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VAPOR GROWTH OF GeSe AND GeTe SINGLE CRYSTALS IN MICRO-GRAVITY

By

H. Wiedemeier*, F. C. Klaessig , S. J. Wey and E. A. Irene
Department of Chemistry, Rensselaer Polytechnic Institute
Troy, New York 12181

SUMMARY

The positive effects of micro-gravity on crystal growth and fundamental properties of the vapor transport reaction were established by analyzing the results of GeSe and GeTe vapor transport experiments performed on board Skylab.

The analysis is based on a direct comparison of GeSe and GeTe crystals and of mass transport rate data obtained on earth and in space. For this purpose, a total of six transport experiments employing different concentrations of transport agent (GeI_4) and two temperature gradients were performed during the Skylab 3 and 4 missions. Extensive ground-based studies demonstrated that the crystal morphology and the mass transport rates of the above systems are affected by the transport conditions, in particular by gravity-driven convection. With increasing contribution of the convective component to the transport process the crystal quality decreases. This shows that on earth the negative effects of convection can only be minimized but not eliminated. The analysis of space and ground crystals is based on a comparison of deposition patterns, growth habits, optical and scanning electron microscopy of as-grown and cleaved crystal faces and thermal etching. The results demonstrate unambiguously a considerable improvement of the space crystals in terms of surface perfection, crystalline homogeneity and defect density. The observation of greater mass transport rates than expected in micro-gravity environment is of basic scientific and technological significance. This indicates that conventional transport models are incomplete and demonstrates that crystals of improved quality can be grown at reasonable rates by this technique in space. These results are of practical importance for the modification of crystal growth techniques on earth.

The combined results confirm the unique conditions of weightlessness for materials processing and for the observation of basic transport phenomena.

INTRODUCTION

Crystal growth by vapor transport is of technological importance in the production of bulk and layer type single crystalline materials used in various

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*Paper presented by H. Wiedemeier.

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electronic devices. It is well established that the properties and performance characteristics of materials are critically dependent on the degree of homogeneity and crystalline perfection which, in turn, are affected by the transport conditions and condensation mechanism of a particular system. Control of these growth parameters under ground-based conditions is limited due to the presence of gravity-driven convective motion in the gas phase.

Crystal growth studies without convective interference in a micro-gravity environment should yield fundamental data for the vapor transport technique and reveal the inherent transport properties of a chemical system. This basic information obtained from the space experiments will enhance our understanding of crystal growth phenomena and will be useful for the improvement of crystal growth techniques on earth. Due to its inherent simplicity in terms of a defined solid-gas phase system, the vapor transport technique is well suited to observe micro-gravity effects and other unexpected phenomena.

This report contains the results of the present evaluation of six crystal growth experiments performed during the Skylab 3 and 4 missions. Four of these experiments were concerned with the growth of GeSe and two of GeTe crystals. Although these systems are presently of limited interest as electronic device materials, their structural properties are favorable for the detection of morphological changes. The conclusions drawn from these exploratory space experiments are readily adaptable to the growth of crystals of other electronic materials.

EXPERIMENT OXJECTIVES

The primary objective of our crystal growth experiments in space was to observe and to measure changes in the mass transport rate of a chemical system and in the morphology of crystals of IV-VI compounds. In the absence of gravity-driven convection and for given experimental conditions, the transport should be controlled by the thermochemical parameters of the solid-gas phase reaction. The crystal habit and morphology should be primarily determined by the crystallographic properties of the respective crystal structures. In addition, information concerning the number and distribution of crystal defects is expected from these experiments.

In view of the structural and thermochemical properties of these materials, any micro-gravity effects on the above parameters should be more pronounced for the GeSe system than for GeTe. The platelet type growth habit of GeSe is very suitable for microscopic and electrical measurements. In addition, thermal etching techniques have been developed for this material in our laboratory. The multi-purpose furnace available for crystal growth on Skylab required the use of a common temperature gradient and heating cycle for a set of three ampules. For this reason, the conditions for the space experiment were selected to yield optimal results for GeSe and supporting data from the GeTe system. The definition of these conditions and the suitability of the above materials for crystal growth in space are based on extensive ground-based studies in our laboratory.

GROUND-BASED STUDIES

Scientific Basis

In a chemical transport reaction [1], a gaseous transport agent reacts at a given temperature with the solid source material to form exclusively gaseous products. The vapor species migrate from the source to the condensation zone of the reaction vessel where, at a different temperature, the reverse reaction occurs with formation of the solid. The necessary concentration gradient is established by means of a temperature gradient. Under optimal experimental conditions well defined single crystals are formed by the condensation reaction. The transport reaction is carried out in evacuated sealed ampules of fused silica which are subjected to the desired temperature gradient in a horizontal two-zone tubular resistance furnace.

The transport of species via the gas phase can be described by diffusion and by gravity-driven convection. In a gravitational field and temperature gradient both transport modes occur simultaneously. It is a unique feature of the vapor transport technique to select experimental conditions such that one or the other mode can be predominant. Under ground-based conditions, the convective contribution to the overall transport process can be minimized, but not eliminated. Based on present models for diffusive and convective gas flow [1], the material flux from the source to the condensation region is affected by the pressure in the transport ampule. At very low pressures of transport agent, the mass transport rate is controlled by the rate of the heterogeneous solid-gas phase reaction, and the material flux is proportional to the concentration of transport agent. At medium pressures, the transport rate is inversely proportional to the total pressure. The overall transport is diffusion controlled in this range. At higher pressures, the material flux increases with increasing total pressure indicating the predominance of the convective transport mode. For the diffusion and convection controlled pressure regions, the heterogeneous solid-gas phase reactions in the source and condensation zone are in the state of near-equilibrium.

Transport Properties of GeSe and GeTe

Mass transport rate studies in our laboratory on GeTe [2] and GeSe [3] using elemental iodine or GeI_4 as the transport agent have confirmed the above models. Details of the experimental procedures and results have been discussed previously [2,3]. These studies demonstrated that the habit and morphology of single crystals grown by this technique are significantly affected by the transport conditions. With increasing contribution of the convective component to the transport process the crystal quality decreases. For GeTe, the crystal habit changes from octahedral bulk type crystals via distorted and hollow octahedra to platelets with nearly macroscopic surface imperfections. The corresponding morphological changes for GeSe from platelet to dendritic type crystal growth are even more pronounced. These observations are explained by gravity-driven convection which causes inhomogeneities and turbulence in the gas phase and negative effects on the condensation process and crystal morphology. The convective component is always operative on earth in the vapor transport system. The observed trend in the change of crystal quality suggests the possibility to grow nearly perfect crystals in zero-gravity environment. The experimental conditions of the above ground-based studies are the same as those employed in space, except for gravity.

EXPERIMENTAL SKYLAB PROCEDURES

The transport experiments were performed in the multi-purpose electric furnace built by the Westinghouse Electric Corporation. The furnace consisted essentially of a cylindrical furnace chamber and an instrumentation compartment. The furnace chamber contained three tubular reaction cavities for the individual metal cartridges and quartz ampules discussed below. Since the Westinghouse facility was a one-zone resistance furnace, the desired temperature gradient and stability were achieved by various heat shields surrounding the quartz ampules in the metal cartridges and by appropriate heat shields in the furnace. The temperature gradient used for the experiments performed during the SL 3 mission was 520 → 420°C with a nearly linear gradient between the hot and cold zone of the reaction chamber.

