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ADVANCED TECHNIQUES FOR IMPROVING LASER OPTICAL SURFACES

RAYTHEON COMPANY

PREPARED FOR
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
ADVANCED RESEARCH PROJECTS AGENCY

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ADVANCED TECHNIQUES FOR IMPROVING LASER OPTICAL SURFACES

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by

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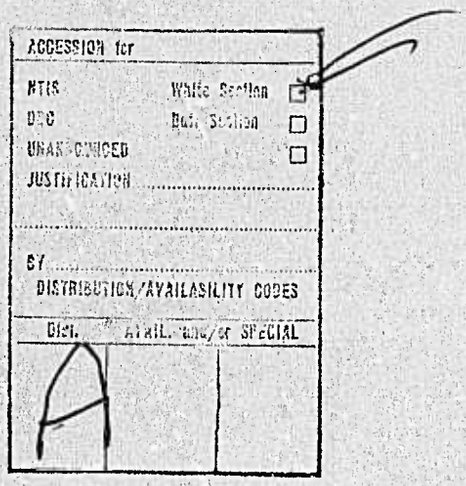

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This program was an eighteen-month study of surface finishing techniques considered to be capable of improving the surface quality of laser optical materials. Chemical and chemical-mechanical polishing, ion-beam polishing, bowl-feed and continuously recycled abrasive "super-polishing" techniques were evaluated for single crystal and polycrystalline potassium chloride and calcium fluoride, and polycrystalline zinc selenide. Optimized conventional grinding and polishing techniques were established for calcium

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fluoride and zinc selenide. Diamond abrasive polishing, using conventional techniques, was shown to produce superpolished surfaces conveniently and reliably on these materials. Optimized chemical polishing techniques were selected for potassium chloride and zinc selenide, and a potentially useful chemical polish for calcium fluoride was identified. Ion beam polishing was shown to be potentially useful only as a final surface cleaning step, preparatory to antireflection coating deposition.

TECHNICAL REPORT SUMMARY

Optical elements of new high-power lasers must eventually handle power densities approaching the fundamental breakdown limits of their component materials. To operate at these levels, the optical elements must be free of such damage-inducing defects as embedded absorbing abrasive particles and field-concentrating pores and microcracks, perhaps as small as 100 angstroms. These are new demands of optical materials which are normally required only to be free of major light-scattering defects (and to have an accurate figure).

This program has been an eighteen-month study of surface finishing techniques considered to be capable of improving the surface quality of laser optical materials. Chemical and chemical-mechanical polishing, ion-beam polishing, bowl-feed and continuously recycled abrasive "superpolishing" techniques were evaluated for single crystal and polycrystalline potassium chloride and calcium fluoride, and polycrystalline zinc selenide. Conventional abrasive polishing procedures for all materials were optimized. The use of zinc sulfide in various forms as an infrared-transparent abrasive for potassium chloride was explored and found to be less useful than conventional polishing followed by chemical polishing.

Conventional polishing of zinc selenide and calcium fluoride is best performed on pitch laps using alumina abrasives. Optimized conditions are summarized in Table VI of the report. Bowl-feed polishing of these materials may be used to improve the conventionally polished surfaces but the results of bowl-feed polishing were found to be difficult to reproduce. Water-based slurries of diamond, used on pitch laps, were found to produce surfaces which were equivalent to the best "superpolished" surfaces. Diamond abrasive polishing consistently produces superior surfaces on these materials.

Relief polishing, differential polishing of the various grains of polycrystalline specimens, was found to be enhanced by soft lap surfaces, and soft or finely-divided abrasives. Diamond abrasives and pitch laps which are just soft enough so that the laps themselves do not produce scratches will minimize relief polishing of polycrystalline specimens.

No completely satisfactory polishing technique for potassium chloride was developed or observed on samples of the material obtained from commercial suppliers. Optically figured surfaces were produced on paraffin laps using alumina abrasives and triacetic glycol slurry vehicles. The most nearly scratch-free surfaces were produced on Politex Supreme* surfaces using alumina or diamond abrasives and isopropanol vehicles. These were poorly figured. Elimination of extraneous particulate matter from potassium chloride polishing stations is a critical limitation of surface quality of polished specimens.

Chemical polishing of zinc selenide may be performed to some extent by several oxidizing solutions. All require the polishing action of a lap surface to remove insoluble reaction products. All produce relief polishing, the appearance of which is also influenced by the etch concentration, polishing time, and choice of lap material. Politex lap surfaces, half molar alkaline potassium ferricyanide, and polishing times of three to four minutes are recommended.

Hydrochloric acid and acetic acid containing chemical polishes for potassium chloride are compared at some length. The surface features which are produced by the solutions are shown to be influenced by the material type, the mechanical polishing techniques used to prepare the surfaces for chemical polishing, and the etch composition. A solution containing four parts hydrochloric acid and one isopropanol is recommended as a chemical polish for potassium chloride. The specimen is immersed in the etch and agitated slowly. This etch will remove approximately three micrometers of material per minute. Infrared absorption measurements made on etched surfaces indicate that the removal of two micrometers of material removes all calorimetrically detectable residues. This etch will produce deep grooves at subgrain boundaries of hot-forged potassium chloride. Surface laser damage produced on HCl-etched forged material did not reveal any tendency of these grooves to act as sites for preferential laser damage.

Acetic acid etchants may be used to polish forged potassium chloride material without producing subgrain boundary grooves if the crystal orientation of the specimen is correctly chosen. This approach should be

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considered only if the subgrain boundary grooves produced by HCl-based etches prove to be unacceptable.

The use of microfiltered solvents and etchants during cleaning and etching of polished specimens is shown to be necessary. Even nominally Electronic Grade reagents may contain particulate matter which can contribute to surface residues.

The utility of ion beam polishing of these polycrystalline materials is shown to be limited to the removal of approximately 2000 angstroms orless as a final preparatory step prior to antireflection coating. Although ion beam polishing was not found to increase the infrared absorptivity of specimen surfaces, surface contamination did occasionally occur in the ion polishing apparatus and the possibility of such contamination should be explored if ion beam polishing is used in component processing.

Finally, several techniques for characterization of finished surfaces are discussed. Of these the most generally useful are Nomarski interference (optical) microscopy, calorimetric absorption, and surface light scattering measurements. Light scattering determinations would be more convenient if a suitable surface replication technique could be developed to avoid the necessity of metallization of the specimen itself.

FOREWORD

This report was prepared by Raytheon Company, Research Division, under Contract No. F19628-73-C-0280 entitled, "Advanced Techniques for Improving Laser Optical Surfaces." This work is supported by the Advanced Research Projects Agency and is monitored by the Air Force Cambridge Research Laboratories, Bedford, Massachusetts.

At Raytheon Company, Dr. C.B. Willingham was the principal investigator of the project. R. Cosgro and F. Taylor performed the experimental polishing work. Optical property measurements were made by Dr. T. Kohane, M. Schapira and T. Varitimos. Scanning electron microscopy was performed by Dr. O. Guentert and X-ray diffraction analysis by D. Howe. Ion beam polishing experiments were performed by Mr. John Gale at Ion Optics, Inc., Winchester Mass. and at Raytheon by C. Dunnrowicz. The zinc selenide polishing effort carried out at Itek Corporation, Lexington, Mass. was directed by W.P. Barnes. Laser damage experiments were conducted at the Air Force Cambridge Research Laboratories with the assistance of Mr. R. Bradbury. Others contributing to the project included Drs. P.A. Miles, D.W. Readey and R.T. Newberg. This report has been given an internal number of S-1856.

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1.0 INTRODUCTION

The goal of this project is to develop surface fabrication techniques which will permit the highest possible laser damage thresholds to be obtained on surfaces of optical components of lasers operating in the 3-5 and 10.6 micrometer spectral ranges. The techniques sought must first of all be capable of producing accurately fabricated optical figures. Further, they must produce surfaces which are free of scratches, of embedded abrasive particles, and of field-concentrating features such as pores and microcracks, perhaps as small as 100 angstroms in breadth.[1] Finally, cleaning procedures which are capable of removing surface solvent and wax or pitch residues must be included, so that the surfaces are prepared to receive adherent antireflection coatings.

This project considers the surface finishing of three materials: zinc selenide, calcium fluoride and potassium chloride. These materials represent three material classes and are themselves important laser optical materials. The finishing of polycrystalline specimens is emphasized because polycrystalline components are or will be fabricated from each of the materials. In the past, most optical materials have been either single crystals or glasses.

This project begins by considering the grinding step which is used for the first rough shaping of the components. Since all the candidate materials fracture by cleavage, it is important to understand the extent to which cleavage cracks driven beneath the surface during grinding re-emerge as damage during polishing. A variety of conventional polishing techniques is explored for each material and optimized choices are made from among them. In this report, a reasonably extensive discussion of both successful and unsuccessful techniques is included in the text. Optimized surface finishing techniques have frequently been regarded as proprietary information by those possessing them. Funded research in this area has made possible a wider distribution of optimized surface finishing techniques and the alternatives from which they were chosen. Recommended procedures are presented more concisely in the Technical Summary.

The superpolishing techniques of bowl-feed polishing and continuously-recycled abrasive polishing are explored. For the latter, as well as for a consideration of techniques for conventionally polishing zinc selenide, Itek Corporation was funded as a subcontractor to this project. Their results are summarized along with Raytheon work, some of which was carried out in parallel.

The double constraints of optical figure and surface perfection require that the abrasive polishing steps be followed by a further treatment to remove the surface damage and remnant abrasive particles. Chemical etching, chemical-mechanical polishing, and ion beam polishing are discussed in this context.

Polished surfaces are inspected and characterized by a variety of techniques including optical microscopy, scanning electron microscopy, and surface light scattering measurements. Laser damage morphologies of chemically polished potassium chloride are reported.

2.0 RESULTS

2.1 Introduction

The experimental work described in this report was conducted in a complex of three cleanrooms constructed for this and other surface evaluation projects. The polishing laboratory contains four 8-inch Strasbaugh polishing units housed in a laminar flow fume hood (Fig. 1). Filtered air is passed around the polishing laps and exhausted from the room. The work area for each polishing unit in the hood is partitioned from the others to prevent abrasives used on one unit from contaminating another. Two of the polishing units are equipped with slurry pumps and can be used for continuously recycled abrasive polishing. Grinding operations can be performed on a fifth Strasbaugh unit, located in a separate room.

The polishing laboratory also contains a clean chemical fume hood, a fitered deionized water supply, filtered dry nitrogen guns, and a pressurized tank which was used to rinse specimens in filtered isopropanol sprays. A Nikon Apophot microscope equipped for Nomarski interference microscopy is used in the polishing laboratory for specimen evaluation.

Surface and bulk light scattering measurements and 10.6 micrometer laser absorption calorimetry were performed in a second laboratory. The metallic films required for the surface light scattering measurements and the scanning electron microscopy were deposited in the third cleanroom of the complex.

2.2 Surface Evaluation

2.2.1 Optical microscopy

Optical microscopy is the most straightforward surface inspection technique available. Defect counts on representative photomicrographs can be used to compare polishing techniques, and defects as small as one or two micrometers can be imaged. Very highly polished surfaces, however, produce low contrast photographs and in all cases photographs are

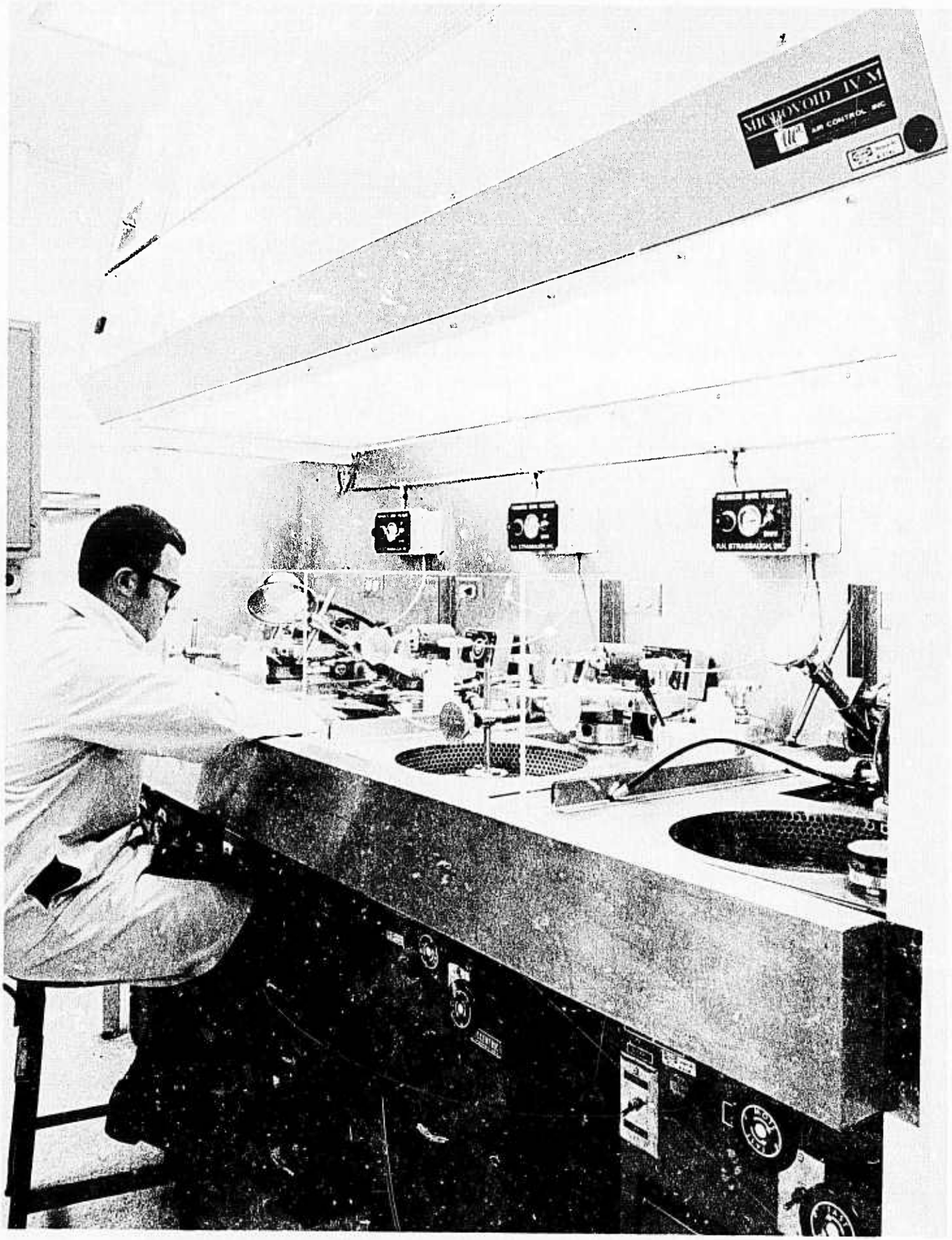


Fig. 1 Raytheon Optical Polishing Facility.

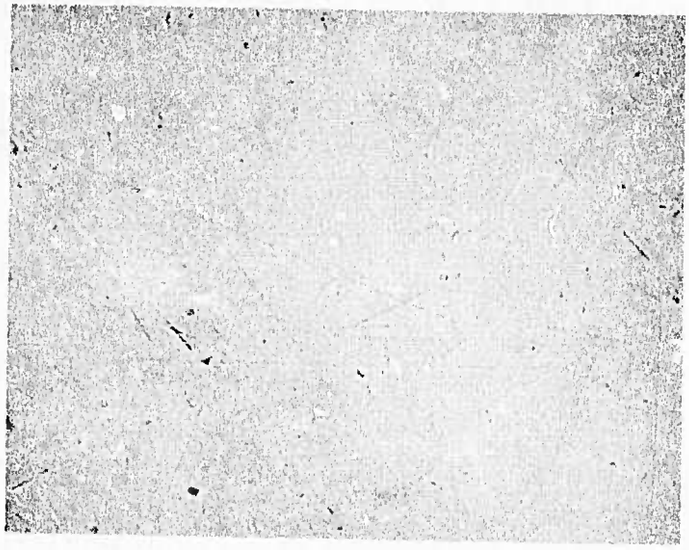
less detailed than the visual image. In this regard, we have found that among Polaroid films Types 52 and 55 are superior to Type 57. These are, however, low speed films which may require inordinately long exposure times to image the low contrast surfaces of highly polished low index of refraction materials.

Two optical microscopes, a Nikon Apophot instrument with an interference microscopy attachment and a Wild M-12 microscope with bright and dark field capability were available for use on the project.

Sample photographs of a zinc selenide specimen polished with Linde-A abrasive for four hours taken with the two microscopes appear in Fig. 2. The Nomarski image (Fig. 2c) is the sharpest of the three. The microstructure of the specimens, made visible by unequal polishing of the variously oriented crystallites in the specimen (relief polishing), can be seen faintly and the image appears to contain more scratches than those taken by the Wild microscope. A statistical comparison of photographs taken by the two instruments, described in Appendix 1, demonstrated that the Nomarski interference micrographs contained significantly more information than the other two, and that there was no significant difference between bright and dark field images in the Wild microscope. This result is somewhat surprising because dark field microscopy, in which the sample is illuminated obliquely by a cone of light surrounding the viewing axis, should be particularly sensitive to scratches. As noted above, the photographs were less detailed than the visual images, and the poor showing of dark field microscopy may have been a photographic problem. Following the statistical comparison, the Nikon/Nomarski microscopy was used exclusively.

2.2.2 Scanning electron microscopy

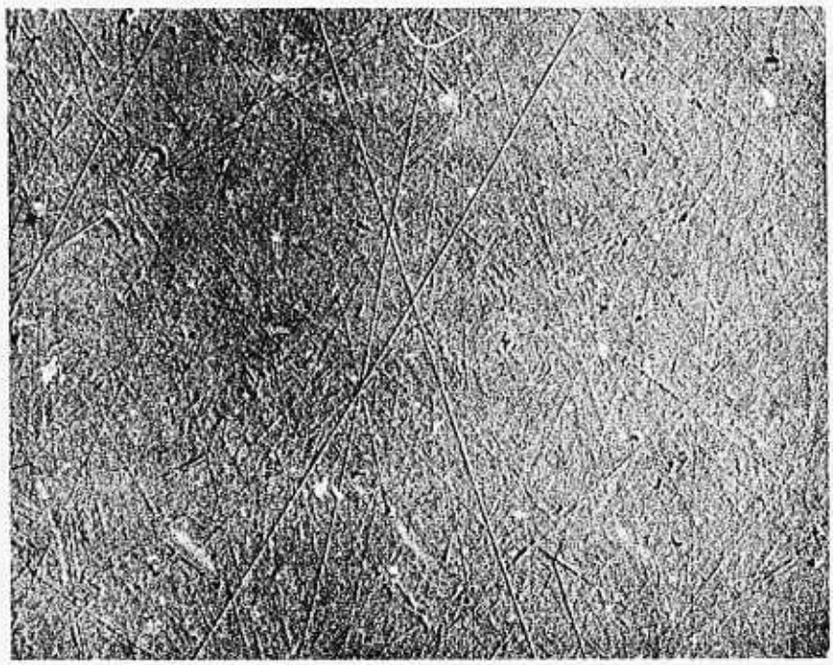
The scanning electron microscope (SEM) scans the specimen surface with an electron beam. Images are formed when an appropriate detector is scanned in synchronism with the electron beam raster. Although secondary electrons from the surface are most commonly imaged, back-scattered electrons, X-ray fluorescence and visible luminescence can also be used.



a. Wild Microscope, Bright Field 183×

b. Wild Microscopy, Dark Field 183×

Fig. 2 Comparison of Optical Microscope Images of Polished Zinc Selenide Surfaces.



c. Nikon Microscope, Nomarski Interference 187X

Fig 2 (Cont'd)

The most striking feature of the SEM is its essentially infinite depth of field which makes it quite useful even at magnifications attainable with optical microscopes. The resolution limit of typical scanning microscopes is approximately 200 angstroms.

