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G R CRONIN ET AL. OCT 83 AIM-013 MDA903-82-C-0159

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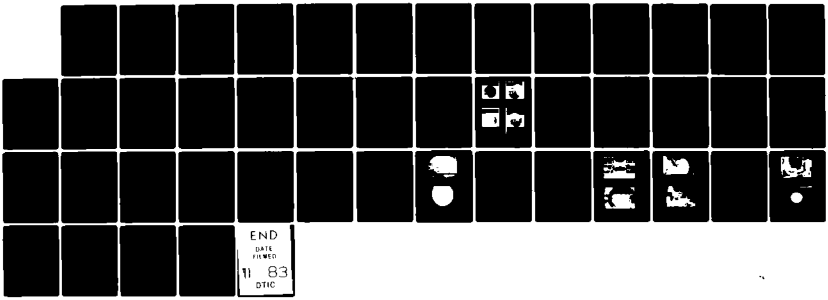

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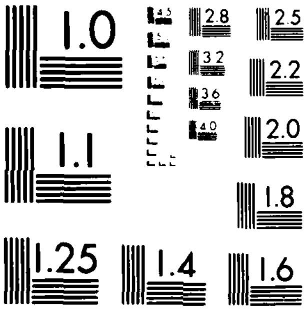

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# LARGE PLATE CdTe SYNTHESIS BY SEALED VESSEL TRANSPORT

GEORGE R. CRONIN, PRINCIPAL INVESTIGATOR
(214) 494-5624

QUARTERLY TECHNICAL REPORT NO. 7

REPORT PERIOD: JULY 1 - SEPTEMBER 30, 1983

SPONSORED BY:

Defense Advanced Research Projects Agency (DOD) ARPA Order No. 4383. Under Contract No. MDA903-82-C-0159 issued by: Department of Army, Defense Supply Service-Washington, Washington, D. C. 20310

AMTIR

**AMORPHOUS MATERIALS, INC.**
3130 BENTON • GARLAND, TEXAS 75042
214/494-5624 – 271-8613

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The seventh quarterly technical report for the program to grow large plates of high purity CdTe in a sealed system covers the period July 1 - Sept. 30, 1983. A process to grow up to 10 inch dia. plates of high purity CdTe with large grain size has been developed. Evaluation results from other workers have confirmed the purity and high resistivity of the resultant materials. Plates have been grown from both tellurium rich and near stoichiometric melt compositions. Optical absorption coefficients at 10 microns as low as .06$\text{cm}^{-1}$ have been measured. A wire saw has been put into operation for substrate wafering and a helium-neon

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20. ABSTRACT (Continued)

laser is now being used for optical orientation of large area single crystals.

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## (CONTINUED)

# SUMMARY

The goal of this program is to use vapor growth to form polycrystalline plates of cadmium telluride (CdTe) 6", 8" and 10" in diameter. The resultant material will be evaluated as substrates for mercury-cadmium-teluride (HgCdTe) growth and as an infrared optical material. Late in the program, mercury vapor will be used in an attempt to grow HgCdTe layers on the large area CdTe plates.

Previous workers have grown large plates of CdTe 6" in diameter transporting the vapor using an inert gas. The starting material was pre-compound. The method to be used in this program was to compound the material and transport the vapor through a filter into the casting chamber for growth in one operation under vacuum. Solid state recrystallization carried out at high temperatures over a long period of time will produce the desired large grain structure.

Results reported in the first three quarters demonstrated the initial process concept was impractical. Vapor transport of compounded CdTe in a sealed evacuated system was too unpredictable. High temperatures coupled with the presence of cadmium oxide caused a high percentage of quartz failures. Program goals could not be reached with the original process approach. The decision was made to convert to a three chamber quartz system in which the cadmium and tellurium vapors entered the plate chamber from separate tubes.

The new process approach was used ten times to produce 6" diameter plates from a stoichiometric melt. Plates weighing almost 2Kgms and possessing the required large grain structure resulted. However, a void region was found to occur between the faces of the plate each time. Growth from sollution was used to eliminate this problem. A plate was grown with grains running from the bottom face to the top face from a solution of approximately Cd45 Te55. Total process time was about 72 hours.

The process was applied to the growth of 8" diameter plates successfully. Some changes had to be made particularly with regards to the sequence of reactant distillation. Plates with large grains several inches in area have been grown. Thickness of material is 0.5" or less with the weight of useful material reaching up to 2Kgm. The material has been found to be high purity by emission spectrographic analysis, high resistivity and to exhibit no or little free carrier absorpton in the infrared. Disks may be generated from the plate by cutting out squares followed by edging.

This quarter marked out first successful attempts at growing 10 inch diameter plates (2) and we also began a series of "seeding" experiments including a return to melts of near stoichiometric composition. A seeded plate, (110), 20cm in diameter and 11mm thick resulted in a 3X improvement in IR transmission at 10 microns. This plate was also grown from a near stoichiometric melt.

A helium-neon laser was obtained for optical orientation purposes and a wire saw was also put into operation for wafering substrates.

For the next quarter we plan to continue the growth of 8 inch diameter seeded plates compounded from near stoichiometric composition and emphasizing the controlled directional freezing so as to produce the largest possible single crystals. We will also begin a series of heat treating experiments under controlled vapor pressure conditions and initiate the preparation of epitaxial layers of HgCdTe.

# I. INTRODUCTION

A crucial problem in the volume production of U. S. Government FLIR systems is the availability of mercury-cadmium-telluride (HgCdTe) detector arrays. Certainly fabrication of the arrays is difficult but the major problem is the availablity of high quality detector material. The production of bulk HgCdTe alloy is a slow, difficult low yield process. The preferred method to produce detector materials is to grow HgCdTe layers epitaxially on a high quality cadmium telluride (CdTe) substrate. However, the availability of high quality CdTe is also limited. Part of the reason for the shortage is that the conventional method for preparing CdTe crystals is to slowly (0.1"/hour) zone refine small diameter (1") crystals using the stockbarger technique. The purpose of this program will be to develop an allternative approac

Large plates of high purity large grain c ium telluride will be grown from the vapor in a sealed s m. Cadmium telluride will be compounded from the element and sublimed through a filter into a separate growth chamb ", 8" or 10" in diameter. Grain size will be increas y solid state recrystallization. Material thus produce ill be evaluated regarding purity, optical homogeneity and suitability as substrates for HgCdTe growth. Attempts will be made to grow HgCdTe layers by mercury vapor deposited on large area plates in situ.

# II. VAPOR GROWTH OF CADMIUM TELLURIDE

## A. General

Cadmium telluride is formed from the group II element cadmium and the group VI element tellurium. All II-VI compounds, as they are called, are difficult to grow because of their melting points and the fact that both constituent elements are volatile. An appreciable vapor pressure exists for each element at the solid melting point which leads to complications for melt growth. For the same reason, vapor growth of the solid becomes attractive.

Solid CdTe may be grown from the vapor at temperatures considerably below its melting point, 1097 ° C, according to the following equation:

$$\mathrm{Cd}\ (g) + \tfrac{1}{2}\,\mathrm{Te}_2\ (g) \rightleftharpoons \mathrm{CdTe}\ (s)$$

Where: g signifies gas or vapor
s signifies solid

The reaction as written is reversible which indicates that solid CdTe will sublime or vaporize into its constituent elements. Thus, the source of Cd or $Te_2$ gas may be either the pure heated elements or a heated source of pre-compounded CdTe solid.

The quality of the CdTe grown from the vapor (or melt) depends upon maintaining the exact radio of 1:1 between the cadmium and tellurium atoms. The presuure of cadmium vapor (pCd) and the pressure of tellurium vapor ($pTe_2$ ) in equilibrium over solid CdTe at the growth temperature is very critacal and a function of temperature. Deviations from stoichiometry will occur if the ratios are not closely controlled. Supplying the vapors from pure elemental sources heated separately and mixed together at the reaction sight is not too accurate. Even the use of inert carrier gasses does not improve the situation to any great extent. Sublimation of precompounded CdTe followed by removal of the vapor to the reaction sight is far more accurate. The compounded material may be weighed to an accuracy of 0.1% or better. The accuracy of the ratios may be maintained through direct sublimation in a closed system or through use of an inert carrier gas in a flowing system.

One quality criteria not mentioned thus far is crystallinity. In melt growth, crystals of one single grain may be grown provided that a seed is used and growth rates are very slow. Such restrictions are also the prime limitation relative to diameter of the crystal. In vapor growth, crystals are grown on other crystal surfaces of the same or similar structure, or they grow on an amorphous substratate with spontaneous nucleation and growth occuring over the entire surface. The first case may produce single crystals provided that growth conditions are carefully controlled. The latter method may produce large grain material provided high growth temperatures are maintained over long periods of time.

## B. Previous Work

The first extensive investigation of the preparation of CdTe was carried out by D. de Nobel (1) of Phillips. The properties, optical, electrical and semiconducting properties of the materials. The liquidus-solidus curve and related pressure-temperature studies have served as the basis for melt growth of CdTe over the years. Discussions related to melt growth will not be repeated here only as they are relative to vapor growth.

L. R. Shiozawa and co workers at Gould (now Cleveland Crystal Laboratories) carried out an extensive investigation beginning in the late 1960's concerning the vapor growth of II-VI compounds generally (2) and cadmium telluride (3) specifically. Diagrams from their papers will be used to discuss the problems involved in vapor growth of cadmium telluride.

Figure 1 shows the simple binary phase diagram of the Cd-Te system (2). The diagram indicates a single compound is formed, CdTe, which has a congruent melting point of 1092 . The term "congruent melting point" indicates that except at perfect stoichiometry, below the 1092 ° C melting point, both Cd rich and Te rich liquids exist in equilibrium with pure CdTe. The point is better illlustratred in the diagram (4) shown in figure 2. Only in a very narrow range of stoichiometric ratios does the pure CdTe and its equilibrium vapor pressure or 0.001 percent. Minimum vapor pressure at all temperature exist along this line. Equilibrium vapor pressure would be exactiy in the right ratio. However, considering the accuracy required, it is more likely that the solid cadmium telluride would be either Cd rich or Te rich. Vapors above the solid would reflect this fact and be larger than those above exactly stoichiometric material.

The pressure of cadmium at the cadmium rich boundry stability field as a function of temperature (2) is shown in figure 3. The tellurium rich (2) is shown in figure 4. In both diagrams, the data is compared to the pressure for the pure element, P Cd (1) and P Te2 (1). For the low temperature, the measured values are very close to those for the pure liquid or close to those corrected according to RAOULT's Law. RAOULT's law states the vapor pressure of a component is lowered by its atomic fraction in a liqiud mixture:

$$P\,Cd = x\ P\,Cd\,(1)$$

Where P Cd is the pressure of cadmium above the the melt

P Cd (1) is the pressure of pure cadmium at the temperature of measurement

X is the atomic fraction of cadmium in the melt.

