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LARGE PLATE CdTe SYNTHESIS BY SEALED
VESSEL TRANSPORT

A. R. HILTON, PRINCIPAL INVESTIGATOR
(214) 494-5624

QUARTERLY TECHNICAL REPORT NO. 2
REPORT PERIOD: MAY 1 - JUNE 30, 1982

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AMORPHOUS MATERIALS, INC.

3130 BENTON • GARLAND, TEXAS 75042

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The second quarterly report for the program to grow large plates of CdTe by vapor transport in a sealed system covers the period May-June, 1982. Altogether 14 attempts have been made to compound CdTe and then transport the material into a separate plate chamber. Plates 6" in diameter have been formed only twice. Progress has been hampered by quartz failure believed due to attack by cadmium vapor. Failure to transfer is believed to be due to deviation from stoichiometry and plugging of the transfer tube between the two chambers. A process change planned for next quarter should eliminate these problems.		

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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-telluride (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-compounded. The method to be used in this program is 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.

The first quarterly report discussed the results obtained in the first 8 attempts to grow CdTe plates. During the current report period, 6 more attempts were made. Plates 6" in diameter have been formed in only 2 of the total 14 attempts. Major problems which have occurred are devitrification of the quartz and failure of the CdTe to transfer from the compound to the plate growth chamber.

Quartz failure has been due mainly to devitrification brought on by exposure to Cd vapor for long periods of time at high temperatures and pressure. Use of pre-compounded material was helpful in minimizing the problem. Also, a practical method was developed to precoat the quartz chambers with carbon formed from acetone.

Failure to transfer was due to problems associated with stoichiometry and by plugging of the transfer tube. Removal of the quartz filter did not prevent plugging. To overcome the stoichiometry problems and increase the transfer tendency, the temperature difference between chambers was increased. The plugging tendency also increased since the Cd and Te vapors formed CdTe rapidly on the first surface reached that was much below the 1097°C melting point.

The conclusion was reached that the program goals could not be met using a two chamber (compound and plate growth) approach. That is, Cd and Te vapors can not be admitted through the same entrance to the growth chamber. A 3 chamber approach will be used instead. One chamber will be reserved for the purification and vapor transport of Cd and a separate chamber for Te. A 3 chamber approach has been used previously to prepare high purity chalcogenide glasses. Preliminary experiments indicate Cd and Te may be transported separately through a filter with no problem.

Plans for next quarter are to use the 3 chamber approach to prepare 6" CdTe plates.

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 availability 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 Cd Te 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 alternative approach.

Large plates of high purity large grain cadmium telluride will be grown from the vapor in a sealed system. Cadmium telluride will be compounded from the elements and sublimed through a filter into a separate growth chamber 6", 8" or 10" in diameter. Grain size will be increased by solid state recrystallization. Material thus produced will 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 insitu.

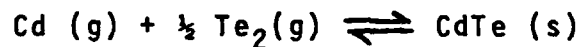
II. VAPOR GROWTH OF CADMIUM TELLURIDE

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 high 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:



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 Te₂ 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 ratio of 1:1 between the cadmium and tellurium atoms. The pressure of cadmium vapor (pCd) and the pressure of tellurium vapor (pTe₂) in equilibrium over solid CdTe at the growth temperature is very critical 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 pre-compounded 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 substrate with spontaneous nucleation and growth occurring 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 results published in 1959 details the thermodynamic 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
|| v| compounds generally (2) and cadmium telluride (3) spe-
cifically. 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 1097°C.
The term "congruent melting point" indicates that except at
perfect stoichiometry, below the 1097°C melting point, both
Cd rich and Te rich liquids exist in equilibrium with pure
CdTe. The point is better illustrated 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
exist. The range is less than one part per hundred thousand
or 0.001 percent. Minimum vapor pressure at all temperature
exist along this line. Equilibrium vapor pressure would be
exactly 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 sta-
bility 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 li-
quid 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 liquid mixture:

