# Final Report

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# Reduction of Convection in Closed Tube Vapor Transport Experiments

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# Reduction of Convection in Closed Tube Vapor Transport Experiments

## Abstract

The primary objective of this effort was to develop a method for suppressing convective flows during the growth of mercurous chloride crystals by vapor transport in closed tubes to levels approaching those obtained in the microgravity environment. Mercurous chloride was chosen because it is a technologically interesting acoustical optical material whose optical properties are believed to be affected by convective flows. Since the Grashof number scales as the cube of the smallest dimension in the flow system, reduction of the size scale can be extremely effective in reducing unwanted convective flows. However, since materials of practical interest must be grown at least on the cm scale, reduction of the overall growth system is not feasible. But if the region just above the growing crystal could be restricted to a few mm, considerable reduction in flow velocity would result. By suspending an effusive barrier in the growth ampoule just above the growth interface, it should be possible to reduce the convective velocity in this vicinity to levels approaching flows in microgravity. If successful, this growth technique will offer a screening test for proposed space experiments that involve vapor transport to see if reduction of convection will result in improved material and will set a new standard against which the improvements obtained in microgravity may be judged. In addition, it may provide an improved method for preparing materials on Earth whose growth is affected adversely by convection. If the properties of this material can be improved, there is a potential commercial interest from Brimrose Inc., who has agreed to fabricate and test devices from the crystals we have grown.

This report describes the development of the growth facility, the purification processes developed for preparing the starting material, and the results from growth experiments with and without the effusive baffle. Mercurous chloride turned out to be a more difficult material to deal with than originally anticipated. At growth temperatures, it is extremely sensitive to practically any impurity which causes it to form oxychlorides and/or to decompose into elemental mercury and bichloride of mercury. We were unable to find a suitable method for protecting the magnetic material used to suspend the effusion barrier from the attack of mercurous chloride vapor.

Although we were successful in growing single crystals of mercurous chloride without the effusion baffle, they exhibited severe microcracking which we attribute to wall-induced thermal stresses. This leads us to believe that uncontrolled convection may not be the most important problem in the development of this material and a new growth process was attempted that eliminates the wall-induced stress. Unfortunately, the grant ran out before this new method could be adequately tested.

## Introduction

It is well-known that convective flows are significant in crystal growth by closed tube physical or chemical vapor transport. Rosenberger [1] has shown that the mass-average no-slip boundary conditions at the walls in a multicomponent system will always lead to a convectively destabilizing density gradient, even if the growth ampoule is oriented in a vertical thermally stabilizing configuration (hot over cold).

Wiedemeier has found different transport rates and strikingly different growth morphologies in PbTe and PbSe grown by both chemical and physical vapor transport in microgravity [2]. Similar results were seen in HgCdTe grown epitaxially by chemical vapor transport [3]. Debe has found a dramatically improved film morphology in copper phthalocyanine grown in microgravity [4]. Van den Berg grew $HgI_2$ by physical vapor transport on Spacelab 3 and on IML-1 and found considerable improvement in the internal order from rocking curve data and in the hole mobility when used as a $\gamma$-ray detector [5].

Exactly how convective flows can affect the surface morphology and, presumably, the defect structure of a crystal is still not well understood, but the works of Vekilov and Rosenberger have shown that flows near the growth interface are perturbed by the growth steps, which in turn produce fluctuations in composition which can cause the growth steps to either bunch-up or spread out [6]. Macrosteps, caused by the bunching up of growth steps, can produce a variety of growth defects.

Singh and co-workers at the former Westinghouse Science and Technology Center (now Northrop-Grumman) have done extensive studies on the effects of convection on the growth of mercurous chloride ($Hg_2Cl_2$) [7-11]. While it has been possible to grow large crystals of this material by closed tube vapor transport, inhomogeneities in the refractive index have remained a major problem in producing material useful for the more demanding acousto-optical device applications. Crystals grown under different convective conditions show a direct correlation between Rayleigh number and the width of both the optical scattering functions and the X-ray rocking curves [11]. This correlation would indicate that convection during the growth process is somehow implicated in the reduction of internal order of the crystal which is reflected in the optical homogeneity.

A growth experiment in microgravity was conducted in conjunction with Northrop-Grumman to determine how much improvement in internal order and optical properties could be obtained by the virtual elimination of convection so that growth could take place under diffusion-limiting transport conditions. Previous space experiments had shown a substantial reduction in the width of the rocking curves for $HgI_2$, which also has a van der Waals bonded, layered structure similar to the mercurous halides [5]. Two 15 mm diameter crystals were grown simultaneously in a transparent furnace provided by the University of Alabama in

Huntsville Consortium for Materials in Space (UAH/CMDS) [12]. The two crystals grew normally for the first 50 hours into the planned 100 hr run when an unexpected purge from another experiment sharing the same vacuum vent line caused a safety interlock (required by crew safety) to terminate the experiment. By this time, sufficient single crystalline material had been grown to analyze, but the uncontrolled shut-down produced much more rapid cooling than planned, resulting in severe lattice strain and cracking of the grown crystals. Post flight analysis revealed single crystalline material of excellent quality away from the cracks, but the amount of such material was insufficient to fully analyze [13].

## Properties of Mercurous Chloride

Mercurous Chloride was chosen for this project because of its potential technological importance if the growth defects can be eliminated and because there was reason to suspect that uncontrolled convection was a contributing factor to these defects.

Mercurous chloride is an acoustical optical material with an unusually low acoustic velocity (347 m/s shear velocity in [110] direction) and high acousto-optical figure of merit, which makes it an interesting candidate for optical delay lines and Bragg cells for optical signal processors. It also has a broad range of spectral transmissivity (0.38-20 microns), which makes it an ideal candidate for wide band acousto-optically tuned filter (AOTF) applications. The transmisivity in the far infrared make it especially attractive for hyperspectral imaging in the thermal infrared. There are presently no other good candidate materials for this application.

The crystalline structure consists of parallel chains of covalently bonded Cl-Hg-Hg-Cl molecules aligned along the crystallographic c-axis with I4/mmm symmetry as shown in Figure 1. The intramolecular bonds are primarily van der Waals, which makes the lattice weak and subject to strain-induced defects. As would be expected from the structure, the material is highly anisotropic mechanically and is optically birefringent ($n_{ord}=1.962$, $n_{extra}=2.621$).

Mercurous chloride has a high vapor pressure and vaporizes congruently, making it an ideal candidate for crystal growth by closed tube vapor transport. It is not possible to grow from the melt because it decomposes before it melts into elemental Hg and $HgCl_2$. Since it is transparent, it is easy to see if the growing boule is a single crystal or if spurious grains have nucleated. If such events occur, the boule can be back-transported and growth restarted under more ideal growth conditions.

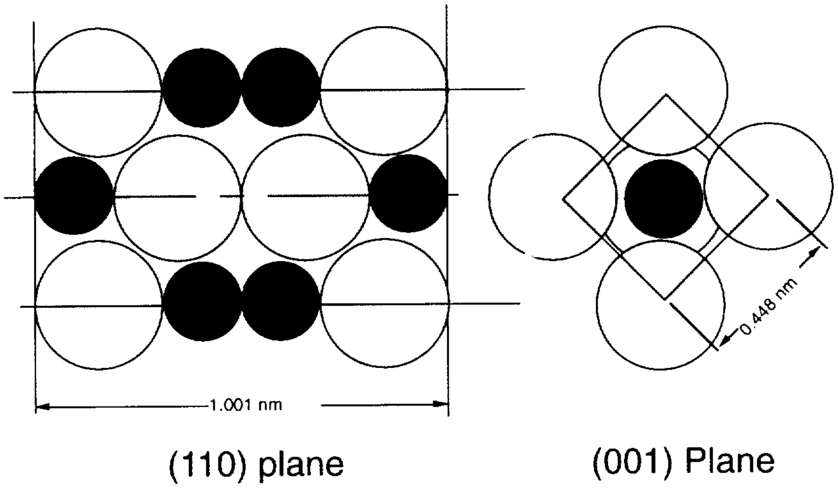

Fig.1. $Hg_2Cl_2$ unit cell. Large circles represent Cl atoms, smaller circles Hg atoms. The linear chains are covalent bonded while the intra-chain bonds are bonded by van der Waals forces. The symmetry is I4/mmm.

## Concept for Approaching Diffusion Controlled Growth in Normal Gravity

During the ground based testing program in preparation for the flight experiment at the UAH/CMDS, a new growth concept suggested itself in which convection could be significantly reduced in normal gravity approaching levels available in microgravity. Convection is suppressed in growth from the melt by application of high magnetic fields but, unfortunately, this technique does not lend itself to vapors which have no electrical conductivity. However, since the Grashof number scales as the cube of the smallest dimension in the flow system, reduction of the size scale can be extremely effective in reducing unwanted convective flows. Since materials of practical interest must be grown at least on the cm scale, reduction of the overall growth system is not feasible. But if the region above the growing crystal could be restricted to a few mm, considerable reduction in flow velocity would result as shown in the following argument.

