Physics Department

Colorado State University

Final Technical Report

January 31, 1970

Including Quarterly Status Report

GROWTH OF CRYSTALS OF THE TERNARY SULFIDES

NASA Grant NGR 06-002-074

A. Introduction

The objectives of this project are:

1) To establish a laboratory for crystal growth.

2) To produce crystals of proustite and pyrargyrite as a test of equipment and technique.

3) To explore additional materials of likely candidacy.

4) To explore possible means of improving optical quality.

5) To make a few preliminary evaluations of the crystals.

It was realized at the outset that all these objectives could not be met during the first year of operation. The major items for crystal growth furnace, controller, enclosure - could not be obtained before the middle of summer. Thus, the efforts up to that time were of necessity preliminary and inaccurate because the gradients were produced at the opening of an oversized surplus tube furnace.

B. Overall Progress

The laboratory was established in Room D-1 of the Engineering - Physics-Mathematics Complex of Colorado State University. Figure 1 shows the research furnace, controller, enclosure and crystal saw and Figure 2 is a sketch of the floor plan of the room showing the general layout of the facilities. The x-ray laboratory is across the hall in D-15 and consists of a G.E. XRD-5 diffraction unit with diffractometer, copper and chromium tubes and cameras -

Laue, two Debye-Scherrer, Buerger precession and Weissenberg. The Department of Physics has recently placed an order to facilitate expanding the unit to a two-tube operation. This would make it possible to use the line focus exclusively for the diffractometer and allow three cameras and tracks to be permanently set up on a second table. This modification, while not accounted to this project, will certainly benefit it by alleviating the congestion and minimizing the adjustment-alignment efforts.

The laboratory is nearly completely equipped as planned a year ago. Some items have still not been delivered, but are only now beginning to be needed -- the two circle goniometer and manipulator, for example.

The profile of the furnace was described in the second quarterly report and the curve is reproduced here, Figure 3. Since then we have taken some additional data with cooling water and stainless steel sleeves included. Typical profiles are given in Figure 4. The effect of the cooling coil is evident in this figure.

Several charges of proustite and pyrargyrite were prepared using various techniques, some of our own inventions as well as those suggested by the literature and personal communications. As expected we found contamination of the charge by water was highly undesirable. Also our attempts to produce a successful charge (in the sense of quality crystal later) from a mixture of the salts Ag_2S and As_2S_3 were not encouraging. The final procedure for preparing charges is to use the elements of 6-nines purity and react at a temperature of the order of 200 C° above the melting point of the compound desired. The vessels are cleaned and prepared in a standard way, the charge loaded in, the vessel pumped and heated to drive off any water vapor, and sealed under a partial atmosphere of argon. The sealed

capsule is heated in an auxiliary furnace in a protective metal tube. The boule is inspected and the growth run initiated. The run takes many hours. Of the several runs made, only two have produced crystals of proustite which we have felt worthy of preliminary examination and expectation of future success. Figure 5 illustrates the vessel and describes the procedure for preparing a charge for a ternary system, Ag-As-S in particular.

The exploration of other materials has not progressed very far. An attempt to grow sulfur crystals by precipitation from a CS_2 solution yielded a few small crystals embedded in a polycrystalline matrix. Some of these small crystals are a few millimeters on a side and show interesting surface morphology and a polarization extinction. This experiment will continue under various controlled conditions.

C. Plans In Current Ready-State.

The Ag-As and Ag-Sb sulfide systems will be further explored with the immediate goal of increasing the size and quality of the crystals produced.

The sulfur-from-solution run will be repeated with attention to temperature and growth rate as well as other solvents.

Gel growth is a term applied to a method of crystal growth in which the mobility of the reactants is decreased by diffusion through a gel. This decreases the growth rate drastically and allows highly insoluble compounds to grow to crystals of several millimeters. The growth of sulfur will be attempted and also an investigation of the possibility of growing various sulfides by this technique.

D. Future Plans

The future plans for the project comprise the fulfilling of the objectives, in particular the exploration of other stoichiometric compounds in

the Ag-As-S and Ag-Sb-S system and the exploration of other ternary sulfide systems, such as Cu-As-S, Ag-Bi-S, As-Pb-S, Cu-Bi-S. Also besides sulfur, one might look at Se-S and Te-S. Going to non-sulfur systems, good candidates are I_2 and several iodides such as Ge I_4, K-Hg-I, Cd I_2, T_1 I_3, K-Bi-I. The chalcogenides comprise a large family of interesting compounds, many of which do not crystallize but instead form glassy materials with, however, appreciable ordering. In the exploratory runs, it is anticipated that several of these will occur and some may be of interest to this project.

