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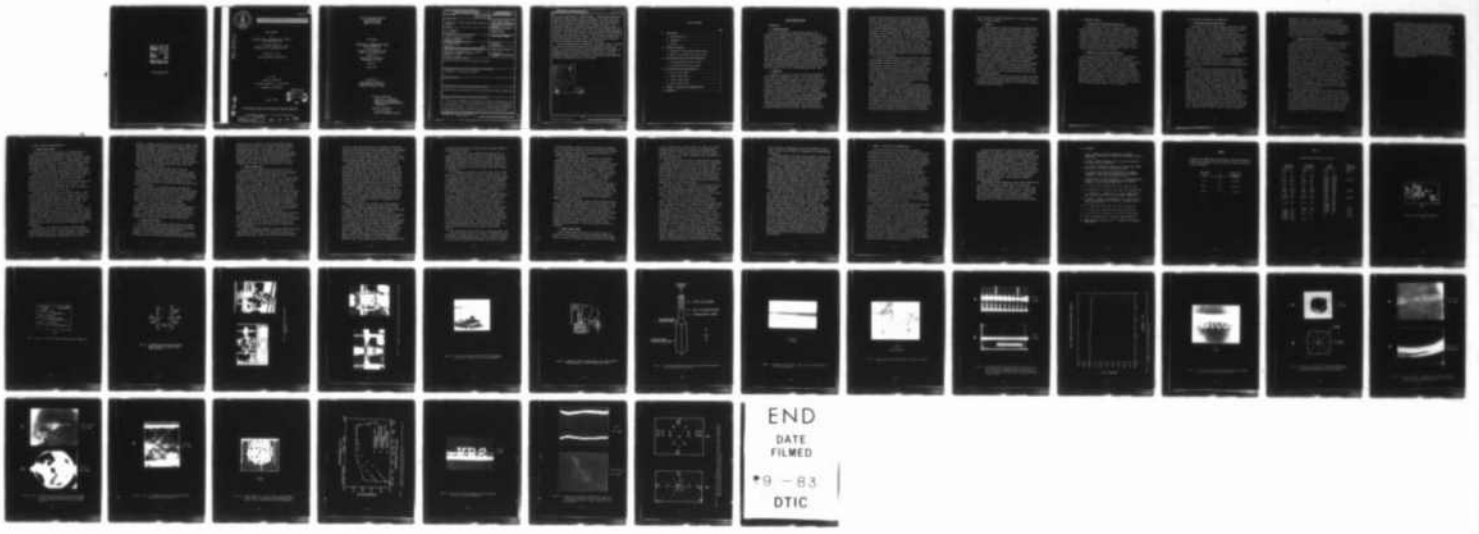

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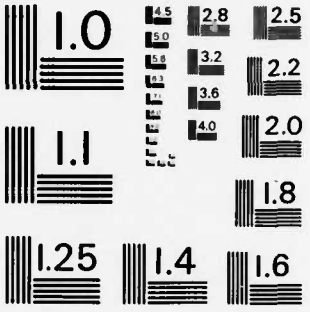

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FINAL REPORT

on

PREPARATION OF INFRARED OPTIC FIBERS USING NEW MATERIALS

for the period of
October 1, 1981 - March 31, 1983
Contract No. N00014-82-K-2001

submitted to the

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STANFORD, CALIFORNIA

August 1983

CENTER FOR MATERIALS RESEARCH

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Center for Materials Research
McCullough Building
Stanford University
Stanford, CA 94305

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This report summarizes an eighteen-month program on the preparation and characterization of optical fibers which have low losses and are transparent in the infrared range. The objectives were to study preparative techniques, compositional and optical properties, and factors which influence fiber growth techniques. The emphasis of this program was on single crystal fibers

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in the size range from 100 - 1000 μm diameter. Single crystal fibers were produced in limited lengths using two techniques: the laser heated pedestal growth technique for high-melting materials, and the capillary-fed fiber growth method for low-melting and for volatile materials. The materials studied were selected from those which have a high potential for low loss at wavelengths greater than 1.5 μm, and included BaF_2, CaF_2, AgBr, and KRS-5. The fibers were analyzed using metallographic, optical, XRD, and energy dispersive analytical techniques. Critical system and growth parameters were studied, and factors which correlated with the occurrence of internal structural and optical defects were identified.

This study demonstrated the feasibility of growing a range of IR fibers with both the laser-heated pedestal and the capillary-fed growth techniques. The strong sensitivity of high melting halides to the presence of background (water and oxygen) impurities, and the lack of an optimum mechanical guiding apparatus for fibers of low-melting materials indicates the need for additional research in these areas.

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FINAL TECHNICAL REPORT

I. INTRODUCTION

A. Program Objectives

This report summarizes an eighteen-month program on the preparation and characterization of optical fibers which have low losses and are transparent in the infrared range. The objectives were to study preparative techniques, compositional and optical properties, and factors which influence fiber growth techniques. The emphasis of this program was on single crystal fibers which could serve in relatively short guiding applications (on the order of a few meters or less), or as active elements in, for example, an integrated fiber optic system. Millimeter and submillimeter diameter single crystal fibers were produced in limited lengths using two techniques: the laser heated pedestal growth technique for high melting materials, and the capillary-fed fiber growth method for low melting and for volatile materials. The materials studied were selected from those which have a high potential for low loss at wavelengths greater than 1.5μm.

B. Background

As opposed to fused silica fibers in which optical absorption rises rapidly at wavelengths in excess of 1 μm, a large number of other glass and crystalline systems are known which have a much wider range of transparency in the infrared (IR). A recent survey article by Goodman (1) lists a number of materials which have potential for low-loss, IR applications. Nassau (2) has recently tabulated the wavelengths at minimum materials dispersion for a comprehensive selection of oxides and halides, Fig. 1. There is also a considerable amount of literature available on low-loss high-power window materials (3-5). While there are not many good glass-formers with minimum dispersion beyond the 2-3 μm range, there are a large number of crystalline compounds which do transmit far into the IR and have minimum dispersion in the 3-10 μm range. These include mostly the

binary and ternary halides, and a few selected oxides and chalcogenides. While one can conceive of using single crystal fibers of such materials for long distance communications, it is more likely they will find application in relatively local guiding applications, or as discrete system components in situations which utilize their non-linear or anisotropic properties. Examples include laser hosts, modulators, mixers, Faraday rotators, and others applicable to fiber and integrated optics. In particular, if the optimum wavelength for ultra low-loss fiber optics turns out to be in the 4-6 μm region, which a number of considerations suggest may be the case, the need for an appropriate solid state laser source around 5 μm will arise. Such a laser source may incorporate a nonlinear fiber optic mixer for example. The growth of cm lengths of oriented single crystal fibers of known nonlinear materials such as $AgGaS_2$, could provide an important link in a fiber optic system.

It is for these applications that we at the Center for Materials Research (CMR) originally undertook the construction of a CO_2 laser-heated pedestal, differential pulling apparatus, Fig. 2, following the original work by Burrus, Stone, and Coldren (6,7). They prepared ruby, sapphire, sapphire-clad ruby, and Nd:YAG, single crystal fibers by this technique. The laser heated pedestal growth technique has a number of significant advantages for the growth of single crystal fibers. This apparatus has been on-line since October, 1980, and early applications included the growth of a wide variety of single crystal oxide fibers as small as 15 μm diameter.

Impressive results had also been reported in the domestic and Japanese literature on the capillary-fed fiber growth method and the "float-zone modified e.f.g." growth of low melting halide fibers such as AgBr (8) and KRS-5 (9). Uniform, IR transparent single crystal fibers were reported to have been grown in lengths exceeding one meter. The limits to optical absorption were reported to be caused by metallic impurities in the source material which could likely be reduced by purification of the source materials and care to eliminate interaction with the crucible or shaper as an additional source. No detailed discussion of the microscopic surface features of these fibers was

given, although the photomicrographs shown in the articles suggested relatively smooth surfaces.

C. Approach

Two major avenues of research were undertaken, although reduced somewhat in scope from the original proposal due to constraints in funding and the limited duration of this program. In the first, fiber growth experiments were carried out on several high-melting halide materials using the laser-heated pedestal growth technique since it was immediately operational and required only the completion of an atmosphere control chamber before initial experiments could be undertaken. The intent was to determine how well the high-melting, fairly reactive, halides could be grown in this type of system.

The second major avenue was to develop a capillary-fed fiber growth apparatus, to become familiar with this technique, and to grow several materials representative of the less-reactive, low-melting halide series. We were interested in identifying fundamental limitations in this type of technique as well as in actually growing the fibers themselves. To reach the current state-of-the-art as rapidly as possible, our first system was modeled closely after the work by Bridges (8) and in fact we actually utilized several of his original system components.

Characterization of the fibers was carried out using a full range of analytical techniques which included optical microscopy, electron microscopy, optical transmission analysis, x-ray diffraction analysis, and energy dispersive analysis.

II. MATERIALS SELECTION

A. Materials for Laser-Heated Pedestal Growth

Two materials were selected for growth by the laser-heated pedestal growth technique: BaF_2(MP = 1280°C) and CaF_2(MP = 1360°C). These two materials exhibit broad transparency in the IR, and were considered representative of the alklaline earth halide class of materials. The choice of CaF_2 coupled in well with fiber growth studies of the NaF-CaF_2 eutectic system being carried out in this laboratory with other sources of funding. Single crystal source material was obtained from the Harshaw Chemical Company in order to ensure the highest chemical purity possible.

B. Materials for Capillary-Fed Fiber Growth

The two materials selected for evaluation of this particular growth technique were AgBr and KRS-5. Both have extended IR transmission, and both had been grown before as single crystal fibers; AgBr by Bridges (8), and KRS-5 by Mimura (9) who used a somewhat different inverted capillary technique where the fiber is pulled downward during growth. One problem with the capillary-fed growth technique is that the melt is contained by a reservoir and therefore must be chemically compatible with the system components, in our case fused silica. Neither AgBr(MP = 432°C) nor KRS-5(MP = 415°C) react significantly with fused quartz. Single crystal material was obtained from the Harshaw Chemical Company for use as feedstock.

III. FIBER GROWTH SYSTEM DESIGN AND CONSTRUCTION

A. Laser-Heated Pedestal Growth System

A photograph of the laser-heated pedestal growth system is shown in Fig. 2. During the course of this program, three major equipment modifications were made: an atmosphere control chamber was constructed and tested; a laser-beam power attenuator was added to the optical system; and a set of microalignment heads was added to the laser sidearms to facilitate positioning of the two beams. Only the first modification (construction and testing of the atmosphere control chamber), was crucial to this program, although the improvements in beam quality afforded by the second and third were deemed highly desirable as well. The second and third modifications were therefore funded entirely by other programs but they did impact growth scheduling on this program to some degree.