For modest values of the Grashof number, $Gr = g\ (\Delta\rho / \rho)\, a^3 / \nu^2$, the maximum convective flow velocity in a vertical cylinder with a radial density gradient is given by $Gr\ \nu /(48\ a)$ [14]. Here $g$ is the acceleration of gravity, $(\Delta\rho / \rho)$ is the relative radial density variation, $a$ is the radius of the ampoule, and $\nu$ is the kinematic viscosity. The thermal and solutal Peclet numbers, which measure the ratio of convective transport to diffusive transport, are given respectively by $v\, L / \kappa$ and $v\, L / D$, where $v$ is the convective velocity, L is the length of the chamber, $\kappa$ is the thermal diffusivity, and $D$ is the chemical diffusivity. Taking $g = 980$ cm$^2$/s, $(\Delta\rho / \rho) = 0.003$ (equivalent to a radial $\Delta T$ of 1°C), $a = 0.75$ cm, $L = 10$ cm, and $\nu = 0.024$ cm$^2$/s (which assumes $Hg_2Cl_2$ to be an ideal gas at 7 atmospheres and 400°C), the $Gr = 2150$ and $v = 1.43$ cm/s. For an ideal gas, $\nu =$

$\kappa = D$. Therefore, the solutal and thermal Peclet numbers are both 600, indicating that convective transport dominates both mass and heat transport. Since everything scales directly as $g$, reducing g by 3 or 4 orders of magnitude would drop the Peclet numbers below 1, which is required for diffusion-controlled transport.

The only other parameters entering into the scaling that one has any control over are the dimensions $a$ and $L$. Since, for device applications, it is not desirable to reduce the diameter of the crystal much below 1.5 cm, this leaves only the length $L$ as a variable. It is not feasible to greatly reduce the length of the growth ampoule, but one could place a effusive barrier just above the growth interface. This barrier would not affect the flows between the source material and the top of the barrier, but could significantly damp the flows in the vicinity of the growth interface where they are believed to do the most damage.

It can be shown [15] that the maximum convective velocity in a narrow horizontal slot with a relative density gradient $\nabla\rho/\rho$ is given by $Gr\ \nu/(72\sqrt{3}\ w)$, but, for this case, the $Gr = g\ (\nabla\rho/\rho)\ w^4/\nu^2$, where $w$ is the vertical width of the slot. The effusive barrier, held at distance $w$ above the growth interface, can form such a slot to restrict the convective flows. If the temperature gradient is 1°C across the radius of the growth ampoule, $\nabla\rho/\rho = 0.004$ /cm and the maximum flow in cm/s is now given by $1.3\ w^3$. If, for example, w is set at 2 mm, v is reduced to 0.01 cm/s. The thermal Peclet number is now given by $v\ a/\kappa$ since $a$ is the dimension over which diffusive transport is to be maintained. Now the Peclet number is reduced to 0.33, well within the diffusion-controlled regime.

The effusive barrier consists porous glass frit in the form of a disc just slightly smaller than the growth ampoule inside diameter. The porous material will allow the vapor to pass through, but will act as a barrier to flow. It is positioned at a fixed distance above the growth interface by a mu-metal ring that interacts with magnets inside the furnace, just outside the growth ampoule. The furnace operating temperatures for most vapor or chemical vapor growth systems are well below the Curie temperature of most magnetic materials, so this should pose no problem. Since the growth front is visible through the transparent furnace, the width of the region between the growth front and the barrier can be monitored and adjusted if necessary by either adjusting the translation rate of the sample or by moving the magnets on the outside of the furnace. Obviously, the effusion barrier cannot be lowered into the tapered region of the growth ampoule in which the seed crystal is grown out to the full diameter, so it will not be effective until the growth front reaches the cylindrical region of the ampoule where the main growth takes place. However, if the thermal conditions are adjusted so that the crystal grows with a slightly convex growth front, any defects that may have formed in the tapered portion of the ampoule should grow out after growth proceeds into cylindrical growth region.

## Development of the Growth Facilities

Shortly after the grant was awarded, Sarwa Tan was hired as a GRA. His first duty was to design and build an enclosure facility for the growth and purification furnaces. A 3 by 5 by 7.75 foot cabinet was fabricated from sheet stainless steel with lexan windows for viewing (see Fig. 2). A 992 cfm blower in a duct connecting the top of the enclosure to a roof ventilator provided a negative pressure to remove any toxic vapors in the event of an ampoule rupture.

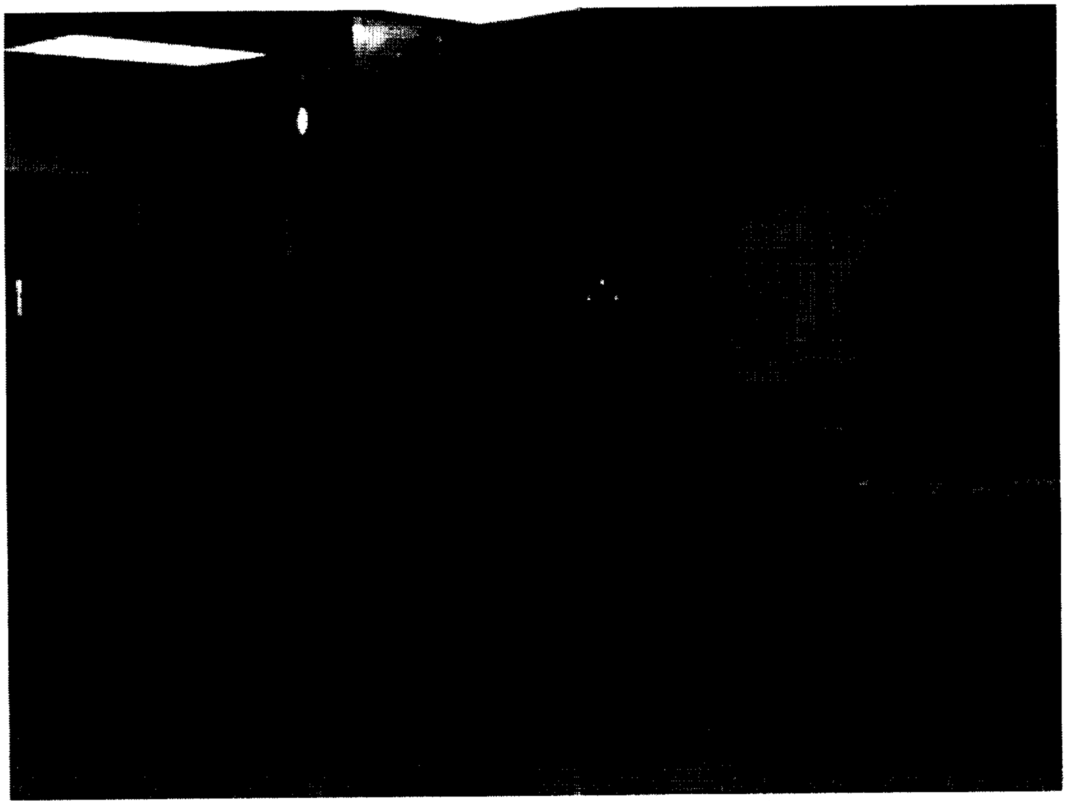

Fig. 2 Growth enclosure and control panel. Metal duct at the top goes to roof vent

A 30 cm long, 2-zone vertical growth furnace was fabricated from 4.2 cm o.d. quartz tubing wound with Ni20%Cr wire. This heated tube is surrounded by a concentric 6.3 o.d. quartz tube to act as a radiation shield as shown below. Temperatures are controlled and monitored by type-K thermocouples.

Low voltage power is provided by two autotransformers and is fed to the heater windings though solid state relays operated by Omega CN9121A PID's for temperature control. The thermal profile is monitored by 4 Omega DP116-KCL thermocouple readers. Fig. 4 shows a block diagram of the control unit.