Using an International Scientific Instruments Mini Sem microscope at Raytheon and a Materials Analysis Corporation instrument located at Photometrics, Inc., Lexington, Mass., we have determined that the SEM does not image the details of highly polished surfaces well. Figure 3 is a comparison of a portion of a calcium fluoride specimen, bowl-feed polished using tin oxide as an abrasive, photographed with the SEM and with the optical (Nomarski) microscope. Its preparation is discussed in paragraph 2.3.4. Both micrographs are taken at approximately 200 diameters. The large scratch was introduced intentionally in the sample's conducting coating to locate the area to be photographed. Surface structure apparent in the optical micrograph cannot be found in the SEM image. At higher magnifications, scratches in surfaces of intermediate quality are imaged (Fig. 4), but transmission electron microscopy of surface replicas, discussed in paragraph 2.2.3, is a better technique. Scanning electron microscopy is useful for identifying surface features which are deeper than polishing scratches but are too small to resolve clearly in the optical microscope. It is also a useful tool for the study of abrasive powders. In Fig. 5, Linde "B" alumina abrasive and another superfine alumina, Alon* fumed alumina are compared. The particle size of the "B" alumina in the photograph is considerably larger than 0.03 micrometers, the nominal average particle size for this material. Note, however, that the larger particles appear to be aggregates of smaller ones. These aggregates are probably produced by the calcining treatment used to produce the material. SEM specimens of abrasives were produced by ultrasonically agitating

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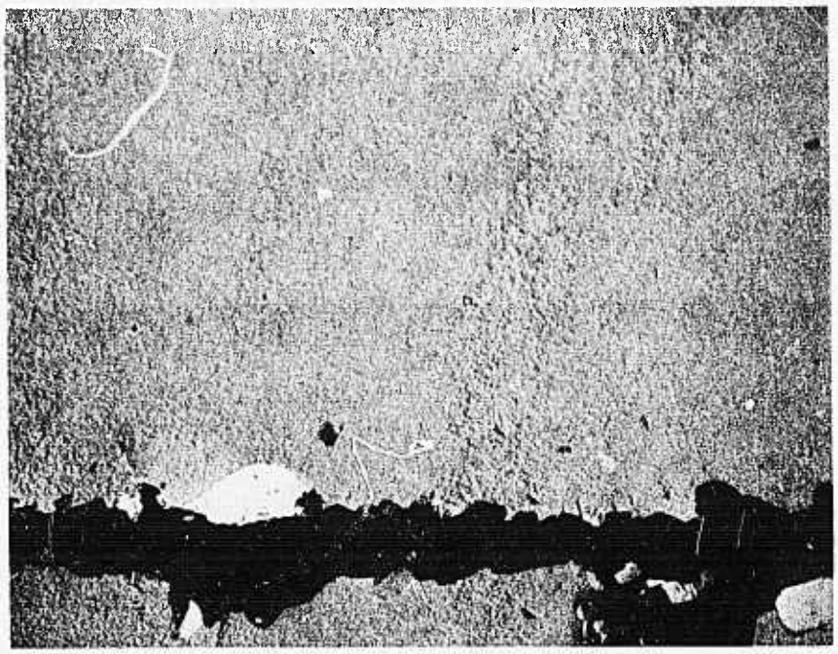
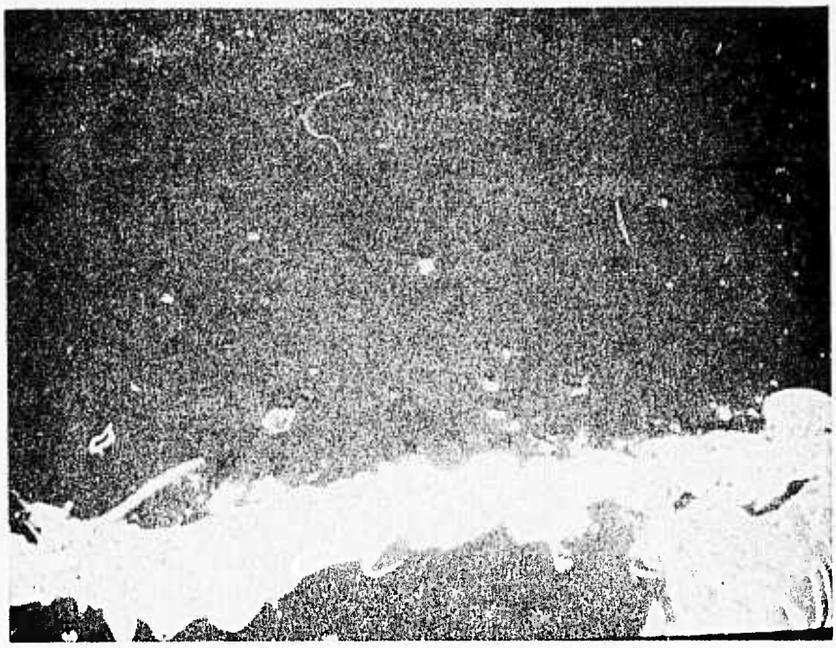


a. Optical Microscope (Nomarski) 186×



b. Scanning Electron Microscope. 200×

Fig. 3 Comparison of Optical and Scanning Electron Microscope Images of Calcium Fluoride Specimen, Bowl-Feed Polished Using Tin Oxide Abrasive.

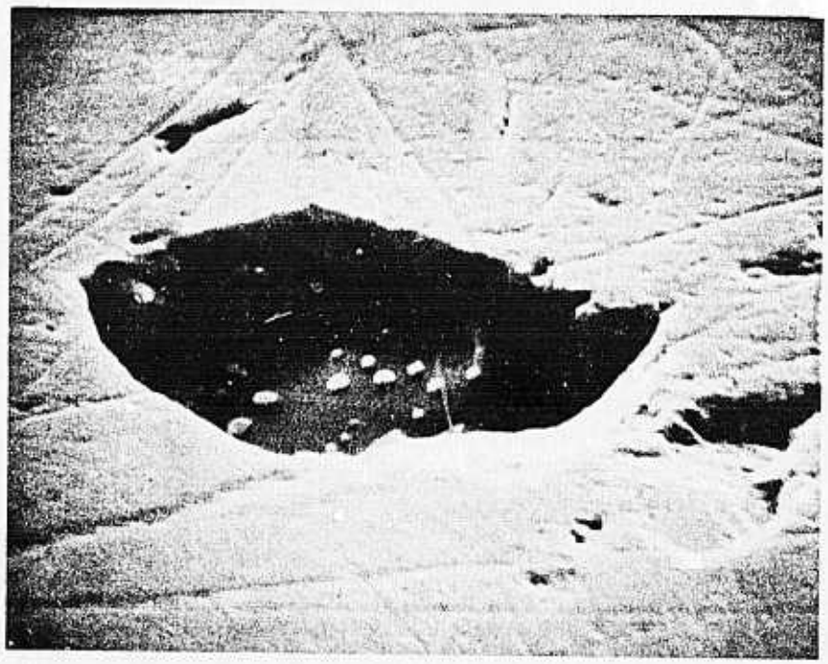
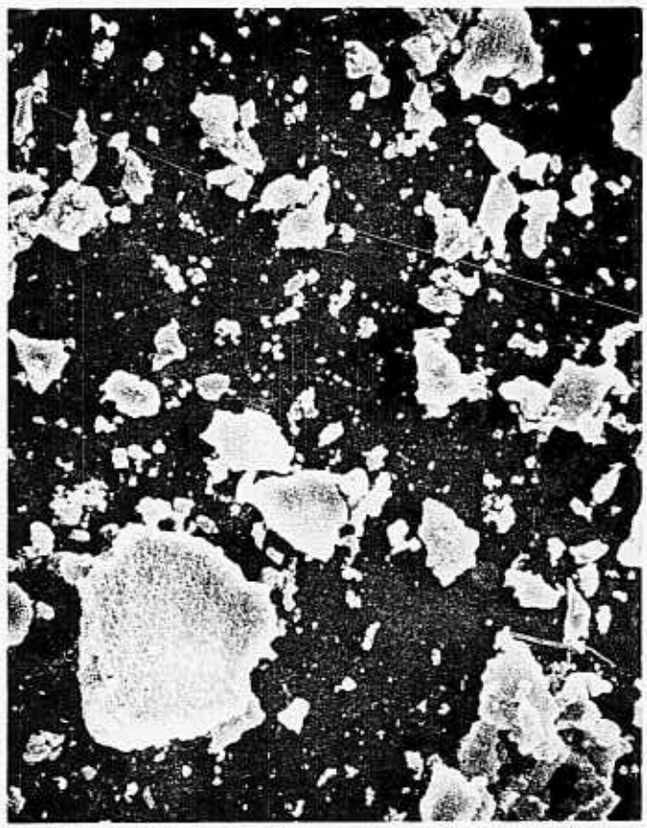
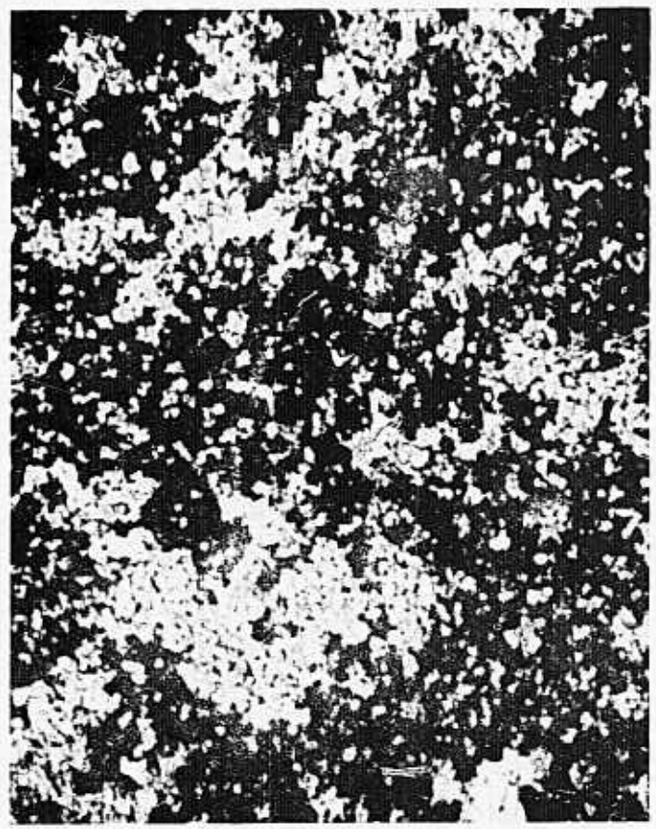


Fig. 4 Scanning Electron Micrograph of Rough Polished Zinc Selenide Specimen. 5000×



a) Universal Type "B" Alumina. 400×



b) Alon Fumed Alumina. 5000×

Fig. 5 Scanning Electron Micrographs of Alumina Abrasives.

very dilute suspensions of the abrasives in methanol and permitting drops of the suspensions to dry on cleaned glass slides. The slides were coated with 500 angstrom aluminum films and photographed in the SEM. The abrasives which appear in Fig. 5 differ at least in their degree of agglomeration. We compare the polishing behavior of these two abrasives in a later section.

2.2.3 Electron microscopy of surface replicas

The most detailed images of surface structures were obtained by transmission electron microscopy of surface replicas.* Replicas are produced by allowing a polymer solution to dry on the surface to be studied. The film which forms replicates the surface faithfully. It is removed from the sample and coated by evaporation first by carbon, then, at near grazing incidence, by a refractory metal. Relief in the replica surface produces "shadows" in the metal layer which are imaged in the microscope. Good replicas have resolutions on the order of 50 angstroms. Figure 6a is a transmission electron micrograph taken at 10,000 diameters of a zinc selenide specimen polished for one hour with Linde B abrasive. The finest resolvable scratches are approximately 100 angstroms across. For comparison, a scanning electron micrograph of the same sample, taken at the same magnification, was featureless. Particulate matter on the surface to be replicated, improper coating of it, or nonuniform removal of the film can cause artifacts in the replica which are difficult to interpret. The circular features in Fig. 6b, a less highly polished zinc selenide specimen, are artifacts. Microscopy of replicas was not widely used during the project because adequate comparison of the polished surfaces could be made by optical microscopy, light scattering, or calorimetric absorption measurements.

2.2.4 Scattering measurements

A surface which is too smooth to be imaged by optical microscopy may still be characterized by measurements of light scattered by it at

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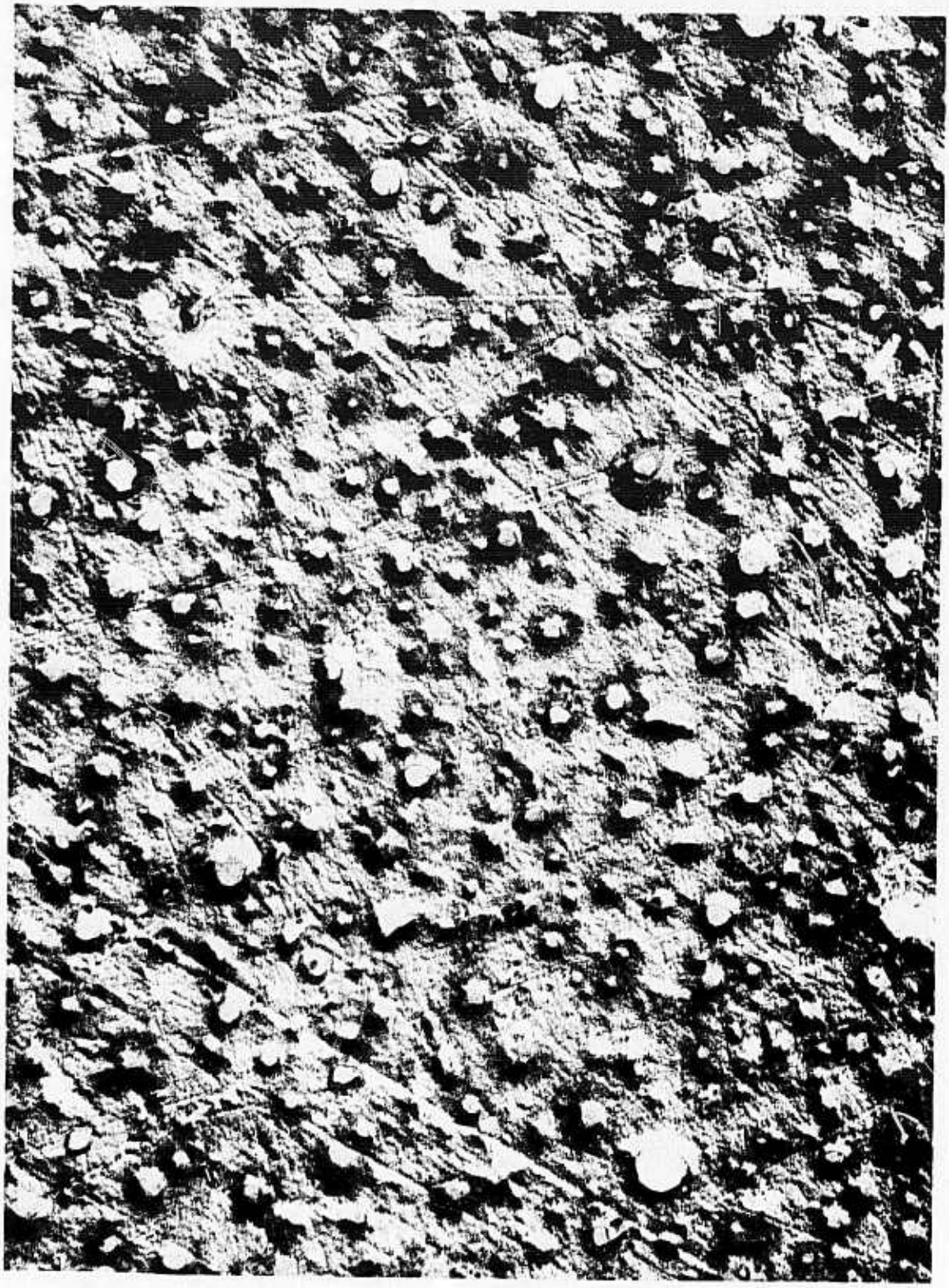
* Work performed at Itek Corporation.

a. Polished One Hours, Linde-B Abrasive

Fig. 6 Transmission Electron Micrograph of Replicas taken from Polished Zinc Selenide Specimens. 10,000×



b. Polished Two Hours, Linde-B Abrasive

Fig. 6 Transmission Electron Micrographs of Replicas taken from Polished Zinc Selenide Specimens. 20,000×

angles away from a directly transmitted beam incident upon it, or a specularly-reflected beam from it. The scattered radiation distribution in the far field is the Fourier transform of the sample surface topography and as such, is the object of analytical attempts to characterize rough surfaces. In this study, the measurements were used only to provide comparative information for surfaces prepared by various techniques.

The apparatus used for scattering measurements is shown schematically in Fig. 7. A 0.5 milliwatt He-Ne laser is used as the source of light at 6328 angstroms. The laser beam is chopped mechanically and strikes the sample which rests on a small platform over point P. The laser, chopper, and sample platform are mounted on an aluminum beam which is attached to a rotating table so that this part of the apparatus may be pivoted around point P through measured angles. Scattered light diverging from the sample and passing through the aperture is focussed by the lens onto an indium antimonide photodiode cooled to liquid nitrogen temperature. The output of the diode is amplified and measured with a lock-in detector.

The measurements reported here were made at an angle of incidence of 45 degrees at various scattering angles. Calling the scattering angle θ, we define a scattering function $F(\theta)$ by

$$F(\theta) = \frac{\text{Power scattered into unit solid angle}}{\text{Total reflected power}} \quad .$$

From the dimensions of the apparatus, the solid angle subtended at the sample by the aperture is calculated as .001058 steradian. (This corresponds to a resolution of about 2 degrees.) Then,

$$F(\theta) = 945 \frac{I}{I_R} \quad ,$$

where I = power measured for angle θ

I_R = power measured for the specular reflection ($\theta = 0$).

To obtain I_R, a filter of optical density 2 was used to keep the power reaching the photodiode at a manageable level.

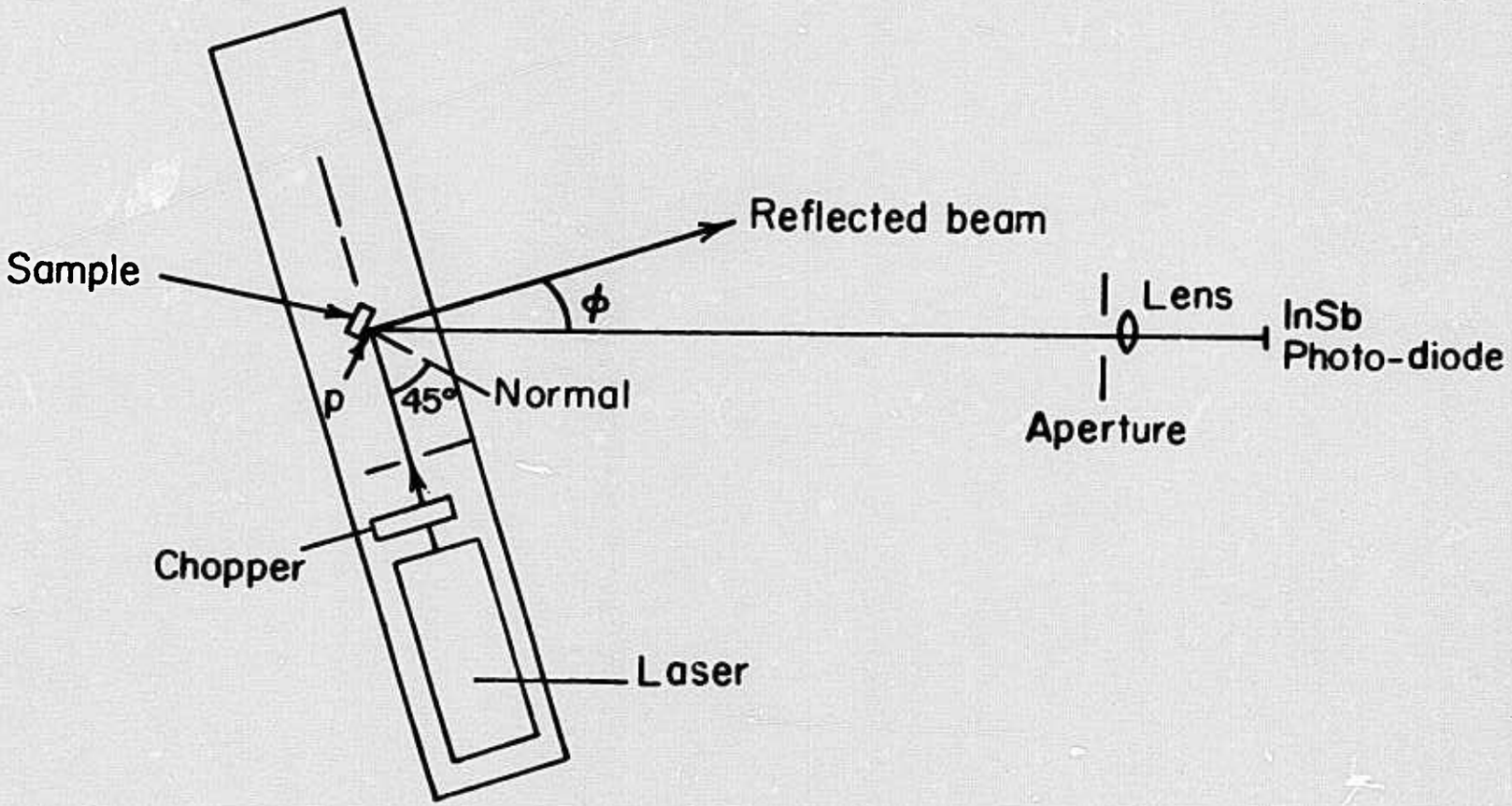


Fig. 7 Scatter Measurement Apparatus - Schematic.