Details of the construction and testing of the atmosphere control chamber, Fig. 3, were given in each of the four quarterly reports (QR's). Details of the laser attenuation and the microalignment heads were given in QR-4.

A persistent and so far unresolved problem with the present atmosphere control system was detected during the growth of BaF_2 and CaF_2 fibers. These materials, being exceedingly reactive at melt temperatures were very sensitive to low levels of oxygen or water vapor contamination inside the atmosphere control chamber. Typically, high purity argon gas, scrubbed in a 750°C titanium sponge reactor, is used as an inert purge gas. The chamber exhaust port is continuously monitored by a "Thermox Oxygen Analyzer" which uses a high temperature ZrO_2 solid state electrolyte as an oxygen sensing element. By tightening seals, we were able to reduce the partial pressure of oxygen to significantly less than 0.1 ppm. Additional testing of the system tightness with a helium mass spectrographic leak detector in the external sniffing mode was carried out. No detectable leaks were found. However, growth experiments on BaF_2 and CaF_2, to be described later, strongly indicate a source of water or oxygen contamination.

Experiments to improve the argon reactor design have failed to significantly reduce the residual background impurity levels. Discussions with the technical staff at the Harshaw Chemical Company reinforced our conclusion that either a reactive fluoride atmosphere or a high vacuum growth chamber are necessary to grow optimally clear BaF_2 or CaF_2 single crystal fibers. Either approach was somewhat beyond the scope of the present program.

B. Capillary-Fed Fiber Growth System

The prototype capillary-fed fiber growth system was completed and underwent initial testing during the third quarter of the program. During that reporting period it was used extensively to carry out growth experiments on AgBr. The initial configuration was preliminary: its sole purpose was to allow us to learn what the critical system parameters were before making a first series of major modifications. We include a photograph of the system partially disassembled in Fig. 4. The main components of the system, shown more clearly in the schematic diagram in Fig. 5 include: (1) a pressurized quartz reservoir and capillary feed tube, (2) a furnace with a separately adjustable afterheater, (3) a cold finger, (4) a fiber guiding x-y stage, (5) a fiber winding drum, (6) a quartz shroud over the growth zone, (7) a pressurization system to pressurize the reservoir and capillary, and (8) precision temperature controllers for the furnace and after-heater. In this system configuration, the fibers are pulled upward during growth. They must also be totally constrained by the mechanical fiber guides because the halide melts studied here have very low viscosity.

The initial modifications made to the system were described in the quarterly reports. Since that time the only serious problem has been fiber guiding. As Bridges did in his original work (8), we rely on a somewhat oversized and slightly curved teflon sleeve to guide the fiber as it is pulled from the melt and wound on the drum. The theory is that the fiber should touch the sleeve in only three places and that the fiber should be mechanically constrained. However, this technique has not proven to be very satisfactory because slight

diameter fluctuations, as they come into contact with the teflon sleeve, cause the free end of the fiber in the melt to move sideways and this introduces a new diameter perturbation. We have tried a number of modifications to the teflon sleeve geometry. However, none have proven totally successful at eliminating perturbations and diameter fluctuations. It was finally concluded that a better solution would be the development of a guiding system using a set of precision, miniature guide wheels. This task seemed to fit better into a major reengineering of the entire growth system and was deferred to a future date when additional funding could be found. It was clear that better use of the time remaining could be spent on growing other IR materials such as KRS-5 with the existing system and on evaluating these fibers.

IV. CRYSTAL GROWTH AND CHARACTERIZATION

A. Growth of BaF_2 Fibers

Growth experiments on BaF_2 fibers were conducted during the fourth quarter as soon as the atmosphere control chamber was operational. Source rods approximately 1 mm^2 were cut from the single crystal material obtained from the Harshaw Chemical Company. Growth experiments were carried out in the atmosphere control chamber using Ti-purified argon as an ambient. Even though BaF_2 is relatively transparent to 10.6 μm radiation, the source rods were readily melted (MP = 1280°C) and the melt which formed appeared to be quite stable.

Crystal growth from the melt was straightforward using a piece of oriented single crystal as a seed. Both BaF_2 and CaF_2 have the fcc fluorite structure and cleave easily on the {111} planes. Oriented seeds of BaF_2 were prepared within a few degrees of the <110> direction using the {111} cleavage planes as a reference. After growth, the cleavage planes in the fiber were found to be perfectly parallel with the cleavage planes in the seed.

Growth rates were typically in the 1-2 mm/min. range. In most respects, BaF_2 behaved much like one of the stable oxides such as YAG. The only significant problem area encountered, however, proved to have serious detrimental effects on the optical quality. The crystal fibers as they were pulled from the melt were quite transparent and looked to be of excellent quality. One to two millimeters above the melt, a solid state precipitate began to form in a characteristic pattern shown pictorially in Fig. 6. Farther up the fiber in cooler regions, the precipitate density continued to increase until at room temperatures, the fibers were quite milky and resembled a ceramic, Fig. 7. After cooling, the residual material in the molten zone and at the top end of the feed rod also displaying a milky appearance.

The identity of the precipitates is so far unknown although considerable effort was devoted to identifying them. The three most likely causes were felt to be: partial decomposition, reaction with water or oxygen in the ambient, and impurities in the starting

material. Although considerable effort was devoted to reducing oxygen and water contamination in the argon ambient to minimal levels, the precipitates remained. Extensive work by R. C. Pastor et al. (10-12) has shown that molten alkaline earth fluorides are strong getters of water vapor and that even in high vacuum, they can react with water desorbed from the vacuum chamber walls. Producers of high optical quality BaF_2 find it necessary to use a PbF_2 flux in order to produce clear material (13). It therefore seems that water vapor and/or oxygen are the most likely cause.

The precipitates are readily visible under high power microscopy. Transmitted light photomicrographs are shown in Fig. 8. Energy dispersive SEM analysis was carried out on metallographically prepared specimens. However, the defect sites appeared to be vacant of any second-phase material. This could have been due to the polishing process and additional preparation methods were pursued, but with no more success.

Precision powder x-ray diffraction analysis specimens were prepared by grinding several lengths of BaF_2 fibers. However, neither survey scanning nor step scanning were able to resolve any additional peaks that did not belong to either BaF_2 or the Si internal standard which was used. We concluded that the total precipitate volume is simply too low (<<1%) to be resolved by this technique.

Assuming that the defect might be due to a reversible decomposition, we undertook a heat-treatment program using several of the grown fibers under an anhydrous HF atmosphere at approximately 1000°C. It was found that once formed, the precipitate could not be removed by this method. Control bars of clear feedstock material remained clear, showing only evidence of mild surface erosion.

B. Growth of CaF_2 Fibers

Growth experiments on CaF_2 fibers yielded results quite similar to those on BaF_2. Seeds this time were prepared within a few degrees of the <111> direction again using the cleavage planes as a reference. As in the previous case, cleavage planes in the grown CaF_2 fibers were found to be perfectly parallel with cleavage planes in the

oriented seed rods. Breakdown to other crystallographic growth directions was not observed. In all cases, the fibers contained unidentified precipitates. Their density in CaF_2 fibers was considerably lower, however, indicating that this material is less reactive than BaF_2, Fig. 9. Post growth heat-treatment experiments were carried out on CaF_2 again using a reactive anhydrous HF atmosphere. As in the case of BaF_2 it was found that once the precipitates had formed, they could not subsequently be removed.

C. Growth of AgBr Fibers

Experiments on the growth of AgBr fibers were carried out extensively in order to characterize the capillary-fed fiber growth system. Although the problem of fiber guiding was never satisfactorily resolved, we were able to grow 0.4 - 0.9 mm dia. fibers to lengths of 30 cm without great difficulty. Typical growth rates varied from 1.5 to 8.4 mm/min. Fiber guiding instabilities did prevent us from quantifying the next most important set of growth parameters which affect fiber diameter uniformity. However, the following set of parameters were observed to have a deleterious effect on growth stability: short term pressure fluctuations in the nitrogen overpressure applied to the melt reservoir (these are caused in part by the need to slowly increase the average pressure to compensate for melt depletion); drafts in the ambient atmosphere; and mechanical vibrations in the system either from the building or its own rotating machinery. Improvements in these areas as well as in fiber guiding would be essential in any future system of this type.

The diameter uniformity of the as-grown fibers was not as good as that obtained in the laser-pedestal growth of well behaved oxide fibers, and typically varied from 0.7 to 0.8 mm dia over a 5 cm length in a typical fiber, Fig. 10. However the surfaces obtained were noticeably smoother over the short range, Fig. 11, than those of typical oxide fibers.

Because of the reported tendency of the alkali halides to grow as single crystals in fiber form (1,6,7) we carried out only a few studies to verify this. Typical Laue diffraction patterns obtained

end-on from AgBr fibers were rather poor in quality, but they were adequate to verify that the fibers were single crystal. The preferred growth direction was generally near the <100> in those crystals studied, but it did vary somewhat and was found to be off by 16° in one of the fibers studied. This tendency is consistent with the <100> planes having the densest packing in the AgBr (NaCl) structure.

Etching studies using 30 wt% $NA_2S_2O_3$ solutions were quite valuable in revealing AgBr fiber structure and orientation. Very brief etching times of less than one minute were found to produce matte bands as reported (8). However, more extended etching times occasionally revealed strong etch rate anisotropy, and some 0.7 mm AgBr fibers etched for periods in excess of 10 minutes displayed a relatively square cross-section, Fig. 12a. Laue x-ray orientation confined that the fast etching rate directions are <110>'s and the slow etch rate directions are <100>'s, Fig. 12b. The etching rates and temperature dependence found is included in Table I. For a variety of applications, it may be desirable to produce bundles of guiding optical fibers. Fibers having relatively square cross-sections would have a considerably higher packing density than would round fibers, and consequently would have a considerably greater percentage of active area.

Two types of defects were revealed in our growth studies on AgBr. In an air ambient, periodic dark regions caused by black inclusions (shown later) and spaced several fiber diameters apart were occasionally observed. These inclusions were attributed to dissociation of the AgBr as it passed through the tip oven which was, by necessity, operated at 100°-150°C above the melting point (MP = 432°C) in order to place the melt/solid interface above the upper face of the furnace where it could be observed. Bridges also experienced this phenomenon (8) and was able to control it by adding gaseous bromine to the ambient. Because of its reactivity bromine was not used in our experiments. The second type of defect appeared as a light, transverse reflecting or refracting feature that had the appearance of a crack or boundary. In thin metallographically prepared sections, these features were not seen, suggesting that they

were really surface-related and likely caused by localized changes in the fiber surface profile.

The physical cause of fiber diameter fluctuations was due to short-term changes in the fiber growth rate and these were due not to changes in the mechanical pulling rate but to thermal instabilities which caused the position of the melt/solid interface to vary. This was readily observable in the microscope during fiber growth and it was possible to observe as well the occurrence of the dark inclusions at the same time.