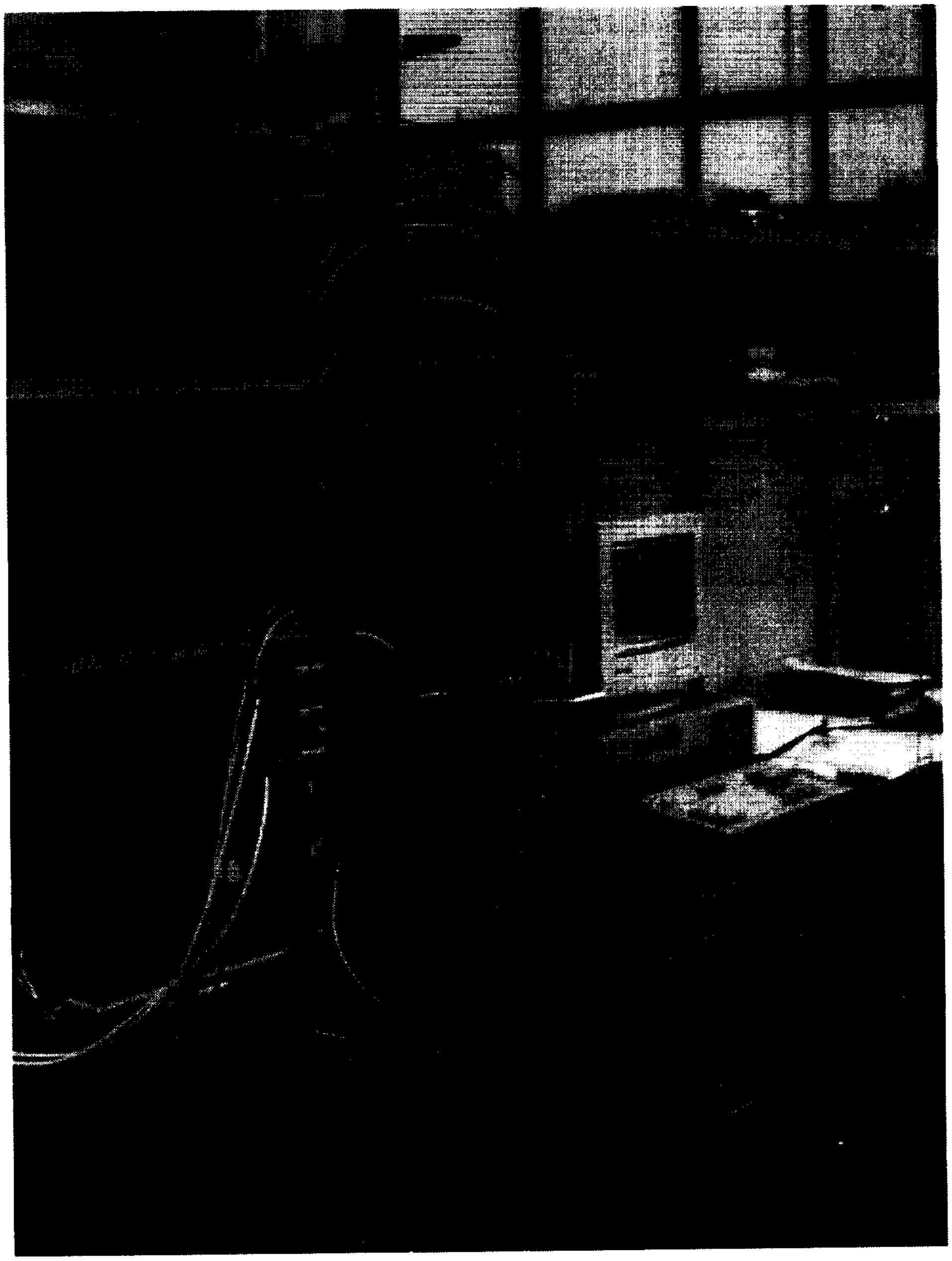

Fig.3 Crystal growth furnace on translation mechanism

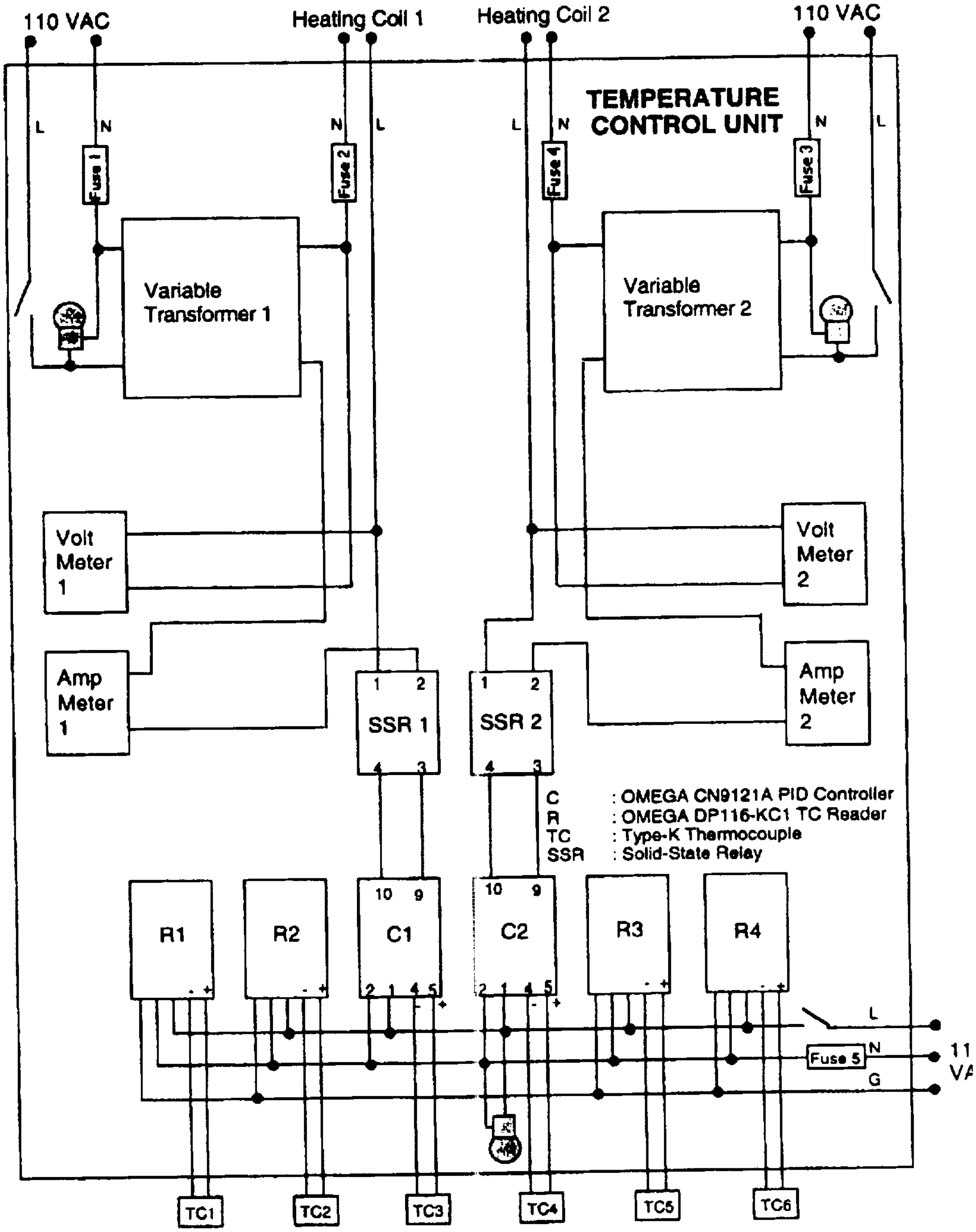

Fig.4 Block diagram of the temperature control unit.

The furnace windings are configured to obtain a typical thermal profile shown in Fig. 5. The source material is held at around 400°C while the growth interface is maintained at 380°C. A 420° hump is provided ahead of the growth interface to provide a fairly sharp gradient in this region to prevent spurious wall nucleation. A translation mechanism moves the growth ampoule so that the growth front stays close to the 380°C isotherm. The system operates at approximately 500 Watts.

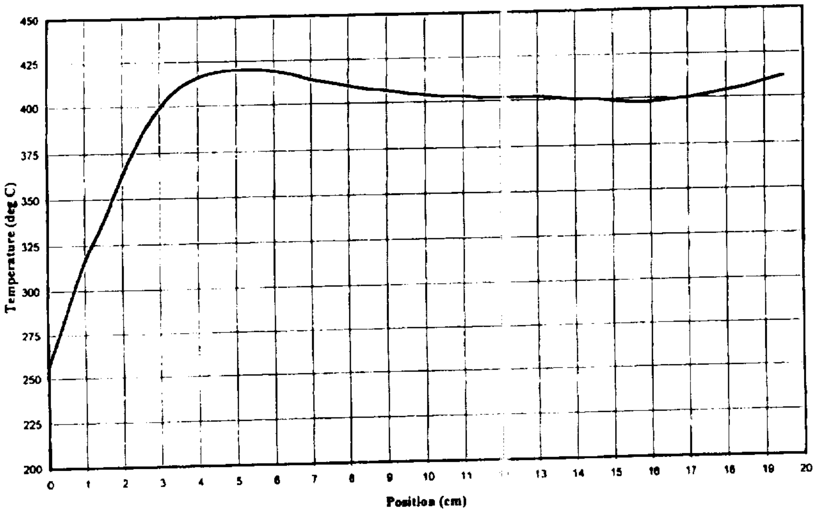

Fig. 5 Thermal profile of the growth furnace.

The heart of the translation mechanism is a Semix 5609M-01 micro-step motor controlled by a Semix RC-233 controller operating through a Semix RD-021M8 driver. A PC computer operating in a stand-alone mode or in a controlled program mode provides the commands through a Semix Link Master RC-002 Current Adapter that converts the computer's RS-232C output to I/O commands to drive the master controller. Fig. 6 shows a block diagram of the translation control system. The stepping motor has 400 steps per revolution. It drives the translation mechanism though a Berg precision speed reducer with a 1000:1 reduction. The nominal translation rate is 5 mm/day.

Growth phenomena is recorded by a Minolta RD-175 digital camera that uses 3 CCD's to achieve full color with 1.75 million pixel resolution. Since the growing crystal becomes bright yellow at temperature, the full color recording is very useful for determining the position of the growth interface relative to the furnace winding so that the temperature of the growth front can be estimated. Since an intervalometer was not available the Minolta camera, the camera was modified to be triggered from the PC controlling the stepping motor.

Purification of the starting material is accomplished by multiple sublimations and condensations. To carry of this process, a horizontal purification furnace was constructed from a 4 cm OD by 27 cm long quartz tube surrounded by an 8 cm OD quartz tube. The temperature control system is similar to that used for the growth furnace. The inner quartz tube is wound to produce a thermal profile shown in Fig. 7. Typically the sublimation chambers are heated to 250-350°C and condensation takes place in a clean chamber held at 100-150°C lower than the sublimation chamber.