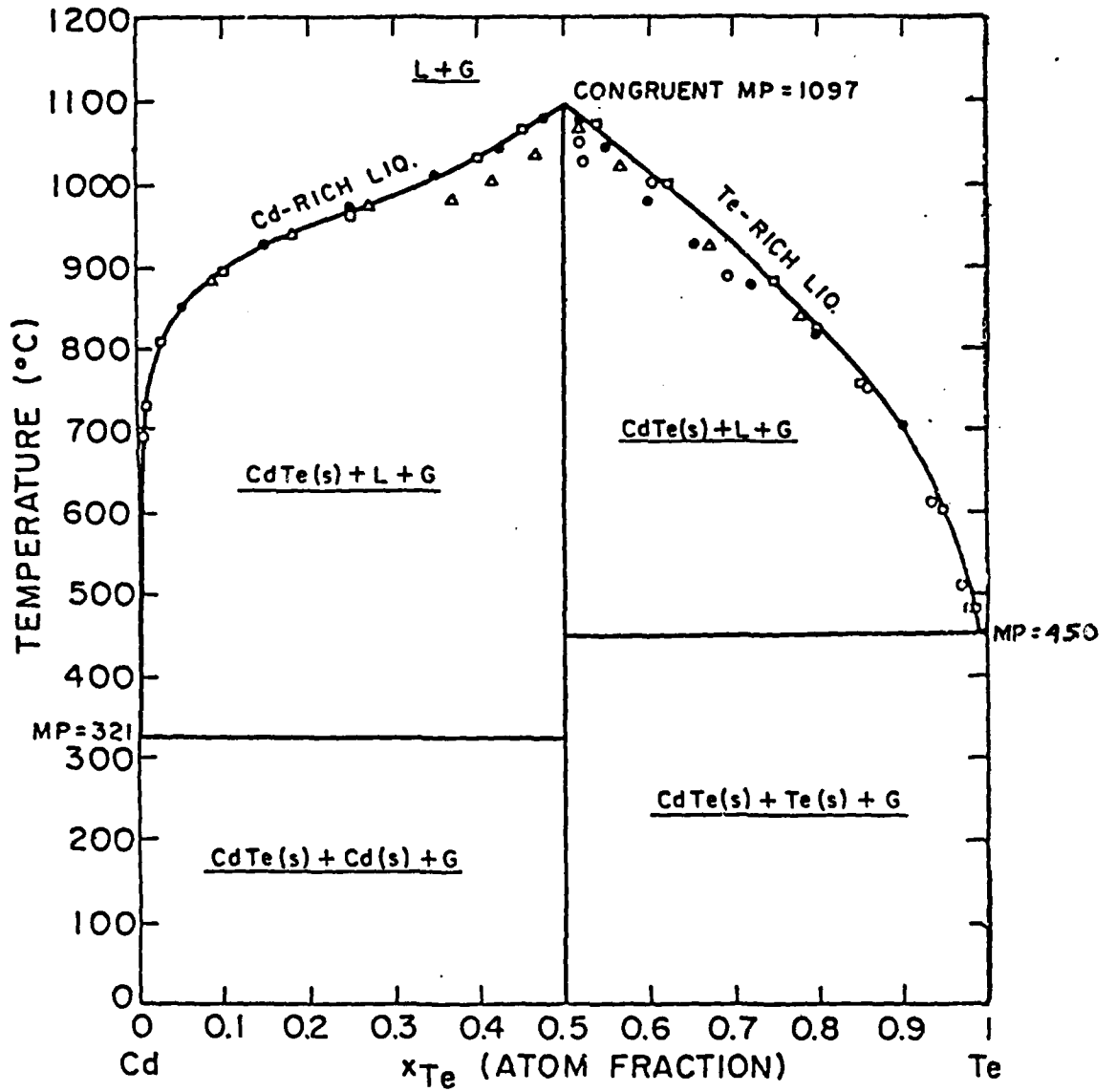


FIG. 1. PHASE DIAGRAM OF THE Cd-Te SYSTEM.

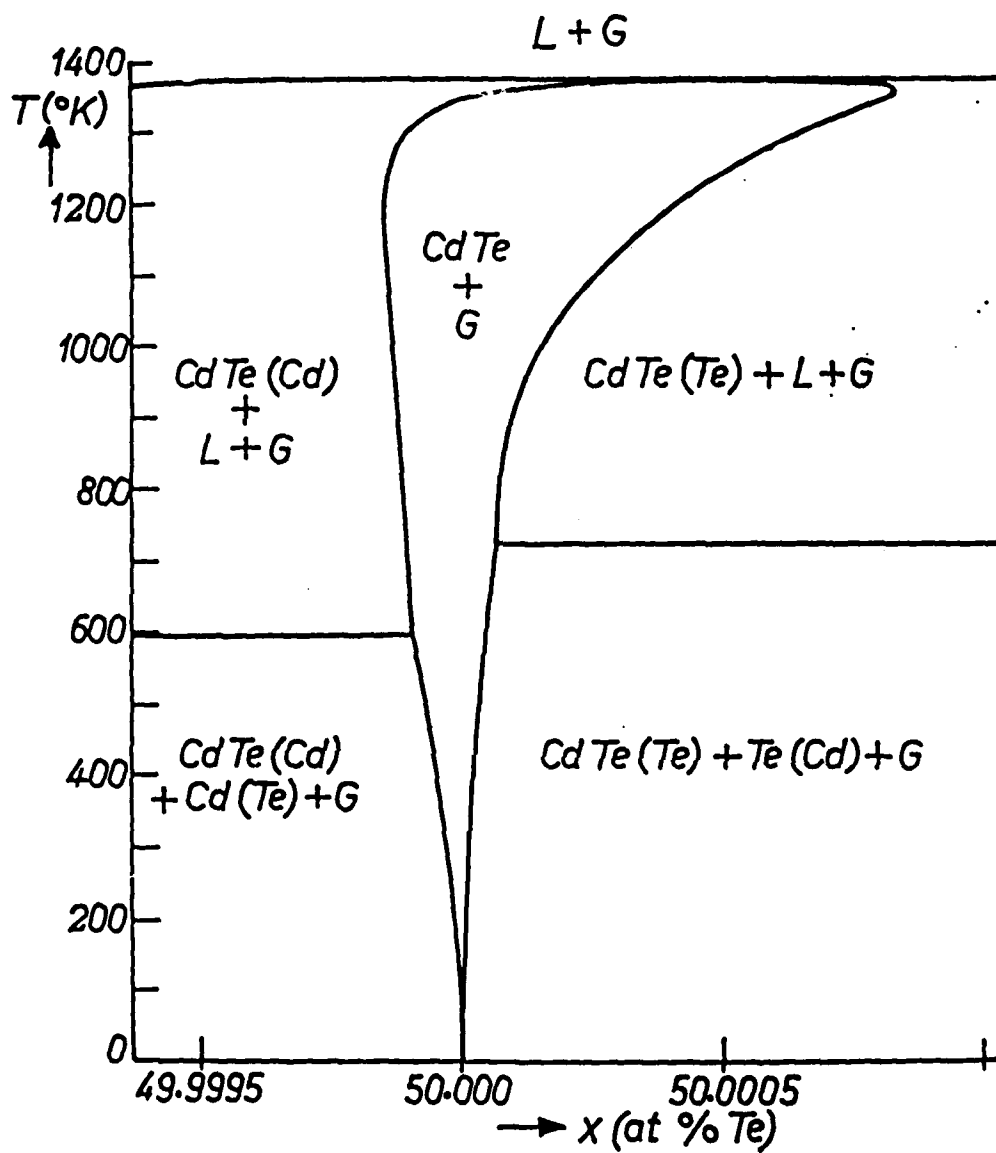


FIG. 2. SOLID STABILITY FIELD OF CdTe.

