoclave Engineers, Inc.,) was thoroughly cleaned and dried. The Teflon seed holder containing the seeds and feed material (HgS) was carefully lowered into place. Approximately 500 ml of fresh solution of 0.5M Na_2S was prepared to which 10 g of powdered HgS was added to presaturate the solution. The solution was carefully poured into the autoclave to nearly the top of the container (~ 2 cm from top) and the plug and pressure flange were properly seated and tightened. The loaded autoclave was then carefully dropped into the heater and support section of the setup and brought to temperature (200 °C). The temperature profile on the outside surface of the autoclave was measured and found to have a 50 °C gradient between the bottom where the feed HgS rests and the top where the seeds are located. This experiment has been underway for several weeks and plans are to continue it for 2-3 months.

c. THM growth: Three more experiments were run during this period: one regular THM run using the standard THM methods and two using a modified THM vapor growth method. The regular THM run again produced the usual polycrystalline solvent-included boule. The modified method, however, holds some hope to produce reasonably good sized crystals in the order of 1 cm by 0.5 cm in size. Fig. 2 (run 26B) shows a photo of a cluster of fairly transparent red crystals of HgS. Fig. 3 shows the regrown HgS before removal from the Pyrex ampoule in which it grew.

Run 26B was conducted in a two-zoned heater, the upper one being ~ 10 cm long and the lower ~ 0.5 cm long. These kanthal elements are supported by a 15-mm-o.d. quartz tube with 1-mm-thick wall. The upper heater was maintained at 300 °C and the lower heater at 460 °C. The ampoule was made of Pyrex glass, the upper section was 8-mm i.d. and 9 cm long and the bottom section was ~ 5 cm long and ~ 4 mm i.d. The solvent (K_2S_4) was precast into the narrow bottom section of the ampoule and HgS powder was gently packed on top to a height of 6 cm. A glass plug was placed on top of the packed powder and the ampoule was evacuated and sealed at an overall length of 14 cm. The charged ampoule was placed in the hot furnace with the bottom tip of the ampoule just where the hottest spot of the lower heater would be. After setting in place for ~ 1 hr, the ampoule was dropped at a rate of 2 mm/day until all the feed material at the top appeared gone. This took ~ 3 weeks. The results were very encouraging. A considerable amount of HgS