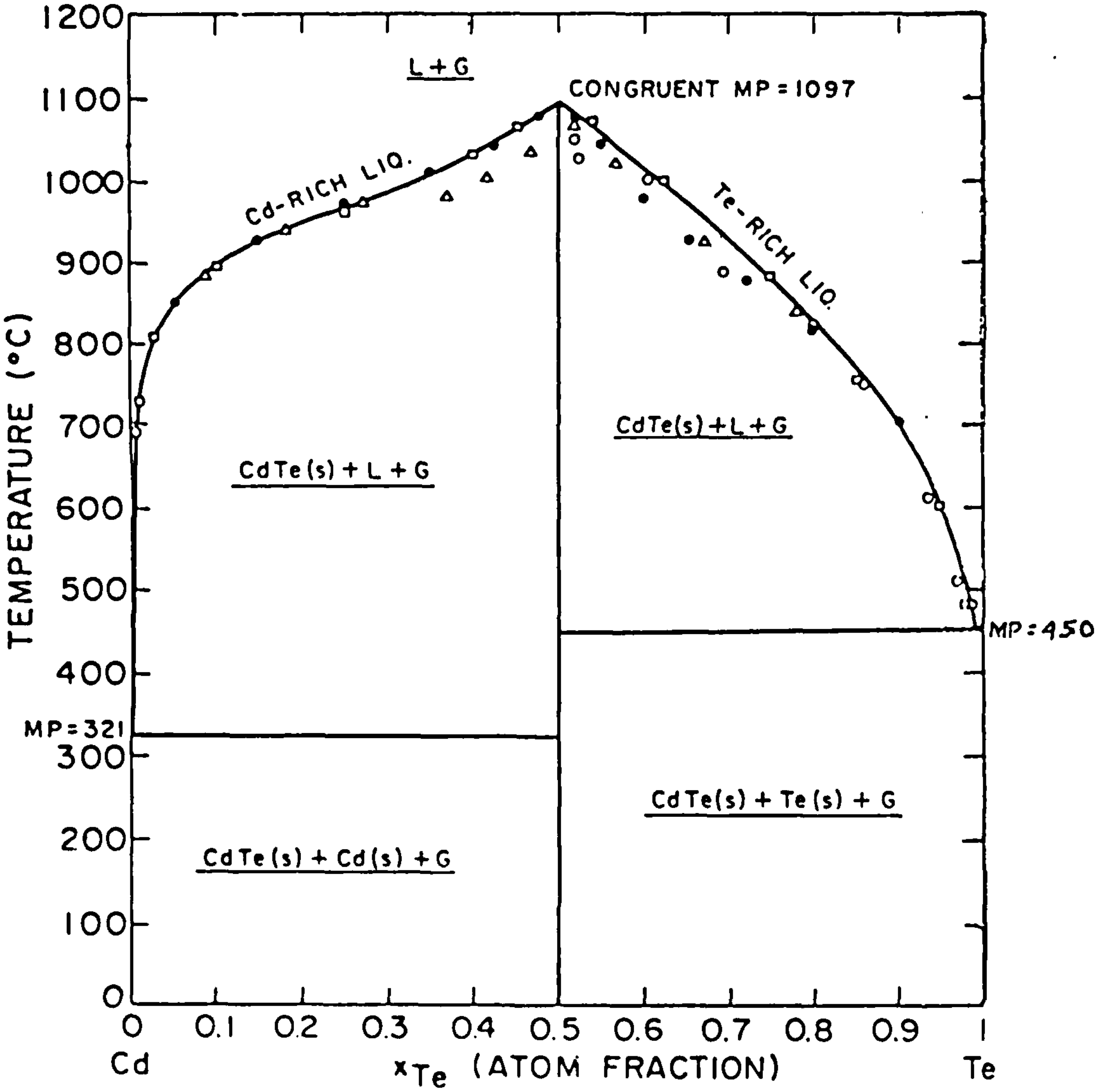


FIG. 1. PHASE DIAGRAM OF THE Cd-Te SYSTEM.

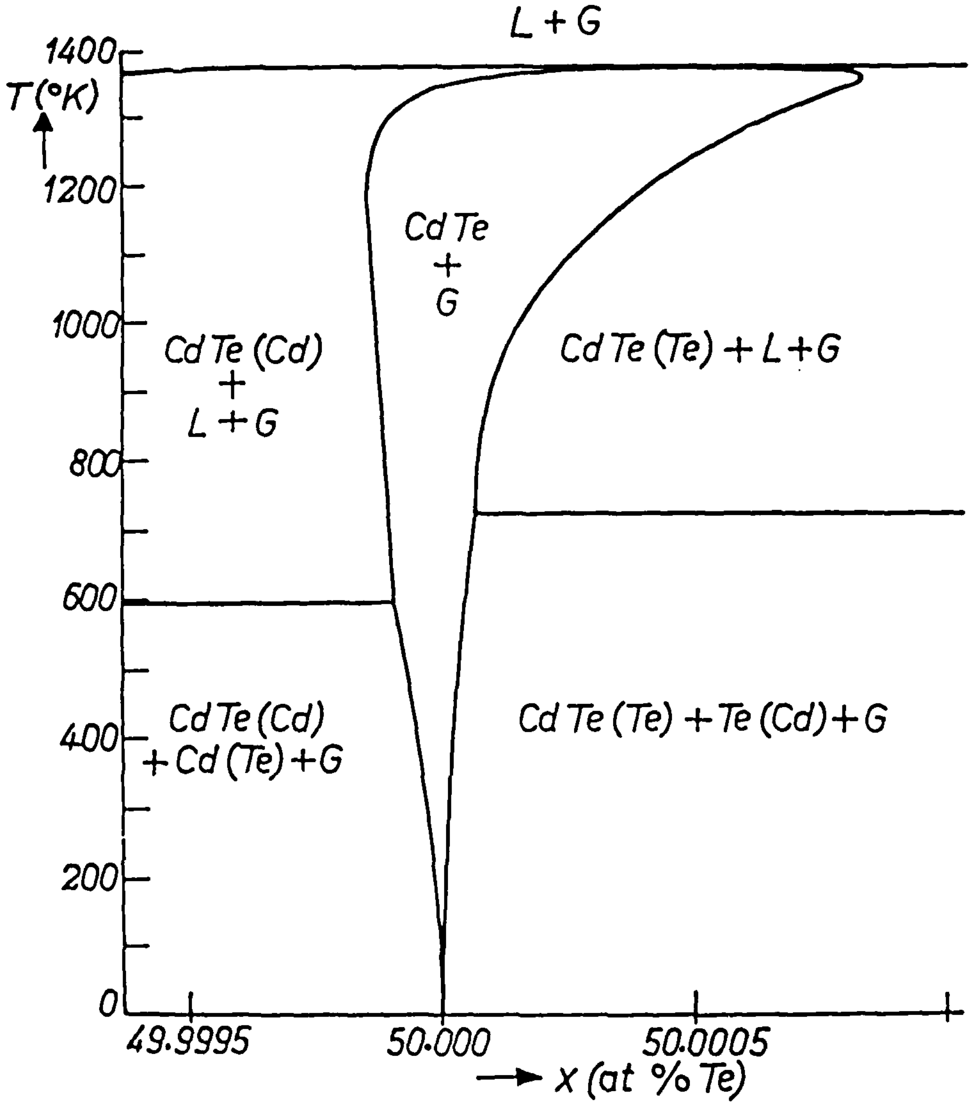


FIG. 2. SOLID STABILITY FIELD OF CdTe.