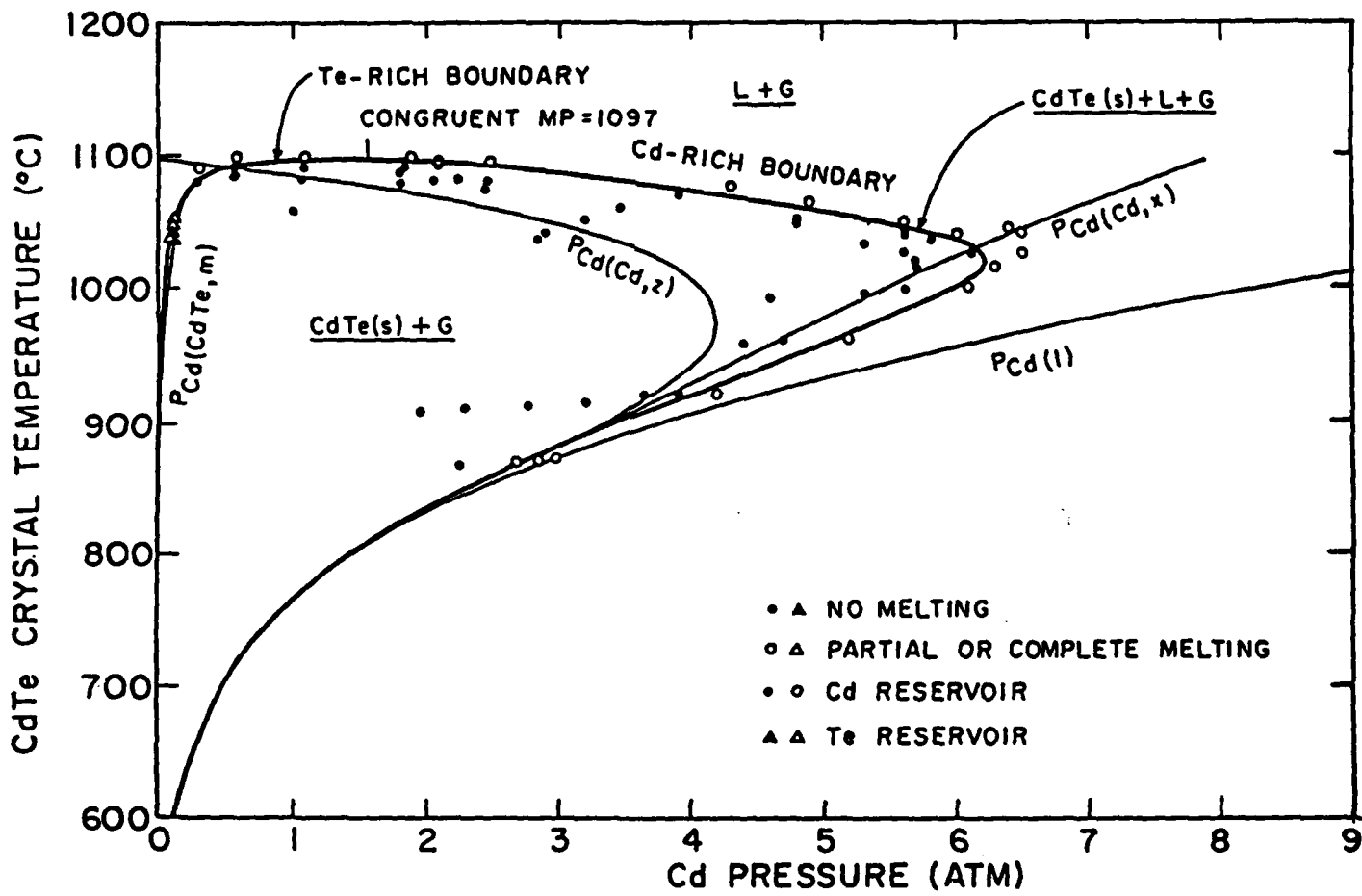


FIG. 3. Cd-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

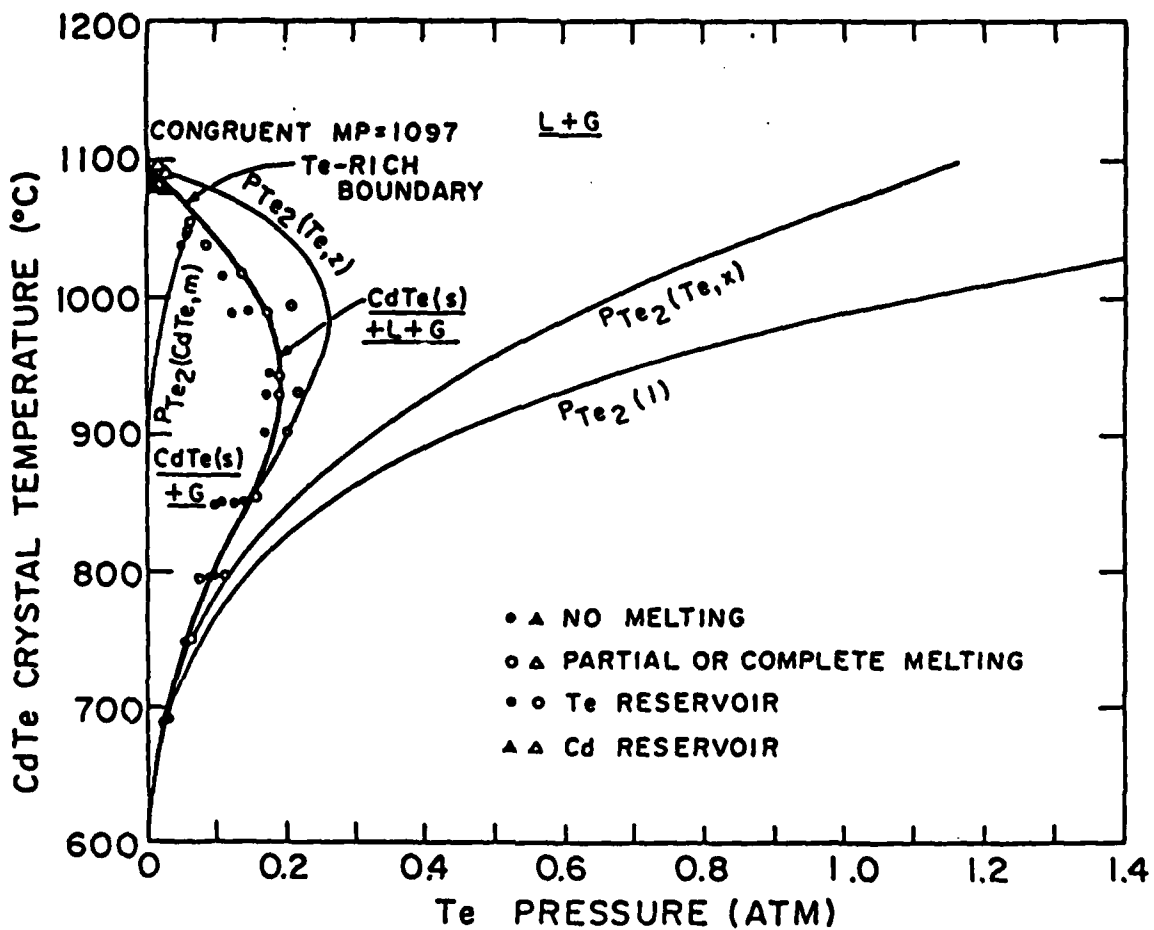


FIG. 4. Te-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

$$P_{Cd} = x P_{Cd}(1)$$

Where P_{Cd} is the pressure of cadmium above 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.

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, 1097°C , is about 1.5 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 inversely proportional to the square root of its molecular weight and directly proportional to its pressure. Therefore, for CdTe sublimation, we find the effusion ratios to be ⁽²⁾