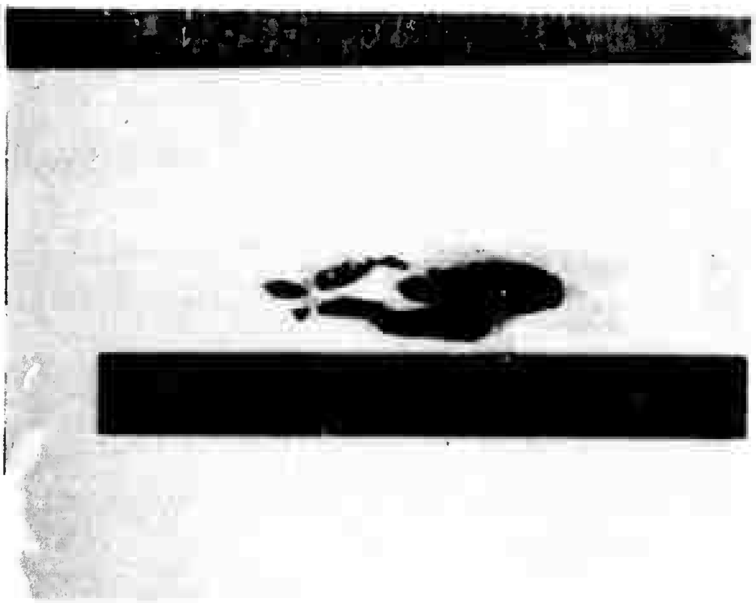

Fig. 2. Shows cluster of HgS crystals separated – run 26B

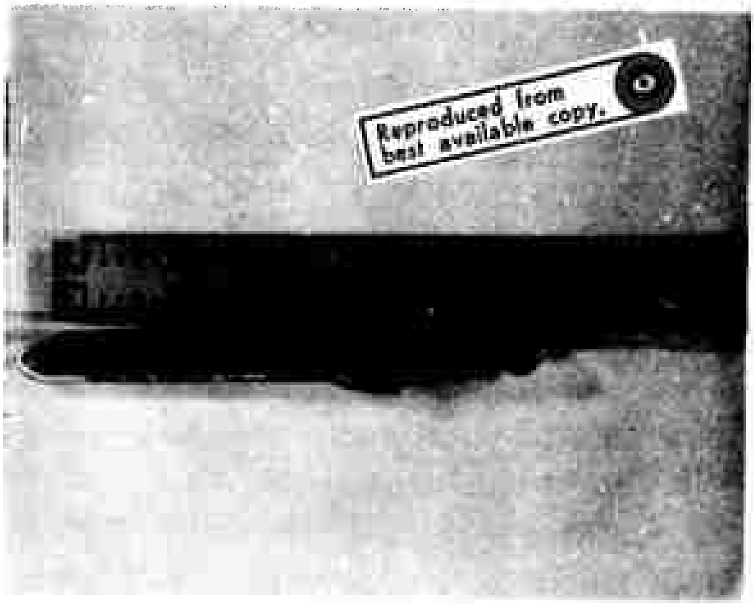

Fig. 3. Shows the regrown HgS before complete removal from lower section of ampoule

regrew as red transparent, good crystalline quality material. A section was polished to 1-mm thickness and the optical transmission checked. Even though the slice was transparent, the impurity content is apparently high enough to give poor results. Only ~ 5% transmission was recorded. The method seemed to hold some promise and so to confirm that this was not an accident a second run (35B) was completed (Fig. 4). Although the crystal quality was not as good this time, it did convince us that the method works. Perhaps by adjusting certain growth, and/or furnace parameters this method can be improved upon.

What seems to be happening here is that instead of creating a single cross-sectional interface between the feed and itself, as normally occurs with THM, the solvent surrounds the regrowth. After ~ 2 days, a space develops between the feed and the solvent. Within this void, vaporized K_2S_4 acts as the transport medium replenishing the solvent with nutrient (HgS) for the growing crystals. The 300 °C upper furnace prevents the solvent from being lost to the feed which hangs on its own, ~ 1 cm above the solvent zone. The fact that the feed is a powder provides the solvent vapor with a large surface area to work on, thus increasing the rate at which the solvent zone receives the feed material. Since K_2S_4 apparently is just not good enough when used as a solvent in the conventional THM approach, the explanation seems to be one of mere surface area and liquid-vapor-liquid transport. We speculate that the process was as follows: The solvent was heated to ~ 450 °C and some of its vapor reached the feed material, whereupon the two combined as a liquid and ran back down to the solvent zone where crystal growth occurs - just below the lower edge of the bottom heater.

In general, there is also some reason to believe the solubility of the HgS in the potassium polysulfides may be affected by which polysulfide one is using, i.e., the more sulfur atoms attached to the molecule, the lower the solubility. The higher the polymer the more viscous the solvent which in turn slows down the diffusion rate of the solute at operating temperature. K_2S_3 melts at 252 °C whereas K_2S_4 melts at 145 °C. The feeling has been that the lower melting K_2S_4 would make a better solvent, but if, in fact, the K_2S_3 is less viscous, it may be a better solvent to try.

2. $Bi_4Ti_3O_{12}$

Three more runs were made during the past 3 months. All were unsuccessful for the following reasons: (1) furnace failure, and (2) vaporization of