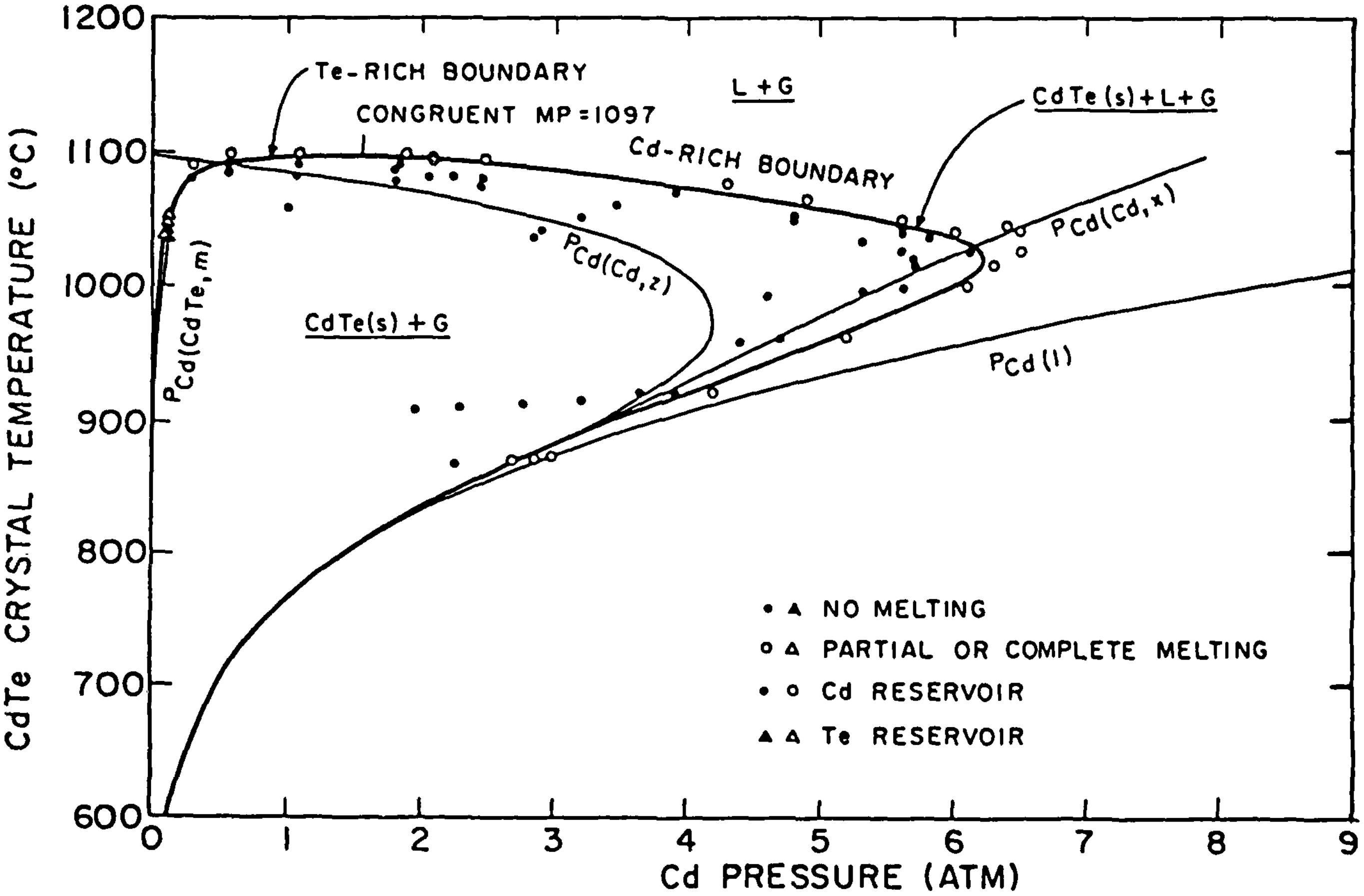


FIG. 3. Cd-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

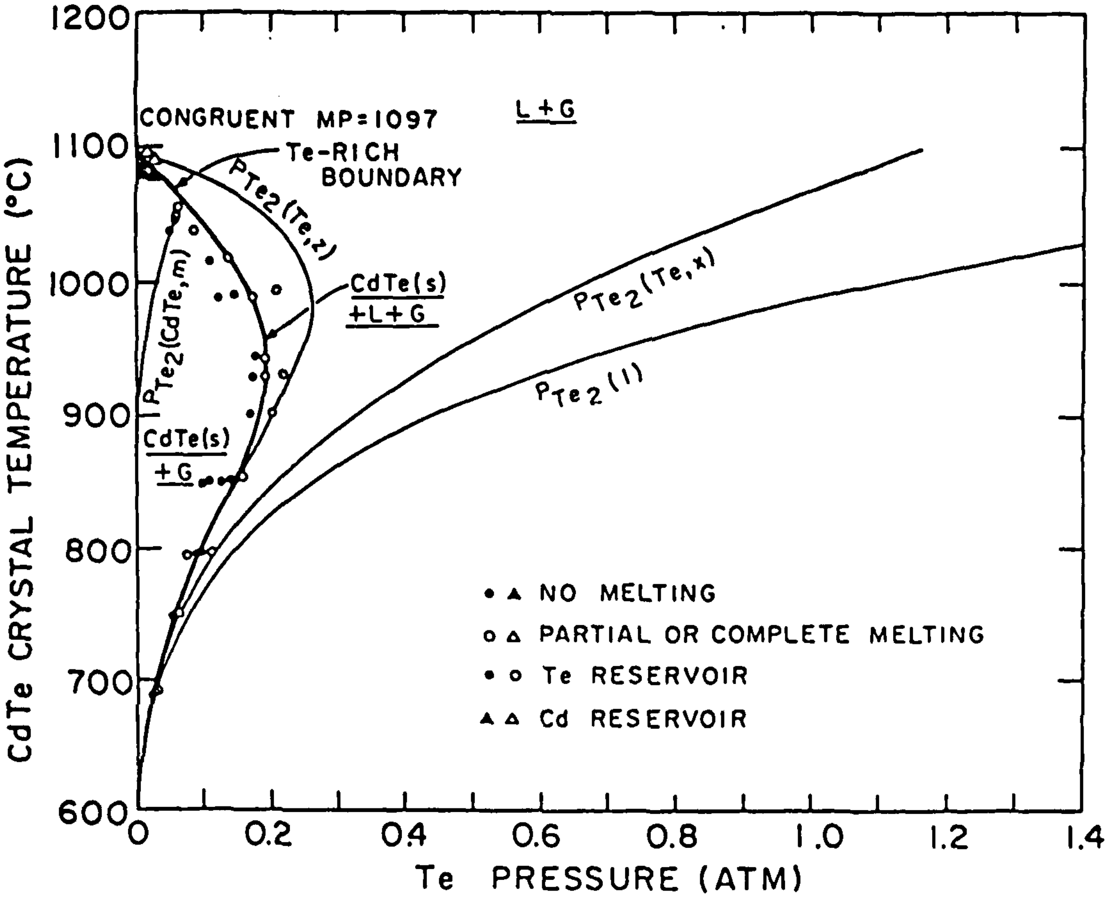


FIG. 4. Te-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

A similar statement may be made for the pressure of tellurium. The calculated curves using X are a simple application of RAOULT's law. Those using the Z subscript indicates that association between the atoms in the liquid are taken into account. The curves labeled with the M subscript correspond to the minimum pressure conditions which exist with only pure Cd Te solid present.

The diagrams indicate that the pressure of cadmium may become very large, 4-6 atmospheres, around 1000 ° C when compounding cadmium telluride. The pressure at the congruent melting point, 1092° C, is about 0.65 atmospheres. The vapor pressure of tellurium is quite low throughout the compounding range. The trick to compounding without an explosion is to stay close to the perfect stoichiometry point and allow time for the liquid phases to become small in quantity. The trick in vapor growth is to be sure that the subliming material is near the stoichiometric ratio so that the resulting vapors are close to the proper ratio. Maintenance of the proper ratio during vapor growth is complicated by the fact that tellurium exists as a diatomic gas, $Te_2$. The effusion rate for a gas is inversly proportional to the square root of its molecular weight and directly proportional to its pressure. Therefore, for CdTE sublilmation, we find the effusion ratios to be$^{(2)}$.

$$R\ Cd/R\ Te_2 = (PCd/PTe_2)\ (MW\ Te_2/MW\ Cd)^{\frac{1}{2}}$$

Where
R is effusion rate
P is pressure
MW is molecular weight

Even though the vapor starts out at the perfect 2/1 ratio, the cadmium atoms move faster changing the effusing gas mixture ratio. For Cd Te, the ratio becomes 1.33 instead of 2. Build up of the excess component may limit the deposition rate in sealed ststem where equilibrium type conditions may be established. The equilibrium constant is given by:

$$K\ Cd\ Te(s) = (PCd)\ (p\ Te_2)^{\frac{1}{2}}$$

The bulid up one component over the other shifts the equilibrium and suppresses further sublimation. Some have used capillary tubes to allow the excess component build up in the vicinity of the source to be pumped away or eliminated. Others have used a carrier gas to carry the subliming vapors, with perfect ratios, to the deposition surface.

### C. Vapor Growth of CdTe Plates

Shiozawa(3) and co-workers at Gould used physical vapor deposition (PVD) to grow CdTe plates up to 6" in diameter. Figure 5 illustrates the type of systems used. Pre-compounded CdTe was sublimed from the hot zone of a furnace to a slightly cooler zone. Best results were obtained when growth temperatures of 1000-1050 °C were used. Recrystallization was allowed to occur over periods up to 400 hours (17 days).

Figure 6 illustrates the type of grain sizes which were obtained. Growth and recrystallization at 950 °C produced small grains. Fast depostion and short growth periods even at the high temperatures produced plates with small grains and voids.

The systems were operated semi-sealed. Argon gas was used as a carrier. Pressures up to 1 atmosphere was used but 180mm, the vapor pressure of stoichiometric CdTe at 1050 °C, was the prefferred pressure. Later versions of the system used graphite parts to minimize the effects of air leaks. Also, inert gas was flowed through the furnace to protect the graphite components.

Plates thus produced were heat treated with both Te and Cd vapors at temperatures of 700-800°C. Treatments were alternated and lasted 1-5 days. Measured absorption at 10.6um was 0.001-0.002 $cm^{-1}$. The effect of heat treating on the infrared transmission of one of their CdTe plates is shown in figure 7. From the transmission for Cd treatment alone, one can see that dual treatment is necessary. After treating with $Te_2$ vapor, almost theoretical transmission was obtained.

## III. APPLICATION OF THE AMTIR METHOD TO THE GROWTH OF CdTe

### A. Preparation of AMTIR-I glass

A simplified diagram depicting the glass compounding and casting process developed by Amorphous Materials, Inc. to produce AMTIR-I, is shown in figure 8. A high purity container is placed in a dual zone resistive heated furnace. Zone 1 contains the round empty chamber which will serve later in the process as the casting mold. Zone 2 contains the glass compounding chamber. The process employed at Amorphous Materials combines all three glass processes (element purifications, compounding the glass and casting the plate) into a single continuous process.

In the first step, both chambers are evacuated and heated to remove moisture. A small amount of aluminum wire is added to the elements to act as a getter of oxides in the molten glass. After several hours, the chamber is sealed