$$R_{\text{Cd}}/R_{\text{Te}_2} = (P_{\text{Cd}}/P_{\text{Te}_2}) \left(\frac{\text{MW}_{\text{Te}_2}}{\text{MW}_{\text{Cd}}} \right)^{1/2}$$

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 a sealed system where equilibrium type conditions may be established. The equilibrium constant is given by:

$$K_{\text{Cd Te(s)}} = (P_{\text{Cd}}) (P_{\text{Te}_2})^{1/2}$$

The build up of 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 deposition and short growth periods even at the high temperatures produced plates with small grains and voids.

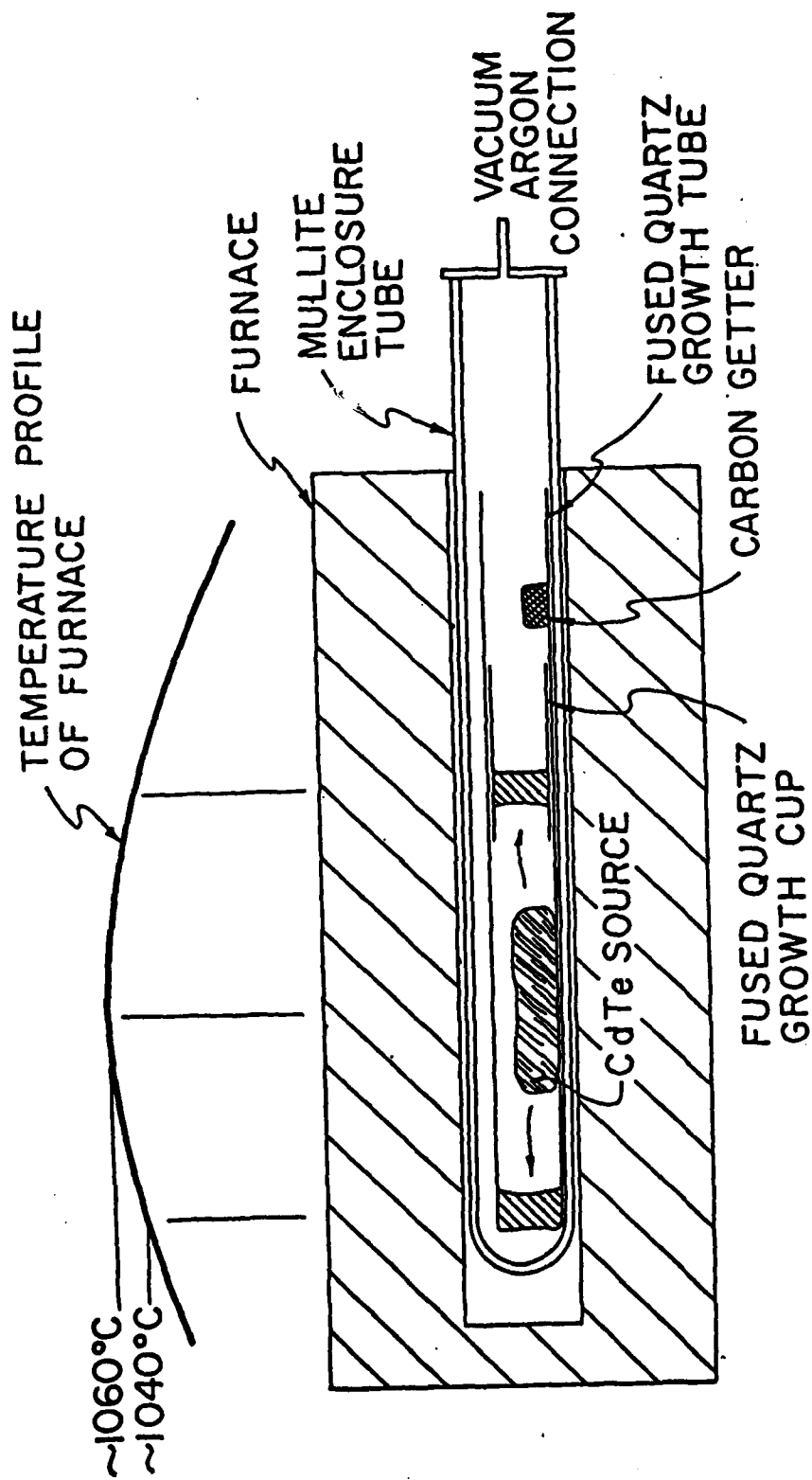
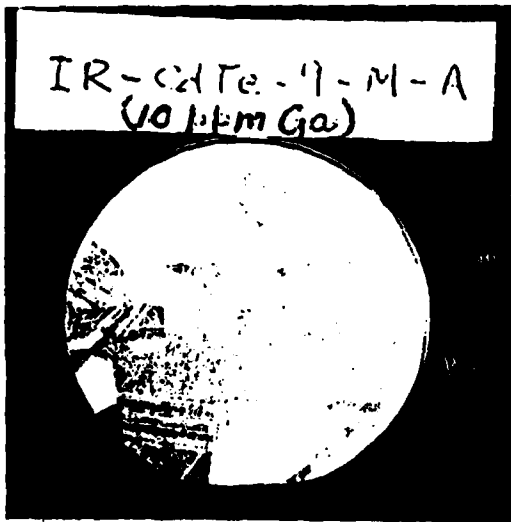
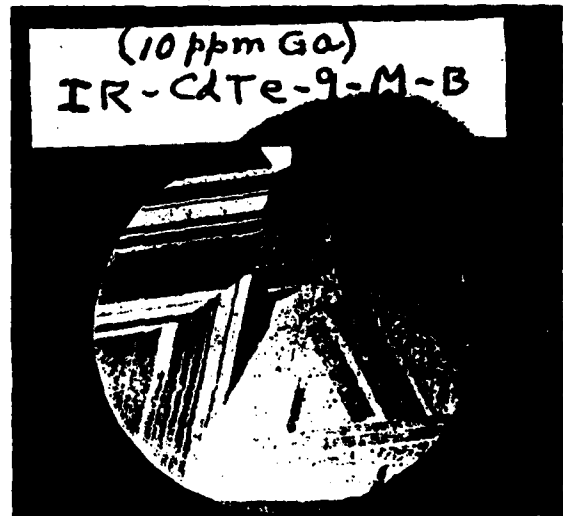


