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Final Report

SPACE PROCESSING OF CHALCOGENIDE GLASS

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Alabama 35812

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Final Report

SPACE PROCESSING OF CHALCOGENIDE GLASS

for

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Alabama 35812

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SPACE PROCESSING OF CHALCOGENIDE GLASSES

1.0 INTRODUCTION

The purpose of this program was to investigate space processing of chalcogenide glasses. This report summarizes the results of this three year effort. Chalcogenide glasses are good infrared transmitters and have good strength, corrosion resistance, and scale-up potential. For these reasons, chalcogenide glasses are considered as potential candidate materials for use as laser windows and infrared fiber optics for transmitting a laser beam through a flexible probe. For fiber optics, is has previously been demonstrated that high quality chalcogenide fiber optics could not be processed due to limitations related to the presence of the 1-g earth environment.

The disadvantage of (earth-produced) chalcogenide glasses is that their infrared absorption is unacceptably high relative to alkali halides, the currently used material for 10.6 μm laser applications. IITRI believes that this limitation of earth-produced chalcogenide is due to optical nonhomogeneities resulting from environmental and container contamination. Processing the glass in space should improve the infrared-transmission of chalcogenide glasses. The containerless, weightless nature of space processing should eliminate: 1) optical inhomogeneities caused by thermal currents and density fluctuations in the 1-g earth environment; 2) contamination from the earth melting crucible by oxygen and other elements deleterious to ir-transmission; and 3) heterogeneous nucleation at the earth melting crucible-glass interface.

The overall objective of IITRI's current program is to determine the manner in which the weightless, containerless nature of in-space processing can be successfully utilized to improve the quality of infrared transmitting chalcogenide glasses. This program is an effort to develop the technique of space processing chalcogenide glass, and define the process and equipment necessary to do so. These goals are accomplished by a series of earth-bound (1-g) processing experiments with As_2S_3 and $G_{28}Sb_{12}Se_{60}$ glasses. Incorporated into these experiments is the use of an acoustic levitation device that will eventually be utilized in the 10^{-4}g space environment to achieve position-controlled containerless processing.

2.0 CONCEPTS OF SPACE PROCESSING

It is necessary to briefly describe some of the concepts being used in this program. The main idea is to take advantage of the near zero "g" environment of space to reduce foreign material contact with the melt by containerless melting, and to eliminate the thermal currents in the melt. It is the defects caused by earth environmental manufacture that causes the glass to overheat in local areas and fracture when exposed to large amounts of infrared radiation. Also, smaller amounts of radiation, although not sufficient to cause thermal fracture, will have distorted wave forms and thus degrade the value of the signal. Therefore, these imperfections must be eliminated.

This program is designed to demonstrate the feasibility of various techniques, processes, and equipment that will be utilized to manufacture chalcogenide glasses in space. Optimum methods, techniques and equipment are defined through evaluation of amorphous character, purity, and homogeneity parameters at various stages of the glass forming process (i.e., from the raw material stage through the melt-quenching stage). The aim of this work is not only to determine optimum preparation techniques, but also to provide guidelines for the design of the actual melting experiment in space, and optimization of the exact chalcogenide composition to be included in the space experiments. The program, therefore, represents the initial phase of an overall systematic effort to insure a high probability of success for the space experiment.

To accomplish the intended improvement in chalcogenide quality, the high-temperature process for making the glass has to be carried on in space at zero "g" where the weightless containerless conditions can be obtained. The preparation for compounding and the final treatment of the material for an optical element can be done on earth without reducing the quality of the space-processed material.

3.0 EARTH PROCESSING VS. SPACE PROCESSING OF CHALCOGENIDE GLASSES

The earth-bound production of chalcogenide glasses involves a five step process: 1) the elemental precursor powders are placed in a silica ampoule, 2) the ampoule is evacuated and sealed, 3) the temperature is slowly increased to the reaction temperature to form the compounded liquid, 4) the ampoule is rocked back and forth for periods up to 48 hours to homogenize the liquid, and 5) the liquid is quenched to form a glass.

The rocking of the ampoule and the resulting mixing of the liquid is necessary to overcome the micro-inhomogeneities resulting from thermal currents and density fluctuations that are due to the presence of the earth's 1-g gravity field. However, these gravity related phenomena are never completely eliminated by this method. Furthermore, this prolonged contact with the crucible material contaminates the chalcogenide with ppm levels of oxygen and other elements deleterious to ir-transmission at a wavelength of 10.6μ.

By going to space to process chalcogenide glasses, both of these problems, thermal currents/density fluctuations and contamination, will be eliminated. The compounding and quenching aspects of the process can be performed in the absence of gravity, eliminating thermal convection. The zero gravity condition provides for the possibility of containerless processing, which will eliminate the contamination effects of the earth melting crucible. Thus, the weightless, containerless aspects of space manufacture has the potential for producing an improved ir-transmitting chalcogenide for use as a large diameter 10.6μ window.

4.0 RESEARCH PROGRAM SUMMARY

Two chalcogenide glass systems were investigated in this program, As_2S_3 and $Ge_{28}Sb_{12}Se_{60}$. As_2S_3, arsenic trisulfide, is a well-characterized system that is considered standard in many respects. $Ge_{28}Sb_{12}Se_{60}$ glasses are currently the best ir-transmitting chalcogenides available.

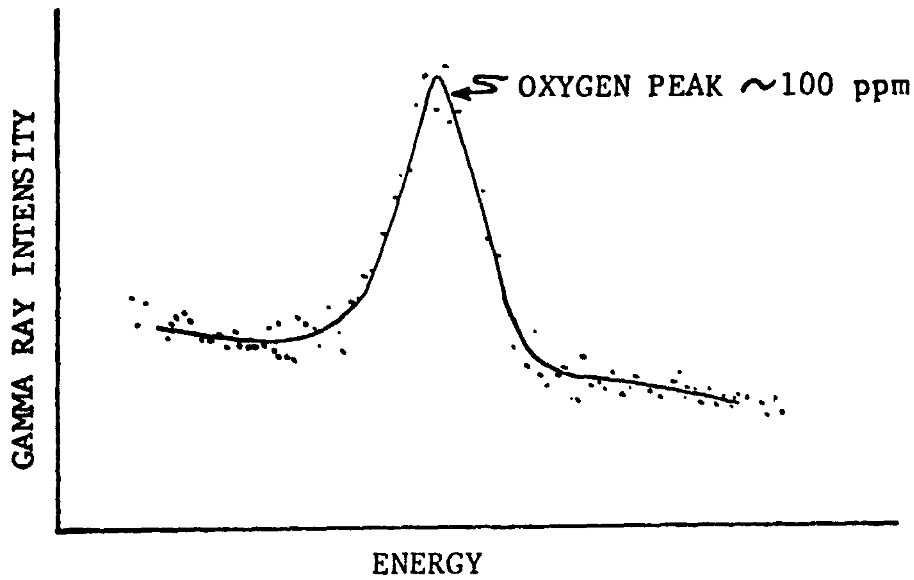
4.1 As_2S_3 Experiments

The As_2S_3 system allowed considerable experience to be gained about the processing of ir-transmitting chalcogenides as well as the nature of the necessary constraints of the in-space experiments. The objective was to develop and evaluate specific techniques, processes, and equipment that are used to a) mix the chalcogenide precursor materials, b) form a homogeneous pellet that can be taken to space for high temperature processing, and c) melt and quench the pellet to form the chalcogenide glass. The idea is to provide firm guidelines for the design of actual in-space experiment.

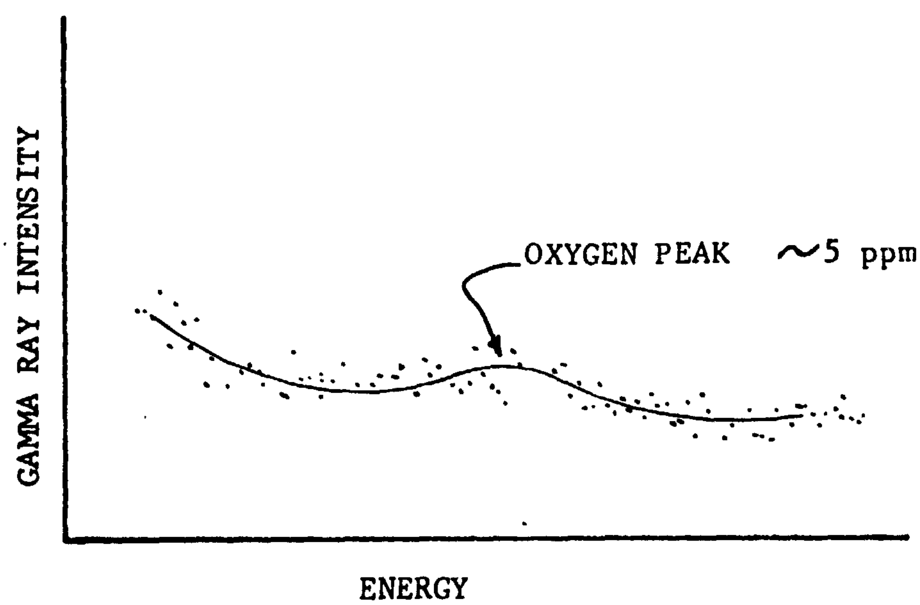
The purpose of the blending phase of the program was to determine the optimum method of preparing a homogeneously mixed precursor powder batch on earth with minimum contamination. Liquid slurry and dry powder methods were investigated. The compounding portion of the program formed a large portion of the first phase effort. The emphasis here was to conduct various glass-making experiments for the purpose of determining the mechanisms of reaction of the precursors. These experiments were generally conducted on cold pressed precursor pellets without rocking the furnace. This is the manner in which the actual in-space melting experiments might eventually be conducted. The ampoule-rocking that homogenizes the glass in 1-g conditions, and also contaminates the glass, will not be necessary under 0-g conditions if suitably pre-mixed precursors are used.

The evaluation stage of the program was conducted at various points in the chalcogenide glass production schedule. In the first phase, for instance, the ir-transmission characteristics of various glasses that were produced were measured using an ir spectrophotometer. Additionally, the low level impurity content of chalcogenide systems was investigated by the CPAA (charged particle activation analysis) technique. Light elements ($1 < Z < 20$) undergo a variety of resonance reactions when bombarded with relatively high energy (0.5 to 2 MeV) charged particles (protons, deuterons, alphas, tritons, etc., from a Van de Graaff Accelerator). Given the bombarding charged particle and its energy, the emitted gamma radiation is characteristic of the target element. With proper calibration, a measurement of the gamma-ray energies and intensities provides a quantitative measurement of the elements present in the sample subjected to charged particle bombardment. Figure 1 illustrates the results of the use of this technique to determine the oxygen content of two chalcogenides. The relative peak heights shown for the cases of 100 ppm oxygen and 5 ppm oxygen illustrates the sensitivity level of this instrument.

A large portion of our first phase effort was spent in preparation for sounding rocket flights. This effort was not a part of the original program plan, but evolved during the course of the first year's work. Short term sounding rocket flights could be used for many preliminary space processing experiments. This approach would provide a relatively inexpensive way of learning of and solving many of the engineering type problems associated with space flight - e.g., effect of actual weightless conditions, effect of actual vibratory, spinning and acceleration (and deceleration) forces on the equipment/experiment, effect of instrumentation on telemetry, etc. To facilitate the processing of chalcogenide glasses under the time constraint of only six to seven minutes of low-g condition in a rocket flight, a new precursor processing technique was conceptualized - hot pressing to form a partially reacted body. Initial work in this area entailed investigations on the proper time-temperature-pressure schedules



CPAA RESULTS: INITIAL IITRI CHALCOGENIDE



CPAA RESULTS: TI #1173 CHALCOGENIDE

Figure 1. CPAA Results for Low-Level Oxygen Contamination

to be employed in hot pressing. This concept was not pursued further, however. The increased contamination that resulted from the hot pressing would negate any benefits to be derived from a short rocket flight.

4.2 $Ge_{28}Sb_{12}Se_{60}$ Experiments

In the second phase of this program, the more complex $Ge_{28}Sb_{12}Se_{60}$ system was studied. This system is equivalent to Texas Instrument's TI-1173 glass and is generally considered to be the best produced on earth. It is anticipated that a glass exhibiting ir-transmission properties better than TI-1173 will eventually be produced in space. For these reasons, TI-1173 glass was chosen as a control standard providing bench-mark data for comparative purposes. The specifics of the processing of this glass are generally proprietary to TI, thus many of the details of the proper temperature-time schedules were developed on the current program. After achieving glass quality comparable to TI-1173, the following additional areas were investigated: 1) purification of precursors, 2) use of gettering agents, and 3) adaptation to processing in inert atmosphere.

4.3 Acoustic Levitation

The final phase of our work involved acoustic levitation. One of the major potential advantages of space for materials processing is that critical stages of the process can be accomplished without the presence of a containment vessel. The containerless aspect of space will be accomplished with the aid of levitation/position control devices that are currently under development for NASA. One such device is the Intersonics, Inc. Acoustic Levitator. This device was supplied GFE to IITRI for use on this program. A cooperative effort was undertaken with Intersonics to work acoustic levitation into the earth-bound chalcogenide processing experimental package. The purpose of this investigation was to investigate all of the aspects of levitation art and science and chalcogenide glass art and science to insure a high probability of success for future space processing missions. Various initial acoustic levitation experiments were conducted. These experiments mainly entailed the levels of stability and control obtainable with this device. Based on this work, recommendations were made to NASA and Intersonics on improvements necessary for this device.

The following sections detail the results obtained in the areas discussed above.

5.0 RESULTS AND DISCUSSION

The following sections discuss the results of the experimental work with As_2S_3 and $Ge_{28}Sb_{12}Se_{60}$. Detailed information about the sample batches referred to in the text is continued in the accompanying tables.

5.1 As_2S_3 Experiments

The concept investigated here is that the benefits to be derived from the weightless, containerless conditions of space involve only the high temperature process. In the 1-g rocking ampoule method it is believed that much of the contamination results from the long duration, high temperature contact of the low viscosity liquid with the silica container. The following sections deal with the feasibility of pressing the batch powders into a homogeneously mixed pellet while on earth, and then compounding the glass in space.

5.1.1 As_2S_3 Precursor Preparation Methods

The objective of the powder preparation phase of the program was to determine the best earth-bound method of obtaining a homogeneous mixed precursor powder batch. Mechanical mixing and liquid slurry mixing methods were investigated. The mechanical method consisted of grinding and dry ball-milling the as-received powders in the proper ratio. The liquid slurry method consisted of mixing the powders in an appropriate liquid to promote uniform particle dispersion, and then evaporating the liquid.

Three organic solvents were selected as the liquid vehicles for the slurry mixing experiments; acetone [CH_3COCH_3], benzene [C_6H_6], and xylene [$C_6H_4(CH_3)_2$]. The criteria considered in the selection of candidate liquid vehicles were: 1) low boiling point, 2) fast evaporation rate, and 3) good wetting properties. Acetone and benzene are well-known solvents having low boiling points ($<100^\circ C$) and high evaporation rates. Xylene also has a low boiling point ($100-200^\circ C$), but has an evaporation rate slightly lower than acetone or benzene. However, xylene exhibits good wetting characteristics and serves as an efficient dispersant.

Reagent grade arsenic and sulfur powders were used in the initial liquid slurry experiments. Two basic types of experiments were conducted. The first involved mixing both powder precursors simultaneously in a given solvent. The second involved mixing each powder separately in a solvent, and then mixing the resulting liquid solutions together. In both cases, the final liquid solution was placed in an ultrasonic bath, and the liquid vehicle evaporated leaving well-dispersed As + S dry powder batch.

The homogeneity of the dry As + S batches prepared by the mechanical and liquid slurry conditions was then qualitatively assessed by examining the processed batches in an optical microscope. Typical results are shown in Figures 2 and 3. Figure 2 represents a case where the mixing was mechanical and no liquid vehicle was employed. Note the large particles present which appear to be large, unmixed individual arsenic and sulfur. Figure 3 represents the case where acetone was used as a liquid vehicle. Again, a few agglomerates are observed. It is believed that these lumps are the result of caking due to the evaporation of the acetone vehicle. Agglomerated particles will not be detrimental if they exhibit the same homogeneity as the non-agglomerated portion of the sample.

Charged Particle X-Ray Spectroscopy (CPXS) elemental analysis was then performed on the mechanically mixed and slurry mixed samples to quantify the degree of homogeneous mixing obtained. A mechanically mixed batch and a slurry mixed batch were each subdivided into four or five parts. Each part was analyzed for amount of elemental arsenic and sulfur present. The results are presented in terms of the ratio of the areas under the sulfur and arsenic peaks. A completely homogeneous mix would exhibit identical sulfur content/arsenic content ratios for all sections of the sample.

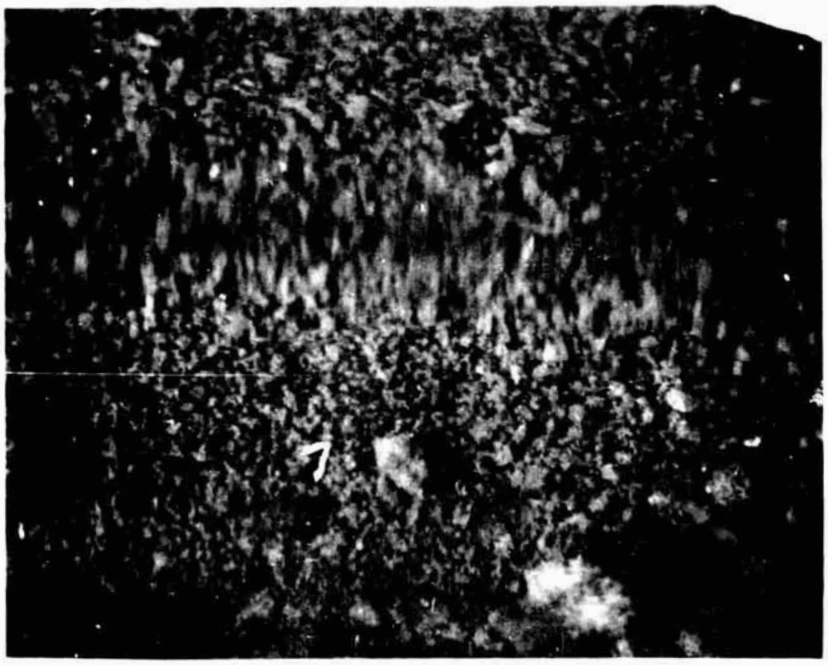


FIGURE 2. Optical Photomicrograph of As+S Batch Prepared by Dry Mechanical Mixing (25X)

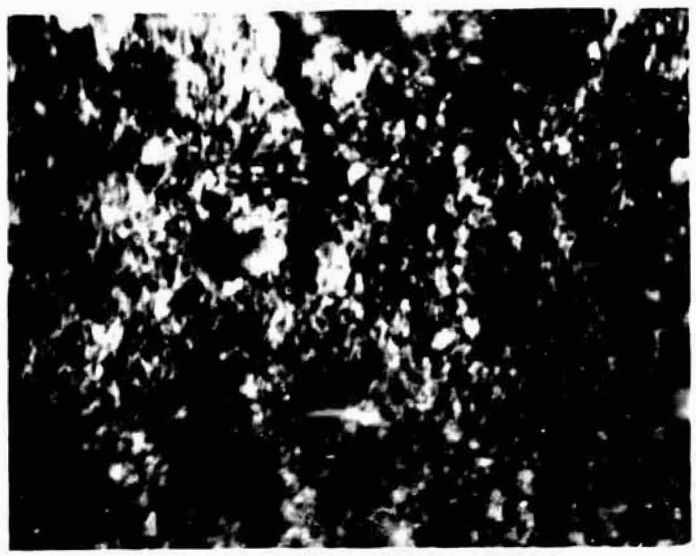


Figure 3. Optical Photomicrograph of As+S Batch Prepared by a Liquid Slurry Technique (80X)

The results of this analysis are presented in Table I, and show that the slurry-mixed batch exhibits significantly greater homogeneity and more uniformly dispersed particles than the mechanically mixed batch. The caked sections of the liquid slurry mixed batches possessed the same composition as the non-agglomerated sections. It can be concluded from these experiments that for space processing of an initially cold pressed precursor pellet, chalcogenides exhibiting better ir-transmission characteristics will be obtained if the precursor powders are prepared on earth using the liquid slurry method rather than the mechanical mixing method.

5.1.2 Cold-Pressed Pellet Processing

Initial experiments in the preparation of As_2S_3 dealt with compounding the elemental arsenic and sulfur powders starting from a cold pressed pellet stage. The object of this was to determine if starting with a cold pressed batch inhibited the reaction process in any manner.

To investigate this the following experiment was conducted. Starting with reagent grade sulfur powder and -325 mesh, 99.5% purity arsenic powder, a cold pressed pellet was prepared and sealed in a silica ampoule. After several attempts to determine the optimum heating schedule, the following schedule proved suitable. The precursor batch was slowly heated (1°C/min) to ~120°C (sulfur M.P.). After a hold period at this temperature, the system was raised to the 650°C reaction temperature at ~2°C/min. After a 16 hour hold period at 650°C (with no rocking to homogenize) the reacted liquid was quenched to form the glass, and subsequently annealed.

Figure 4 is a photograph of the processed chalcogenide and ampoule. Note the small amount of sulfur condensed on the upper part of the ampoule. This phenomenon can be accounted for by dealing with the stoichiometry of the compounded glass.

