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**CRYSTAL GROWTH OF ZnSe AND RELATED TERNARY
COMPOUND SEMICONDUCTORS
BY PHYSICAL VAPOR TRANSPORT**

Contract Number:

NAS8-39718

Final Report

Principal Investigator:

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(Formerly Universities Space Research Association)

Submitted to:

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FINAL REPORT
CRYSTAL GROWTH OF ZnSe AND RELATED TERNARY COMPOUND
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CONTRACT NAS8-39718

March 1, 1993 to September 30, 1997

Purpose and Scope of the Research:

The task was a joint collaboration including scientists from the Universities Space Research Association (USRA), NASA/Marshall Space Flight Center (MSFC) working in the Space Sciences Laboratory, and in the laboratories of Marquette University Materials Science and Metallurgy Program, and Hughes Santa Barbara Research Center. Other contributors included the Center for Photonic Materials and Devices, Department of Physics, Fisk University and the Department of Materials Science and Engineering, State University of New York at Stony Brook.

The task included investigating ZnSe and related ternary semiconducting alloys, e.g., ZnS_xSe_{1-x} , $ZnTe_xSe_{1-x}$, and $Zn_{1-x}Cd_xSe$. These materials are useful for opto-electronic applications, such as high efficient light-emitting diodes and low power threshold and high temperature lasers in the blue-green region of the visible spectrum. Given the recent demonstration of its optical bi-stable properties, ZnSe is also a possible candidate material for digital optical computers.

The investigation consisted of extensive ground-based studies, preparing for a flight experiment. This investigation included both experimental and theoretical efforts. Task objectives were: (1) to characterize ground-based crystal growth as a basis for comparative analysis of crystals grown in μg ; and (2) obtain experimental data and perform analyses required to define optimum parameters for flight experiments.

Phase I

The first six months of this study, the Preliminary Definition Phase (Phase I), was concentrated on the binary compound ZnSe:

- (a) purification of starting materials of Se by zone refining;
- (b) synthesis of ZnSe starting materials;
- (c) heat treatments of these starting materials;
- (d) vapor transport rate measurements;
- (e) vapor partial pressure measurements of ZnSe;
- (f) crystal growth of ZnSe by physical vapor transport
- (g) various characterizations on the grown ZnSe crystals.

In this investigation, ground-based studies were performed of the crystal growth of ZnSe by physical vapor transport in closed ampoules in preparation for flight experiments in low gravity condition. The following are the specific tasks resulting from the ground-based studies:

- (a) Established quantitative correlations between growth parameters, growth interface shapes, compositional redistribution, densities and distributions of dislocations, impurities, low angle grain boundaries, second phase inclusions, and other structural properties of the crystals grown by physical vapor transport.
- (b) Evaluated the contribution of gravitationally driven convection in the growth process by performing experiments under various vapor transport orientations relative to the gravitational direction (i.e., horizontal, vertically stabilized, and destabilized configurations).
- (c) Developed a two-dimensional model for delineating the effects of mass transport and heat transfer on the distribution of alloy composition, structural defects (dislocation), impurities, and the solid-vapor interface shapes during the physical vapor transport process in order to establish a fundamental understanding of the crystal growth process.
- (d) Established the partial pressure 3-phase curves of the vapor species in this system by measuring the optical absorption of the vapor phase coexisting with the condensed phases.
- (e) Evaluated the fundamentals of the current vapor transport theories by performing measurements of the partial pressures of the individual species and the vapor transport rates on the same ampoules.
- (f) Performed opto-electric characterization on the crystals and, thus, established the correlations between the electrical and optical characteristics of the grown crystals and the processing parameters.
- (g) Evaluated the potential benefits of microgravity processing for device applications by fabricating devices from ground-grown crystals.

Starting Materials

The ZnSe starting material was synthesized in-house from ultra-high pure starting elements, provided by commercial vendors. A zone refiner was used to purify the starting element.

Vapor Partial Pressure Measurements

Using an optical absorption technique, the partial pressures over one ZnSe sample were measured between 980° and 1090°C. It was confirmed that the predominant vapor species are Zn and Se₂ and the congruently subliming composition is inside the homogeneity range in this temperature range.

Heat Treatment of Starting Materials

In the physical vapor transport process, the transport rate is at its maximum when the source materials sublimes congruently, i.e., the vapor phase has the same composition as the solid phase. Because vapor partial pressures coexisting with the solid phase depend strongly on the small deviation from stoichiometry of the solid, it is almost impossible to weigh out the amount of elements by reproduction to form the compounds that have certain values of partial pressures. One method to adjust the stoichiometry of the starting materials, which makes the samples sublime more congruently, is to bake out the materials under dynamic vacuum condition. The change in stoichiometry stops when the materials sublime congruently. The other method is simply the distillation of the materials. The purpose of the heat treatment process, together with vapor partial pressure measurements, is to reproduce the same stoichiometry - as close to congruent sublimation as possible - for the source materials so that the transport rate is the highest and the same during each growth run.

All of the ZnSe starting material used in Phase I was from Cleveland Crystals, Inc., with purity of either 99.995% or 99.999%. These materials were treated by either (a) being baked out at about 1080°C under dynamic vacuum condition for about 10 minutes, or (b) being distilled by subliming the material from one end of the ampoule and depositing it on the other end under dynamic vacuum condition.

Transport Rate Measurements

The transport rates of ZnSe materials under a temperature gradient were measured by a direct, *in situ* technique which gives the amounts of mass transported at different time intervals. All the materials inside a transport ampoule were collected and loaded into an optical cell and the stoichiometry of the materials were determined by partial pressure measurements at Marquette University.

Simultaneous measurements of partial pressures and transport rates were also performed, establishing and confirming the theory of vapor transport rate in a closed ampoule.

Crystal Growth Experiments

A three-zone growth furnace was used to produce a sharp thermal gradient which resulted in a well-defined position for the supersaturated vapor phase and consequently, a well-defined solid vapor interface. Using this method, large single crystals of ZnSe were grown consistently. Growth experiments in seeded, unseeded, horizontal, and vertical growth configuration were conducted.

Using the original three-zone furnace configuration resulted in growth interfaces for some crystals being concave toward the solid. After analyzing the thermal environment near the interface, an adiabatic zone (2.5 to 5 cm thick) was inserted between the central zone heater and the cold zone. This change resulted in an improvement of growth interface.

Characterization and Results

Samples were examined by optical, scanning electron, and atomic force microscopy. The growth orientations were determined by Laue X-ray diffraction. The facet surface of ZnSe-5 crystal was determined to be (110) planes and the growth direction of ZnSe-6 was [331]. (Figures showing results of these and other tests were provided in the final report for Phase I and are attached as Attachment 1.)

Fisk University performed Atomic Force Microscopy (AFM) and Differential Scanning Calorimetry (DSC). (Results shown in final report for Phase I.)

A (110) slab was cut almost parallel to the growth direction of the ZnSe-6 crystal and was lapped and chemomechanically polished in 2% Br ethylene glycol solution. This slice was sent to State University of New York at Stony Brook for synchrotron radiation analysis.

A part of the ZnSe-6 crystal was also sent to the Santa Barbara Research Center where for studying the technique to put on ohmic contact for the Hall measurement and to perform cathodoluminescence measurement. A double-crystal diffractometer was set up in the laboratory and rocking curve diffractometry was performed.

Existing optical transmission and photoluminescence equipment were modified and measurement on ZnSe crystals were conducted.

Phase II

Phase II of the contract authorization to proceed was awarded 1 December 1993, and contract performance start up was 6 January 1994. The Phase II tasks were a continuation of the Phase I tasks with emphasis on the ternary systems, such as ZnSeS, ZnTeSe, and ZnCdSe. The primary objective of the ground-based investigation was to obtain the experimental data and conduct analyses required to define the optimum growth parameters for upcoming flight experiments. Most of this objective was accomplished in Phase I for the binary systems. The Phase II work continued, adding the ternary systems, processing data for analyses and refinement leading to a flight experiment.

The proposed flight experiment was declined by NASA in early 1995 after a Science Concept Review on September 29, 1994. Activity on this contract was held to a minimal level after the contract was de-scoped in 1996, when Dr. Ching-Hua Su's salary and related benefits were returned to NASA when he became a Civil Servant. Dr. Yi-Gao Sha continued the research for USRA. His research centered primarily on theoretical calculations for mass flux and composition in ZnSe-based ternary physical vapor transport systems and transport experiments.

Work on this contract was halted as of September 1997.

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Publications:

Ching-Hua Su, Yi-Gao Sha, M.P. Volz, D.C. Gillies, F.R. Szofran, S.L. Lehoczky, W. Zhou, M. Dudley, Hao-Chieh Liu, R.F. Brebrick, and J.C. Wang. Invited paper, "Ground-based Research of Crystal Growth of II-VI Compound Semiconductors by Physical Vapor Transport," presented at the 8th Annual Symposium on Microgravity Science and Space Processing, 32nd AIAA Aerospace Science Meeting, Reno, Nevada, January 10-13, 1994 (paper No. 94-0564 published in AIAA proceedings).

K.T. Chen, M.A. George, Y. Zhang, A. Burger, Ching-Hua Su, Yi-Gao Sha, D.C. Gillies, and S.L. Lehoczky, "Selenium Precipitates in ZnSe Crystals Grown by the Physical Vapor Transport," presented at the 1994 March meeting of the American Physical Society, March 21-25, Pittsburgh, Pennsylvania.

Yi-Gao Sha, Ching-Hua Su, W. Palosz, M.P. Volz, D.C. Gillies, F.R. Szofran, S.L. Lehoczky, Hao-Chieh Liu, and R.F. Brebrick, "Mass Flux of ZnSe by Physical Vapor Transport," submitted to J. Crystal Growth, June 1994.

Kuo-Tong Chen, M.A. George, Y. Zhang, A. Burger, Ching-Hua Su, Yi-Gao Sha, D.C. Gillies, and S.L. Lehoczky, "Selenium Precipitation in ZnSe Crystal Growth by Physical Vapor Transport," submitted to J. of Crystal Growth, July 1994.

Yi-Gao Sha, Ching-Hua Su, W. Palosz, M.P. Volz, D.C. Gillies, F.R. Szofran, S.L. Lehoczky, Hao-Chieh Liu, and R.F. Brebrick, "Mass Flux and Crystal Growth of ZnSe by Physical Vapor Transport," presented at the 8th International Conference on Vapour Growth and Epitaxy (ICVGE-8), Freiburg, Germany, July 24-29, 1994.

Travel:

The various meetings/conferences noted above in publications.

3/23-4/2/94 Ching-Hua Su, Milwaukee, WI, to discuss selenium precipitates at Marquette University.

4/7-4/14/96 Yi-Gao Sha, Materials Research Society Meeting.

7/97 Meeting by Ching-Hua Su at Santa Barbara Research Center with Co-I, Dr. S. Sen, and her co-workers on the responsibility of the center in future work .

Contract Administration Activities:

Base Contract: Period of Performance: February 22, 1993 - August 21, 1993
Value: \$89,873
Funding: \$89,873

Modification Number 1: No-cost extension through November 30, 1993
Modification Number 2: Increased value by \$419,600 to \$509,473. Extended through May 31, 1996. Additional funding of \$50,127
Modification Number 3: Additional funding of \$210,000
Modification Number 4: Revised NASA Form 1018 distribution instructions and reporting period
Modification Number 5: Descope of requirements and decreased value by \$145,480 from \$509,473 to \$363,993
Modification Number 6 Additional funding of \$13,993. Fully funded
Modification Number 7: No-cost period of performance extension to December 31, 1996
Modification Number 8: No-cost period of performance extension to September 30, 1997

Contract Completion:

Total Contract Value:	\$363,993
Funded Value:	\$363,993
Total Estimated Cumulative Costs:	\$358,126
Estimated Total Costs at Physical Completion:	\$358,126
Physical Completion:	100%

Physical completion of the Statement of Work was accomplished within existing funding. Because of changes in approach and research pursuits, as well as the de-scope of the statement of work, the reduced funding was adequate to complete the research at a lower total cost than initially proposed.