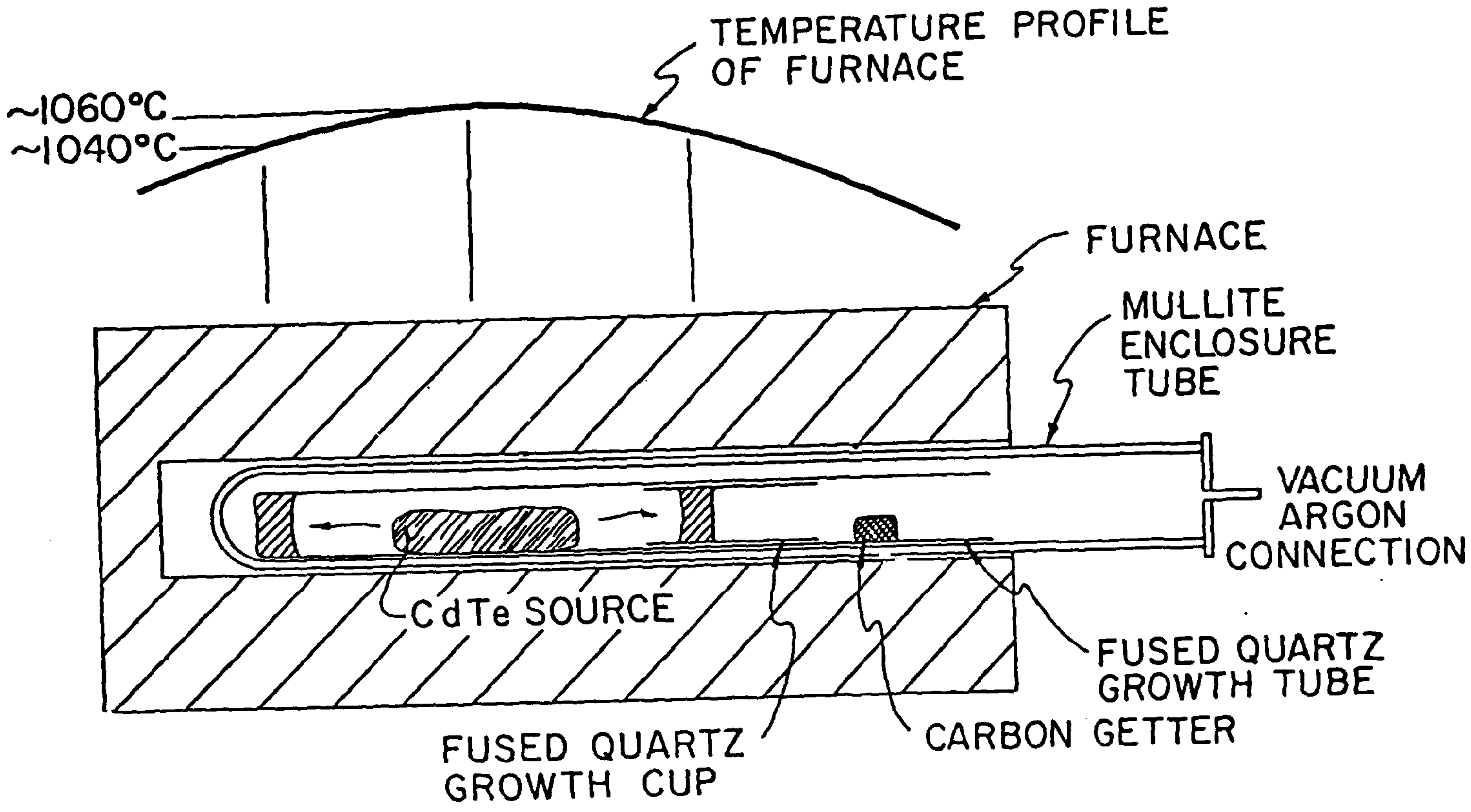


FIG. 5. HORIZONTAL SYSTEM FOR CRYSTAL GROWTH BY GRAIN GROWTH

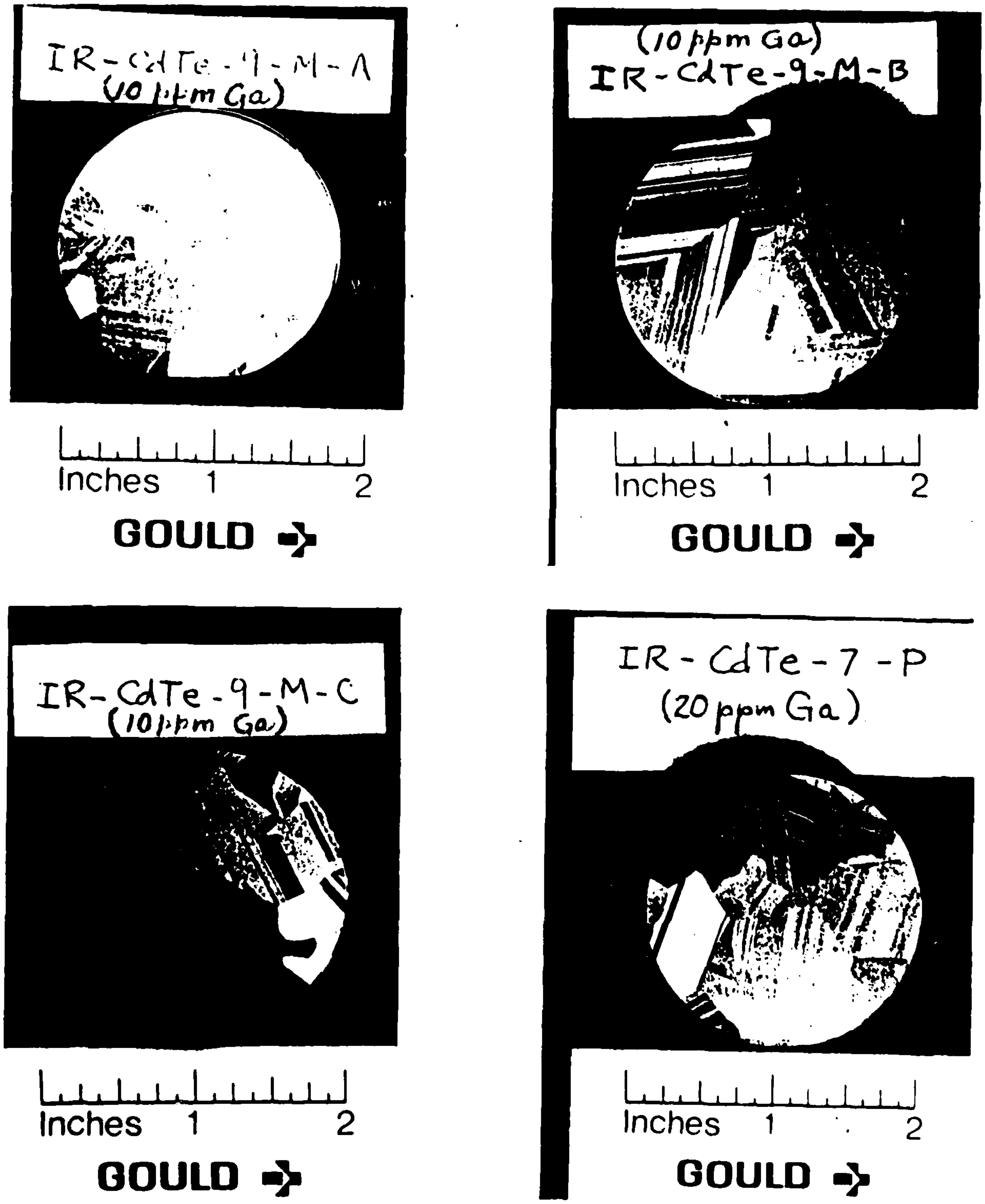


FIG. 6. Lapped Surfaces of CdTe Window Blanks Highlighting Grain and Twin Patterns.

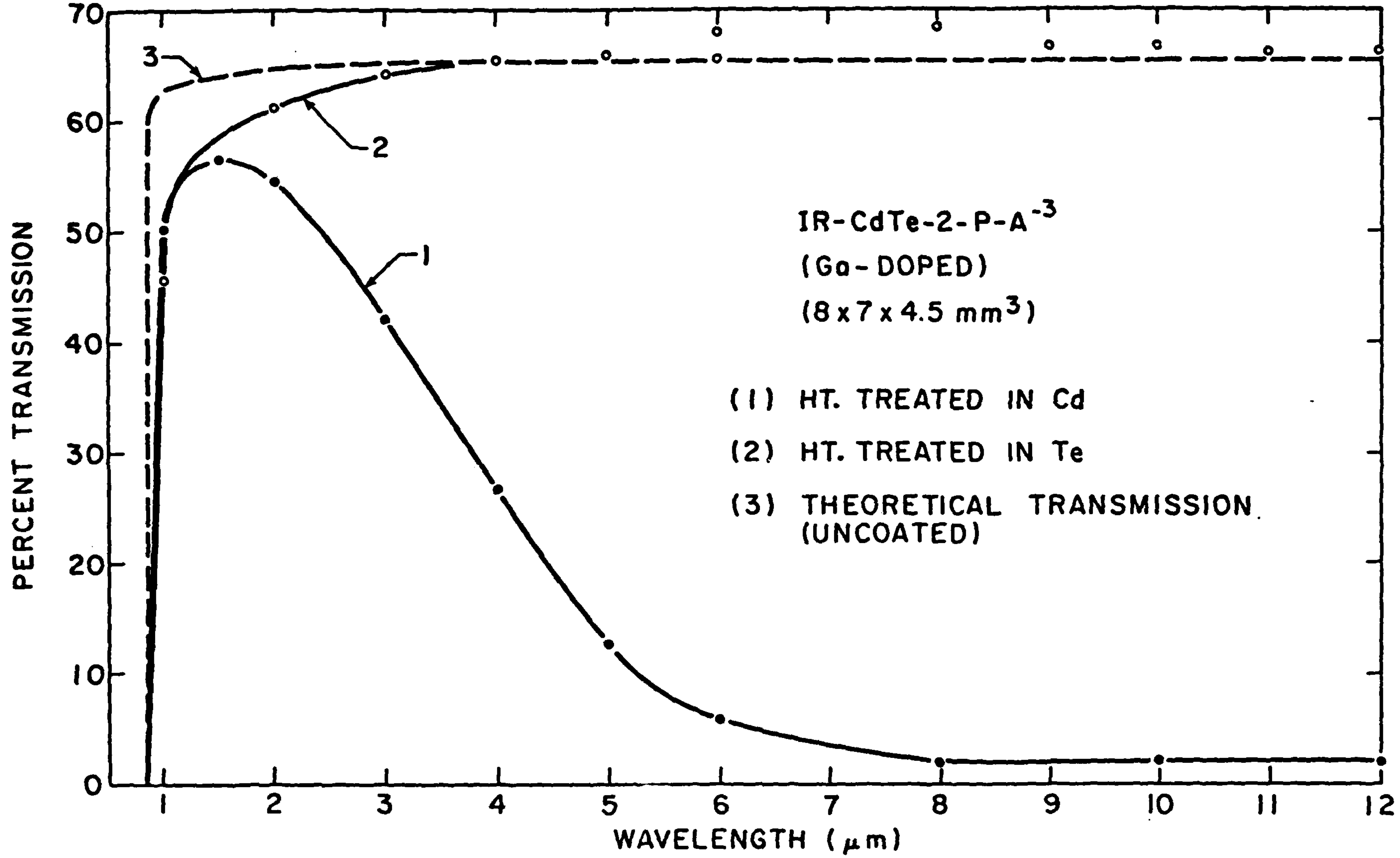
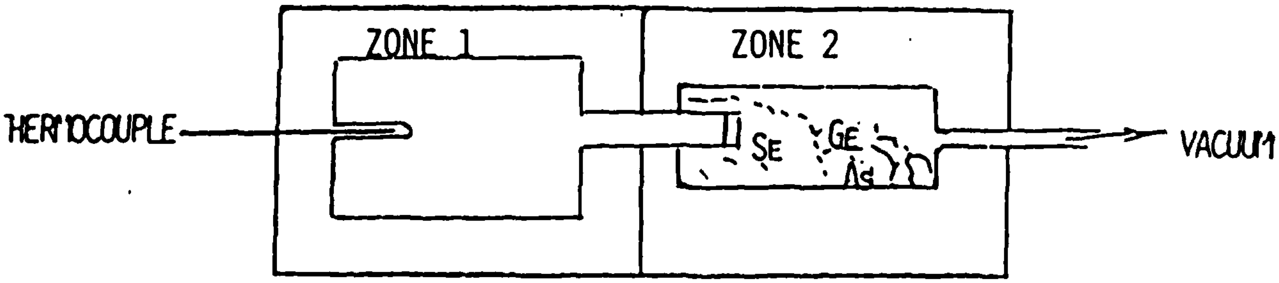
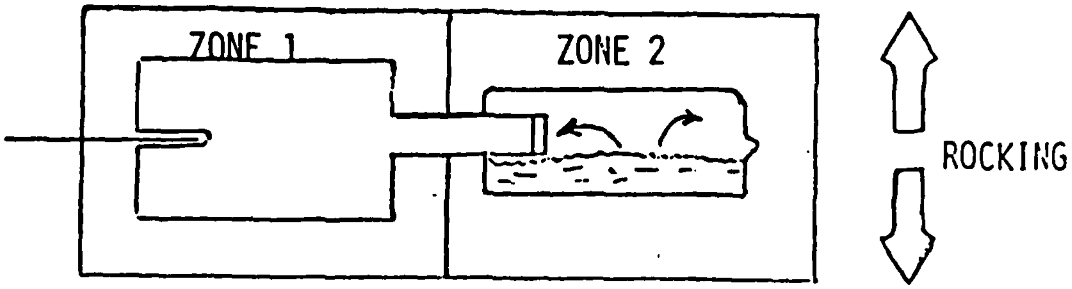


FIG. 7. OPTICAL TRANSMISSION OF Ga-DOPED CdTe

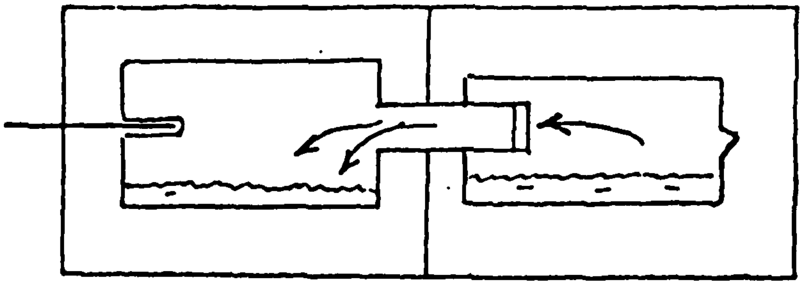
FIGURE 8. GLASS PROCESS DIAGRAM



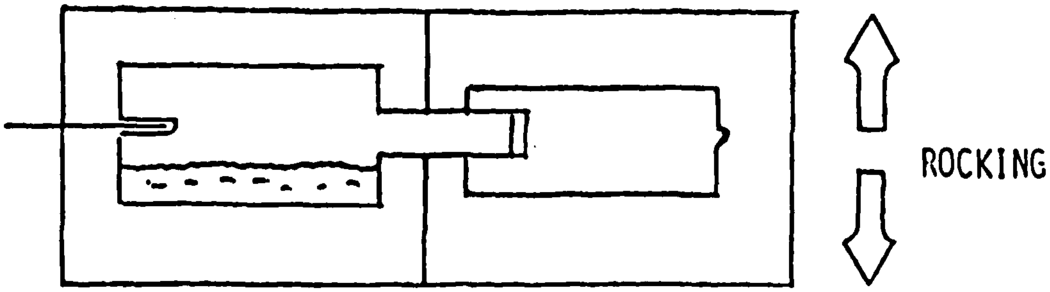
PURIFICATION



COMPOUNDING



DISTILLATION



CASTING

off while still under vacuum by heating and collapsing the pumping tube. The furnace is closed and need not be opened again until the glass is quenched.