FIG. 5. HORIZONTAL SYSTEM FOR CRYSTAL GROWTH BY GRAIN GROWTH



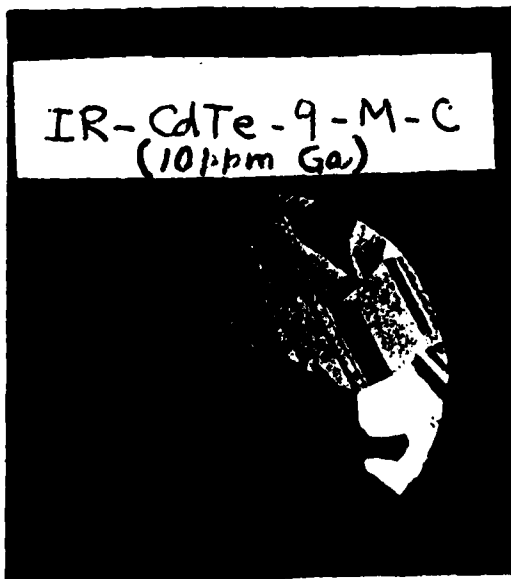
Inches 1 2

GOULD →



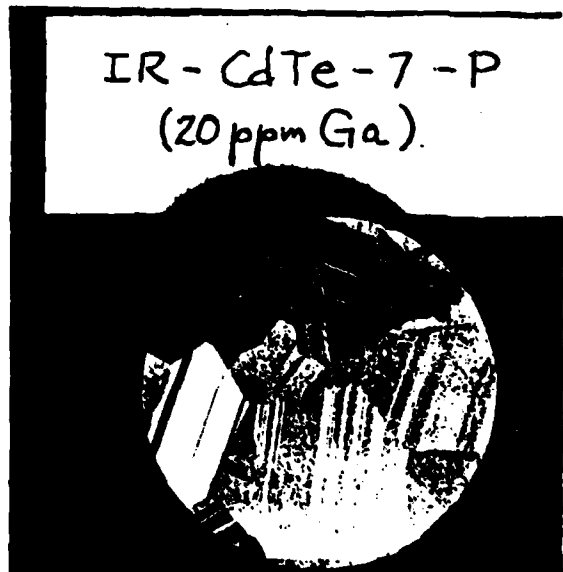
Inches 1 2

GOULD →



Inches 1 2

GOULD →



Inches 1 2

GOULD →

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

The systems were operated semi-sealed. Argon gas was used as a carrier. Pressures up to 1 atmosphere was used but 180 mm, the vapor pressure of stoichiometric Cd Te at 1050°C, was the preferred 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 Te₂ and Cd vapors at temperatures of 700-800°C. Treatments were alternated and lasted 1-5 days. Measured absorption at 10.6μm 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 Te₂ vapor, almost theoretical transmission was obtained.

III APPLICATION OF THE AMTIR METHOD TO THE GROWTH OF CdTe

A. Preparation of AMTIR-1 glass

A simplified diagram depicting the glass compounding and casting process developed by Amorphous Materials, Inc. to produce AMTIR-1, is shown in figure 8. A high purity quartz 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.