Samples on which scattering measurements were to be made were first coated with an opaque aluminum film to raise the scattered intensities to measurable levels. This requirement makes it extremely inconvenient to follow the course of a polishing sequence because the specimens must be demounted from their polishing blocks in order to be coated. Once demounted, they cannot be simply remounted so that the surface is accurately aligned with other specimens and regrinding is usually required to bring all specimens into the same plane. The metallization requirement also makes scattering measurements on large optical elements inconvenient.

Since the scattering behavior of the metallized specimens depends only upon their surface relief, accurately-reproduced surface replicas taken from the specimens and metallized should be equivalent substitutes for the originals. During the course of this project, a brief attempt was made to develop an acceptable replication technique for polished surfaces. In order to make the developed technique useful for evaluating surfaces of all materials and usable in most optical shop situations, several restrictions were placed on it. First, the technique must be capable of reproducing detail on the scale of a few hundred angstroms so that irregularities on the order of one quarter wave high and larger would be reproduced. This requirement eliminated the use of mold release agents on the surfaces. Second, no heating of the specimen was permitted. Replicating compounds were required to set up in no more than 12 hours (overnight). Third, replicas which were on the order of one centimeter diameter and flat to within a few wavelengths were required in order to provide a reasonable statistical representation of the replicated surface. Finally, the replicas were required to be thermally stable to the extent that aluminum metallization by thermal evaporation in a conventional vacuum system was practical.

Results of a number of trials are summarized in Table I. No really adequate technique was developed by the termination data of this study. We do believe, however, that this approach warrents further effort. Surface replicas could be used to evaluate either angular-dependent or total integrated surface scatter and provide quantitatively-determinable indications of average surface quality.

TABLE I

COMPOUNDS USED FOR SURFACE REPLICATION OF ZnSe

Replicating Compound	Supplier
1) Collodion	Allied Chemical Company Morristown, N.J.
2) Opticoat	Spawr Optical Research Corona, California
3) Replicating Tape	Ladd Laboratories Burlington, Vermont
4) RTV Silicone Rubber Molding Compound No. 664	G.E. Silicone Product Dept. Waterford, N.Y.

The first two compounds are polymer solutions which were poured onto the surfaces. Various concentrations and layer thicknesses were used. Collodion could not be stripped from the surface in pieces which were large enough for scattering measurements. Opticoat, a stripable coating used for protection of optical surfaces was removable, but distorted during evacuation and metallization.

The replicating tape is a polymer which is softened in acetone, pressed against the surface, allowed to harden, and stripped away. The technique is widely used for preparing electron microscope replicas but we were unable to obtain replicas of sufficient area using very thin tape or of sufficient flatness using thicker tape. This procedure can probably be made to work.

The RTV compound is a room temperature curing rubber which sets overnight without shrinkage. It was poured onto the surfaces of the specimens and retained by masking tape walls. The set rubber did replicate the coarser features of polished surfaces but ignored finer scratches and introduced extraneous surface features. These were caused by incomplete deaeration of the liquid which left remnant pores (air bubbles) at the interface.

2.2.5 Absorption measurements

The vacuum chamber of the 10.6 μm laser calorimeter is shown in Fig. 8. This chamber is a pyrex cross with a 6 inch i.d. vertical arms and 4 inch i.d. horizontal arms. Evacuation of the chamber is accomplished through an opening in the base plate with a standard diffusion pump vacuum system. The side arms are fitted with KCl windows to allow entrance and exit of the laser beam. The sample is mounted in a ring attached to a rod which passes through a seal in the top plate. This rod may be moved vertically, and the entire chamber horizontally, to permit probing of different parts of the sample. The sample is mounted in the ring with four nylon screws, one of which also serves to press a thermocouple junction against the sample. The reference junction for the thermocouple is attached to a polished aluminum block also in the chamber but away from the laser beam, and the thermocouple leads pass through sealed holes in the top plate.

A Coherent Radiation Model 42 laser, capable of 50 W at 10.6 μm, is used as power source, and a Coherent Radiation Model 201 Power Meter measures the power coming out of the exit window. The output of the sample thermocouple is amplified with a Keithley Model 148 nanovoltmeter and displayed, along with the output of the power meter, on a strip chart recorder. The absorption coefficient may be calculated either from the actual temperature rise of the sample or from the slope of the temperature rise, both appropriately corrected for heat loss. To facilitate the calculations, a computer program has been written which requests the pertinent data, provides the refractive index and specific heat for commonly measured materials and performs the calculations. The computer program does not assume that the fraction of power absorbed is small, and the output gives the fraction absorbed and the absorption coefficient (uncorrected for any surface absorption).

2.3 Abrasive Polishing

2.3.1 Introduction

Materials to be superpolished by any technique must first receive the best possible conventional optical polish. Conventional polishing

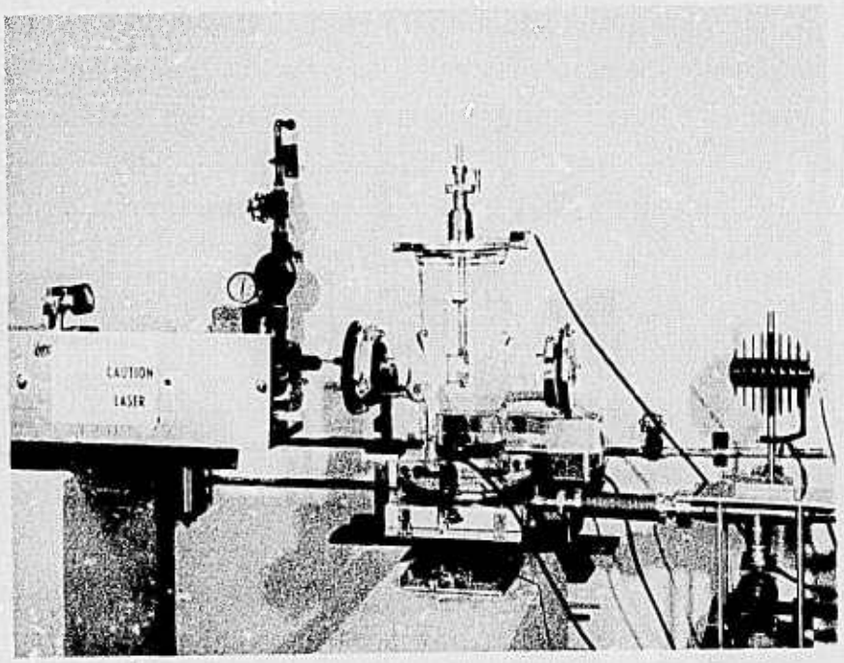


Fig. 8 Raytheon Research Division 10.6 Micrometer Laser Calorimeter.

establishes the optical figures of the pieces and the quality of the polish determines the demands placed upon the superpolishing step. Conventional polishing for this project is performed on standard optical polishing machines. Workpieces, mounted on an aluminum disc having flat, parallel faces are oscillated over the surface of the rotating lap by an eccentric arm.

The pressure on the work is adjusted by loading the arm, and the work is free to rotate as it moves over the lap surface. The optical figure is controlled by adjustments of the motion of the workpieces relative to the lap (which must itself be flat); the operator's skill is an important component of optical figure control. Optical figures were determined by observing the curvature of interference fringes produced between the workpiece and an accurate optical flat held in contact with the workpiece, under illumination from an unfiltered low pressure mercury discharge. Curvature of the fringes by an amount equal to the separation of the fringes implies a deviation from planarity of approximately 2500 angstroms on the workpiece. Samples used in this study were considered to be adequately flat when the curvature was less than half the fringe spacing.

The surface figure and defect density produced by a polishing operation may be determined by any of the numerous variables in the process. Thus, the choices of lap material, rotation rate, applied pressure, abrasive, slurry vehicle and slurry concentration all contribute to the surface character. Further, since polishing is carried out as a series of operations using progressively finer abrasives, the results of each step depend upon the outcome of all preceding steps. Finally, the role of the operator is substantial.

While polishing procedures must be optimized experimentally, some generalizations can be made. First, optical figure control is difficult to maintain when cloth or other very soft or yielding lap surfaces are used. Optical finishing is most commonly carried out on laps surfaced with pitch, less frequently on one of a variety of other waxes.

Pitches and waxes having a variety of hardnesses are available. In general, harder surfaces are selected for polishing harder materials, and conversely. Pitch which is too hard will force abrasive into the workpiece and scratch it. Since pitch hardness is strongly temperature-dependent, the operating temperature is an important parameter. The Raytheon polishing laboratory was maintained at 74°F; comments below relative to choice of pitch should be taken in that context.

Second, slow lap rotation and light loading of the work tend to produce more perfect surfaces. Figure control is easier when low rotation rates are used. The polishing of calcium fluoride and zinc selenide described below was carried out on laps rotating at approximately 30 revolutions per minute (the lowest rate available) with pressures of 1.5-3 pounds per square inch (1-2 grams per sq. millimeter) applied to the work. Potassium chloride was usually polished by hand on stationary laps at pressures approximately a tenth as large. Some potassium chloride was polished on rotating (30 revolutions per minute) beeswax laps.

Third, application of the abrasive is the least well controlled parameter in the operation. A considerable portion of an experienced operator's skill is an intuitive feel for when to add abrasive, how much to add, and whether it should be added from the top or bottom of the slurry container (a particle size selection). In these experiments, abrasives were applied "as needed" by shaking small quantities of the slurry onto the lap with a paint brush - standard optical practice.

Abrasive choice is best made by experiment. The polycrystalline specimens dealt with during the project are susceptable to "relief polishing," a surface feature produced on polished specimens by a dependence of the polishing rate upon the orientation of the individual crystalline grains within the material. Relief polished surfaces having grain-to-grain height variations as large as 2000 angstroms may be produced easily by incorrect abrasive choices. As detailed in paragraph 2.3.5, we find that the tendency toward relief polishing is minimized on CaF_2 and ZnSe, by using diamond abrasives and the hardest pitch lap material which does not itself scratch the surfaces.

2.3.2 Grinding

The first step of the polishing process uses a coarse (typically 9-30 micrometers) alumina abrasive to bring the sample surfaces into the same plane and remove damage introduced by any previous sawing or grinding operations. Successive steps typically grind an amount of material equal to two to five times the diameter of the abrasive particles used in the previous step from the specimens to minimize the remnant subsurface damage. For many optical materials, especially amorphous ones, microfractures introduced by the grinding abrasives extend only a few abrasive grain diameters into the workpiece and this procedure is sufficient. Single crystals of the materials used in this study, however, are all easily cleaved; in polycrystalline specimens, grinding operations may easily drive cleavage cracks into the material to a depth at least equal to the grain size. That grinding proceeds at least in part by cleavage is clearly shown by Fig. 9, a scanning electron micrograph of a ground zinc selenide specimen. Cleavage fracture is found in ground surfaces of the other materials as well. Preliminary sawing and rough grinding operations may induce cleavage damage well below the physical surface.

The most serious defects found in the most highly polished specimens of calcium fluoride and zinc selenide produced during the report period are small pits, frequently flat-sided, with associated scratches as shown in Fig. 10, an optical micrograph of a bowl-feed polished calcium fluoride specimen. In order to determine the extent to which remnant cleavage cracks in ground surfaces contribute to defects in polished surfaces, the polishing of a series of "standard ground" surfaces was followed as detailed below.

Specimens of CaF_2 and ZnSe were first conventionally polished, then ground with the abrasive compound to be studied. The ground surfaces were then polished with 'A'-type alumina (0.3 micrometer nominal particle size). The polishing was interrupted periodically, the thickness of the material removed was measured with a dial gauge (accurate to plus or minus approximately two μm), and photomicrographs of three randomly selected areas on the surface were taken. Surface defect densities were then determined by counting the number of remnant pits in the photographs and by computing the average surface area fraction covered by the pits. This

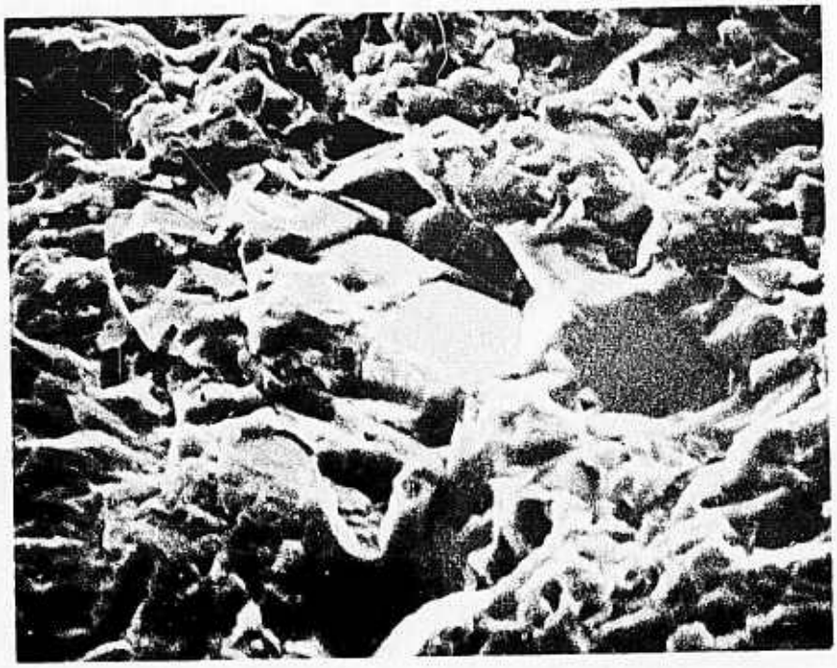


Fig. 9 Scanning Electron Micrograph of Cleavage Produced During Grinding of Zinc Selenide. 3000×

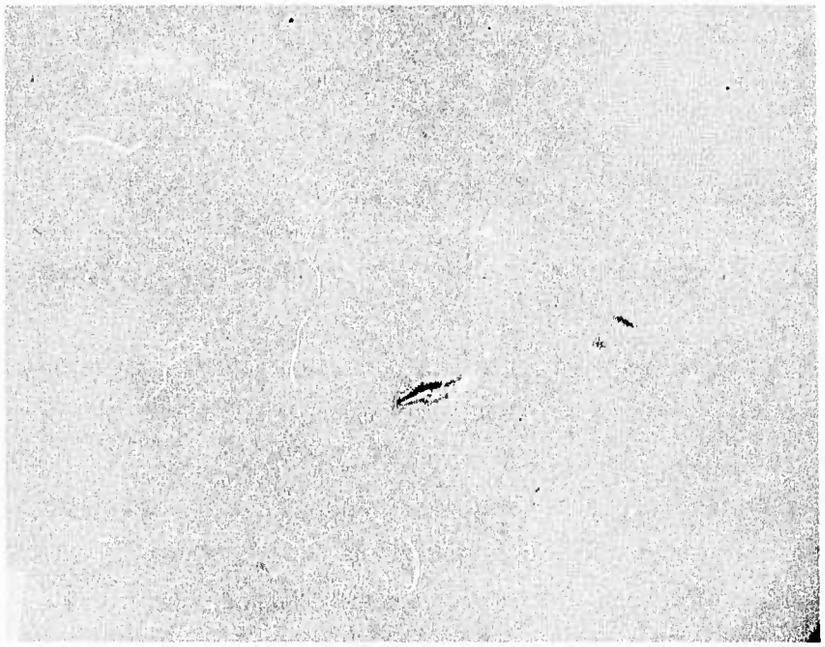
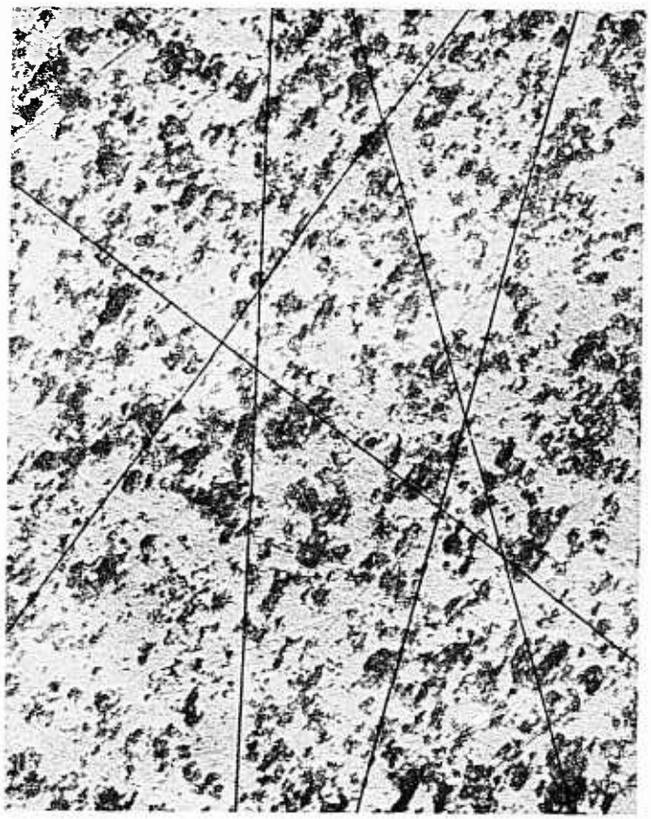


Fig. 10 Cleavage Damage in Bowl-Feed Polished Calcium Fluoride (Optical Micrograph). 766X

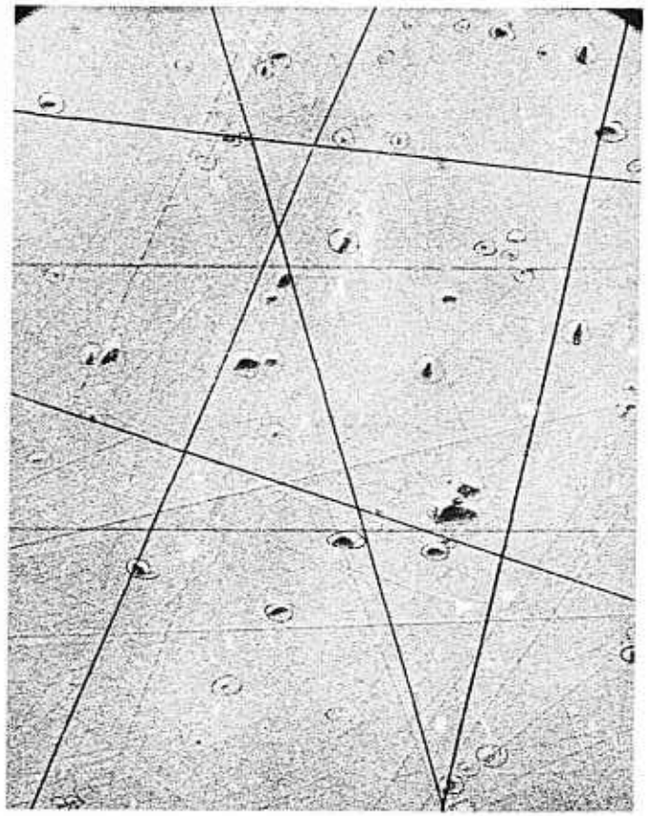
second measure, useful only above a few percent coverage, is computed by measuring the fractional length of lines drawn randomly across the photograph which intersect pits.

Microstructural changes which accompany the polishing of polycrystalline calcium fluoride surfaces generated by twelve micrometer nominal grain diameter abrasives are summarized in Fig. 11. Defect densities taken from photographs of the process are correlated with polishing time and material removal in Fig. 12. The defect density is seen to fall rapidly as material is removed until a layer which is only slightly thicker than the nominal abrasive diameter has been polished away (Fig. 11d). At this point, the surface quality is optimized, for continued polishing (Fig. 11e) begins to produce new scratches and some pitting at grain boundaries. This latter degradation was observed by both Raytheon and Itek. The extent of the degradation appears to depend more upon additional parameters such as the quality of the polishing of the beveled edges of the specimens than on remanent cleavage damage. Cleavage damage introduced during grinding varies strongly in extent with the orientation of the grain being ground, as shown in Fig. 13, a photograph of an intermediate stage of the polishing of a CaF_2 specimen ground with 5 micrometer abrasives. This specimen also degraded as it was "overpolished" but the pits which appeared during the degradation occurred randomly over the entire surface which indicates that some effect other than remnant grinding damage was responsible.