The temperature is raised in both chambers while rocking the furnace. The casting chamber is heated to prevent premature transfer of the elements from the compounding chamber. The furnace is rocked for several hours to insure that all the elements have reacted properly and are uniformly mixed.

Rocking is stopped and the glass casting chamber cooled to allow transfer of the compounded glass into the casting chamber. Distillation occus through a porous quartz filter which removes all particulate matter. The distillation generally takes 12-15 hours. The amount of material passed through the frit varies depending upon diameter and thickness. A 6" diameter plate 2" thick requires about 4Kgms of glass while a 8" diameter plate 2" thick requires 7Kgms of material. It is interesting to note that the purity of the finished material improves with quantity prepared. The total amount of impurities from quartz walls, vaccuum system. etc. remains constant while the ending concentration decreases with increase in mass. The distilled glass is mixed by rocking. The glass is then allowed to cool while rocking down to the casting temperature range. Rocking is stopped and the furnace leveled up. The glass is rapidly cooled using compressed air to the anneal range 370 ° C. The glass is annealed 6-8 hours before being allowed to cool to room temperature.

AMTIR-I glass is compounded in very unique and valuable high purity quartz containers. Casting chambers 6", 8" and 10" in diameter are routinely prepared. Methods have been worked out to open the chambers with a diamond saw so that the cast plate may be removed without breaking. The chambers are cleaned up and resealed for reuse. The compounding tubes are not saved. The impurities within the high purity beginning reactants are left behind during the distillation. The residues are sometimes quite large indicating the effectiveness of the method in reparing high purity solid materials.

## B. Modification for Vapor Growth of CdTe

The temperature range involved in cadmium telluride compounding and solid state recrystallization is 1050-1100 ° C, well above the compounding temperature used for AMTIR-I. However, the furnaces are of sufficient caliber to reach and maintain these temperatures continuously. Times involved are much longer. From start to finish the AMTIR-I process requires 48 hours to produce a plate. High quality cadmium telluride grown from the vapor with solid state recrystallization (grain growth method) requires 300-400 hours (12-17 days) to produce good quality material 1" thick.(3) For a 6" diameter plate, 2700gms of cadmium telluride would be grown. Considering all these factors, the procedure carried out would be as follow:

1. The correct amounts of high purity cadmium and tellurium will be weighed out and placed in the compounding chamber as before. For a 6" plate, about 2700 grams will be required. High purity aluminum wire will be added (10-20ppm) to serve as an oxide getter. The casting chamber may need to be carbon coated using graphite formed from the pyrolysis of acetone.

2. The compounding and casting chambers will be heated to 200°C to remove moisture and the chamber will be tipped off.

3. The casting chamber will be heated to 1100° C. The compounding side will be heated to the boiling point of cadmium (765°C) and rocking begun. Over a period of hours, the temperature will be increased to 1100° C while rocking to insure complete compounding of the cadmium telluride.

4. Rocking will cease and material transfer begun. The casting chamber side will be reduced to a temperature of 1000-1050 C to bring about transfer of material to the plate side. The high temperature will be maintained so that grain growth will be a continuous process. Particulate matter and oxide impurities will remain behind in the compounding chamber. The time involved may be as long as 10-15 days.

5. After completion of the run, the cadmium telluride plate will be removed from the chamber using a horizontal glass saw as is done for AMTIR plates.

## C. Program Objectives

A large diameter, thick, high purity, large grain plate of cadmium telluride will be formed. Individual large grains 1-4cm$^3$in volume will be visible in the surface of the plate after lapping and light etching. Evaluation and treatment of the plate depends upon the desired use.

First emphasis of the program will be to establish the growth parameters using 6" diameter chambers. Purity of resultant material will be verified by chemical analysis. Electrical, mechanical and optical evaluation techniques established, scale up for 8" diameter and 10" diameter plates will occur.

Substrates will be cut out of 6", 8" and 10" diameter plates for evaluation for HgCdTe epitaxial growth. Disks 2" in diameter and 0.1" thick will be prepared for evaluation by groups disignated by DARPA.

Disks 2"D x 0.25 " thick will be prepared for optical homogeneity verification. The disks will be polished flat and paralled in order to carry out MFT based image spoiling tests. Additionally, lenses will be fabricated for evaluation in the U. S. Army small imager FLIR common Module.

The last goal of the program will be to grow large area HgCdTe layers in situ. Mercury vapor will be admitted into the 6", 8" and 10" diameter CdTe growth chambers in an attempt to produce layer growth of the right composition.

D. Vapor Gowth Results

The results obtained in 14 attempts to prepare CdTe plates using a stoichiometric vapor approach was dicussed in detail in Technical Report No. 2. The major difficulties encountered are summarized below:

1. Numerous quartz failures occured probably due to the attack of cadmium vapor at high temperatures and moderate pressures.

2. Formation of solid CdTe in the filters caused plugging. The use of filters had to be abandoned early to aid attempts to transfer the stoichiometric material from the compounding chamber to plate chamber.

3. Sublimation of stoichiometric material in a vacuum system is difficult to control and unpredictable. Excess of one component relative to another will shift equilibrium conditions.

4. Deposition does not always occur where desired.

5. Analytical results reported in Technical Report No. 3 did not demonstrate a purity improvement over the reactants. Filters were not used.

6. Trying to pass Cd and Te vapors through the same entrance at the same time to the plate chamber is the cause of major problems.

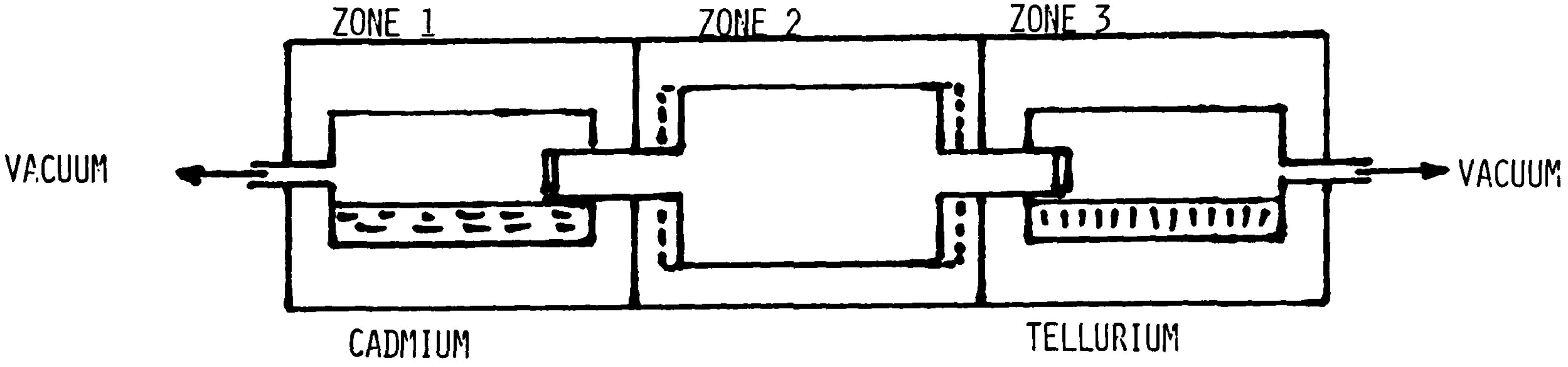
## E. Vapor-Melt Growth Method

The conclusion reached from the vapor growth results was that the Cd and Te vapors could not enter the plate chamber through the same entrance. A three chamber zone approach would be required if the program goals were to be met. A diagram depicting the modification of the AMTIR method is shown in figure 9.

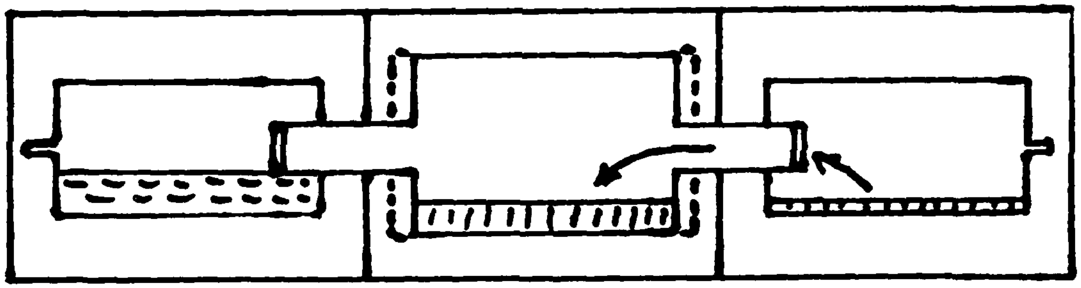
The elements are melted and purified while being pumped from both ends. After this step is completed and the chambers sealed, one element is transferred into the plate chamber and condensed as a liquid. In this case, Te is transferred first. Condensation as a liquid in the bottom of the chamber insures CdTe plate growth will occur where it is most desired. Notice the plate chamber is wrapped with quartz wool insulation to insure uniform temperature.

The second step involves compounding CdTe by transferring Cd vapor into the chamber. After the melt is compounded, air may be blown on the bottom of the chamber to promote crystal growth from the center and the bottom of the melt. The procedure, equipment used and early results were reported in Technical Report No. 3.

