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SEMI-ANNUAL PROGRESS REPORT

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GROWTH OF ZINC SELENIDE SINGLE CRYSTALS BY PHYSICAL VAPOR TRANSPORT IN MICROGRAVITY

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Principal Investigator

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1. Crystal Growth Studies

1.1 Task

Optimization of growth parameters for large (20 mm diameter and length) zinc selenide single crystals with low structural defect density.

1.2. Earlier Status

As previously reported, we attempted to grow zinc selenide and zinc sulfoselenide crystals by physical vapor transport (PVT) in closed ampoules. The ampoule configuration used is depicted in Fig. 1. Early runs yielded some cm-size ZnSe crystals. However, later we were not able to reproduce the growth of such crystals. Most ZnSSe experiments resulted in polycrystalline material with very small grain size. Even in the earlier, successful runs with ZnSe, a ring of small crystals formed around the main crystal on the wall near the coldfinger. This clearly indicates that the radial temperature gradient in the nucleation and growth tip is insufficient to prevent parasitic nucleation and growth. In addition, the transport rates obtained at 950 °C, the temperature limit of the gold-coated silica tube furnaces used, were much lower than those reported in the literature for higher temperatures.

With the change in the Principal Investigator, from Dr. Elmer Anderson to Dr. Franz Rosenberger, the crystal growth efforts were redirected. It was decided to exclusively apply the Effusive Ampoule PVT technique (EAPVT), that was developed for CdTe under NASA auspices (F. Rosenberger, M. Banish and W. Duval, NASA Techn. Memorandum 103786, December 1991) to the growth of ZnSe. In this technique, the accumulation of transport-limiting gaseous components at the growing crystal is suppressed by continuous effusion to vacuum of part of the vapor contents. This is achieved through calibrated leaks in one of the ground joints of the ampoule.

Other advantages of this technique and the apparatus used are:

- Temperature capability up to 1050 °C.
- Reduction of the vapor incongruency problem through minimization of the temperature difference between source material and growing crystal.
- Minimization of the formation of thermal stress-induced structural defects through minimization of the axial temperature gradient across the growing crystal.
- Predetermination of the crystals orientation and suppression of grain boundary formation through the use of seeds.
- Determination of optimal thermal conditions for etching and growth within a few runs through in-situ optical monitoring of the seed/crystal surface morphology.