In the existing literature on the growth of AgBr, CsI, and CsBr fibers there is little information on optical characterization. One of our primary objectives was to learn how to prepare and characterize IR-transmitting fibers. Our initial emphasis was in the preparation of longitudinal thin sections to observe optical and structural uniformity along the lengths of the fibers, and the preparation of thin axial sections to observe radial features. A longitudinal thin section showing opaque defects of unknown composition is shown in Fig. 13a. These defects correlated with the dark regions mentioned in the previous paragraph and tended also to occur in regions of rapid diameter fluctuation. We observed these defects both in our own fibers and occasionally in a few sample fibers grown elsewhere (14). An axial thin section from a clear section of fiber is shown in Fig. 13b and it shows the presence of fine, opaque inclusions located near the perimeter of the fiber. The central region of the fiber appears to be quite free of defects. Because these fine inclusions are not visible when looking through the side of an unmounted section of fiber, we have not ruled out the possibility that they are caused by the mounting procedure itself. Axial sections from regions containing dark bands show extensive internal features, however, and leave no doubt that they were caused by growth instabilities, Fig. 13c.

Thin cross-sections, when analyzed under crossed-polarizers, show the presence of internal strain, Fig. 13d and e. Additional work will be required to determine whether this is a grown-in feature or whether it is an artifact of mounting and polishing. AgBr plates and lenses

do not show extensive internal strain by this technique, suggesting that the effect may be inherent in the fiber growth process. Identification of defects of this nature constitutes the first step in improving low-melting halide fibers.

A major interest was to obtain some measure of the spectral transmission of AgBr fibers compared to the single crystalline starting material. Samples for this purpose were prepared by mounting a bundle of fibers in a plastic resin and then preparing optically ground surfaces normal to the growth axis. A photograph of a 4 mm thick cross-sectional slice is shown in Fig. 14. After the mounting resin was blackened to prevent stray transmission, this sample was evaluated using dual beam spectrophotometry in a survey made to determine if there were any spectral features present. The transmission spectrum was found to be relatively featureless, Fig. 15, and it compared well with that of the starting material. Published transmission data does show higher short wavelength transparency than we found in either the starting material or in our grown fibers. Part of this could be due to slight photodecomposition which appeared to occur over a several month period with only periodic exposure to ambient room-light conditions.

No serious attempt was made to obtain specific absorption data at discrete wavelengths. These measurements are quite difficult to make on moderate lengths of fibers because of end-face fabrication, and in our particular case, surface scattering caused by local diameter perturbations would have dominated. In addition AgBr fibers are dense and rather easily deformed. This complicated the difficulties of end-face fabrication to the point that we seriously studied only fiber lengths that could be totally encapsulated or otherwise fully supported during preparation, in other words lengths of around one centimeter.

D. Growth of KRS-5 Fibers

Growth of KRS-5 fibers was carried out during the final two quarters of this program using the capillary-fed fiber growth method. Prior to this work, the growth of single crystal fibers by the upright

capillary technique had not been reported. The system used to grow the KRS-5 fibers was identical to that used for the AgBr fibers including the use of a pure silver cold finger positioned slightly where the capillary tip in order to sharply localize the position of the melt/solid interface.

In most respects, KRS-5 was found to behave similarly to AgBr in the capillary-fed system with only one minor exception. Considerably more material condensation was noted on the cold finger as fiber growth proceeded than in the case of AgBr. This did not affect fiber growth however, and, in fact, KRS-5 fibers were somewhat easier to grow. Growth was initiated by dipping a platinum wire into the melt and from that point on the fibers grew readily. Growth rates were varied from 1.5 to 8.4 mm/min. No attempt was made to determine the complete range of stable growth conditions.

Surfaces were found to be quite smooth on a local scale, Fig. 16, but due to the shortcomings in the mechanical fiber guiding system, the long range straightness and diameter stability was somewhat poorer. Single crystal KRS-5 fibers were grown in the 0.4 to 0.8 mm dia range to lengths of 22 cm without serious difficulties.

An initial concern was the actual composition of the grown fibers. (KRS-5 is near the minimum melting composition in the TlBr-TlI solid solution system. Its composition is approximately 58m% TlI - 42m% TlBr and it melts at about 415°C.) The condensate on the cold finger was yellow in color and when analyzed by powder x-ray diffractometry, it proved to be pure TlBr. Consequently, it was assumed that the grown fibers could be deficient in TlBr. Precision x-ray powder diffraction analyses were therefore carried out on the grown fibers as well as on the starting material. No significant differences were found, Table II. Several possibilities could account for this: (1.) The compositional shift may be too small to be detected, or (2.) sublimation from the melt exposed at the capillary tip may be congruent, with the sublimate composition being the same as the melt composition, but with only TlBr condensing on the cold finger. Subsequent inspection of the growth system did reveal the presence of an unidentified clear crystalline material in the location

of the capillary tip suggesting that the second possibility is more likely. In any case, no evidence of condensation on the growing fiber was detected.

The optical quality of the KRS-5 fibers appeared to be quite good except for the presence of a few dark inclusions which tended to occur in regions where obvious growth and diameter perturbations occurred, Fig. 17. In thin axial sections, the fibers appeared to be uniform and transparent. Attempts to fabricate 1 cm long rods with optically flat and parallel faces for absorption measurements were not very successful, however. Microscopic evaluation of these rods end-on suggested internal structure which caused large index variations and strongly distorted the transmission. Except for obvious minor diameter variations no corresponding internal structural features were visible from the sides of these rods under microscopic examination. A large part of the difficulty was attributed directly to a lack of effective diameter and growth rate control during the growth process.

KRS-5 like thallium bromide has a body centered cubic structure, space group m3m. It was of great interest to learn if KRS-5 fibers had a strongly preferred growth direction. Initial attempts to obtain Laue diffraction patterns from mechanically-polished ends of grown fibers were unsuccessful due to work damage and smearing. No suitable chemical polishing etch was found. Ultimately, however, suitable faces were prepared using 0.05 μm Linde A polishing compound suspended in undiluted liquid soap and a Buehler metcloth. Clear Laue diffraction patterns were then obtained, Fig. 18, and these showed that the preferred growth direction corresponded almost exactly with the <110>. This is consistent with the densest plane being the {110} in the CsCl structure. No attempt was made to seed KRS-5 fibers in any other crystallographic growth directions due to time constraints. Such a program would be of great fundamental interest: it would be important to determine if stable growth could be achieved in other crystallographic directions and if there would be any variation in optical quality.

V. SUMMARY: CONCLUSIONS AND RECOMMENDATIONS

At the end of this brief research program, a number of conclusions and observations can be made. The program has been very successful from our point of view in extending single crystal fiber tewchnology into the infrared regime. The diversity of this program has allowed us to study two very different crystal growth techniques, to evaluate them using a number of potentially important materials, and to develop a variety of analytical techniques that have not here-to-fore been applied to single crystal fiber sturctures.

We have clearly demonstrated that the laser-heated pedestal growth technique can be used to grow single crystal fibers of high-melting alkaline earth halides such as BaF_2 and CaF_2. Melts of these compounds were shown to be stable in an inert atmosphere and single crystal fibers could readily be grown. What was concluded to be reactivity with ambient water or oxygen impurities proved to be a troublesome problem area in terms of producing optically clear fibers. Fibers of BaF_2 with its more reactive cation contained considerably more precipitation than fibers of CaF_2. It is strongly recommended that additional fiber growth experiments be carried out in reactive atmospheres containing CF_4, HF, etc., in order to determine if the precipitation phenomenon can be avoided.

Our growth experiments on the low melting halides, AgBr and KRS-5 using the capillary-fed fiber growth method were even more successful. Optically clear fibers of either material could be grown easily using the configuration where the fibers are pulled upward from the melt. This is the first time single crystal KRS-5 fibers have been grown by this technique. We have also shown that localized optical defects such as dark inclusions tended to be coincident with growth rate instabilities. One fundamental limitation of the "pull up" capillary growth system is that the level of the melt in the capillary delivery tube depends totally on inert gas counter pressure over the melt in the attached reservoir. A strong advantage of the inverted, "pull down" configuration is that only gravity and surface tension are relied on to position the melt at the end of the capillary (we assume here that the melt wets the capillary).

A more serious limitation of either the "pull up" or "pull down" configuration is the need for a mechanically sophisticated fiber guiding system. Any mechanically fixed fiber guiding scheme will tend to produce periodic perturbations spaced as far apart as the distance between the fiber guider and the capillary tip. It appeared in our experiments that a mechanically "live" fiber guider would be required to accommodate diameter perturbations (such as occur during initial seeding) without causing simultaneous perturbations at the melt/solid interface. The requirements for such a system include bidirectional operation, zero mechanical "slop," low drag, and zero mechanical abrasion of the fiber surfaces. These requirements suggest a challenging design problem.

Our experiments do not suggest that single crystal optical fibers will offer an alternative to glassy fibers for long distance communications. In lengths of a few meters or less, we have shown that a variety of halide materials appear feasible. Growth system constraints are tight, however, and considerable attention must be paid to controlling composition and reaction with background impurities, and to providing very precise mechanical fiber guiding.

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TABLE I

Etching rates of AgBr single crystal fibers in 30% $Na_2S_2O_3$ solutions. Etching occurs primarily on the {110} surfaces leaving a relatively square cross-section.

Temperature (°C)	Etching Rates (mm/min)
5°C	1.1×10^{-2}
22°C	2.4×10^{-2}
60°C	8×10^{-2}

TABLE II

POWDER DIFFRACTION DATA ON KRS-5

Starting Material		Residual Material		Fiber Grown		Silicon Standard
d(A)	I	d(A)	I	d(A)	I	d(A)
4.12	3.6	4.13	5.04	4.12	4.12	
-	-	-	-	3.48	1.69	
3.14	15	3.14	9.0	3.135	13.5	3.1355
2.92	100	2.92	100	2.91	100	
-	-	-	-	2.55	5.1	
2.38	1.2	2.38	2.0	2.37	2.44	
-	-	-	-	2.035	5.8	
2.06	10.4	2.06	15.8	2.055	13.5	
1.92	5.2	1.92	8.16	1.92	1.35	1.9201
1.84	1.0	1.84	2.28	1.81	1.5	
-	-	-	-	1.74	1.0	
1.682	30	1.68	30	1.68	30	
1.638	5.6	1.635	2.04	1.635	2.81	1.6374
-	-	-	-	1.6	6.7	
-	-	-	-	1.51	0.2	
1.455	5.4	1.455	7.32	1.455	5.6	
-	-	-	-	1.405	0.8	
-	-	-	-	1.372	1.2	
-	-	1.355	1.2	1.355	1.0	1.3577
1.302	7.6	1.305	7.8	1.303	6.0	
1.245	1.0	-	-	1.24	1.2	1.2459
1.188	0.6	1.19	1.1	-	-	
1.109	5.0	-	-	-	-	1.1085
1.107	2.0	-	-	-	-	
1.10	7.0	1.102	7.2	-	-	

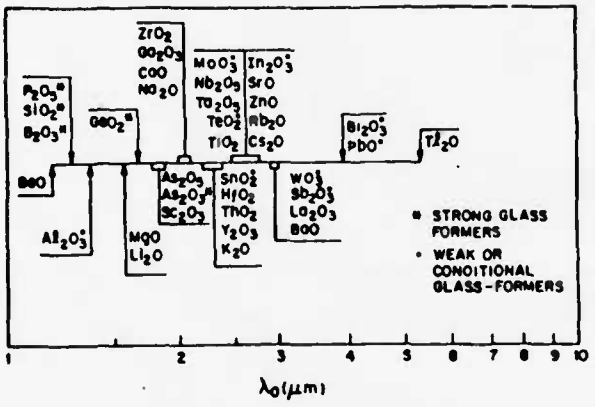


Fig. 1a. The λ_o values of oxides (4).