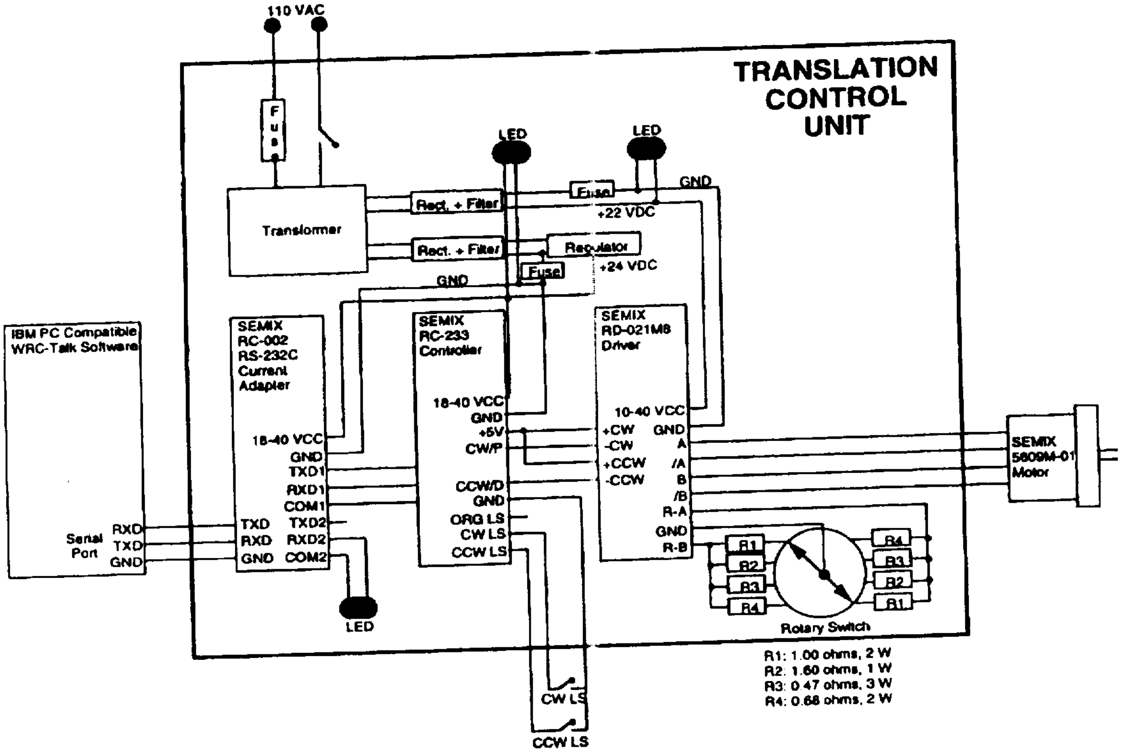

Fig. 6 Block diagram of translation control unit.

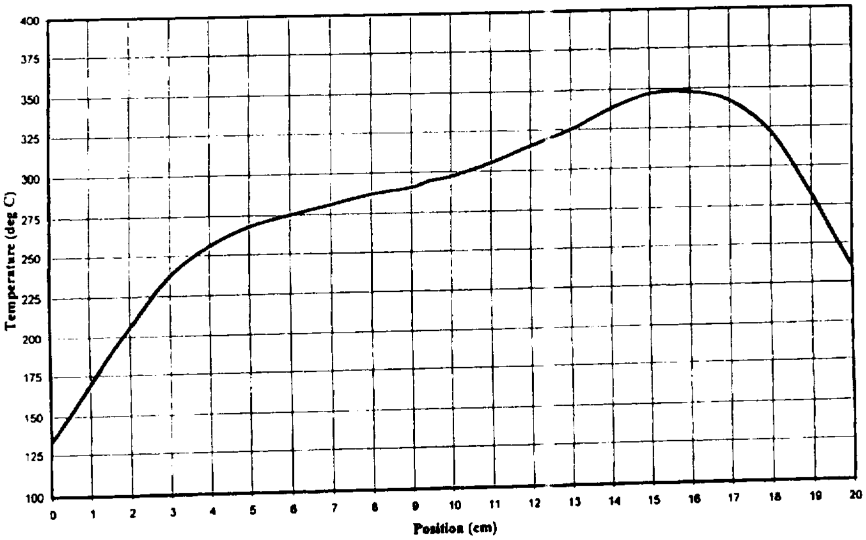

Fig.7 Thermal profile of the purification furnace.

The vacuum system used to pump down the ampoules consists of a two-stage Varian SD-450 rotary pump with a Varian Turbo-V250 turbomolecular pump with a pumping speed of 200 liters/minute, capable of an ultimate vacuum of $2 \times 10^{-10}$ Torr. Two thermocouple gages and a Bayard-Alpert ionization gage are used to monitor the vacuum. A cold trap is placed between the vacuum system and the ampoule to trap any mercurous vapor generated during ampoule sealing.

Several Mitchell laboratory furnaces capable of 1200°C are available for high temperature bakeout of the growth and purification ampoules.

## First Growth Experiments

The first growth experiments carried out by Sarwa Tan utilized one of the two growth ampoules from the previous flight experiment shown in Fig. 8. It was decided to carry out a number of growth experiments before attempting to use the effusive barrier in order to gain more experience in the growth technique before complicating things with the barrier. The quartz growth ampoule and cartridge shown below were fabricated in the UAH/CMDS glass shop. The growth ampoules are 15 mm inside diameter (I.D.) and 100 mm long with wall thickness of 1.5 mm. These ampoules are hermetically sealed inside of evacuated 22 mm I.D. quartz cartridges which provide a second level of confinement as well as structural support for the growth ampoules during launch and landing. The small knob on the end cap keeps the charge in place during the pre-launch handling and throughout the launch phase. This particular design was chosen to avoid applying stresses to the growth ampoule from thermal expansion and contraction of the source material.

The highly purified compact slug of mercurous chloride (provided by Northrup-Grumman) was loaded into the quartz growth ampoule, whose large end was open at this point, and was positioned near the tapered end. The end of the long 10 mm outside diameter (O. D.) stem remains sealed at this point. A loose fitting quartz end cap with the small knob at its center was then inserted into the source end of the growth ampoule which has a small detent to hold the end cap in the proper position. The ampoule is then evacuated to $10^{-5}$ $-10^{-6}$ Torr before glass welding the end cap in place with an oxy-methane torch

The $Hg_2Cl_2$ charge was then back- transported to the source end by placing the ampoule in a gradient furnace in which the $Hg_2Cl_2$ at tapered end is held at 460°C while the source end is held at. 435°C. This procedure allows for thermal expansion of the source material when it is brought back up to 400°C during the growth run.

The sealed end of the stem was then cut off and an 8 mm diameter $\langle 110 \rangle$ oriented seed (also provided by Northrop-Grumman) was inserted so that it rested next to the capillary tube in the growth ampoule. A loose fitting quartz rod was then inserted to hold the seed in place, allowing sufficient space for thermal expansion. The growth ampoule is again evacuated to $10^{-5}$ - $10^{-6}$ Torr through the stem, which is then glass welded to the quartz rod to form the final seal. After sealing the ampoules, vacuum was verified with a Tesla coil and the ampoules were inspected under 10x magnification for cracks and other flaws.

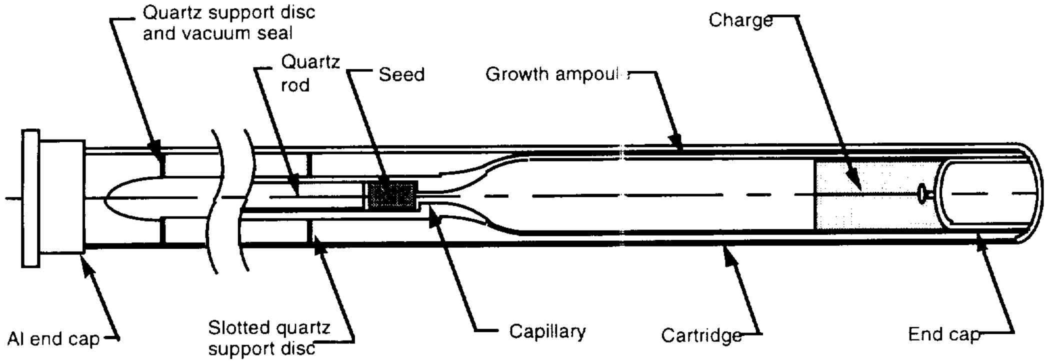

Fig. 8. Schematic of flight cartridge and growth ampoule.

The growth ampoule is then inserted into the cartridge. The stem portion just behind the seed is supported by a quartz disc that has been slotted to allow for the passage of gas during cartridge evacuation. A second quartz disc near the end of the stem provides the rear vacuum seal for the cartridge. The source end of the growth ampoule is glass welded to the forward end of the cartridge during the final evacuation and sealing operation. An aluminum end cap is potted to the other end of the cartridge. This end cap mates with the translation mechanism which moves the cartridge in and out of the heating zones.

When this ampoule was returned from the Spacehab 4 (STS-77) flight, it had a partially grown crystal, but the premature shutdown of the furnace had caused the crystal to crack. Knowing this, we elected not to open the ampoule. Instead Sarwa was able to carefully back-transport the grown crystal to the original starting configuration without destroying the seed. He then proceeded to re-grow the crystal. However, as the source material sublimated away, the small knob at the top of the growth ampoule, which had been designed to support the charge under low gravity conditions, was unable the hold the source in the vertical configuration and the charge fell into the growing crystal.

It was clear that a new ampoule design was required. The first attempt placed a small chamber at the top of the growth ampoule connected by a straight tube to the growth ampoule. The purified material from the original flight sample was crushed and loaded into this chamber. This was later modified by curving the tube and placing a small hole in the side of it to prevent source material from falling through the tube onto the growing crystal. Since no seed was available, a sharp conical recess was designed into the growth ampoule to act as a nucleation site.