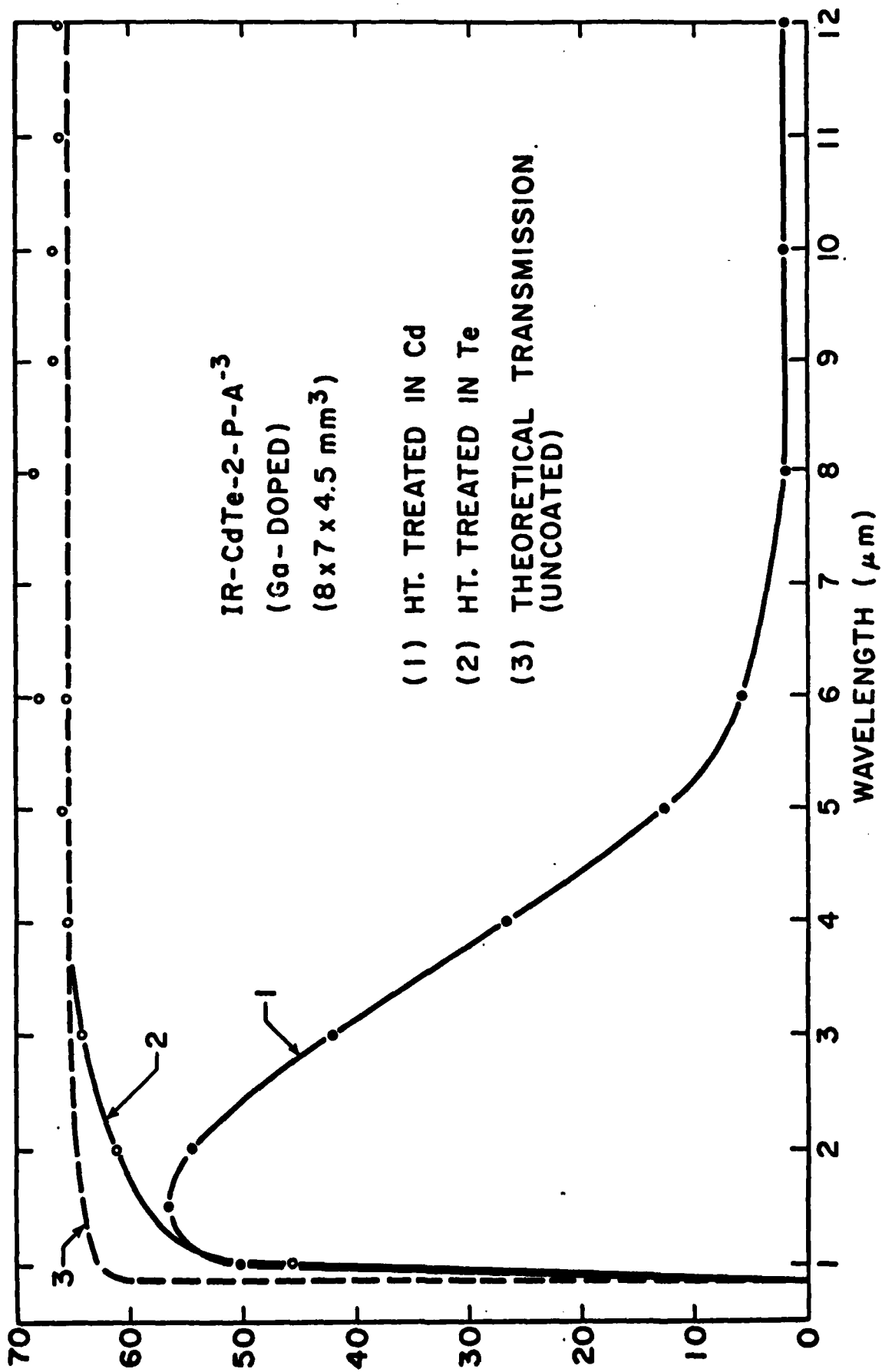
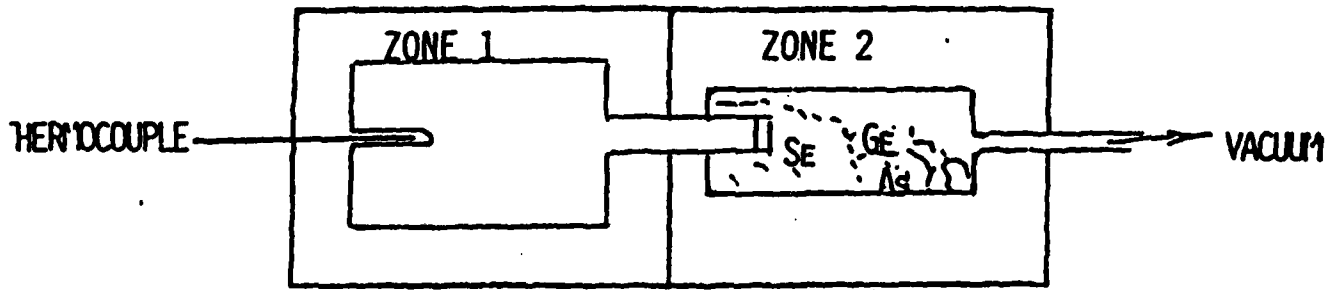
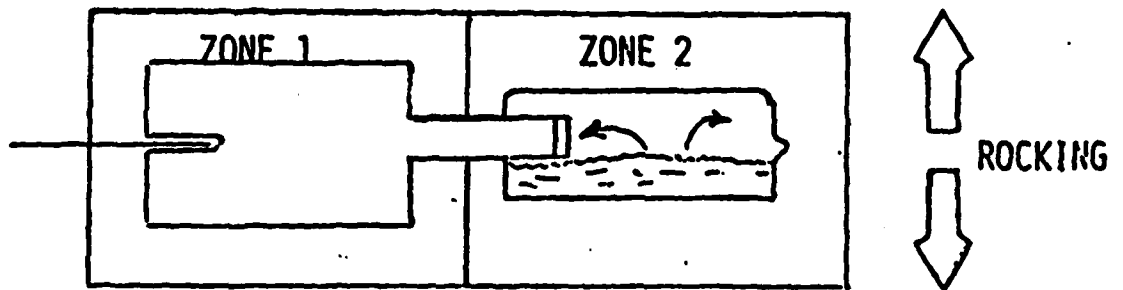