In order to increase the range of experimental conditions a temperature gradient of 412 → 346°C was employed for the second series of transport studies carried out on the SL 4 mission. The primary goal of the SL 4 experiments was to confirm the unexpected mass transport rates observed during the SL 3 mission discussed below. In addition, supporting evidence for the morphological changes in crystal habit was expected.

The transport ampules were made of fused silica tubing of 13.7 mm inner diameter and 150 mm in length. Close to one end the ampule contained three shallow indentations to hold the source material in place. The other ampule end was sealed after loading at a pressure of 10^{-6} torr or less. Prior to loading the cleaned ampules [2,3] were outgassed at a temperature of about 1000°C for 10 hours and a vacuum of 10^{-6} torr. The polycrystalline starting materials GeSe and GeTe were synthesized by annealing stoichiometric mixtures of high purity elements (99.999%) and subsequent sublimation of the product [2, 3]. The crystallographic identity of the materials was established by X-ray diffraction techniques. High purity GeI_4 (99.999%) was used as a transport agent. The ampule designated 3A in this experiment contained 2.0 gm of GeSe and 14.28 mg of GeI_4 per cm^3 tube volume. Ampule 3B was loaded with 1.0 gm GeSe and 1.28 mg/cm^3 GeI_4, and ampule 3C contained 1.0 gm GeTe and 7.14 mg/cm^3 GeI_4. After sealing the ampule, the starting material was quantitatively sublimed to the source end. For the temperature gradient 520 → 420°C, these conditions corresponded to a high (GeSe, 3A), low (GeSe, 3B) and medium (GeTe, 3C) contribution of the convective component to the overall transport under ground-based conditions. This set of ampules was used for the SL 3 mission experiments.

For the SL 4 mission experiments the back-up ampules 5A, 5B and 5C were employed. The quantities of GeSe and GeTe and the initial amounts of transport agent GeI_4 used in these ampules was the same as in the corresponding SL 3 transport tubes. Due to the lower temperature gradient used for the SL 4 experiments (412 → 346°C), a partial precipitation of transport agent occurred in ampules 5A and 5C during transport. No precipitation of GeI_4 occurred in ampule 5B. The resulting pressure conditions corresponded to a medium (GeSe, 5A and GeTe, 5C) and to a low (GeSe, 5B) convective contribution to the overall transport under ground-based conditions.

The transport tubes were enclosed with the proper heat shields in evacuated metal cartridges by Westinghouse. These cartridges were inserted into the multi-purpose furnace by the astronauts. The chemical transport reactions for the GeSe and GeTe systems and the experimental conditions employed for the studies in micro-gravity environment are summarized in Table I. The GeI_4 pressures are calculated for the mean temperature of the gradient and ideal gas conditions.

Table I

TRANSPORT REACTIONS AND
EXPERIMENTAL CONDITIONS

$$GeSe(s) + GeI_4(g) = 2\ GeI_2(g) + 1/2\ Se_2(g)$$

$$GeTe(s) + GeI_4(g) = 2\ GeI_2(g) + 1/2\ Te_2(g)$$

ΔT: 520 → 420°C (SL 3 Mission)	
GeSe (3A)	$P(GeI_4(g)) = 1.50$ atm
GeSe (3B)	$P(GeI_4(g)) = 0.13$ atm
GeTe (3C)	$P(GeI_4(g)) = 0.75$ atm
ΔT: 412 → 346°C (SL 4 Mission)	
GeSe (5A)	$P(GeI_4(g)) = 0.42$ atm
GeSe (5B)	$P(GeI_4(g)) = 0.12$ atm
GeTe (5C)	$P(GeI_4(g)) = 0.60$ atm

After initiating the heating cycle aboard Skylab 3, a temperature of 520°C at the source end and of 420°C at the condensation region of the ampule were achieved after 2.75 hours. These conditions were maintained (± 3°C) for 33 hours, during which transport and crystal growth occurred. After termination of the experiment, cooling of the ampules to ambient temperature took place in the multi-purpose furnace over a period of about 12.5 hours. The heating cycle for the SL 4 experiments consisted of a heat-up period of 1.5 hours, a soak-time of 34 hours during which the temperature remained constant within ± 3°C, and a cool-down period of 7 hours.

The cartridges were returned to the George C. Marshall Space Flight Center. Radiographic examination of the ampules in the cartridges showed that none of the ampules had any mechanical damage. After opening the metal cartridges, the ampules were brought to our laboratory for further evaluation of the experiment. An opened cartridge and a ground-based GeSe transport ampule are shown in Fig. 1. A similar ampule used for the space experiment was inserted into the section of the cartridge shown next to the ampule in Fig. 1. This part fit into the upper half of the cartridge which was sealed at the right edge of the first section. The ground-based ampule reveals the dendritic type deposition of GeSe typical for convection controlled transport conditions.

RESULTS AND DISCUSSION

After recording the deposition profile of transported material in the closed ampules, the tubes were opened and the crystals and residual source materials were carefully removed for further examination.

Crystallographic Identification of Transport Product

The crystallographic identification of space grown crystals was established by means of Debye-Scherrer and Laue X-ray diffraction techniques. The results in terms of lattice parameters and crystallographic orientation of as-grown faces are summarized in Table II together with corresponding data of ground-based crystals.

Table II

CRYSTALLOGRAPHIC PARAMETERS OF
SKYLAB AND GROUND-BASED CRYSTALS

System	Lattice Parameters (Å) a_0	b_0	c_0	Orientation (hkℓ)
		SL 3 MISSION		
GeSe (Ground-Based)	4.383 ± 0.01	3.827 ± 0.01	10.770 ± 0.02	(001)
GeSe (M556-3A)	4.387 ± 0.01	3.840 ± 0.01	10.768 ± 0.02	(001)
GeSe (M556-3B)	4.387 ± 0.01	3.836 ± 0.01	10.787 ± 0.02	(001)
GeTe (Ground-Based)	5.982 ± 0.003	$\alpha = 88.25 \pm 0.05°$		(111)
GeTe (M556-3C)	5.981 ± 0.003	$\alpha = 88.30 \pm 0.05°$		(111)
		SL 4 MISSION		
GeSe (M556-5A)	4.386 ± 0.01	3.835 ± 0.01	10.783 ± 0.02	(001)
GeSe (M556-5B)	4.375 ± 0.01	3.826 ± 0.01	10.757 ± 0.02	(001)
GeTe (M556-5C)	6.072 ± 0.01	$\alpha = 87.20 \pm 0.2°$		(111)

A comparison of the data in Table II shows that the lattice constants of the respective systems are identical within limits of error. There is no change in the orientation of native faces of crystal platelets. Within the detection limits of X-ray diffraction techniques there is no measurable effect of micro-gravity on the crystallographic parameters of space grown crystals. The increase in the unit cell dimensions of GeTe (5C) can be explained by the formation of a limited solid solution between GeTe and transport agent which was anticipated under the experimental conditions of the SL 4 mission. The above results are expected in view of the relative magnitude of chemical bonding and gravitational forces.