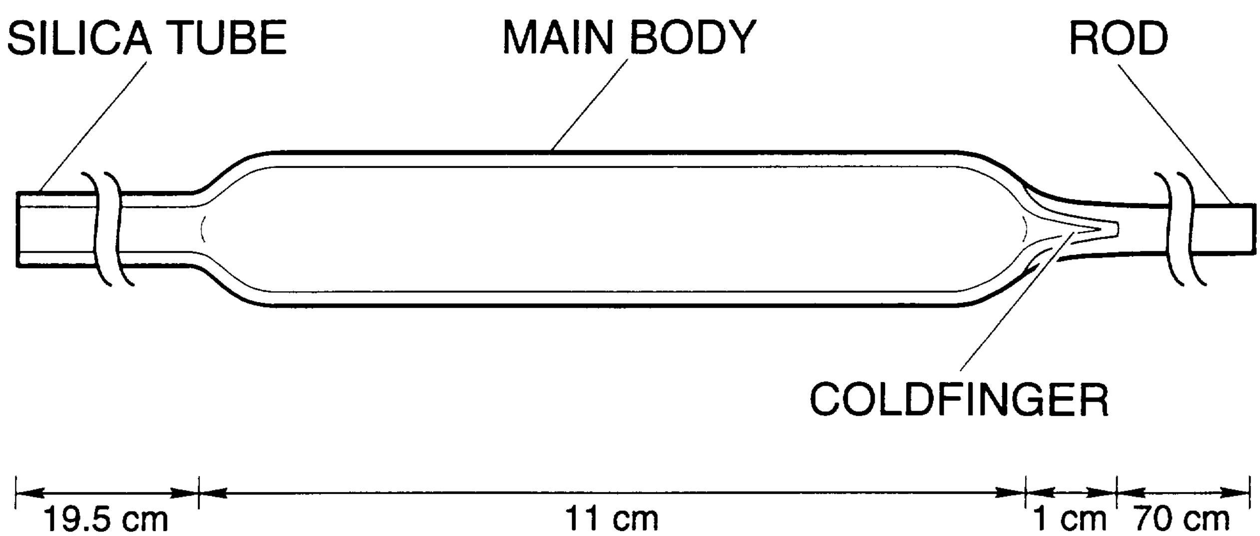


Fig. 1. Growth ampoule for closed system PVT.

However, earlier exploratory runs of our EAPVT setup with ZnSe revealed the following shortcomings:

- Extensive operation at and above 1050 °C, necessary to obtain good vapor epitaxial growth on ZnSe seed plates, led to frequent failure of some of heating elements.
- Thermal radiation leakage through the gold-coated windows, used for optical access to the seed region, caused an intolarable deformation of the temperature profile as evidenced by an irregular habit of the growing crystal boule.
- The source material was previously condensed onto the closed end of the source chamber in a separate heating cycle. On cool-down, or renewed heat-up after the introduction of a seed plate, the large difference in thermal expansion between silica glass and zinc selenide which sporadically sticks to the wall, often caused cracking of the ampoule.

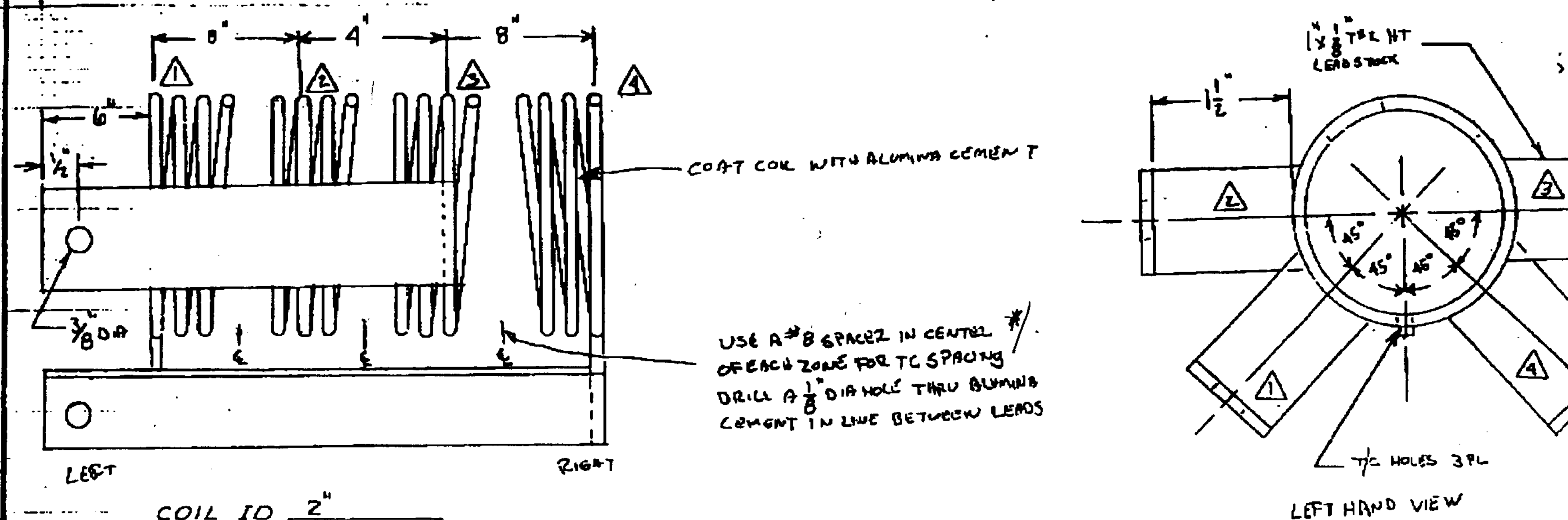
During the reporting period we have worked on remedying these shortcomings.