The microstructures presented in Fig. 14 were typical of those produced by the polishing of ground zinc selenide surfaces. In this instance an M-12 (12-micrometer grinding abrasive) surface is being polished with 0.3 micrometer 'A' type alumina. A total of 64 micrometers of selenide was removed during the experiment; this corresponds to five times the grinding compound diameter and is on the order of the selenide grain size. In this case, the surface is nearly developed after 1.75 hours which corresponds to the removal of 12 micrometers (Fig. 14c) and no significant changes occur from 2.75 hours (15 micrometers removed), (Fig. 14d) through 19.25 hours (64 micrometers removed).

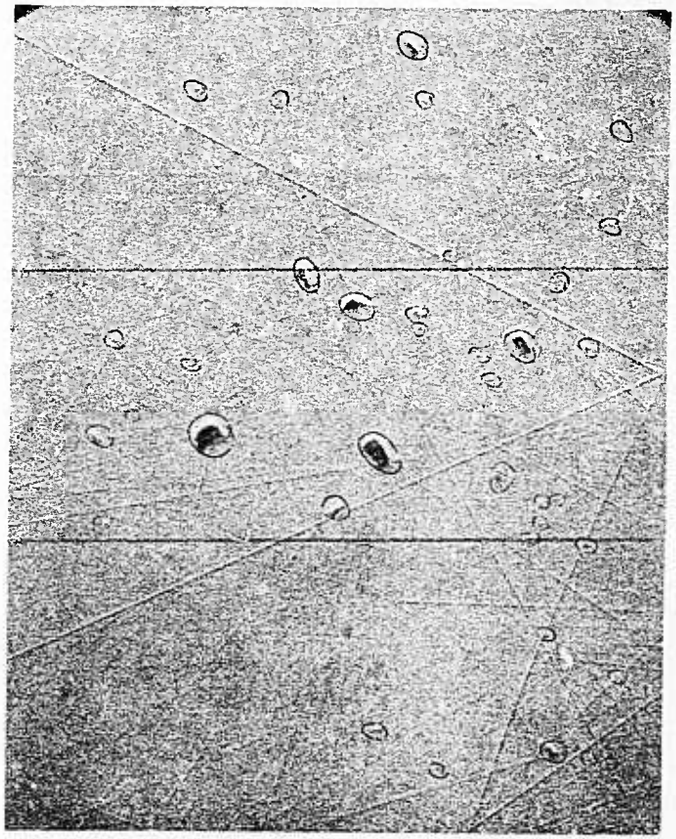


a) Time: 10 Minutes. Removal: 3 μm

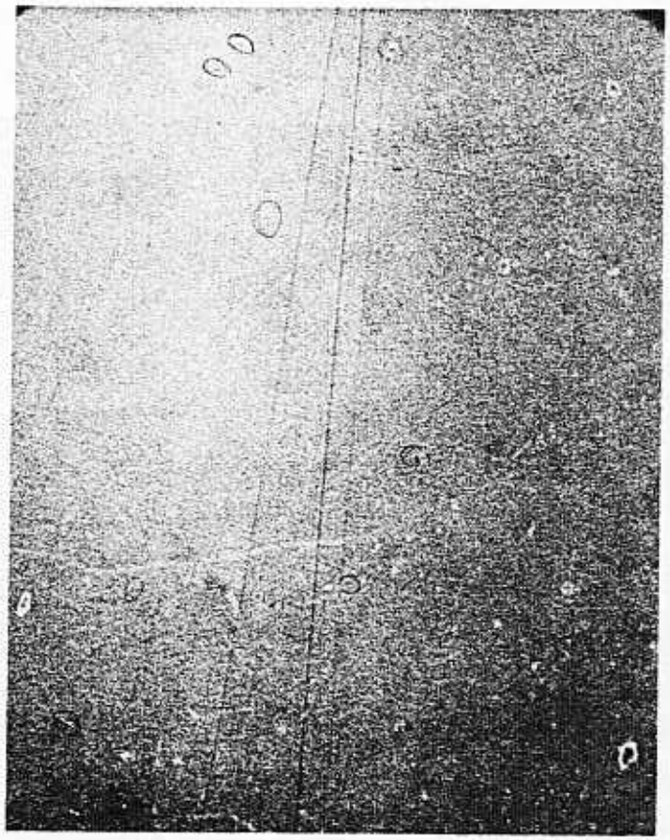


b) Time: 180 Minutes. Removal: 8 μm

Fig. 11 Microstructure Produced During Polishing of Ground Polycrystalline Calcium Fluoride Surface Produced by Twelve-Micrometer Alumina Grinding Abrasive. 187×



c) Time: 240 Minutes. Removal: 12 μm.



d) Time: 360 Minutes. Removal: 15 μm.

Fig. 11(Cont'd)

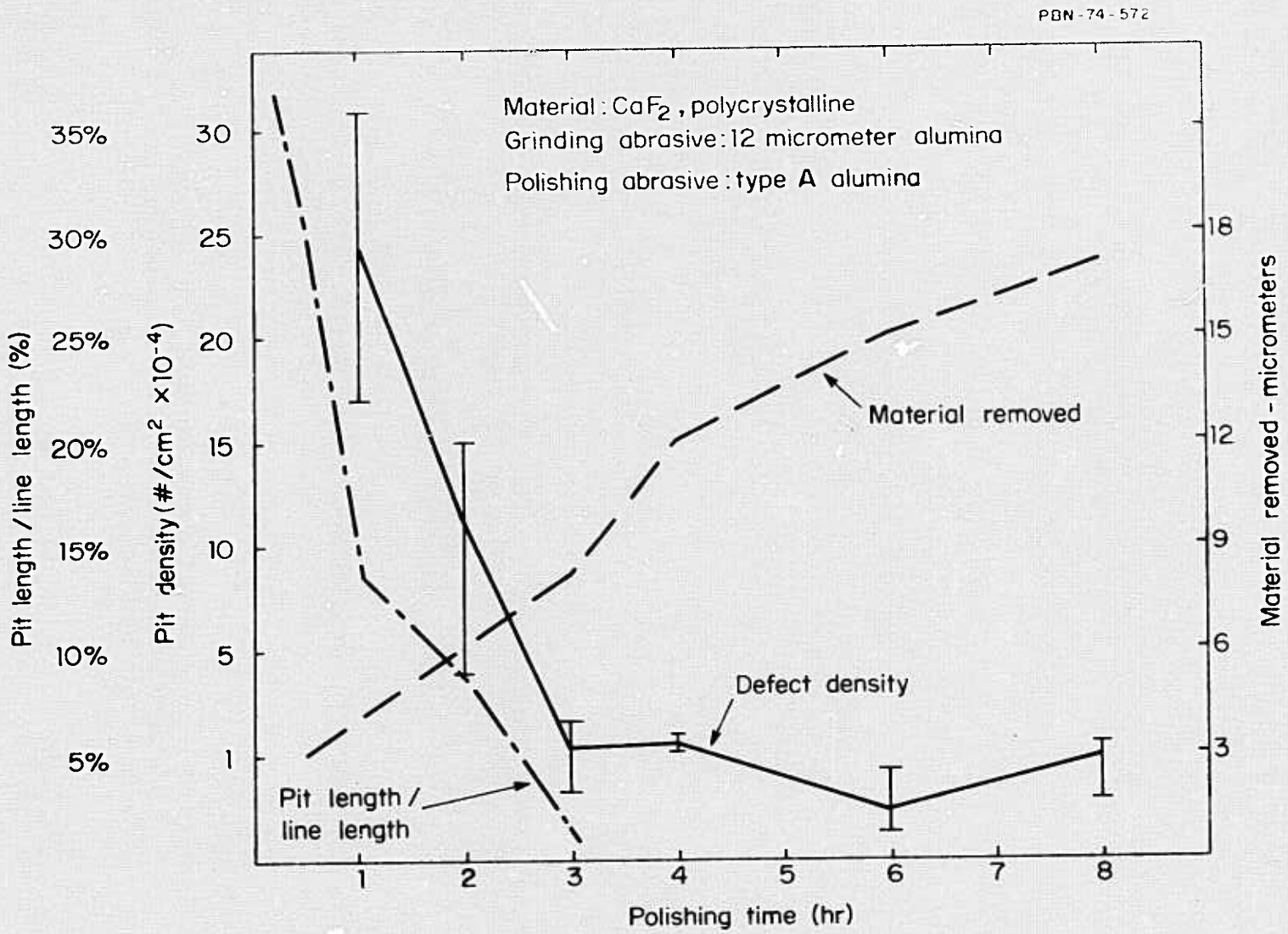
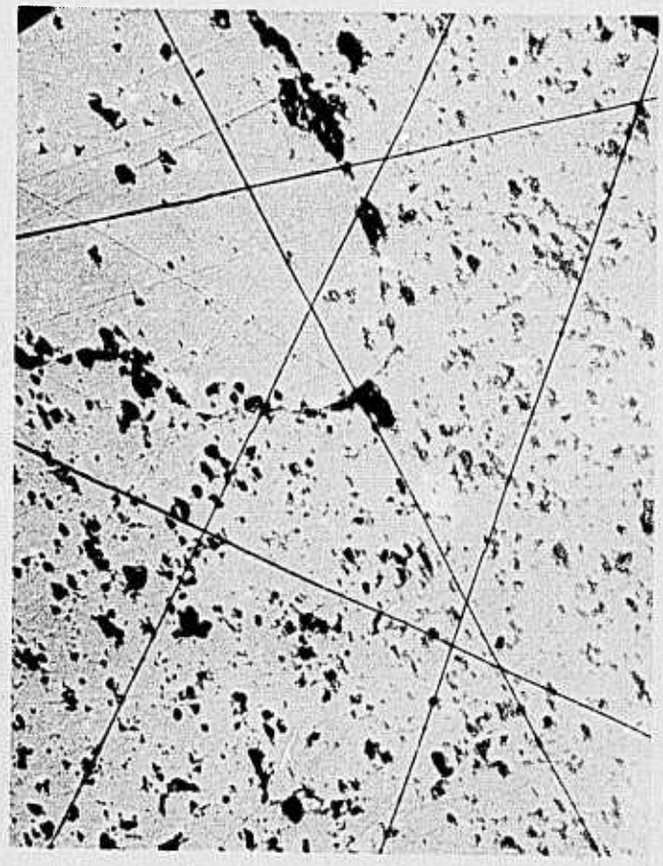
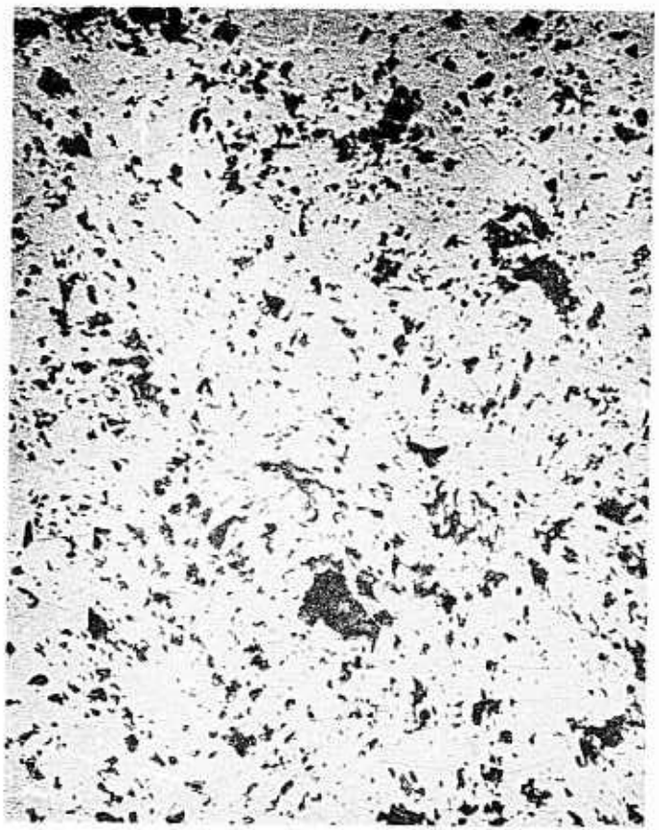


Fig. 12 Surface Defect Density vs Polishing Time and Material Removal for Ground Polycrystalline Calcium Fluoride Surface Produced by Twelve-Micrometer Alumina Grinding Abrasives.

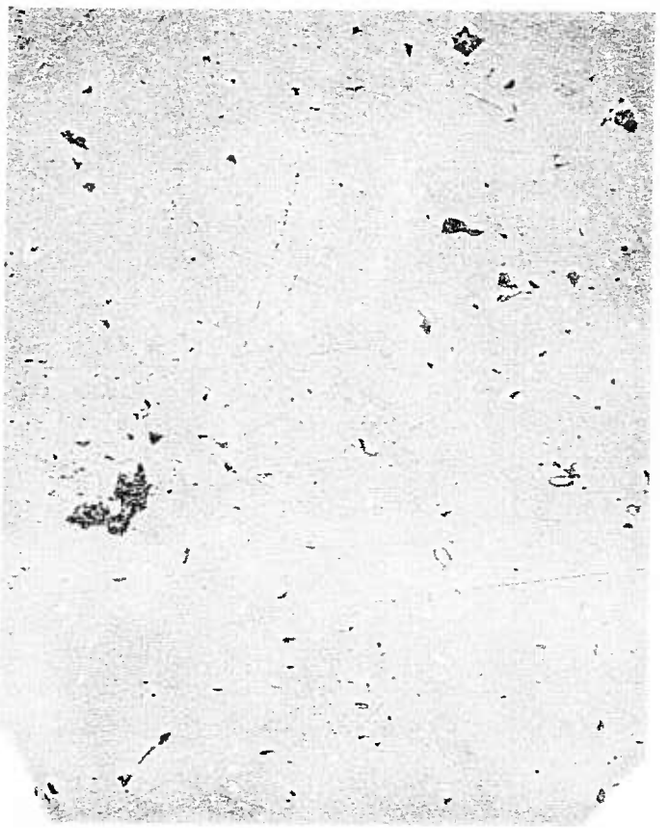


Time: 10 Minutes. Removal: Unmeasurable.

Fig. 13 Microstructure Produced During Polishing of Ground Polycrystalline Calcium Fluoride Surface Produced by Five-Micrometer Alumina Grinding Abrasive. 187×



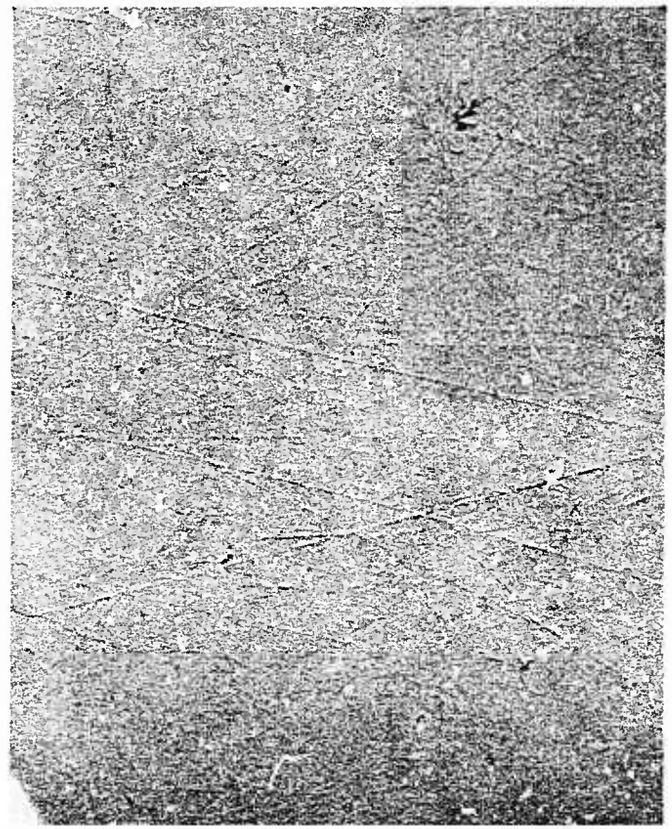
a) After 15 Minutes Polishing, 3 μm Removed. 187×



b) After 45 Minutes Polishing, 5 μm Removed. 187×

Fig. 14 Microstructures Produced During Polishing of Ground Polycrystalline Zinc Selenide Surface Produced by Twelve Micrometer Alumina Grinding Abrasive.

c) After 1.75 Hours Polishing, 10 μm Removed. 187×



d) After 2.75 Hours Polishing, 15 μm Removed. 187×

Fig. 14(Cont'd)

e) Time: 480 Minutes. Removal: 17 μm.

Fig. 14 (Cont'd)

Figure 15 summarizes the microstructure analysis taken from the photographs. Error bars on the pit count line correspond to the range of pit counts determined in each set of the three photographs. As in the calcium fluoride case, the surface typical of the polishing abrasive is formed soon after a surface layer comparable to the final grinding abrasive is removed. Scratches on the surface are probably caused by the material which breaks away to form the pits; occasional scratches may be found terminating in pits in most of the photographs in Fig. 14.

That these pits tend to be associated with grain boundaries in the material is shown in Fig. 16 which contains unetched and etched views of the same area of a selenide surface polished with 'A'-alumina. These defects are no more than a micrometer or two deep and have been present at more or less the same density throughout the removal of the total 64 micrometers. It would seem reasonable to associate them with bulk defects already present in the selenide material.

The chemical vapor deposition process used to produce zinc selenide has been steadily improved over the past eighteen months so that such defects are now uncommon. Grain boundaries are nevertheless a potential source of damage during polishing, especially as the improving surface begins to fit very closely to the lap. Under these conditions, very large forces may be generated across the two surfaces if they are allowed to become too dry, and these forces may be large enough to pluck material from the surface.

In order to assess the depth of damage produced by the original grinding operations, a Blanchard-ground block of ZnSe specimens was polished with A-type alumina and the defect counts were correlated with material removal as above. The defect count reached steady-state after approximately 40 micrometers had been removed and remained so through the removal of another 60 micrometers. We conclude that grinding-induced cleavage damage can be removed from the polycrystalline fluoride and selenide materials by a series of grinding steps in which layers two to three times thicker than the nominal diameter of the

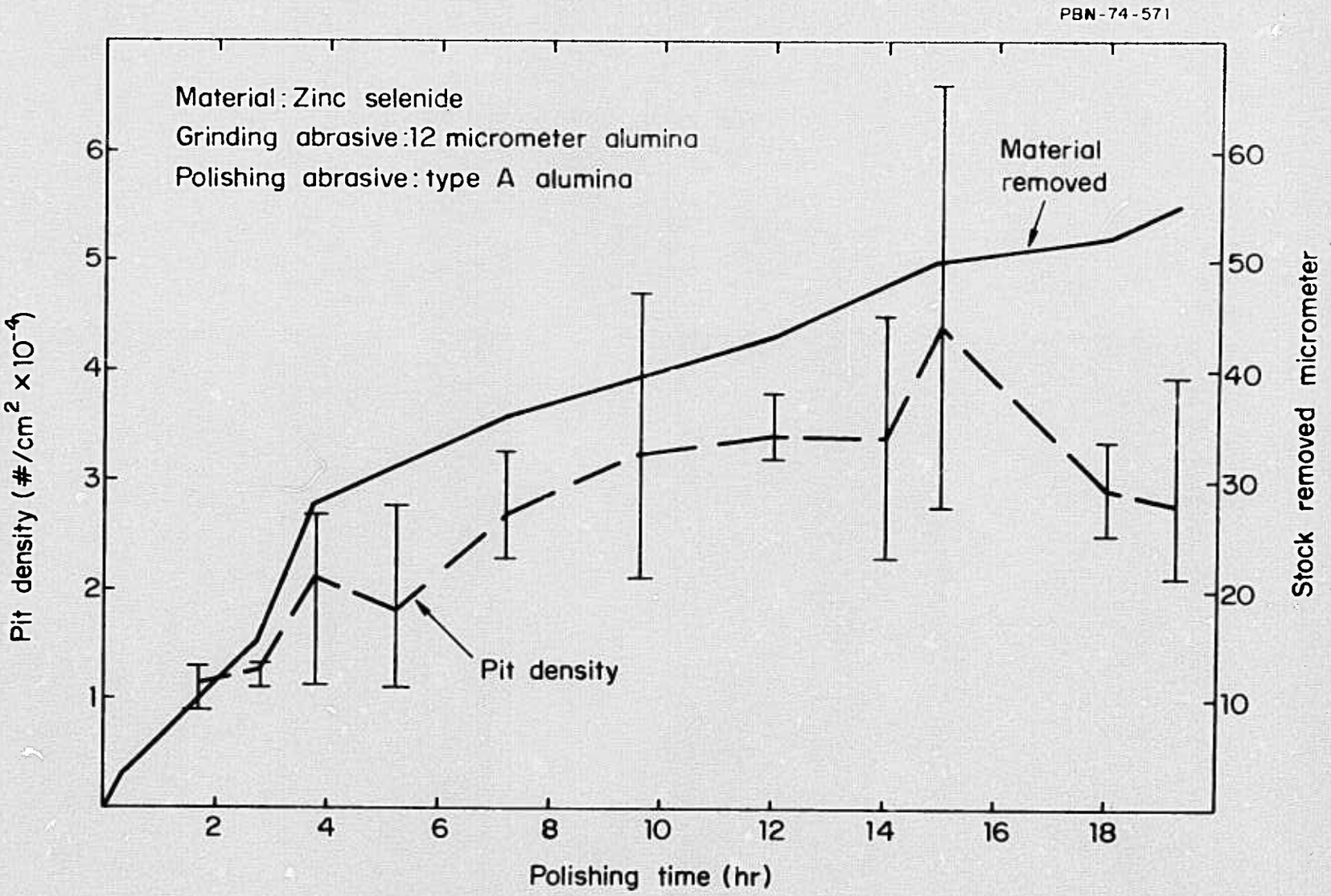


Fig. 15 Surface Defect Density vs Polishing Time and Material Removal for Ground Polycrystalline Zinc Selenide Surface Produced by Twelve-Micrometer Alumina Grinding Abrasive.