Figure 5 illustrates the ir-transmittance of As_2S_3 produced in this manner (i.e., from a cold pressed pellet) as a function of

TABLE I

CPXS POWDER BATCH HOMOGENEITY RESULTS

Powder Mixing Method and Sample Number	Ratio of Sulfur Content to Arsenic Content
Mechanical #1	1.802
Mechanical #2	1.296
Mechanical #3	1.527
Mechanical #4	1.868
Mechanical #5	2.579
Slurry #1	2.189
Slurry #2	2.015
Slurry #3	2.277
Slurry #4	2.373

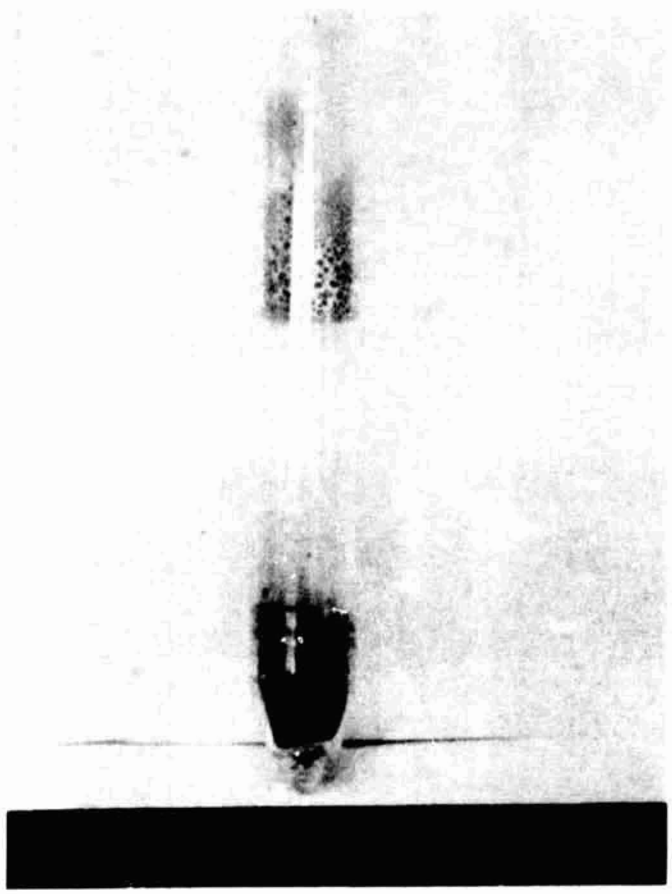
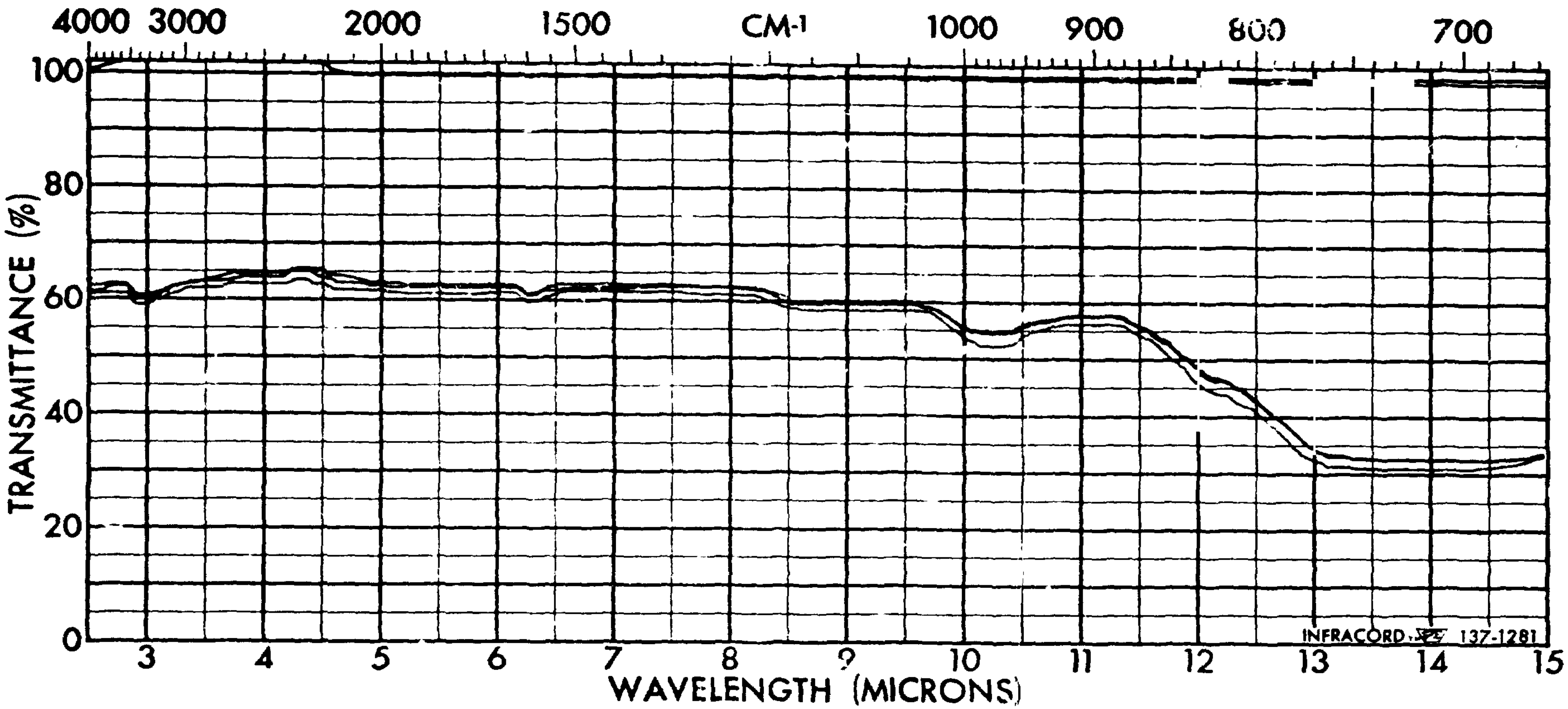


Figure 4 Photograph of Processed Chalcogenide and Ampoule



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE As_2S_3 (99.5% Arsenic, lab grade sulfur)	Color: slightly reddish brown	1. Sample Size = .42 x .39 inch	Small sample size; small
Cold Pressed Pellet Mel:ed in Sealed Ampoule	PURITY	2.	particle of unmelted
(BDR-11)	PHASE	DATE 5/29/74	senic in sample.
	THICKNESS 0.088 inch	OPERATOR MAA	

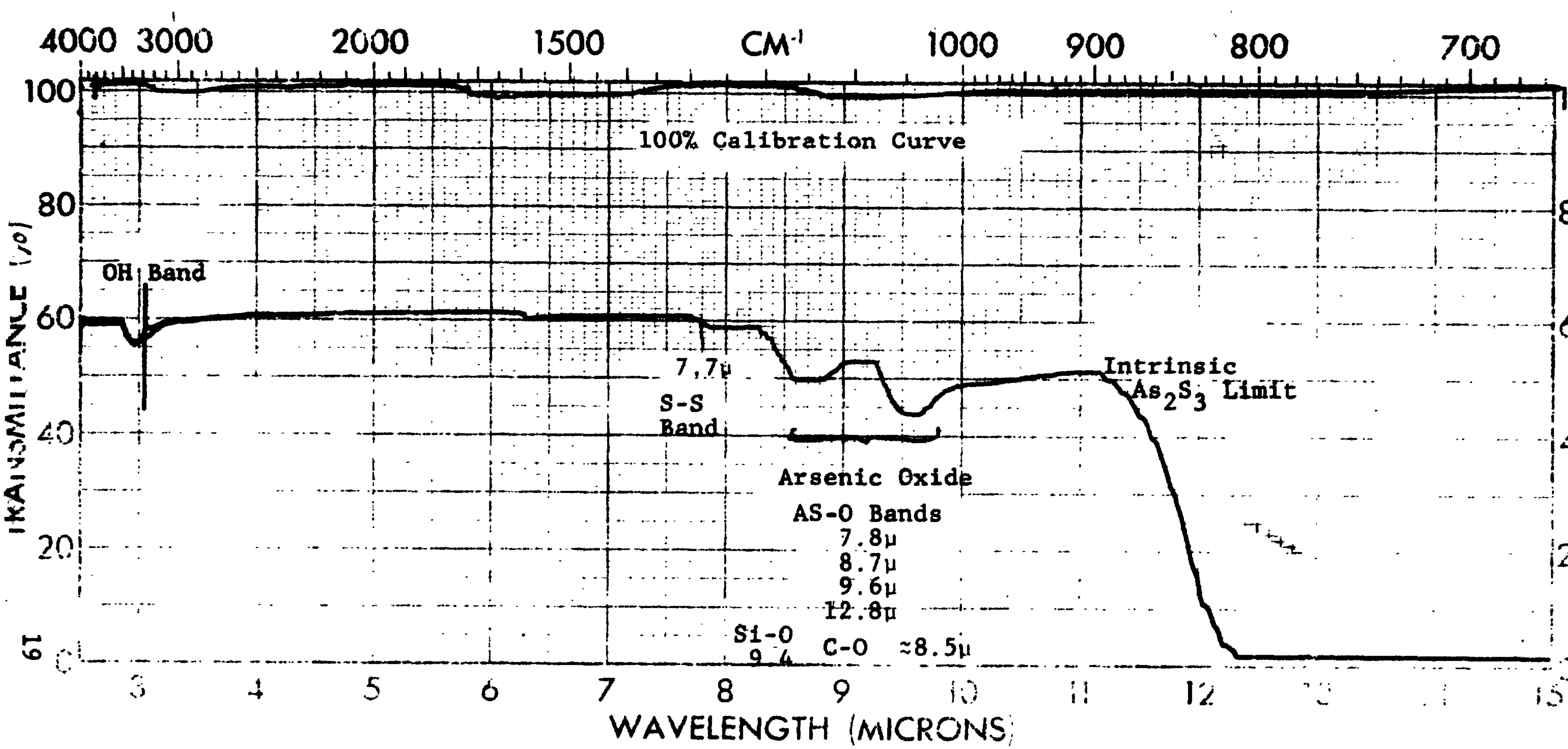
SPECTRUM NO.
SAMPLE

Figure 5 Infrared Transmittance of As_2S_3 Processed from a Cold-Pressed Pellet wavelength. Figure 6 illustrates the ir-transmittance of a commercially available As_2S_3 produced by the rocking ampoule method. The similarity of the transmission characteristics of these two samples leads to the conclusion that the concept of producing chalcogenides from cold pressed precursor pellets is valid.

5.1.3 Possible Use of Sounding Rocket Flights

Having gained some knowledge regarding the mechanism of reaction of chalcogenide precursors, attention was turned to the constraints of space manufacture and particularly the constraints of NASA's Space Processing Program. Successful reaction of mixed As + S powders via a solid-liquid reaction in a sealed container requires relatively long heating times. This is due mainly to melting point differences and vapor pressure considerations for the constituent elements. Ideally, however, materials systems that required heating times in minutes rather than hours are desirable. With such a system, many preliminary space processing experiments could be performed in sounding rockets.

Although not part of the original scope of work, a preparation technique was conceptualized for As_2S_3 that might reduce the in-space processing times considerably. This preparation technique involves hot pressing the precursor powders. The reasoning proceeds as follows. In a sealed container where arsenic and sulfur powders are reacted, the melting point disparity (120^oC for sulfur, $>600^oC$ for arsenic) dictates that heating is done slowly so that the solid arsenic can react with the liquid sulfur. Sulfur is kept in the liquid state by its own vapor pressure above the melt. Too rapid heating will cause the pressure above the melt to rise to a level sufficient to fracture the SiO_2 container before the arsenic is fully reacted. The general idea of the hot pressing concept is to provide the pressure necessary to keep the sulfur molten while still in the low temperature, highly viscous sample preparation stage (i.e., on earth). This will produce a



SPECTRUM NO. 1

SAMPLE As_2S_3

Commercial Material

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND

1.

2.

DATE 9/10/74

OPERATOR

In sulfur rich glass the S-S bands are located at 7.7μ, 10.15μ and 11.9μ.

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

Figure 6 Infrared Transmittance of Commercial As_2S_3 Glass.

PART NO 137-1261

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

partially reacted sample that will withstand the forces of liftoff better than a cold pressed pellet. The final high temperature reaction to form As_2S_3 will be accomplished in a relatively short time in space (hopefully minutes instead of hours), and thus be amenable to preliminary sounding rocket experiments.

The initial hot pressing experiments were aimed at determining the feasibility of the hot pressing concept, and to get a rough idea of the temperature, pressure, and time boundaries for this concept to be successful. The feasibility of partially reacting arsenic and sulfur powders by hot pressing was investigated using the apparatus illustrated schematically in Figure 7. The precursor powders were contained within the mold/plunger system. This system was heated with a wire-wound heater, and inserted into a standard Instron testing machine. The upper plunger was connected to the upper (movable) Instron crosshead. The force necessary to deform the plunger was monitored with a strain gage type load cell.

Several initial hot pressing experiments were conducted. The variables studied were temperature, pressure, and time. Temperatures ranged from 100° to 400°C. Pressures ranged from 500 to 2000 psi. Hot pressing times ranged from 15 to 30 min. It was found that for temperatures less than 200°C for pressures ranging from 500 to 2000 psi, the hot pressed product appeared visually as relatively unreacted powders, similar to the visual appearance of a cold pressed As + S pellet. For processing temperatures between 250° and 400°C, at any pressure from 500 to 2000 psi, much material was extruded at the upper plunger-mold wall interface. The extrusion appeared high in sulfur and presumably was due to the rapid volatilization of the sulfur precursor.

However, at a temperature of 200°C with an applied pressure of 2000 psi minimum extrusion occurred. A section of the mold-plunger-sample system is shown in Figure 8. Upon removing and polishing, the hot pressed sample appeared distinctly metallic,

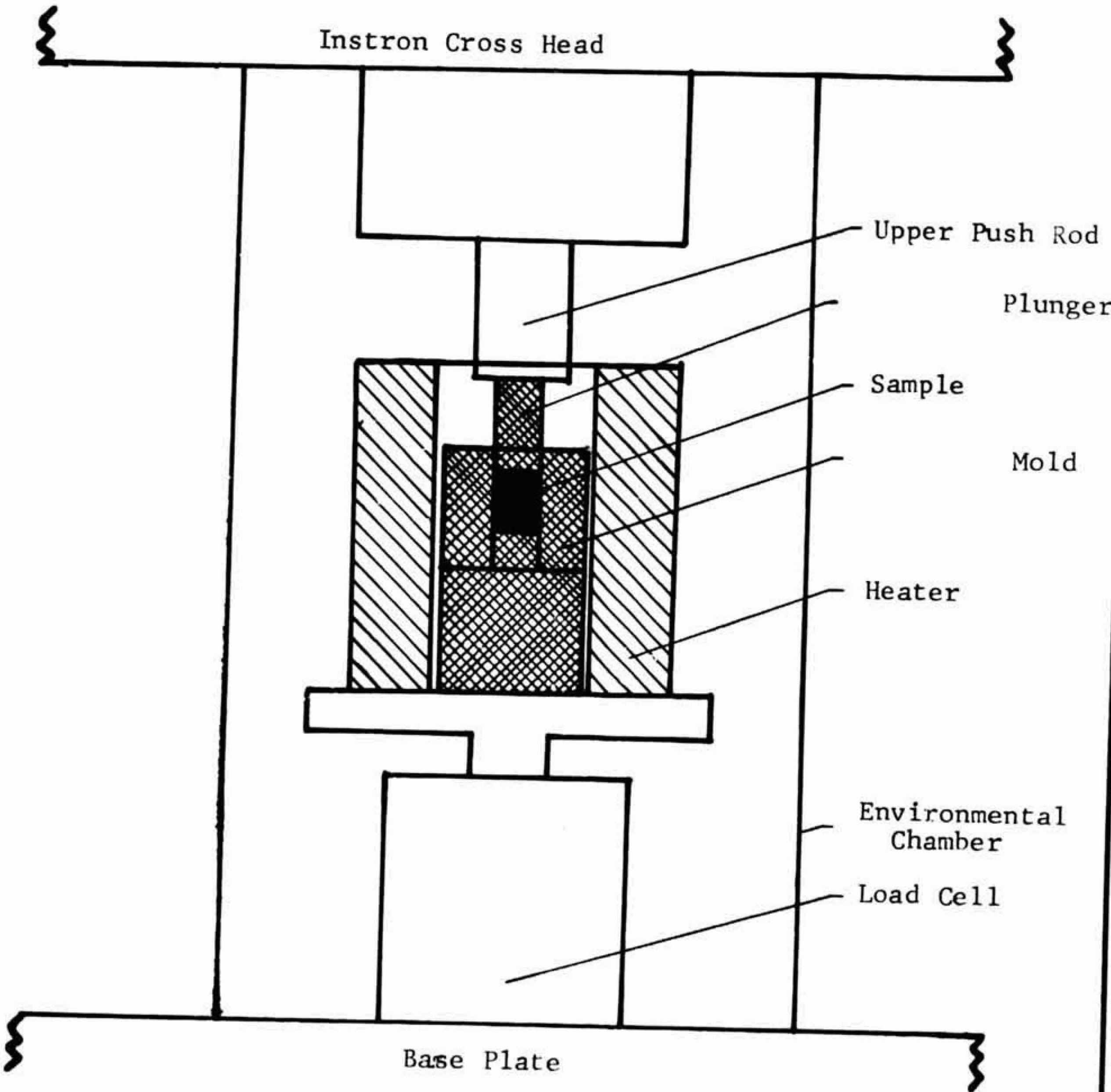


Figure 7. SCHEMATIC OF CHALCOGENIDE GLASS PRECURSOR PROCESSING EQUIPMENT

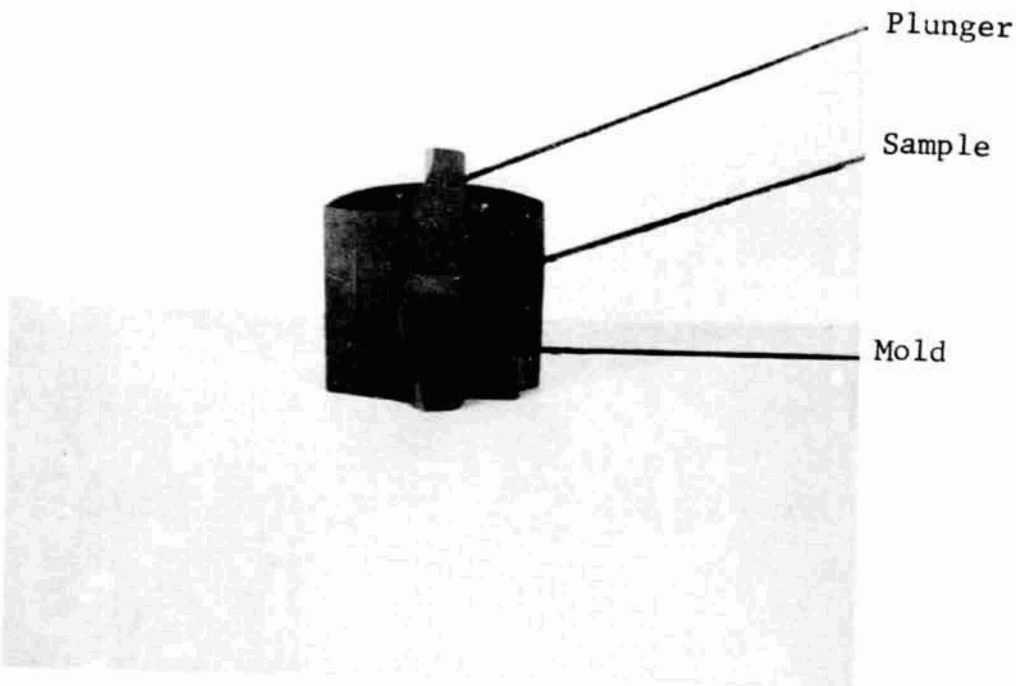


Figure 8 Sectioned View of Hot Pressed Arsenic And Sulphur Precursors

a rough qualitative indication that significant As + S reaction had occurred.

This sample was submitted for CPAA analysis. The first result of this analysis was that the arsenic to sulfur ratio for this hot pressed material was similar to that of a commercially available As_2S_3 glass analyzed by CPAA. The second result of the CPAA analysis on the hot pressed As + S sample was that significant carbon contamination was present at a depth of a few microns. This contamination is presumably related to diffusion from the graphite mold employed. To eliminate this problem subsequent hot pressing experiments were conducted in a stainless steel system.

At this point, an additional variable, time, was added to the As + S hot pressing experiments. Following the 200°C, 2000 psi schedule that gave promising results in the initial experiments, additional batches were hot pressed for times up to a few hours. No apparent differences in these samples processed for varying times were visually observed.

In order to more quantitatively assess the quality of the hot pressed samples that visually appeared to have undergone a significant $2As + 3S \rightarrow As_2S_3$ reaction, X-ray diffraction analyses were conducted to indicate the amount of crystallinity present. The precursor arsenic powder is crystalline. Thus a comparison of X-ray analyses of a mixed As + S powder batch prior to hot pressing with a hot pressed pellet should provide a qualitative indication of the degree of chemical reaction obtained by hot pressing After chemical reaction the arsenic should be relatively amorphous. Thus, a significant drop in crystallinity should be observed in the hot pressed samples. This evaluation technique can be made semi-quantitative, in a comparative sense. For instance, changes in the hot pressing schedule can be quantified by assignment of a number corresponding to, say, the area under the arsenic peak or the height of the arsenic peak in a diffraction pattern.

This analysis was applied to the "best" preliminary hot pressed sample (200^{o}C, 2000 psi) with results shown in Table II. This semi-quantitative result indicates that although the initial hot pressed samples appeared significantly glassy, there remained a substantial amount of unreacted (crystalline) arsenic. This result indicates that the time-temperature-pressure hot pressing schedule must be altered in a manner to promote more complete reaction.

Further hot pressing experiments were conducted at higher temperatures and pressures to promote more complete reaction. These experiments invariably lead to much extrusion of the low melting sulfur at the upper plunger-mold wall interface. To circumvent this problem, other time-temperature-pressure schedules were investigated. For instance, for hot pressing similar materials with widely different melting points, La Course(1) has found it convenient to use the following schedule: 1) slowly raise the temperature to slightly above the lowest M.P. in the system (120^{o}C for sulfur in our case) with no applied pressure, 2) slowly raise the temperature to the desired pressing temperature, and 3) apply the desired pressure. Presumably, this schedule permits the formation of a relatively thick colloidal solution that will not extrude easily before the arsenic is completely reacted. Additionally, this schedule provides for better pressure control as the sulfur volume rapidly increases during the ring-to-chain structure transformation.

Through these experiments, it has been demonstrated that the concept of hot pressing the precursor powders to reduce the time necessary for higher temperature processing appears feasible. However, much work will be required before a sounding rocket flight. It is our belief, however, that this work should be de-emphasized in the future. The most promising route to improve chalcogenide glasses will be through the utilization of future manned orbital flights that do not have the constraint of only 6 - 7 minutes of weightlessness that exists in a Sounding Rocket flight. Sounding

TABLE II

X-RAY ANALYSIS OF VIRGIN AND HOT PRESSED As+S BATCHES

Sample	Number Indicating Relative Height of Arsenic Peak
1. Virgin As+S Precursor Powder Batch	79
2. "Best" Preliminary Hot Pressed Sample	71

Rocket experimentation will provide valuable engineering-type information, but it is highly doubtful that an improved chalcogenide will be produced in any such flight. It is IITRI's belief that the 6 - 7 minute time constraint of a Sounding Rocket flight is much too stringent to permit the production of improved chalcogenides. More time is needed due to the melting point differences of the constituent elements. This problem will be partially eliminated by hot pressing the precursors, but at the sacrifice of increased contamination.