FIG. 7. OPTICAL TRANSMISSION OF Ga-DOPED CdTe

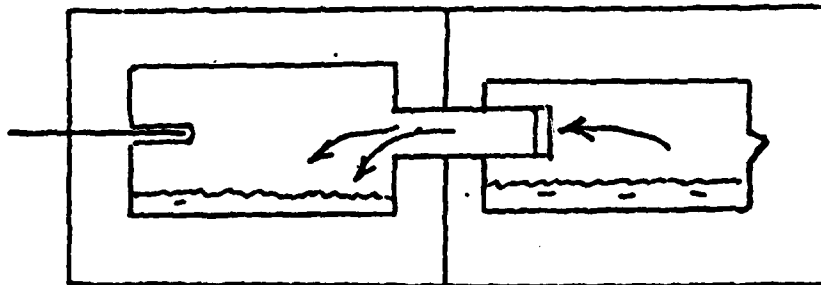
FIGURE 8. GLASS PROCESS DIAGRAM



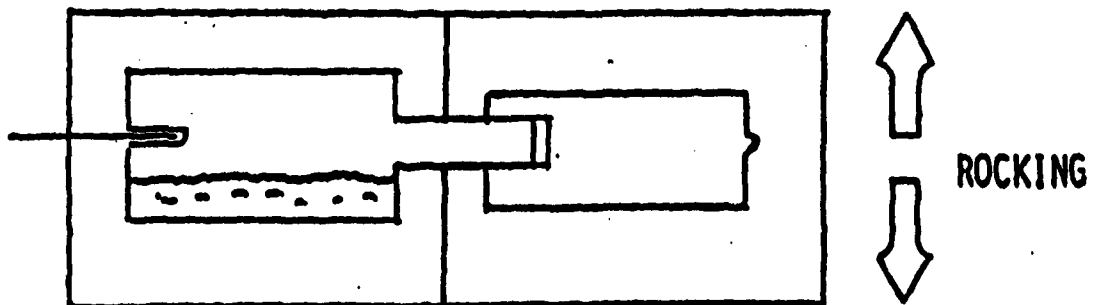
PURIFICATION



COMPOUNDING



DISTILLATION



CASTING

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 chambers is sealed 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 occurs 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, vacuum 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-1 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 preparing high purity solid materials.

B. Modification for Vapor Growth of Cd Te

The temperature range involved in cadmium telluride compounding and solid state recrystallization is 1050-1100°C, well above the compounding temperature used for AMTIR-1. 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-1 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 follows:

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 1-4cm³ 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 will be

IV. RESULTS FOR THE QUARTER

A. Equipment Changes

The Barber Colman 521 overtemp control units were modified so that control up to 1200°C could be attained. The units are used on both the R & C furnaces to guard against exceeding the safe temperature limits for quartz during the long periods of crystal growth. Double thermocouples are used in both the R & C furnaces to provide both temperature control and overtemperature protection.

B. Plate Growth Summary

Results obtained in the first 8 attempts to vapor grow cadmium telluride plates were presented in the first quarterly report. Only the last four involved use of 6" chambers as had been originally scheduled. Six more attempts have been made since the last report. Conditions and results for all 14 runs are summarized in table I.

Examination reveals that a plate was actually grown in only two cases, runs 6 and 7. Even then, pre-compounded CdTe was used as the source material. Use of a filter between the two chambers was abandoned early. In no case was cadmium telluride compounded from the elements and vapor transported through a filter to form a plate in a separate chamber.

Various difficulties accounted for the failure to achieve our goals thus far. The major difficulties encountered were quartz failure and transfer failure. Each are discussed below.

TABLE I. CdTe PLATE GROWTH RESULTS

RUN NO.	PLATE SIZE in	CHARGE KGMS. E/PC	TRANSFER COND. R/C	GROWTH COND. R/C	TIME HRS.	RESULTS
1	8	5E	1060/1020	1060/1020	52	No. Transfer, CdTe in R side, IR Trans.
2	8	3.3E	1060/960 1060/900	1060/900	48	No Transfer, CdTe in R side, Good IR Trans.
3	8	3.4E				Chamber Imploded at 900°C, filter plugged
4	8	3.3E				Chamber Imploded at 1000°C
5	6	2.2E	1060/1020			Power Failure, Fractured Quartz
6	6	2PC	1060/975	1060/975	30	Thin, Wedged Plate, Plug in Transfer Tube
7	6	2PC	1060/980	1090/1050	100	Insulated Chamber, Carbon Coated, 6"Dx0.4" Excellent Plate
8	6	2.2E	1100/1060	1100/1060	70	No Transfer
9	6	2.2E	1090/980			Quartz Failed
10	6	2PC	1050/980	1050/1050	100	Transfer tube plugged, No Transfer
11	6	2.2E	1070/950			Quartz Failed
12	6	2.2E	1070/980			Quartz Failed
13	-	2E	900/700			Precompound Material, No Transf.
14	6	2PC	1070/960	1070/1060	72	No Transfer, Tube Plugged

E Elements PC Pre-Compounded
R Compound Chamber C Plate Chamber

Quartz Failure

Exact Stoichiometry between the elements is extremely important. Weighing must be carried out accurately. The only way that you can be sure that stoichiometric CdTe has been produced, free of tellurium or cadmium rich material, is to raise the temperature in slight excess of the 1097°C Congruent melting point. Until that point is reached, high pressures of Cadmium vapor are experienced. The high pressures cadmium vapor devitrifies the quartz during the long periods at high temperature.

The precompounded material has already passed through the stage of high cadmium pressures. When a chamber is loaded with pure cadmium telluride, the highest pressure which may be expected is 1.5atm at 1097°C. Since the transport is attempted at 1050-1070 with the vapor rapidly condensing in the C chamber, one may expect that total cadmium pressure is considerably below the 1.5 atmospheres maximum.