Band Gap of ZnSeS ZnSeTe and ZnCdSe

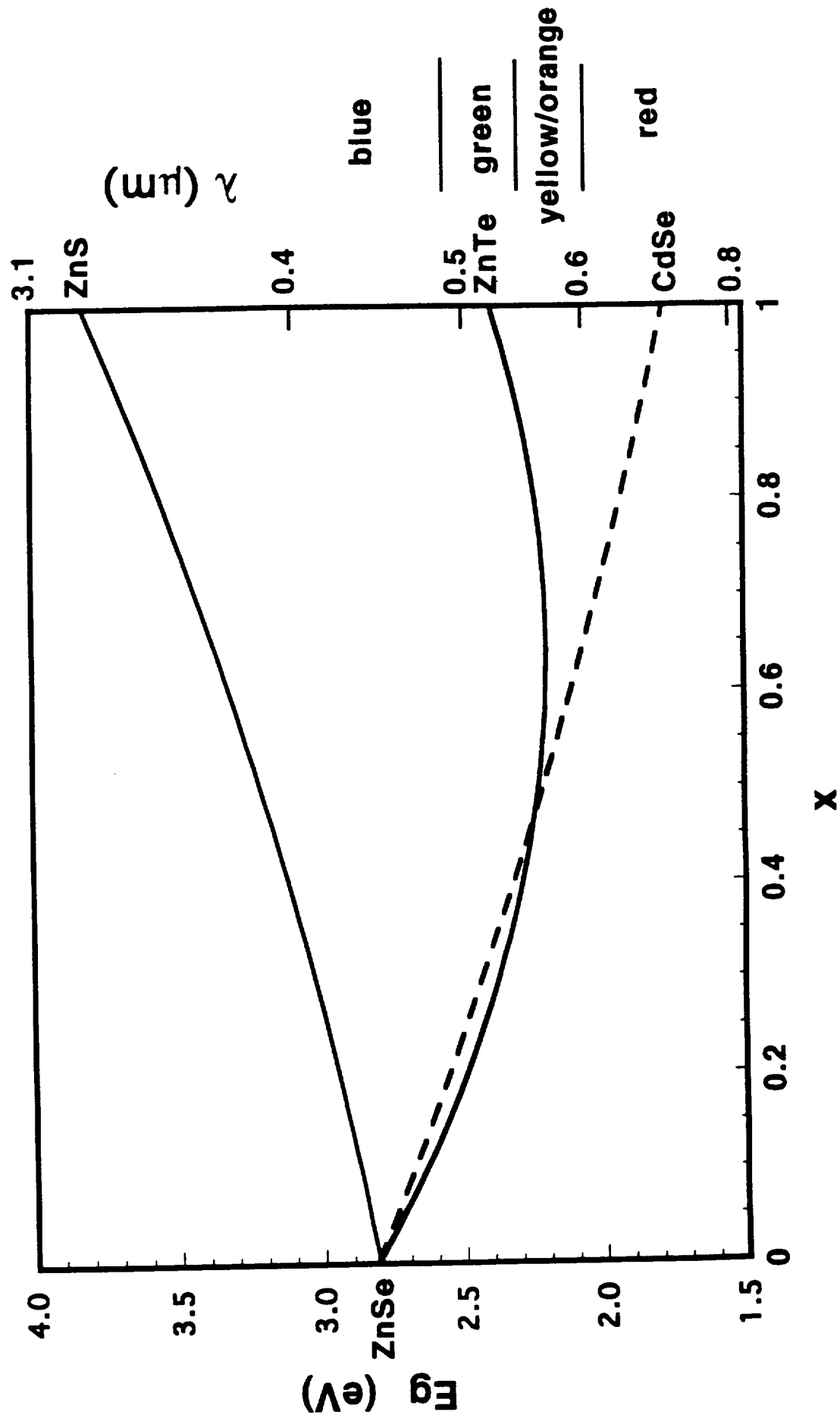
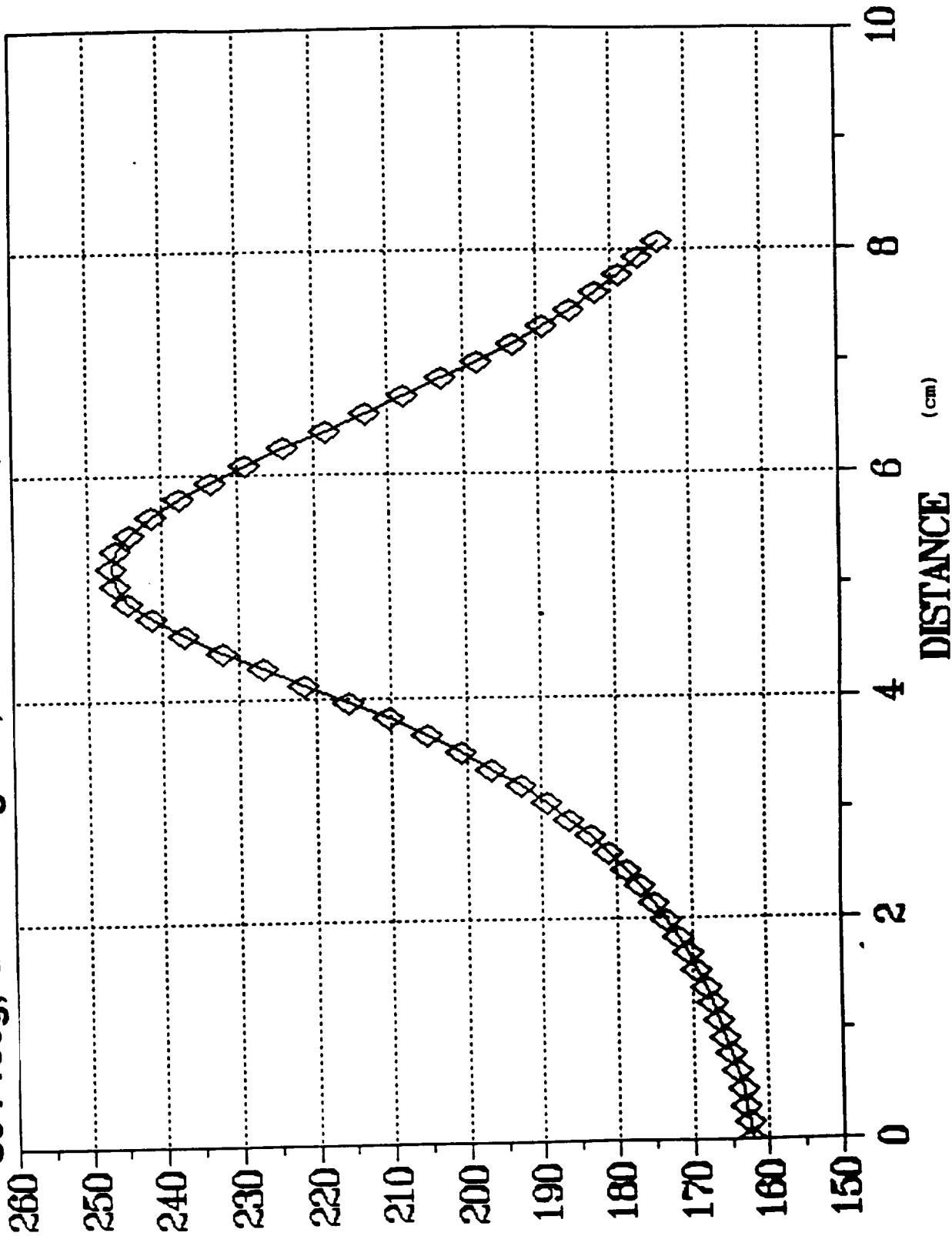