5.2 $Ge_{28}Sb_{12}Se_{60}$ Experiments

The following sections discuss the $Ge_{28}Sb_{12}Se_{60}$ glass experiments involving: 1) processing parameters, 2) precursor treatment, 3) high purity glasses, 4) use of gettering agents, and 5) processing in inert atmosphere.

5.2.1 Processing Parameters of $Ge_{28}Sb_{12}Se_{60}$ Glass

Studies were conducted to establish the processing parameters of $Ge_{28}Sb_{12}Se_{60}$ glass. In these experiments the glasses were compounded using reagent grade materials having a purity of 99.5%. The reason for using low purity materials initially was to economically study processing parameters such as reaction temperature and time, ampoule size, and quantity of the reactants. Thus, in the initial experiments high infrared transmission of the glass was not required.

Time and temperature schedules were selected from the published data on TI 1173 glasses (References 2 and 3). The literature information does not specify a particular compounding temperature, rather a very broad range of temperature. Hence, experiments were conducted at selected temperatures within the range of 800-925^{o}C.

The batch compositions were formulated in a glove box filled with a pure and dry argon gas, and the batch materials were transferred to a quartz ampoule. The ampoule was evacuated (4.5 x 10^{-4} Torr) for 16 hours and then sealed with an oxy-hydrogen torch.

The glass inside the sealed ampoule was melted in a rocking furnace. The furnace was rocked for various lengths of time at 800-925°C and the glass was then air quenched. The ampoule containing the glass was then annealed for twelve hours at 300°C.

These experiments indicated that glasses could not be compounded at temperatures below 800°C even when soaked for 16 hours. It was also observed that the compounding of $Ge_{28}Sb_{12}Se_{60}$ glass at higher temperatures (900-925°C) resulted in a surface reaction with the quartz ampoule as evidenced by adherances of the annealed glass to the quartz ampoule wall. It was thus established that the glass should be compounded within a temperature range of 800-900°C, preferably near the lower end of this region.

Following these preliminary processing studies, experiments were also conducted to establish the relationship between the quartz ampoule size and the quantity of the batch material. In earlier experiments with As_2S_3 glasses, it was observed that during glass melting the ampoule would explode due to high pressure buildup from gaseous arsenic and sulfur components, while using a 20 gram batch in a 37 cc ampoule. The initial experiments with $Ge_{28}Sb_{12}Se_{60}$ has established that the ideal batch size for a ~ 37 cc ampoule is 15 grams.

Following these experiments, various additional compositions corresponding to $Ge_{28}Sb_{12}Se_{60}$ glass were formulated. The glasses were made from reagent grade materials using the previously described procedure. Annealed glasses were ground and polished and their infrared transmission was measured to determine the effect of impure batch constituents. Composition No. 28 had a very porous structure probably due to insufficient mixing during the rocking operation. The other two glasses (29 and 30) possessed the lustrous dark appearance of TI 1173. Transmission characteristics of these polished glasses were measured on a Perkin Elmer

Infrared spectrophotometer and the transmission curves are presented in Figures 9 and 10.

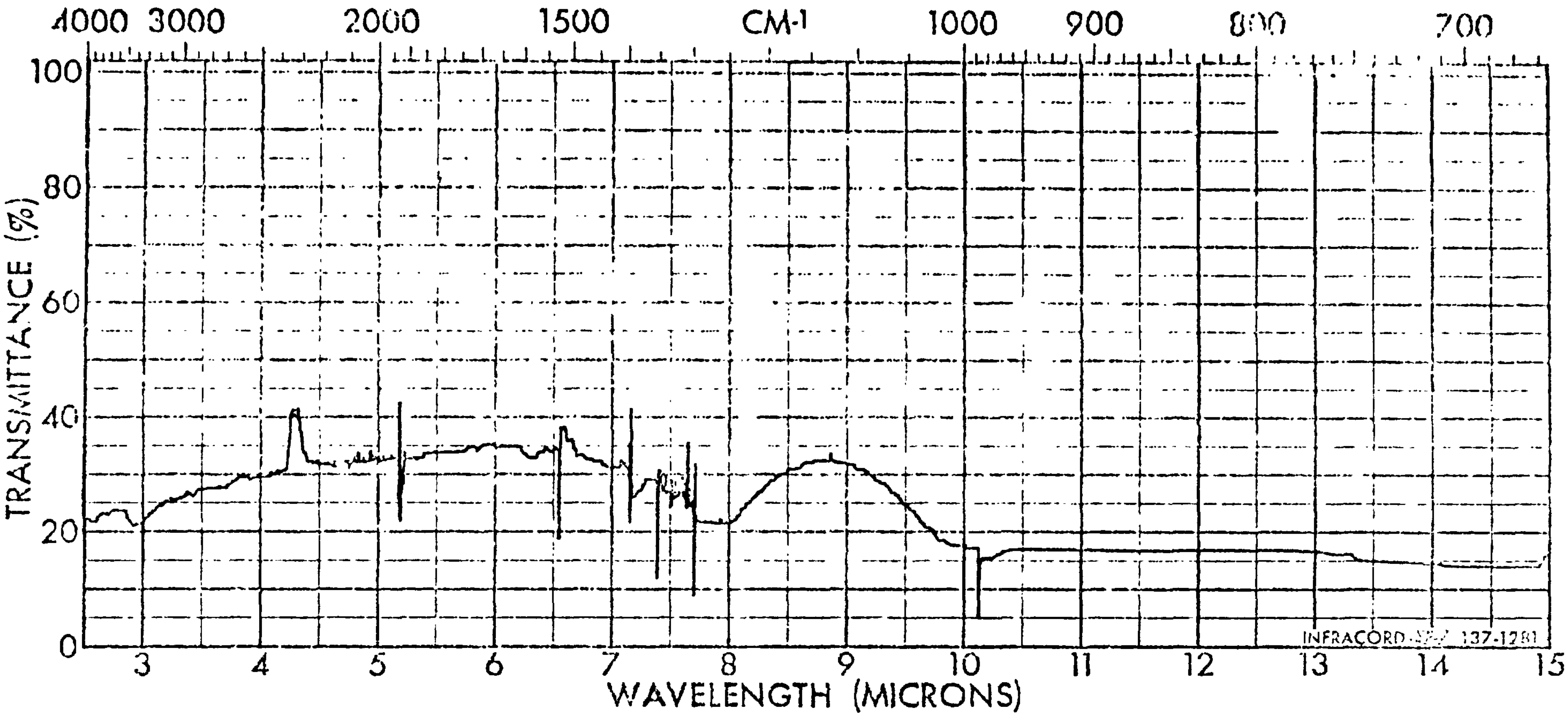
When studying these transmission curves, it should be remembered that these glasses were prepared using reagent grade materials. The erratic pattern in Figure 9 is due to noise background from the instrument. The noise was dampened while running the pattern for Glass No. 30 and Figure 10 presents a clear pattern. The transmission hump around 8-10 microns is not observed in TI-1173, and is probably characteristic of the impurities in the reagent grade materials.

The experiments described above served to establish the basic processing parameters of $Ge_{28}Sb_{12}Se_{60}$ glass using precursor materials of reagent grade purity. The work described in the following sections deals with the use of high purity precursors.

5.2.2 Precursor Treatment Experiments

It is common practice to treat precursor materials to remove surface oxygen. Texas Instruments passes hot hydrogen gas over the as-received precursor powders. The treatment described in this section involves a vacuum distillation technique.

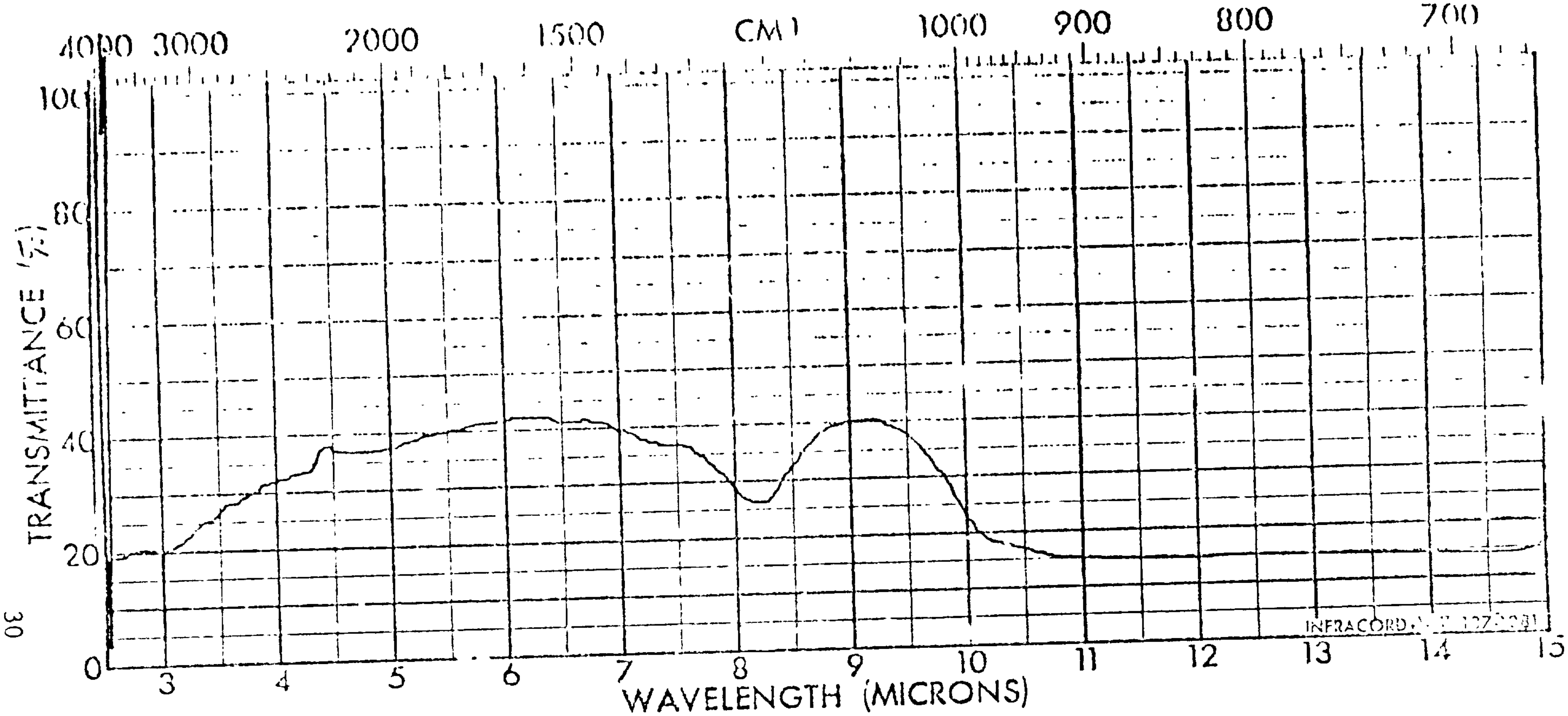
Ultra high purity powdered materials (Ge, Se and Sb all of purity 99.999%) were procured. Table III presents suppliers' analyses of the high purity materials. The surface impurities, primarily surface absorbed oxygen, were removed by vacuum distillation. In this technique the materials were sealed separately in an evacuated ampoule. The ampoule was then transferred into a vertical tube furnace, and the lower (metal containing) end of the tube was heated. The absorbed oxygen was driven off and collected at the cold upper end of the ampoule. The ampoule was held overnight at the treatment temperature, which was much lower than the melting point of the particular material being treated. For germanium the treatment temperature is 450°C, for antimony 400°C, and for selenium it is 150°C.



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE 29, 10 gram		1.	Erratic lines on the
$Ge_{28}Sb_{12}Se_{60}$	PURITY Low Reagent Grade, 99.5%	2.	pattern are due to
	PHASE	DATE 3/19	instrument noise.
	THICKNESS 2 mm	OPERATOR	

SAMPLE

Figure 9 Infrared Transmission



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE 30		1.	
$Ge_{28}Sb_{12}Se_{60}$	PURITY Reagent Grade, 99.5%	2.	
	PHASE	DATE 3/19/75	
	THICKNESS 2 mm	OPERATOR Akb-an	

SPECTRUM NO
SAMPLE

Figure 10 Infrared Transmission

Table III Suppliers' Analyses of the High Purity Materials

Material	Percent Purity	Form	Supplier
Germanium	99.999	Powder	Atomergic
Germanium	99.999	Bar	Eagle-Picher Industries, Inc. Quapaw, Oklahoma
Selenium	99.999	Powder	Atomergic
Selenium	99.99	Pellet	Kawecki-Berylco Industries New York, New York
Antimony	99.999	Powder	Atomergic
Antimony	99.999	Bar	Cominco American, Inc. Spokane, Washington

The vacuum distilled materials were transferred into a dry argon-filled glove box, and a stoichiometric batch composition corresponding to $Ge_{28}Sb_{12}Se_{60}$ was formulated. The weighed batch composition was then put into a clean and dry quartz ampoule. The ampoule was evacuated to remove possible oxygen contamination by placing it under vacuum (4.5 x 10^{-6} Torr) for 16 hours, after which it was sealed with a torch.

The batch inside the sealed ampoule was compounded by melting in a rocking furnace for 15 hours at 820°C, followed by air quenching. The quenched glass was again remelted in an inert atmosphere of argon, and the glass was annealed from 275°C to room temperature in 10 hours.

Ten glasses compounded using the above procedure all exhibited the characteristic metallic lustre of the TI-1173 glass. They were ground and optically polished, and their optical transmission in the infrared region was measured.

None of these glasses showed any transmission in the infrared region of interest. Samples of the 'as-received' and vacuum distilled powder precursor materials were analyzed by the Center for Trace Characterization, Texas A & M University, College Station, Texas. Their analyses indicated that the concentration of oxygen in the 'as-received' high purity selenium powder was 275 $\pm$ 15 ppm, and that this was only reduced to 250 ppm after vacuum distillation.

Discussions with the Texas Instrument, Inc. technical group (Reference 4) indicated that although the high purity (99.999%) germanium, antimony, and selenium powders are free from metallic impurities, the purity level drops considerably when all the elements including oxygen are taken into account. The purity of the fabricated form of material such as powder, is considerably lowered due to the high surface area available for adsorption of O_2. The oxygen contamination would also be present in non-powdered forms such as bar or pellet; however, it would be several orders of magnitude lower due to smaller surface area of the bar or pellet. Therefore, it was recommended that the starting materials should be of high purity (99.999%) and in the form of bars or pellets.

Based on these analyses, it was decided to fabricate the $Ge_{28}Sb_{12}Se_{60}$ glass using commercially available high purity bars or pellets.

5.2.3 Processing and Evaluation of High Purity $Ge_{28}Sb_{12}Se_{60}$ Glasses

Infrared transmitting $Ge_{28}Sb_{12}Se_{60}$ glasses were processed using the high purity (99.999%) germanium, selenium and antimony precursors in the form of bars and pellets. Table III presents the pertinent details on these materials. Stoichiometric batch compositions corresponding to $Ge_{28}Sb_{12}Se_{60}$ were formulated. Table IV presents the composition and processing parameters investigated. An optimum stepwise procedure for processing the glass by conventional earth methods was also established. During the processing of the glass, several improvements were made in the vacuum system. The processed glasses were evaluated for their infrared transmitting characteristics.

5.2.3.1 Glass Processing Procedure

Based on our experiments and consultations with Texas Instruments, Inc. (Reference 4), a glass processing procedure for high purity bars and pellets was adapted. The following sequential procedure outlines the steps:

1. All glass batch preparation was performed in a glove box having a continuous flow of pure and dry argon gas.

2. Individual constituents (chunks or pellets of germanium, selenium and antimony) were accurately weighed and transferred to a clean and dry quartz ampoule purged with the argon gas.

3. The ampoule was heated to 105°C and simultaneously placed under vacuum for 16 - 24 hours; then sealed.

Table IV

COMPOSITION PROCESSING PARAMETERS AND CHARACTERISTICS OF IITRI'S $Ge_{28}Sb_{12}Se_{60}$ GLASSES

Run No.	Composition (Grams)				Surface O_2 Removal Temp. °C	Pressure Torr.	Reaction Temp. °C	Time at Reaction Temp Hours	Density of Glass Grms/cc	Transmission 2-8μ %	Transmission 8-14μ %	REMARKS
	Ge	Sb	Se.	% Dopant Al								
TI-1173	$Ge_{28}Sb_{12}Se_{60}$			--	--	--	--	--	4.71	60-63	63-58	Small Absorption Band Around .3μ.
41	3.75	2.7	8.55	--	200	18.0×10^{-3}	843	16	--	60-60	--	Absorption Bands at 2.9, 6.3, 8-0 and a Bell Shaped Band 11-14μ.
42	3.75	2.7	8.55	--	101	12.5×10^{-3}	845	16	5 06	51-52	52-50	Absoroption Band Between 12-14μ.
43	3.75	2.7	8 55	--	175	$8\ 3 \times 10^{-6}$	884	16	4.92	41-42	42-	Strong Bance @ 2 9,3,8 and a Bell Shaped Band 11-14μ.
44	3.75	2.7	8.55	--	105	5.0×10^{-5}	884	16	4.94	44-45	45-42	Bell Shaped Band Between 11 5-14μ.
45	3.75	2.7	8.55	0.33	105	$3\ 5 \times 10^{-5}$	867	16	4 79	28-34	34-18	
46	3.75	2 7	8.55	0.10	105	2.6×10^{-5}	884	16	4.69	60-63	63-52	No Absorption Bands.
47	3.75	2.7	8.55	0.05	105	1.6×10^{-5}	884	16	4 69	42-44	44-40	No Absorption Bands.
48	3.75	2.7	8.55	0.10	105	1.2×10^{-5}	884	41	4 62	41-41	41-40	No Absorption Bands.
49	3.75	2.7	8 55	0.10	105	1.0×10^{-5}	884	21	4 71	50-54	54-48	No Absorption Bands.
50	3.75	2.7	8.55	0.05	105	1.5×10^{-5}	834	21	4.61	46-48	48-42	No Absorption Bands.
51	3.75	2.7	8 55	0.10	105	8.3×10^{-4}	825	21	4.68	51-53	53-48	No Absorption Bands.
52	3.75	2.7	8.55	0.10	105	8.3×10^{-6}	800	66	4.70	60-63	63-52	No Absorption Bands.

4. The sealed ampoule was transferred into a rocking furnace. The temperature was gradually raised to about 600°C in four hours and held constant for 1-1/2 hours.

5. The temperature was raised to 700°C in one hour and held constant for another half an hour.

6. The temperature of the rocking furnace was raised to the final reaction temperature (800-900°C) in one hour and held constant for 16 to 24 hours.

7. The temperature of the rocking furnace was lowered to 600-700°C and held at that temperature for 1/2 to one hour.

8. The glass was quenched (inside the sealed ampoule) to room temperature.

9. The ampoule containing the glass was annealed at 275°C for 16 hours.

10. The annealed glass was removed and ground and polished using the standard optical glass polishing technique.

In the course of establishing this procedure, it was determined that the use of double cold-trapped oil diffusion vacuum system was superior to the use of a turbo-molecular system. Figure 11 presents the details of the oil diffusion system which provided vacuum as low as 10^{-6} Torr.

5.2.3.2 Infrared Transmission

All the processed high purity glasses were evaluated in terms of their infrared transmission characteristics. The infrared transmission of the ground and optically polished samples (5 mm thick) were measured in the 2-15 micron region using a Perkin Elmer Model 21 spectrophotometer.

It has been observed that this model spectrophotometer quite often develops background noise and other instrument related bands which interfere with the actual transmission characteristics of the sample. For this reason, before measuring the transmission of the glass sample, the spectrophotometer was run blank (without

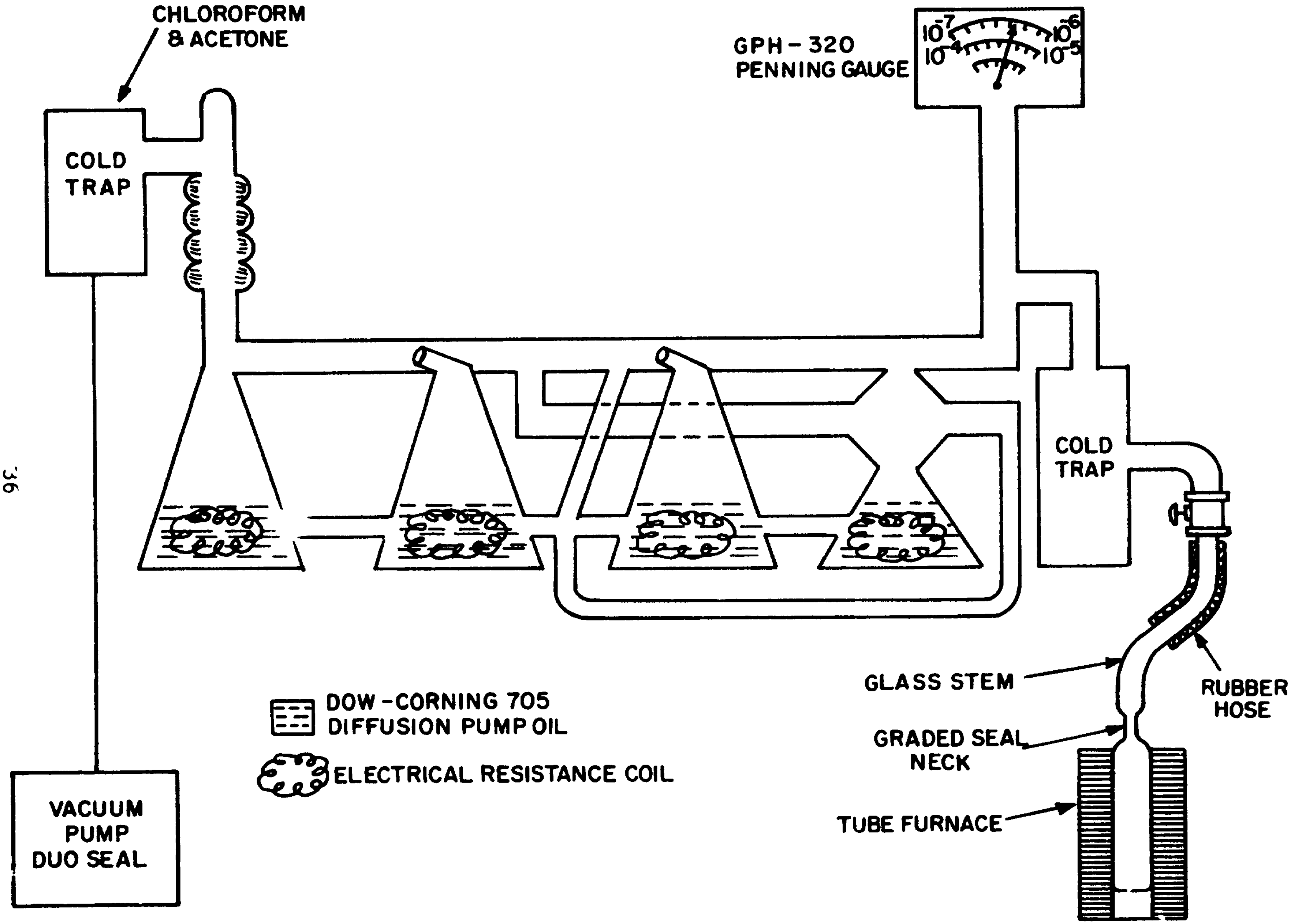


Figure 11 Diffusion Vacuum Pump System

the sample) so as to locate the background noise and other instrument related absorption or inverse absorption bands. It is a normal practice not to run the blank at 100% full-scale so that the magnitude of the inverse absorption bands can be established. Blank runs were made at 90% full-scale and the instrument related bands were observed at 4.25, 9.75, 12.5 and 15 micron regions. Before measuring the transmission characteristic of the glass sample, the scale was returned to 100% full-scale so as to measure the true transmission.