50 Microns

a) Unetched Surface

50 Microns

b) Etched Surface

Fig. 16 Polishing Damage on ZnSe. 378×

abrasive used in the previous step are removed. Thicker layers can easily be removed (and usually are), but these results demonstrate that extensive grinding may be avoided if it is necessary to preserve a maximum component thickness. For the Blanchard-ground ZnSe specimens we examined, a 100 μm surface layer contained all the surface damage which prevented the production of a good conventional finish, but since initial grinding procedures are variable, this initial removal step should either be re-established by each fabricator, or the 100 μm layers should be substantially exceeded.

2.3.3 Conventional polishing

Typical specimens used for polishing experiments during the course of the project are summarized in Table II. Conventional polishing results obtained for any material may be assumed to be applicable to all examples of that material investigated during the course of the project. Relief polishing is of course absent on single crystalline materials and may vary significantly in severity among specimens containing only a few grains. Abrasives used during the experiments are summarized in Table III, lap surfaces in Table IV, and slurry vehicles in Table V. Diamond abrasives, used without binders in water slurries, were also used to polished ZnSe and CaF_2. They are discussed separately in paragraph 2.3.5.

2.3.3.1 Zinc selenide

Parallel studies of conventional polishing of zinc selenide were conducted at Raytheon and at Itek Corporation. Both studies reached substantially the same conclusions. Soft pitch laps. alumina abrasives, and a slurry vehicle containing equal parts of ethylene glycol and water produced the best surfaces. The soft Cycad pitch used by Itak was softer than the pitch used at Raytheon, which probably accounts for the more frequent relief polishing they observed. We show in paragraph 2.3.4 that relief polishing is promoted by soft lap surfaces. B-type alumina was used by both Itek and Raytheon to improve conventionally polished surfaces produced with A-type alumina, although both laboratories found the improvement difficult to reproduce. Figure 5 contains a scanning electron micrograph of a B-type specimen which exhibits a considerable agglomeration. Some of the agglomerates are apparently capable of scratching the relatively soft selenide specimens under conditions which would permit harder materials to break them down.

TABLE II

SAMPLES USED FOR POLISHING EXPERIMENTS

Material	Dimensions	Grain Size	Fabrication
ZnSe	38 mm dia. disc 4 mm thick	50-150μm	Chem. Vap. Deposit, Raytheon
ZnSe	12 mm dia. disc	50-150μm	Chem. Vap. Deposit, Raytheon
KCl	25 mm disc	Single Crystal	Harshaw Chemical Co.
	38 mm $\times$10 mm disc	5-70μm	Hot Forged, 100 ppm Eu, Honeywell Ceramics Center
	25 mm $\times$10 mm	8-20 mm	Fusion Cast, 100 ppm Sr addition, Raytheon Material
	Irregular, Ave. 25 mm Sq. $\times$4 mm	1-3 mm	Optovac Single Crystal Hot Forged at Raytheon
CaF_2	Discs 12 to 51 mm dia. $\times$6 mm thick	10-20 mm	Fusion Cast at Raytheon
	38 mm disc	200 μm	Hot Pressed, Irtran 3 from Eastman Kodak
	30 mm dia. discs	Single Crystals	Optovac
	Irregular 25 mm Square $\times$4 mm	1-3 mm	Optovac Single Crystal Hot Forged at Raytheon

TABLE III

ABRASIVES USED FOR CONVENTIONAL POLISHING

Abrasive	Compositions	Particle Size (Micro-meters)	Materials Polished ZnSe	CaF_2	KCl	Comments
Diamond	Carbon	3	X			Scratched
Diamond	Carbon	1	X			Surface
Diamond	Carbon	0.25	X			
Microgrits	Al_2O_3	30	X	X	X	Grinding Compounds
Microgrits	Al_2O_3	12	X	X	X	See grinding discussion
Microgrits	Al_2O_3	9	X	X	X	
Microgrits	Al_2O_3	5	X	X	X	
"C"-Alumina	Al_2O_3*	1.0	X	X	X	Rough Polish
"A"-Alumina	Al_2O_3*	0.3	X	X	X	Intermediate Polish
"B"-Alumina	Al_2O_3*	0.06	X	X	X	Finest polish - highest quality surface on all materials
Barnesite No. 85	Cerium Oxide (impure) + 2nd phase	NM	X	X		
Barnesite No. 924	Cerium Oxide (impure)	NM finer than No. 85	X	X		
Tin Oxide	SnO_2		X	X	X	Difficult to clean from KCl
Liquid ZOX-E†	ZrO_2 in aqueous suspension	NM	X			
ZnS	ZnS	1	X		X	No polishing on ZnSe, similar to all others on KCl

* Supplied by Union Carbide as Linde-A, etc. or by Universal Shellac and Supply as Universal-A, etc. No difference in properties found between the two suppliers

† Universal Shellac and Supply.

TABLE IV

LAP SURFACES USED FOR CONVENTIONAL POLISHING

Material	Function	Comments
Cast Iron	Grinding all materials	
Glass	Grinding all materials	Preferred final grinding surface
Paraffin	Polishing KCl	Figure control relatively easy, difficult to prevent material from digging into lap
Beeswax	Polishing KCl, ZnSe	Figure control difficult. Work does not dig into surface
Lead	Polishing ZnSe Using 0.25μm diamond paste	Produced badly scratched surface
Kemet Lead*	Diamond Polishing using water soluble paste for CaF_2, ZnSe	Product scratched surface
Swedish Pitch** No. 73	Polishing CaF_2, ZnSe	
Swedish Pitch + 0.2 wt. % linseed oil	Polishing CaF_2, ZnSe	Produced highest quality surfaces
Soft Cycad Pitch***	Polishing CaF_2 ZnSe	
Hard Cycad Pitch	Polishing CaF_2 ZnSe	
Hard Cycad and Various Linseed Oil Additions	Polishing CaF_2 ZnSe	Permits Pitch hardness adjustments

* A lead-epoxy composite obtained from Engis Corp, Morton Grove, Illinois

** Obtained from Universal Shellac and Supply Company

*** Obtained from Cycad Products, Crystal Lake, Illinois.

TABLE V

SLURRY VEHICLES USED FOR CONVENTIONAL POLISHING

	Materials Polished			
	ZnSe	CaF_2	KCl	Comments
Light Oil	X			Used with diamond paste
Water	X	X		
Water: Ethylene Glycol 1:1	X	X		Best vehicle used
5 Percent Acetic Acid in Water	X			
Ethylene Glycol			X	Etches slightly
Triacetic Glycol			X	Does no react with KCl, reacts slightly with pitch laps. Best vehicle for pitch and wax lap polishing of KCl
Isopropanol			X	Used with synthetic lap surfaces and alumina abrasives for KCl
Hyprez W-Lubricant* Spray	X	X	X	Used with water-soluble base diamond pastes but reacts with pitch

* Obtained from Engis Corp., Martin Grove, Illinois.

Typical zinc selenide surfaces produced by conventional techniques are presented in Fig. 17. Polishing schedules for ZnSe and CaF_2 appear in Table VI. These conditions were determined for groups of the materials mounted on 4-6 inch diameter aluminum specimen blocks. Typical specimen areas during a polishing run were on the order of 50-100 cm^2.

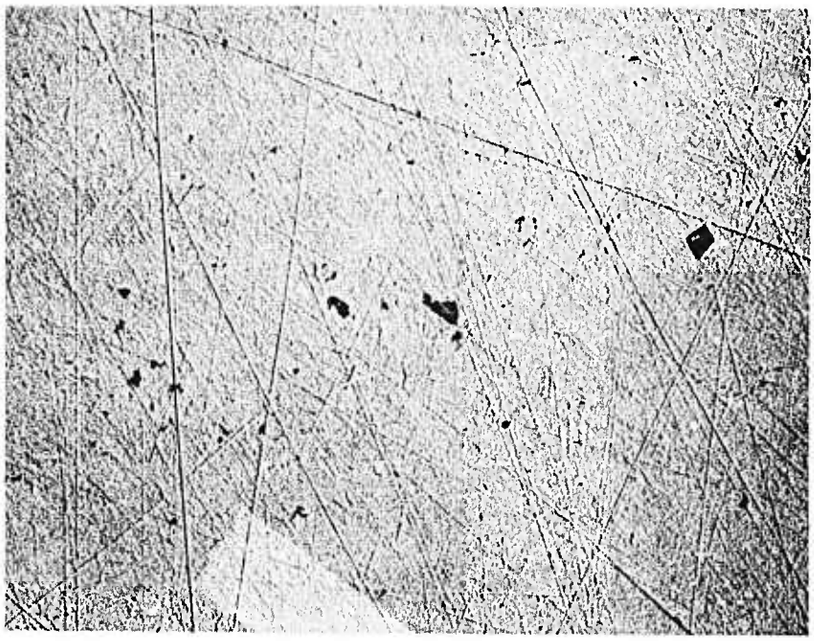
2.3.3.2 Calcium fluoride

The procedures developed for zinc selenide work equally well for calcium fluoride. In this case, the material will be used at wavelengths at which the alumina abrasive should not absorb significantly. Relief polishing of polycrystalline specimens is a more serious problem for calcium fluoride than for zinc selenide. The point is considered in more detail in connection with bowl feed polishing, but it is worth noting here that attempts to produce extremely high quality conventionally polished surfaces on polycrystalline CaF_2 surfaces using very fine B-type alumina or fumed alumina and soft pitch laps will typically produce relief polishing.

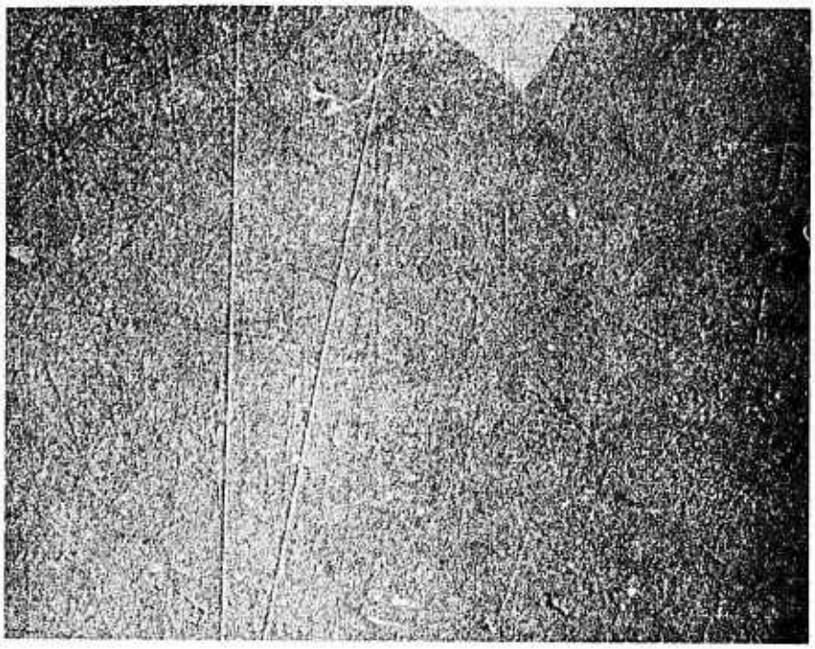
Calcium fluoride polishes easily and surfaces which appear quite smooth to the unaided eye (because of the low index of refraction) and lightly sleeked under the microscope (Fig. 18) can be produced with conventional techniques and A-type alumina without significant relief polishing. For the highest quality surfaces, diamond polishing on pitch laps is preferred.

2.3.3.3 Potassium chloride

Potassium chloride is by far the softest of the three materials and is the most difficult to polish. Pitch and wax laps used to polish KCl during the project were listed in Table IV. In addition, the cloth and synthetic lap surfaces listed in Table VII were explored, these using propanol-alumina slurries. The silk and cotton sheet materials



a. Type C-Alumina Abrasive. 187×



b. Type A-Alumina Abrasive. 187×

Fig. 17 Surfaces Produced During Conventional Polishing of Zinc Selenide.

c. Type B-Alumina Abrasive. 187×

Fig. 17 (Cont'd)

TABLE VI

A. TYPICAL POLISHING RUN FOR ZINC SELENIDE

Operation	Abrasive	Slurry	Lap	Time	Material Removed (μm)	Removal Rate (μm)/ min
Grind	9μm alumina	H_2O	Cast Iron	10 min	70	7
Grind	5μm alumina	H_2O	Glass	10 min	30	3
Polish	"C"-Alumina	H_2O/ glycol	Swedish No. 73 Pitch + 0.2 wt. % Linseed Oil	1 hour	10	0.16
Polish	"A"-Alumina	H_2O/ glycol		1 hour	5*	0.06
Polish**	0-1/2 μm diamond powder	H_2O		1.5 hours	Unmeasurable	

* A minimum time and maximum materials removal rate estimate. Actual polishing time is determined by the simultaneous achievement of acceptable optical figure and optimized surface. Removal rate is highest in the first hour during which time the remnant "C"-alumina surface is replaced by the "A" surface.

** See paragraph 2.3.5.

TABLE VI

B. TYPICAL POLISHING RUN FOR CALCIUM FLUORIDE

Operation	Abrasive	Slurry	Lap	Time	Material Removed (μm)	Removal Rate μm/min.
Grind	9 μm Alumina	H_2O	Cast Iron	20 min.	60	3
Grind	5 μm Alumina	H_2O	Glass	20 min.	30	1.5
Polish	"C"-Alumina	H_2O/glycol 1:1	Swedish Pitch No. 73 + 0.2 wt. % Linseed oil	1.3 hrs.	9	0.12
Polish	"A"-Alumina	H_2O/glycol	Swedish Pitch No. 73 + 0.2 wt. % Linseed oil	1 hr.*	6	0.1
Polish**	0-1/2 μm Diamond	H_2O	Swedish Pitch*** No. 73 + 0.2 wt. % Linseed oil	1.5 hr.	Unmeasurable	

***

If polycrystalline specimens relief polish, use harder pitch. If specimen surfaces do not improve rapidly with diamond, soften and repress lap.

a) C-Type Alumina Abrasive, 1/2 Hour from Ground Surface.

b) A-Type Alumina Abrasive, 3 Hours from C-Alumina Surface.

Fig. 18 Microstructure of Conventionally Polished Calcium Fluoride (Irtran 3). 187×

c) B-Type Alumina Abrasive. Deep grooves in all photos are pores in body of specimen which also contribute to scratch density.

Fig. 18 (Cont'd)

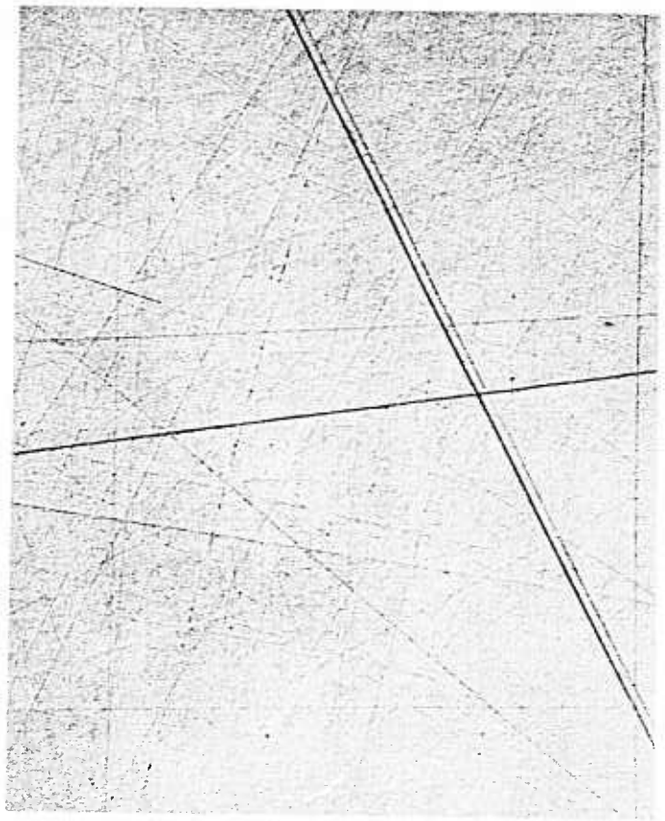
were stretched over polyethylene sheets on cast iron laps. The others had self-adhesive backings.

TABLE VII

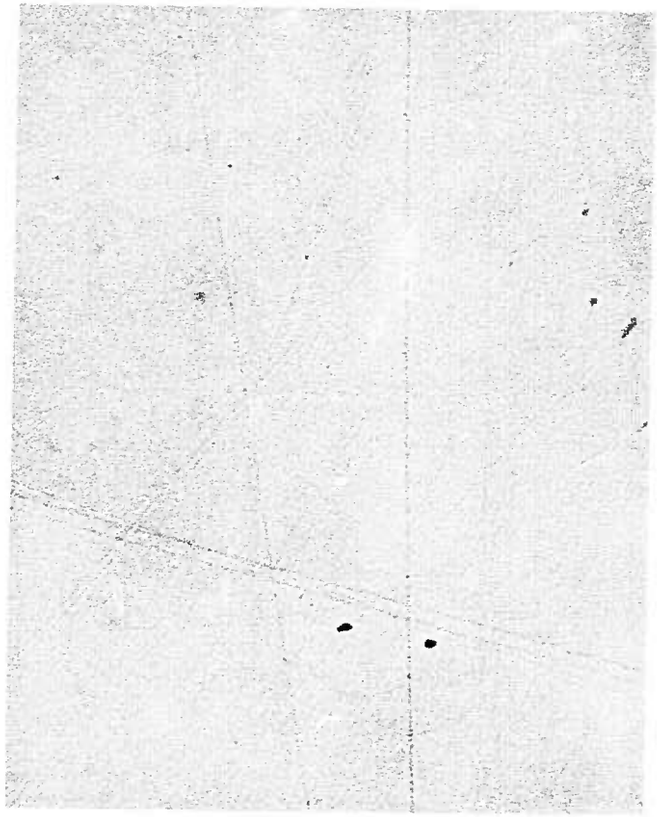
SYNTHETIC LAP SURFACES USED TO POLISH KCl

Material	Supplier
Silk, AB selected	Buehler, Ltd. Evanston, Ill.
Pellon XP-5	J.I. Morris Co., Southbridge, MA
Pellon Par-W	J.I. Morris, Co., Southbridge, MA
Alphalap (billiard cloth)	J.I. Morris, Co., Southbridge, MA
Politax Supreme	Geoscience Corp., Stamford, CT
Cotton Bed Sheet	

Of these, the most nearly scratch-free surfaces were obtained using the Politex material, B-type alumina and propanol. The best of these (Fig. 19a) are similar in quality to a commercially polished specimen obtained from Janos Optical Co., Newfane, Vt., (Fig. 19b). The surface scratches in both specimens (as in all specimens produced during the project) are considerably wider than the nominal abrasive diameter and probably caused by abrasive agglomerates and other extraneous particulate matter which we were unable to eliminate by washing the fresh lap surfaces in filtered isopropanol and performing the polishing in the clean hood. In the case of the pitch and wax laps, some galling of the wax surfaces appears to produce especially severe scratches. Freshly made wax laps were routinely worked with triacetin and clean glass surfaces before they were used to polish the halides in order to minimize extraneous wax particles. Figure 19c is a typical KCl surface produced with A-type alumina on a paraffin lap using triacetin (triacetic glycol) as a slurry medium. The use of this compound, which does not react perceptibly with KCl surfaces, was first described by H. Bennett.[3] Potassium chloride specimens (38 mm diameter) which were flat to within approximately one wave (at 5460 angstroms) were produced using the paraffin laps without inordinate difficulty, but these contained the

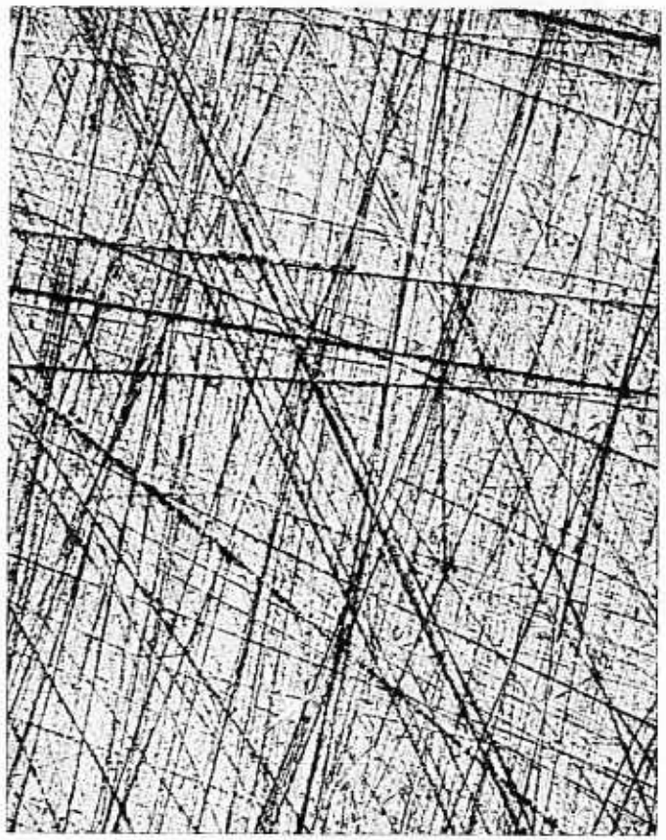


a) Politex, B, and Propanol



b) Janos Optical

Fig. 19 Microstructures of Conventionally Polished Potassium Chloride.



c) Triacetin, A, Paraffin.