Figure 1

Se : 150g, 25cm long rod, M.P. = 217 °C; Trans. rate = 1.91 cm/hr



◇ TEMP

Figure 2

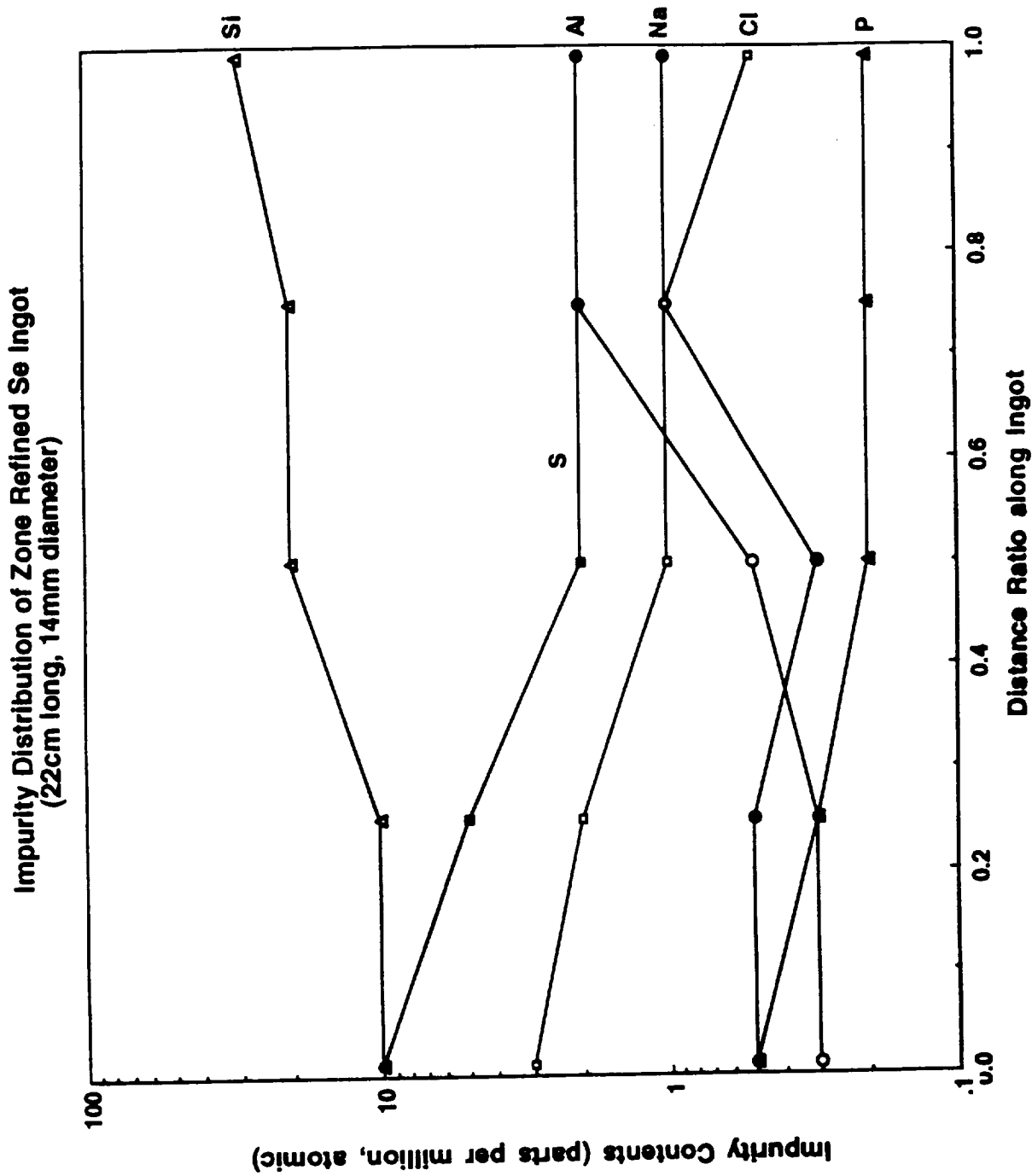


Figure 3

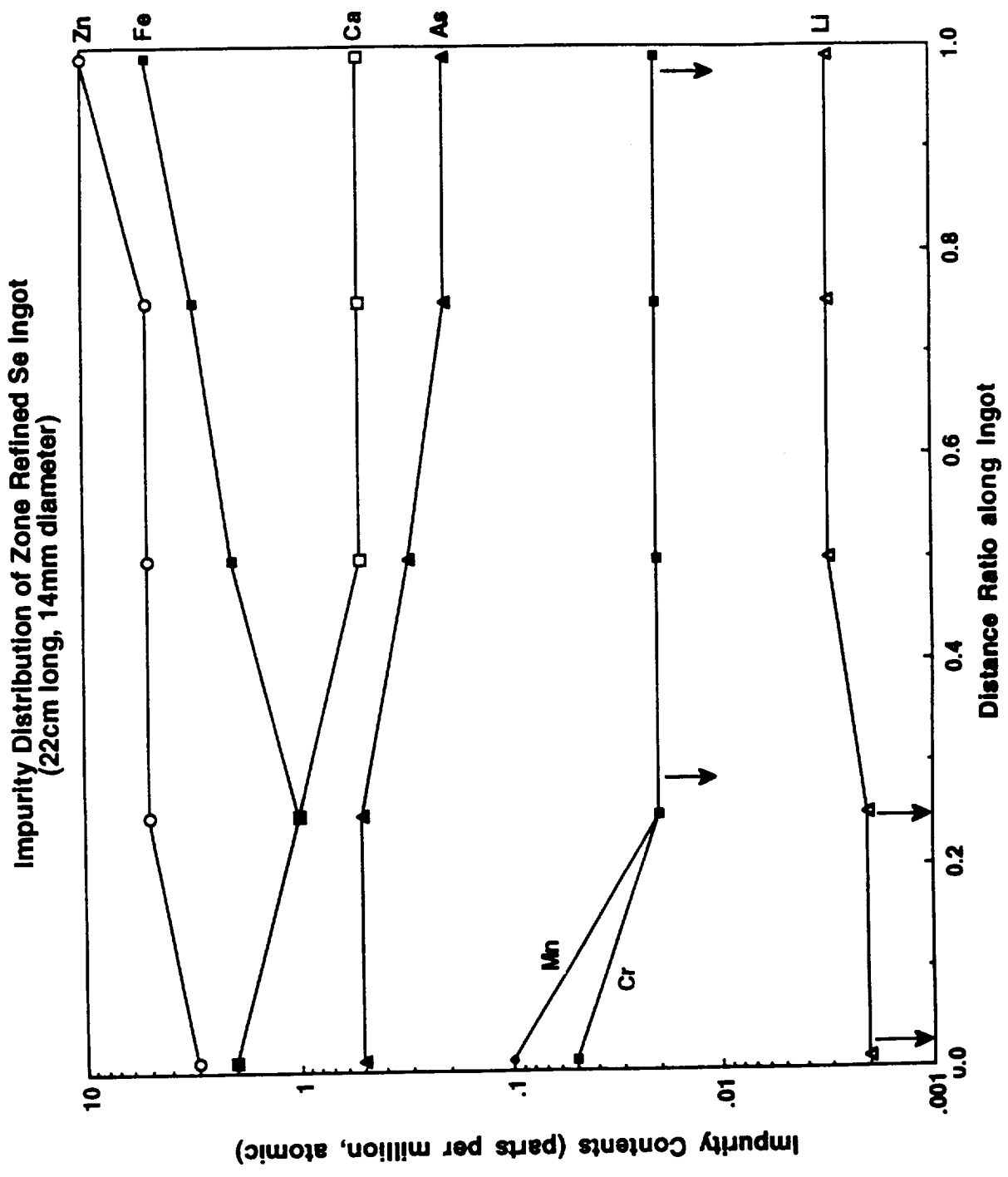


Figure 4

Illustration for Heat Treatment of ZnSe Starting Materials

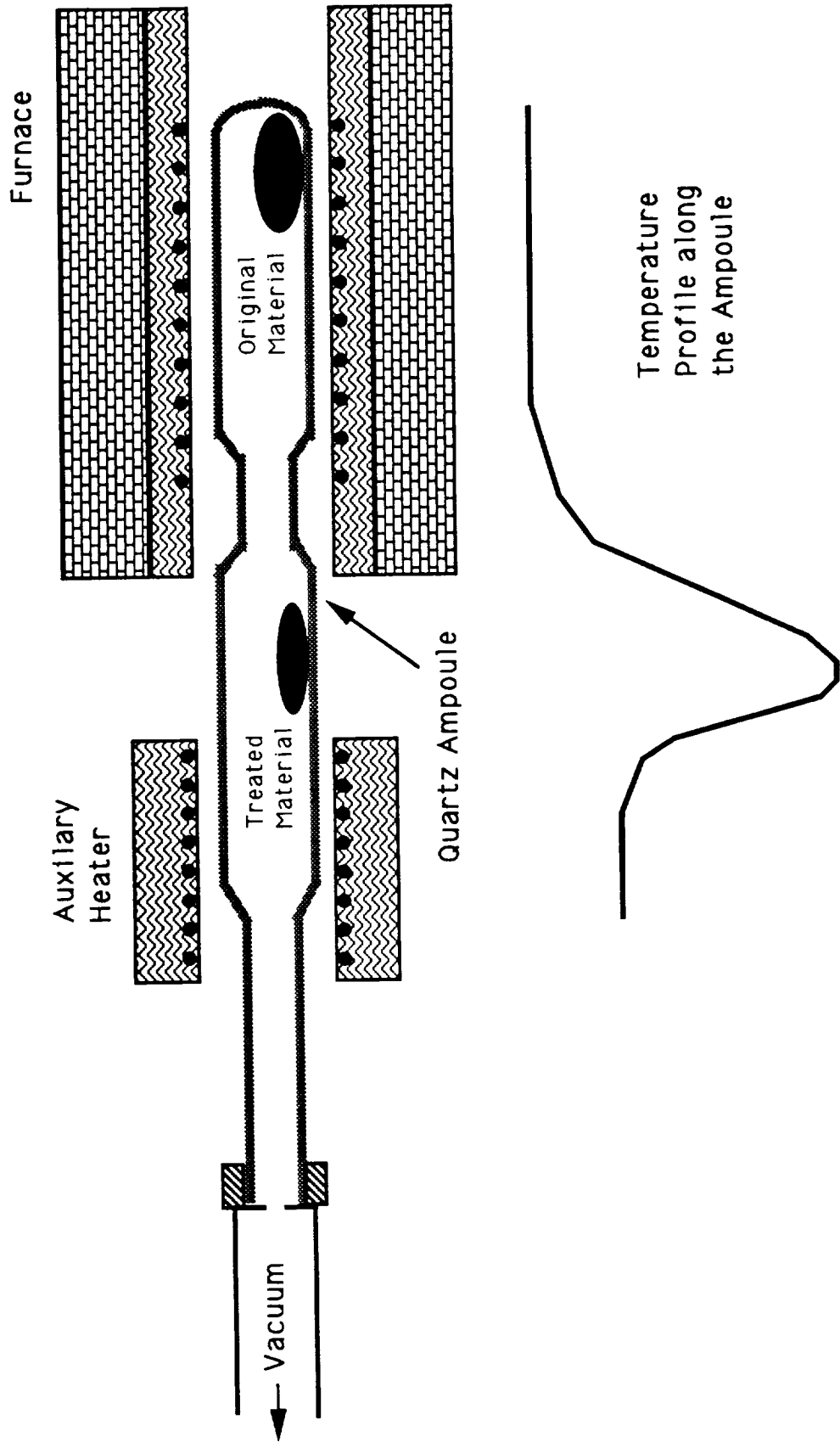


Figure 5

Illustration for Transport Measurement of ZnSe

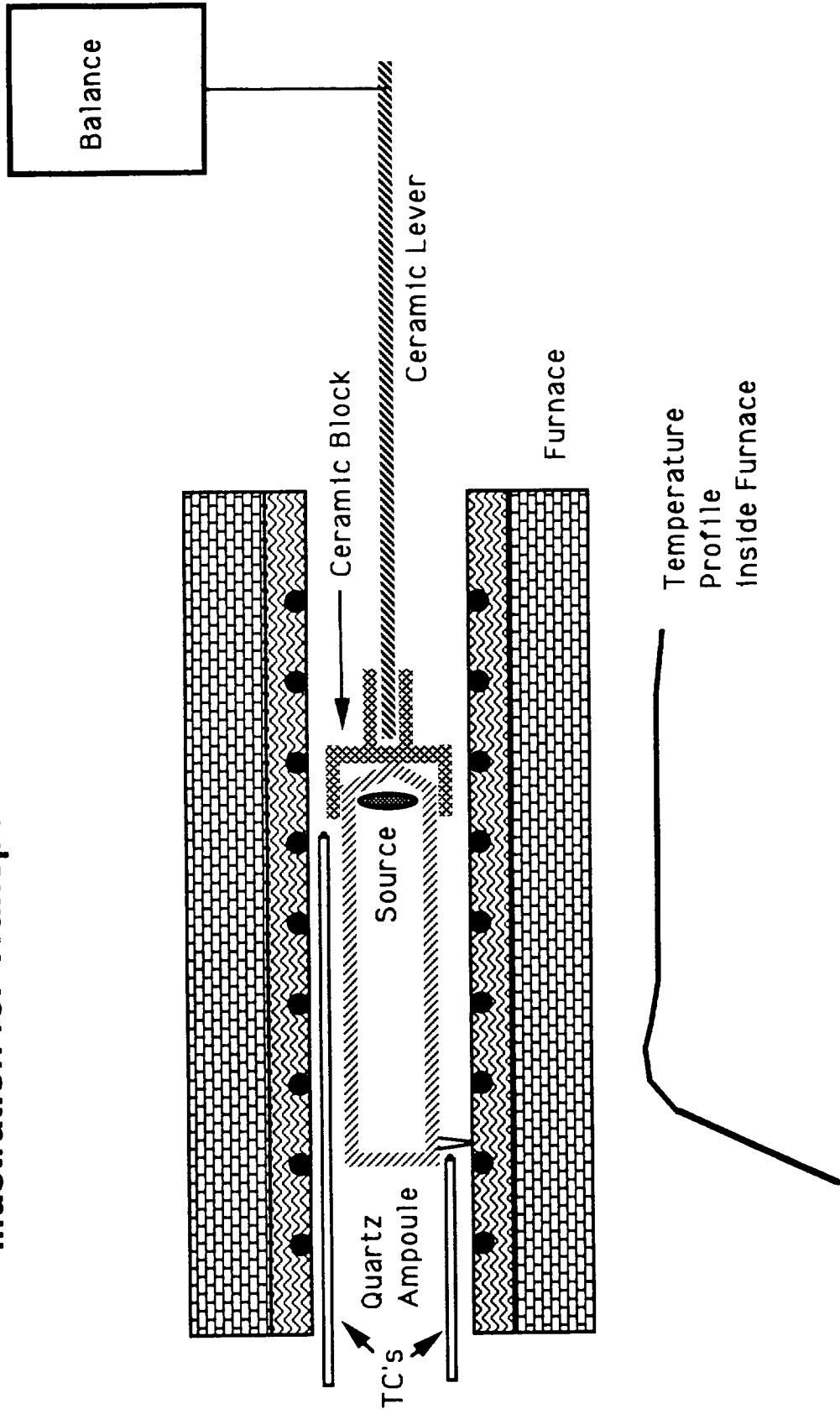


Figure 6

ZnSe Transport Results (ZST-2) with baseline correction

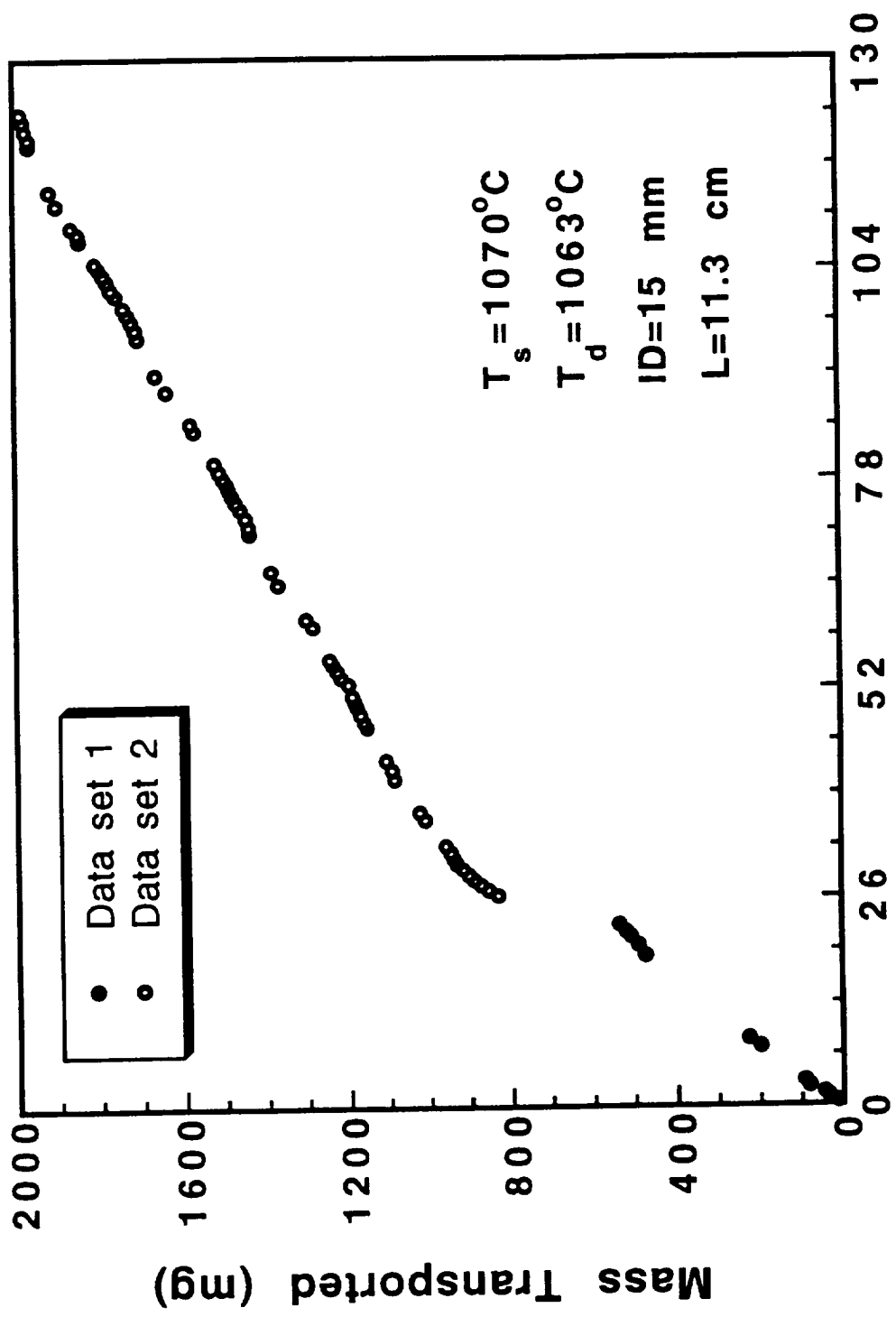


Figure 7

ZnSe Mass Transport Rate (ZST-2)