The internal inhomogeneities, possible impurities and optical defects in the glass were examined using an infrared microscope (Model D manufactured by Research Devices, Inc.). This added facility has greatly improved IITRI's capability to qualitatively identify the causes of poor ir-transmission in chalcogenide glass.

5.2.3.3 Evaluation of High Purity Glasses

Table IV presents details which include the composition and the processing parameters of the glasses to be discussed in this section. The processing parameters include 1) the surface-oxygen removal temperature, 2) the vacuum pressure, 3) the molten glass reaction temperature, 4) the molten glass reaction time, 5) the density of the processed glass, and 6) the optical transmission characteristics of the processed chalcogenide ($Ge_{28}Sb_{12}Se_{60}$) glass in the 2-8 micron and 8-14 micron regions. Complete optical transmission characteristics of these glasses are discussed below. Density and optical characteristics of Texas Instruments-manufactured TI-1173 glass determined at IITRI is presented in Figure 12.

Glass compositions No. 41 and 42 were fabricated using a vacuum of 12 -18 x 10^{-3} Torr, which proved to be not sufficient to drive out all the oxygen and oxygen-related impurities from the system. This resulted in absorption bands at 2.9, 6.3, 8.0 microns and a strong bell-shaped band between 11-14 micron regions (see

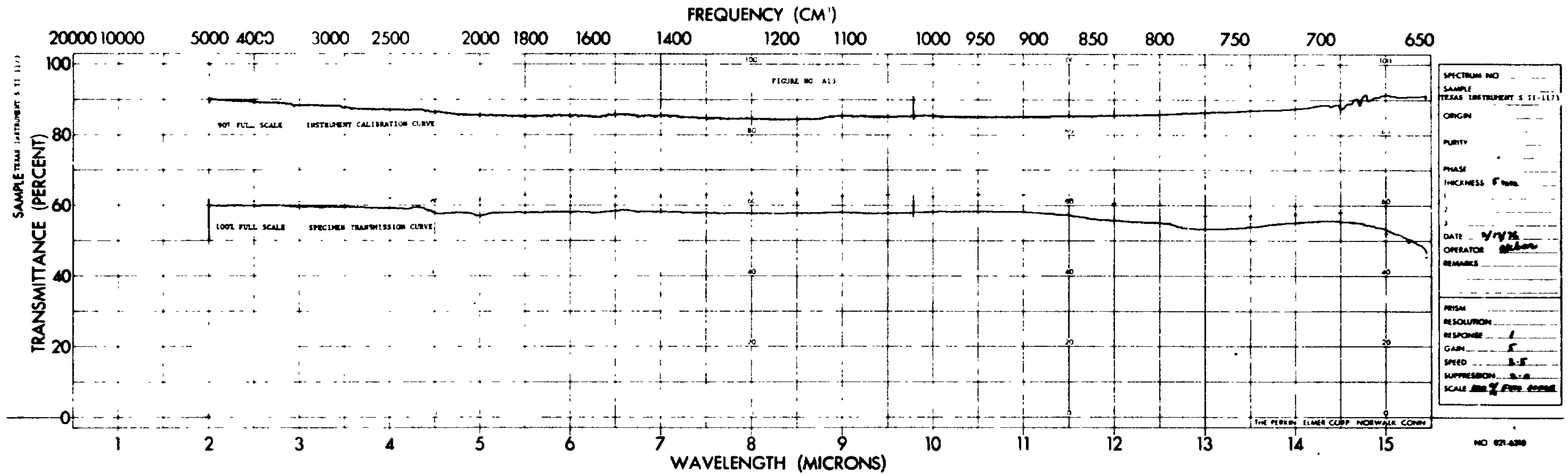


Figure 12 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$ (Texas Instruments TI-1173)

Figures 13 and 14). Figure 15 presents a photograph of glass taken by an infrared microscope. The dark spot in the picture shows an area of inhomogeneity which is directly related to the processing defects of the glass.

Glass composition Numbers 43 and 44 were fabricated using the diffusion pump vacuum system as shown in Figure 11. This improved vacuum system was intended to eliminate the oxygen-related absorption bands. However, the transmission characteristics of these glasses in Figures 16 and 17 again exhibited strong absorption bands. This phenomenon was discussed in detail with Texas Instrument, Inc. staff (Reference 4). It was emphasized that the vacuum system alone would not be sufficient to eliminate all the oxygen and related impurities, and that it is necessary to add pure aluminum which acts as a getter for oxygen. The optimum quantity of aluminum additive should be determined by actual experimentation. Composition No. 45 included 0.05 grams of aluminum which corresponds to 0.33% of the total batch constituents (15 grams). The glass was reacted for 16 hours at 867°C. The resulting poor transmission indicated the possibility that the quantity of aluminum added (0.05 grams) as a dopant was too high (Figure 18). In composition No. 46 and 47, reduced quantities of aluminum were added. These (reduced quantities) were 0.015 grams and 0.008 grams corresponding to 0.1% and 0.05% respectively. These glasses were reacted for 16 hours at 884°C. Figure 19 and 20 present the infrared transmission of these glasses. Composition 46 had an excellent transmission of 60% whereas composition 47 had a relatively low transmission of 42%. These experiments showed that the beneficial effects of aluminum addition in removing -OH related absorption bands is not simply a linear function of the amount added.

These results indicate the need to establish further the optimum quantity of aluminum dopant necessary to improve optical characteristics. Four glasses (Nos. 53-57 shown in Table V) having the stoichiometric composition of $Ge_{28}Sb_{12}Se_{60}$ and containing