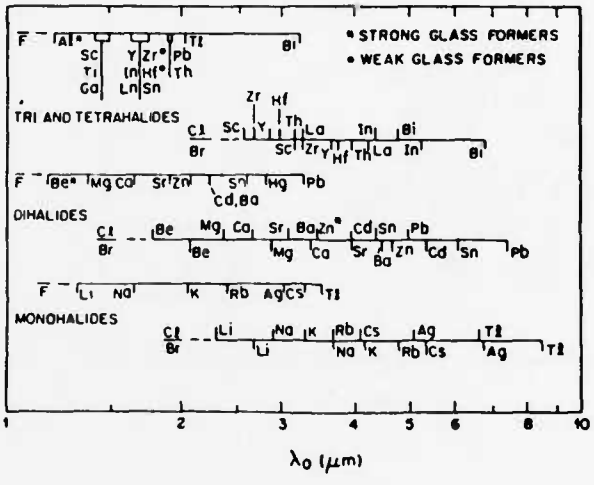


Fig. 1b. The λ_o values of fluorides, chlorides, and bromides (4).

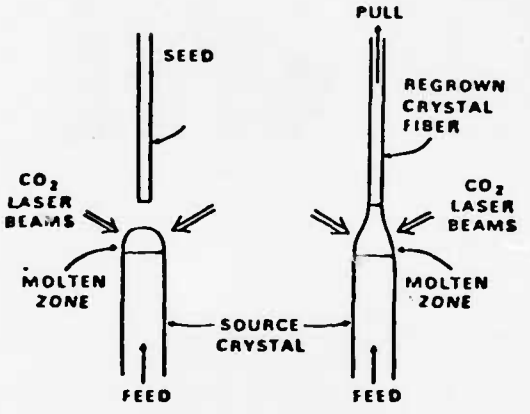


Fig. 2a. Configuration of laser-heated pedestal growth technique for single crystal fibers and rods.

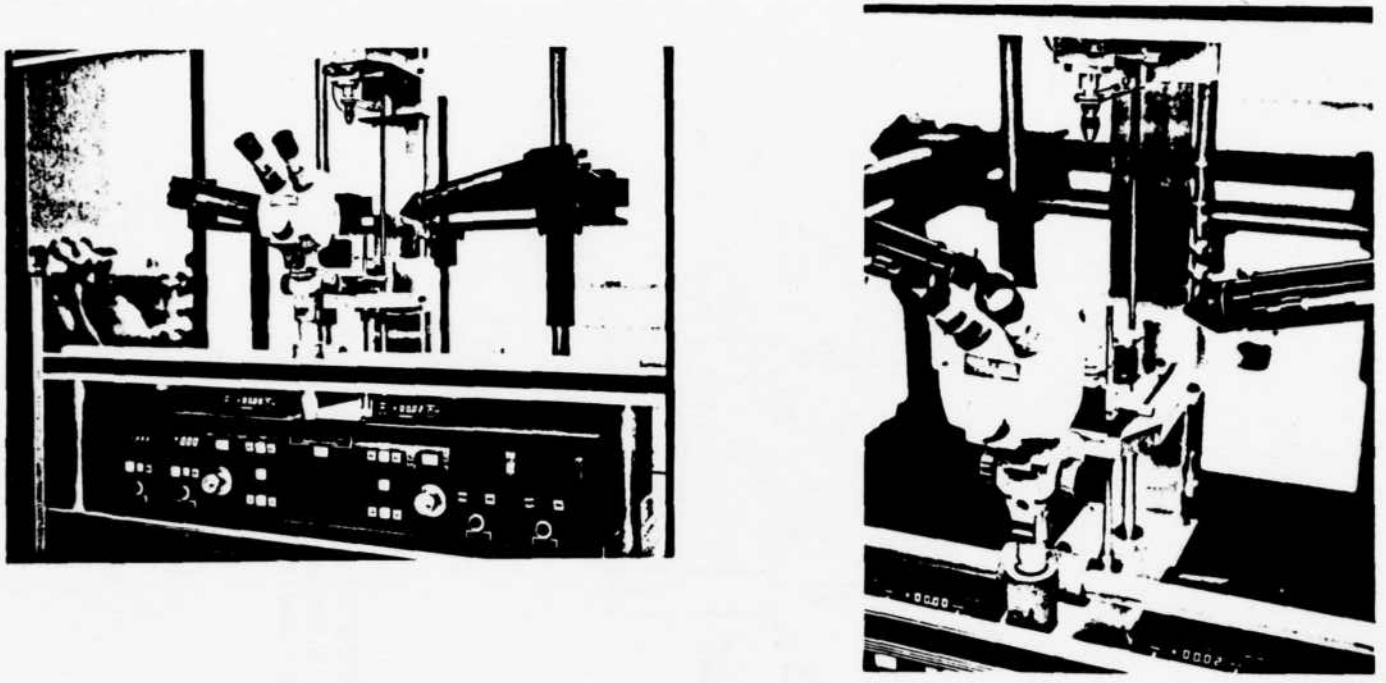


Fig. 2b. Laser-heated pedestal growth apparatus.

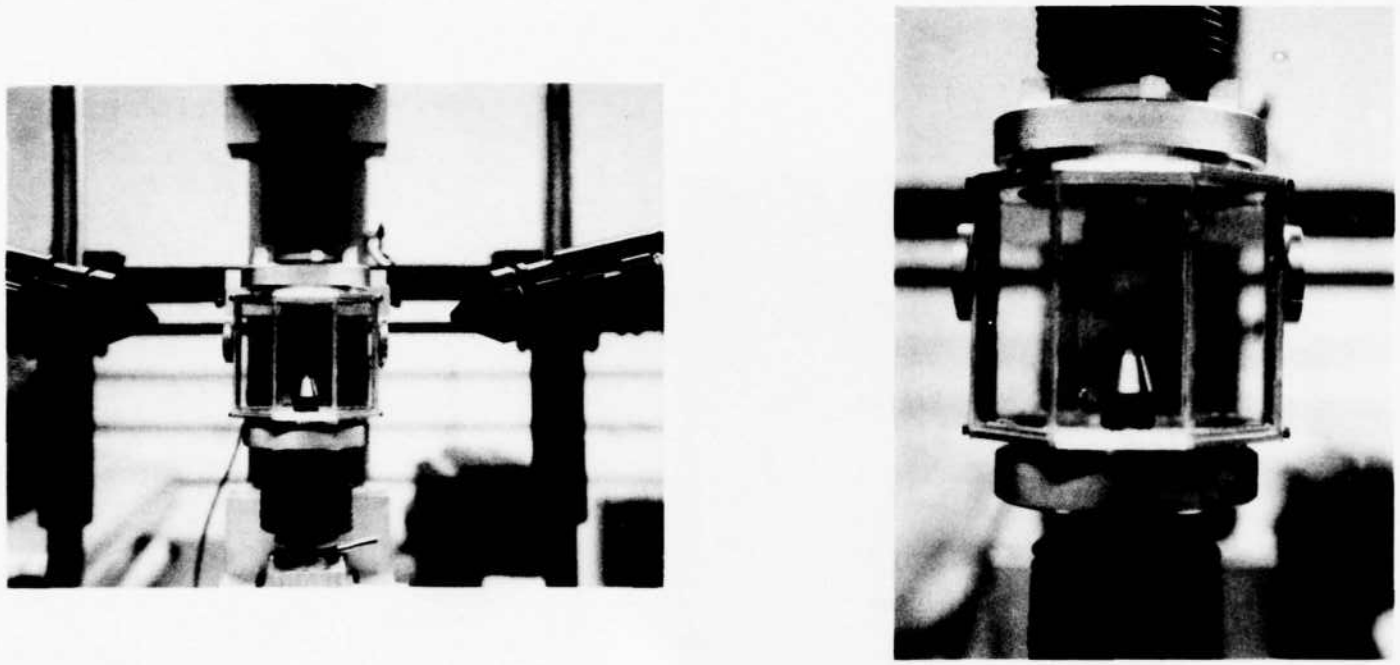


Figure 3: Atmosphere control chamber on the laser-heated pedestal growth system.

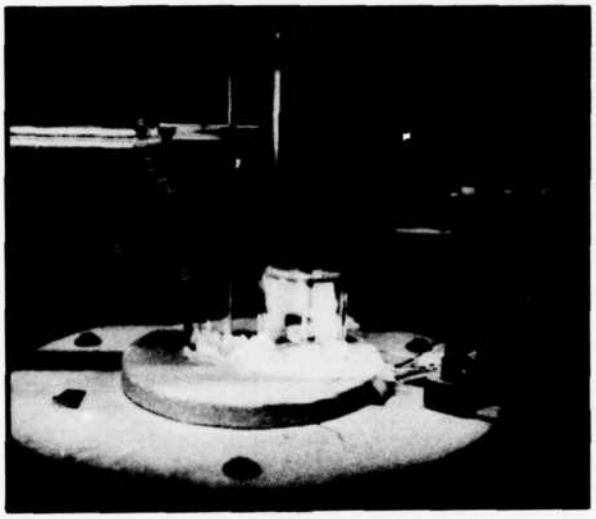


Figure 4: Photograph of preliminary capillary-fed fiber growth system used to identify critical system parameters.

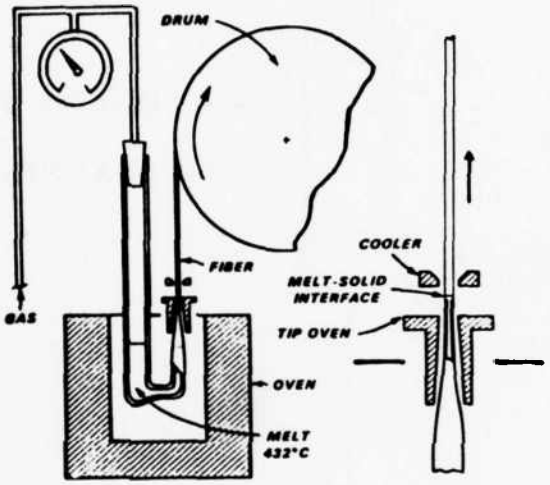


Figure 5: Schematic diagram of capillary-fed fiber growth apparatus from Bridges et al., OPTICS LETTERS 5, 85 (1980).