Mass Transport Rates

A summary of the mass transport rate or flux data observed in micro-gravity and under ground-based conditions is given in Tables III and IV.

Table III

MASS TRANSPORT RATE UNDER
MICRO-GRAVITY AND GROUND-BASED CONDITIONS

SL 3 MISSION (520 → 420°C)

System	Mass Flux $((\text{moles/cm}^2 \cdot \text{sec}) \times 10^{-9})$			Ground-Based Transport Mode
	Micro-G	1-G	Extrapolated Diff. Mode	
GeSe (A)	~ 5	39	$\sim 4 \times 10^{-1}$	High Convective
GeSe (B)	~ 10	5.3	~ 3	Low Convective
GeTe (C)	~ 3	2.5	$\sim 2 \times 10^{-1}$	Medium Convective

A comparison of these data reveals a rather significant result. The flux in micro-gravity is greater than expected if gas phase diffusion would be the only parameter contributing to the material transport from the source to the condensation region. For systems (A) and (C) the difference between observed and predicted mass fluxes is about one order of magnitude. These observations indicate the existence of other than gravity-driven convective transport components contributing to mass flux in a reactive solid-gas phase system. Thermodynamic and kinetic considerations suggest that the additional transport modes are related to the thermochemistry of the gas phase reaction and to secondary effects of the temperature gradient. These factors have been largely ignored in the conventional treatment of transport phenomena.

The above trend in the mass transport rates is confirmed by the flux data of the SL 4 transport experiments listed in Table IV.

Table IV

MASS TRANSPORT RATE UNDER
MICRO-GRAVITY AND GROUND-BASED CONDITIONS

SL 4 MISSION (412 → 346°C)

System	Mass Flux $\{(\text{moles/cm}^2\cdot\text{sec}) \times 10^{-9}\}$			Ground-Based Transport Mode
	Micro-G	1-G*)	Extrapolated Diff. Mode	
GeSe (A)	$\sim$0.8	0.9	$\sim$0.1	Convective
GeSe (B)	$\sim$1.8	0.8	$\sim$0.5	Diff. + Conv.
GeTe (C)	$\sim$1.0	1.7	$\sim$0.1	Convective

*) Based on 420 → 350°C temperature gradient

Despite the lower temperature gradient and the associated partial precipitation of transport agent for the SL 4 experiments, the flux data of Table IV are in good agreement with the overall pattern observed during the SL 3 mission.

The technological significance of these results is the possibility of growing crystals in space at reasonable rates and improved quality by this technique. The scientific importance is the demonstration that the conventional transport models are incomplete.

Morphological Characteristics

A comparison of ground-based and space grown crystals reveals distinct morphological differences of the as-grown faces and crystal habits.

Representative GeTe crystals (Table I, system 3C) are shown in Fig. 2. Crystals obtained under ground-based conditions (Fig. 2a) show distorted surfaces of the platelets and needles. Aggregation and twinning are frequently observed. Nearly all octahedral type crystals grown under these conditions reveal partially hollow growth habits. The corresponding space crystals (Fig. 2b) have considerably more compact habits. The as-grown faces of these crystals show a higher degree of smoothness and crystalline perfection. The edges of these crystals are better defined. The apparent slight difference in the metallic luster of the ground-based and space crystals is due to a partial condensation of the residual gas phase during the cool-down period of the multi-purpose furnace. In our laboratory, this is avoided by removing the ampule from the furnace and quenching the residual vapor phase at the source region.

The typical appearance of the condensation region of a GeTe ground-based and space transport ampule is shown in Fig. 3. The curvature of the dendritic-type crystals is characteristic of the GeTe deposition pattern under convection controlled transport conditions (Fig. 3a). This pattern strongly indicates turbulent flow of the gas phase in the ground-based ampule. Under micro-gravity conditions no such pattern is observed (Fig. 3b).

A rather interesting phenomenon is observed on some of the as-grown faces of GeTe crystals obtained in ampule 3C under micro-gravity conditions (Fig. 4). The triangular pattern reveals three-fold symmetry which is characteristic of the (111) orientation of the GeTe crystal face. This pattern is probably due to a very slow condensation of vapor species which can lead to a decoration of the defects in the (111) plane. Since such a decoration effect requires a rather homogeneous and undisturbed condensation, this phenomenon is difficult to observe under ground-based conditions due to localized convective interference.

A representative selection of ground-based and space grown GeSe crystals (Table I, system 3B) is shown in Fig. 5. The concentration of transport agent used in this case corresponds to the onset of the convection controlled range in a gravitational environment. For this reason, the external morpological differences are expected to be less pronounced than for systems 3C and 3A (Table I). However, the difference in surface quality between ground-based (Fig. 5a) and space crystals (Fig. 5b) is obvious. The as-grown faces of the ground crystals have steps and ledges while the space crystals reveal a more uniform surface. A comparison of internal faces of GeSe (system B) crystals will be discussed below.

The most pronounced difference in growth morphology was predicted and observed for GeSe (Table I, system 3A). The GeI_4 pressure employed yields a convention controlled transport mode under ground-based conditions. A typical view of the condensation region of a GeSe ground-based (high convective) transport ampule is compared to the corresponding space ampule (3A) in Fig. 6. The ground-based ampule (Fig. 6a) shows clearly the dendritic type growth and distinct curvature of the individual dendrites. This morphology reveals the effects of convective turbulence on crystal habit. In the absence of convective interference individual well-developed single crystal platelets (Fig. 6b) are obtained. The space ampule 3A (Fig. 6b) contains the largest GeSe single crystal grown under present experimental conditions. (The photographs of Fig. 6 were taken through the quartz wall of the closed ampules.)

Close-ups of the two sides of the largest GeSe single crystal platelet (system 3A) grown in space are shown in Fig. 7. The actual dimensions of this platelet are about 4 mm in width and 16-18 mm in length. The thickness is about 50 μ. The spotty appearance of the native surfaces is due to the above mentioned partial condensation of residual gas phase during the cool-down period.

The lower temperature gradient employed for the SL 4 experiments (412 → 346°C) yielded smaller transport rates as compared to the SL 3 mission experiments. In addition, the lower temperature of the condensation region leads to a reduction in mobility of species on the surface of the crystal. This results in a decrease of crystal size and quality. However, despite these restricting parameters a comparison of ground-based and space crystals grown in the above temperature gradient confirms the trend observed for the morphological changes of the SL 3 crystals.

This is illustrated in Fig. 8 for GeSe ground-based and space (5B) crystals. The major difference here is that the ground crystals (Fig. 8a) reveal a higher growth rate in the c-direction (perpendicular to the (001) plane) relative to the space crystals (Fig. 8b) which show a preferential growth parallel to the (001) plane. This yields single crystal platelets with (001) orientation. This observation is interesting with respect to the orthorhombic structure of GeSe which is characterized by primary bonding within the (001) double-layers and secondary bonding between adjacent planes of two sets of (001) double-layers. Based on these bonding properties, the predominant growth of (001) platelets is expected under near-ideal conditions. This is also in agreement with the corresponding results (GeSe, 3B) of the SL 3 experiments. In addition, the as-grown faces of the space crystals (Fig. 8b) show a higher degree of crystalline perfection. The spotty appearance of the surface of the space grown material is due to the above discussed condensation of residual vapor species during the cool-down period.