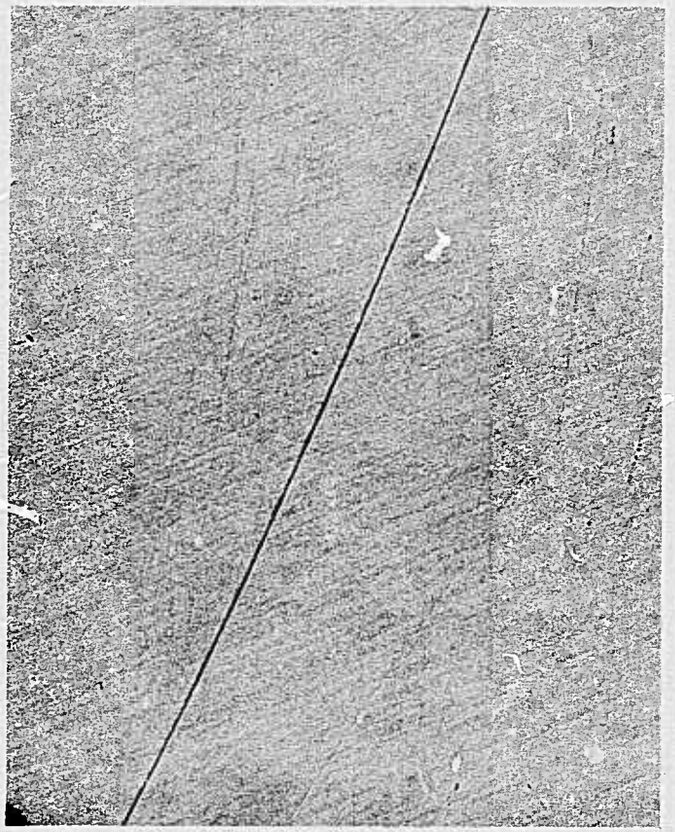
Fig. 19 (Cont'd)

rather deep scratches shown in Fig. 19. The cleaner specimens produced by the Politex laps were several waves convex. We were unable to combine the good features of the two approaches.

In this context, we point out that the Harshaw Chemical Company routinely produces, by proprietary techniques, the highest quality alkali halide surfaces we examined during the course of the project. They produce two grades, a standard window polish and a laser finish which appear as Figs. 20a and 20b, respectively. Microscopically, the standard window polish appears to be superior to the laser polish. This difference was observed for each of four "laser-polished" and twelve "window polished" specimens inspected. Note that the larger scratches in both these specimens were introduced at some time subsequent to the polishing step, probably while packaged in the paper envelopes in which they were shipped. Although no optical figure specification was placed on the specimens, which were 25 millimeters in diameter, several of those measured were flat to within approximately one half wave over their surfaces with a several wave roll at the edges. Others were quite convex. One laser polished specimen contained several grains separated in height by approximately one fringe step. This relief polishing might prove troublesome if Harshaw's techniques were used to polish polycrystalline cast materials to exacting tolerances. Hot forged potassium chloride, which is more likely to be used in high power laser applications would not exhibit this relief polishing so long as the initial boule were a true single crystal.

2.3.4 Bowl-Feed polishing

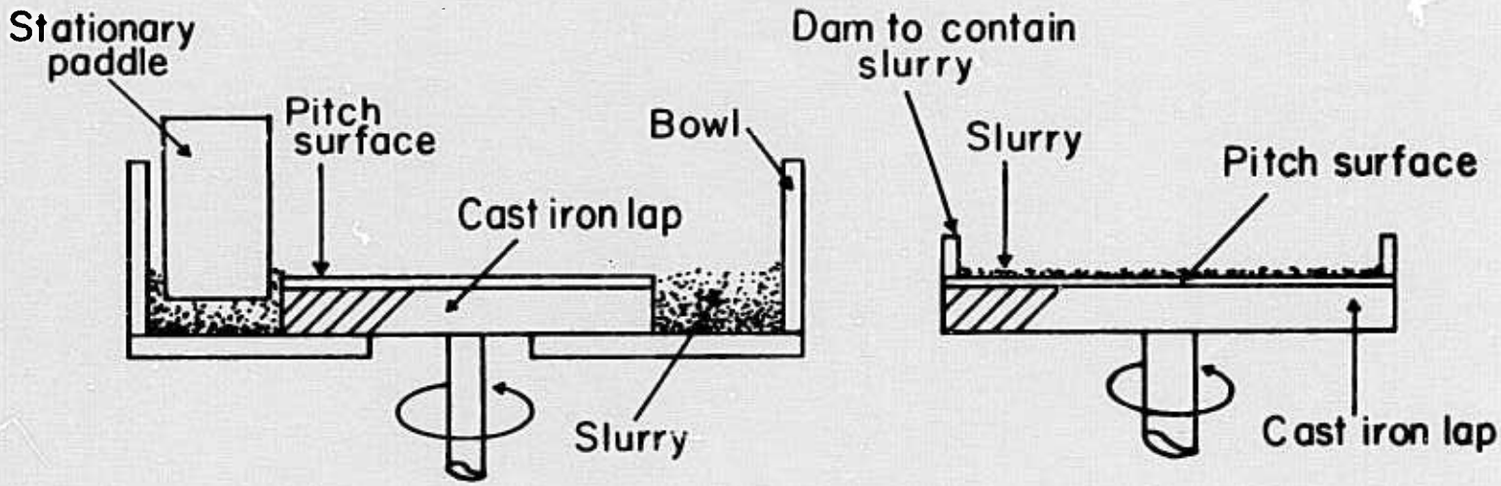
Bowl-feed polishing is a technique widely used for finishing surfaces of fused silica and metal super-reflectors. Surfaces having root mean square deviations from planarity as small as 5 angstroms have been reported.[4] Figure 21a shows schematically a polishing lap adapted for bowl-feed polishing. The bowl, which rotates with the lap, contains an abrasive slurry which just covers the lap surface when the lap is stationary. When the lap is in motion, the slurry moves radially outward and the stationary paddle directs the upper portion of the slurry back onto the lap surface.



a) "Window Polish"

b) "Laser Polish"

Fig. 20 Conventionally Polished Potassium Chloride Produced by Harshaw Chemical Company.



a. Bowl Feed Used at Raytheon.

b. Submerged Lap Used at Itek.

Fig. 21 Bowl-Feed Polishing Laps - Schematic.

As polishing proceeds, the bowl permits the coarser abrasive fractions to settle out of the active slurry volume. Further reduction of the abrasive particle size is thought to be caused by the action of the workpiece on the lap.

The variation of the procedure shown in Fig. 21b was used by Itek Corporation for their superpolishing experiments. They have used it successfully in other systems. In this variation, however, there is no "gutter" area surrounding the lap, so superpolishing must occur by abrasive breakdown alone. And since the workpiece cannot be run out past the edge of the lap, the operator has less control of the optical figure.

Bowl-feed polishing of CaF_2 and ZnSe was carried out by filling the bowl to just cover the lap surface with a slurry containing 10 percent by weight of the chosen abrasive in filtered, deionized water (from a Millipore "Super-Q" purification system). Softened pitch laps similar to those described in the preceding section were rotated at approximately 30 revolutions per minute. The pressure on the workpieces was similar to that reported for conventional polishing. Samples used for bowl-feed polishing were first finished with Universal Type A or B alumina abrasive.

The bowl-feed polishing assembly was allowed to run for several hours before the workpieces were put on the lap. During this time, a layer of sedimented abrasive built up on the bottom of the bowl. Liquid lost by evaporation was made up by addition to the lap surface to avoid stirring of the slurry pool. Following the first tabulated zinc selenide polishing, a drop of the slurry was extracted from the top surface of the pool for scanning electron microscopy. Several bowl-feed polishing runs performed at Raytheon are summarized in Table VIII.

Itek Corporation polished a block of zinc selenide specimens for two hours on the lap shown in Fig. 21b using Linde A abrasive (which is coarser than the abrasive used for bowl-feed polishing at Raytheon).

TABLE VIII

BOWL-FEED POLISHING EXPERIMENTS

Material	Abrasive	Time (hr)	Removal Rate (μm/min)	Results
ZnSe (3 pieces, 1 in. square)	Univ. B (Alumina)	4.5	0.03	Surface Improvement
ZnSe (single 1 in. square piece)	Univ. B (Alumina)	4	NM	Surface Degradation
CrF_2, polycrystalline	Univ. B (Alumina)	4	None detectable	Surface Improvement
	Barnesite No. 924	3.25	0.01	Degradation
	Tin Oxide	4	NM	Degradation

Microscopic examination of the specimens indicated that, while they contained some pits and scratches, the surface quality had improved.

Itek also evaluated the use of continuously-recycled abrasive polishing of zinc selenide. In this technique, the slurry is continuously played onto the lap surface by a pump. The extent to which the coarser abrasive fractions are allowed to settle out of the slurry can be controlled to some extent. The procedure has been used successfully by Itek to polish glass and metal surfaces with abrasives other than alumina, but they found that both 'A'- and 'B'-type alumina settled out of suspension too rapidly to produce any significant polishing of the zinc selenide specimens. A wetting agent (Everflow, marketed by Universal Shellac Co.) was used in an attempt to obtain better abrasive suspension, but it degraded the selenide surfaces.

The preliminary results of bowl-feed polishing of both CaF_2 and ZnSe were quite encouraging. 'B'-type alumina abrasive dramatically improved the surfaces of both materials. Scratches in the zinc selenide surface could be seen in the microscope, but were too fine to photograph clearly.

The function of abrasive breakdown in the process could not be determined from the micrographs taken of the abrasive extracted from the bowl after the experiments. The largest particles in a scanning electron micrograph taken of a sample of the final slurry were as large as the largest particles in the as-received abrasive.

The improvement produced by bowl-feed polishing of zinc selenide is demonstrated by the scattering measurements presented in Fig. 22, in which a bowl-feed polished sample is compared with a specimen polished by conventional techniques using the same abrasive type. The bowl-feed polished specimen improved by approximately a factor of three at all angles. The Itek submerged lap superpolish specimen, which was finished with A-alumina,was comparable in quality to a conventional polish using the finer grade B-alumina.

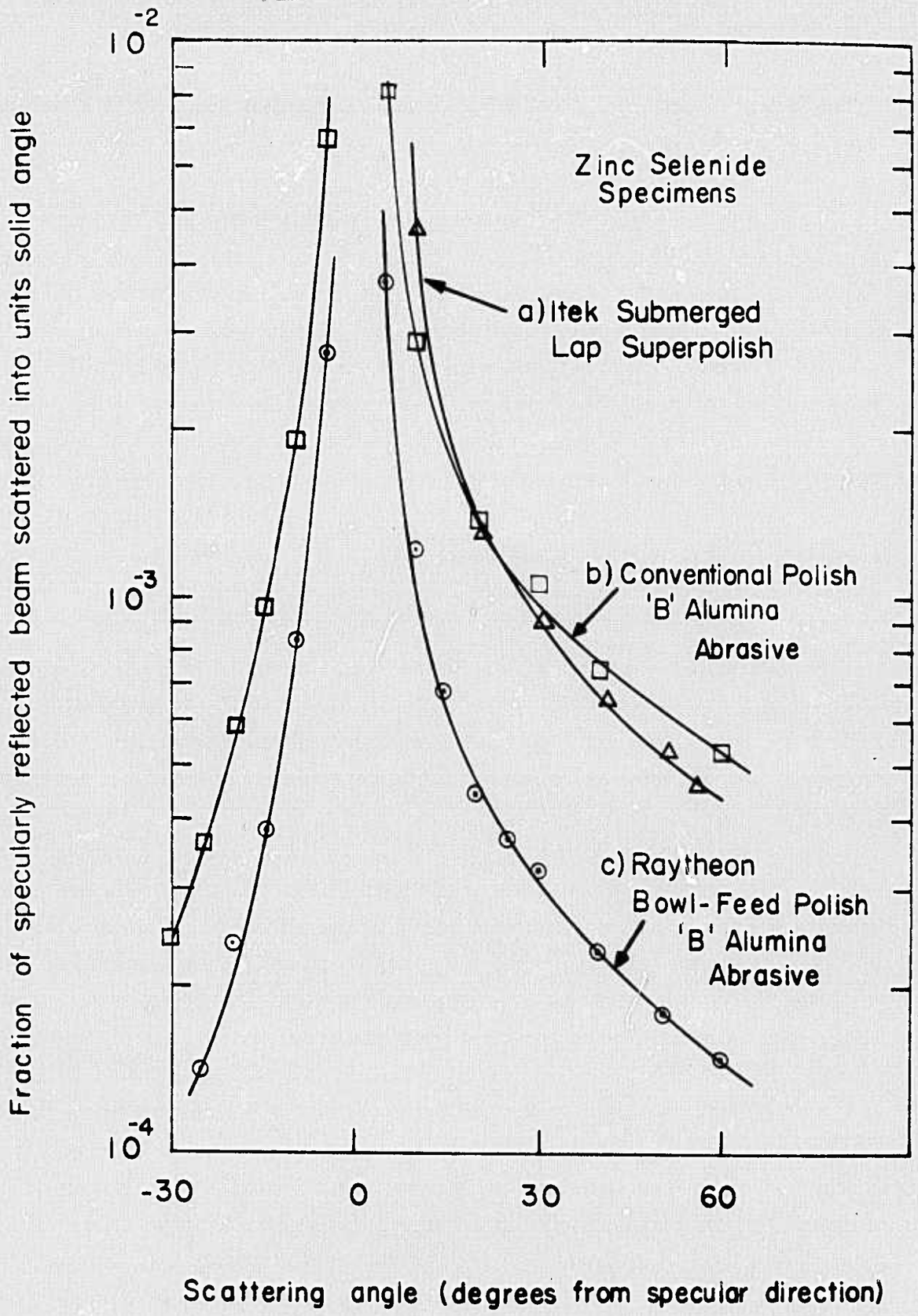


Fig. 22 Light Scattered Into Unit Solid Angle vs Scattering Angle - Selenide Samples.

Figure 23 compares bowl-feed and conventionally polished polycrystalline calcium fluoride. The improvement in this case is by approximately an order of magnitude. Microscopically, the bowl-feed polished calcium fluoride specimen is more nearly scratch-free than the zinc selenide sample. The only scratches visible on the calcium fluoride specimens were associated with surface pits which are probably the result of grinding damage introduced during the earliest processing steps. The importance of all the processing steps cannot be overemphasized. As was the case with zinc selenide, no grain boundary relief was produced on these specimens.

Tin oxide and Barnesite No. 924 abrasives degraded calcium fluoride surfaces during bowl-feed polishing runs. Figure 24 illustrates the scratches and relief polishing produced by Barnesite. Surface structure produced by tin oxide was shown in Fig. 3.

A zinc selenide specimen worked as a single piece did not improve but degraded, probably because it was too small to be held against the lap over its whole surface. At the end of the experiment, the specimen had become convex and covered with new scratches; both defects were probably caused by the leading edges of the specimen "digging into" the lap surface.

The above results were obtained during the first half of the program after which the bowl-feed laps were set aside and other areas of the program pursued. When bowl-feed polishing activity was renewed toward the end of the program in order to produce specimens for independent evaluation and rms surface roughness determination, two problems which had not been apparent in the earlier experiments arose. First, the scratch removal, which had been easily achieved in the earlier experiments, could only be reproduced by extensive cleaning and recleaning of the apparatus and remaking and reworking of the lap surface. Second, relief polishing, especially of polycrystalline cast calcium fluoride, became a serious problem. A block of cast polycrystalline CaF_2 consisting of one 45 millimeter diameter piece surrounded by six 20 millimeter pieces was being prepared when the extent of the problem was first realized. Figure 25 is a micrograph of an isolated grain in one of the pieces. This

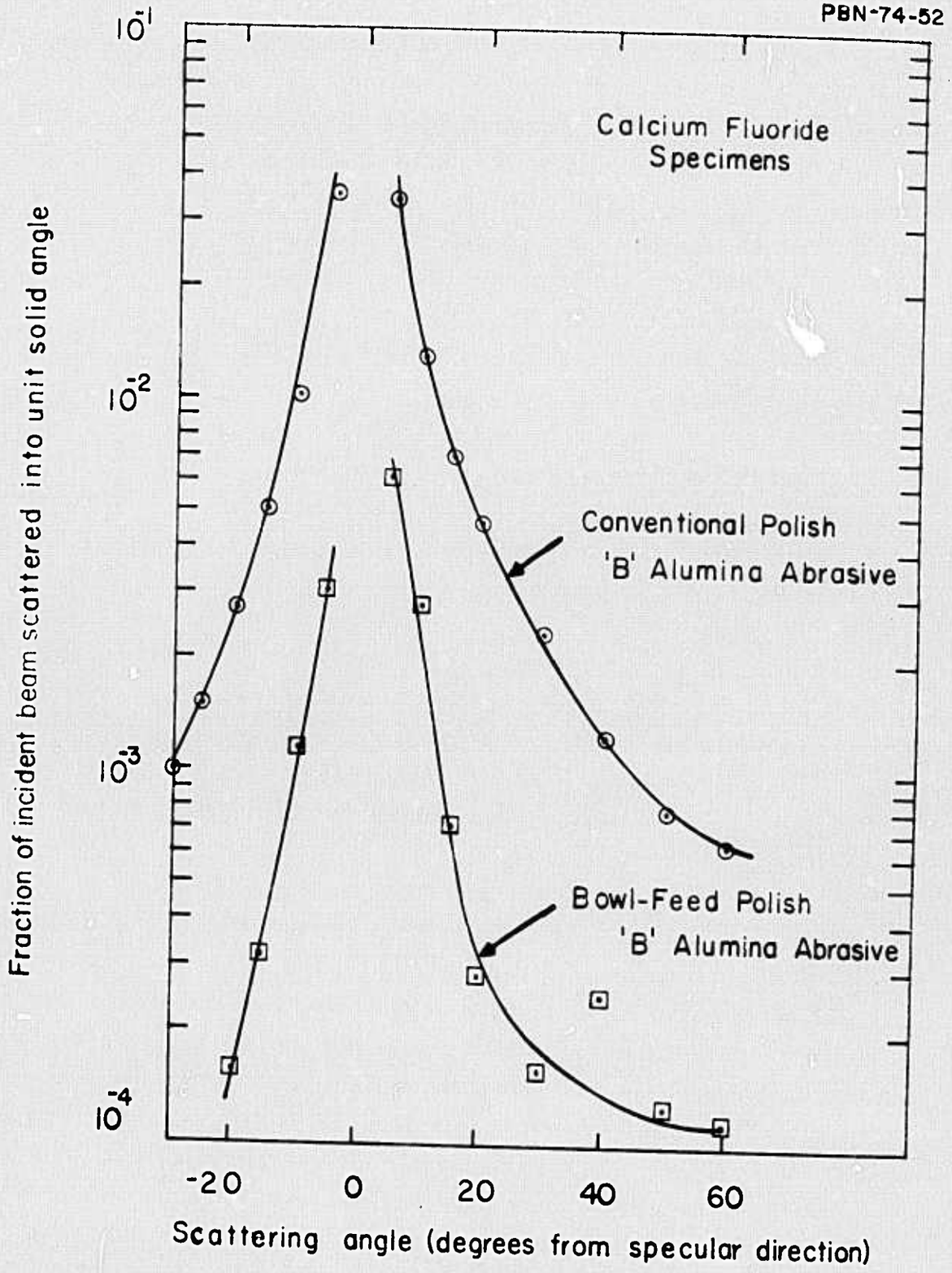


Fig. 23 Fraction of Incident Beam Scattered Into Unit Solid Angle vs Scattering Angle, Calcium Fluoride Specimens.