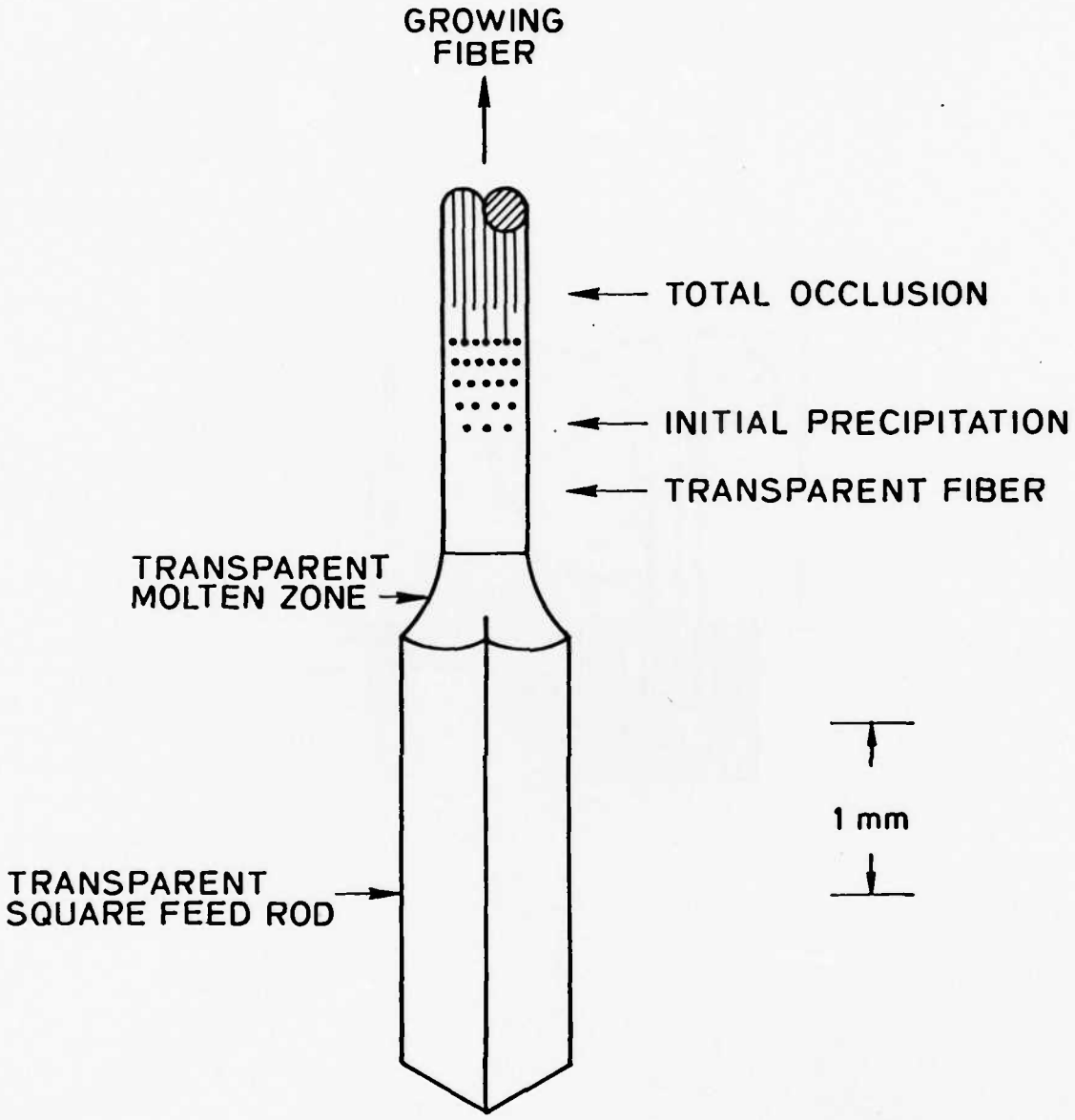


Figure 6: Pictorial representation of solid state precipitation observed during the growth of BaF_2 fibers.

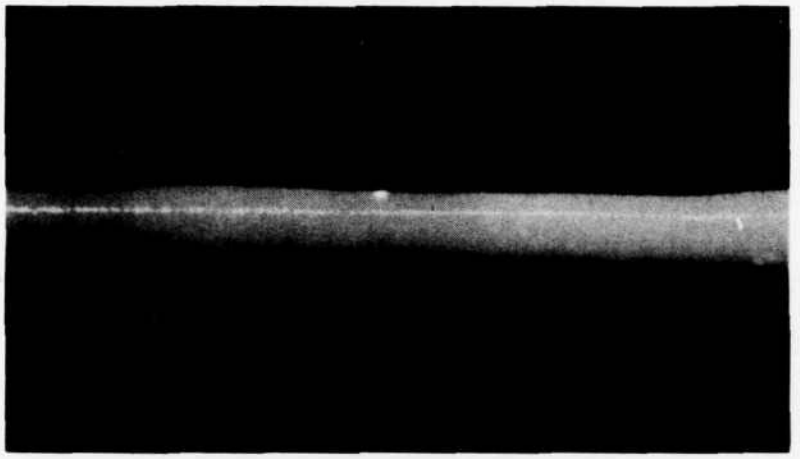
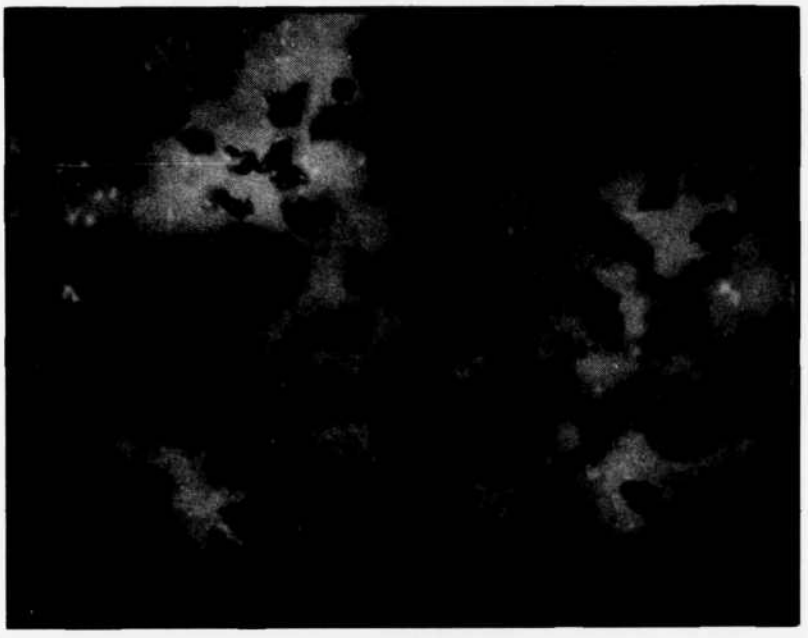


Figure 7: Photograph of an 0.5 mm dia. BaF_2 fiber with a high density of scattering precipitates.



10 microns

Figure 8: Transmitted light photomicrograph of precipitates in BaF_2 fiber.

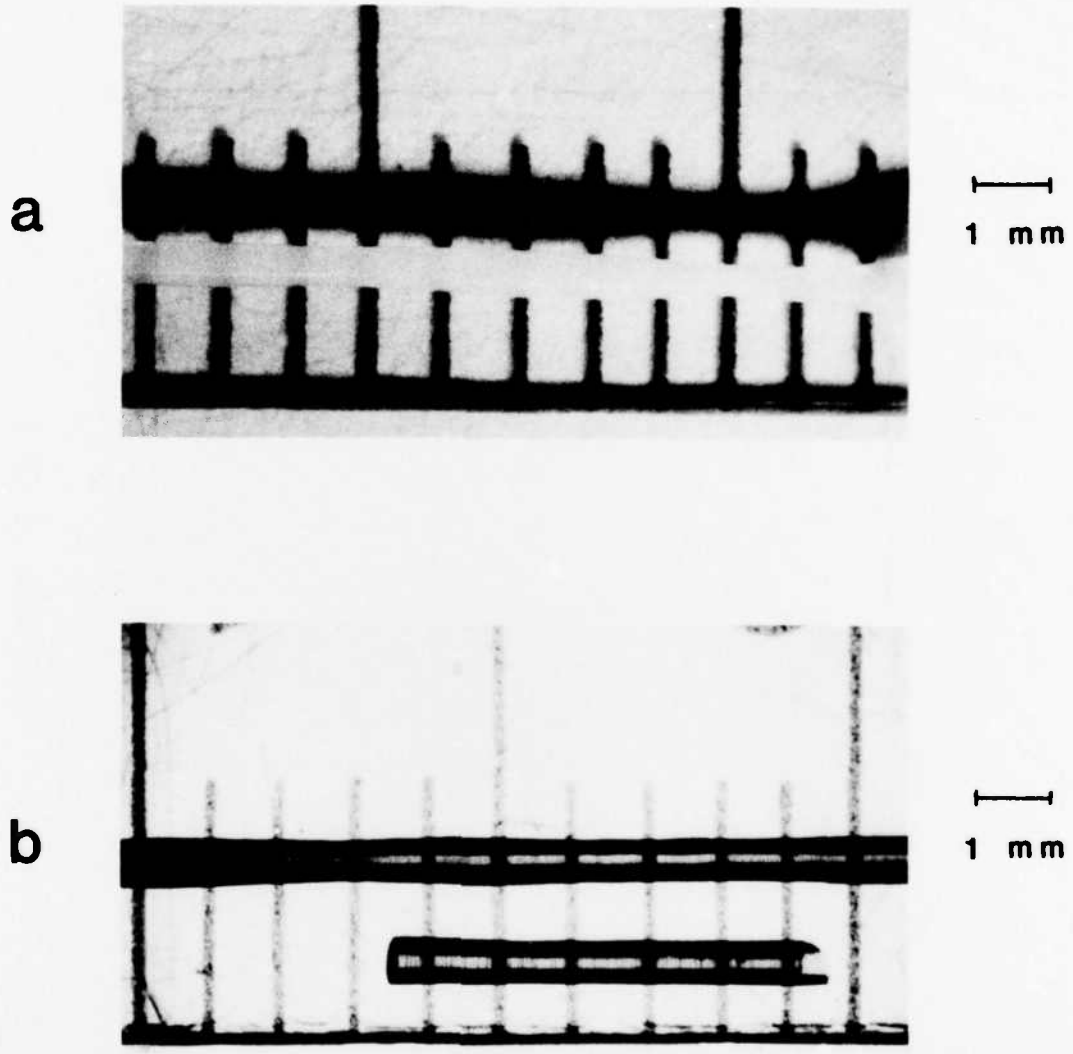


Figure 9: Photomicrographs of CaF_2 single crystal fiber in (a) incident light and (b) transmitted light. The incidence of scattering centers is significantly lower in CaF_2 than in BaF_2, and these fibers are much more transparent than typical BaF_2 fibers.