Analogous to the SL 3 results, the morphological differences between ground and space crystals are more pronounced for the GeSe system (5A) corresponding to high-convective transport under ground-based conditions. This is illustrated in Fig. 9. Ground-based GeSe transport leads to massive aggregation of smaller GeSe platelets and to polycrystalline condensation (Fig. 9a). (This corresponds to dendritic aggregation for the higher temperature gradient of the SL 3 experiments.) Under micro-gravity conditions individual single crystal platelets of (001) orientation (Fig. 9b) are obtained. The apparent roughness of the surface of the space crystals is caused by the above mentioned precipitation of transport agent due to supersaturation during growth and the condensation of residual vapor species in the cool-down period. However, despite these secondary reactions imposed by the experimental conditions of the SL 4 mission, the characteristic morphological differences between ground and space condensation are clearly exhibited.

The combined experimental evidence from the changes in deposition pattern and crystal habits demonstrates unambiguously the positive effects of micro-gravity on the external morphology and quality of crystals. The results of scanning electron microscopy and thermal etch studies discussed below are consistent with the above conclusions.

Scanning Electron Microscopy Studies

Scanning electron photomicrographs (400X) of cleaved faces of GeSe ground-based and space grown (3B) crystals compared in Fig. 10 show interesting morphological differences.

The irregular cleavage pattern of the ground-based crystal (Fig. 10a) is partially due to crystalline inhomogeneities causing a nonuniform separation of (001) layers upon cleavage. The origin of the holes in cleaved faces of ground-based crystals is not yet unambiguously identified. Other cleaved faces of ground crystals revealed shallow indentations. Present data indicate that some of these cavities could be native defects. The rather homogeneous cleavage pattern of the space crystal (Fig. 10b) reflects the higher degree of crystalline perfection. The diagonal edge is due to cleavage and represents the border between (001) planes of different depths with respect to the native surface. Both crystals were cleaved in the same manner which emphasizes the differences in crystallinity of the space and ground-based material.

Scanning electron photomicrographs (1000X) of the native edges of GeSe ground-based and space (3B) crystals in Fig. 11 reveal a pronounced difference in crystalline perfection. In both cases the crystal area at the left-hand side of the photograph is the (001) face of the crystal platelet. The edge is perpendicular to the (001) face. The edge of the ground-based crystal (Fig. 11a) shows regions of crystalline imperfections containing holes which penetrate into the bulk of the material. The morphology of a cleaved (001) face (perpendicular to the edge) will be affected by the location of the cleavage plane with respect to edge inhomogeneities. This could explain morphological differences of cleaved GeSe faces of ground-based crystals. The nearly perfect edge of the space crystal (Fig. 11b) is consistent with the high quality of cleaved (001) faces.

The morphological differences between GeSe dendrites obtained under ground-based high-convective conditions and GeSe single crystal platelets obtained in space (3A) are illustrated in Fig. 12 by scanning electron microscopy (200X). The native surface of the dendrite (Fig. 12a) reveals a series of steps which mark the onset of growth of different segments of the dendrite. In the presence of convection currents the onset of new layers is not always perpendicular to the growth direction of the preceeding crystal leading to the observed curvature of dendrites. The irregular growth also explains the formation of macroscopic cavities which penetrate into the bulk of the dendrite. The overall morphology of the cleaved (001) face of the space crystal (Fig. 12b) reflects the degree of homogeneity of the gas phase and condensation process under micro-gravity conditions.

Thermal Etching Studies

In order to investigate the effects of micro-gravity on crystalline perfection for the bulk of the material, internal faces of GeSe (system 3B) crystals are examined by thermal etching and optical microscopy. Due to the bonding properties of GeSe the single crystal platelets can be cleaved parallel to the (001) plane. For the etch studies, freshly cleaved GeSe crystal platelets are mounted in the hot stage of a metallographic microscope. Under vacuum ($\sim 10^{-4}$ torr) the temperature of the crystal is gradually raised until a change in surface morphology is first observed. Based on studies in our laboratory, at this temperature any mass-loss from the crystal surface is very small and changes in surface morphology are mainly due to a mobility of species on the surface [4,5]. In addition, the surface mobility is initiated at surface defects.

The cleaved faces of GeSe ground-based specimens selected for thermal treatment were of the highest quality and were indistinguishable at magnification 500X from the space crystals. The results of a short-term thermal etching (5 min at about 190°C) of inner planes of ground and space crystals (3B) of GeSe are shown in Fig. 13. The ground crystal (Fig. 13a) is completely covered with thermal etch pits. The average density of pits based on the upper left and lower right areas of Fig. 13a is about 8×10^5 cm^{-2} and the diagonal length of the largest pits is approximately 8×10^{-3} cm. The number and distribution of etch pits is related to the corresponding quantities of defects in this plane. The morphology of the space crystal (Fig. 13b) is considerably less affected by short-term thermal etching. The density of pits based on the entire area of Fig. 13b is in the order of 10^3 cm^{-2}, and the diagonal length of the largest pits is in the low 10^{-3} cm range. Allowing for large error limits in the etch pit count of the space crystal, there remains a significant difference compared to the density of pits of the ground crystal. This indicates a higher degree of crystalline perfection and homogeneity of the space grown material. (The edge in the upper right area and the line in the right section of Fig. 13b are due to cleavage of the crystal.)

The above observations are supported by the results of long-term etching of GeSe single crystal platelets at the same temperature for 2.5 hours. After extended time periods, mass-loss from the crystal causes a complete roughening of the surface. Representative areas of thermally treated internal (001) faces of ground and space (3B) crystals are shown in Fig. 14. The differences in surface morphology are obvious. The density of etch pits in the upper left quadrant of the ground-based crystal in Fig. 14a is about 8×10^5 cm^{-2}. The diagonal length of the largest well defined etch pit in the lower right corner of Fig. 14a is about 10^{-2} cm and the depth is approximately 33×10^3 Å. These etch pits reveal the two-fold symmetry of the (001) plane. In addition, the surface of the ground-based crystal has developed several nearly macroscopic etch pits in the lower left area of Fig. 14a. The high reflecting broad region in the upper right section of Fig. 14a is a large step to a lower (001) plane. The morphology of the ground crystal is contrasted by the much more uniform appearance of the (001) face of the space crystal in Fig. 14b. The density of etch pits based on the entire area of Fig. 14b is 4×10^4 cm^{-2}, the average diagonal length is about 4×10^{-3} cm and the depth of the larger pits is approximately 17×10^3 Å. The etch pits reveal the two-fold symmetry of the crystal plane. There are no macroscopic changes of the space crystal even after extensive thermal etching.

A comparison of the results of thermal etching shows that the number of etch pits of the space crystal after long-term etching is at least one order of magnitude lower than the density of pits for the ground-based crystal after short-term etching. The overall morphology of the (001) plane of the space crystal after short and long thermal treatment reveals a higher degree of perfection than the plane of the ground-based crystal. Based on the relation between the effects of thermal etching and crystalline imperfections, the combined experimental information from the etch studies demonstrates the improved quality of the space grown crystals.