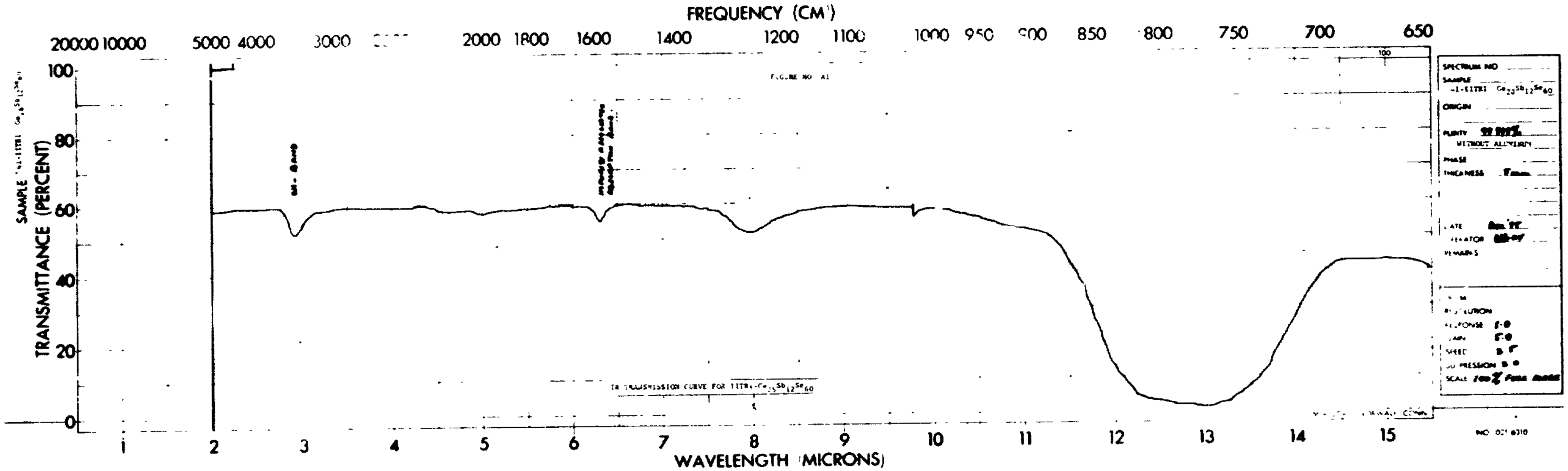


Figure 13 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 41

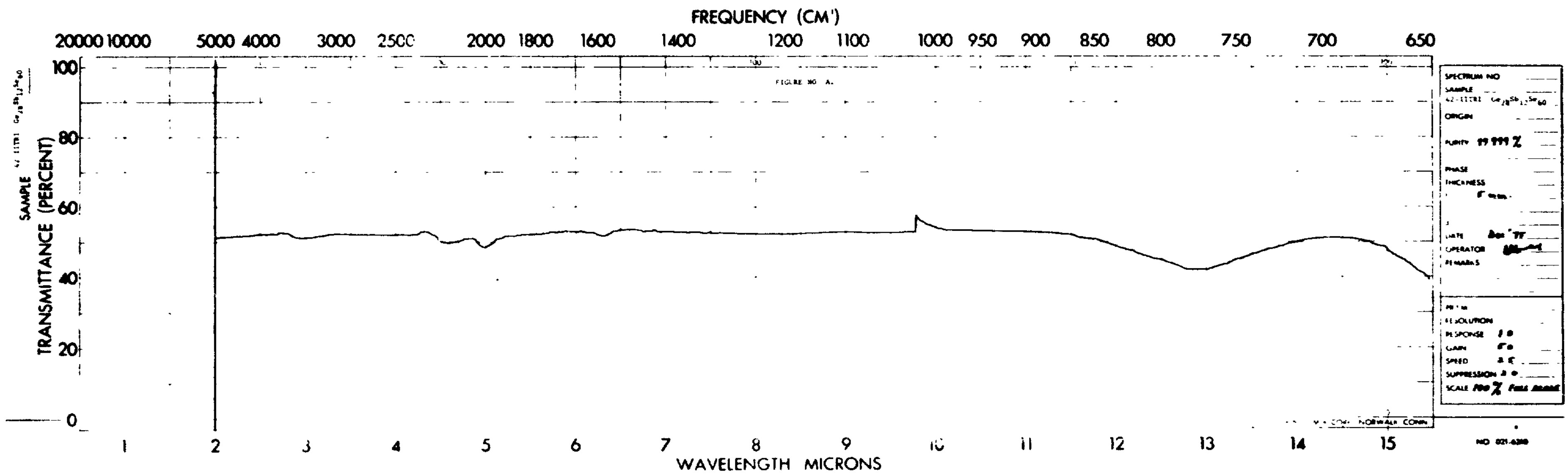


Figure 14 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 42

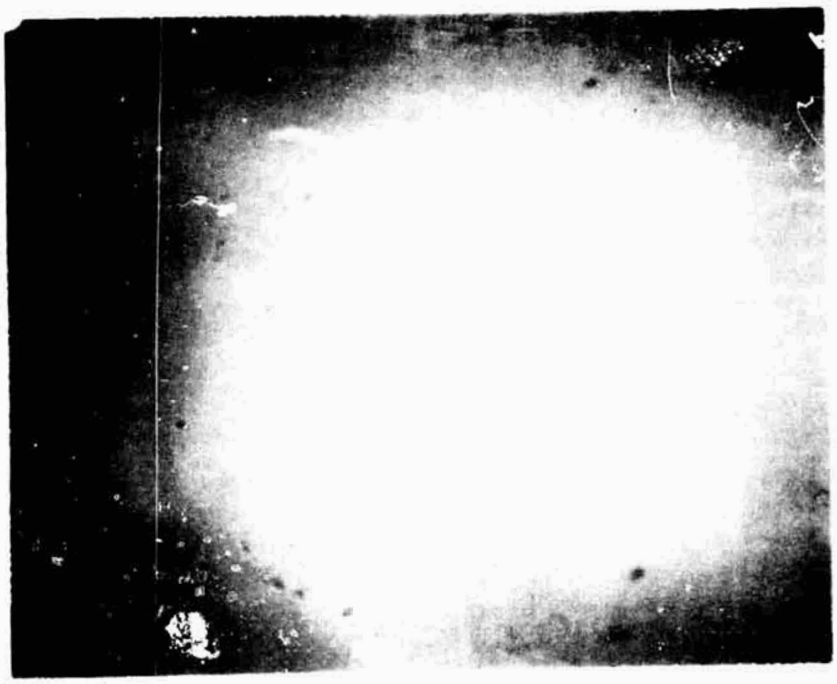


Figure 15 Infrared Microscope Picture of IITRI $Ge_{28}Sb_{12}Se_{60}$ Glass

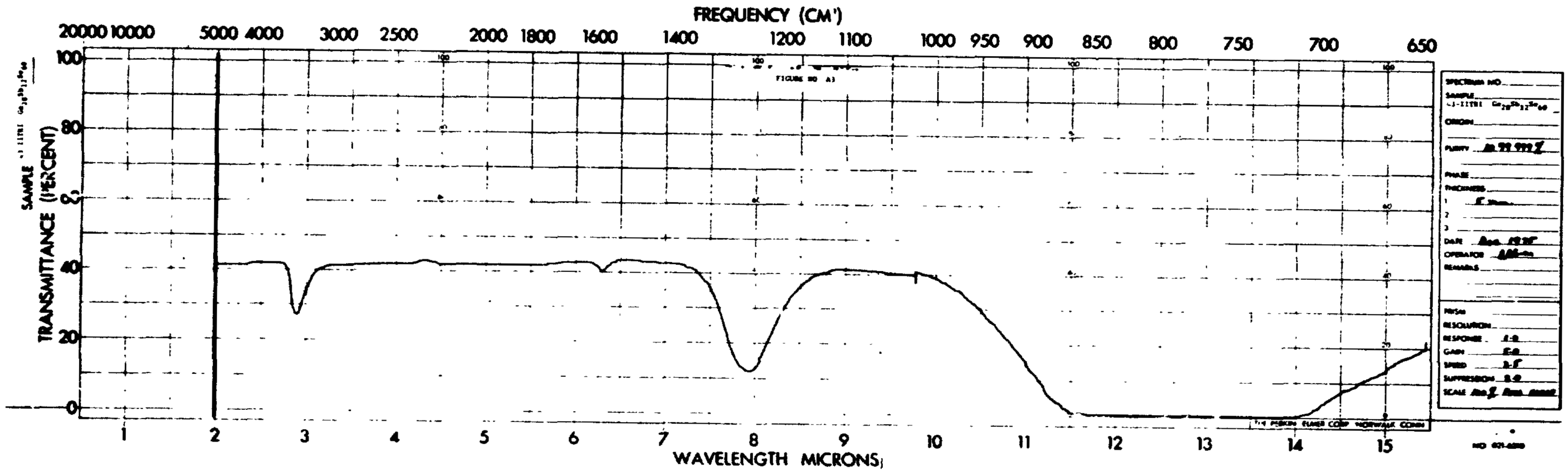


Figure 16 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 43

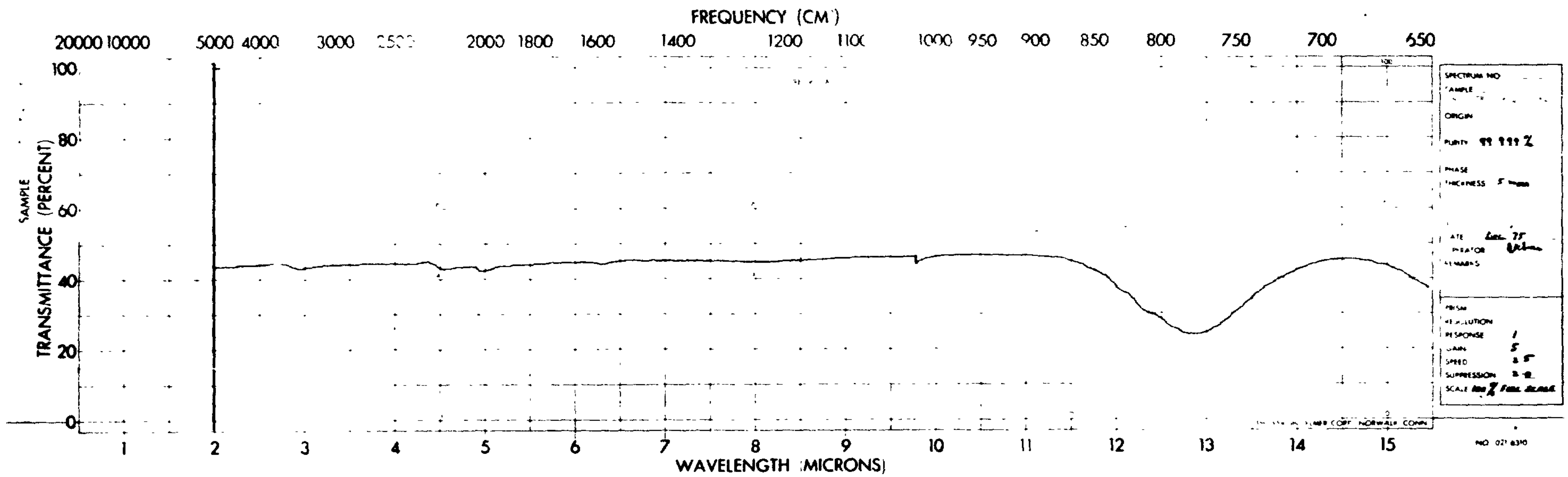


Figure 17 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 44

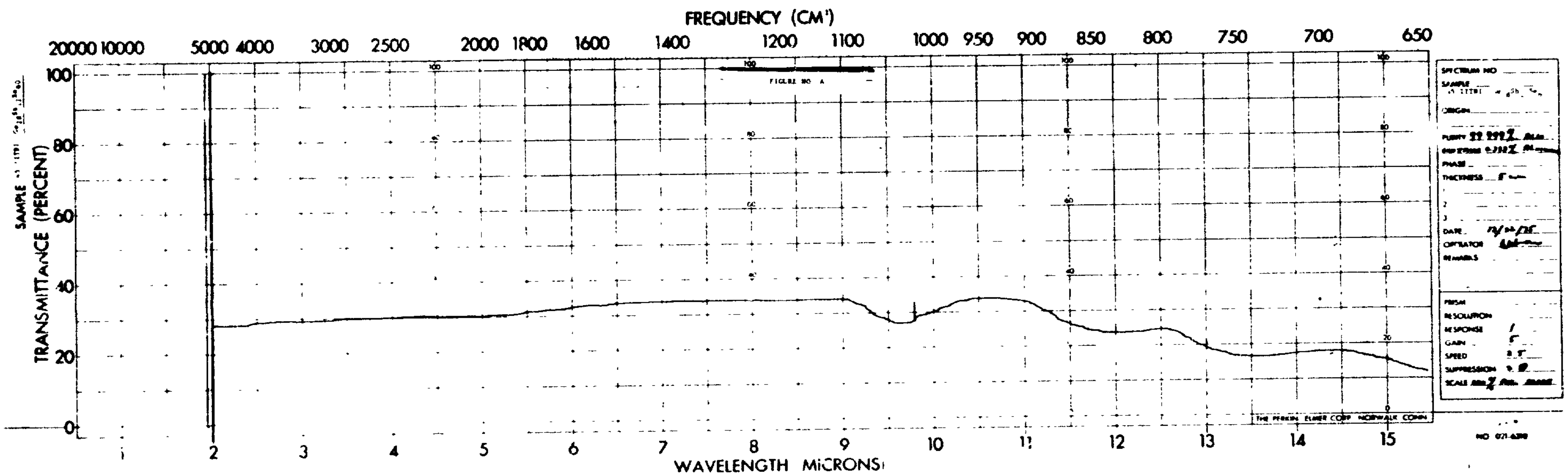


Figure 18 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 45

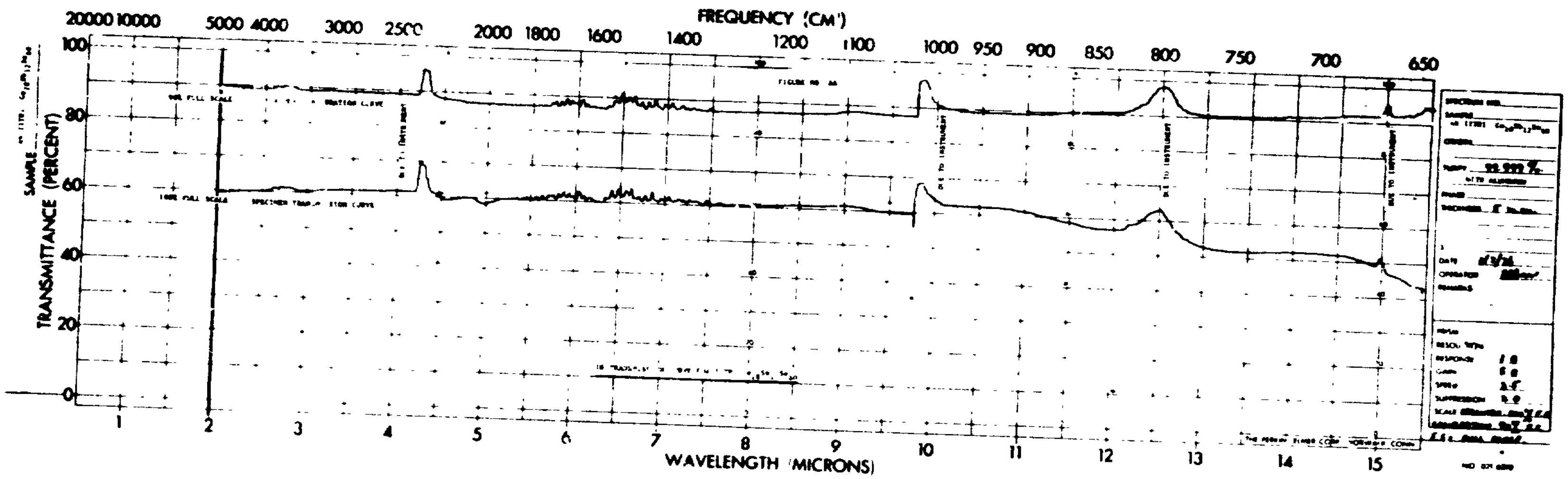


Figure 19 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$ Sample No. 46

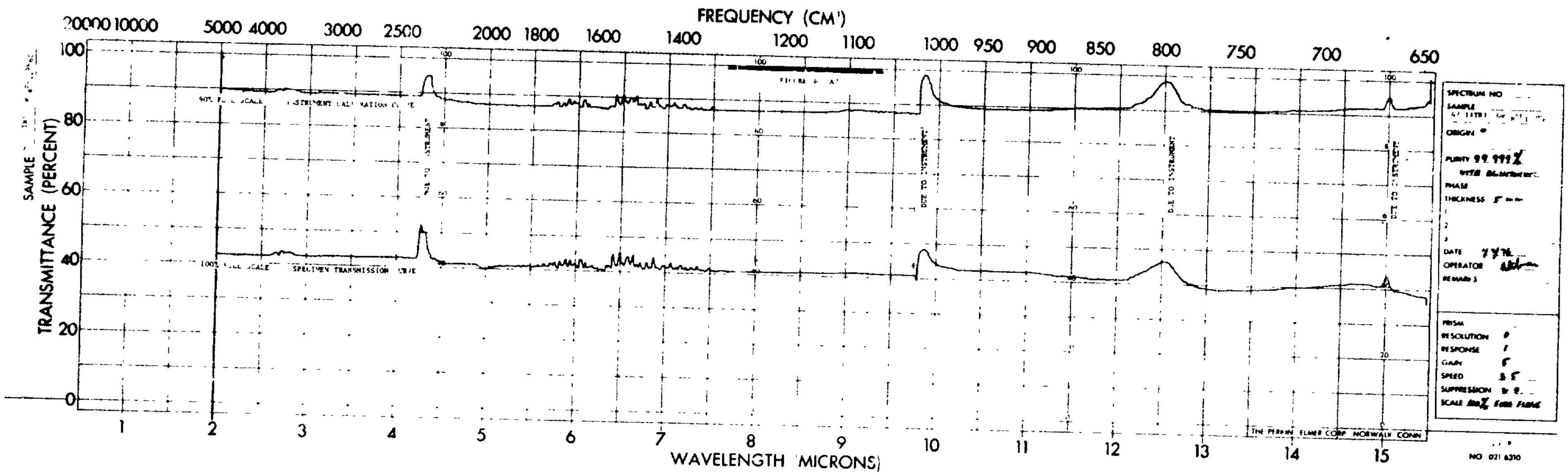


Figure 20 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 47

Table V

COMPOSITION PROCESSING PARAMETERS AND CHARACTERISTICS OF IITRI'S $Ge_{28}Sb_{12}Se_{60}$ GLASSES

Run Number	Composition (Grams) Ge	Sb	Se	Dopant Al	Surface I_2 Removal Temp. °C	Pressure Torr.	Reaction Temp. °C	Time at Reaction Temp. Hours	Density of Glass Grms/cc	Transmission 2-8μ Percent	Transmission 8-14μ Percent	REMARKS
TI-1173	$Ge_{28}Sb_{12}Se_{60}$				--	--	--	--	4.71	60-63	63-58	Small Absorption Band Around 13μ.
53	3.75	2.70	8.55	--	105	7.4×10^{-6}	825	19	4.67	61-64	64-48	Large Bell-shaped Absorption Band Around 12.8μ.
54	3.75	2.70	8.55	0.0038	105	6.8×10^{-6}	825	24	4.65	50-55	55-48	No Absorption Bands.
55	3.75	2.70	8.55	0.0006	105	1.0×10^{-5}	825	23	4.70	54-59	59-53	No Absorption Bands.
56	3.75	2.70	8.55	0.0158	105	3.3×10^{-6}	830	23	4.69	56-63	63-55	No Absorption Bands.
57	3.75	2.70	8.55	0.0008	105	2.9×10^{-6}	830	23	4.68	57-63	63-55	No Absorption Bands.
58	3.75	2.70	8.55	--	105	5.0×10^{-5}	825	24	4.66	--	--	Strong Absorption. Powdered (-325M) Batch Material could not be Processed.
59	3.75	2.70	8.55	0.0008	105	5.0×10^{-5}	825	70	4.72	--	--	Sample Damaged. Powdered (-325M) Batch.
60	3.75	2.70	8.55	--	--	5.0×10^{-5}	837	24	4.59	65-65	65-46	Excellent Transmission Curve Except for Bell-Shaped Absorption Band Around 12.8μ due to the Absence of Aluminum.

varying quantities of aluminum dopant were prepared. The aluminum content ranged from 0.0006 grams to 0.158 grams in a 15 gram batch. The quantity of the dopant (0.0158 grams) necessary to eliminate the 12.8μ absorption band was established as described above. A batch composition containing no aluminum was also prepared and was used for reference purposes (Run No. 53). Weighed quantities of the high purity batch ingredients were transferred into a quartz ampoule. The ampoule was placed under vacuum to remove oxygen contaminants. It was then sealed and processed in a rocking furnace for about 20 hours at 825°C. The glasses were quenched, annealed, ground and polished and their infrared transmission characteristics determined.

Among these glasses, composition No. 53 (without aluminum) has good transmission ranging from 61% - 64% between 2-8μ region and 64% - 48% between 8-14μ region (5 mm thick), shown in Figure 21. However, the absence of aluminum causes a strong bell-shaped absorption band around 12.8μ. This has been attributed to the formation of Se_8 rings (as discussed by Lucovsky[5]), originating in the selenium metal.

Among the glasses containing aluminum dopants, those containing the minimum quantity (No. 55, Figure 23) do not have as good a transmission as the one having the maximum quantity (No. 56, Figure 24). In between these extremes, composition No. 57 (Figure 25) containing 0.0008 grams resulted in a glass having a transmission ranging from 57-63% between 2-8μ and 63-55% between 8-14μ. The improved transmission can be attributed to the optimum quantity (0.0008 grams) of aluminum that was incorporated as dopant. In the 8-14μ region, this glass compares well with the TI-1173 ir-characteristic shown in Figure 12.

5.2.3.4 <u>Effect of Reaction Time</u>

A series of experiments were conducted to establish the effect of reaction time on the optical transmission characteristics of the glass. Run No. 48 (refer to Table IV) was processed by

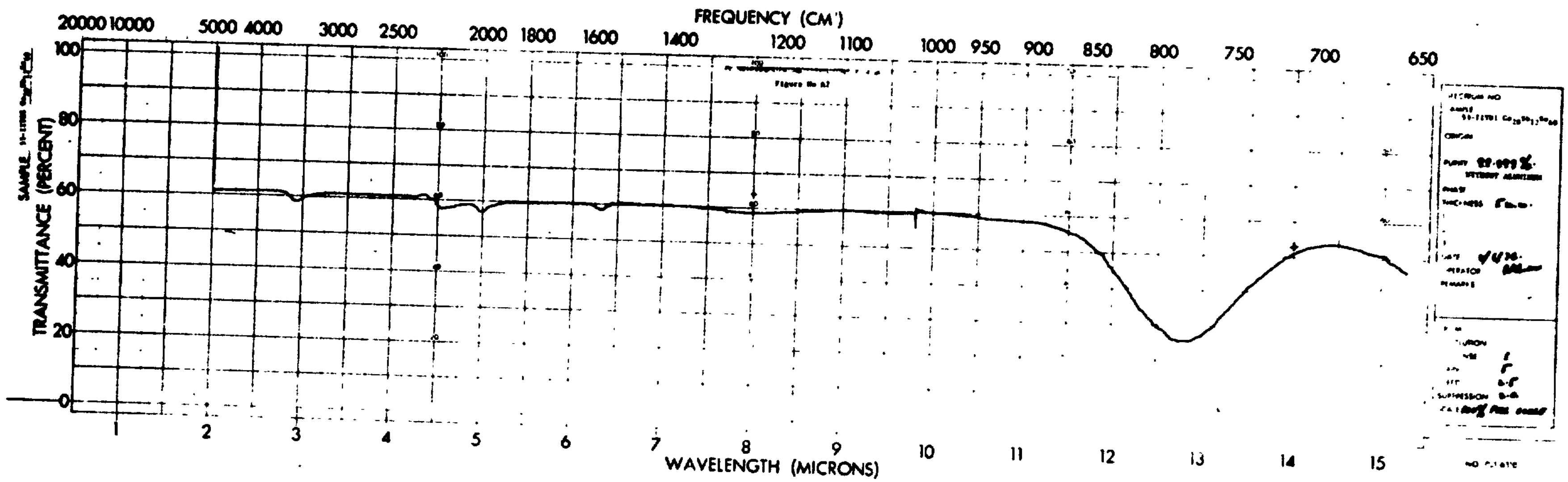


Figure 21 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 53

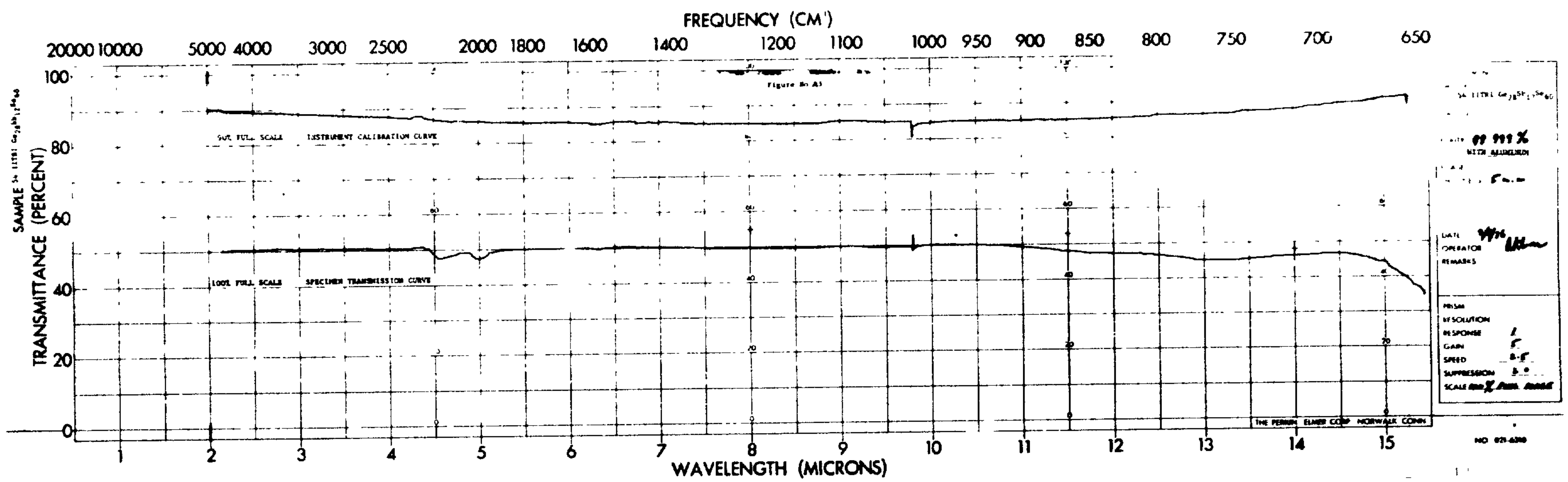


Figure 22 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 54

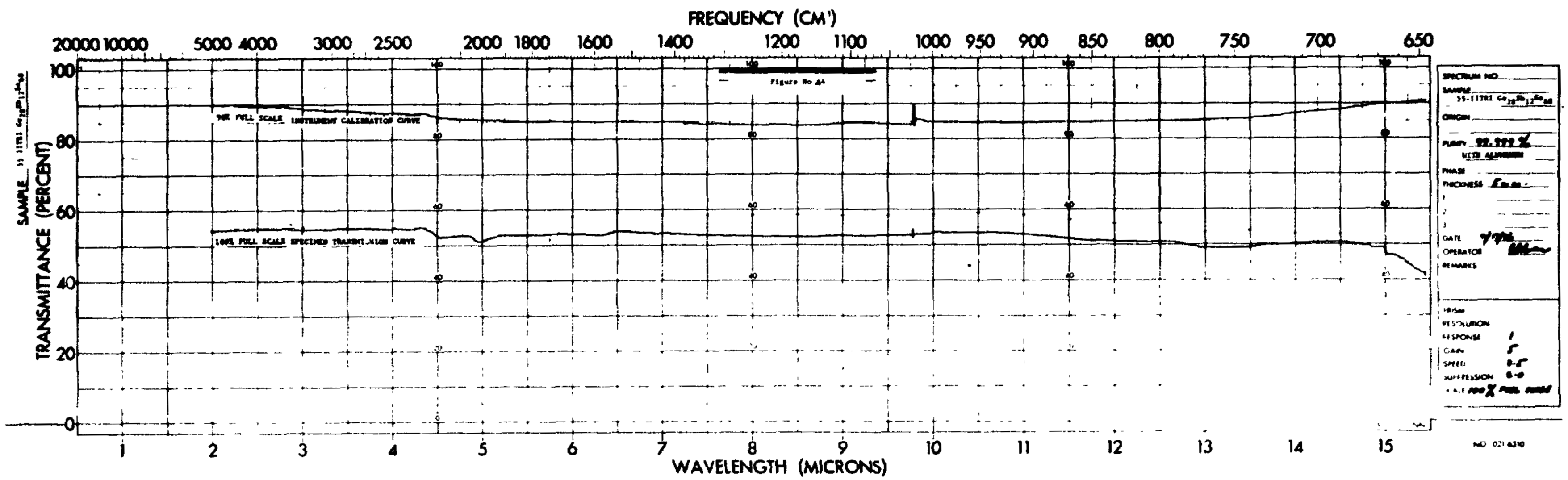


Figure 23 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 55

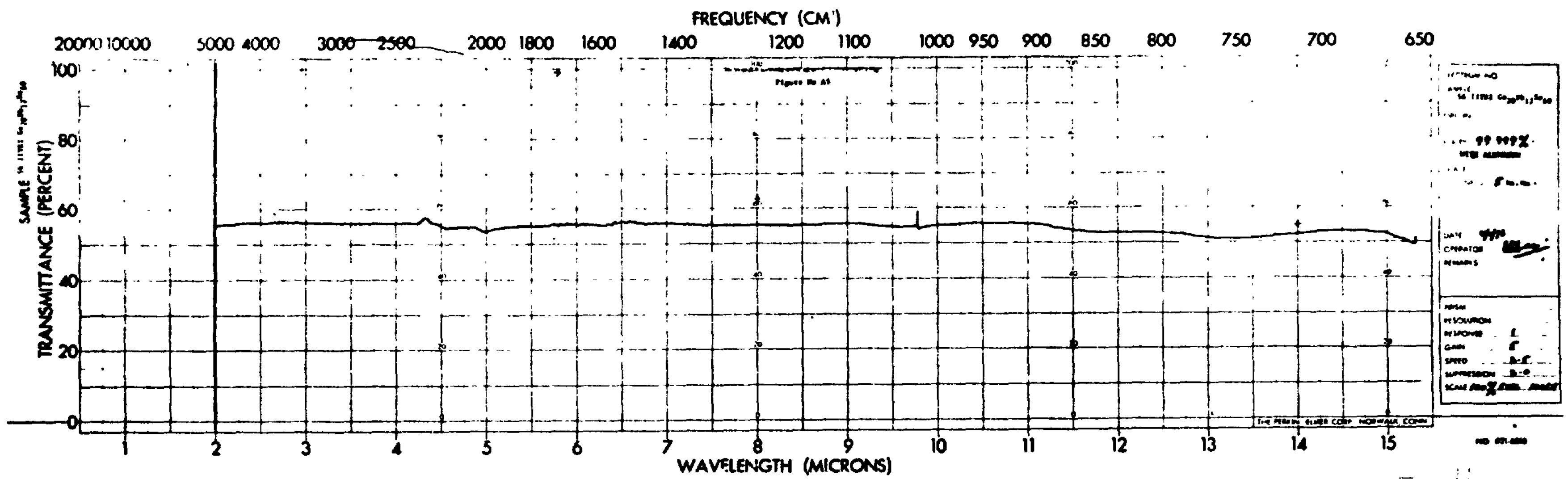


Figure 24 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 56

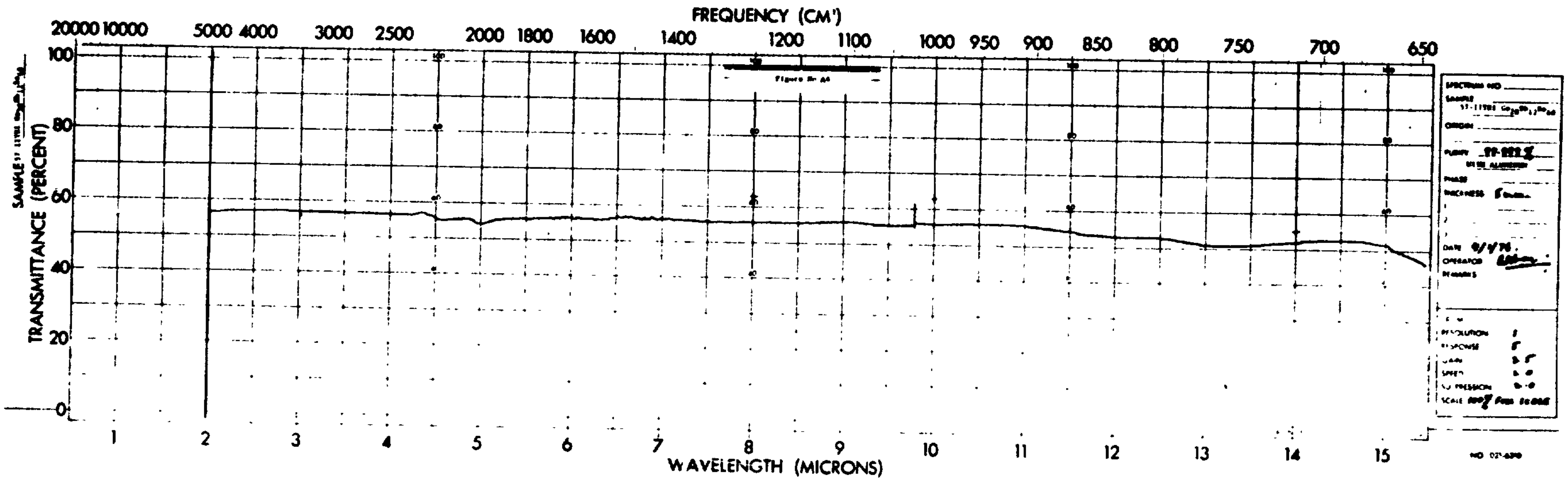


Figure 25 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 57

keeping the aluminum content (0.0158 grams) and reaction temperature (884°C) constant and increasing the reaction time to 41 hours. The result presented in Figure 26 showed that under these controlled conditions the increased reaction time did not improve the transmission characteristic of the glass. Further, it was also observed that higher reaction temperatures would initiate a reaction between the container (quartz ampoule) and the processed glass. This effect was quite pronounced in presence of large quantities of aluminum.

At this stage a series of experiments were conducted to establish the relationship between the glass reaction time and temperature. The purpose of these experiments was to correlate the time/temperature factors with 1) power availability in the in-space processing chamber, 2) time constraints of a given space processing mission, and 3) the operational characteristics of the acoustic levitator.

Four glasses (Nos. 49 to 52) were processed at progressively lower temperatures (884, 834, 825, and 800°C) while keeping the reaction time at a constant 21 hours, except in run No. 52 where visual observation indicated a need for a longer reaction time of 66 hours. The infrared transmission characteristics of these glasses indicated a definite relationship. At lower reaction temperatures, the molten glass requires a longer reaction time to obtain a maximum transmission of the glass. Composition No. 52 provides a good example of this phenomenon. The glass was processed at 800°C for 66 hours, and the compounded glass had a transmission around 63%. Refer to Figures 27 - 30.

5.2.3.5 Processing in Inert Atmosphere

Experiments were conducted in which the regular batch ingredients (bars and pellets and without aluminum dopant) were processed in an inert atmosphere of argon. This is a critical experiment, because the acoustic levitator requires an atmosphere (as opposed to vacuum) for its operation.