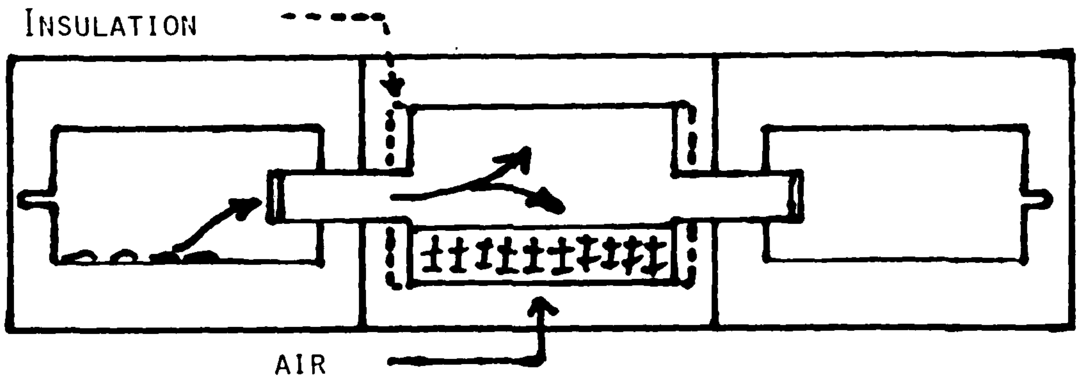
FIGURE 9. THREE ZONE MELT GROWTH PROCESS



REACTANT PURIFICATION



TELLURIUM TRANSFER



CADMIUM TELLURIDE GROWTH

## IV. RESULTS FOR THE QUARTER

### A. CdTe Plate Fabrication

During the quarter four large diameter CdTe plates were fabricated using chalcogenide glass compounding techniques. Two of the plates are 10 inch in diameter, the third was a 6 inch diameter plate and the fourth was 8 inch. (see table I)

Plate #47

This plate, 10 inches in diameter, was compounded from 3.1Kg 5 nines grade cadmium and 4.3Kg 5 nines grade tellurium. This represents a melt composition of approximately 55% atomic tellurium and 45% atomic cadmium. The compounding process was carried out as before by the slow distillation of first cadmium, then tellurium into a central evacuated chamber. The distilled vapors in both cases were filtered by means of a quartz fiber plug placed near the entrance to the central chamber. The cadmium is slowly transferred to the central chamber over a time period of about four hours at 750 C (vapor pressure approximately one atmosphere). Then the tellurium is transferred at 800 C (vapor pressure approximately 150mm) over a time period of 8 - 10 hours.

After material transfer, the central chamber is placed on an automatic temperature program which is designed to bring the CdTe to just above the melting point (1092 C). This is followed by a slow cooling cycle to promote the growth of large area crystals, a quench cycle, and finally a slow anneal cycle.

During the slow cool from above the melting point cycle, a low volume (1-2 lit./min.) air flow is directed on the bottom center surface of the central quartz chamber. The purpose of this cooling air is to ensure that the freezing is initiated at the center of the plate and crystal growth occurs outward towards the periphery. The complete temperature cycle is shown in Figure 10.

After cooling, the quartz chamber is sawed open and the CdTe plate is easily removed, intact, with no evidence of sticking or chemical reaction with the quartz. The resulting plate was typically about one inch thick, however, the upper half to two - thirds of the plate showed large evidence of dendritic growth and tellurium entrapment at the grain boundaries. The plate was also covered with a crust of dull grey powder which we believe is amorphous tellurium. The grain pattern of this plate was noticeably different from that observed on all previous plates. The crystal pattern formed two distinct regions over the plate area. One region, circular, about 5 inches in diameter was situated in the center portion of the plate. The grains in

## TABLE 1. THREE CHAMBER MELT GROWTH RESULTS

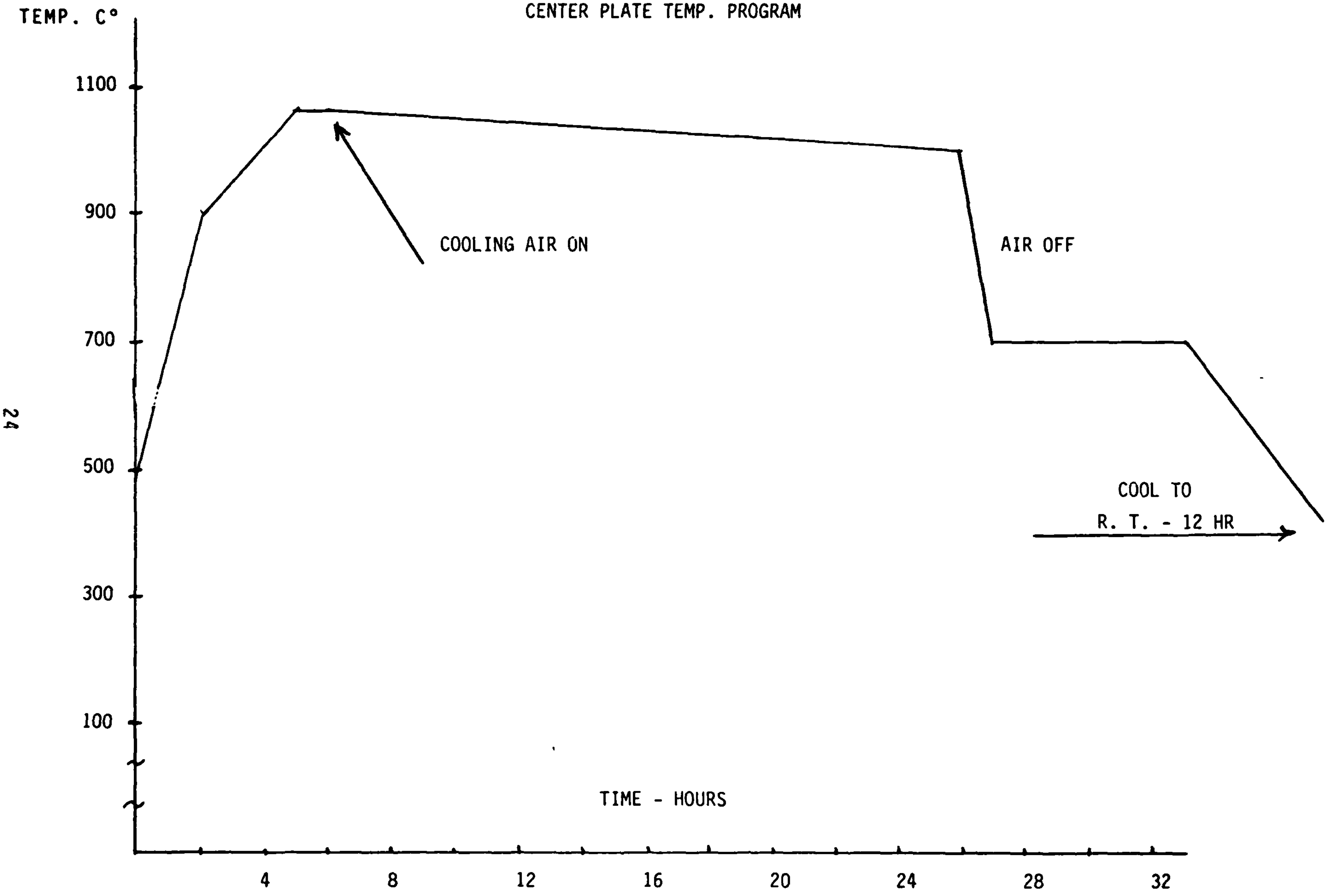
| RUN NO. | TYPE | SIZE | CONDITIONS | RESULTS |
|---|---|---|---|---|
| 26 | Solution | 2Kgms.6" | Cd 45 Te55, 1090-800 Air 24Hrs. | Lg. Grain, 1 layer |
| 27 | " | 6Kgms.8" | " " | Cd did not transfer. |
| 28 | " | " " | " " | " " |
| 29 | " | 4Kgms.8" | Cd45 Te55, 1090-800, 24Hrs. Air | Most of Cd did not transfer |
| 30 | " | 2.5Kgms.8" | Cd45 Te55, 1050-800, 24Hrs. Air, Cd transferred first | Small grain plate 0.3" thick |
| 31 | " | " " | Cd45 Te55, 1050-800, 24Hrs. Tellurium transferred while Cd cooled | Most of Cd did not transfer, thin plate |
| 32 | " | " " | Cd 45 Te55, 1075-800 Air, | Thin plate, most Cd did not transfer |
| 33 | " | " " | Cd45 Te55, 1075-800 | Cd did not tranfer, poor quality |
| 34 | " | " " | Cd45 Te55, 1075-800 Air, | Small grain, thin plate |
| 35 | " | " " | Cd45 Te55, 1075-800 | Cd did not transfer |
| 36 | " | " " | Cd transferred first, used check valve | Quartz failed |
| 37 | " | " " | Cd transferred first 1085/cooled, 6°C/HR | Good plate |
| 38 | " | " " | Same | Excellent plate |
| 39 | " | " " | Cd48 Te52, 1095, 3°C/HR | Good plate |
| 40 | " | 3.3Kgms.8" | Cd42 Te58, 1050, 3°C/HR | Good plate |
| 41 | " | 4.8Kgms.8" | Cd45 Te55, 1085, 5°C/HR | Good plate |
| 43 | " | " " | Cd45 Te55, 1060, 3°C/HR | Excellent plate |
| 44 | " | " " | Cd45 Te55, 1060, 3°C/HR New Furnace | Fair plate |
| 45 | " | " " | Repeat of 44 | Excellent plate |
| 46 | " | 7.7Kgms.10" | Cd45 Te55, 1060, 3°C/HR | Quartz failed |

TABLE 1. CONTINUED

| RUN NO. | MELT COMP. | SIZE | CONDITIONS | RESULTS |
|---|---|---|---|---|
| 47 | 55% Te<br>45% Cd | 10 inch<br>7.4Kg | Air Cooled | Plate intact - Two Regions of Crystal Growth Upper Plate Region Dendritic |
| 48 | 55% Te<br>45% Cd | 10 inch<br>7.4Kg | Air Cooled | Same As Above |
| 49 | 55% Te<br>45% Cd | 6 inch<br>2.4Kg | Air Cooled<br>Seeded Melt | Large Area Single Crystals, Upper Half of Plate Dendritic |
| 50 | 50% Te<br>50% Cd | 8 inch<br>3.1Kg | Air Cooled<br>Seeded Melt | Large Area Single Crystals, No Dendritic Growth, Good IR Transmissio Finished Plate 11mm Thick |

FIGURE 10

CENTER PLATE TEMP. PROGRAM



this region were relatively small, averaging about 0.25cm$^2$ in area. This area was surrounded by the second region composed of larger elongated crystals. These crystals average about 5cm in length and one cm wide. Orientations of these crystals were examined under the helium-neon laser and about 20%, roughly one in five appeared to be very close to a (111) orientation. An equal number of (110) orientations were also observed. The majority of the crystals however, in both regions were of undetermined orientation. (see figure 11)

Plate #48

This plate was compounded essentially identically with the previous plate #47. It was 10 inches in diameter, compounded from 3.1Kg high purity cadmium and 4.3Kg high purity tellurium, representing, as before, a 55% atomic tellurium composition.

The weight of this plate after compounding was 7.2Kg indicating about 97% of the total constituents were accounted for as having transferred to the central chamber. That is, 3% was left behind after vaporization as residue. The results were strikingly similar to the previous 10 inch plate. Again, two distinct regions of crystals were observed. The large area crystals surrounding a central portion of small crystals indicating that the freezing of this plate occurred in two separate patterns.

As before the upper surface of the plate was covered with dendritic growth, voids and amorphous tellurium. (see figure 12)

Plate #49

This plate was compounded in a 6 inch diameter chamber from 1.0Kg 5 nines cadmium and 1.4Kg 5 nines tellurium representing again a 55% atomic tellurium concentration.

The cadmium and tellurium transfer temperatures as well as the heating and cooling cycles were indentical with the two previous plates.