A cleaved section of a ground-based GeSe dendrite and the cleaved (001) face of the corresponding space platelet (3A) are compared in Fig. 15. The internal face of the dendrite (Fig. 15a) reveals a distinct line pattern and the curvature typical for the macroscopic habit of dendritic growth. The face of the GeSe space crystal (Fig. 15b) appears to be mirror smooth under these conditions. (The magnification applied for the dendrite is 250X and for the crystal platelet 500X.) The edge in the plane of the space crystal is due to cleavage and represents the boundary between layers of different depths with respect to the native surface.

The results of thermal etching (30 min, ∿190°C) of cleaved faces of a ground-based GeSe dendrite and the corresponding single crystal platelet (3A) grown in micro-gravity (Fig. 16) are consistent with the external morphological differences between these growth habits. Thermal treatment of the dendrite face (Fig. 16a) caused the formation of large aggregated etch pits and nearly macroscopic ledges. This observation demonstrates that removal of mass due to vaporization is highly irregular with respect to the surface area as a result of the intrinsic inhomogeneities of the dendritic crystal. The morphology of the thermally etched (001) face of the space crystal (Fig. 16b) is considerably more homogeneous. The well defined etch pits reveal the two-fold symmetry of the (001) plane. The average diagonal length of the larger etch pits is about 5×10^{-3} cm, their depth is approximately 3×10^{4} Å and the etch pit density is in the low 10^{5} cm^{-2} range. The absence of steps even after extensive thermal treatment of the (001) face of the GeSe space crystal reveals a very uniform removal of mass from the surface. This in turn requires a rather homogeneous crystalline structure of the surface and subsurface layers. The combined differences between the growth habits and the thermal etch patterns of GeSe dendrites and platelets demonstrate unambiguously the positive effects of micro-gravity on external morphology and bulk crystalline perfection.

CONCLUSIONS

The combined experimental evidence from the analysis of space grown crystals confirms the predicted positive effects of micro-gravity on crystal quality. This is based on a comparison of macroscopic crystal habits, deposition patterns, optical and scanning electron microscopy, and the results of thermal etching of cleaved crystals obtained under ground-based and micro-gravity conditions.

In addition to improved crystal quality, a second major result of the Skylab experiment M556 is the observation of greater mass transport rates than expected in micro-gravity environment. This observation is of scientific and technological significance with respect to the theoretical extension of conventional transport models and the possibility of growing higher quality crystals at reasonable rates by the vapor transport technique in space. Continuing ground-based studies indicate that the interaction between gravity-driven and other convective components causes turbulence and the negative effects on crystal quality as observed on earth. The ultimate goal of these studies is to approximate the effects of micro-gravity on crystal quality under earth-bound conditions.

The internal consistency of results obtained for two materials (GeSe and GeTe), two different temperature gradients and various pressures of transport agent strongly support the validity of the above conclusions.

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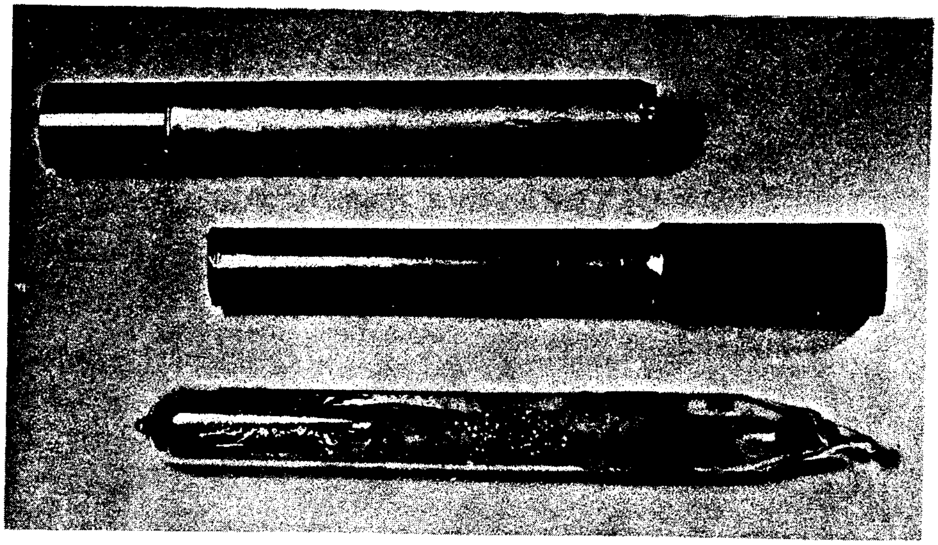

FIGURE 1. METAL CARTRIDGE FOR TRANSPORT AMPULE USED IN SKYLAB EXPERIMENT. THE QUARTZ AMPULE SHOWN WAS USED FOR GROUND-BASED STUDIES. THE AMPULE IS 150 mm LONG, 13.7 mm INNER DIAMETER AND REVEALS THE DENDRITIC DEPOSITION OF GeSe TYPICAL FOR CONVECTIVE CONDITIONS.

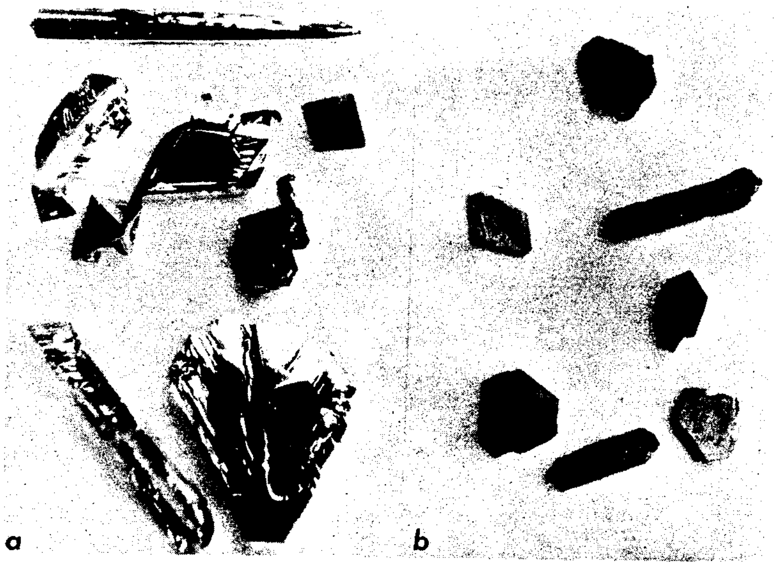

FIGURE 2. REPRESENTATIVE GeTe CRYSTALS OBTAINED UNDER BROUND-BASED CONVECTIVE (a) AND SPACE (b) CONDITIONS. THE LENGTH OF THE GROUND-BASED (a) NEEDLE IS ABOUT 4mm AND THE EDGE LENGTH OF THE HOLLOW OCTAHEDRA ABOUT 0.7 mm. THE LENGTH OF THE SPACE (b) NEEDLE IS ABOUT 2mm AND THE AVERAGE EDGE LENGTH OF THE PLATELETS IS 1mm.