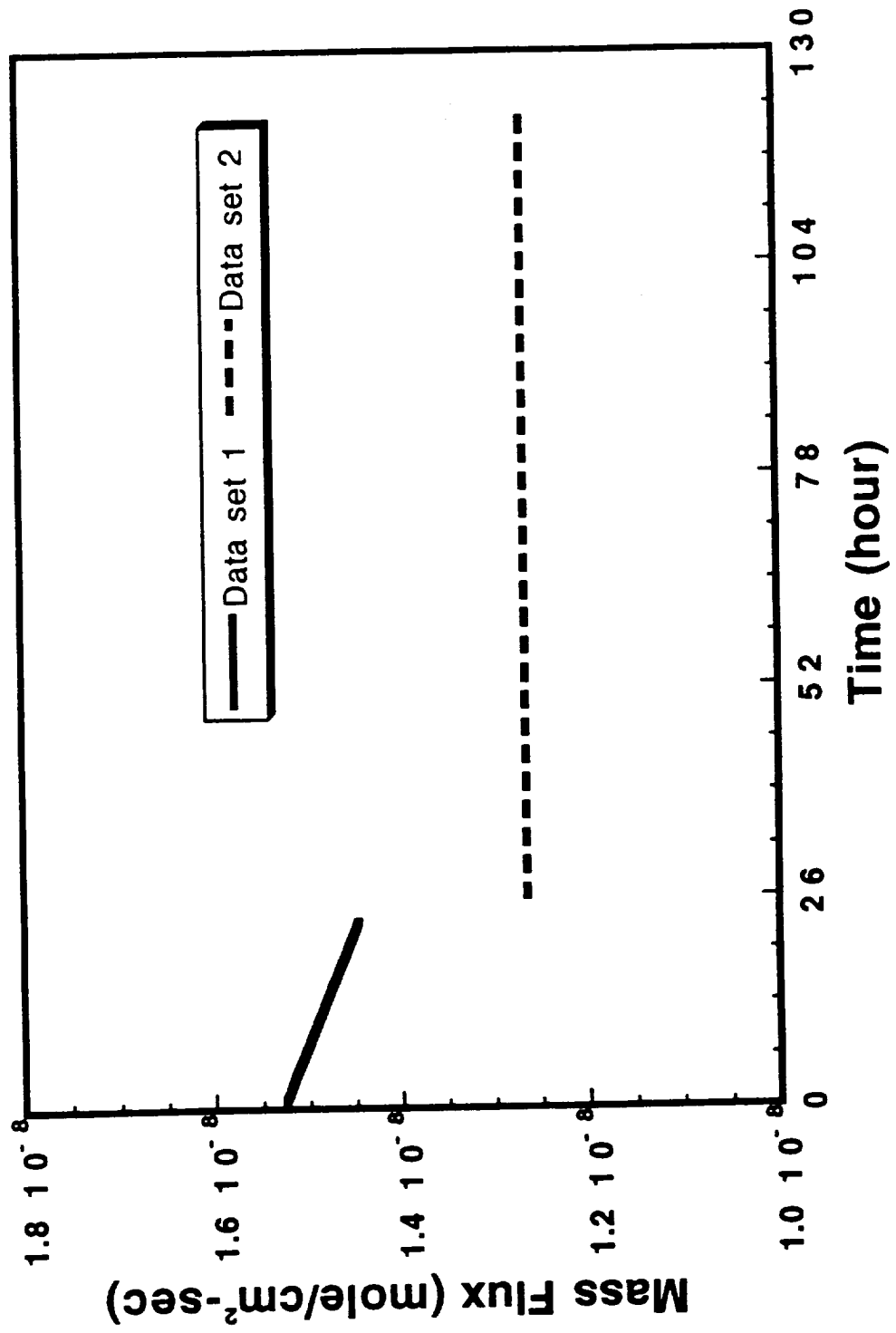


Figure 8

ZnSe Transport Results (ZST-4)

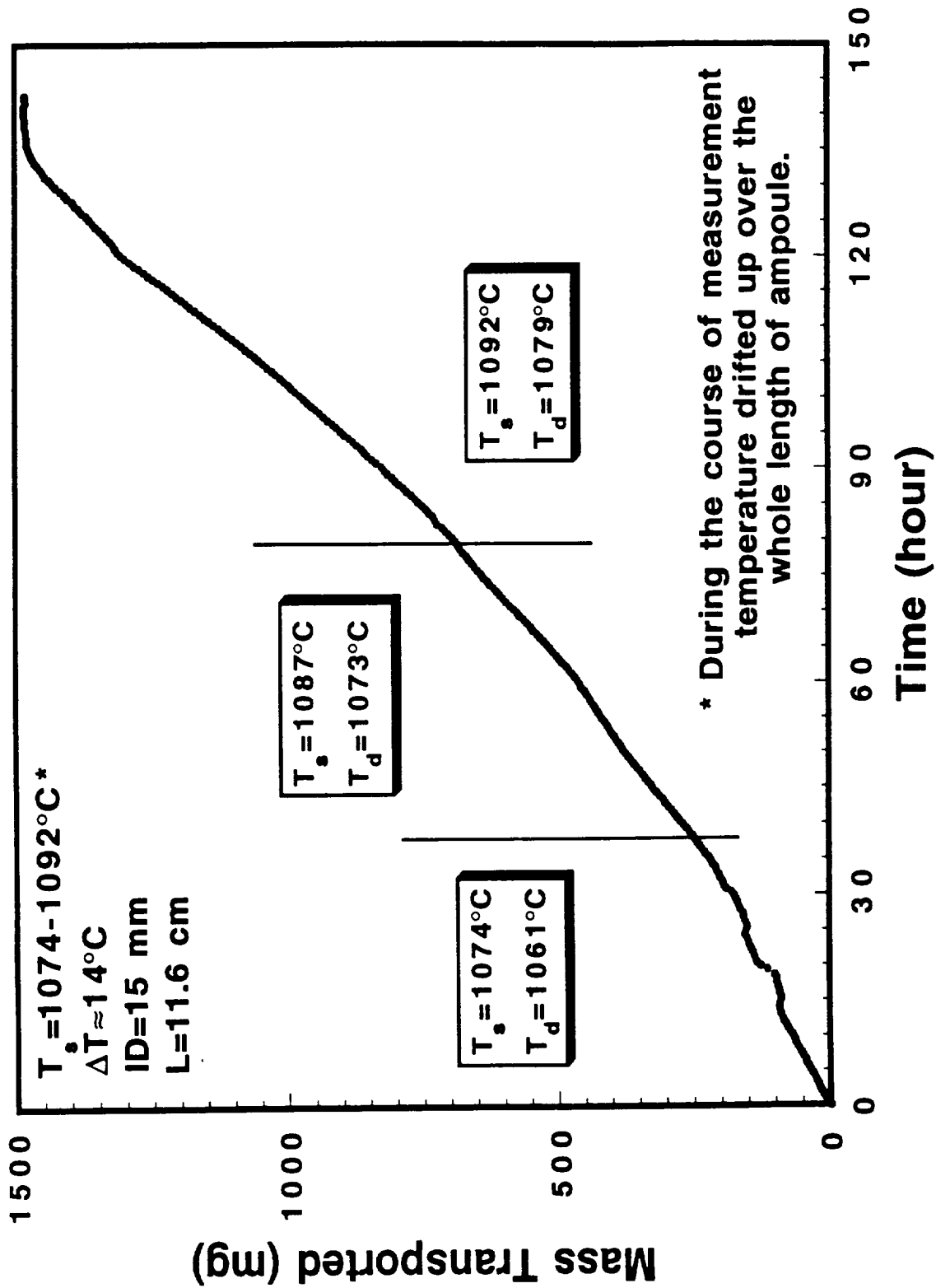


Figure 9

ZnSe Mass Transport Rate (ZST-4)

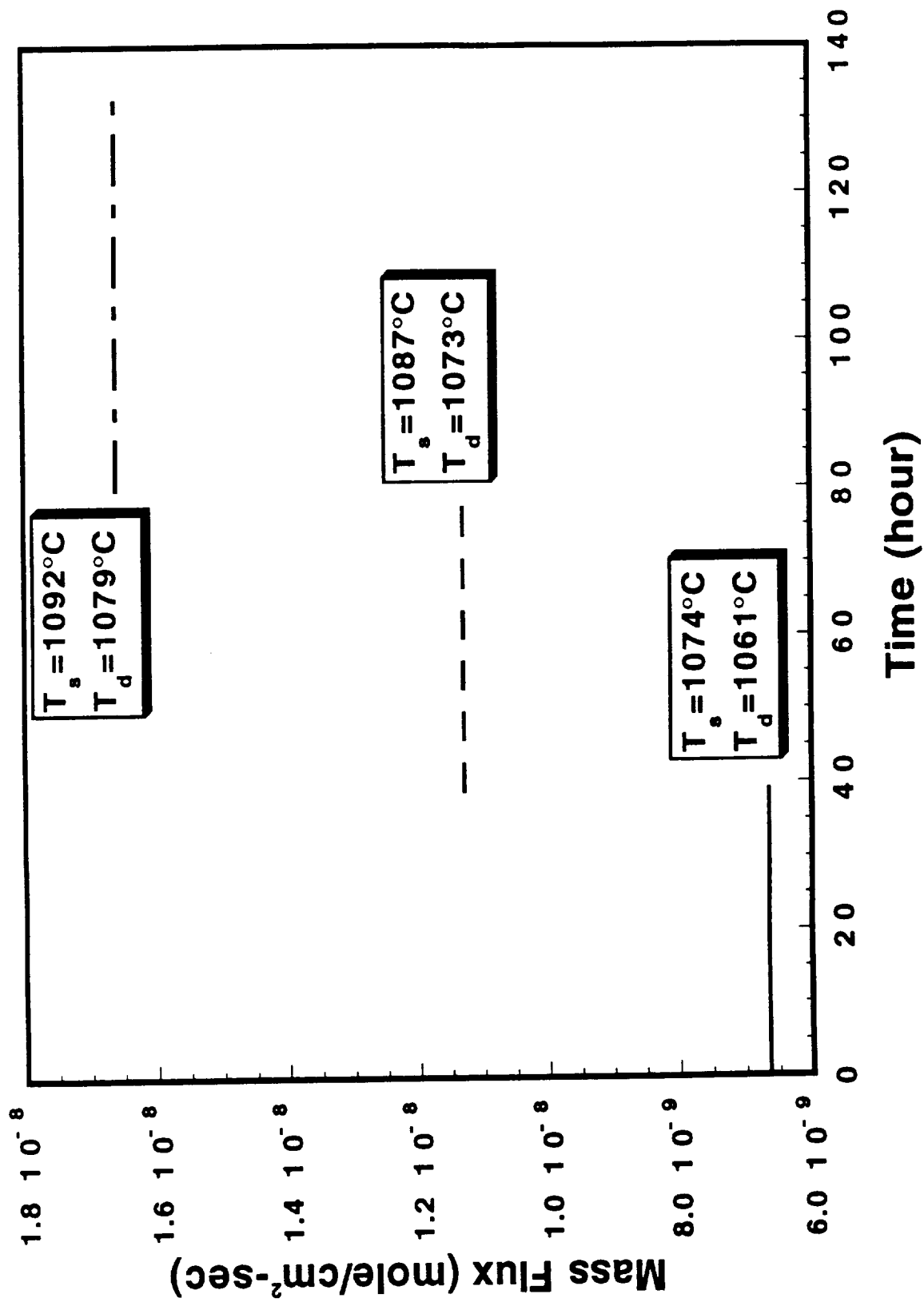


Figure 10

ZnSe Transport Results (ZST-4, run 2)

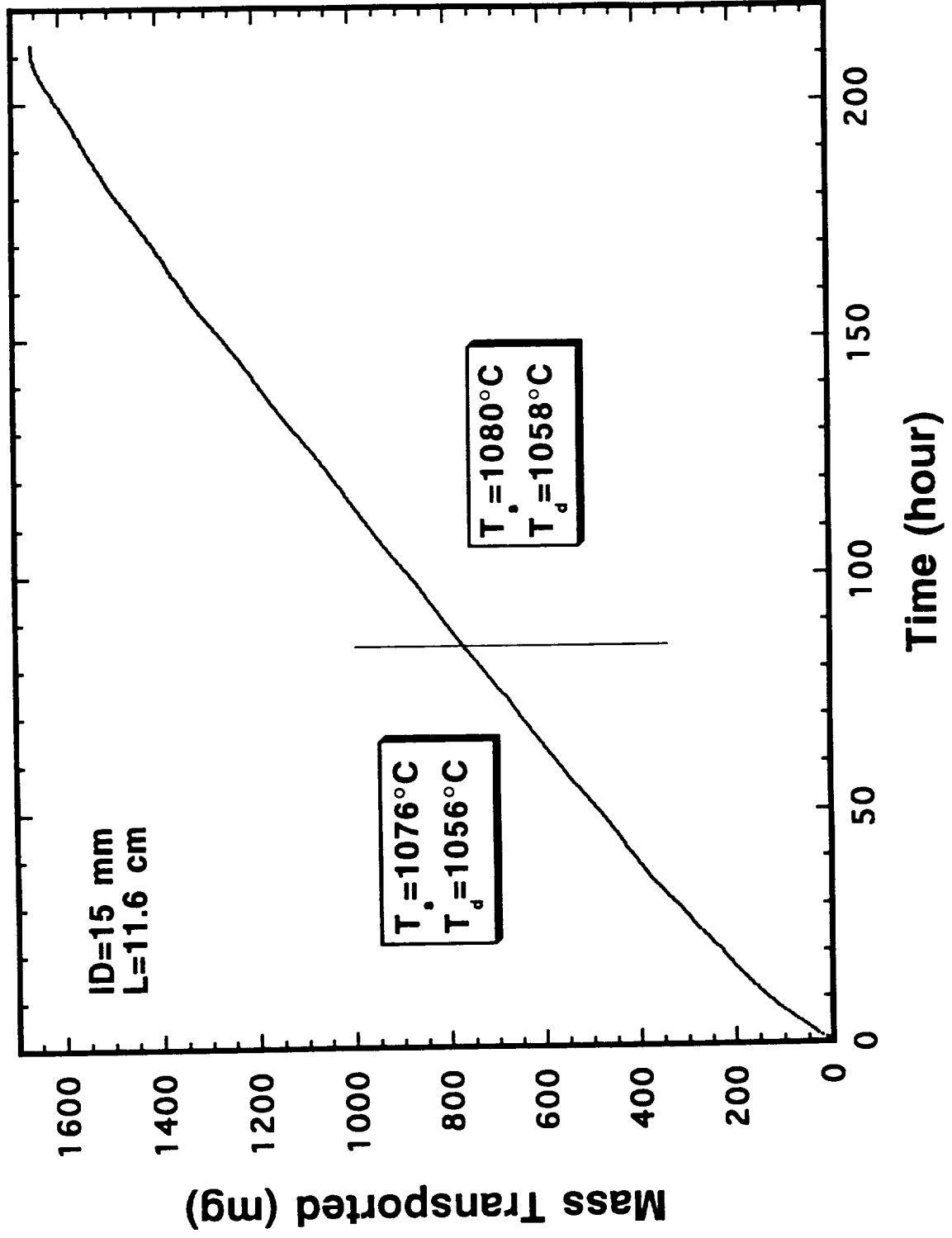


Figure 11

ZnSe Mass Transport Rate (ZST-4)