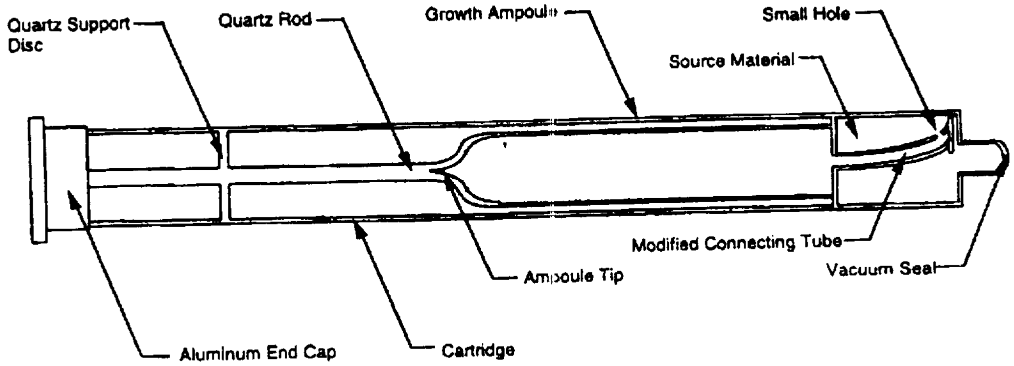

Fig.9. Modified growth ampoule. The connecting tube at the top is slightly curved and the hole is in the side to prevent any material from falling through the tube onto the growing crystal.

The new ampoules were cleaned with acetone, then $HNO_3$, followed by a rinse with DI-water, and dried at 600°C for several hours. After loading the powdered starting material, the ampoule was evacuated to $10^{-6}$ Torr using a $LN_2$ cold trap to prevent any sublimating vapor from entering the turbomolecular pump.

The first attempt with the straight tube grew a crystal approximately 5 cm long; however small bits of the starting material falling through the tube caused spurious nucleation resulting in several large grains in the grown crystal. Traces of Hg were seen in the bottom tip of the growth ampoule, indicating some decomposition of the $Hg_2Cl_2$ into Hg and $HgCl_2$ It turns out that this decomposition can be caused by light, trace quantities of water vapor and/or other impurities.

The source material was again recovered by crushing the grown crystal from the previous attempt. Another crystal was grown using the growth ampoule with the curved pipe. This time the crystal grew to length 47mm with a 15mm diameter. Unfortunately, a 4 hour power interruption cause by a thunderstorm some 60 hours into the growth process cause a crack which propagated though the entire crystal. After this experience, we obtained an auxiliary backup power supply to prevent such reocurrences.

A plot of the growth temperature estimated form the position of the growth interface in the furnace is shown in Fig.10. The first nucleation occurred at 360°C and the initial growth rate was 7.66 mm/day. The growth front reached a stable isotherm of 378°C after about 20 hours but then for unexplained reasons stopped as the translation carried the growth front into the cooler regions of the furnace. It is not clear if the hole in the delivery pipe became clogged of if the growth front had become contaminated with some impurity. After the power was reestablished, the crystal resumed its growth at a rate of 7.6 mm/day until it reached a stable isotherm of 387°C after an additional 85 hours. Here it grew at the translation rate of 5 mm/day for an additional 30 hours when the source material was totally consumed.

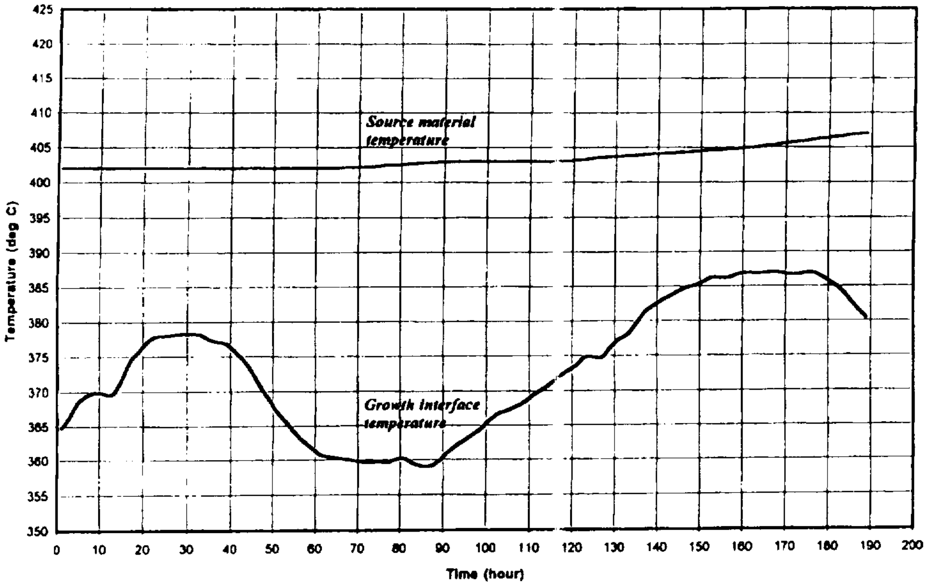

Fig. 10. Temperature history of the growth interface on the third run. For reasons that are not understood, the crystal stopped growing after some 40 hours and the translation carried the interface deeper into the cold zone. The crystal then resumed its growth at 7.66mm/day until it reached a stable isotherm, after which it grew at the translation rate of 5 mm/day.

The next growth experiment used material we purified. Here the ampoule tip was initially placed at the 390°C isotherm and slowly lowered into the cooler region of the furnace, expecting first nucleation to occur somewhere close to the growth temperature of 380°C. However nucleation did not occur until around 345°C. Even after 40 hours the growth interface was still below 345°C so the translation rate was lowered to 4 mm/day. The crystal then grew at a relatively stable rate of 4.36 mm/day until it reached a stable isotherm of 353°C. At this point the crystal was growing nicely with a faceted convex growth front when at 160 hours into the run, material that had nucleated on the wall above the growing crystal detached and fell onto the growing interface causing new grains to form. The new grains grew somewhat faster, leveling out at the 363°C isotherm. The temperature history of the growth front is shown in Fig. 11.

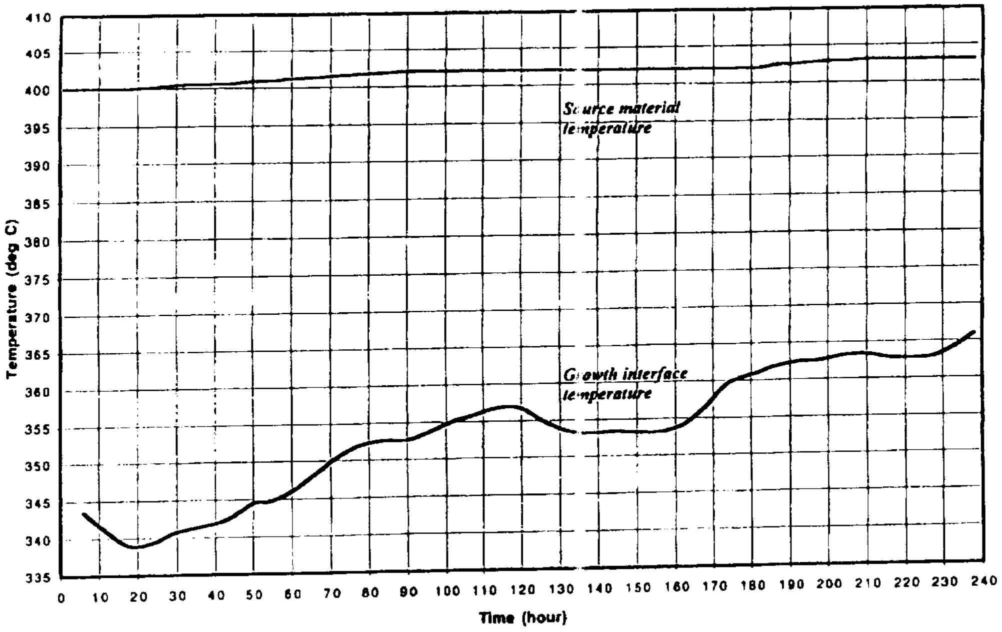

Fig.11. Temperature of the growth interface during the fourth run. In this case the interfacial temperature was considerably lower than in the previous run. The translation was lowered to 4 mm/day. Eventually the growth reached a stable isotherm of 353°C. At 160 hours, a crystallite that had nucleated on the wall, came loose and fell onto the growth interface causing new grains which grew faster.

Why the growth temperature in the two runs were so different is not clear. One possibility was that since the growth was self-seeded, the orientation of the growing crystal may be different in the two cases. The easy growth direction for this material is along the [001] direction in which growth is twice as fast as along the [110] direction. We were not successful in obtaining good Laue diffraction patterns form these crystals, so we have no way of confirming if this is the reason for the different growth behaviors. Attempts to obtain backscatter Laue patterns from the third crystal showed only a few highly distorted spots indicating a high degree of lattice strain that could be interpreted that growth was along the [001] direction. No usable Laue pattern could be obtained for the fourth crystal.

Unfortunately for us, at bout this time Sarwa Tan received a very attractive offer form the University of Minnesota to pursue his Ph.D. in physics working in low-dimensional superconductivity under Dr. Allen Goldman and decided to accept. He completed his thesis and left UAH with his M.S. in physics.