While all other growth conditions were identical with those used to prepare previous plates, this represented our first attempt at "seeding". The "seeding" was carried out as shown schematically in Figure 12-A. A small flow of cooling air was directed on the seed portion of the bottom of the quartz chamber to ensure growth initiating from this region. The results indicate that this indeed did take place. The single grain which grew in the center of this plate was the same orientation, (110), as that used for the seed and the total crystal pattern was indicative of a freezing process which proceeded from the center of the

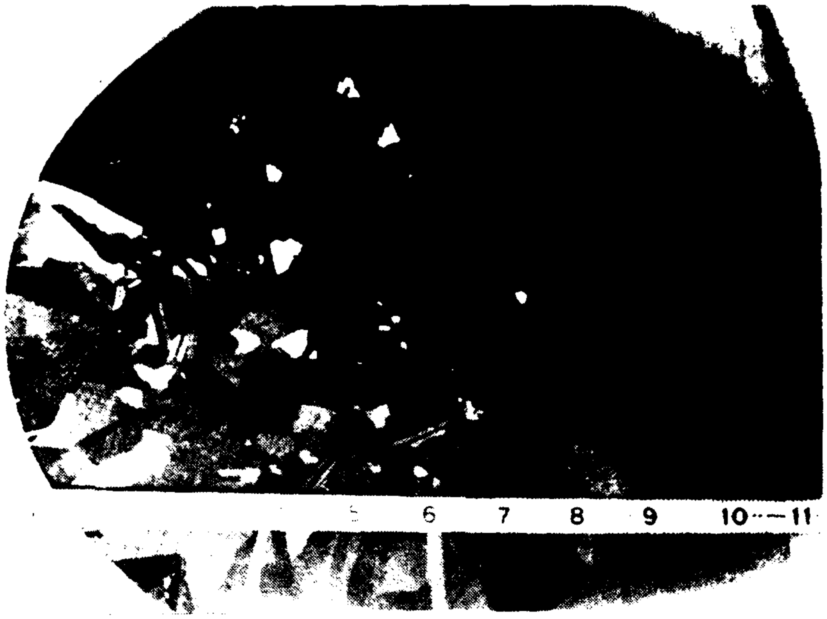


Figure 11
10 in. dia. CdTe plate showing large grain growth along outer edge of plate

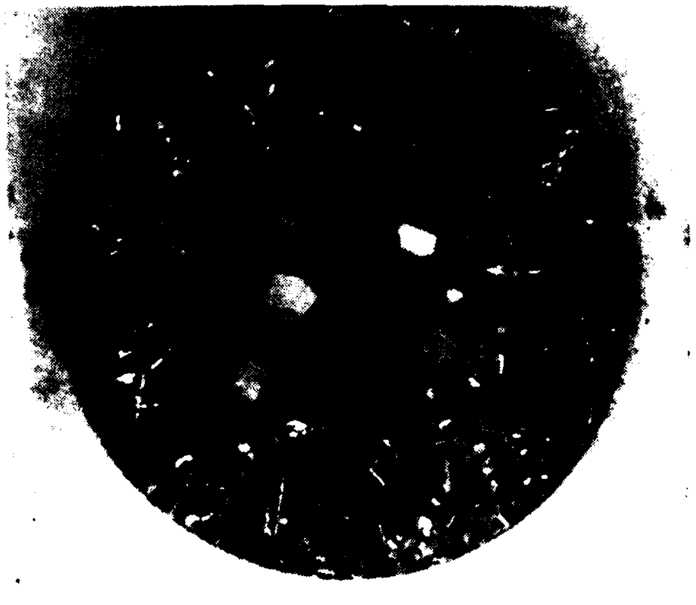


Figure 12
Back side (upper surface) of 10 in. dia. CdTe plate showing center region of well compounded material and outer edge of dendritic growth

FIGURE 12-A
DIAGRAM OF "SEEDED" MELT

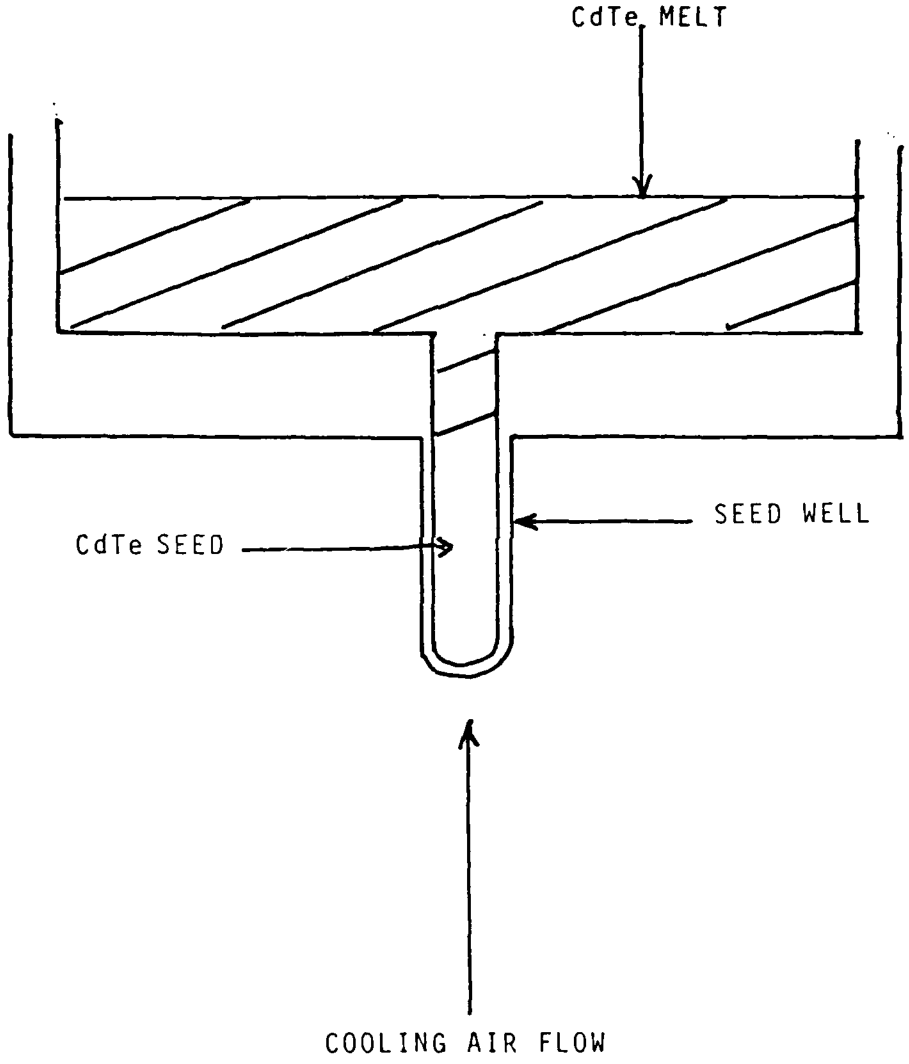


plate outwards towards the periphery. As a result, this plate showed some extremely large single crystal areas. Over 50% of the crystals averaged 2 inches or more in length and 0.3-0.5 inches wide with some up to 1.5 inches wide. Like previous plates, however, the upper half of the thickness of this plate was composed of dendritic, tellurium rich material with many voids. A thick scale of amorphous tellurium also covered the upper surface of the plate.

### Plate #50

Since the seeding experiment of Plate #49 produced encouraging results an attempt was made to repeat the seeding experiment but with a nearly stoichiometric melt composition. By this means we hoped to avoid the dendritic growth and voided regions which had always been observed previously with tellurium rich melts. Plate #50 was compounded in an 8 inch diameter quartz chamber from 1.45Kg high purity cadmium and 1.64Kg high purity tellurium. The cadmium, in cylindrical bar form, was etched in concentrated HCl for 5 minutes just before loading. This produces a cleaner, oxide free surface and the nonvolatile residue left behind after vaporizaton is greatly reduced. The tellurium is loaded into the chamber in chunk form without any pretreatment. The temperature cycle of this run was similar to the previous 3 runs with one exception. For plate #50 the temperature was maintained just above the melting point (1092° C) for an interval of four hours before the slow cooling cycle began. Again, a (110) oriented seed was placed in the chamber recess and when the cooling cycle started, a small jet of air (1-2 l/min.) was directed on the bottom of the chamber where the seed had been placed. (see figure 13 and 14)

Plate #50, after lapping, is shown in Figure 15. After grinding, lapping and polishing both sides, the plate was 11mm thick, 20cm in diameter (8 inches) and weighed 2.1Kg. There was no evidence of dendritic growth, nor was there any grey residue of amorphous tellurium remaining on the surface. The large area single crystal in the center of the plate indicated a (110) orientation, the same as the seed which was used. The grain pattern of this plate also showed evidence of a directional freeze which proceeded from the center outward and from the bottom of the plate upward. After polishing, an infrared transmission scan from 2.5 to 25 microns was performed. At 10 microns the transmission was 58.9% and an absorption coefficient of approximately 0.06cm was calculated. This represents an improvement over material measured previously of nearly 3X.

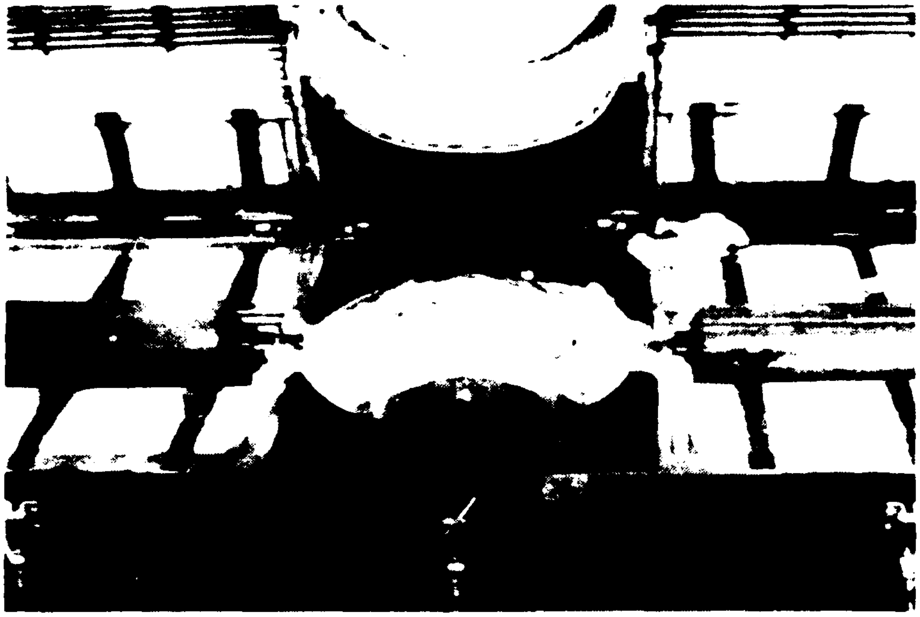


Figure 13
3 - zone furnace with 8 inch diameter chamber after compounding

Figure 14
Center chamber of 3 - zone furnace after commpounding 8 inch diameter plate