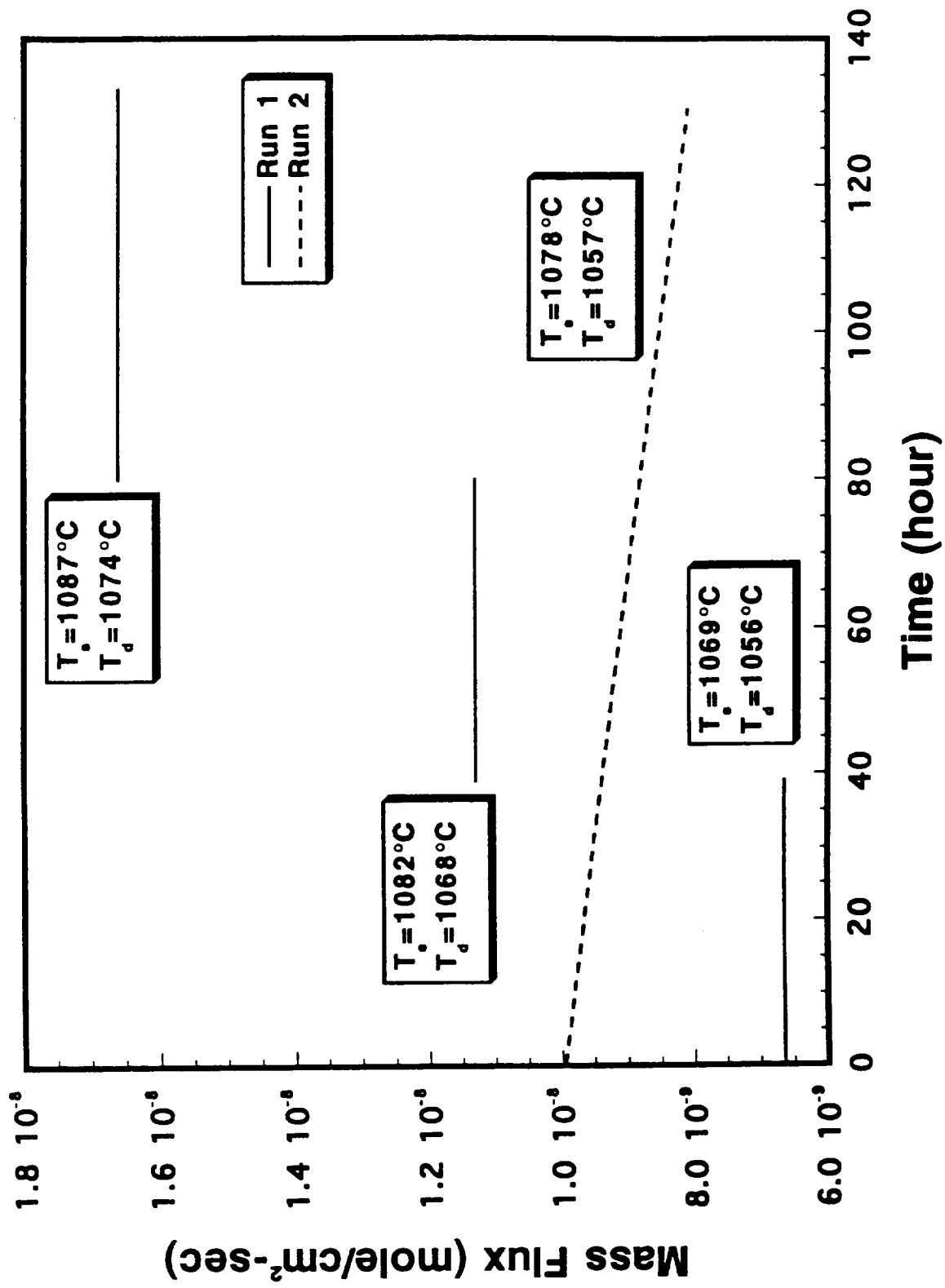


Figure 12

ZST-4

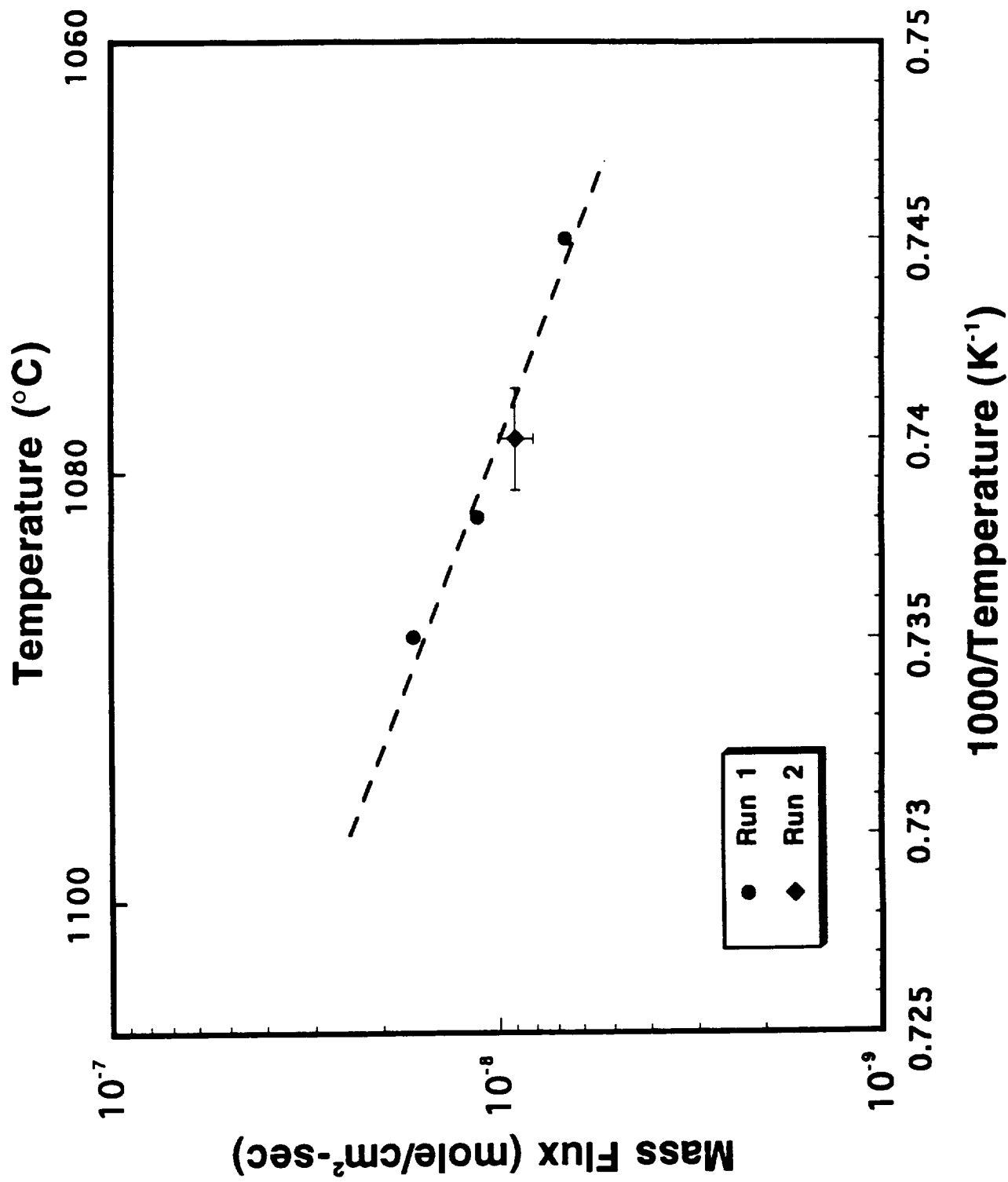


Figure 13

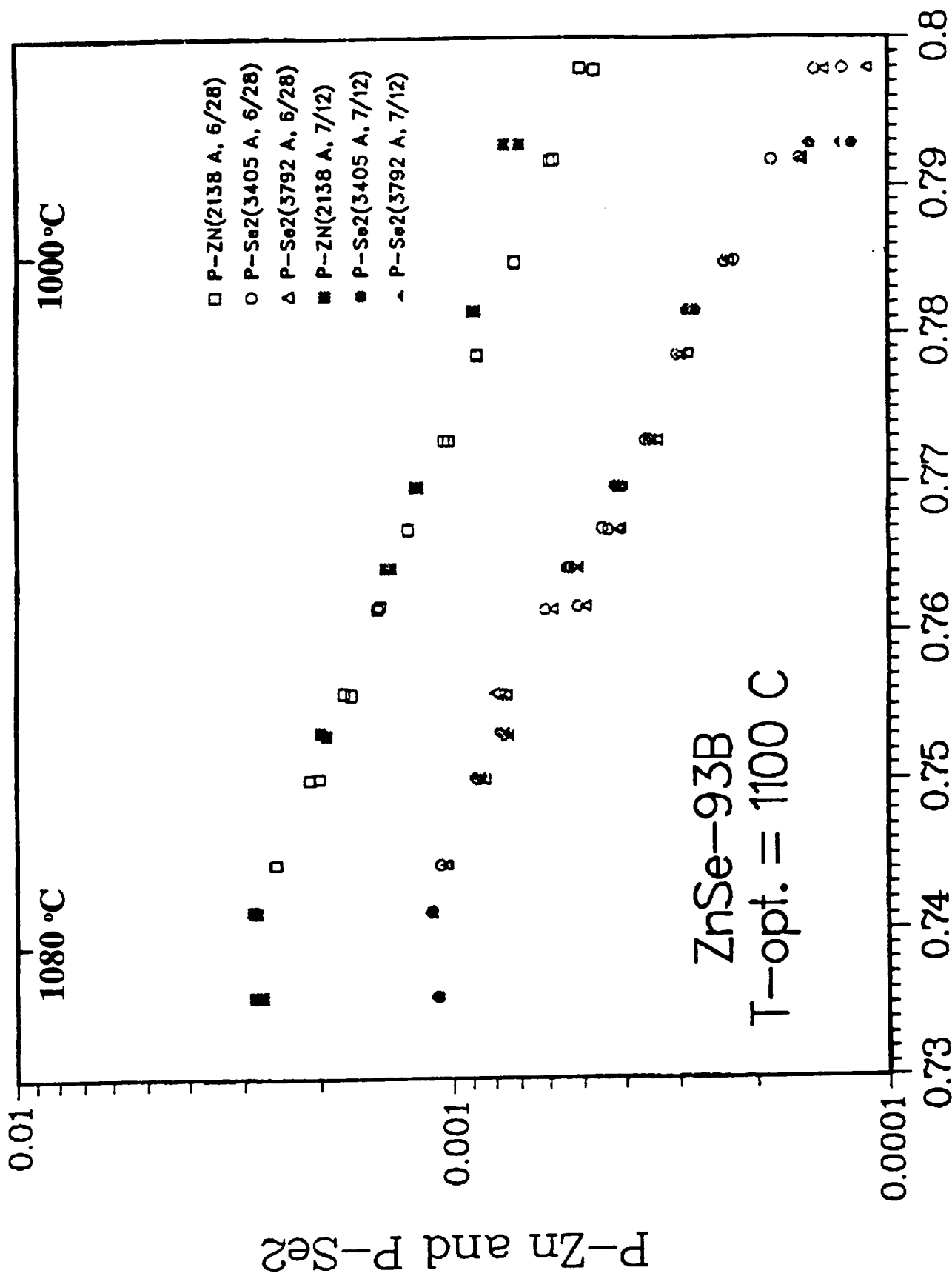


Figure 14

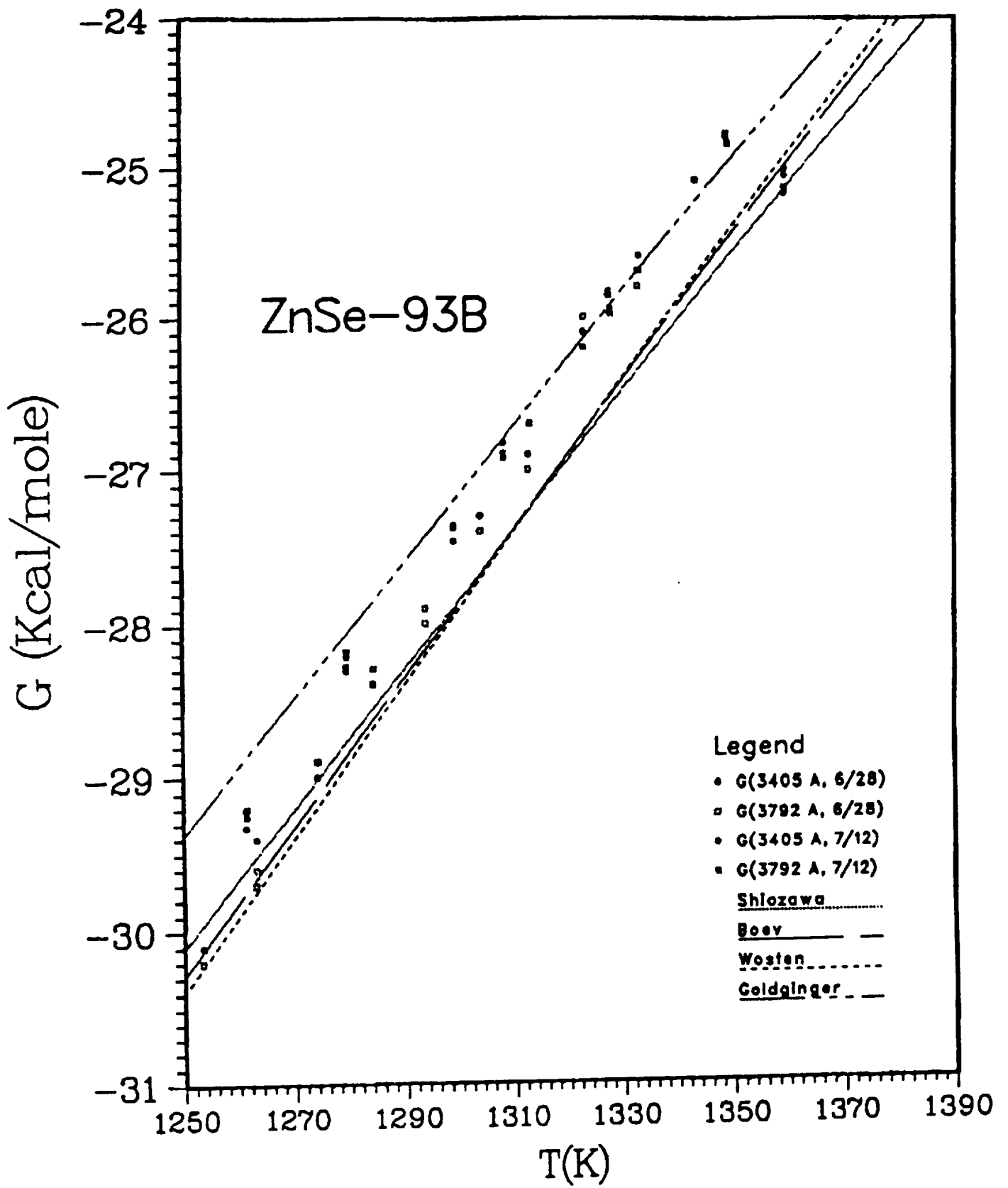


Figure 15