## Material Purification

The mercurous chloride available from Aldrich is supposed to be 99.5+% pure. However, this level of purity is far below what is needed for successful crystal growth. Sarwa Tan first attempted to purified using the multiple sublimation process developed by Westinghouse [8]. A column of 8 Pyrex chambers are interconnected by smaller diameter tubes as shown below. After cleaning and vacuum baking the column, the first chamber is filled with the starting material. This material is them vacuum baked under vacuum at 110°C to drive off moisture and other impurities that can form oxychlorides of mercury and catalyze decomposition of the mercurous chloride. The column is then vacuum sealed and placed in the purification furnace.

The first chamber is heated to ~350°C and placed in the gradient region of the furnace so that the subliming material condenses in the second chamber. When most of the starting material has been transported, the tube connecting the first and second chamber is sealed off by a torch without losing the vacuum conditions in the column. The second tube is then heated to transport the partially purified material into the third tube and the process is repeated until the highly purified material is deposited into the final chamber.

We quickly found that heating the first chamber to 350°C formed quantities of black sticky material (identified by Singh as pinchite $Hg_5Cl_2O_4$ [xx]) that was transported into the second chamber and beyond. Also traces of Hg were found indicating the decomposition had occurred. Even reducing the temperature to 250°C helped, but did not eliminate the transport of the impurities. Sarwa Tan then modified the design of the column by placing glass frits with decreasing porosity in the ends of each chamber as indicated in Fig. 12.

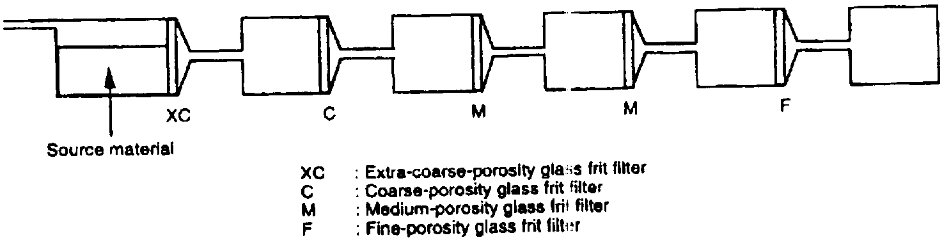

Fig. 12. Modified design of purification column with glass frit filters to prevent transport of solid materials.

A second problem with the published Westinghouse purification column design also quickly became apparent when attempting to duplicate it. With the connecting tubes in the middle of the chambers, the sublimated material tends to deposit circumferentially in the next chamber. When that chamber is then heated during the next purification cycle, thermal expansion causes the chamber to crack resulting in a loss of vacuum. It was then necessary to remove the powder form the cracked chamber in a dry box and transfer it manually into a new column and start over. This turned out to be an extremely time consuming process, plus the loss of vacuum re-exposes the material to moisture in the ambient air.

XRD spectra of the as-received mercurous chloride powder form Aldrich and the purified material are shown in Fig. 13 and 14. The as-received material shows all of the allowed reflections of mercurous chloride with no apparent impurity peaks in the background noise (this method is not particularly sensitive for trace impurities). The (110) reflection dominates the spectrum of the purified material with all of the weaker reflections suppressed. We believe this is a result of the faster growing (110) faces of the sublimated crystallites making up the purified material which provide more (110) planes.

After Sarwa Tan had to leave to start the fall semester at U. Minnesota, a new GRA, In-Seok Shin was been recruited and trained on the project. In-Seok redesigned the purification facility to include a large aluminum heat sink to support the ampoules in which the material condenses. An infrared line heater was procured and mounted above the ampoule with the condensing material in order to encourage the material to condense on the bottom of the ampoule instead of around its inside circumference. After several more broken ampoules caused by material condensing around the filters, In-Seok was able to fine-tune the heaters so that multiple sublimations could be made without breakage.

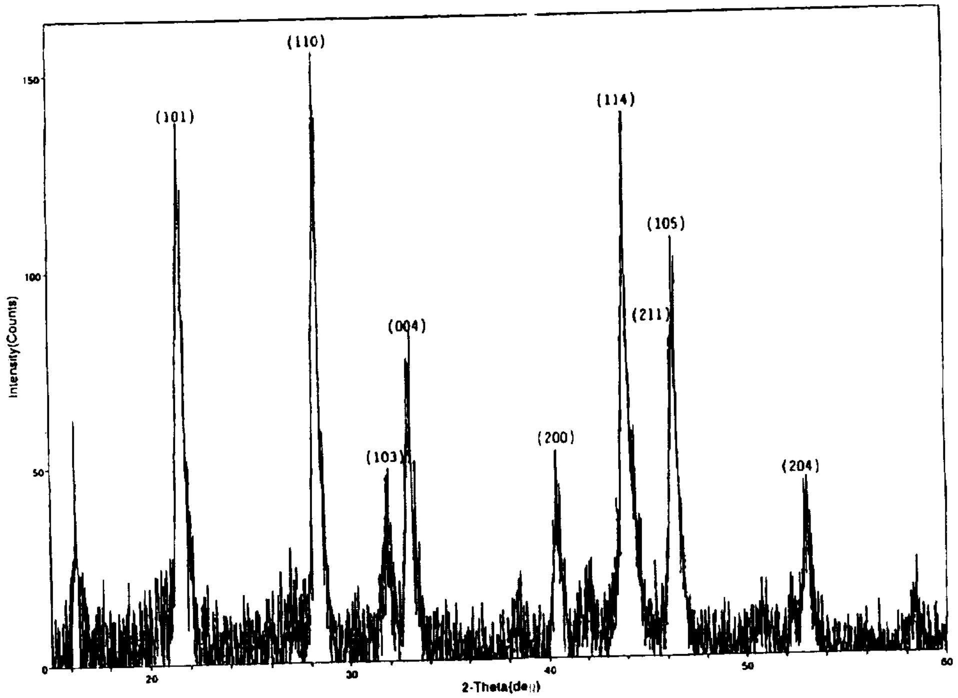

Fig.13. XRD spectrum of mercurous chloride as received from Aldrich Chemical Co. All observed peaks correspond to allowed reflections for this material.

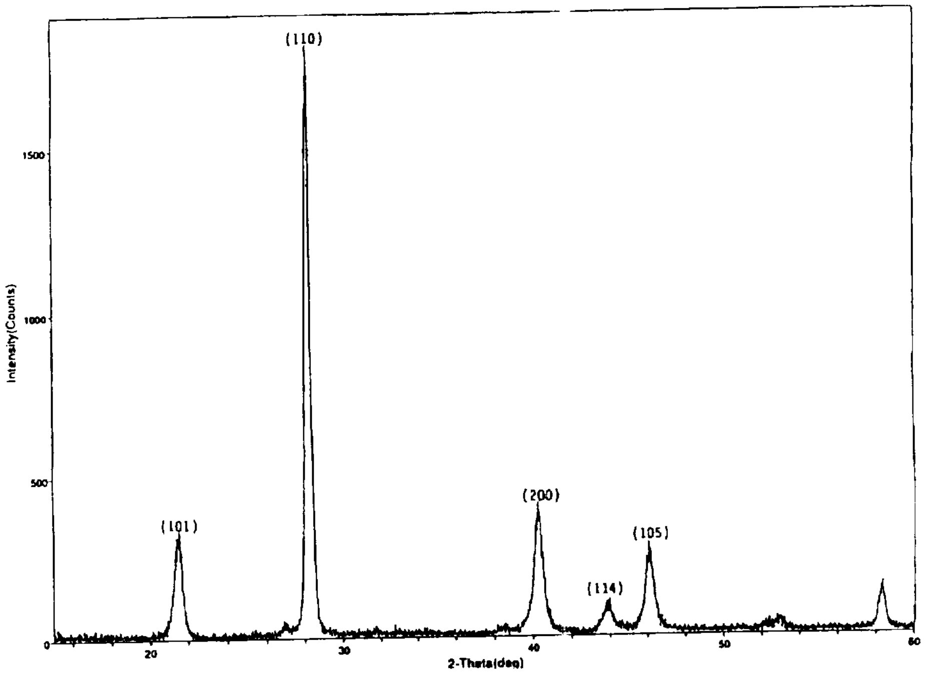

Fig. 14. XRD spectrum of purified mercurous chloride. Note the dominance of the (110) peak with many of the weaker peaks suppressed. We believe this is caused by the fast growth of the crystallites along the [110] direction, resulting in many more (110) plains.

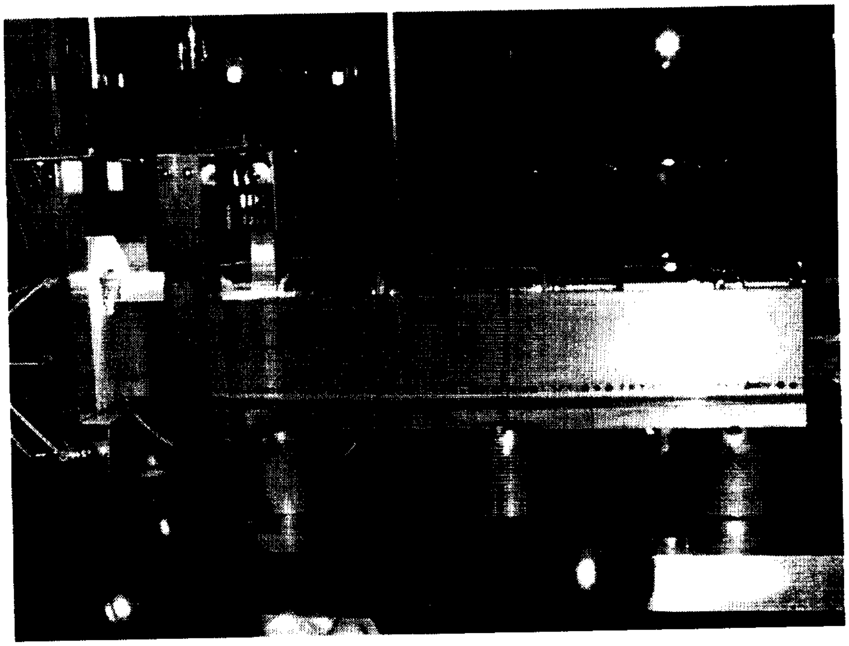

Fig. 15. Aluminum heat sink and line heater (upper left) used to produce a vertical gradient to prevent material from depositing concentrically in the growth ampoule.