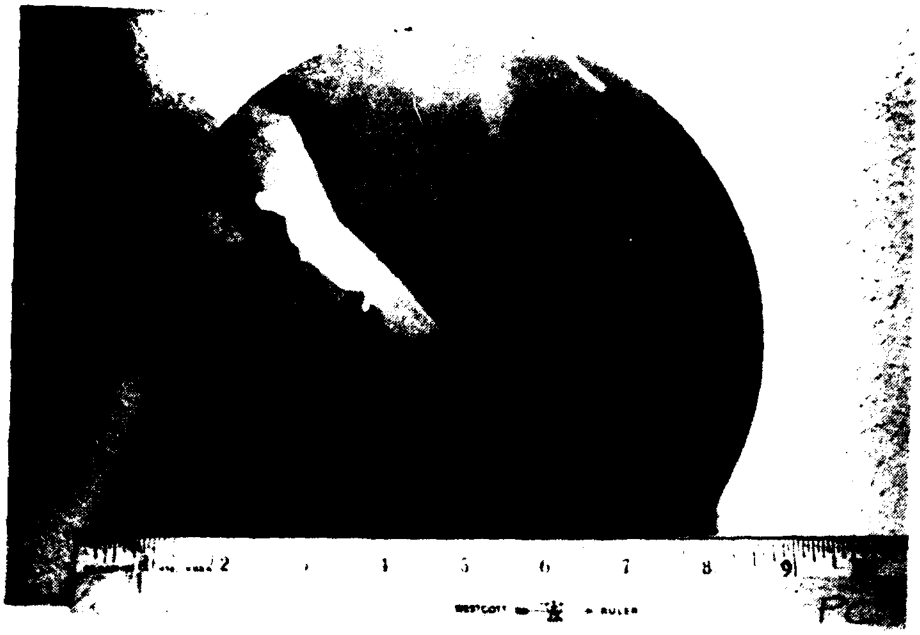


Figure 15
8 inch diameter CdTe plate after lapping (seeded plate)

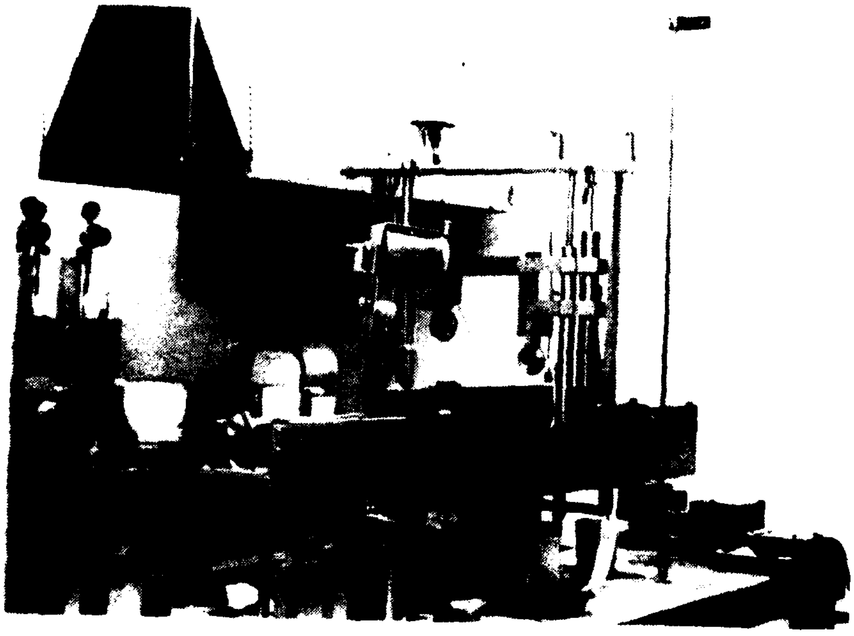


Figure 16
Wire saw for wafering 2 inch diameter CdTe substrates

### B. Optical Orientation Using A Helium-Neon Laser

During this quarter we also aquired a helium-neon laser from Meles Griot, Model No. 05-LHR-111, for use in optical determination of crystal orientation. Using this technique it was determined that a substantial fraction of the larger single crystal areas on a given CdTe plate were either (111) or (110) or very close ( ±10° - 20° ) to these orientations.

### C. Optical Applications

Previous reports have pointed out that infrared optical quality cadmium telluride is different from substrate material. Small grain low absorption material is required for lenses and windows. A lens can be designed, polished and tested before the end of the program. The precise refractive index will be required to calculate the radius of curvature for a lens which can be tested in our Diversified Optics MTF system.

A computer program has been written to calculate transmission of various optical materials from precise refractive index data. The most readily available data is from Kodak for IR TRAN 6, hot pressed cadmium telluride. Using the Kodak data, assuming an absorption coefficient of 0.01cm$^{-1}$ for 1-14um, and a thickness of 1cm, the IR transmission was calculated. The computer print out is shown in table II. Notice that the calculated transmission under these circumstances, agrees with the 65% previously used in judging the absorpton of material. Excellent quality material as that produced by II-VI Inc. is said to approach a level of 0.001cm$^{-1}$ throughout the range. Our goal then must be to reduce absorption in our material to that level.

### D. Wafering CdTe Substrates

During this quarter we also put into operation a wire saw (Laser Technology Model 2008) for wafering CdTe substrates. The Laser Tech. wire saw is ideally suited for cutting large diameter (2 inch) substrates. (see figure 16 and 17) For best results, the cutting action is obtained with a 10 mil diameter stainless steel wire used in conjunction with an abrasive slurry. The slurry is made up in approximately 300 ml. batches using a 2:1 by volume ratio of ethylene glycol to 400 mesh silicon carbide powder. Pure glycerin was also evaluated as an abrasive carrier but appeared to be too viscous in most instances. We also evaluated a diamond impregnated 8 mil diameter wire without the SiC slurry but longer wire life was achieved by using the 10 mil dia. stainless steel wire. With a slurry dripping rate of approximately one drop per second a cutting rate of nearly 3 inches per hour was achieved using a weight adjustment of approximately 100g.

Figure 17
Wire saw (close up)

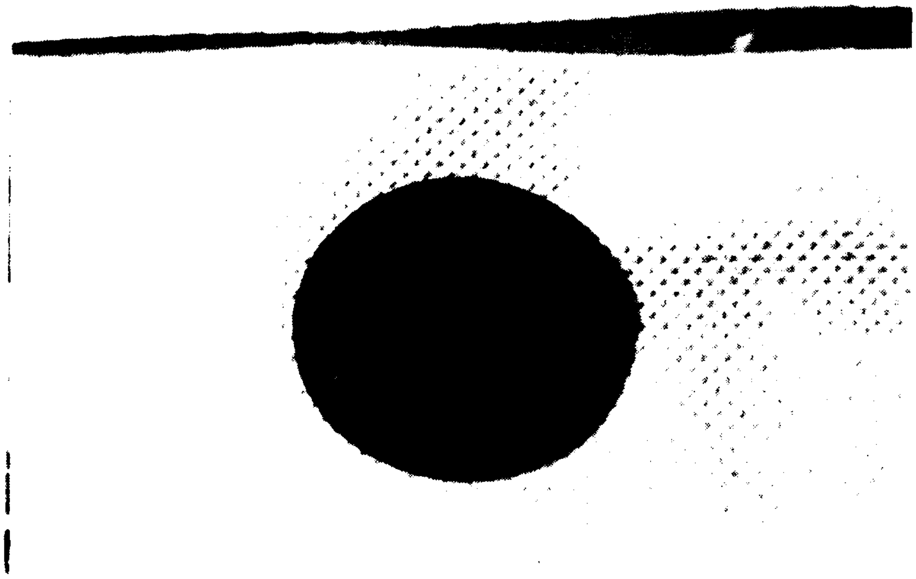


Figure 18
2 in. dia. CdTe substrate with large single crystal areas

Surface finish was usually very smooth with only a trace of "ridging" which could easily be removed by light lapping. Two inch diameter slices were sawed into .080 in. thick substrates and then hand lapped on each side to a final thickness of .070-.075 in. Substrate polishing by chemical-mechanical techniques was not attempted this quarter. The hand lapping was carried out using the same 400 mesh silicon carbide powder used in the wire sawing process. The final surface finish produced by lapping on a flat glass plate is well suited for crystal orientation determination by optical means, i. e., a helium-neon laser.

## E. Status and Plans

With regard to the plans for this quarter which we had outlined previously we did prepare the first two 10 inch diameter plates and evaluated the material.

The use of this material as substrates for liquid phase epitaxy of HgCdTe layers at this location has been postponed until the next quarterly reporting period. We did, however, send out some 2 inch diameter substrates to other organizations independently working on LPE techniques in HgCdTe. Samples were sent to Raytheon, Texas Instruments, Inc. and Ford Aerospace. We are expecting some results of their evaluation in the very near future. (see Figure 18)

Finally, the work on vapor phase heat treatment of melt grown plate material is underway and will be reported on during the next reporting period.

TABLE II.

CALCULATED IR TRANSMISSION FOR CADMIUM TELLURIDE

| WAVE LENGTH | IR INDEX | ABSORPT. | (cm) THICKNESS | R | TRANSM. |
|---|---|---|---|---|---|
| 1.00 | 2.838000 | 0.010000 | 1.0000 | 0.229341 | 0.619969 |
| 1.06 | | 0.010000 | 1.0000 | 1.000000 | 0.000000 |
| 1.50 | 2.742000 | 0.010000 | 1.0000 | 0.216715 | 0.636744 |
| 2.00 | 2.714000 | 0.010000 | 1.0000 | 0.212980 | 0.641773 |
| 2.40 | | 0.010000 | 1.0000 | 1.000000 | 0.000000 |
| 3.00 | 2.695000 | 0.010000 | 1.0000 | 0.210431 | 0.645221 |
| 4.00 | 2.688000 | 0.010000 | 1.0000 | 0.209490 | 0.646499 |
| 5.00 | 2.684000 | 0.010000 | 1.0000 | 0.208951 | 0.647231 |
| 6.00 | 2.681000 | 0.010000 | 1.0000 | 0.208547 | 0.647780 |
| 7.00 | 2.679000 | 0.010000 | 1.0000 | 0.208277 | 0.648147 |
| 8.00 | 2.677000 | 0.010000 | 1.0000 | 0.208007 | 0.648515 |
| 9.00 | 2.674000 | 0.010000 | 1.0000 | 0.207603 | 0.649066 |
| 10.00 | 2.672000 | 0.010000 | 1.0000 | 0.207332 | 0.649434 |
| 11.00 | 2.669000 | 0.010000 | 1.0000 | 0.206927 | 0.649987 |
| 12.00 | 2.666000 | 0.010000 | 1.0000 | 0.206521 | 0.650540 |
| 13.00 | 2.663000 | 0.010000 | 1.0000 | 0.206116 | 0.651095 |
| 14.00 | 2.660000 | 0.010000 | 1.0000 | 0.205709 | 0.651650 |

## V. PLANS FOR NEXT QUARTER

1. Continue the growth of 8-inch diameter plates from near stoichiometric melts using seeding techniques and prepare thick (one-inch) samples without dendritic growth or voided regions.

2. Carry out a series of heat treatment experiments under varying conditions of time, temperature, and cadmium or tellurium vapor pressure to lower the absorption coefficient still further.

3. Develop a non contact chemical polishing technique suitable for preparing substrates with damage free surfaces.

4. Begin a series of experiments to deposit epitaxial layers of HgCdTe by liquid phase epitaxy on both oriented and non oriented CdTe substrates.

5. Prepare a 10 inch diameter plate from a near stoichiometric melt which has large area single crystal regions and evaluate the material regarding optical quality and orientation.

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