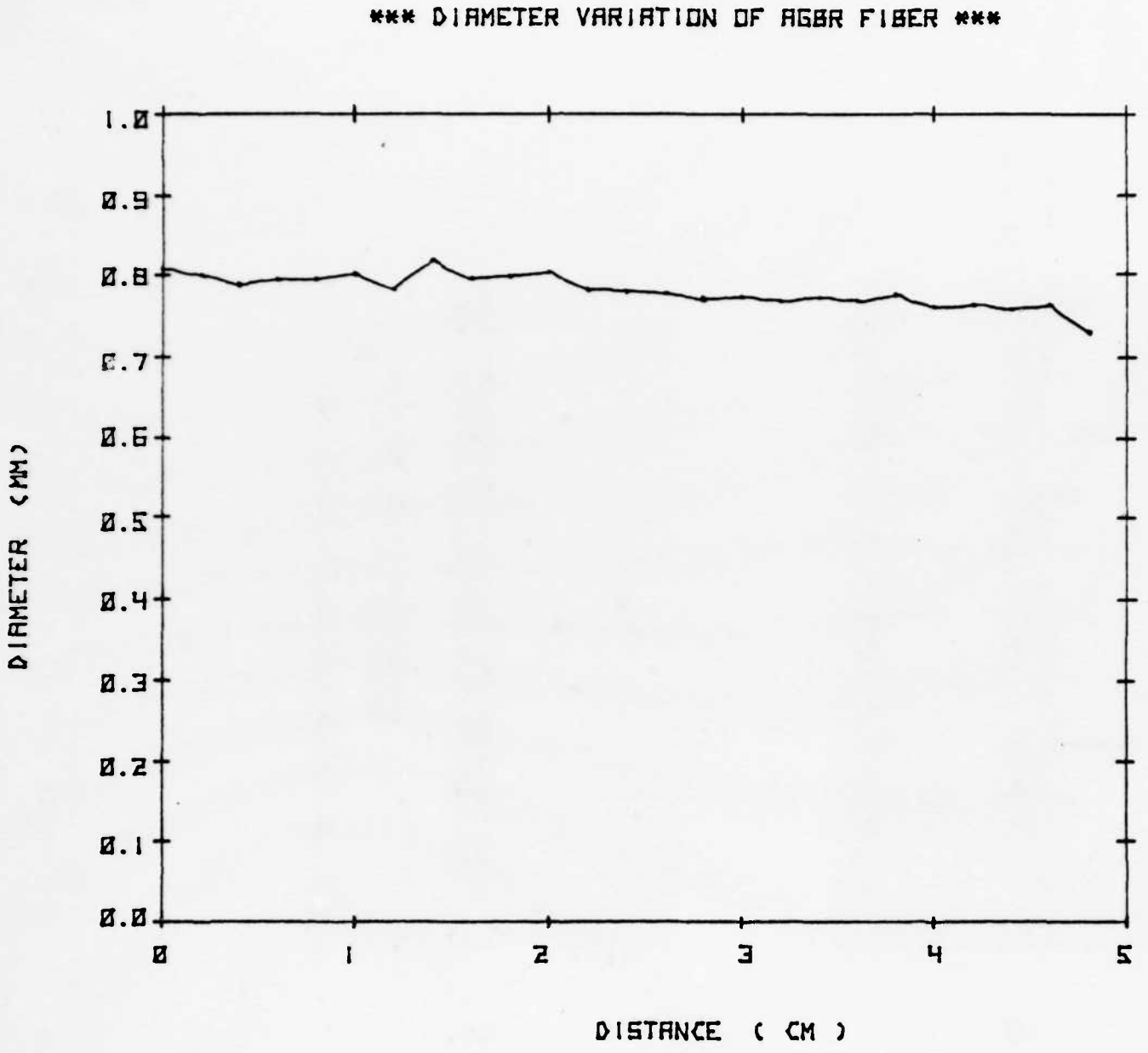
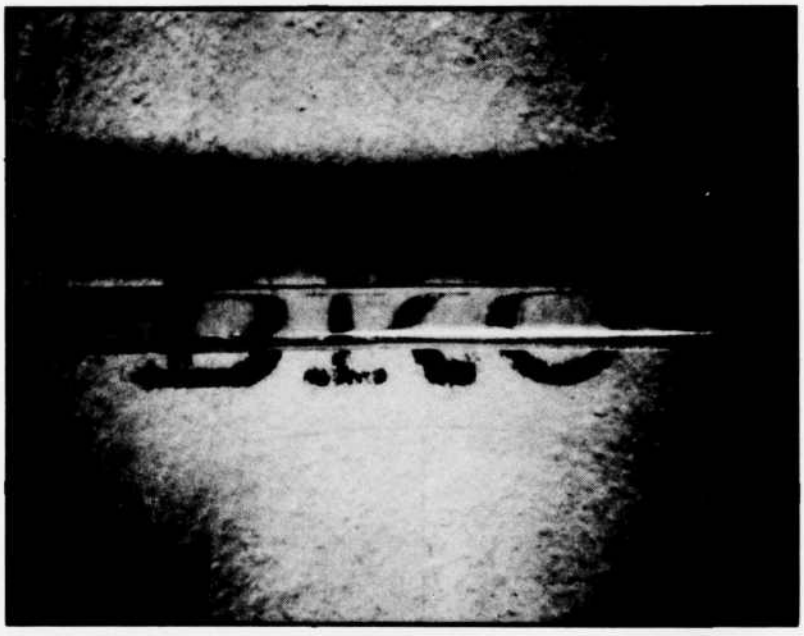


Figure 10: Diameter of a typical 5 cm AgBr fiber as determined with an optical microscope having a $\pm$ 2 μm resolution travelling stage.



1 mm

Figure 11: Photograph of a recently grown AgBr fiber having improved diameter uniformity and surface smoothness.

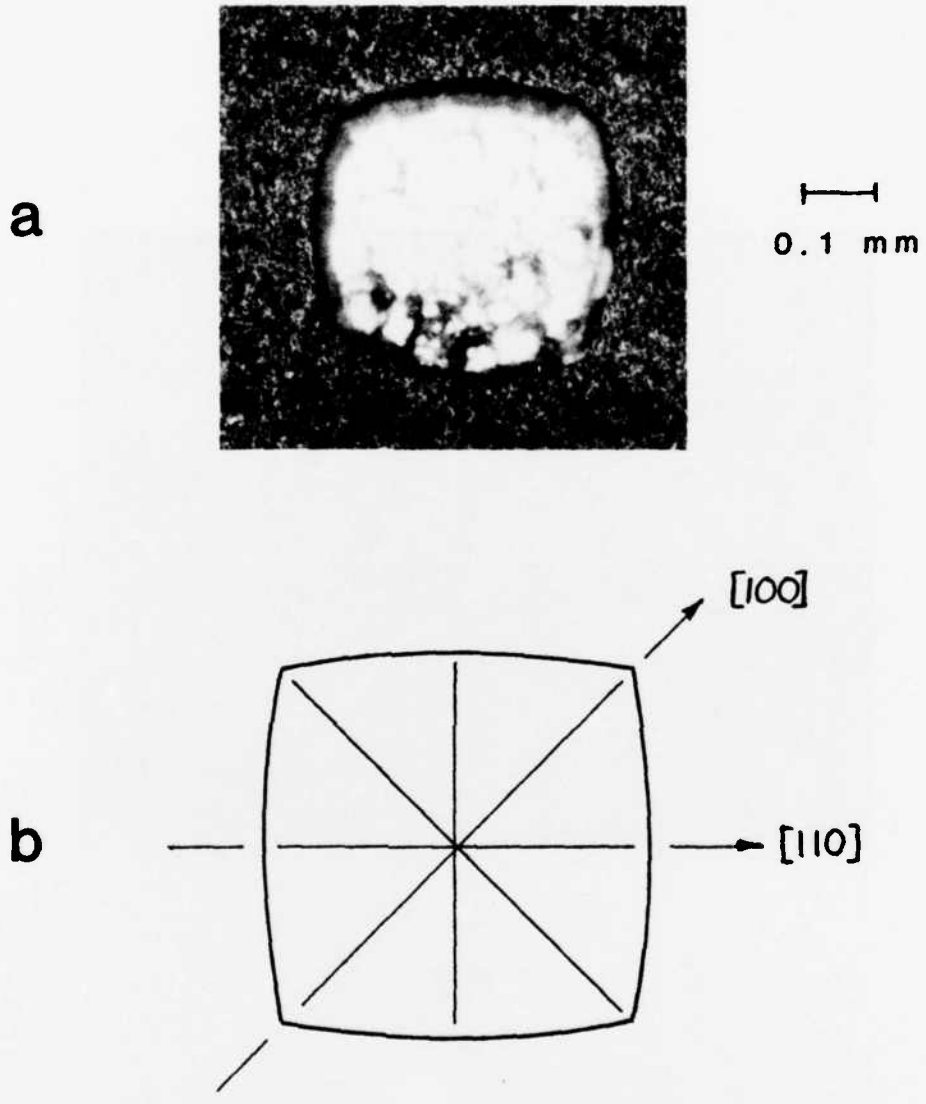


Figure 12: (a) AgBr fiber etched for 10 minutes in 30% $Na_2S_2O_3$ solution, cross-sectional view. (b) Schematic orientation of fiber cross-section obtained by Laue XRD.