Carbon coating was used to attempt to avoid the quartz failure. Double chamber (R & C) quartz units were placed in the furnace empty. A long tube had been left on the R side. Both chambers were evacuated and heated to 800°C. Acetone vapors were allowed to enter. An excellent dark carbon film formed on the walls of both chambers. The furnace was cut off and allowed to cool to room temperature. The unit was removed from the furnace and the long tube on the R side removed using the glass saw. The unit could then be loaded in the usual manner with a 2Kgms charge of CdTe without disturbing the protective carbon film. Undoubtedly, some protection was realized. However, quartz failure continued to occur.

One adverse effect of carbon coating was visibility. In the transfer attempt, a temperature difference of at least 100°C (aided by air blown on the bottom of the plate chamber) was provided for an overnight period. It was essential to verify visually that the charge material in the R side had been removed by sublimation to the C chamber. The furnace was opened for a fast look. However, the temperature on the R side is above 1000°C. At that temperature, especially with carbon coating on the walls of the chamber, it becomes very difficult to see because of light emission. Several times we thought the material had transferred and set the temperatures for 100 hours of recrystallization only to find out later that the material was still in the R side. A run and several days of time were thus wasted.

D. Failure to transfer

Sublimation may be stopped if one of the components, tellurium in this case, builds up in the vicinity of the source. To compensate for this possibility, we have attempted to use perfectly stoichiometric materials and large temperature differences between the R & C chambers. The lower temperature on the C side is below the boiling point of tellurium, 990°C. However, the melting point of CdTe is 1097°C. If the vapor comes into contact with a cooler surface before reaching the C chamber, CdTe will form. Such has been the case. The transfer tube between the two chambers has been the site of CdTe deposition. So much so that in at least half of the runs, a CdTe plug was found in the transfer tube. Quartz wool insulation failed to keep the plugging from occurring. Earlier speculation that the filter was being attacked may have been erroneous. The plugging was probably due to CdTe formation.

fraction was left behind in part and part deposited on the top of the pure tellurium. These results illustrate the real possibility of preparing high purity CdTe provided low temperature distillation through a filter is used.

F. Process Change

The inescapable conclusion is that three chamber preparation will be required if program goals are to be met. Three chambers preparation has been used previously (4) to prepare high purity chalcogenide glasses. A diagram of the apparatus used is shown in figure 9. The two materials prepared in this manner were a Ge-Sb-Se glass (TI1173) and a Ge-As-Se glass (AMTIR-1). There is no obvious reason why the method can not be applied to CdTe with excellent results. The only complication is that the plate chamber temperature will have to be raised to near or over the 1097°C melting point. The method will actually assume a vapor-melt preparation method. Such methods have been used successfully in the preparation of gallium arsenide.

No further attempts will be made using a two zone approach. All efforts will be concentrated on developing the three zone approach.

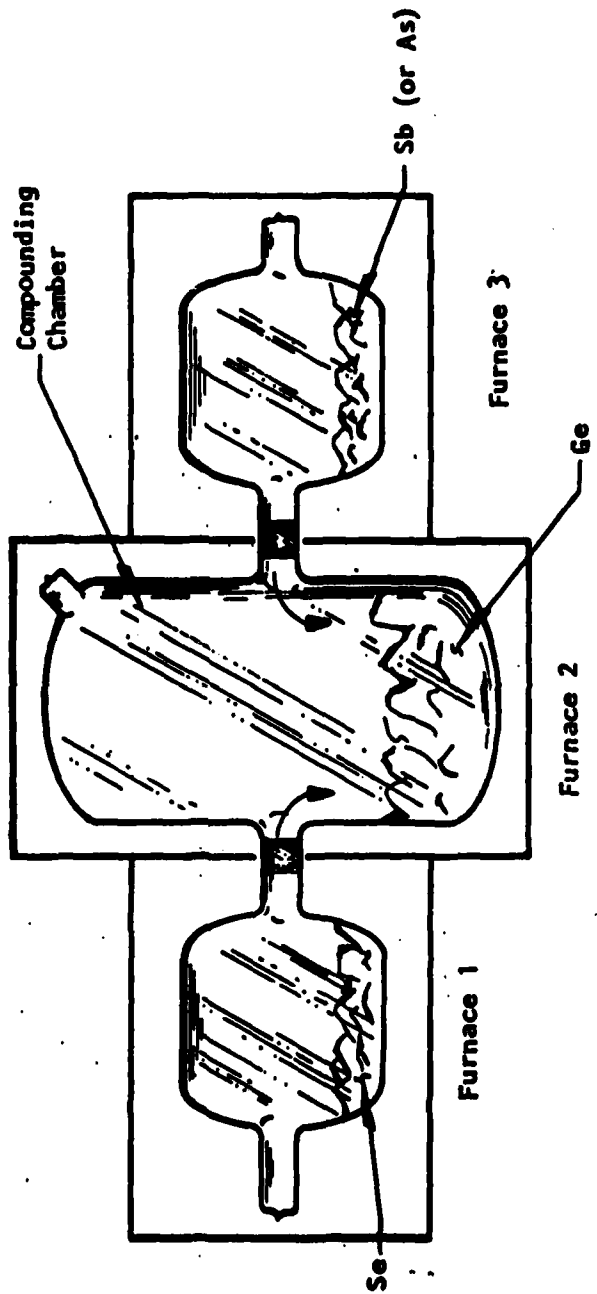


Figure 9. PREPARATION OF HIGH PURITY GLASSES

V. PLANS FOR NEXT QUARTER

1. Construct a new furnace enclosure large enough to accommodate a three zone furnace.
2. Establish power sources capable of controlling the temperatures of a three zone furnace.
3. Develop a quartz fabrication technique to provide a three zone compounding chamber. The two end chambers will be equipped with large diameter caps for easy material loading. Each compounding chamber will be separated from the plate chamber by a standard filter.
4. Prepare a 2Kgm high purity 6" diameter plate using the new method.

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