Illustration for Simultaneous Measurement of Transport Rate and Partial Pressure

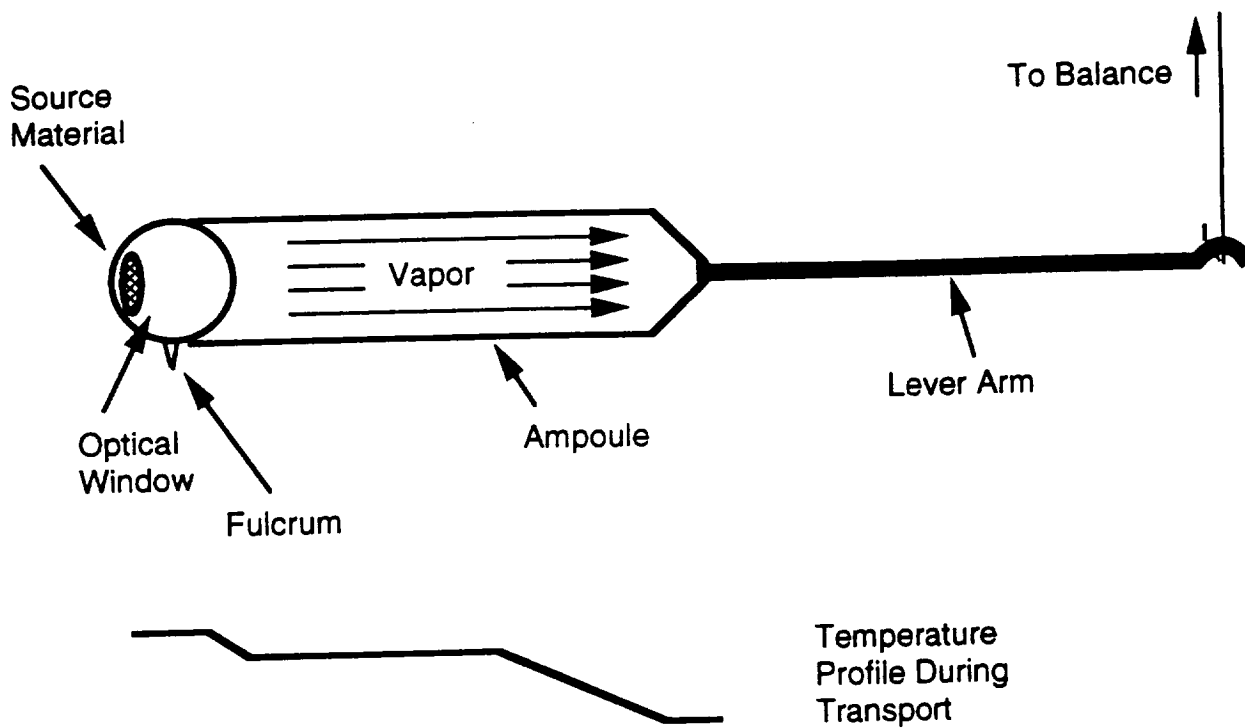


Figure 16

ES002

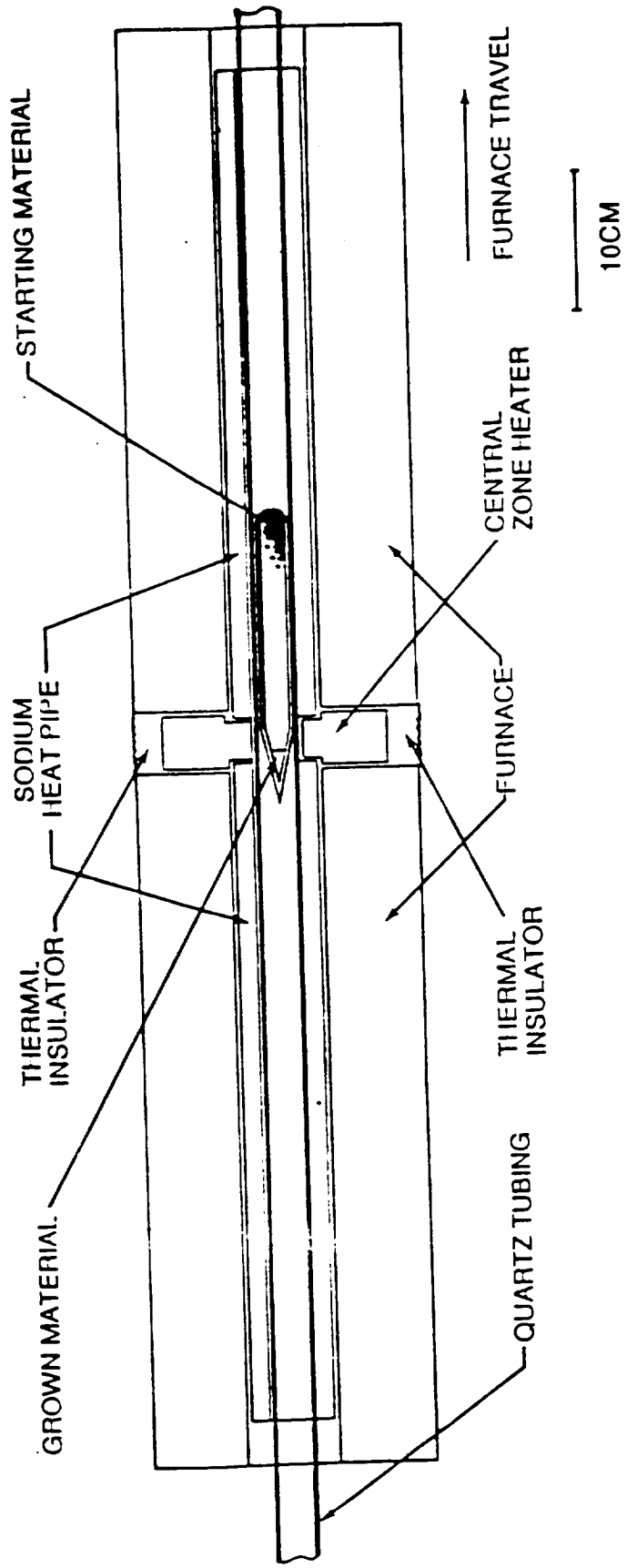


Figure 17

Thermal Profile for ZnSe-5