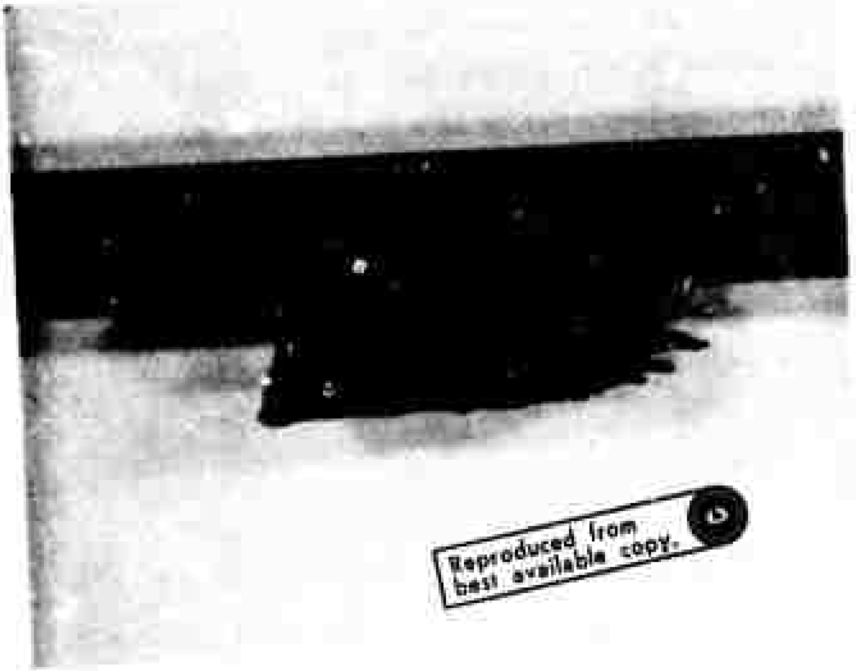

Fig. 4. HgS regrowth by THM vapor transport technique — run 35B

solvent causing separation in the solvent zone. The regrowth has been of very small crystalline size and very porous. The last run (38B) did produce a solid regrown section of ~ 1.2 cm long and 1-cm diameter but this regrowth was from feed pellets which consisted of a 10:1 mixture of $Bi_2O_3 + TiO_2$ (the other runs were ~ 5:1 by wt). The material was checked for transmission characteristics (see Fig. 5). Definite X-ray characterization is still outstanding at this time but the general growth habit is such that one can be fairly sure that another bismuth titanate with a stoichiometry different from $Bi_4Ti_3O_{12}$ resulted.

The procedure used in this work is as follows. Powdered Bi_2O_3 and TiO_2 are thoroughly mixed in the proper amounts. The mixed powder is pressed into pellets ~ 15 mm long and 9 mm in diameter and sintered overnight in a muffle furnace at 900 °C. Two pellets are placed on top of a 1-cm precast zone of Bi_2O_3 in a 1-cm-diameter platinum crucible. A platinum lid is placed over the charge in the crucible which is ~ 5 cm long and open at the top. The charged crucible is dropped through a THM furnace. The temperature in the center of the furnace is set at 1050 °C where the furnace element itself is ~ 1100 °C. The dropping rate in general is ~ 3 mm/day.

3. $A^{II} B^{IV} C_2^{V}$ compounds

$CdGeAs_2$: Several boules of $CdGeAs_2$ were synthesized during the past quarter for the use as feed material for the THM regrowth.

The procedure used is to weigh into a clear quartz 1-cm-i.d. ampoule the proper proportions of Cd, Ge, and As metals. The ampoule is immediately evacuated and sealed to prevent oxidation of As metal. The sealed ampoule is placed in a horizontal furnace preheated to 450 °C. After 1 hr, the temperature is raised slowly to 600 °C and left overnight. The following day the temperature is brought to 730 °C. During this time, the ampoule is rotated periodically by an attached kanthal wire which extends out of the furnace. When assured that the melt is complete and homogeneous, the ampoule is removed from the furnace and plunged vertically into a dewar of liquid nitrogen. The liquid N_2 quench is necessary in order to prevent oxidation of the casting which invariably cracks the ampoule as it passes through its phase transformation (630°C). Very good quality castings have been produced this way and only hair line cracks have been found occasionally which have no effect on use as feed material for THM.