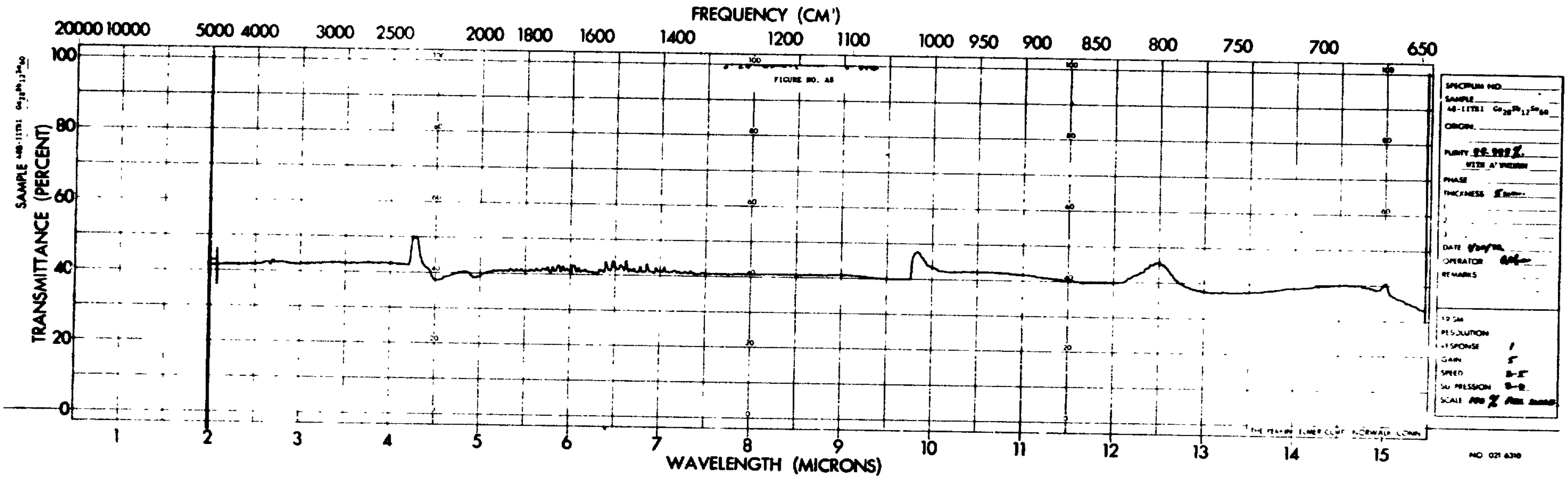


Figure 26 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 48

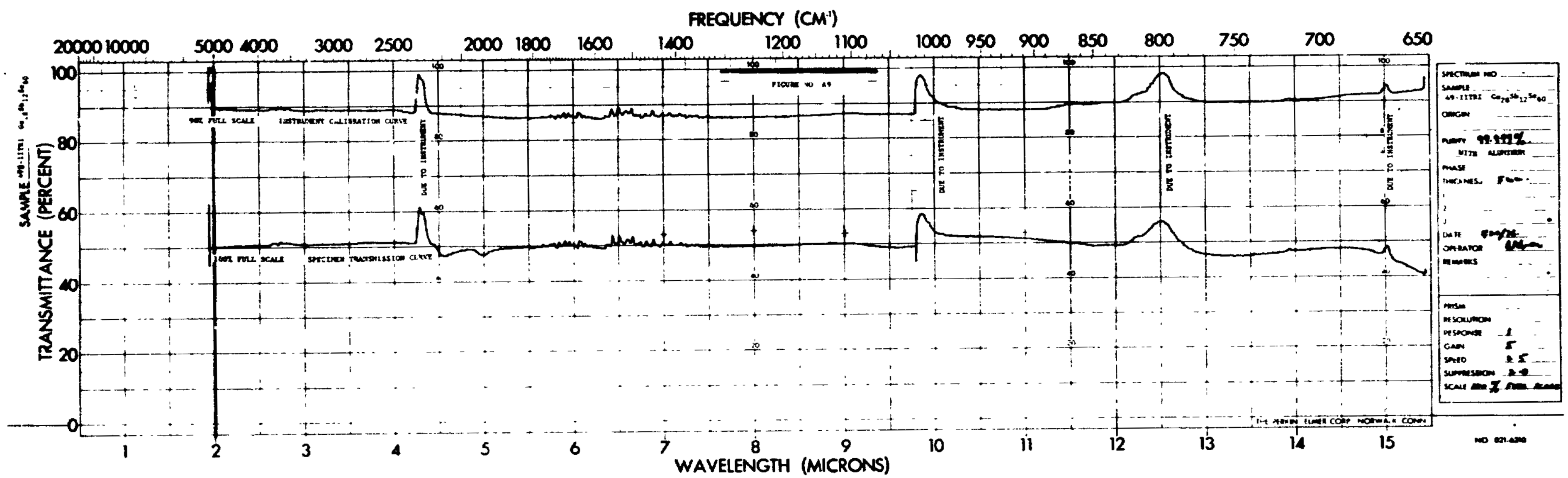


Figure 27 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 49

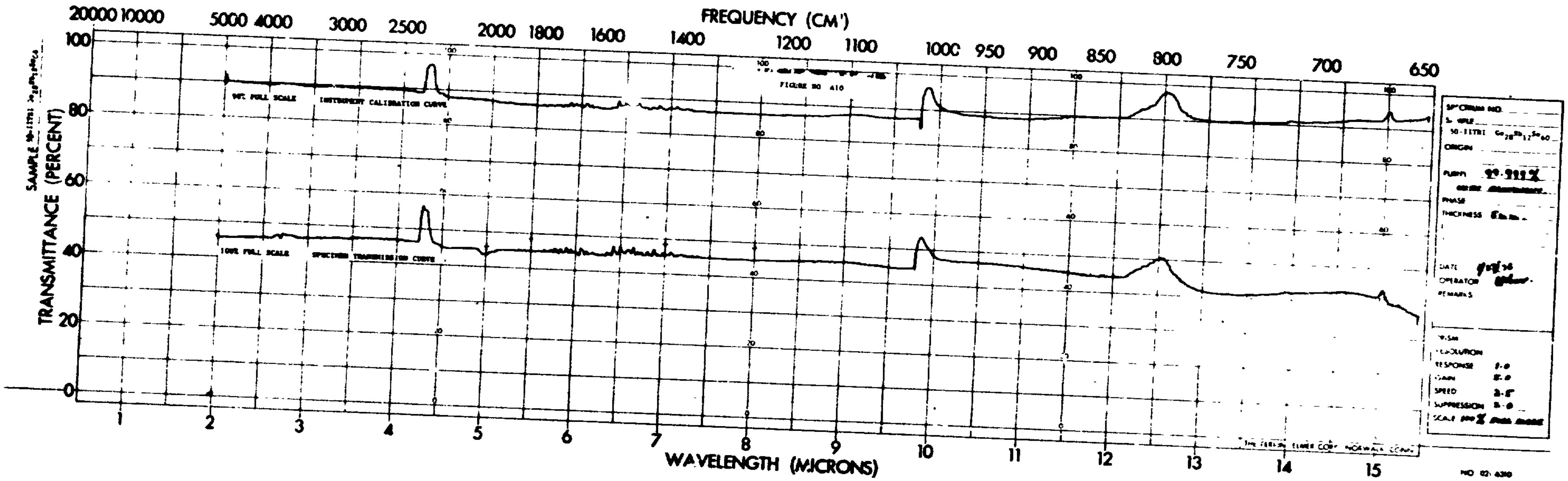


Figure 28 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 50

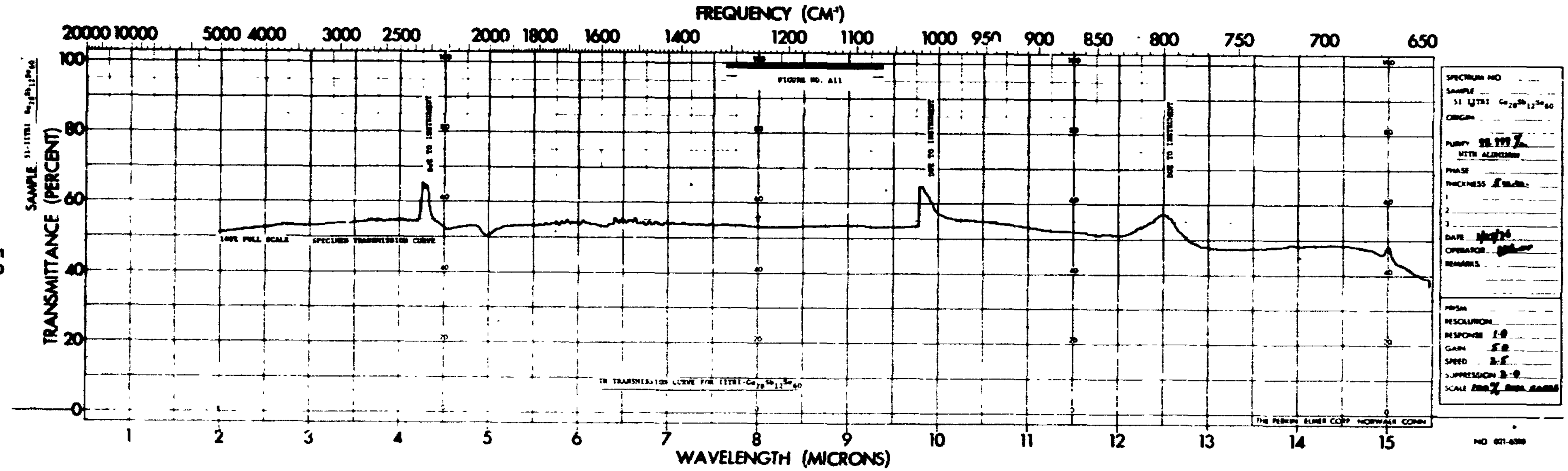


Figure 29 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 57

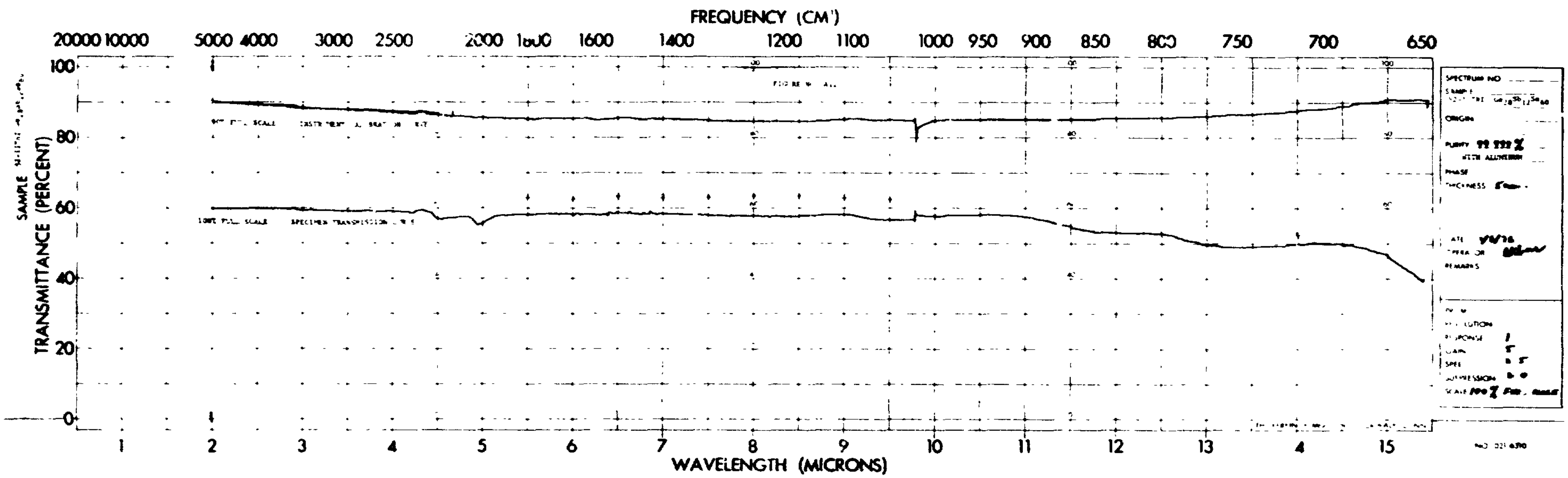


Figure 30 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 52

The design of the quartz ampoule was modified so as to accommodate a continuous flow of argon. Figures 31 and 32 show photographs of the ampoule, and Figure 33 presents the details of the processing system.

The ampoule was placed in a vertical furnace and the main outlet was connected to the diffusion pump through a series of cold traps. Commercial argon gas, purified through an oxygen gettering furnace, was allowed to enter the ampoule through a side inlet. The ampoule was 'rocked' by an air-controlled vibrator and the furnace and ampoule temperatures were closely monitored. The procedural details are as follows:

> Stoichiometric batch composition corresponding to $Ge_{28}Sb_{12}Se_{60}$ was weighed and transferred into the modified quartz ampoule. The ampoule was placed in the furnace system. Purified argon gas was flushed into a previously evacuated (5×10^{-6} Torr) system at a flow rate of 2 ml/min.
>
> The reason for flushing argon was to drive out any residual oxygen from the system. Argon was once again let into the system and was maintained throughout the experiment at a flow-rate of $\simeq$ 8 ml/minute and a pressure ranging between 2 - 4 psi.
>
> The furnace (containing the ampoule) was heated at a rate of 90°C/hour. After it reached a temperature of 650°C, the heating rate was reduced to 24°C/hour until it reached the glass reaction temperature of 840°C. The molten glass was held at this temperature for 19 hours, cooled, and finally quenched. Similar heating schedules have been used in the previous experiments. The quenched glass was annealed, ground and polished.

One glass was processed by this technique (run No. 60, Table V). Figures 34 and 35 present the photographs of the top and bottom of the processed glass. The bottom portion (which was in contact with the base of the ampoule) had several pits (holes) and could be due to the presence of argon trapped during quenching. The sample was ground and polished. Figure 36 presents the ir transmission characteristic of the glass.