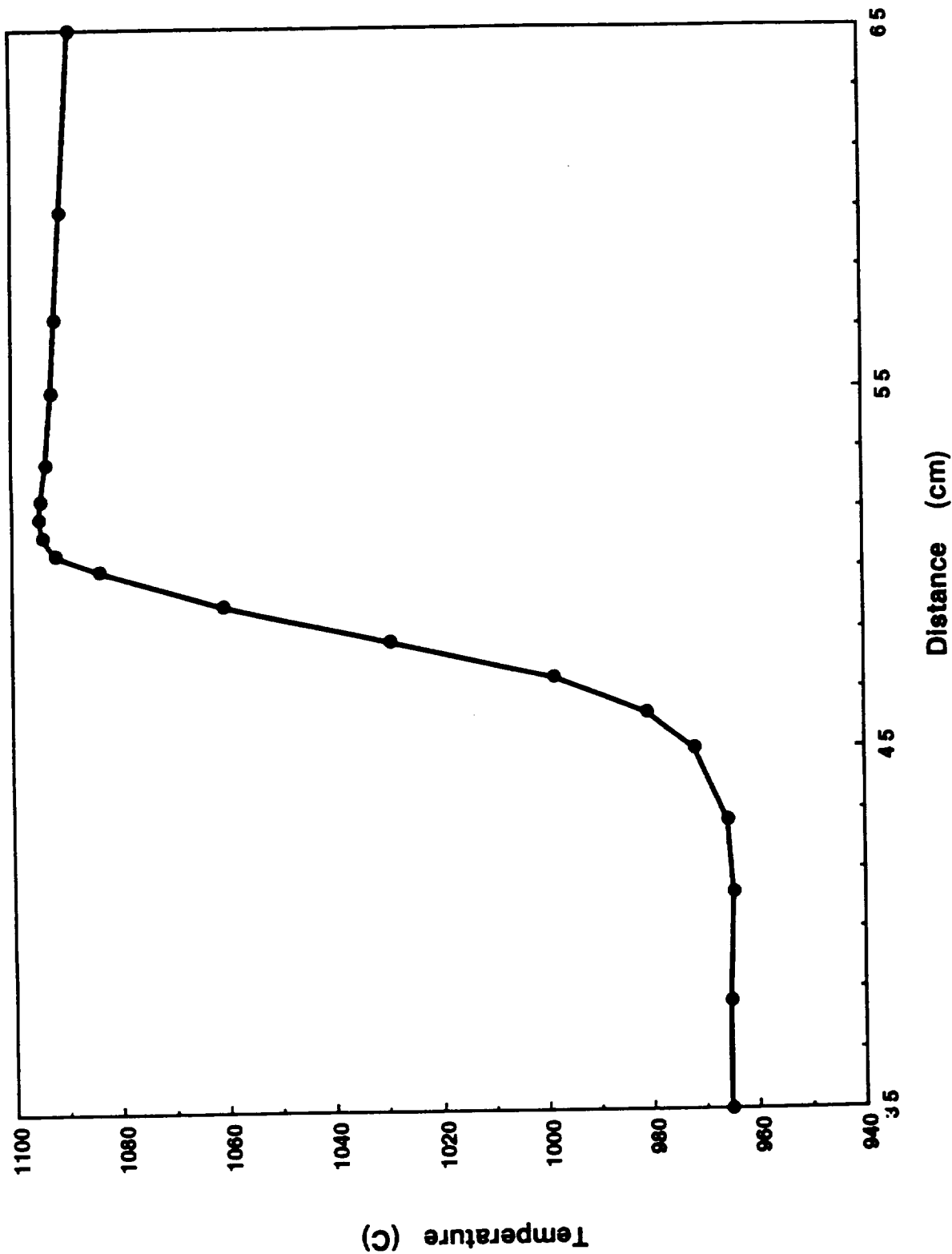


Figure 18

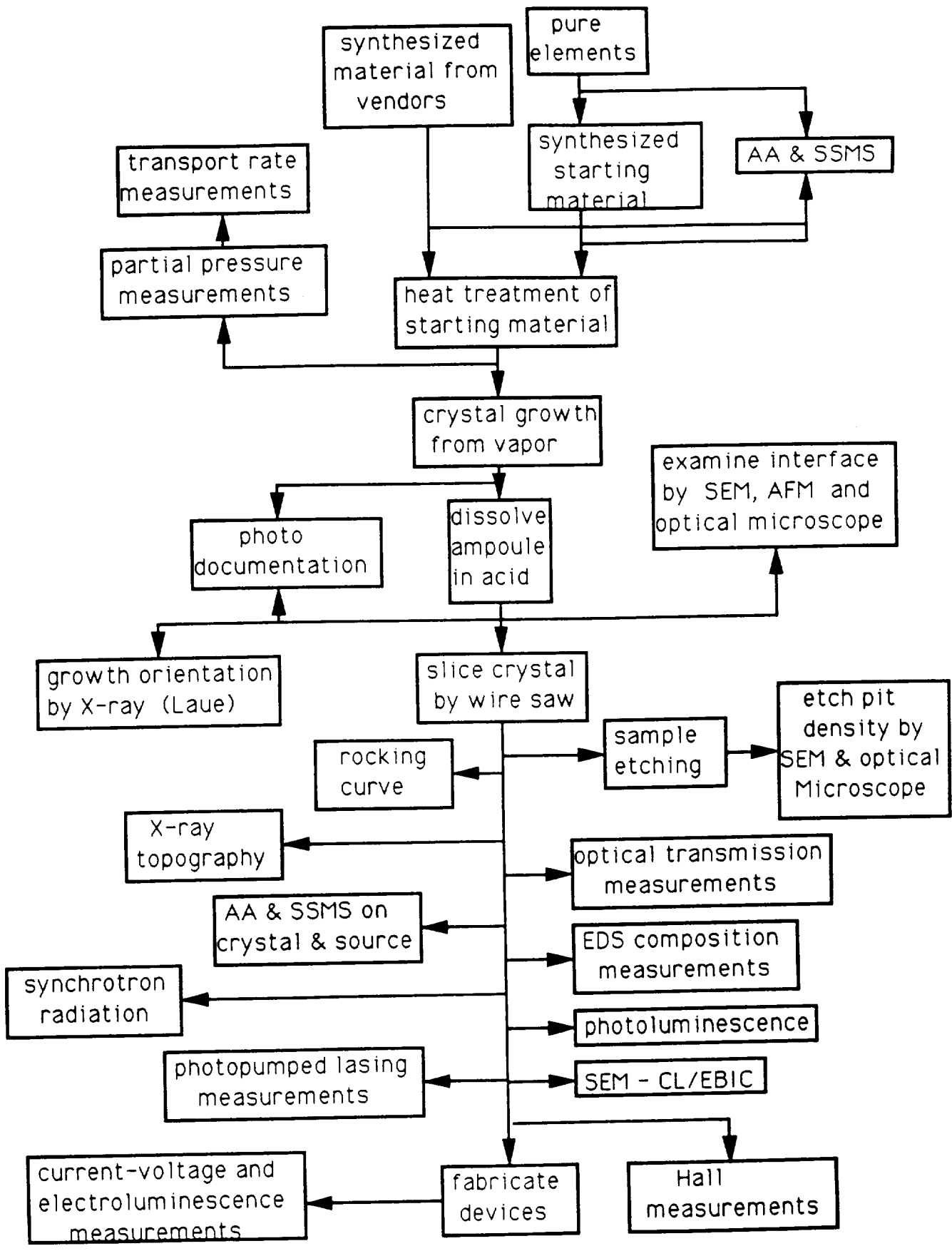


Figure 19 Flow chart of characterization plan

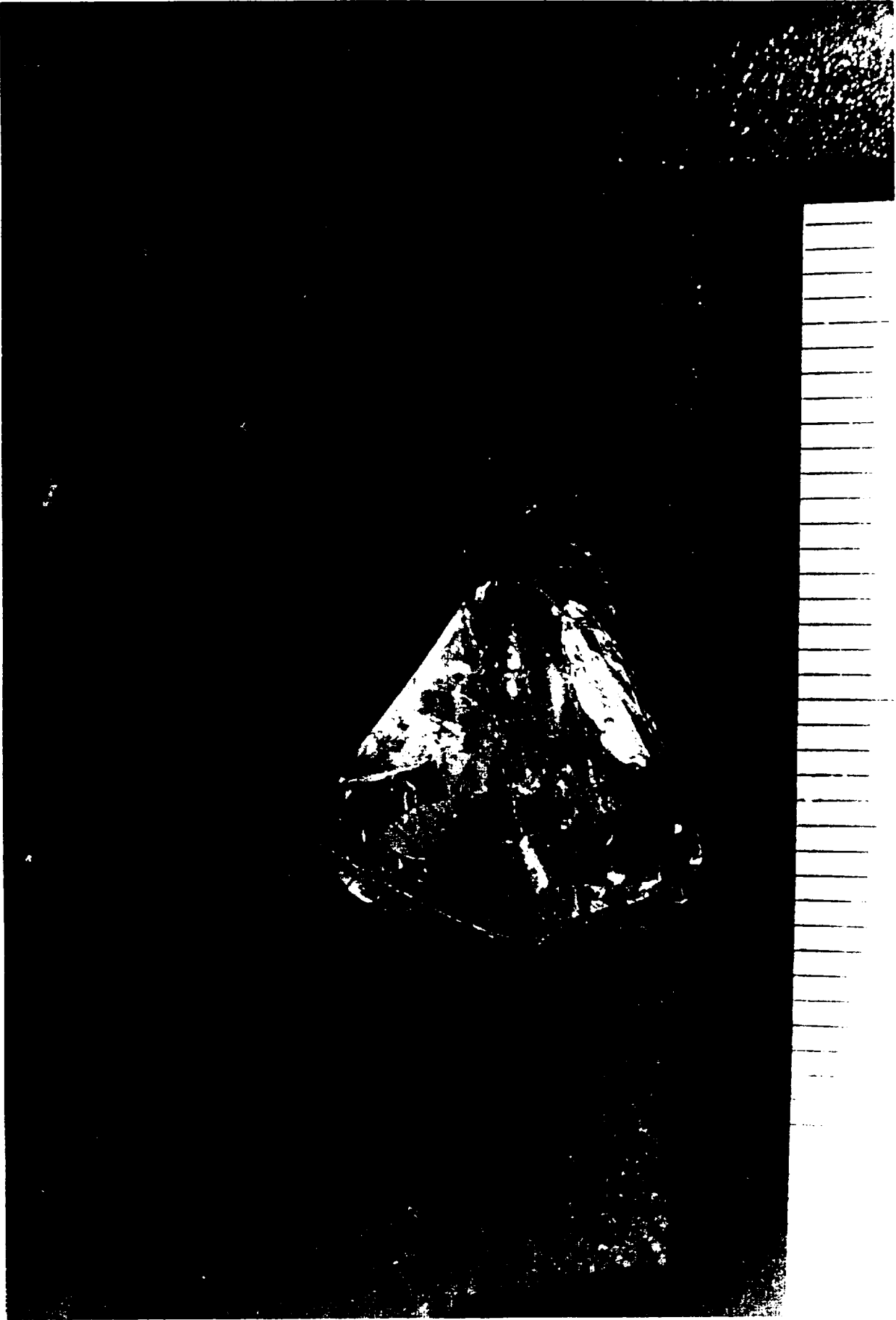


Figure 20

ZnSe-6 Clear.