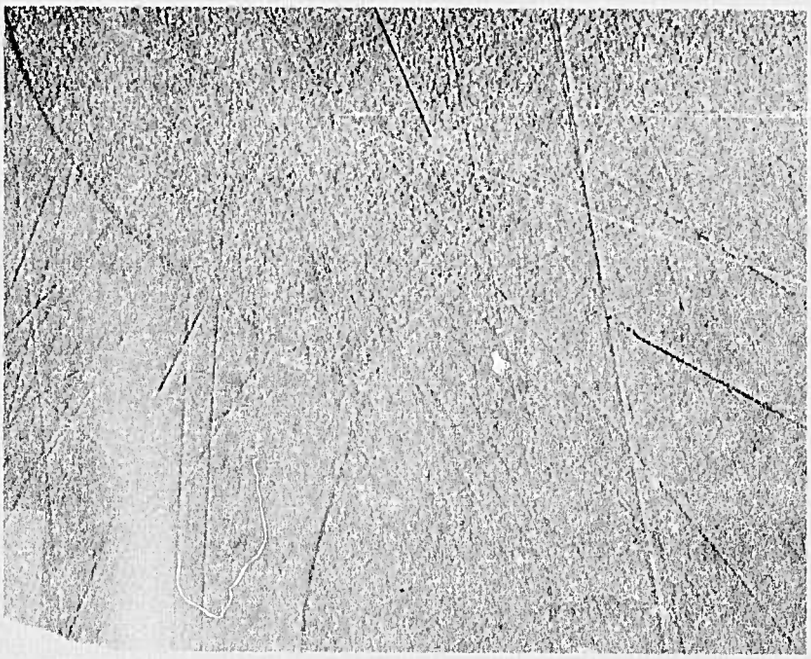


Fig. 24 Polycrystalline Calcium Fluoride Specimen, Bowl-Feed Polished with Barnesite No. 924 Abrasive. 187×

Fig. 25 Relief Polishing in Bowl Feed Polished Calcium Fluoride.

specimen was bowl-feed polished, using B-type alumina abrasive for 2 hours. The original surface, which was produced by conventional polishing techniques and A-type alumina, contained the pits and scratches which characterize the A-surface, but no relief polishing. Relief polishing only appears when very fine polishing is attempted. In this case the surface relief is approximately 2400 angstroms measured interferometrically, which is a little worse than $\lambda/20$ at 3.8 micrometers and clearly unacceptable.

A second investigation of the bowl feed polishing technique was carried out in an attempt to eliminate the relief polishing problem. The grain size of the cast CaF_2 specimens on the block described above is approximately one centimeter, so the smaller ones contain only three or four grains and the large ones approximately ten. Individual grain boundaries were therefore easily relocated under the microscope for comparison of the effects of the various polishing treatments which were used. Since alumina abrasives had already been shown to produce superior surfaces, three aluminas; A-type, B-type, and Alon fumed alumina were chosen for comparison. SEM photographs of the latter two appear in Fig. 5. Pitch laps having a variety of hardnesses were used and both bowl-feed and conventional polishing techniques were attempted. Pitch hardness was adjusted by means of linseed oil additions to either hard Cycad pitch or Swedish Pitch No. 73. Hardness measurements for the various pitch compositions are presented in Table IX. Data points were taken on a Kentron microhardness tester using a one gram load. Two aspects of the Table deserve comment. First, the soft Cycad pitch used by Itek Corporation during their study of zinc selenide polishing was considerably softer than the pitch used at Raytheon. We will see below that the soft pitch probably contributed to the difficulty they experienced with selenide relief polishing.

Second, the 0.2 percent oil addition to the Swedish pitch and the 0.1 percent addition to the hard Cycad appear to have caused slight increases in hardness. This unexpected result was repeated on a second set of Swedish pitch specimens and is probably caused by the volatization of more light pitch components during the stirring (which is used to homogenize the pitch-oil mixture) than are replaced by the small oil additions. Most of the combinations of pitch hardness and abrasive type were used to bowl-feed polish the block of CaF_2 specimens described above. Between bowl-feed treatments, the specimens were reground with 5 μm Microgrit (alumina) grinding compound and repolished with A-type alumina. The B-type and Along aluminas were also used as abrasives for conventional polishing.

TABLE IX

KNOOP HARDNESS AND POLISHING CHARACTERISTICS OF OIL-PITCH MIXTURES USED TO POLISH POLYCRYSTALLINE CALCIUM FLUORIDE

Pitch Composition (Linseed Oil in wt. %)	Knoop Hardness	Remarks
Cycad (Hard)	0.61	Scratches Surface
Cycad (Hard) + 0.1%	0.64	Scratches Surface
Cycad (Hard) + 0.2%	0.52	Scratches Surface
Cycad (Hard) + 0.3%	0.40	Scratches Surface
Cycad (Hard) + 1.0%	0.30	
Swedish No. 73 + 0.2%	0.26	
Cycad (Hard) + 2.0%	0.20	
Swedish No. 73	0.18	Relief Polishing at Specimen Edges Worst for first Abrasions
Cycad (Hard) + 3.0%	0.17	
Cycad (Hard) + 4%	0.05	
Swedish No. 73 + 1%	0.04	Figure Control Becomes Difficult
Cycad (Soft)	0.04	Relief Polishing Worse

Results of this series of experiments may be summarized as follows: First, no completely satisfactory set of polishing conditions was determined. Second, relief polishing was favored by either finer abrasives or softer lap surfaces. Third, either B-type alumina or Alon could be used to produce scratch-free surfaces; the latter abrasive was the more reliable. The most nearly perfect surfaces, which still exhibited relief polishing, were produced using bowl-feed polishing, Alon alumina, and the harder Swedish pitch surface. In order to obtain the optimized surfaces both the pitch and abrasive had to be compromised. Harder pitches and coarser (A-type) abrasives both produced scratched surfaces.

The results may be explained as follows: The hardness of a crystalline material (and by analogy, its resistance to abrasion in a polishing situation) is dependent upon its orientation. When the technique being used to polish a polycrystalline aggregate removes material very gently, orientation-dependent differences in grain hardness may be large enough to produce relief polishing. Soft lap surfaces, fine abrasives, and soft abrasives all polish more gently than their opposites, and therefore tend to enhance relief polishing. Conversely when the polishing action is more rigorous, the abrasive-lap combination determines the material removal rate and the relief polishing disappears. The observations of relief polishing associated with the relatively soft Barnesite and tin oxide abrasives on CaF_2 and with ZnS on KCl are consistent with this model of relief polishing. Syton, an alkaline colloidal silica suspension, was used as a chemical-mechanical polish for CaF_2 and found to produce relief polishing even when neutralized, probably because the silica abrasive is both finely divided and relatively soft.

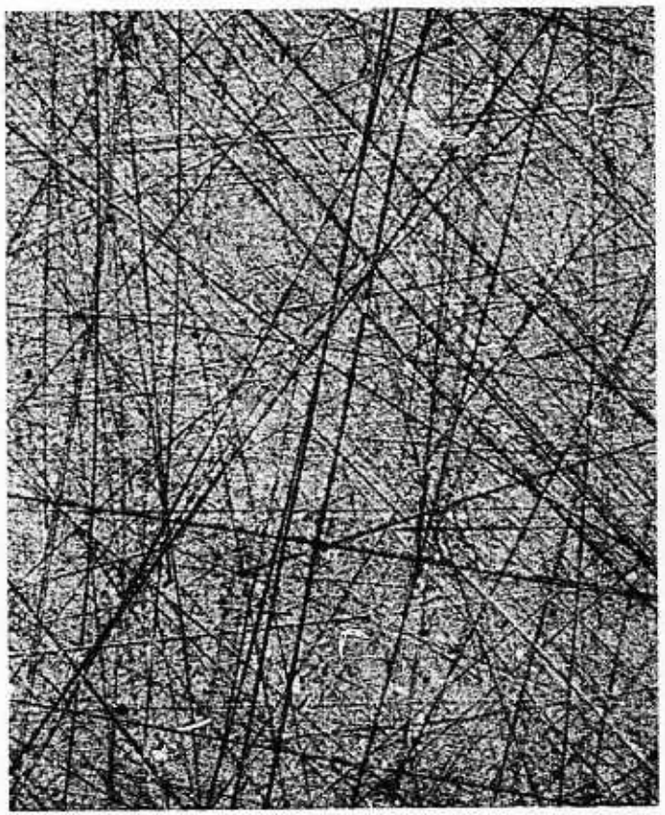
The results of this series of experiments indicate that either harder lap surfaces or harder abrasives should be useful for improving CaF_2 surfaces without causing relief polishing. Pitch surfaces harder than those which produced the best bowl-feed polished specimens generally scratched the surfaces. A harder abrasive, diamond, was shown to be a most effective solution to the problem. Results are discussed in the next paragraph.

Finally, bowl-feed polishing of potassium chloride using triacetin as the slurry medium was attempted. A 4-inch diameter beeswax lap was mounted inside an 8-inch diameter bowl for the experiments. Potassium chloride single crystals conventionally polished with 'A'-alumina (on a beeswax lap using triacetin) were bowl-feed polished with 'B'-alumina in triacetin. Results are summarized in Fig. 26, where the initial 'A'-surface (Fig. 26a) is seen first to improve (Fig. 26b) and then to degrade with further polishing (Fig. 26c, d). The initial bowl-feed polished surface is the highest quality abrasive polish produced on potassium chloride using wax laps during this project, but the improved surfaces were very difficult to reproduce. Further, the beeswax lap surfaces tended to separate from their aluminum backing plates after long immersion in the triacetin. The deterioration may have been caused by surface contamination introduced when the specimens were inserted in the microscope, by coarse agglomerates of the alumina abrasive, or by bits of wax produced by galling of the lap surface. Attempts to improve the surfaces by using Alon or refined B-type alumina and by working the wax lap with a glass flat to eliminate loose bits of wax were largely unsuccessful.

Concluding, although bowl-feed polishing was shown to be capable of producing the most nearly scratch-free surfaces on zinc selenide and calcium fluoride specimens produced during the course of this project, relief polishing and lack of reproducibility limit the usefulness of the technique. Potassium chloride surfaces were improved by the technique but no really outstanding finishes were produced. Bowl-feed polishing may become still more unwieldly when it is extended to the finishing of larger pieces. It was to this end that Itek's experiments with continuously-recycled abrasive polishing were directed. This evaluation of the super-polishing techniques precipitated our renewed investigation of diamond abrasive polishing late in the program.

2.3.5 Diamond abrasive polishing

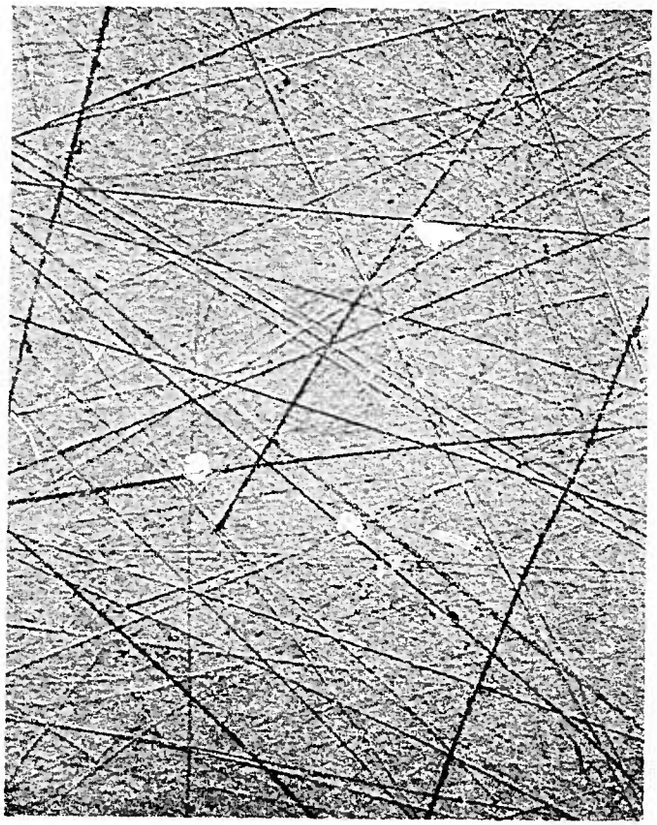
Diamond abrasives were used to produce the optimized abrasive polishes on both zinc selenide and calcium fluoride. The use of diamond in the form of oil-based pastes was explored very early in the program



a) Original Surface. 187×

b) After 15 Minutes. 187×

Fig. 26 Potassium Chloride Bowl-Feed Polished in Triacetin Slurry of 'B' - Alumina.



c) After 45 Minutes. 187×

d) After 60 Minutes. 187×

Fig. 26 (Cont'd)

during which time they were used in conjunction with cast iron laps for grinding and rough polishing and with soft lead laps for fine polishing. These treatments produced badly scratched surfaces. Since oil-based pastes could not be used with pitch laps and alumina abrasives appeared to be acceptable, attempts to use diamond ceased. When relief polishing was recognized to be a limiting feature of superpolished polycrystalline CaF_2, attempts to use diamond abrasives were renewed. The hardness of diamond, it was hoped, would produce the same polishing rate on all fluoride orientations.

Loose diamond powder in a water slurry was used, as summarized in Table X, on pitch laps. The abrasive was shaken with water and added dropwise to the operating lap. When the specimen surfaces began to improve, the lap surfaces were considered to be charged with diamond and further slurry additions were made from the water over the settled diamond. The lap rotation rate and specimen pressure used for previous abrasive polishing were retained. Occasionally the rapid surface improvement which generally characterized the technique did not occur. In these cases softening the lap surface slightly with a torch and pressing it with a glass flat to produce a fresh surface restored the proper polishing behavior. In some instances this reworking was repeated two or three times before the lap polished properly, but in all cases the proper action was obtained. We note that while we did not attempt to use it, 0.1 μm diameter diamond powder is available and might produce still finer surfaces. We did use 3-micrometer diamond powder as a replacement for A-type alumina. It produces a surface which is more highly scratched than the alumina surface, but it polishes to an identical surface when the finer diamond is applied.

Results obtained by diamond polishing of polycrystalline CaF_2 are presented in Fig. 27, a comparison of light scattering measurements taken from conventionally polished, bowl-feed polished, and diamond polished specimens. The diamond polished specimen was taken from a block consisting of the four one-inch diameter specimens which relief polished most severely during the bowl-feed polishing studies. No relief polishing could be detected on any specimen of the group after diamond polishing. The polishing technique is summarized in Table X.

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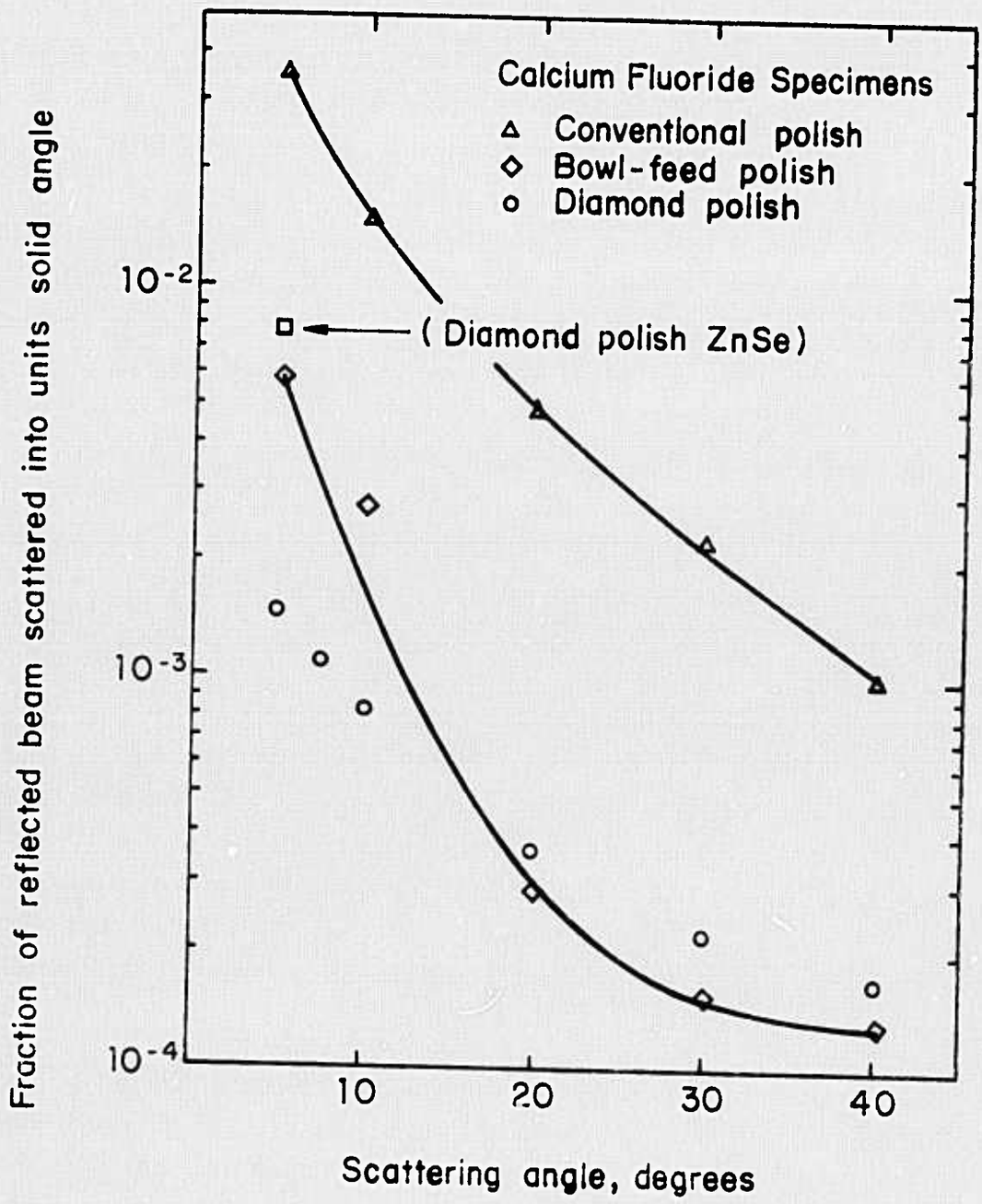


Fig. 27 Light Scattered into Unit Solid Angle vs Scattering Angle-Diamond Abrasive Polished Calcium Fluoride Specimens.

TABLE X

DIAMOND POLISHING OF POLYCRYSTALLINE CaF_2

Preliminary Sample Preparation	Standard A-Alumina Conventional Polish
Abrasive	O-$\frac{1}{2}$ μm loose diamond powder*†
Slurry Vehicle	Water
Lap	No. 73 Swedish pitch +0.2 percent Linseed oil
Polishing Time	1.5 hours, < 3 μm
Material Removal from A-Surface	Unmeasurable

* Obtained from Engis Corporation, Morton Grove, Illinois.

† A diamond paste in a water-soluble base was also used on the pitch laps, but without success.