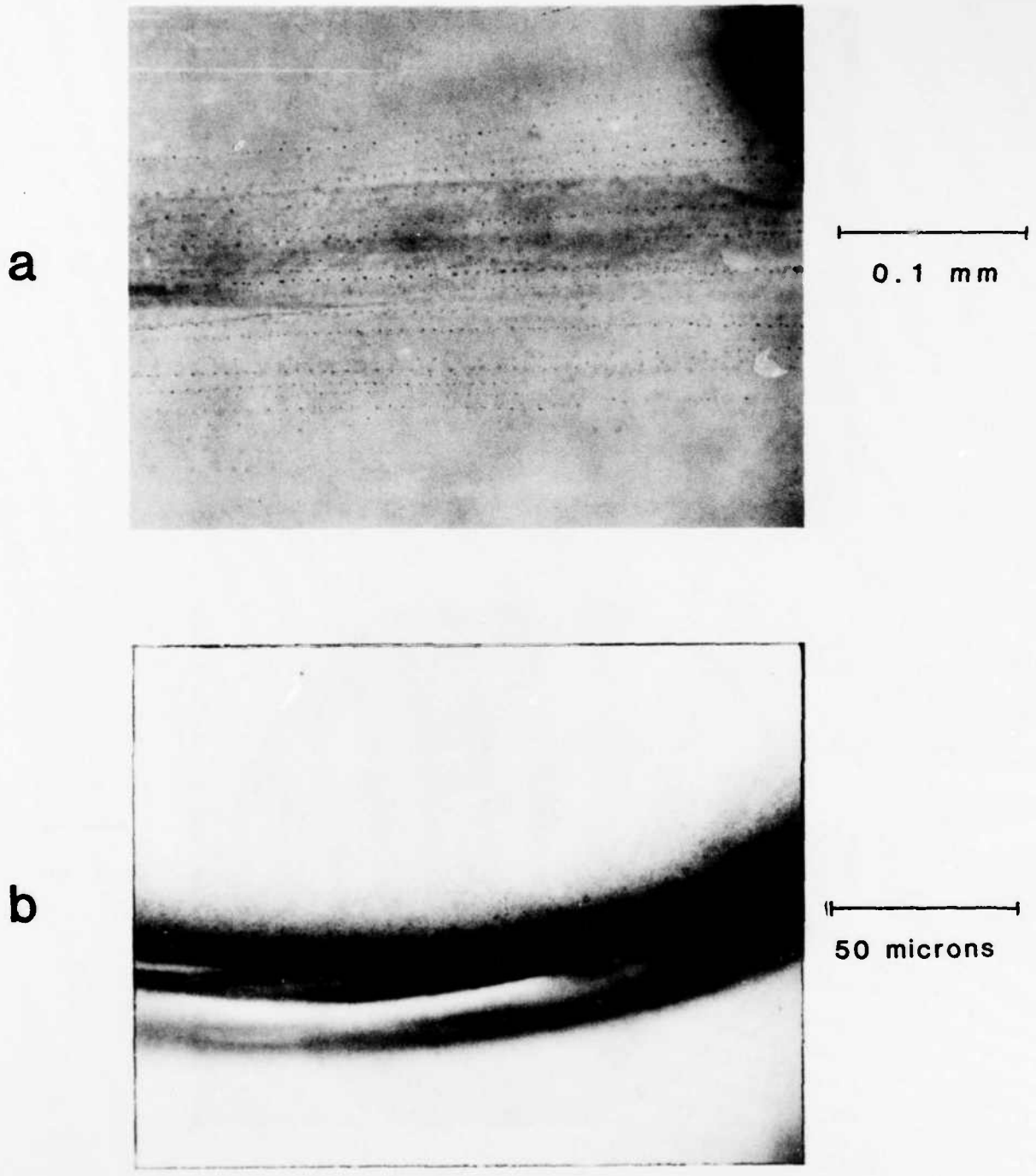


Figure 13: AgBr thin sections. (a) Longitudinal thin section sharing opaque inclusions. (b) Axial thin section, clear in center, but with fine precipitates near perimeter.

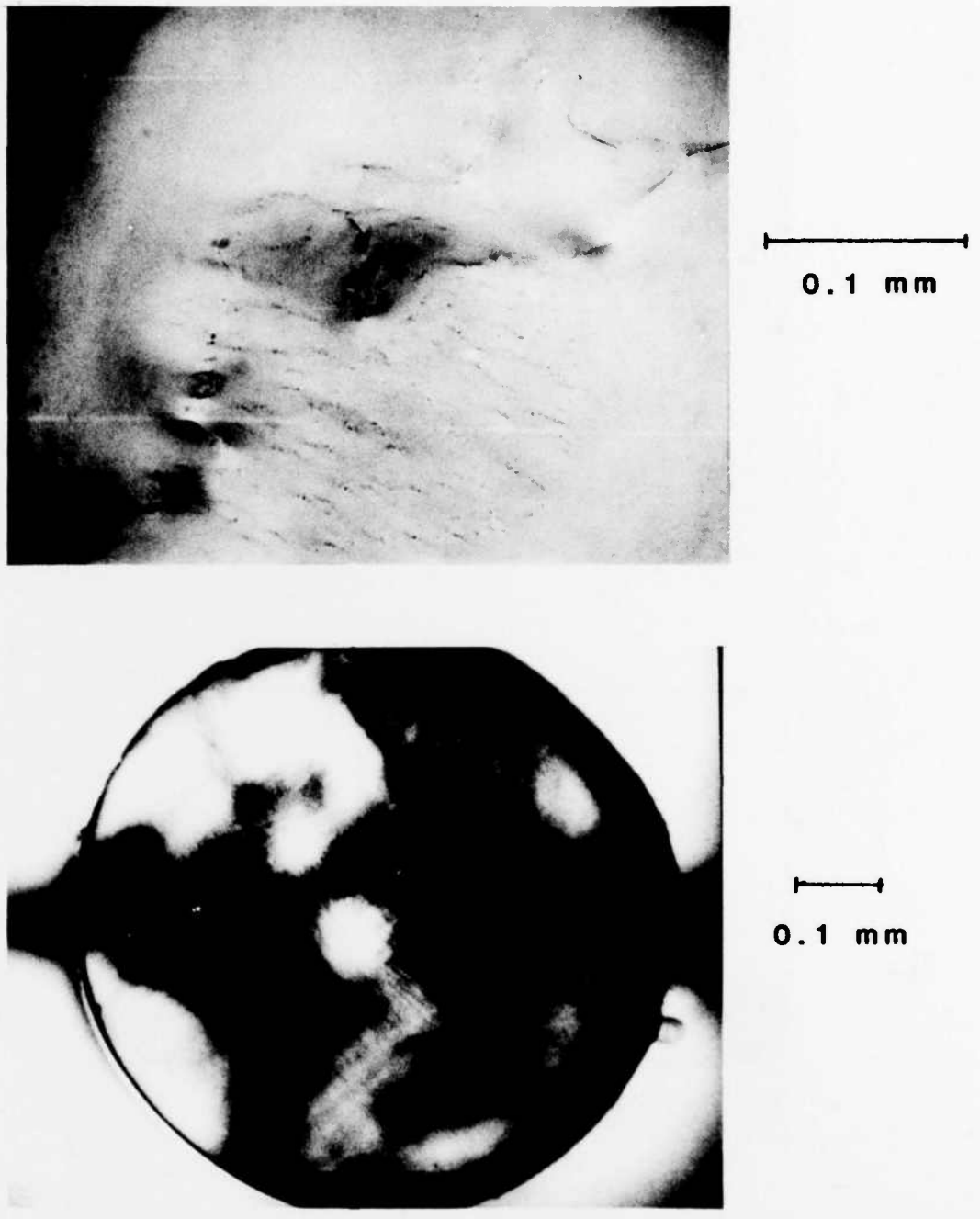
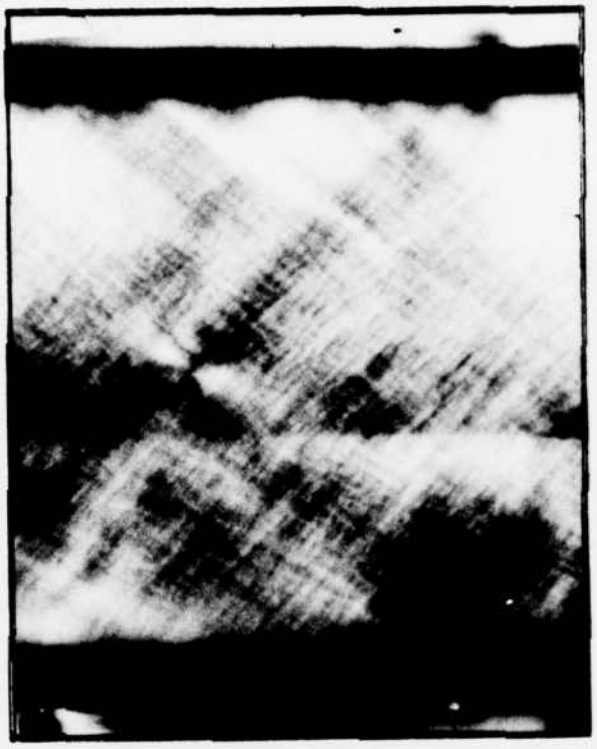


Figure 13 Cont: (c) Axial thin section showing core structure caused by obviously unstable growth conditions. (d) Axial thin section showing internal strain under crossed polarizers.

e



0.1 mm

Figure 13 cont: (e) Longitudinal thin section showing internal strain under crossed polarizers.

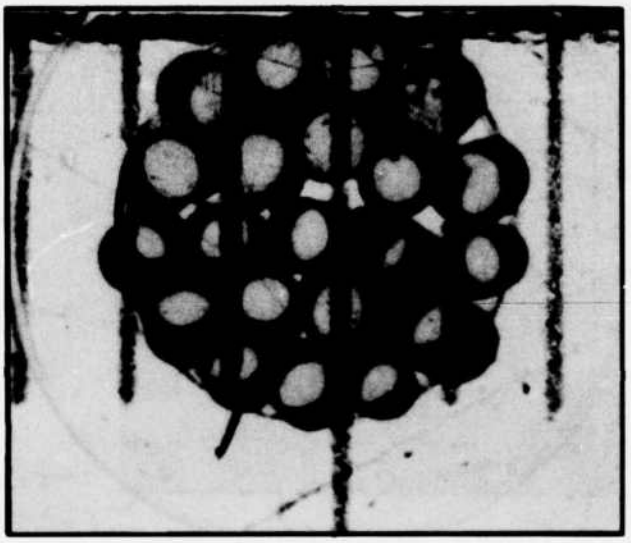


Figure 14: Photomicrograph of a bundle of AgBr fibers approximately 4 mm in length. The ends have been polished flat and parallel to allow measurements of optical transmission.