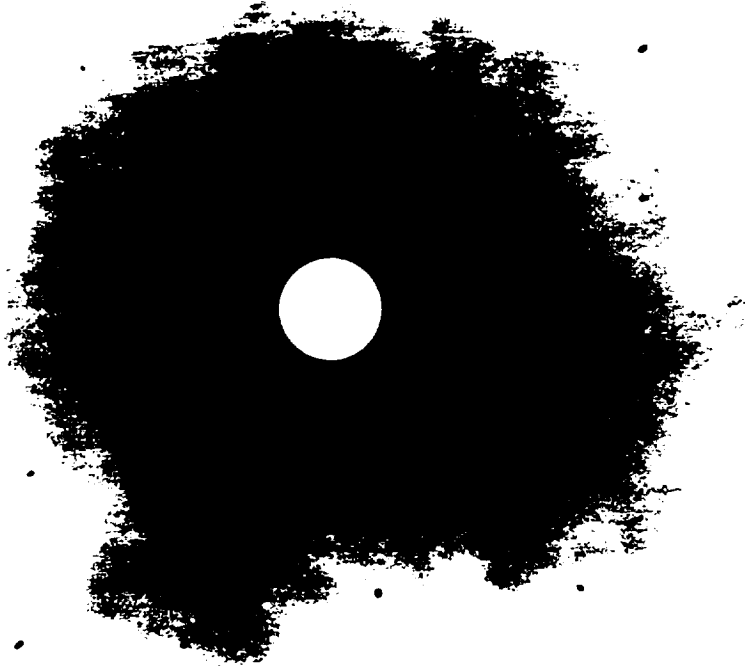


Figure 21

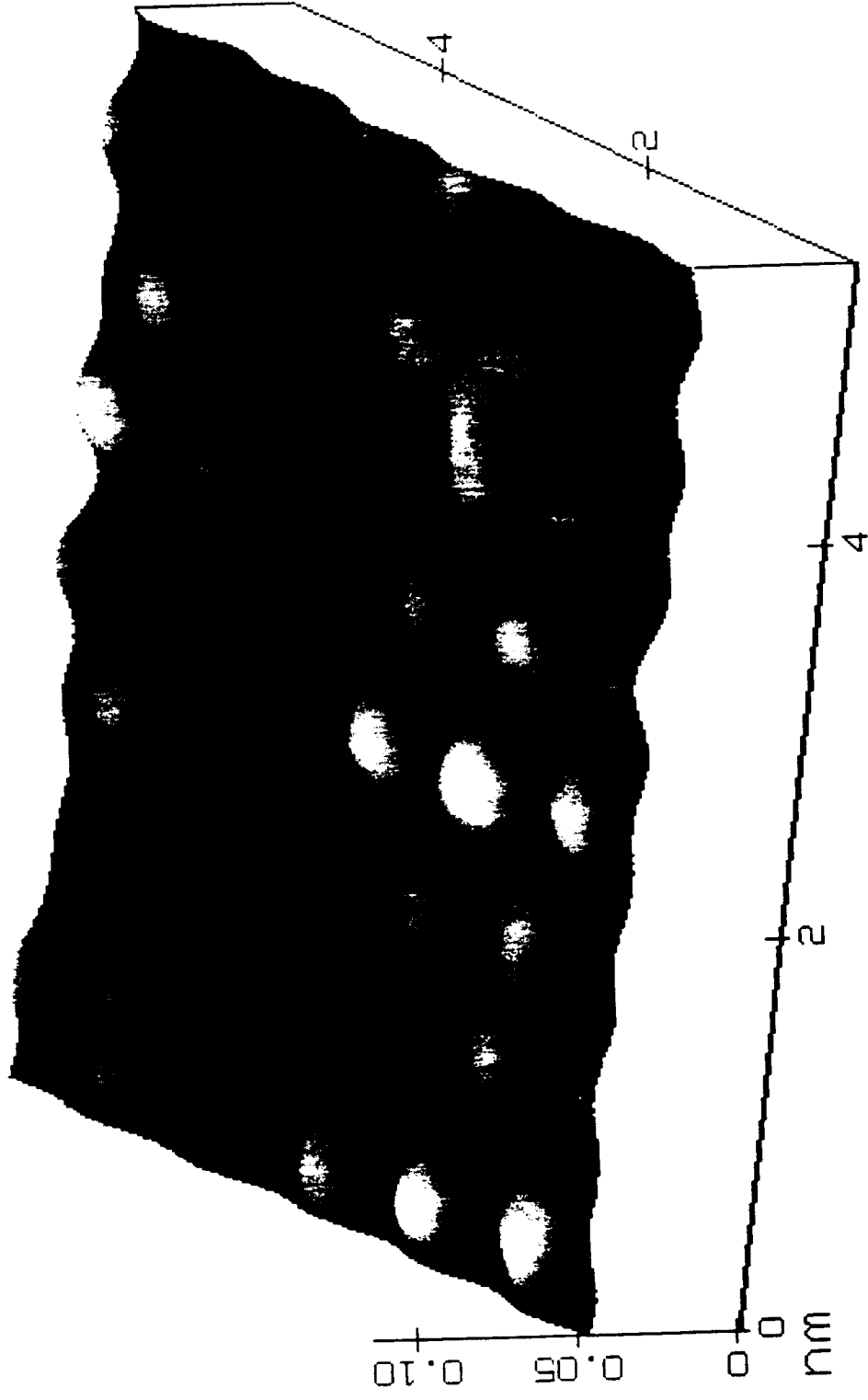


Figure 22 **Atoms on a ZnSe surface**

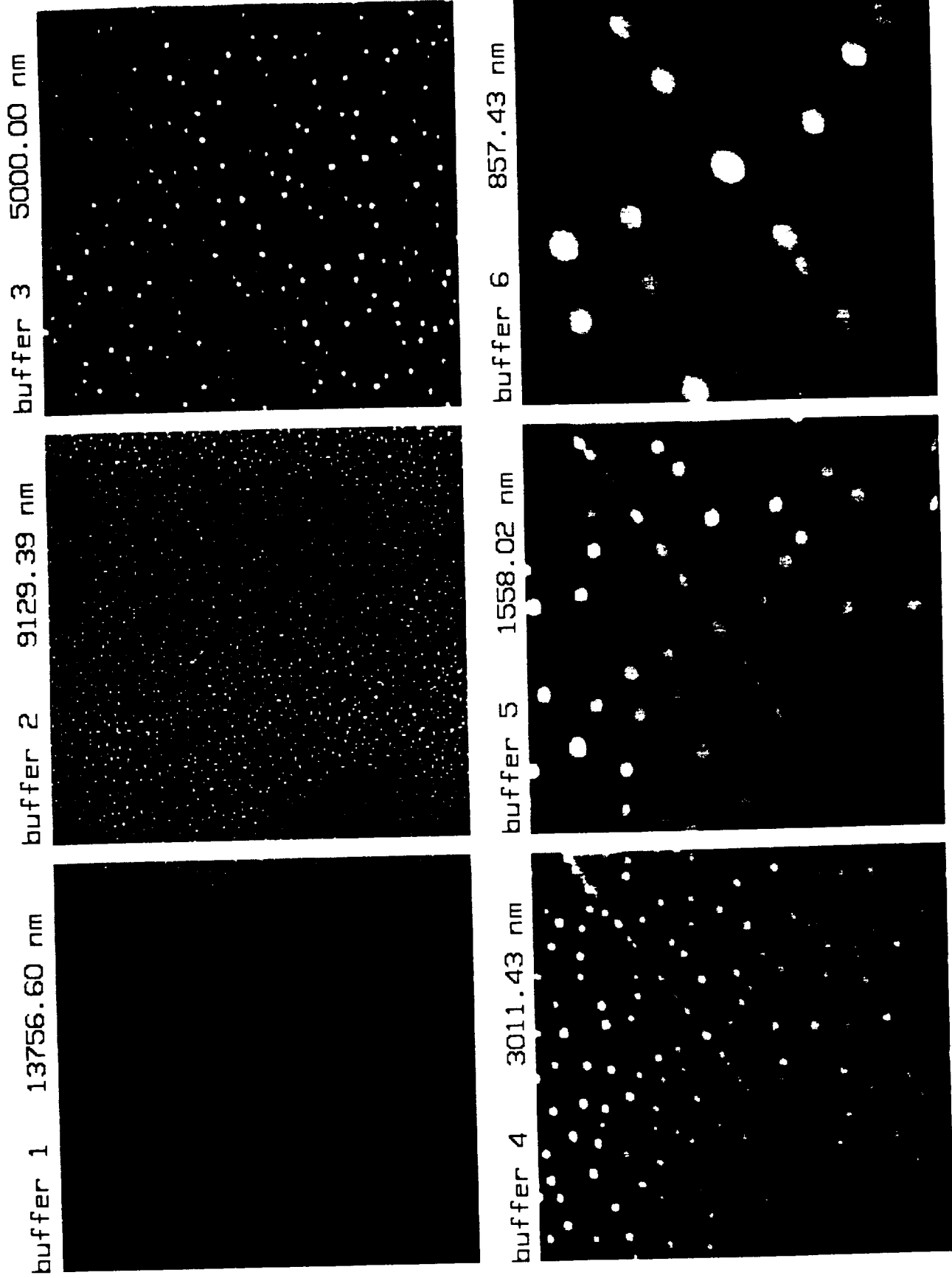


Figure 23 **Freshly cleaved ZnSe showing precipitates**

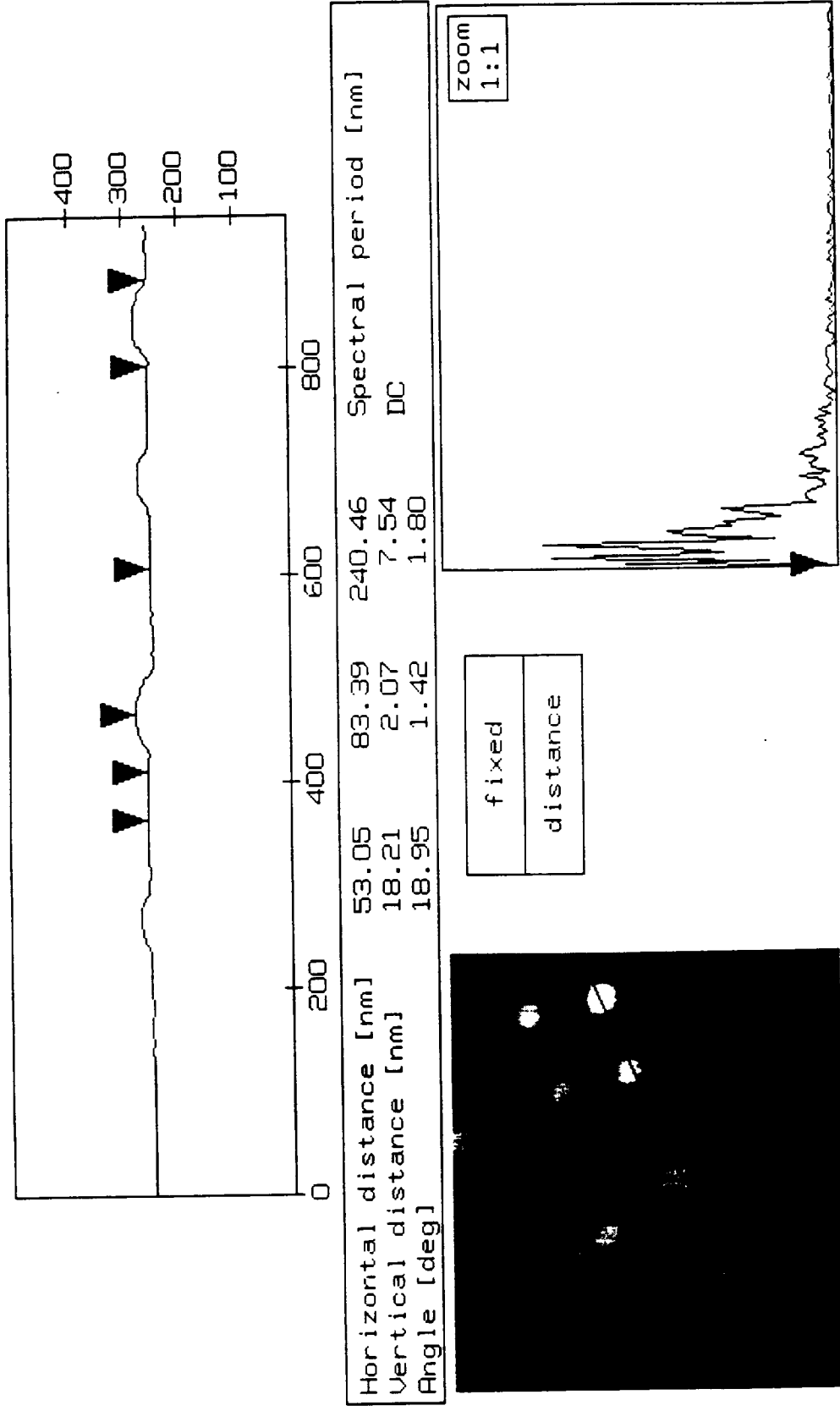


Figure 24

Cleaved ZnSe surface, profile of precipitates

10 kV

19 mm

x 3000

5 μm

Z
25943
22511
21899

2

ZnSe-6



Figure 25

DSC OUTPUT

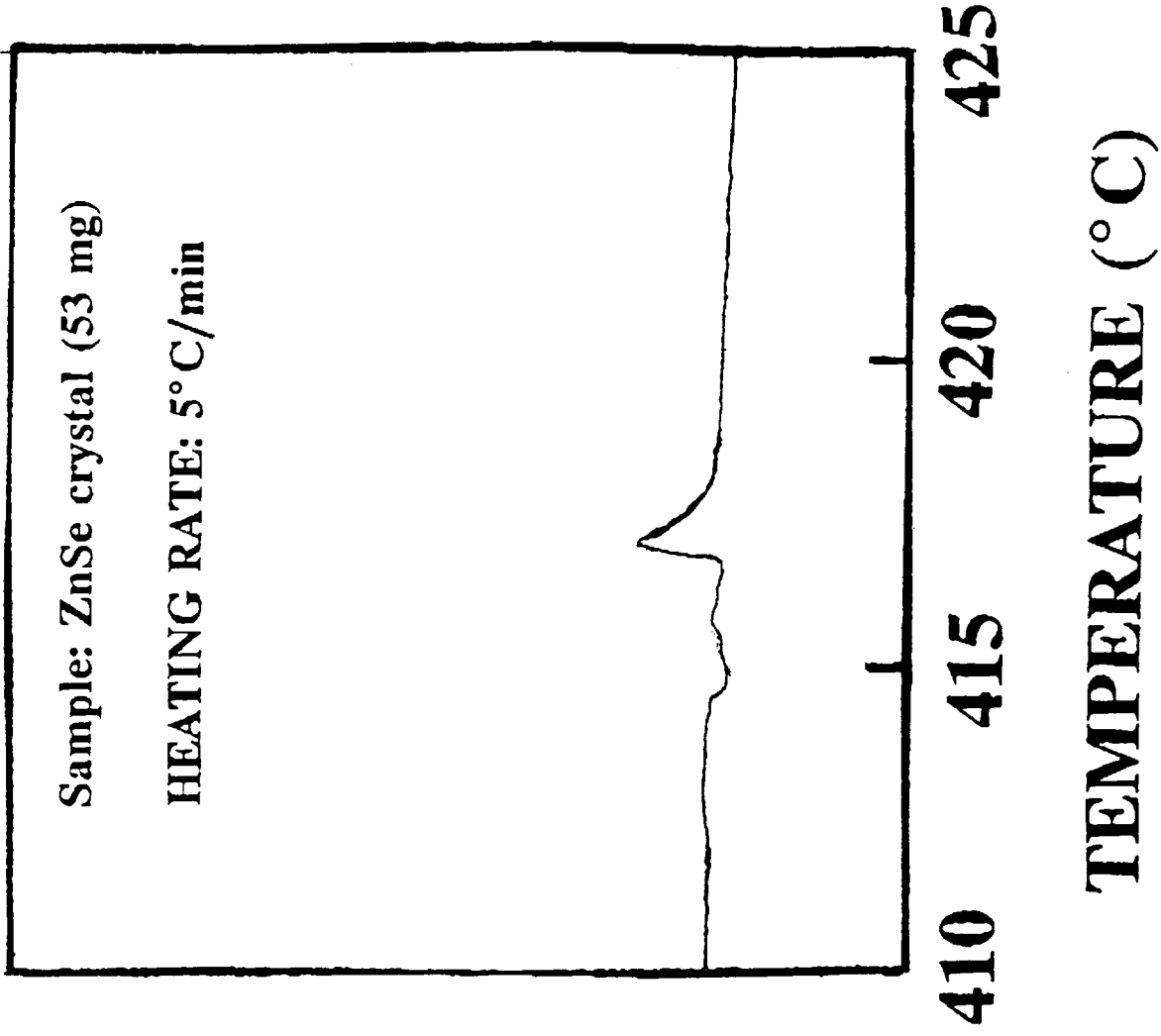
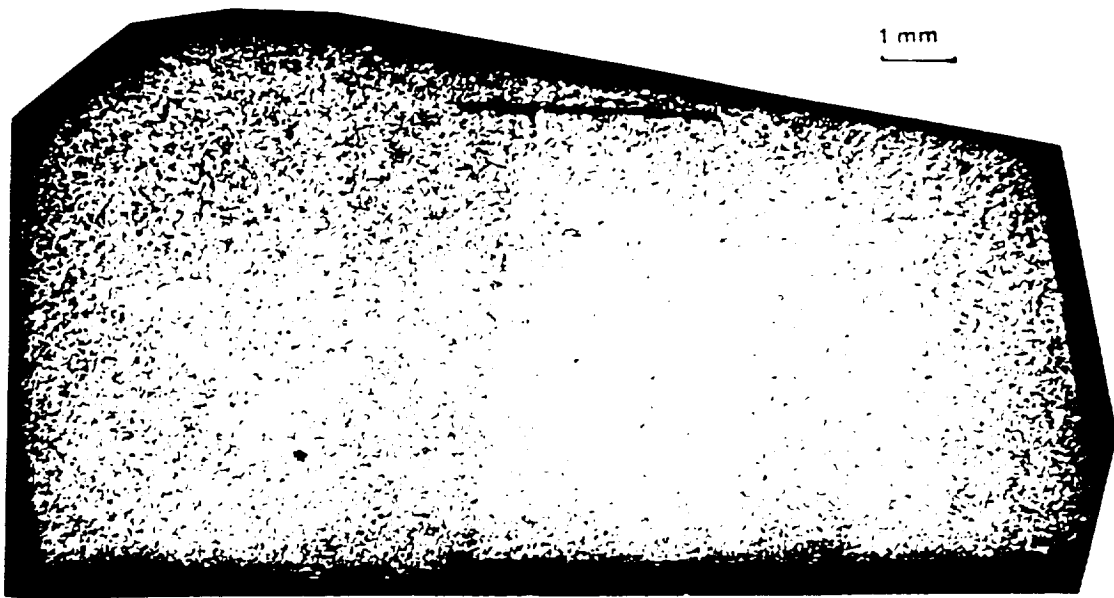


Figure 26



ZnSe - 6 Optical Microscope (after polish and etch in 2% Br Ethylene Glycol)



1 mm

Reflection Topograph



Figure 27

Transmission Topograph