FIGURE 3. DEPOSITION PATTERN OF GeTe CRYSTALS UNDER GROUND-BASED CONVECTIVE (a) AND MICRO-GRAVITY (b) CONDITIONS. LENGTH OF INDIVIDUAL DENDRITES (a) IS 1.5-4mm.

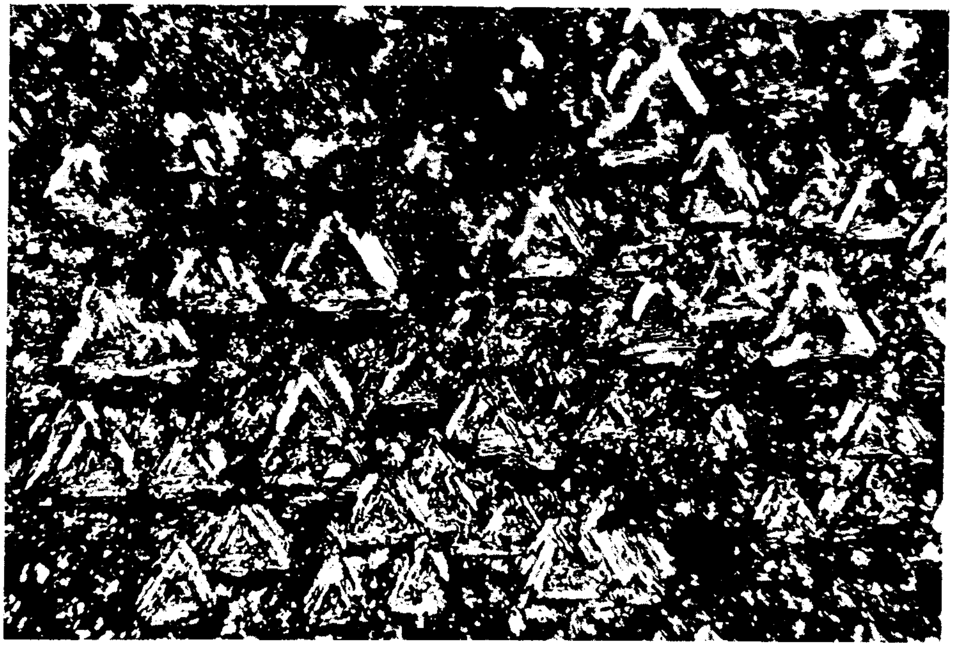

FIGURE 4. PHOTOMICROGRAPH (300X) OF (111) NATIVE FACE OF GeTe SPACE-GROWN CRYSTAL (3C). TRIANGULAR PATTERN INDICATES POSSIBLE DECORATION OF DEFECTS.

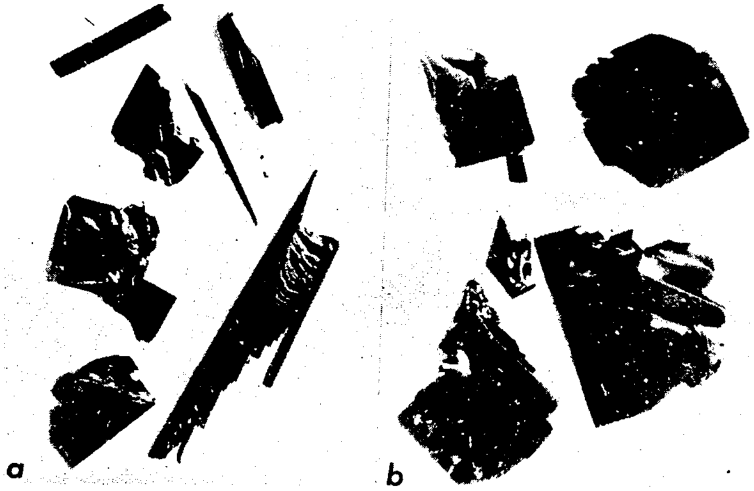

FIGURE 5. REPRESENTATIVE GeSe CRYSTALS (3B CONDITIONS) GROWN ON EARTH (a) AND IN SPACE (b). THE EDGE LENGTH OF THE GROUND-BASED CRYSTALS (a) IS 1-5mm AND OF THE SPACE CRYSTALS (b) 2-5mm.

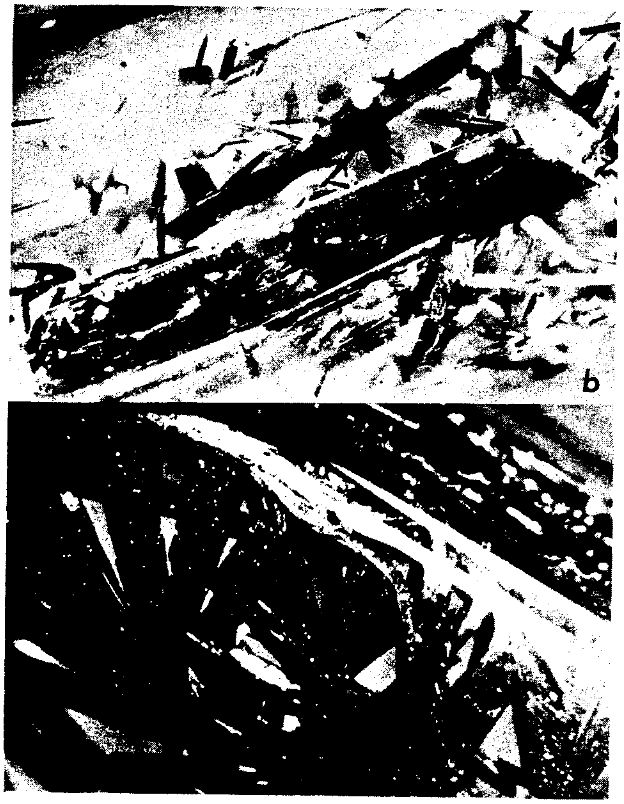

FIGURE 6. VIEW OF THE DEPOSITION REGION OF A GeSe (3A CONDITIONS) GROUND-BASED (a) AND SPACE (b) TRANSPORT AMPULE. EDGE LENGTHS OF SPACE CRYSTALS (b) RANGE FROM 0.2-18mm.

FIGURE 7. FRONT AND BACK SIDE OF THE LARGEST GeSe SINGLE CRYSTAL PLATELET GROWN UNDER MICRO-GRAVITY CONDITIONS (3A). DIMENSIONS ARE 4 X 8 18mm, THICKNESS IS ABOUT 50 µ.