E. Personnel

Besides the principal investigator, a graduate student, John Kitterman, has contributed to the project, handling most of the routine details of the operation of the laboratory and cooperating directly with the principal investigator in the handling of the materials and charge preparation. Maintenance of the laboratory and control of the growth runs was handled by Kitterman and a senior Eric Rogers.

Rogers left for graduate school in the Fall and Kitterman left at the end of January upon completion of the experimental work for his Ph.D. thesis. Another senior, Jon Gustafson, contributed to the project during the summer, and a sophomore, Dan Marvel, helped during the Fall.

Dale R. Wonder
Principal Investigator

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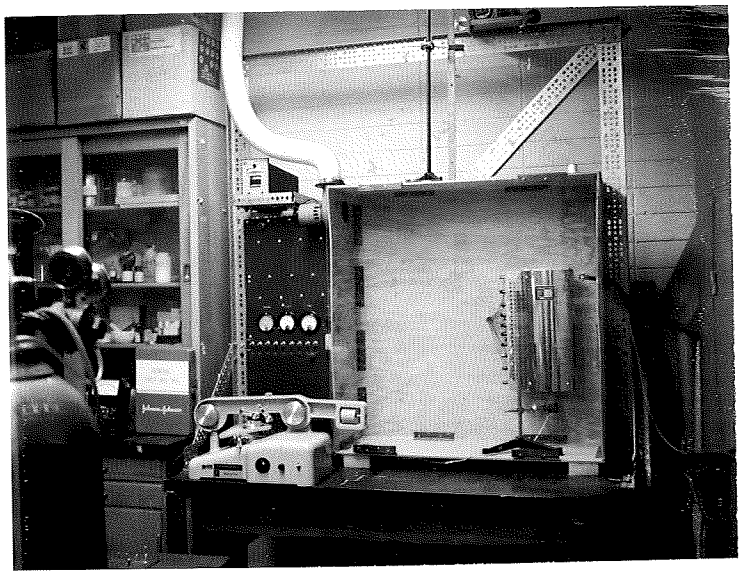
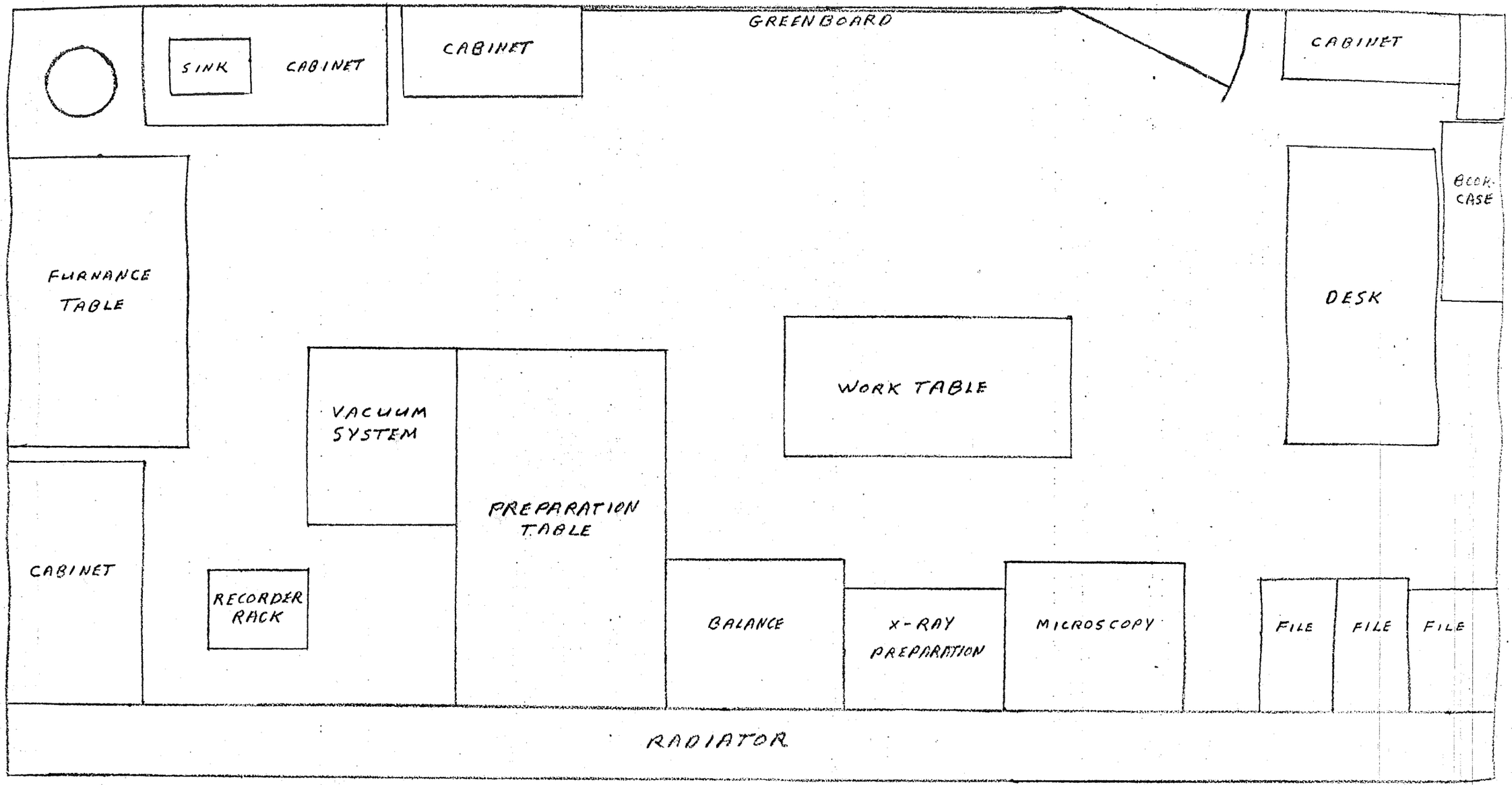