However, the final powder still had to be removed from the final purification chamber and ground into a powder for loading into the growth ampoules. Even though this process was done in a dry box, some exposure to moisture and to other possible contaminants could not be avoided. It was later found that one could start with commercially available material in a properly cleaned and baked-out quartz growth ampoule and grow a slug of polycrystalline material. This slug could then be placed in another growth ampoule and used to grow a fair quality crystal that was at least optically clear. The individual quartz growth ampoules are easier to clean and can be baked out at higher temperatures than the multistage purification apparatus. Also, the material is kept in the form of a compact slug, which eliminates the large surface area of a powder that can easily become recontaminated. The process can be repeated until the desired purity is obtained. However, again the process is extremely time consuming.

Joo Soo Kim later came up with a simpler purification method. Instead of locating the connecting tubes at the center of the purification chambers, he alternated them above and below the centerline as shown below.

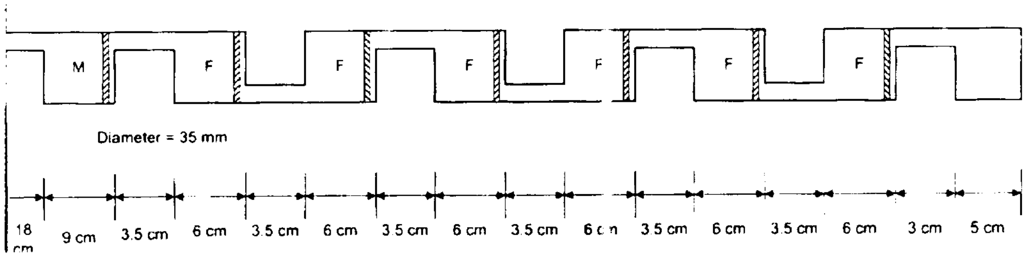

Fig. 16. Purification column developed by Joo Soo Kim. The over and under arrangements prevents the concentric deposition of the sublimate and makes the chambers less susceptible to breakage when reheated.

By a careful regime of heating the material to be transported and transporting through the upper tube so the sublimate would not longer be deposited concentrically, he was able to eliminate the breakage problem.

## Second Generation Growth Experiments

The growth ampoules were cleaned with HF, acetone, ethanol, and repeatedly rinsed with DI-water. They were dried at 150°C for several hours in air and then vacuum baked at >800°C at $10^{-5}$-$10^{-6}$ Torr. The slug of starting materials was loaded into the upper chamber of the growth ampoule. The growth ampoules were then evacuated to $10^{-6}$ Torr and sealed with an oxy-methane torch. Instead of the curved delivery pipe developed by Sarwa Tan, In-Seok Shin mounted a glass frit between the source region and the growth region to prevent any material from dropping on the growing crystal. Using this technique, he was able to grow two optically clear crystals 25 mm diameter by 47 cm long. After the starting material was exhausted, the crystals were slowly cooled at 10-15°C per hour.

These two crystals were sent to Brimrose Corp. for analysis. They were optically clear with no visible grain structure. One apparently grew along the [100] direction. It produced a nice rainbow effect when backlit and viewed perpendicularly to the optical axis. Brimrose, however, ran into the same problem we had when they attempted to get Laue X-ray diffraction patterns from the crystals. They could only get a few Laue spots, not enough to orient the crystal. They suspected that the material is highly strained, or that micro-cracking has occurred on a scale too small to be seen with normal optical inspection. Even though we were unable to obtain the orientation of the crystalline axes, we requested that Brimrose cut small sections of one of the crystals to be used as seeds. Inspection of these sections did indeed reveal micro-cracking throughout the sections. Obviously the crystals were not of device quality.

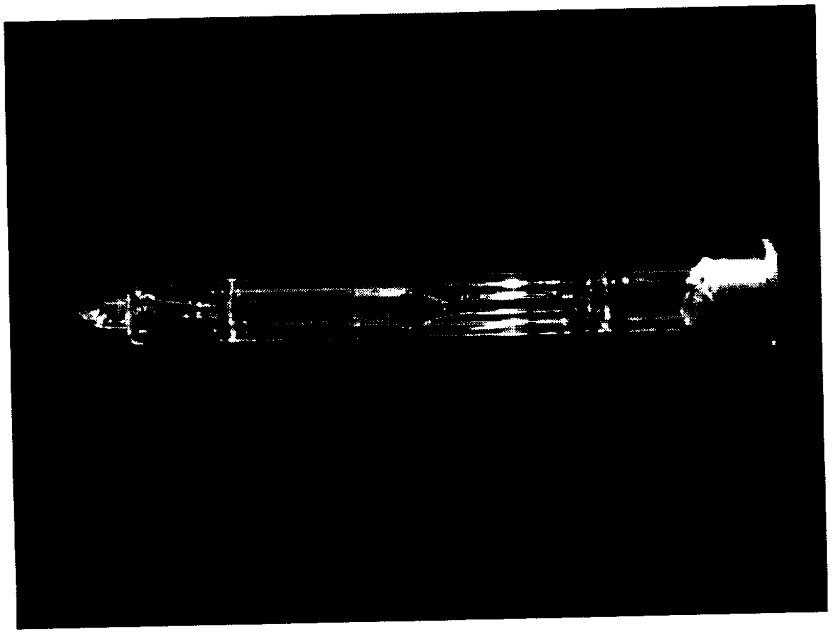

Fig. 17. One of the single crystal of mercurous chloride grown by In-Seok Shin that was sent to Brimrose Inc. for analysis.

Since then In-Seok grew three more crystals, but all had one or more large cracks making them unsuitable for device evaluation. Why these crystals cracked and the earlier ones did not is unclear since we tried to follow identical procedures in all cases.

We also noticed that the grown crystals tended to darken with time, even though they were stored on light tight containers. We submitted one of the crystals to our Laboratory for Materials and Surface Science for XPS analysis. We had hoped to be able to determine the valence state of the Hg to see if we had $Hg_2Cl_2$ or $HgCl_2$ on the surface so we could tell if the materials was decomposing. The measurement were inconclusive, confirming only the presence of Hg.

## Growth Experiments with an Effusive Barrier

In the meantime, In-Seok had also designed the magnetic suspension to hold the effusive barrier in place. The first concept used a glass frit effusive barrier just slightly smaller than the inside diameter of the growth ampoule with four small Fe-Nd magnets inserted at 90° intervals around the circumference into the frit. The exterior magnet consisted of a ring of Co-Sm magnets with like poles facing the center. The idea was to place the ring magnet around the quartz radiation shield of the furnace and levitate the frit above the ring magnet so that the growth interface could be seen. The fallacy of this scheme quickly became apparent when we attempted to assemble the growth ampoule with the magnets inside. The magnets became overheated when the ampoule was being sealed and lost their magnetism.

We then decided to encase the frit in a mu-meta ring and use a much simpler external positioning set of two magnets located on opposite sides of the quartz growth ampoule inside the growth furnace. The scheme seem to work as the furnace was being heated up, but suddenly we lost magnetic control as we neared the growth temperature. We then discovered that the particular mu-metals we had chosen had a Curie temperature of only 380°C. Even more disturbing, the mercurous chloride vapor had severely attacked the mu-metal ring and had decomposed into Hg and mercuric chloride.

At about that time, In-Seok received a very attractive offer from Motorola and elected to leave with his M.S. rather than stay for his Ph.D. It became necessary to recruit another GRA, Joo Soo Kim, and train him from the beginning.

Joo Soo located some some mu-AD-48 alloy tubing with the right diameter that has a Curie temperature well above 400°C. We knew we had to somehow protect the mu-metal from the attack of the mercurous chloride vapor. We considered gold coating the ring, but we first had to make sure the gold would not be attacked by the vapor. We sealed some gold foil in an ampoule with mercurous chloride and heated it to 420°C for several days. We saw no evidence of attack or decomposition. Joo Soo that had the mu-metal ring vapor coated with Au, fixed the porous frit inside the ring and prepared the ampoule for a growth experiment.

The magnetic positioning worked well for the first several hours, but then the baffle became frozen in place, Severe corrosion could be seen between the ring and the ampoule wall and Hg could be seen in the bottom of the ampoule.

Thinking that the vapor deposited Au may not have been thick enough to protect the mu-metal ring, Joo Soo found a company that could dip the rings in molten Au. Another experiment was prepared with the same results.

At this point we began to have serious doubts that we could protect the magnetic material required to suspend the baffle in the growth ampoule from the corrosive environment. We were also concerned about the microcracking we had seen in the more successful crystal growth experiments and decided that maybe convection was not the primary problem in the growth of mercurous chloride.

## New Growth Method

Given the anisotropic properties of the mercurous chloride crystals and their propensity for breaking ampoules due to thermal expansion, we suspected that perhaps the ampoule walls may be responsible for the lattice strain and optical inhomogeneities that have plagued the production of this material. We decided to try growing mercurous chloride without wall contact from a seed mounted on a heat sink, similar to the method developed by EG&G for growing mercuric iodide. Only we didn't have a suitable seed to grow from.