1.3. Work Performed

We have redesigned the furnace to be used for this project. As schematically shown in Fig. 2, a custom-designed heating element, consisting of three independently controllable zones, forms the core of the new furnace. The elements were laid out for gauge 5 heating wire, which will drastically increase their life time. A 1/4" gap is provided between the 2 center turns in the center zone, to accomodate the optical monitoring of the etching/growth process. One of the outer zones will determine the source temperature. The center zone, in combination with the other outer zone and the seed pedestal light pipe will determine the crystal temperature and its gradient.

The new heating element and the corresponding high-current transfoemers have been received. The water-cooled shell and insulation arrangement for the element are being designed and constructed.

For the optical monitoring of the crystal's vapor-solid interface we are working on a new approach. The gold-coated windows (see Section 1.2) will be replaced by a low-power microscope. This device, which has been conceived in our laboratory, consists of two silica lenses, which are contained in the high temperature part of the furnace, and a room-temperature 10X eyepiece. For efficient light collection and maximizing the field of view, the front lense is positioned in close proximity of the 1/4" gap in the center zone of the heating element. To provide better viewing of the crystal top and to minimize heat losses through the microscope, it will be mounted oliquely to the crystal axis. The optical axis of the microscope will be passing through the insulation of the upper, source heating zone, rather than along the shortest radius out



COIL ID 2"
GAUGE 5, TYPE A-1 WIRE. LENGTH 35 FT WEIGHT 3 LBS

* Mod. (9/30): Wind uniformly, except for 1/4" spacing between 2 center turns in center zone (Space for microscope viewing)

Thermcraft		
COIL LAYOUT		
SCALE	NTS	DRAWING NO. B-

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Fig. 2.

to room temperature.

Prototype tests of this microscope arrangement in another high-temperature furnace have been encouraging. The assembly to be used in the ZnSe is being constructed and built into the insulation/shell arrangement of the new furnace.

The demountable ampoule has been partly redesigned for the growth of ZnSe; see Fig. 3. The source chamber has now a partition with a filling tube. The prepurified source material is introduced through this tube and rests initially in the trough between the ampoule wall and filling tube. During heat-up, with the seed already in place, the source material compacts in the coolest region of the source chamber and thus, occupies a thermally well defined position from the beginning of the downward transport to the seed. In addition, we have bent the transport-limiting capillary. Straight capillaries appeared to slightly raise the temperature of the center of the crystal-vapor interface through some "light-pipe effect" from the hotter source material zone.

In order to better control the radiative heat losses through the seed pedestal, the light pipe (coldfinger, see Fig. 3) will rest in a graphite cup, the temperature of which will be monitored with a thermocouple.

During the next six months, the furnace arrangement will be completed and optimized for the growth of large ZnSe single crystals.

2. Modelling of Physical Vapor Transport Rates

2.1. Task

Development of a 3-D numerical model for the transport rates to be expected in physical vapor transport under a given set of thermal and geometrical boundary conditions, in order to provide guidance for an advantageous conduct of the growth experiments.

2.2. Earlier Status

After failure of all accessible, commercial codes to reproduce definitive experimental results obtained with the iodine/carbontetrabromide system (see earlier reports) we have modified a 3-D spectral code, that was developed at the CMMR for Bridgman modelling. After introduction of the proper boundary conditions and subroutines for the composition-dependent transport properties, the code reproduced the experimentally determined transport rates for the two cases with strongest convective flux contributions to within the experimental and numerical error. These are the two most difficult cases to compute.