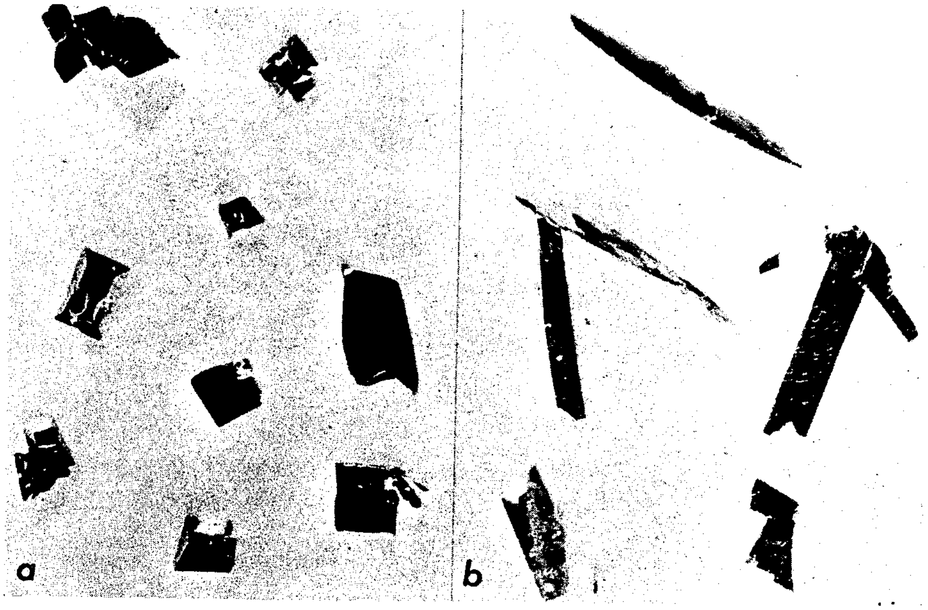

FIGURE 8. REPRESENTATIVE GeSe CRYSTALS (5B CONDITION) GROWN ON EARTH (a) AND IN SPACE (b). AVERAGE DIMENSIONS OF GROUND-BASED (a) CRYSTALS ARE 1-2mm AND OF SPACE CRYSTALS (b) 1mm WIDTH AND 5mm LENGTH.

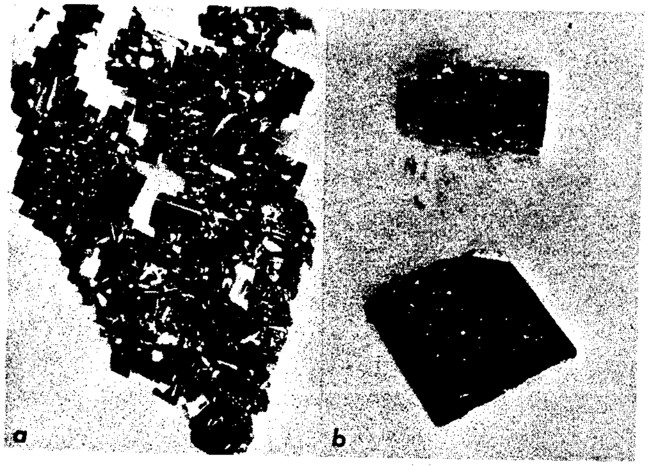

FIGURE 9. REPRESENTATIVE GeSe CRYSTALS (5A CONDITIONS) OBTAINED UNDER GROUND-BASED (a) AND MICRO-GRAVITY (b) CONDITIONS. TOTAL LENGTH OF CRYSTAL AGGREGATE (a) IS 5mm. EDGE LENGTHS OF SPACE CRYSTALS (b) IS 0.8-1.5mm.

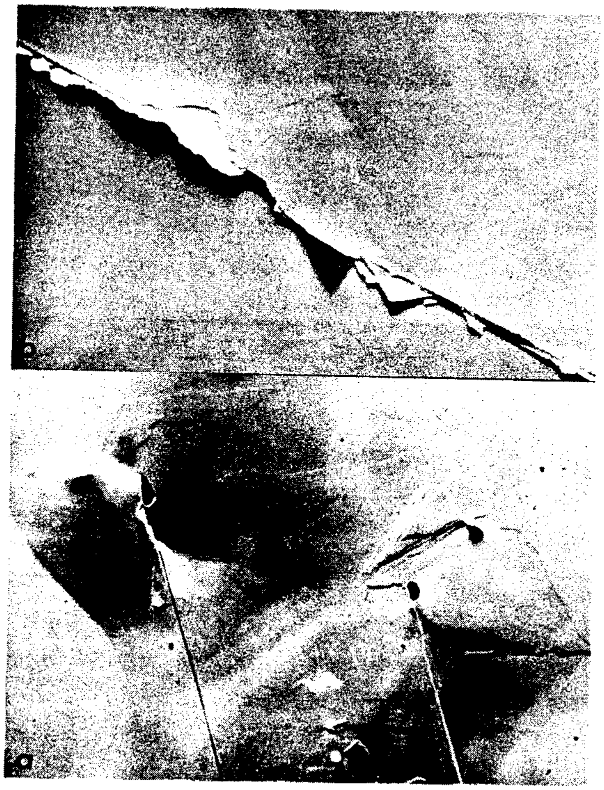

FIGURE 10. SCANNING ELECTRON PHOTOMICROGRAPHS (400X) OF CLEAVED (001) FACES OF GeSe (3B CONDITIONS) CRYSTALS GROWN ON EARTH (a) AND IN SPACE (b).

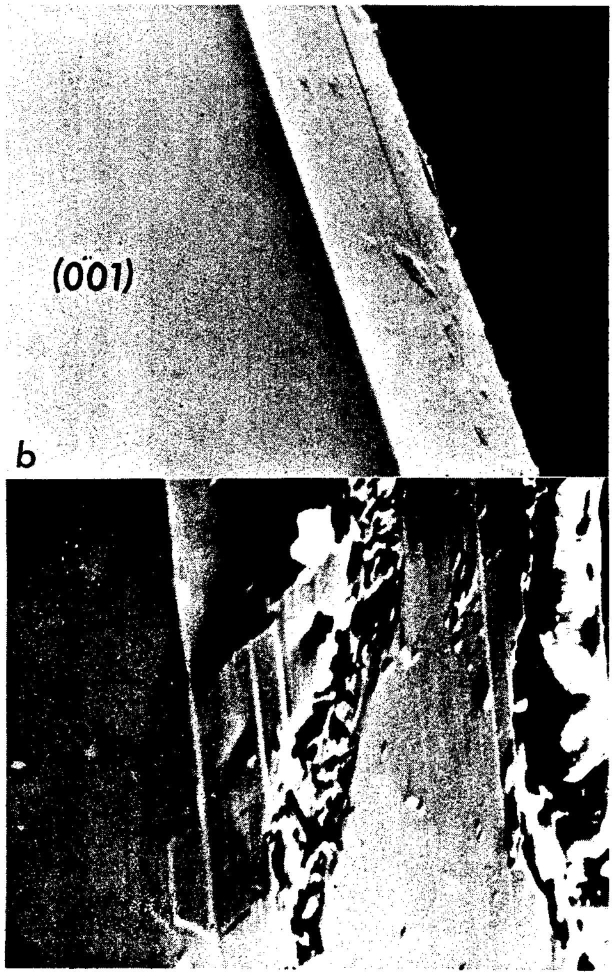

FIGURE 11.

SCANNING ELECTRON PHOTOMICROGRAPHS (1000X) OF NATIVE EDGES OF GeSe (3B CONDITIONS) CRYSTALS OBTAINED UNDER GROUND-BASED (a) AND MICRO-GRAVITY (b) CONDITIONS.

FIGURE 12.