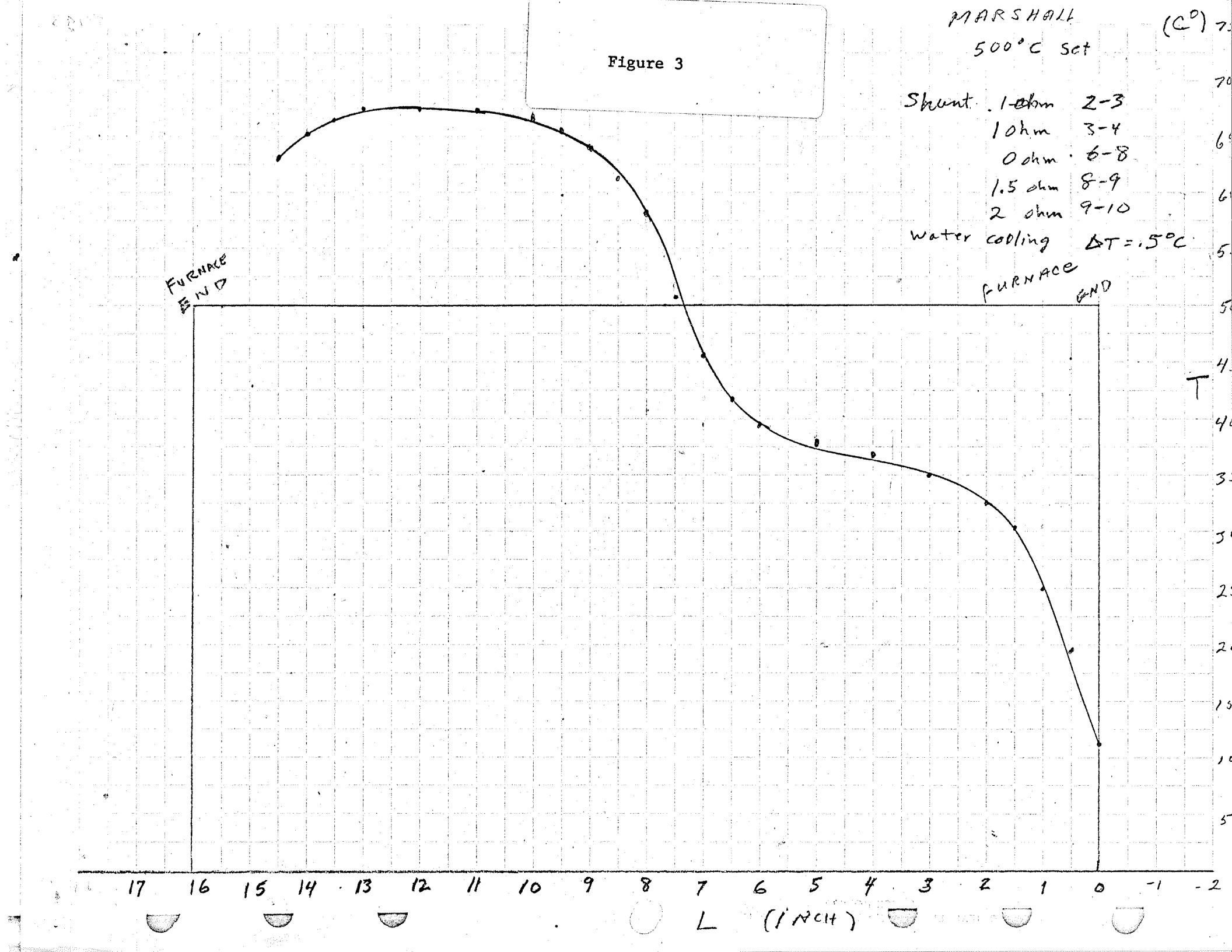
Figure 1. Furnace, control unit and crystal saw.