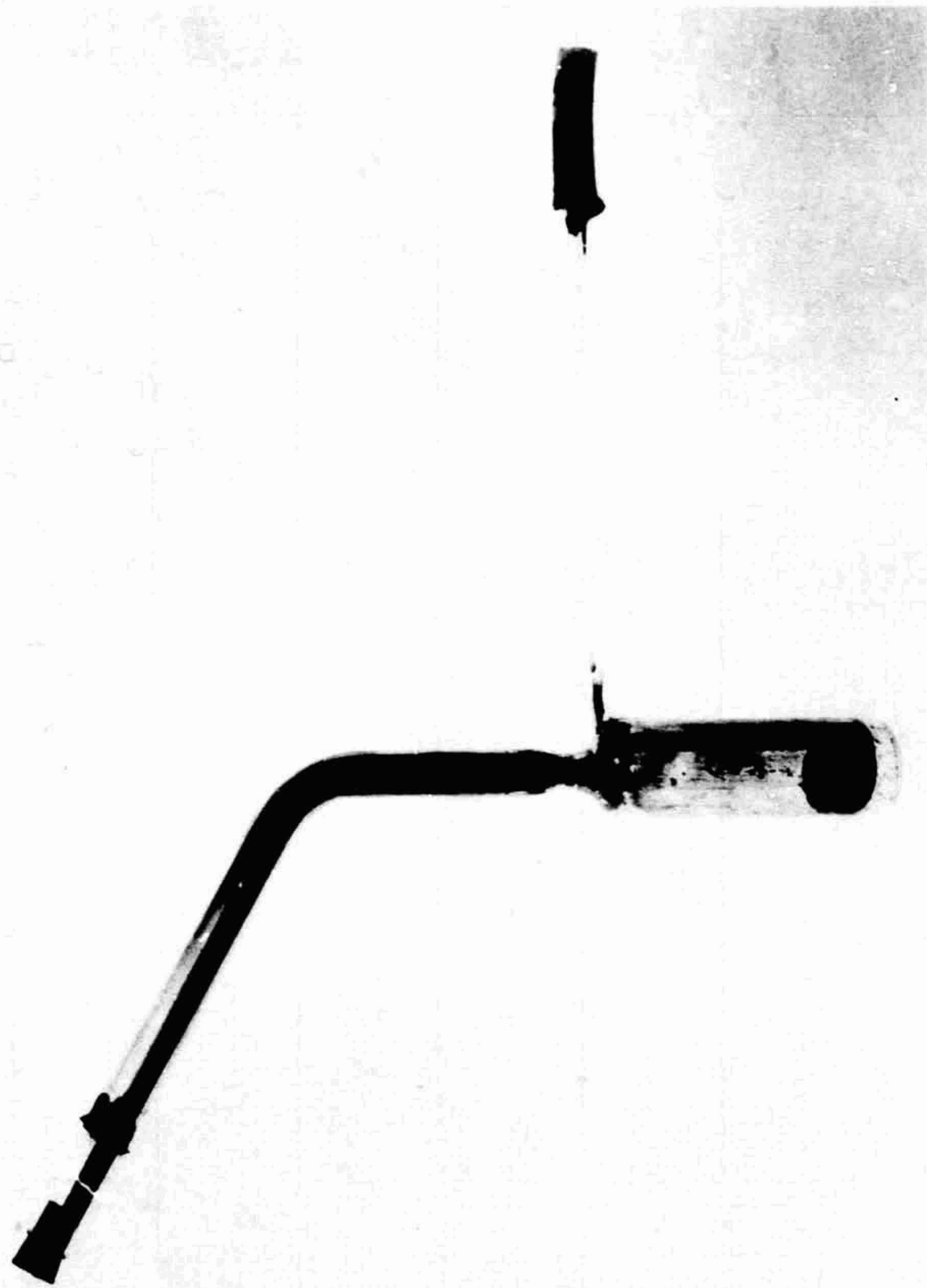


Figure 31 Glass Melting Ampoule with an Inlet for Inert Gas

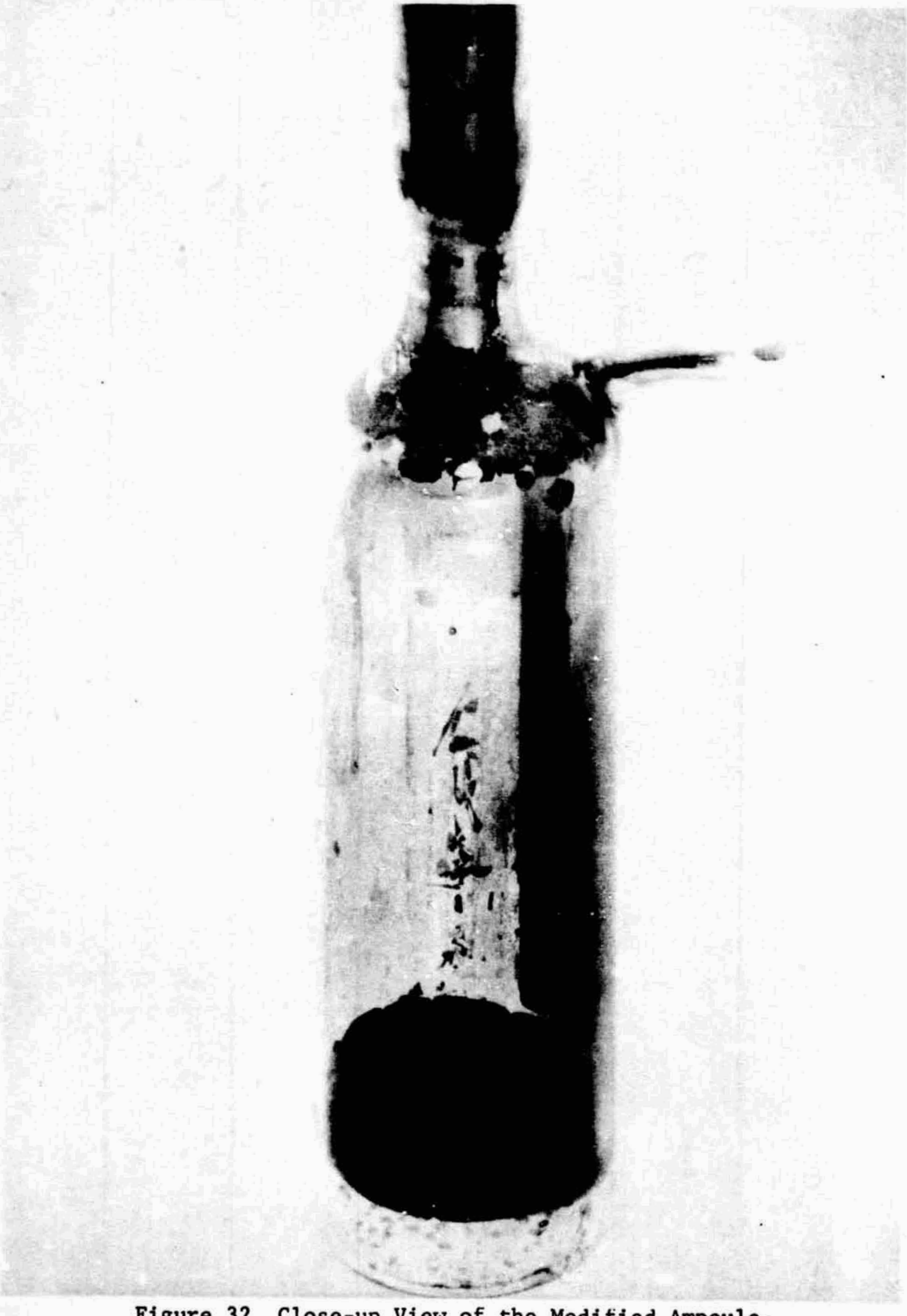


Figure 32 Close-up View of the Modified Ampoule

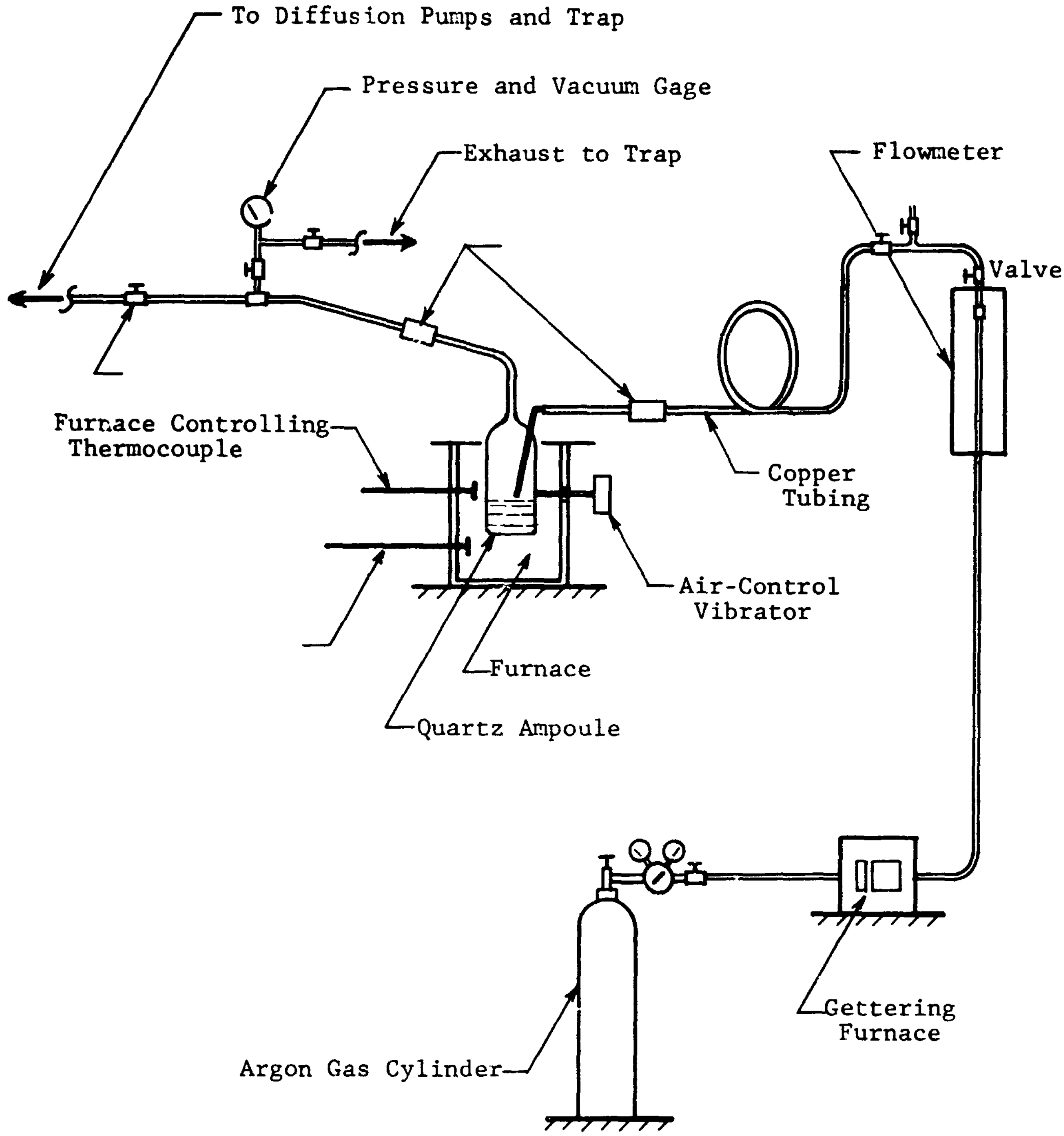


Figure 33 System for Processing of Cnalcogenide Glass in an Inert Atmosphere

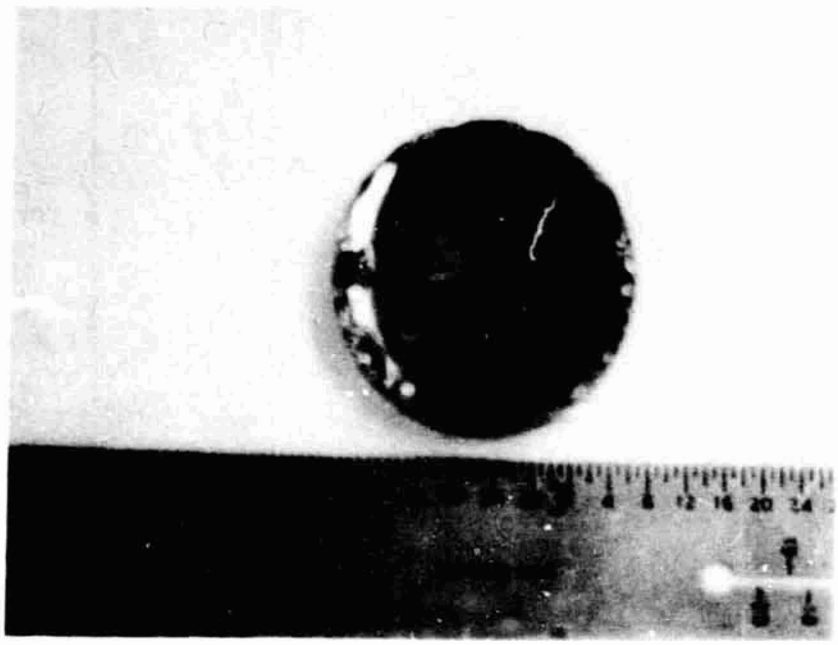


Figure 34 Top View of Argon Process $Ge_{28}Sb_{12}Se_{60}$ Glass. (Run No. 60

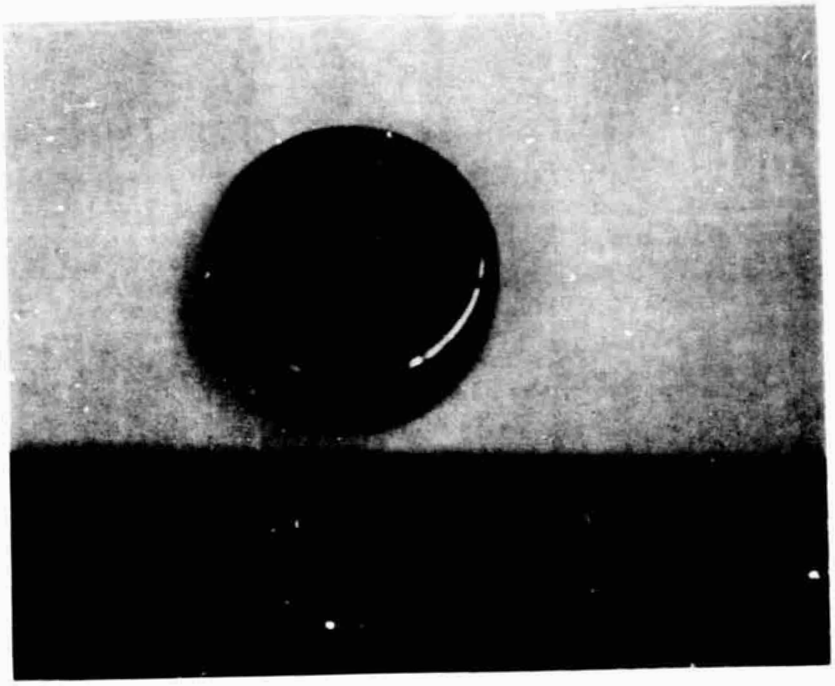


Figure 35 Bottom View of Argon Processed $Ge_{28}Sb_{12}Se_{60}$ Glass (Run No. 60)

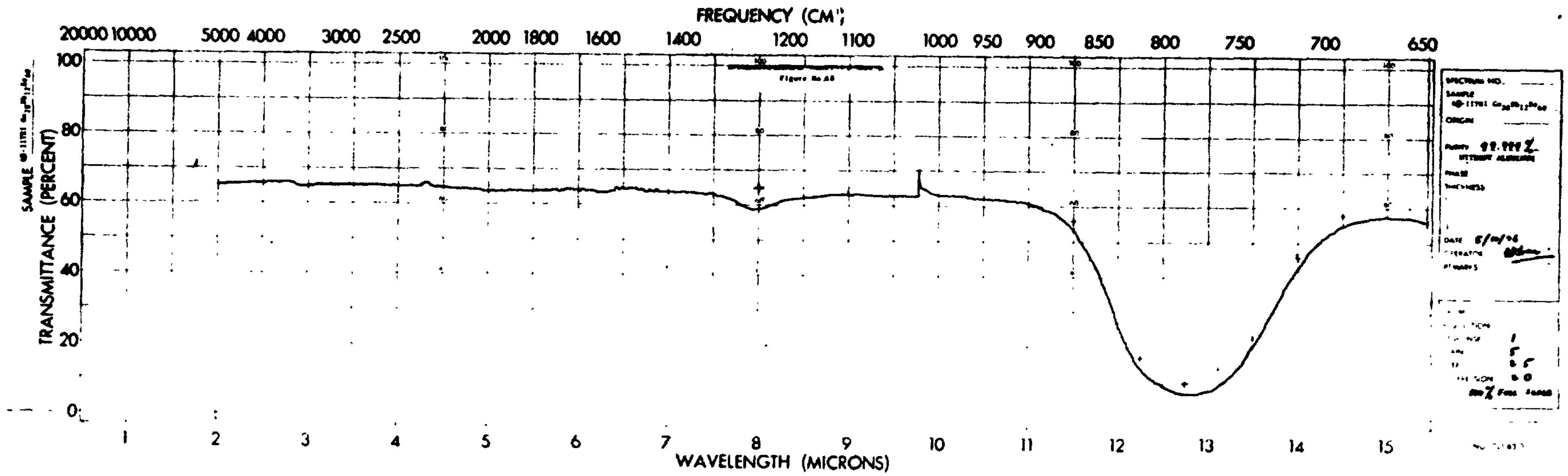


Figure 36 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 60

The transmission characteristic shows that this is the best glass we have processed. The transmission is around 65% over the entire 2-12μ region with the characteristic bell-shaped absorption band around 12.8μ. This higher transmission is an improvement over glasses processed under vacuum. It could be that the continuous flow of argon during the entire processing is an improved technique to eliminate oxygen-related impurities.

The result of using an argon atmosphere during processing is very encouraging as this demonstrates that the glass can be successfully processed in an inert atmosphere which will be present in the acoustic levitator.

Two additional glasses (run Nos. 61 and 62) were processed by this procedure to determine the reproducibility of the process. No aluminum dopant was added. Table IV presents the composition and processing parameters of these two glasses. Figures 37 and 38 present the infrared transmission characteristics (in the 2-14μ region) of these processed glasses. The transmission characteristics of TI-1173 glass (produced at Texas Instruments) measured at IITRI are shown in Table VI, Figure 12. Very good agreement with the TI-produced glass is illustrated.

During these studies two important observations were made. The first relates to the degassification of the ampoule and the second relates to the flushing of argon gas. Degassification of the ampoule involves the initial heating of the ampoule (prior to flushing of argon) to 100°C under a vacuum of 10^{-6} Torr for 12 - 16 hours. It has been established that this is one of the critical operations in IITRI's processing of high quality $Ge_{28}Sb_{12}Se_{60}$ glass. This operation expels moisture and oxygen-related surface contaminants from the batch materials and from the ampoule walls.

The second important observation relates to the continuous flow of purified argon gas during the entire processing period.

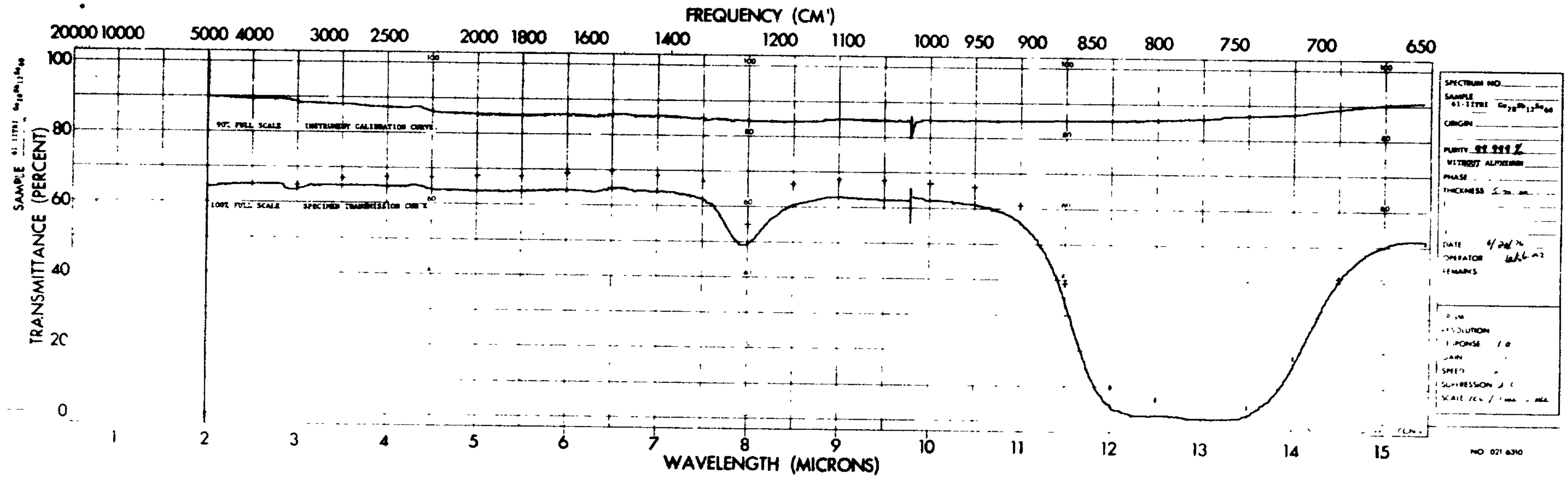


Figure 37 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 61

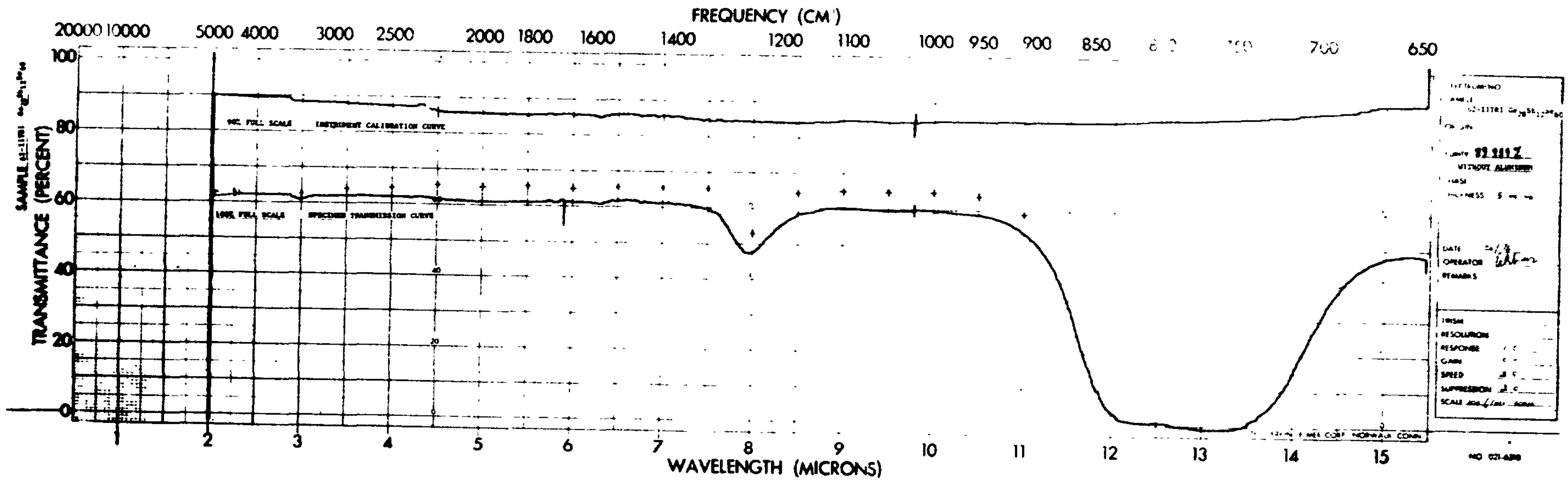


Figure 38 Infrared Transmission of $Ge_{28}Sb_{12}Se_{60}$
Sample No. 62

Table VI

COMPOSITION, PROCESSING PARAMETERS AND CHARACTERISTICS OF IITRI'S $Ge_{28}Sb_{12}Se_{60}$ GLASSES

Run Number	Composition (Grams)				Surface O_2 Removal Temp °C	Pressure Torr	Reaction Temp °C	Time at Reaction Temp Hours	Density of Glass Gms/cc	Transmission 2-8μ Percent	Transmission 8-14μ Percent	REMARKS
		Sb	Se	Dopant Al								
TI-173	$Ge_{28}Sb_{12}Se_{60}$				--	--	--	--	~ 71	60-63	63-58	Small Absorption Band Around [illegible]
61	3.75	2.70	8.55	--	105	2-4x10^{-6}		16-18	4.66	65-67	-	Characteristic Absorbtion Bands @ 9 & 13M
62	3.75	2.70	8.55	--	105	2-4x10^{-6}		16-18	4.69	65-67	-	" " " " " " "

Previous work had shown several pits (holes) on the bottom portion of glass processed in the argon atmosphere. However, such pits were eliminated in the newly processed glasses. This flaw was eliminated by proper control of the argon flow-rate during the processing period.

The experiments involving a static and dynamic inert gas atmosphere (argon) were successful. The dynamic argon atmosphere was found to be very effective in removing oxygen-related impurities. Glass produced in this manner showed improved infrared transmission when compared to the vacuum ampoule method used in earth processing. Additionally, enough experiments of this nature were conducted to indicate good reproducibility in results.

5.3 Acoustic Levitation-Containerless Processing

Position control devices will be used to stabilize containerless samples during in-space processing. One such device is described by Whymark[6] and was supplied to IITRI for use on this program for the purpose of integrating its use into our earthbound chalcogenide experiments.

The acoustic levitation/position control device is pictured in Figures 39 and 40. The basic operation of this device is that an acoustic force field is established within the containment cylinder (Figure 41) and the sample material is constrained to holes (energy minimums) in the sound field. The high temperature process is performed in the furnace region of the tube. The sample is then moved to a cooler portion for quenching (Figure 41).

Experiments were conducted wherein various materials were levitated at ambient room temperature to gain experience with the device and to investigate the level of stability and control attainable.

Initial experiments were conducted with low density styrofoam spheres up to several millimeters in diameter (Figure 42).