SCANNING ELECTRON PHOTOMICROGRAPHS (200X) OF THE NATIVE SURFACE OF A GeSe GROUND-BASED DENDRITE (a) AND OF THE CLEAVED (001) FACE OF A SPACE-GROWN GeSe (3A) CRYSTAL (b).

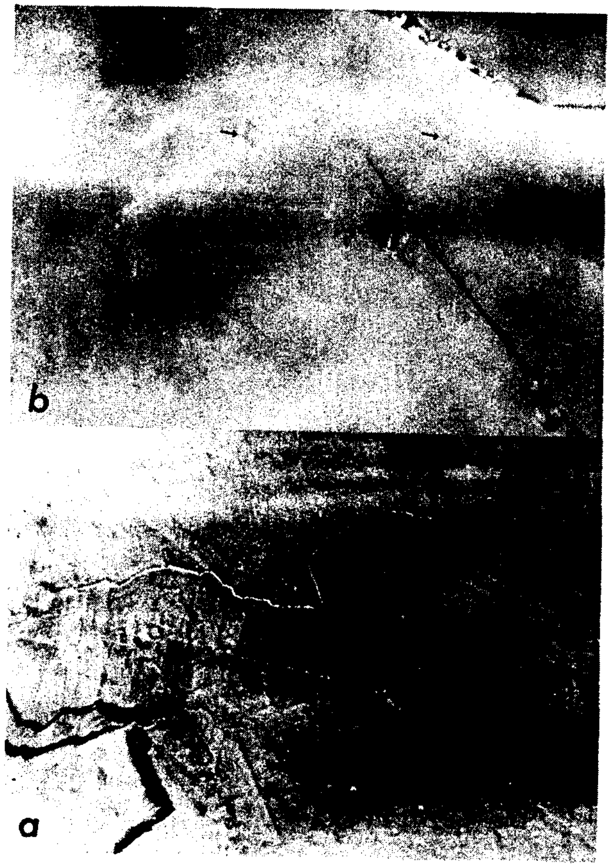

FIGURE 13.

OPTICAL PHOTOMICROGRAPHS (125X) OF CLEAVED (001) FACES OF GeSe (3B CONDITIONS) SINGLE CRYSTAL PLATELETS OBTAINED ON EARTH (a) AND IN SPACE (b) AFTER THERMAL ETCHING (5 MIN, ~190°C). THE LOCATIONS OF TWO OF THE THERMAL ETCH PITS OF THE SPACE CRYSTAL (b) ARE INDICATED BY ARROWS.

FIGURE 14.

OPTICAL PHOTOMICROGRAPHS (125X) OF CLEAVED (001) FACES OF GeSe (3B CONDITIONS) SINGLE CRYSTAL PLATELETS GROWN ON EARTH (a) AND IN MOCRO-GRAVITY (b) AFTER THERMAL ETCHING (2.5 HR, ~190°C).

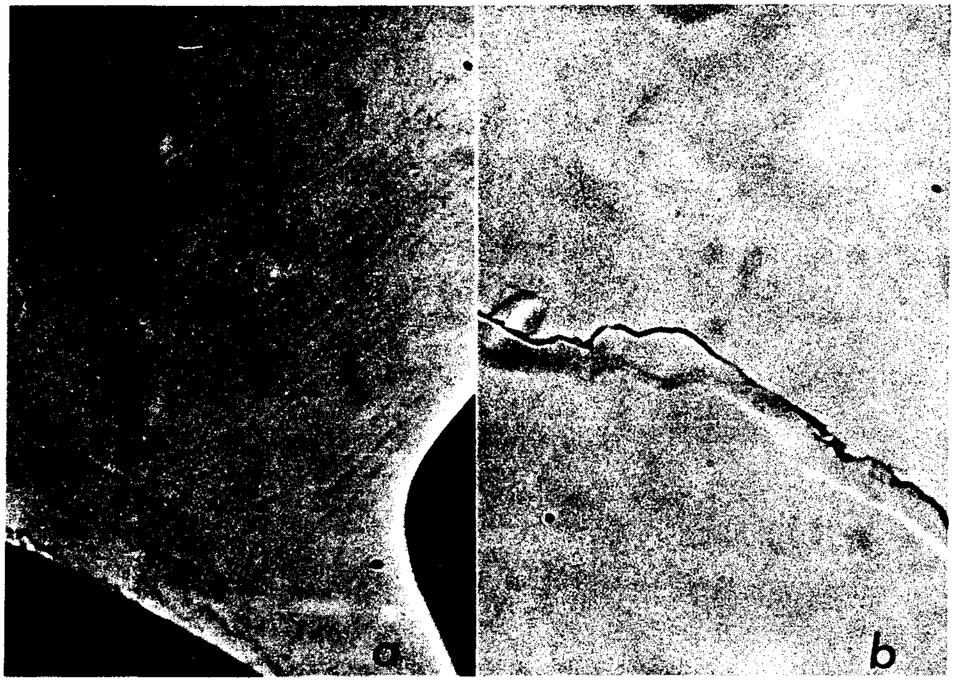

FIGURE 15. OPTICAL PHOTOMICROGRAPHS OF A CLEAVED SECTION OF A GeSe GROUND-BASED DENDRITE (a) (250X) AND OF A CLEAVED (001) FACE OF A SPACE-GROWN GeSe (3A) SINGLE CRYSTAL PLATELET (b) (500X).

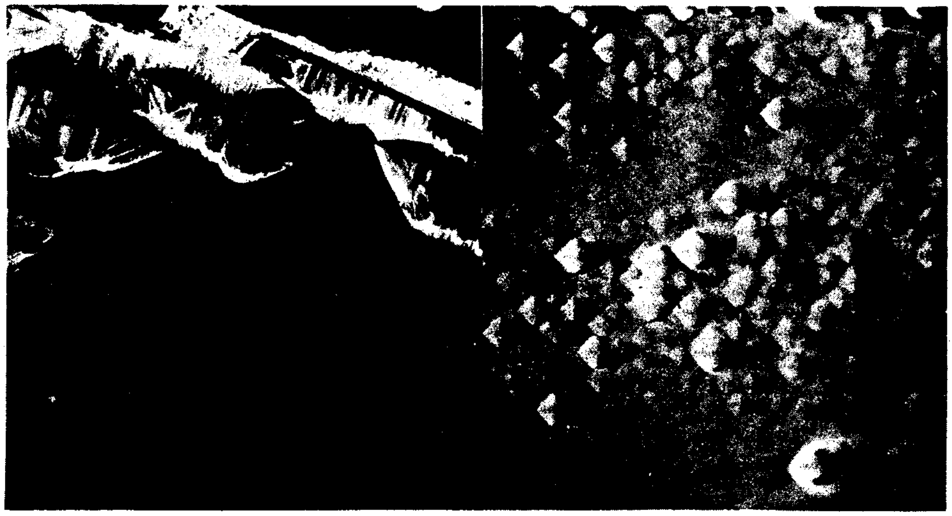

FIGURE 16. OPTICAL PHOTOMICROGRAPHS (125X) OF A CLEAVED GeSe GROUND-BASED DENRITE (a) AND A CLEAVED (001) FACE OF A SPACE-GROWN GeSe (3A) CRYSTAL PLATELET AFTER THERMAL ETCHING (30 MIN, ~ 190°C).