C. S. U. LABORATORY FOR CRYSTAL GROWTH

Figure 2

Figure 3


MARSHALL
500°C set
(C°)
Shunt .1 ohm 2-3
1 ohm 3-4
0 ohm 6-8
1.5 ohm 8-9
2 ohm 9-10
water cooling ΔT = .5°C
FURNACE END
FURNACE END
T
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
L (INCH)

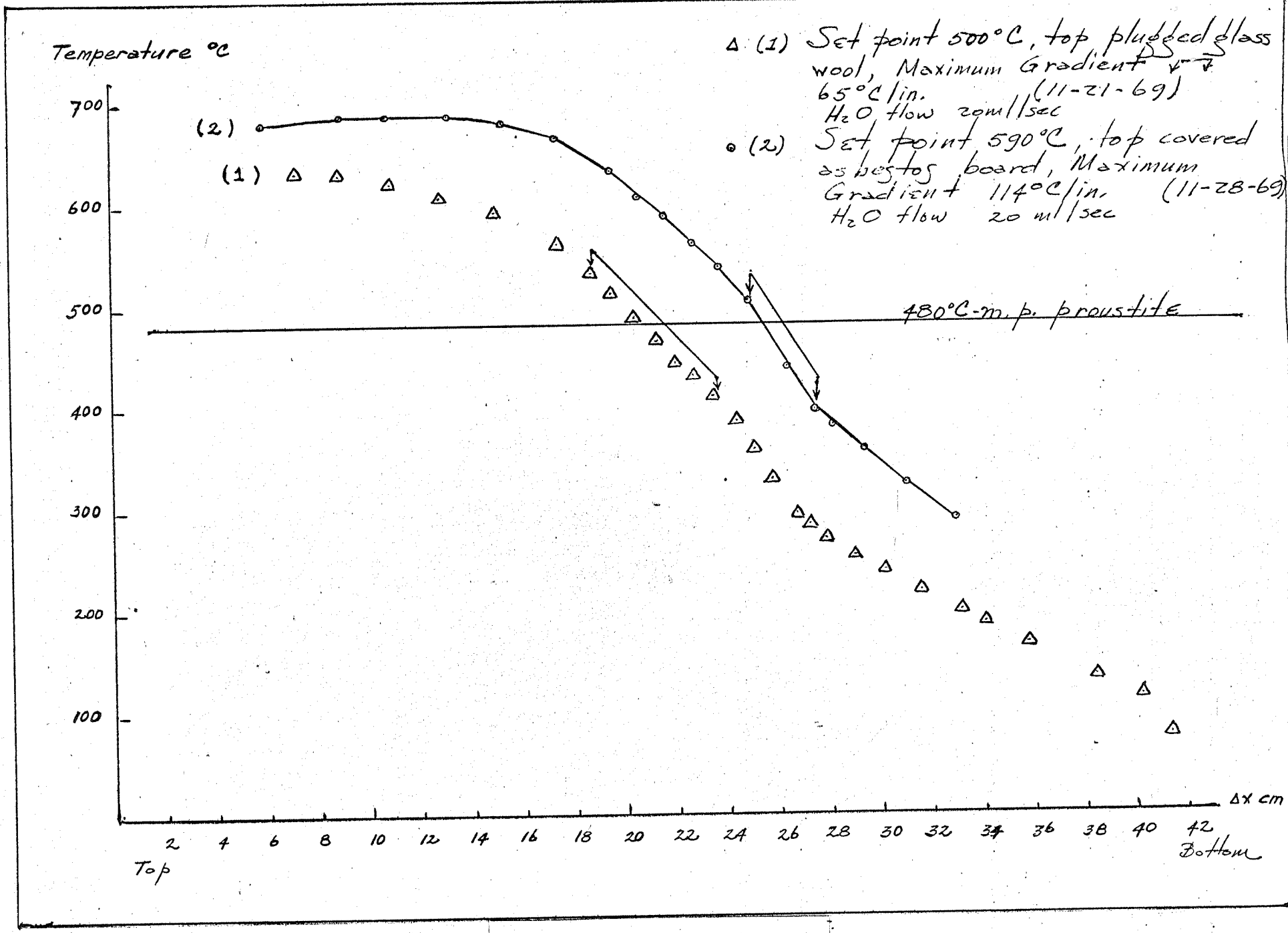
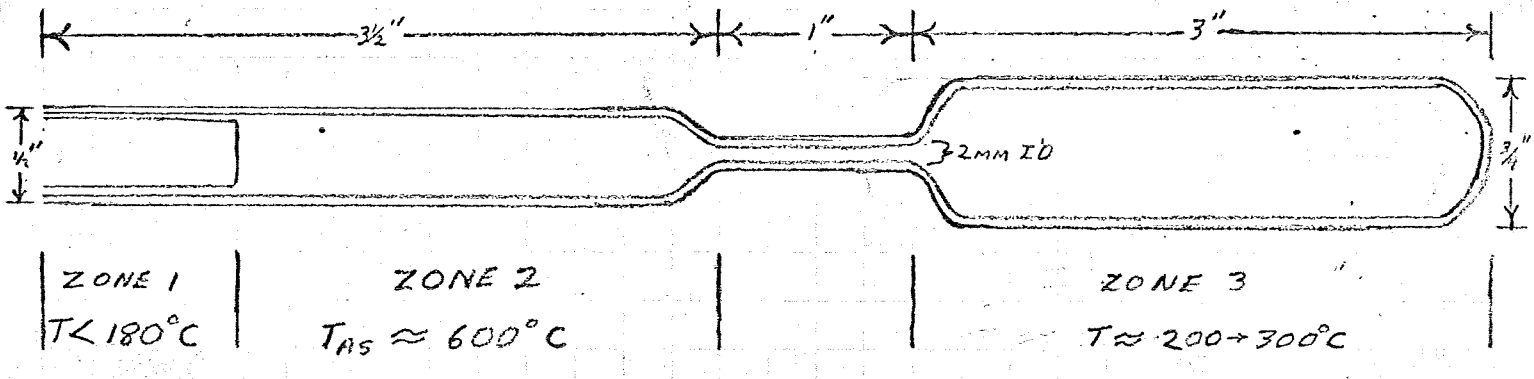

Temperature °C
700
600
500
400
300
200
100
(2)
(1)
480°C-m.p. proustite
Δx cm
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
Top
Bottom
Δ (1) Set point 500°C, top plugged glass wool, Maximum Gradient 65°C/in. (11-21-69)
H2O flow 20ml/sec
○ (2) Set point 590°C, top covered asbestos board, Maximum Gradient 114°C/in. (11-28-69)
H2O flow 20 ml/sec

Figure 4



PROCEDURAL STEPS

1. Match, clean, dry tube, cup charges.

2. Load Ag, As, S charges.

3. Heat whole tube to 150° C and pump, 20 minutes. Cool.

4. Seal ring - keep As charge cool (zone 2 at < 100° C)

5. Heat zone 2 to ~ 320° C, cool zone 1 and zone 3 to < 100° C, 30 minutes until distillation of As_2O_3 is completed into zone 1.

6. Heat zone 2 to 600° C, zone 3 to ~ 200° C, cool zone 1 <100° C, 20 minutes until distillation of As into zone 3 is completed. Cool.

7. Seal at capillary.

8. React in protected reaction furnace. Cool.

9. Inspect.

Figure 5