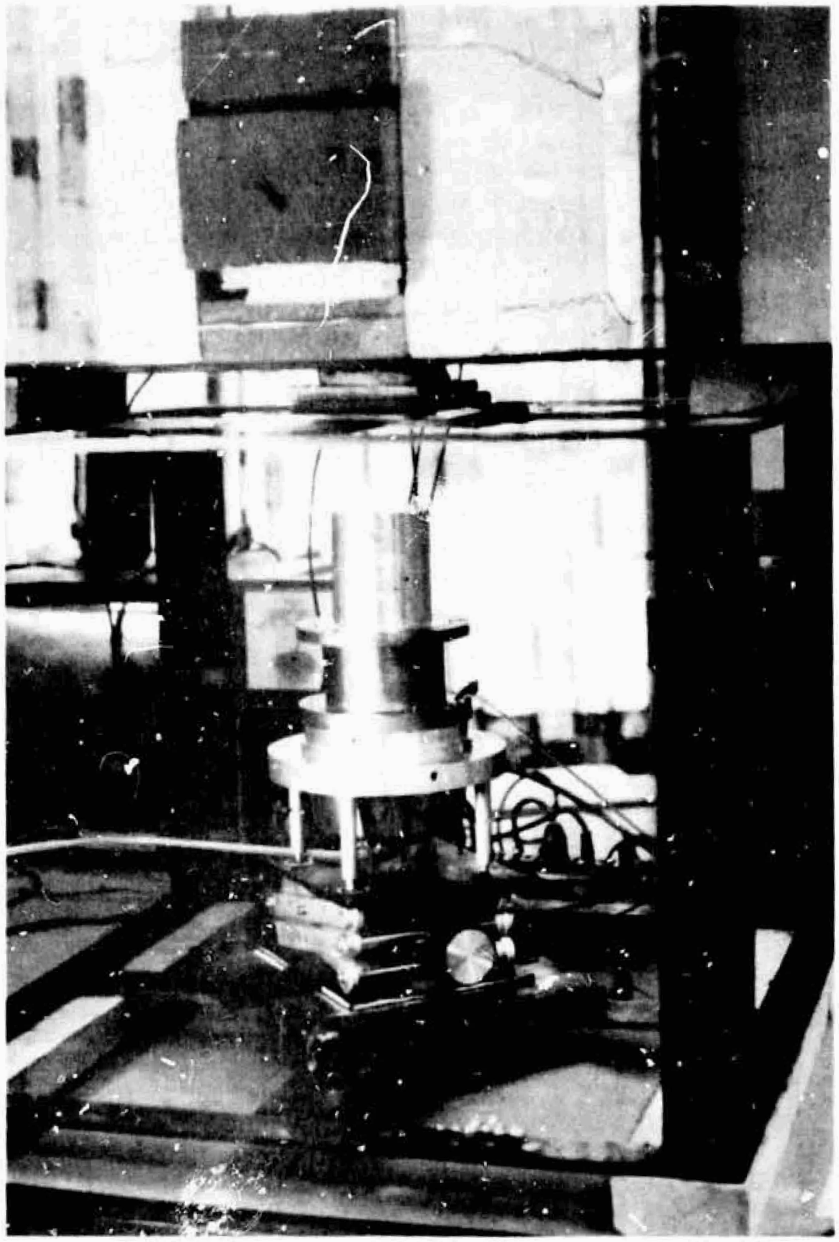


Figure 39 Photograph of Intersonics Acoustic Levitator

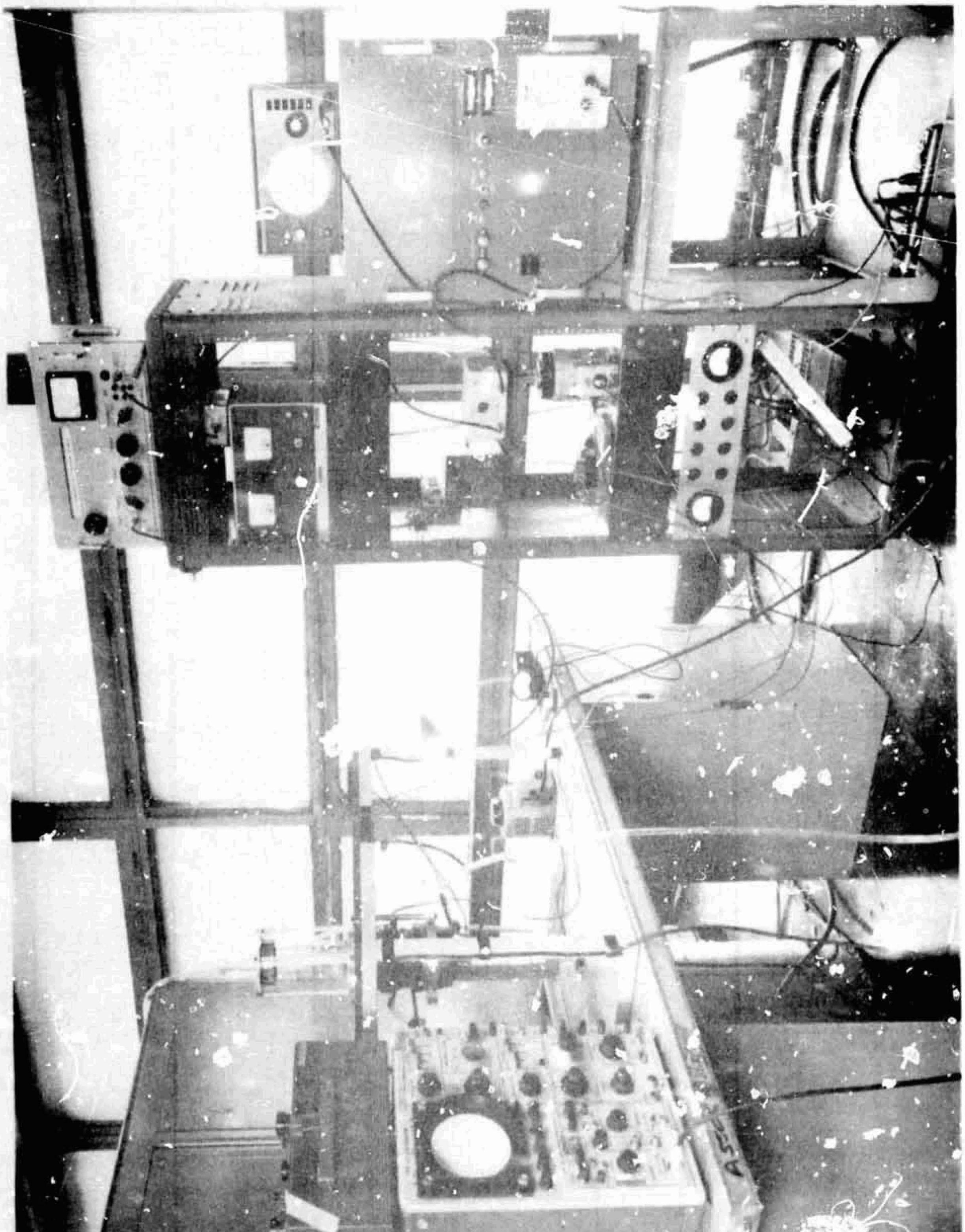


Figure 40 Acoustic Levitator Unit

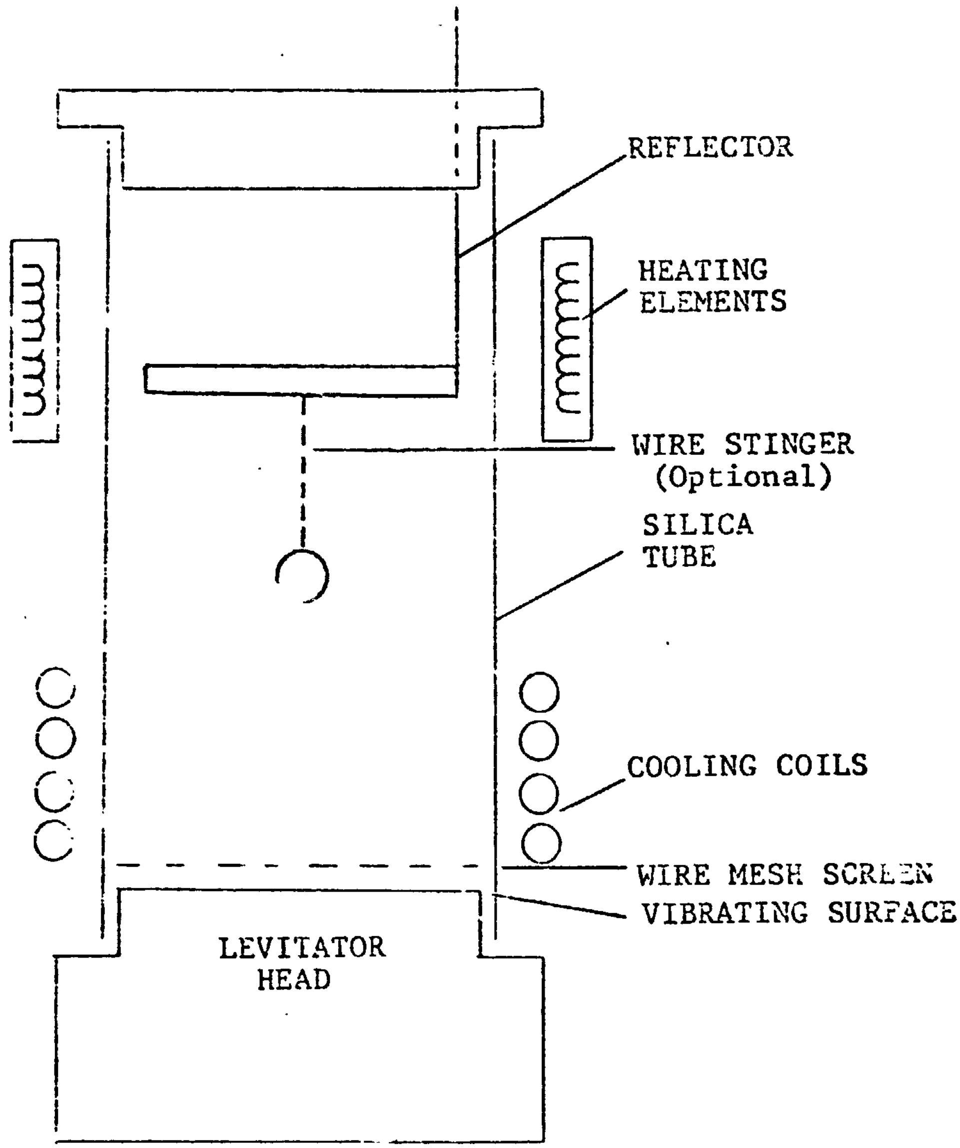


FIGURE 41 Levitation Melting

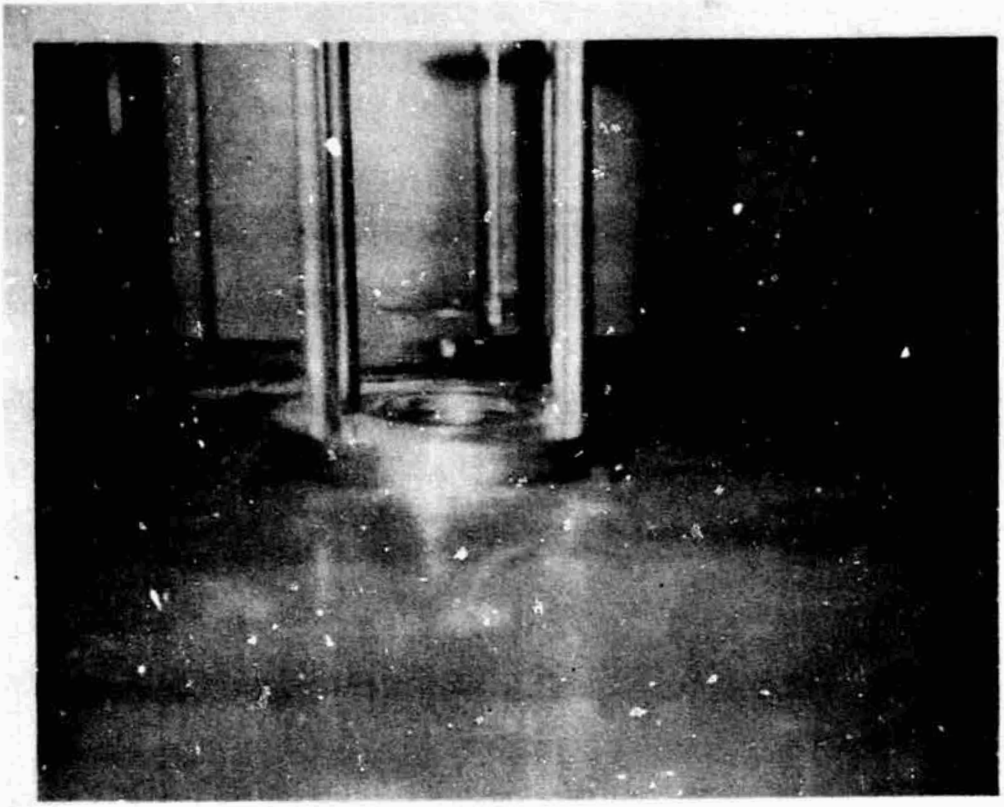


Figure 42 Room Temperature Levitation of Polystyrene Sphere

Excellent stability and control were obtained with this low density material. Levitation was successfully conducted for periods up to 90 minutes, which provides a good indication of the potential of this system for making glass melting experiments in space.

The next series of levitation experiments were conducted using 5mm diameter, 2 mm thick polystyrene discs. Levitation was accomplished for periods up to 20 minutes. However, it was difficult to maintain stable levitation without the sample spinning. Under these conditions of 1-g levitation, the main drive coil of the acoustic levitator frequently burned out. In an attempt to eliminate this problem, convective cooling was applied to the coil area.

The addition of convective cooling permitted operation at higher power levels. Several levitation experiments were conducted with 3-5 mm diameter soda-lime glass beads. With the unit operating at maximum power (determined by a maximum permissible current density for the 24 gauge wire of the main drive coil) a glass bead could be levitated only for short periods (few seconds). For our earth-bound processing experiments to be successful, we will need more stability, control, and time that has been obtained in these glass bead experiments. In the weightless in-space environment, however, much lower power levels will be required for levitation since the earth's 1-g gravity force will not be acting on the sample materials being levitated.

At this point in our acoustic levitation experiments, various components of the system were returned to Intersonics, Inc. for subsequent Drop Tower testing at MSFC. R.R. Whymark reports[7] that these experiments were very successful. Suitable sample injection and stable levitation were obtained for 1/4 and 3/8-inch diameter aluminum spheres at $\simeq$ 800°C under the short duration of near-weightlessness attained during the tests. It is significant that the power required for this levitation was very small as compared to the power necessary for 1-g earth levitation.

This indicates that the problems of stability and control that we have been experiencing in the earth experiments will be greatly diminished in space.

When the levitator system components were returned to IITRI with an improved drive coil, another series of experiments were initiated. These experiments included high temperature levitation of molten polystyrene, and room temperature levitation of commercial As_2S_3 glass. These experiments lead to several modifications of the device, and are described as follows.

5.3.1 High Temperature Experiments

Experiments were conducted to study the high temperature control and stability of the acoustic levitator. Figure 43 shows the furnace/chamber system. Polystyrene discs about 1/4" in diameter and 1/16" thick were levitated at room temperature. When the temperature was raised to ~ $400^{\circ}F$ ($\sim 200^{\circ}C$), stable levitation was maintained. However, when enough time had elapsed to melt the polystyrene disc, the molten disc would splatter out of the minimum energy well and splash on the silica tube. Reducing the size of the specimen did not improve this situation. Apparently, when the molten material flattens and spreads out, it exceeds the boundaries of the minimum energy nodal point. Therefore, larger minimum energy nodal points are required if 1/4" diameter samples are to be processed. Whymark indicates[7], however, that 1/8" diameter samples will be successfully levitated in the liquid state.

5.3.2 As_2S_3 Glass Experiments

Room temperature levitation experiments were also conducted using As_2S_3 (arsenic trisulphide) glass developed during the course of this program.

These experiments resulted in only short periods of successful levitation and frequent burn-out of the levitator drive coil

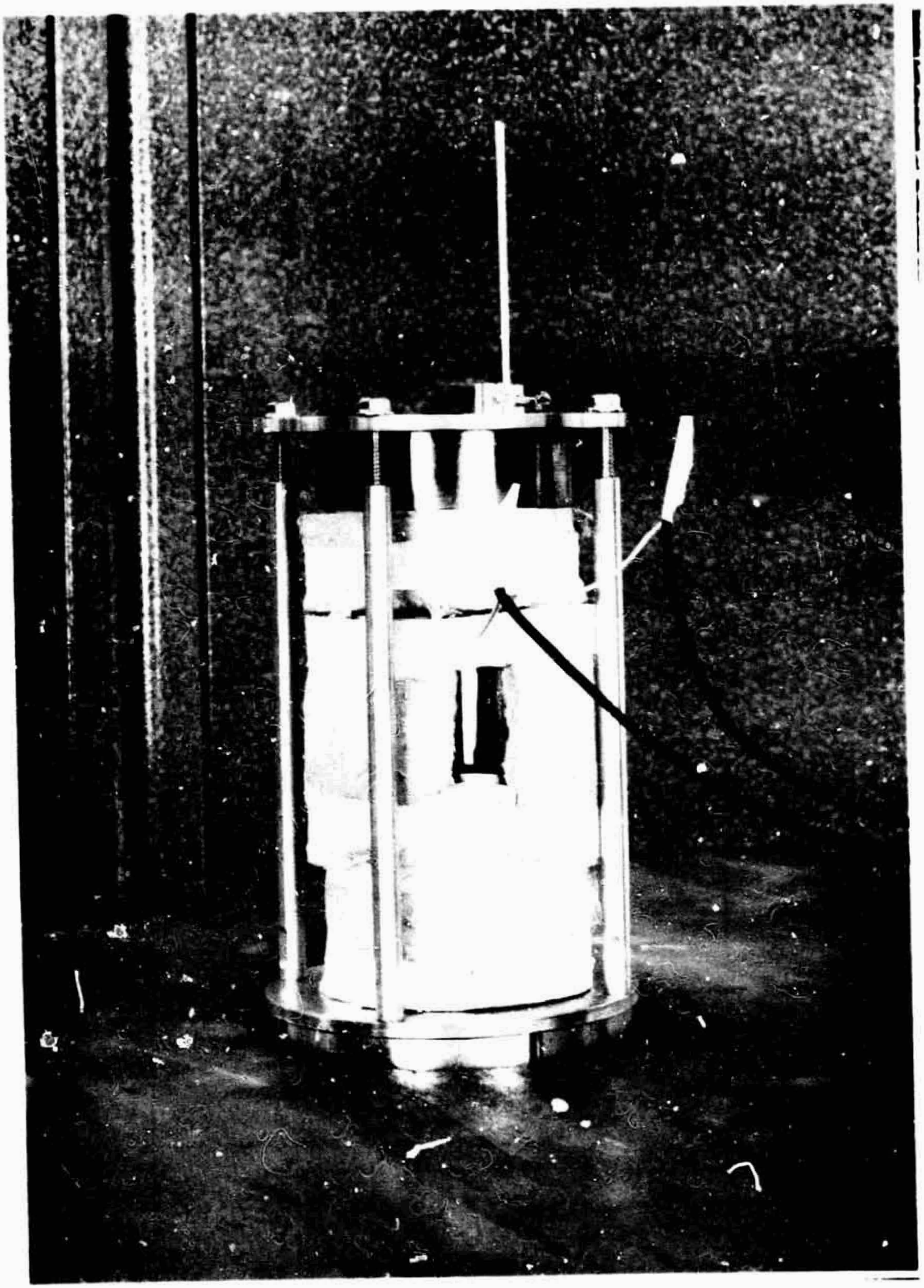


Figure 43 Acoustic Levitator - Furnace/Chamber System

due to the high power level required during operation. These experiments led to several modifications of the device and general observations regarding its operation which are as follows:

1. Water-cooled levitator head: In earlier experiments with low density materials (0.9 gm/cc) it was determined that the addition of convective cooling permitted operation at higher power levels. For the higher density As_2S_3 glass (3.4 gm/cc), this cooling method was insufficient. Water cooling was then added (Figure 44). This resulted in successful operation at higher power levels, but not high enough to be adequate for long term As_2S_3 melting experiments.

2. Bottom Screen: The purpose of the wire mesh screen located near the bottom of the levitation chamber (Figure 41) was to assist in the acoustic 'lift-off' of the sample. It has been determined that use of a stinger type wire device instead of the screen permits more suitable introduction of the sample into the acoustic field. Additionally, it has been found that elimination of the wire screen results in more stable levitation.

3. Chamber diameter/vibrator diameter: The levitator was provided with a chamber consisting of a 2-1/4 inch diameter silica tube. R.R. Whymark had suggested (Reference 7) that a portion of the stability problems that had been encountered were perhaps due to the small size of this chamber relative to the vibrator head diameter causing sound wave interference patterns. To check this, 5 mm glass beads were levitated using a 4-inch diameter chamber. This resulted in increased stability and successful levitation for periods of time up to 15 minutes.

4. Plunger Frequency: Another operational problem that was observed with the acoustic levitator was an unstable plunger oscillation frequency. Operating properly, the plunger had a free air resonance of 20 KHz as established at Intersonics, Inc. However, during testing it was observed that this frequency varied unpredictably between 15-20 KHz, necessitating continual retuning

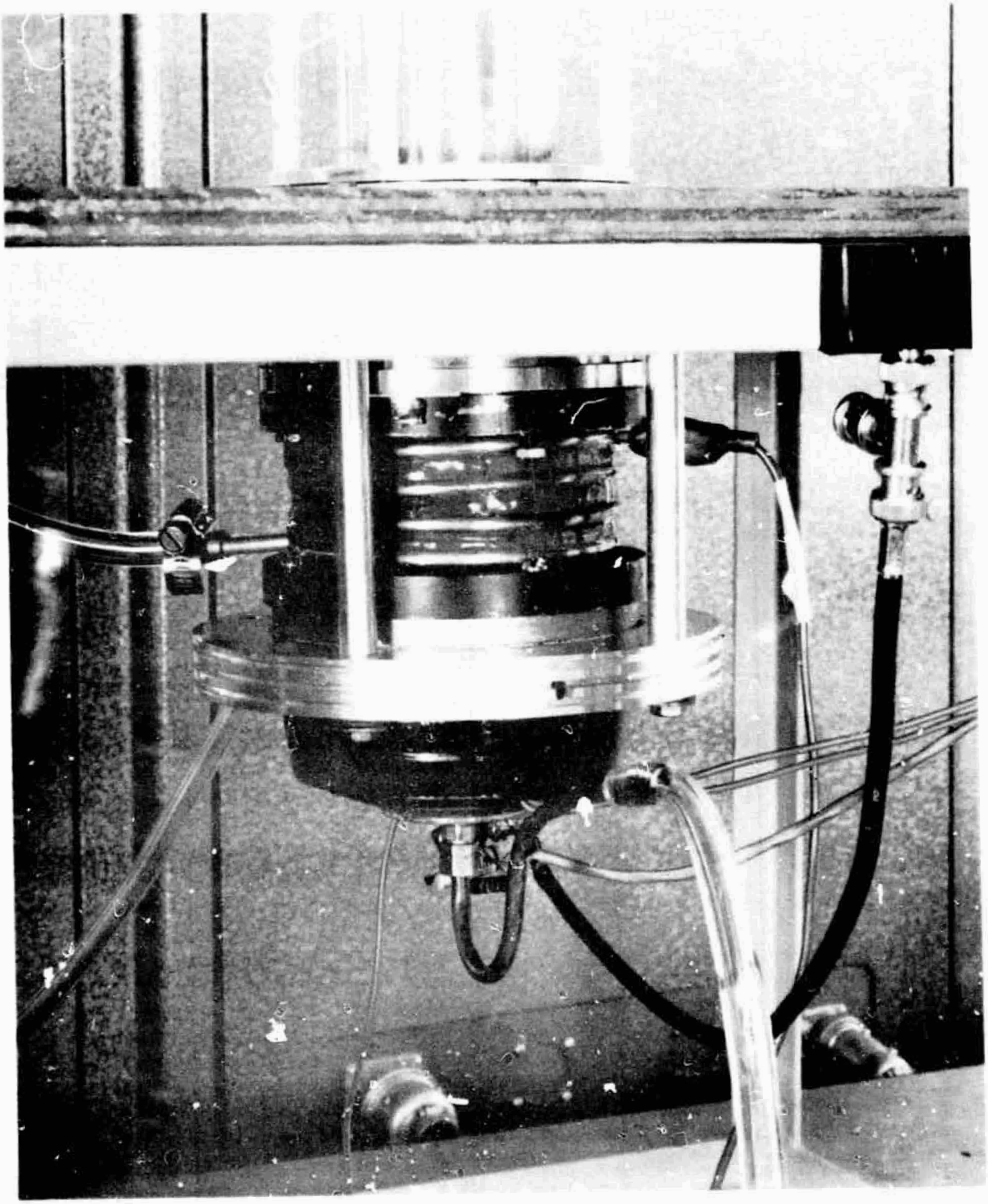


Figure 44 Acoustic Levitator Head with Water-Cooled Coils

of the feedback circuit. This situation was probably a major cause of our inability to levitate in a stable manner for long periods of time. It is believed that more stable electronics are required to solve this problem.

5. Reflector Position: Referring to Figure 41, it has been observed that levitation improved with decreasing distance between the reflector and the vibrating head. For the current application, a sufficiently large reflector to vibrator distance will be necessary to accommodate suitable heating and cooling sections within the chamber.

All these factors were discussed in detail with the Intersonics, Inc. and MSFC personnel. Both had recognized the limited capability of the existing unit. The existing MSFC/Intersonic device was not designed for long term levitation in a 1-g field. It was determined that to meet the requirements of IITRI's present ground-based program, modification of the device was necessary. IITRI's general requirements for the levitation/position control device that were discussed with Intersonics and MSFC personnel are listed as follows:

1. Stability and control during long term (8-10 hour) experiments.
2. Operation under 1-g conditions.
3. High temperature operation (up to 900°C).
4. Use with typical high density chalcogenide glasses and precursor constituents.
5. Use with solid spherical or disc-shaped samples up to 8 mm diameter; and liquid disc samples up to 4 mm diameter.
6. Use with a p ging gas atmosphere.
7. Ability to change the shape of liquid samples in a controlled manner as described by Whymark (Reference 6).

Based on this experience by IITRI, and the suggested modifications, Intersonics is presently completing construction on an improved acoustic levitation/positioning device, designed specifically for use in ground-based programs.

6.0 CONCLUSIONS

On this program, experience has been gained about the general behavior of ir-transmitting chalcogenides as well as the nature of the necessary constraints of the in-space experiments. We have dealt with the basic materials science of the chalcogenide systems, and also incorporated acoustic levitation into our experimental package. The concept here is that earth-bound experiments will demonstrate that all the compatibility conditions and constraints of in-space processing are satisfied. In this manner we can work towards confidence that early in-space processing experiments will be successful.

Several conclusions have been reached during this phase of the program. They are outlined as follows:

1. Laboratory experiments conducted at IITRI have established the techniques, processes and equipment necessary for the production of high purity chalcogenide glasses. This gives IITRI a baseline from which to work in developing the techniques that will eventually be used in space.
2. The processing techniques developed at Texas Instruments, Inc. have been successfully adopted for IITRI -- $Ge_{28}Sb_{12}Se_{60}$ glass. These processing techniques have been adopted within the constraints of 1-g environment (by conventional earth manufacturing methods).
3. The $Ge_{28}Sb_{12}Se_{60}$ glasses that have been processed at IITRI have optical transmission around 63% (5 mm thick) which is comparable to Texas Instrument's $Ge_{28}Sb_{12}Se_{60}$ glasses (TI-1173).
4. The concept of going to space with a cold-pressed pellet is valid, as long as we can achieve a high degree of homogeneity in our earth-mixed precursor powders.

5. A highly homogeneous cold pressed pellet can be prepared on earth using the liquid slurry method of particle mixing. This method was shown to be greatly superior to the mechanical dry mixing method.

6. Laboratory experiments have established, however, that the use of precursor materials in powdered form increases the oxygen contamination of the processed glass. This indicates that high purity precursor materials in bar or pellet form should be used (whenever possible).

7. The addition of the MSFC Acoustic Levitation/ Position Control Device to the IITRI experimental package permits investigation of all of the trade-off aspects of chalcogenide glass production prior to an actual space flight. In this manner the facility and the experiment can be developed together to insure a high probability of success for early missions.

8. Modifications were made at IITRI on the MSFC acoustic levitator in an attempt to improve levitation stability during long-time experiments. Room temperature experiments on As_2S_3 glasses and high temperature experiments on polystyrene were conducted. These experiments have established the need for additional modifications in the acoustic position control device to facilitate stable, long term, high temperature levitation under 1-g conditions.

7.0 FUTURE WORK

It is recommended that future work in this area concentrate heavily on the use of the acoustic position control device to achieve containerless processing conditions. The main efforts should be on achieving stable, long term levitation under 1-g conditions. Emphasis should be placed on the non-contact mechanical mixing phenomenon that has great potential for increasing the homogeneity of the chalcogenide glass while maintaining a very high degree of purity. This technique entails a form of non-contact mechanical mixing that can be performed with the acoustic levitation device by rhythmic variations in the sound field intensity. This work can proceed when a suitably modified acoustic levitator becomes available to IITRI.

8.0 CLOSURE AND ACKNOWLEDGEMENT

Based on the results and conclusions arrived at in this work, it is IITRI's belief that substantial progress has been made in the area of processing of chalcogenide glasses and adapting the processing parameters for future in-space missions.

We acknowledge the very many helpful suggestions made by Dr. A. R. Hilton, Texas Instruments, Inc., during the course of this work. These have been extremely valuable and are greatly appreciated.

Respectfully submitted,
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