Joo Soo was looking for a dissertation topic for his Ph.D. in Mechanical and Aerospace Engineering and proposed to design and construct a suitable furnace using computational fluid dynamics to model the convective flows and heat transfer inside of the growth ampoule. Since we didn't have a suitable seed to grow from, he designed a self-seeding capability in the base of the furnace, similar to the method used for our previous closed tube vapor transport experiments. However, after the self-seeded crystal grows through the tapered portion of the ampoule, it is no longer confined by the ampoule walls and can grow freely in all directions.

While developing the thermal model, several growth ampoules were fabricated in the UAH glass shop and some preliminary experiments attempted. The crystals seeded successfully and grew through the tapered part of the ampoule. However, when they reached the expanded portion of the ampoule, they grew much too fast to achieve good quality single crystals.

Joo Soo now has the first phase of his model complete that predicts the flows and heat transfer inside the ampoule given fixed thermal boundary conditions on the ampoule. He now needs to add the growing crystal to the model and compute the temperature at the growth interface. He then needs to compute the radiative and convective heat transfer between the furnace and the growth ampoule so that he can configure the system to give the desired temperature at the growth interface.

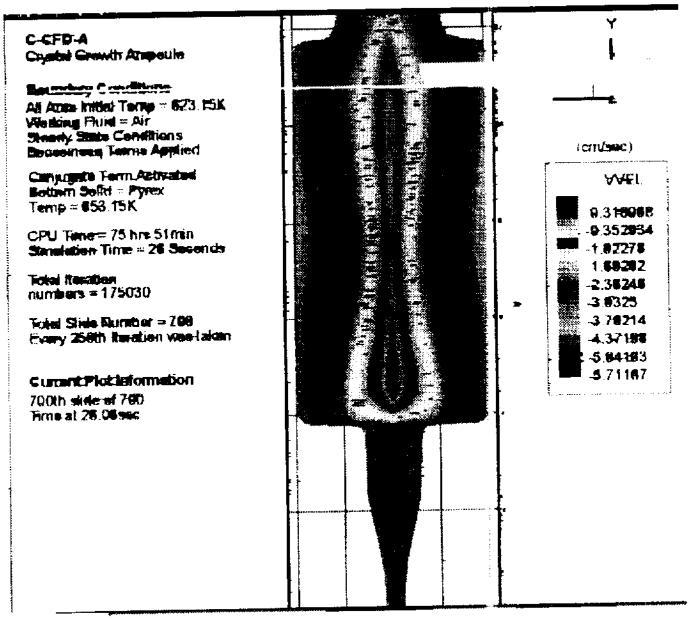

Fig. 18. First result of CFD modeling of flow in the new growth ampoule. The ampoule walls are held at constant temperature while heat is being extracted from the bottom stem. Shown are the contours of vertical velocity. The vapor inside the ampoule rises along the walls and descends along the centerline.

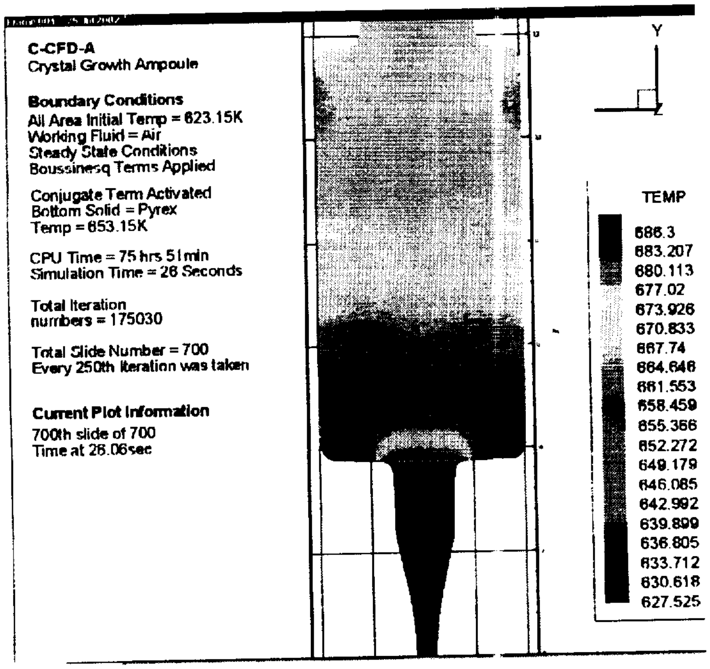

Fig.19 Computed thermal profile inside the new type growth ampoule.

Even though the thermal model is not complete, sufficient insight was obtained from the previous experiments and the computations dine to date to slightly tweak the furnace and the growth procedure and successfully grow a single crystal by this method (see Fig. 20).

Unfortunately, this grant expired before he could complete these tasks and he is seeking additional support.

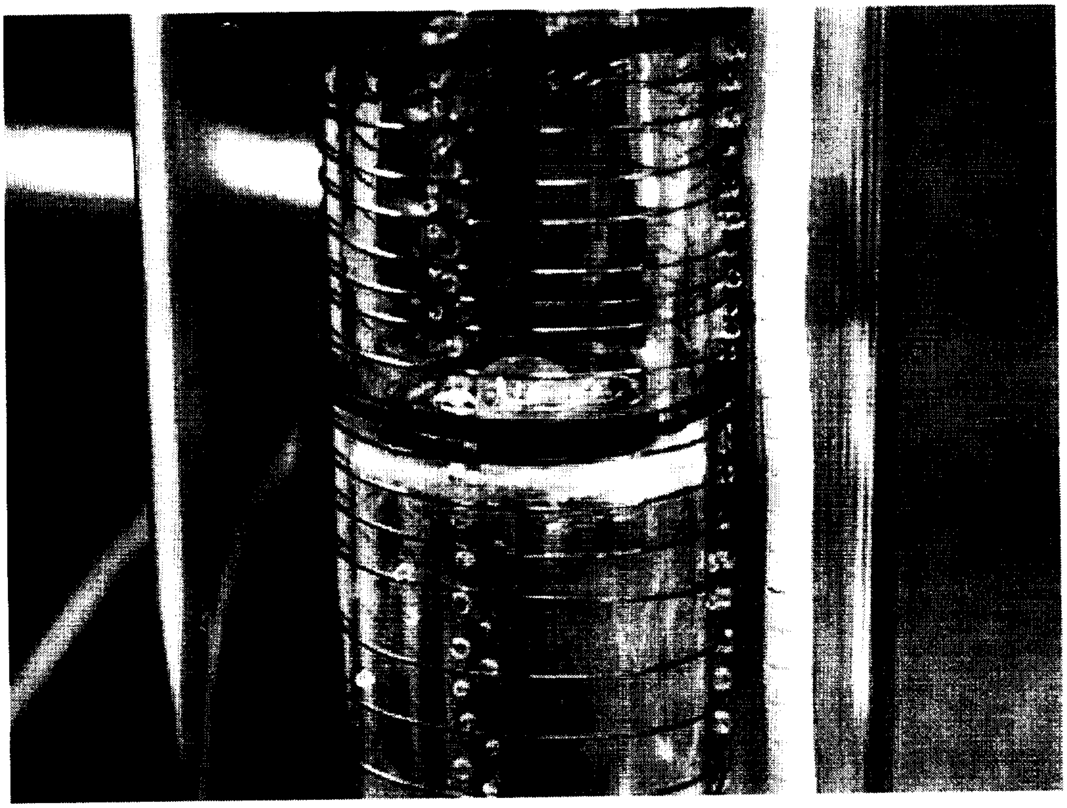

Fig. 19 Single crystal grown by self-seeding wall-less growth method developed by Joo Soo Kim. Multiple facets may be seen on the growing face of the crystal.

## Conclusions

UAH has developed an excellent facility for growing crystals by closed tube vapor transport. Novel methods for purifying mercurous chloride and for suspending the starting material above the growing crystal were developed by incorporating porous glass frit to prevent the transport of solid impurities and an over-under arrangement of the tubes connecting the chambers in the purification column to prevent the partially purified sublimate from depositing concentrically and breaking the ampoule during the heating for the next purification stage.

Single crystals of mercurous chloride were successfully grown, but were not of device quality. The crystals appeared to be highly stressed which may explain the difficulty we had in obtaining good Laue diffraction patterns and the microcracking we observed. We suspect that wall confinement and thermal expansion and contraction are responsible for this stress.

A technique for magnetically positioning an effusive barrier was successfully demonstrated, but we were unable to protect the magnetic material inside the ampoule from the corrosive attack of the mercurous chloride vapor. This concept could still be useful for more benign systems.

We now believe the problems in growing device quality mercurous chloride are more related to wall-induced thermal stresses than to uncontrolled convection. Consequently, we developed a new growth technique, similar to the method used for growing mercuric iodide, that avoids wall contact. Preliminary results have been obtained in CFD modeling of the convective flows and heat transfer in the growth ampoule developed for this process and a single crystal has been grown by this method. The grant funding ran out before this work on this new growth method could be completed.

Mercurous chloride has great technical promise for unique applications that require acousto-optical materials with wide spectral transparency, especially in the thermal infrared. No other material has been successfully produced that fills this niche. We believe that our new wall-less growth technique shows great promise in alleviating some of the problems in producing device quality mercuric chloride, but we have not yet been able to fully test the concept.

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