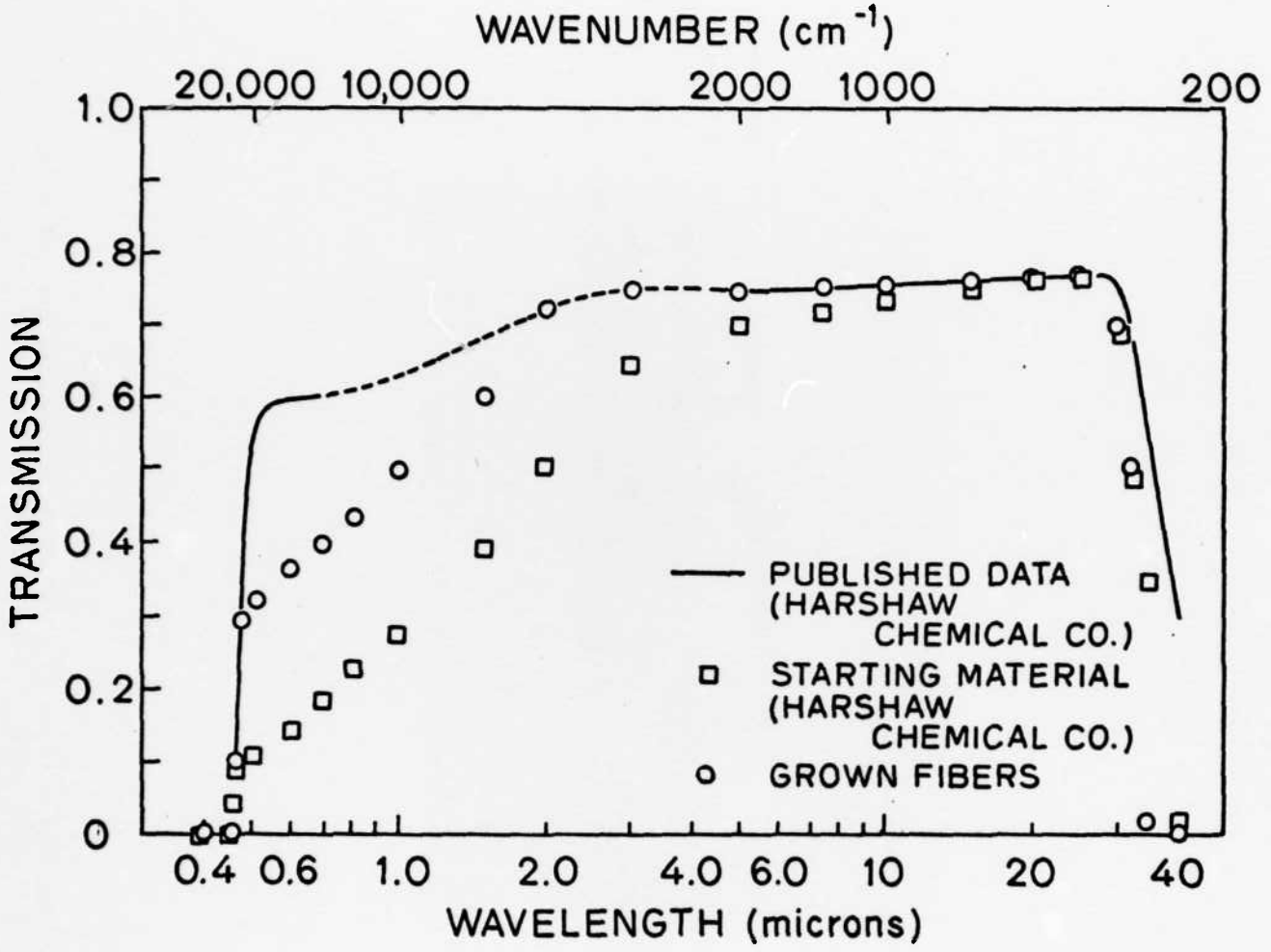
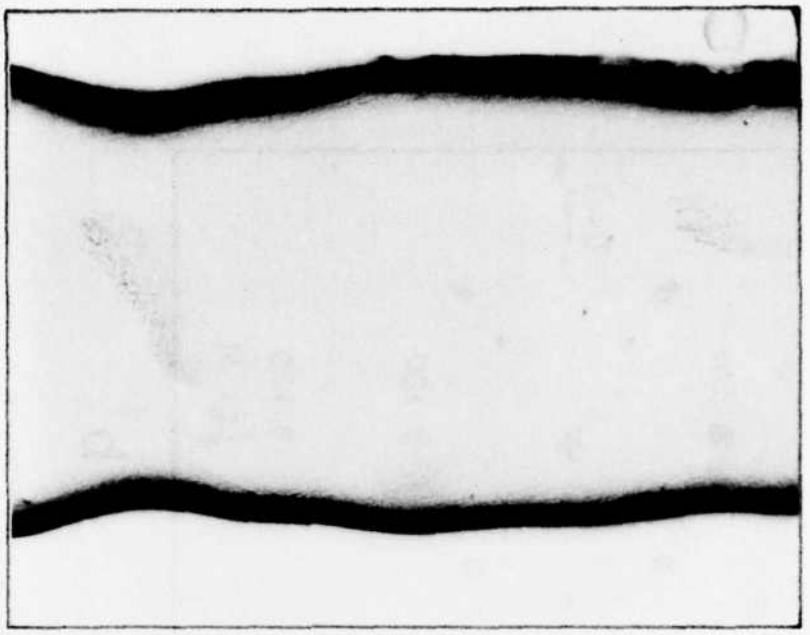
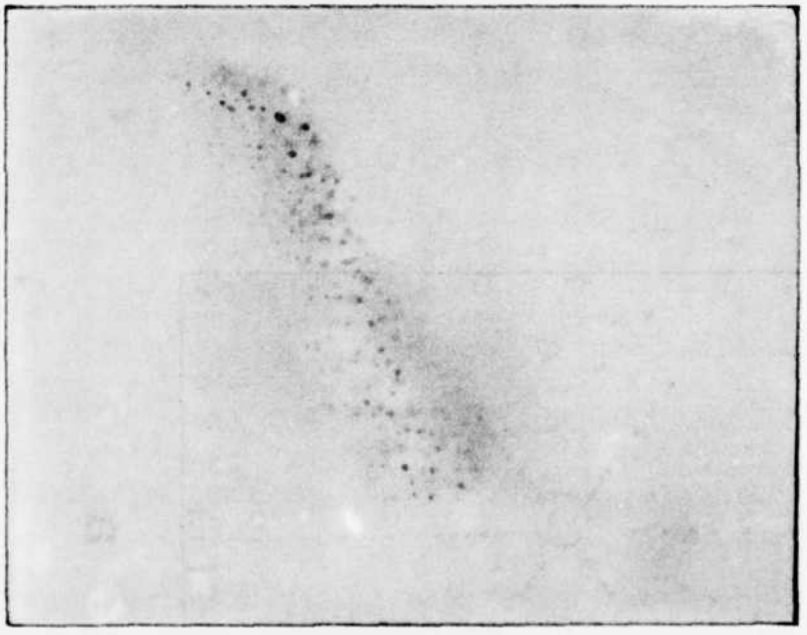


Figure 15: Transmission measurements on bundled AgBr fibers compared with starting material. All data was normalized at 20 μm.

Figure 16: KRS-5 fiber in incident light showing good diameter uniformity and surface smoothness.



0.1 mm



0.1 mm

Figure 17: Longitudinal thin section of KRS-5 fiber showing the occurrence of defects that appear as voids. They tend to occur whenever there is a sharp "necking in" of the fiber diameter.

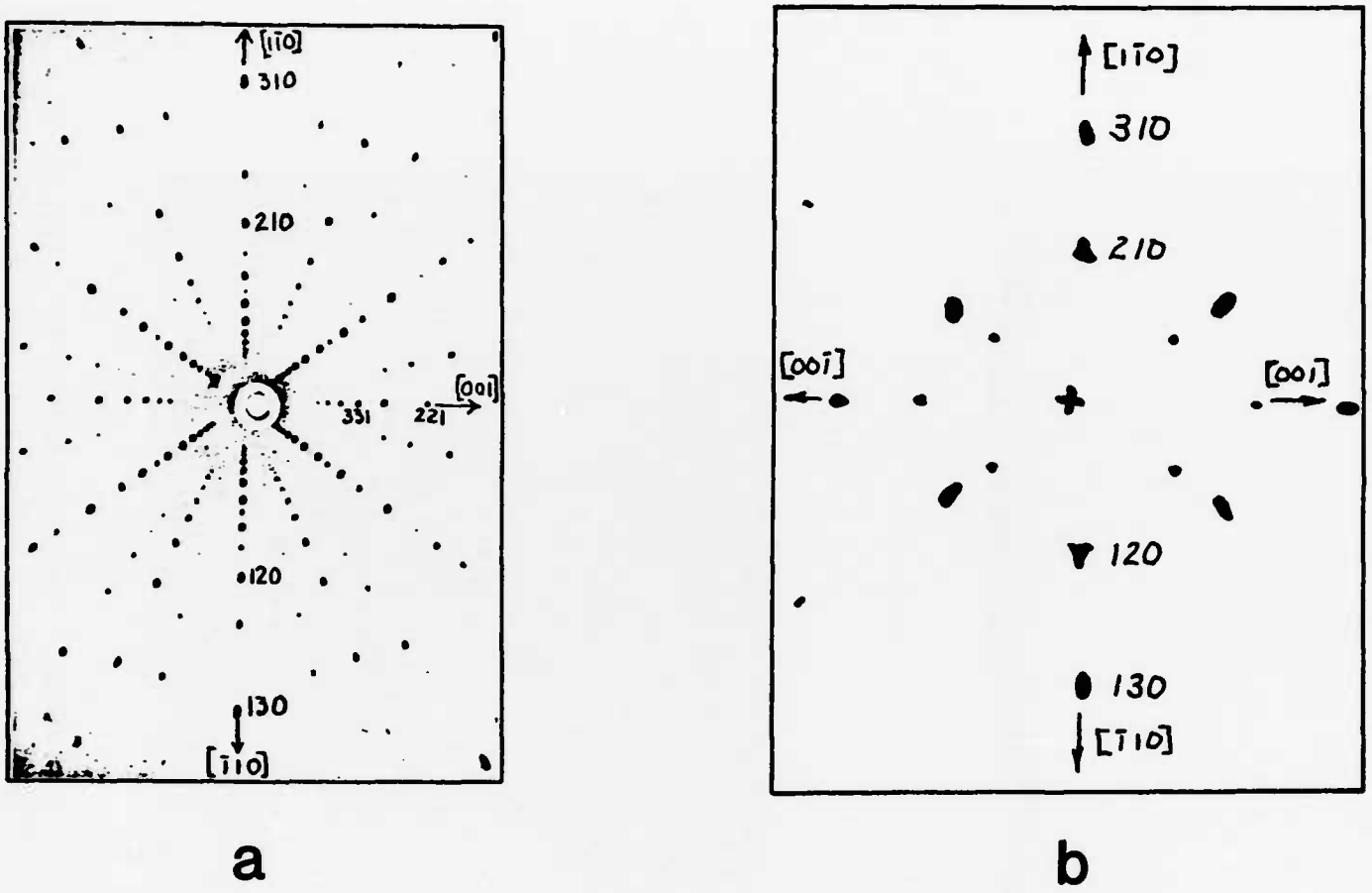


Figure 18: Laue orientation of KRS-5 fiber. (a) Typical bcc crystal with beam approximately parallel to [110]. (b) KRS-5 XRD Laue pattern partially indexed, showing fiber grew within a few degrees of the [110] direction.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