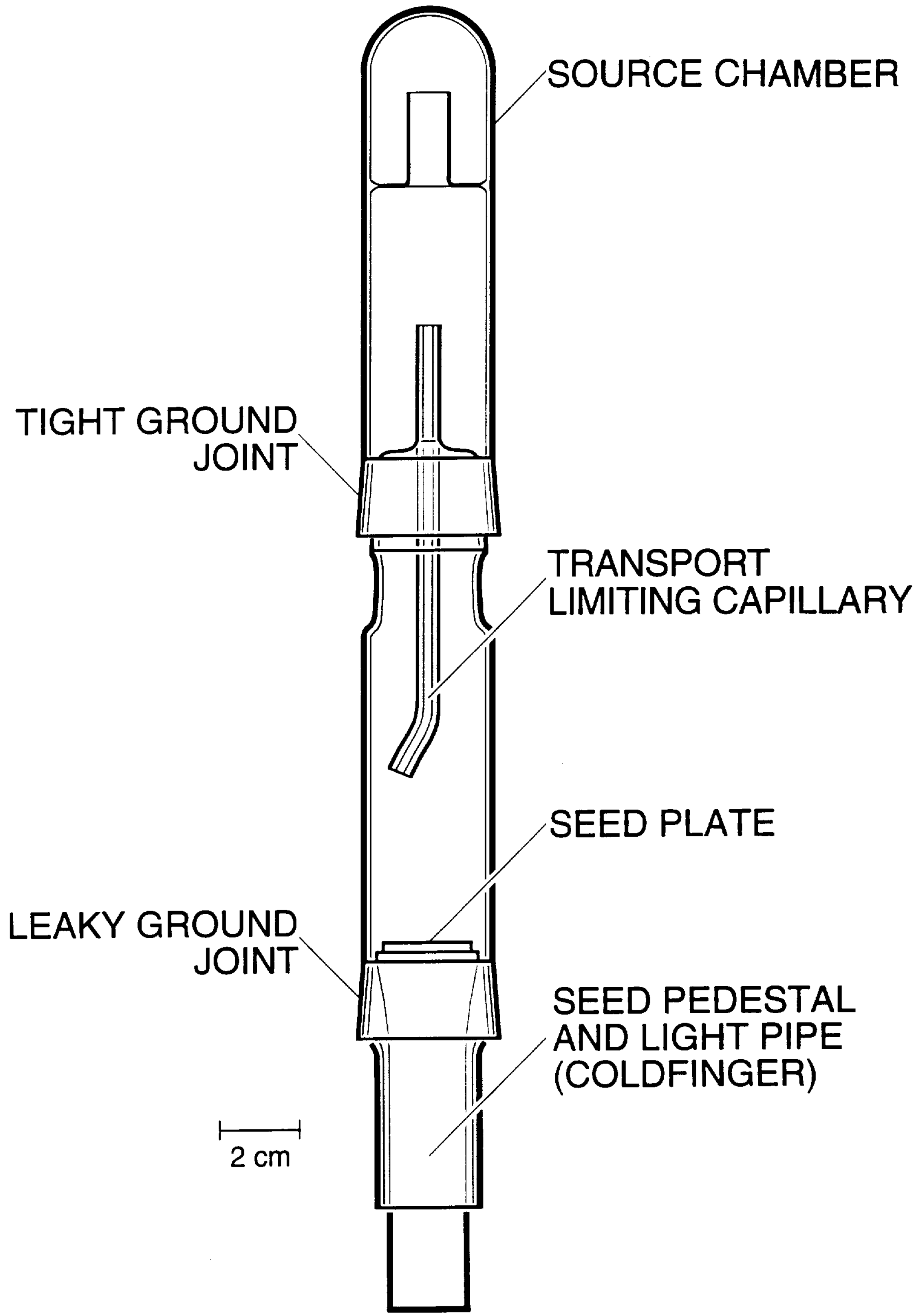

Fig. 3. Demountable ampoule for effective PVT.

2.3. Work Performed

During the reporting period, solutions were obtained for the remaining 13 cases for which we have well defined experimental results. The solutions reveal a very intricate interplay between thermal and solutal convection, and further empasize the necessity of realistic, 3-D descriptions of vapor transport processes.

During the next six months, we will evaluate the computational results and present them, together with the experimental work, in a comprehensive publication. This material will, for the first time, represent a computational PVT transport model that contains all the essential transport physics of sublimation-condensation experiments for a wide range of thermal and compositional parameters.