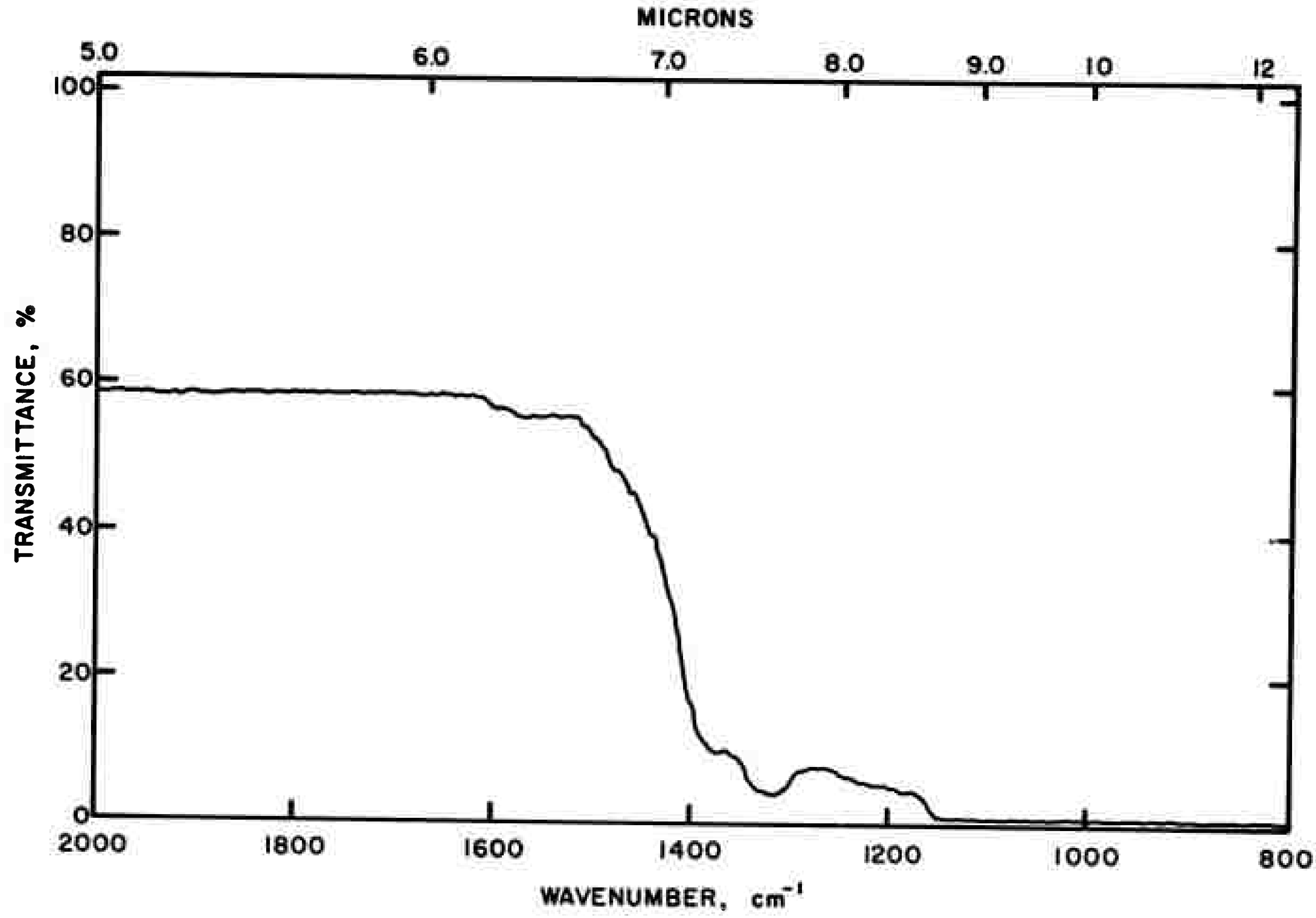

Fig. 5. Bi_2O_3-TiO_2 by THM Bi_2O_3 solvent growth temperature 1080°C – run 33B

So far, we have tried Sn, Cd, Bi, Pb metals as solvents. The solubility of the compound in both Cd and Bi is too low at the growth temperature (~ 600 °C) to be useful. Sn and Pb do pass completely through the casting. The regrown material so far is very polycrystalline and not transparent to IR. Sn is not as promising as the Pb. In the case of tin, the initial material has a deficiency of Ge and a substitution of Sn but nearer the top of the regrown ingot, X-ray checks show that the $CdGeAs_2$ contained only traces of tin in the lattice. This would suggest the Ge should be added to the Sn at the beginning, thus establishing an equilibrium condition and not changing the stoichiometry of the regrowth. Fig. 6 shows the regrown $CdGeAs_2$ from run 30B using Sn as solvent. The material regrown using Pb as the solvent, from a standpoint of purity of material, was much better but the crystallinity was poor. The boule contained many grain boundaries and probably solvent inclusions. The Pb in the regrown ingot was almost undetectable by fluorescent X-ray analysis. A slice of this run (40B) was polished and checked for optical transmission but perhaps due to the grain boundaries and impurity absorptions, no transmission was observed.

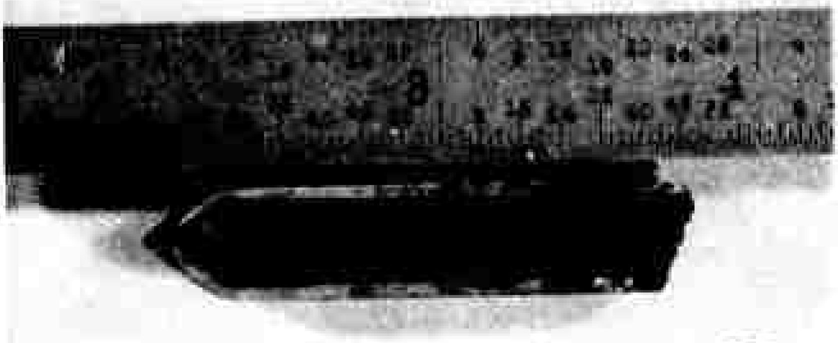

Fig. 6. THM grown $CdGeAs_2$ using tin as solvent

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