The diamond polishing techniques used for CaF_2 were repeated on ZnSe specimens producing the results summarized in Fig. 28. Again the best bowl-feed results were repeated. Although no further scattering measurements were made, the technique was used to polish several additional sets of microscopically similar ZnSe and CaF_2 specimens.

Finally, after the close of this project, the diamond polishing techniques were used to polish a 6-inch diameter cast CaF_2 disc. In this case, approximately half fringe steps were produced at some grain boundaries. We believe, however, that the use of slightly harder pitch laps should substantially eliminate this problem and recommend diamond polishing as the optimum abrasive polishing technique for both calcium fluoride and zinc selenide.

2.3.6 Transparent abrasive polishing

Abrasive particles embedded in optical surfaces may be considered to be a universal feature of conventional abrasive polishing. To the extent that they absorb incident laser radiation, they may be sites for preferential

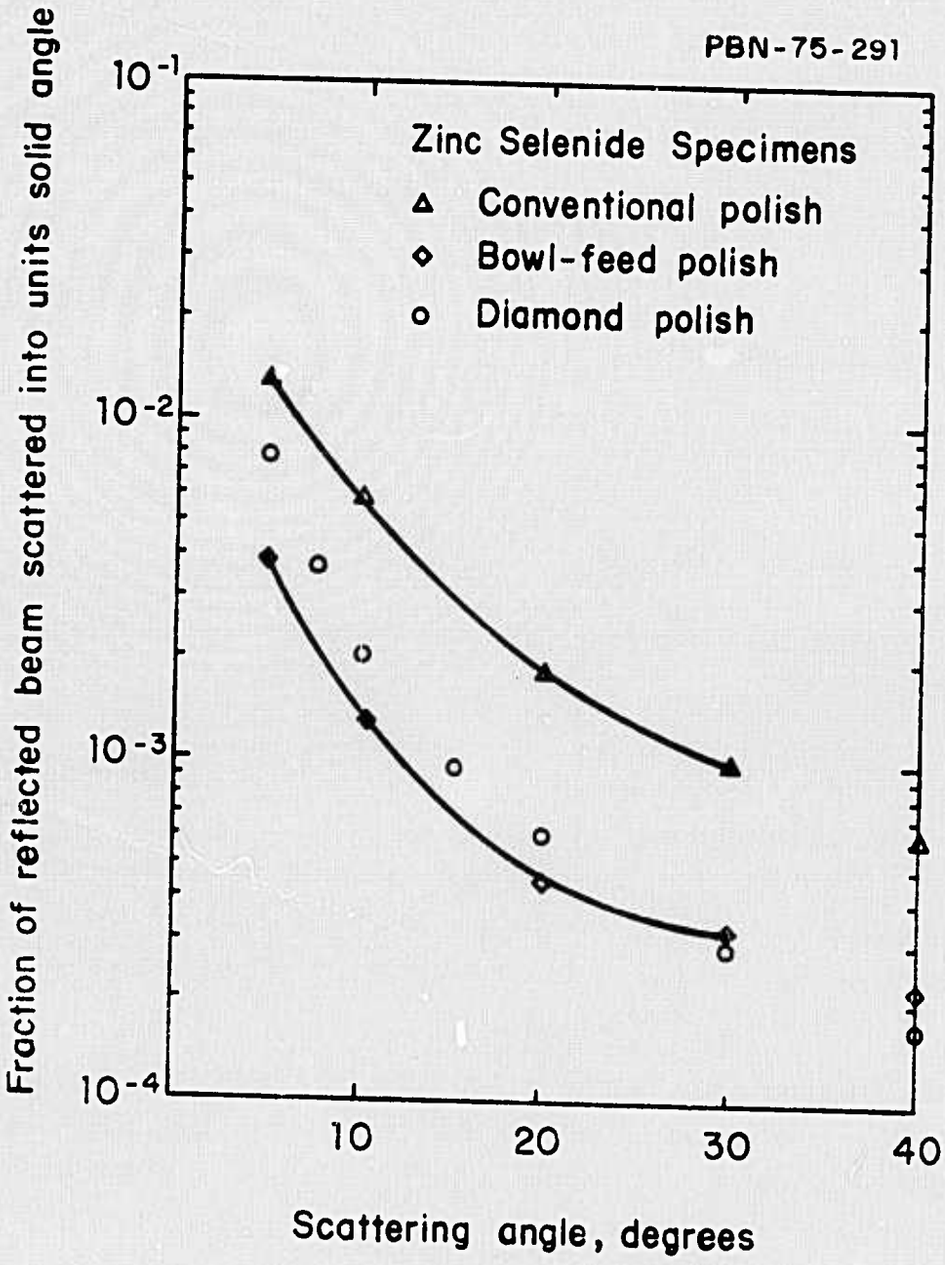


Fig. 28 Light Scattered into Unit Solid Angle vs Scattering Angle - Diamond Abrasive Polished Zinc Selenide Specimens.

damage. One of the surface finishing techniques assessed by this project was the use of abrasives which are transparent to the laser radiation. When the program was proposed, transparent abrasives were thought to be particularly important for the polishing of components for laser operating in the 8 to 14 micrometer wavelength range where aluminum oxide and other common abrasive materials are quite opaque. Potassium chloride and zinc selenide were chosen as specimen window materials and zinc sulfide, which is harder than both, as a candidate abrasive material. Diamond, an abrasive used for other reasons during the project might also be considered to be a transparent abrasive since in single crystal form, it is transparent to well beyond 14 micrometers. Industrial-grade diamonds used as abrasives, however, contain considerable quantities of graphite, which would be quite opaque. The third sample material being studied for this program, calcium fluoride, will be used for lasers operating at wavelengths where aluminum oxide itself is a transparent abrasive.

During the course of this program, acceptable chemical and mechanical polishing procedures were developed for zinc selenide which, although they made use of absorbing abrasives, nonetheless raised the CW selenide damage threshold (to CW 10.6 micrometer radiation) well above power levels at which thermally-induced optical distortions would limit the usefulness of practical selenide optical elements. Damage measurements are presented in the final report for contract No. DAAH01-72-C-0194. Pulsed laser damage appears to be the result of breakdown at bulk defects. The use of zinc sulfide as an abrasive for potassium chloride, therefore, became the entire transparent abrasive effort.

Zinc sulfide (Knoop hardness 250), is approximately 30 times harder than potassium chloride (Knoop hardness 8) and is capable of removing stock from chloride surfaces. During the first six months of the program, zinc sulfide abrasives were shown to remove material from potassium chloride surfaces and to produce a rough polish. Hardened forms of zinc sulfide were subsequently produced and evaluated.

Hardened sulfides were produced by precipitation from aqueous solutions containing intentional impurity additions. Impurity atoms or

ions in crystalline materials which cause strains in the lattice immediately surrounding them make plastic deformation of the material more difficult because the strain fields impede the motion of the dislocations which is responsible for the plastic deformation. In ionic crystals, very substantial hardening effects may be produced by the substitution of ions having a valence which is different from that of the normal lattice ion. Figure 29 illustrates the change in yield point, a physical property closely related to hardness, which is obtained by divalent additions to alkali halides. This is the phenomenon being used to produce strengthened halide window materials. In the case of zinc sulfide, two substitution schemes were attempted for the precipitates; single substitution of trivalent gallium for divalent zinc and double substitution of gallium and monovalent silver for zinc. In the former case, two gallium ions replace three zinc ions; one lattice site remains vacant. The double substitution replaces two zinc ions by a gallium-silver pair. The coupled substitution was attempted because it was expected to be significantly more soluble in the zinc sulfide lattice than the single gallium addition and capable of increased hardening. Zinc sulfide-selenide solid solutions produced as bulk solids by chemical vapor deposition were also evaluated as abrasives after first being ground to appropriate particle sizes.

Pure and hardened sulfides were precipitated in the apparatus shown schematically in Fig. 30. Nitrogen containing ten percent hydrogen sulfide is bubbled through the heated, stirred solution from which the sulfide precipitates. Evaporating water is returned to the reactor by the condenser and excess hydrogen sulfide is trapped in gas scrubbers which contain potassium hydroxide solutions. Pure and gallium-doped zinc sulfides were precipitated from acidic half-molar solutions of zinc chloride to which appropriate gallium chloride additions had been made. Pure zinc sulfide and sulfides containing one-half, one, and two atomic percent of gallium were produced. The gallium-silver substitution was attempted from an acidic nitrate solution because of the insolubility of silver chloride. A ten atomic percent replacement of zinc by gallium/silver was attempted. The extremely low solubility of silver sulfide caused it to precipitate as a separate phase in this case and no doubly substituted material was produced.

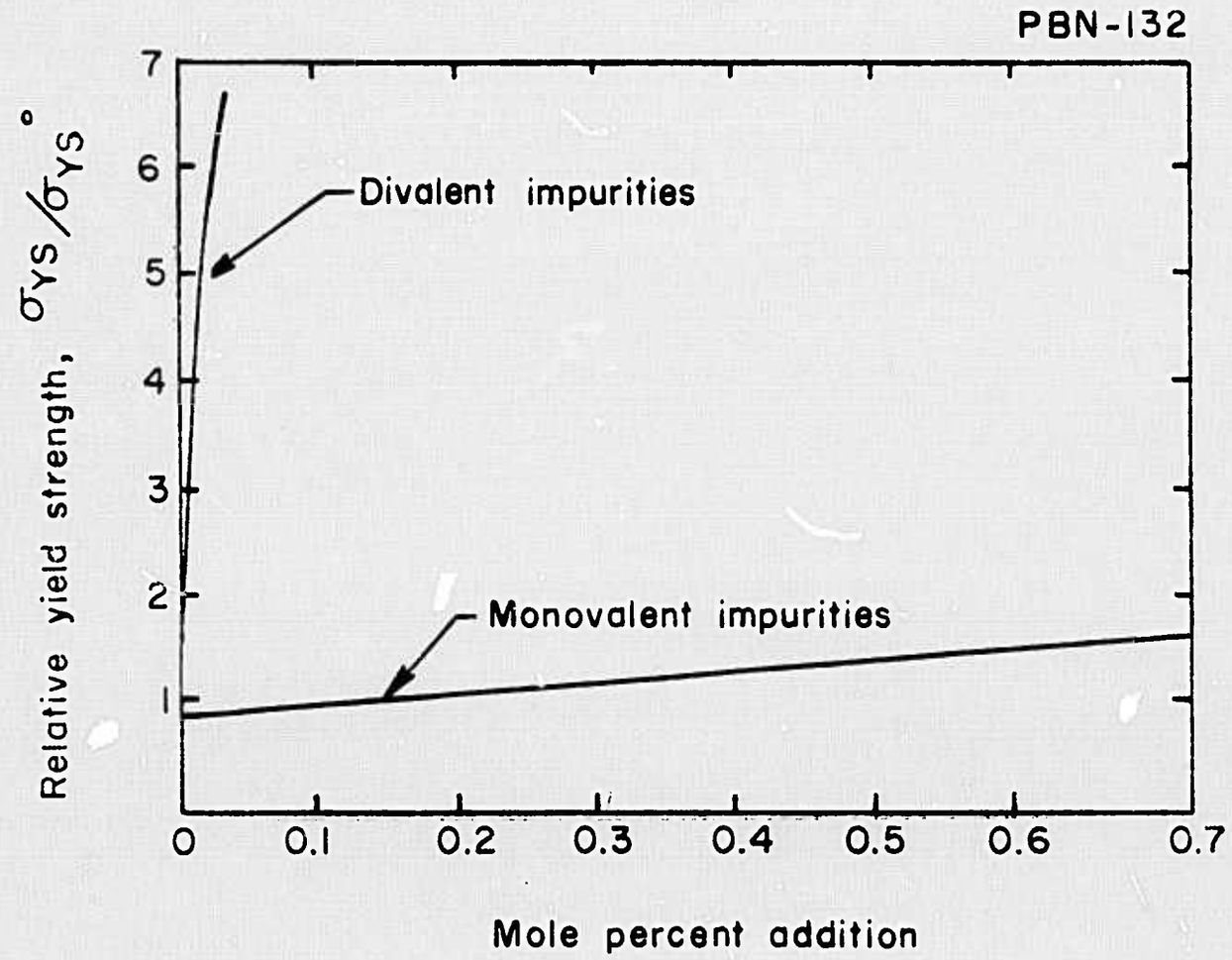


Fig. 29 Hardening Effects of Impurities in Alkali Halides.

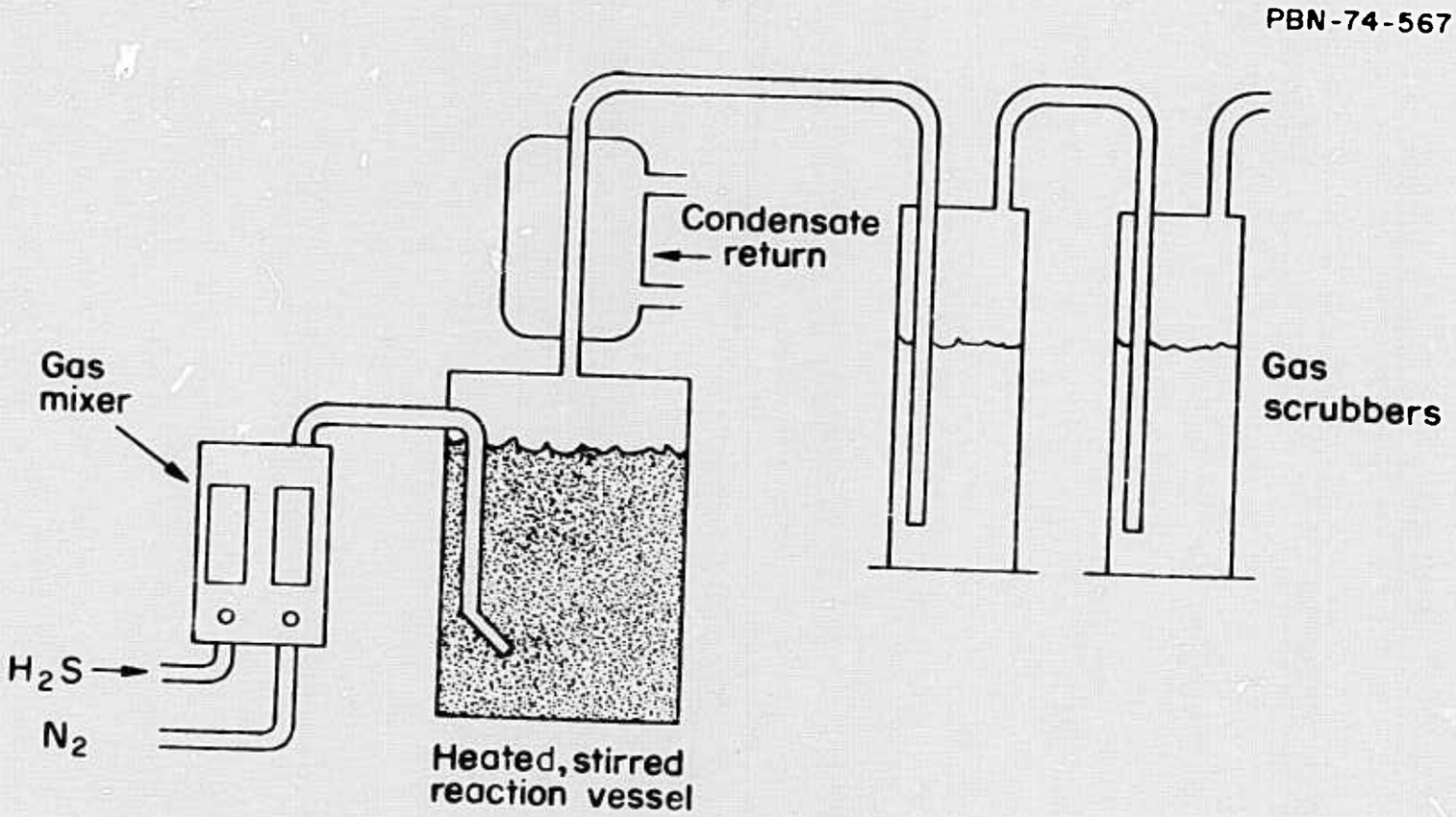


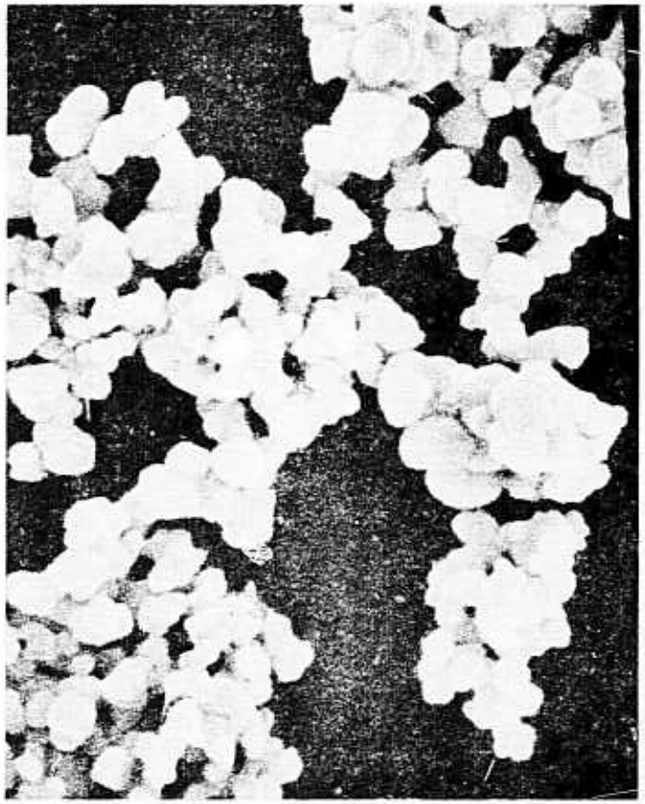
Fig. 30 Precipitator for Zinc Sulfide Preparation.

Pure and gallium-doped zinc sulfide precipitated as more or less spherical particles, one to three micrometers in diameter. Figure 31a is a scanning electron micrograph of as-precipitated pure zinc sulfide. X-ray diffraction analysis of the precipitates showed them to be poorly crystallized mixtures of both the cubic and hexagonal zinc sulfide polymorphs. Heat treatment of the powders improved their crystallinity (as determined by a sharp decrease in the breadth of X-ray diffraction lines) and revealed the polycrystalline character of the precipitated spherulites. Figure 31b is a photograph of a zinc sulfide precipitate annealed in hydrogen sulfide at 800° C for one-half hour.

The pure and the two gallium-doped sulfides were used as-precipitated and after annealing to polish potassium chloride. The polishing was carried out on beeswax laps which were rotated at approximately 30 rpm, using glycerol triacetate (triacetin) as the slurry vehicle. Single crystal and polycrystalline potassium chloride samples were polished. Both hand polishing, in which the work was loaded by only its own weight, and machine polishing, in which the pressure on the material was approximately one-half pound per square inch, were used during the course of the experiments.

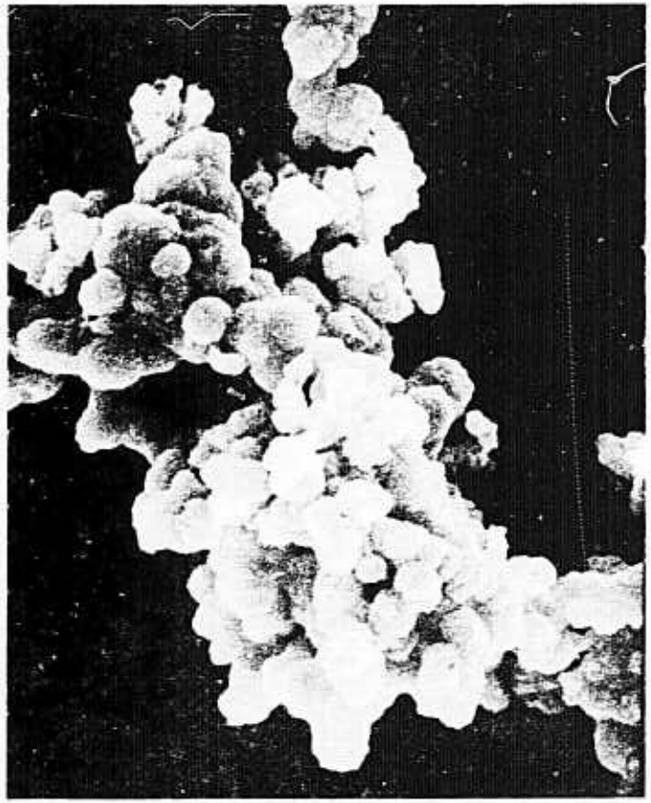
Surfaces produced by the various sulfide materials did not differ significantly. They were generally characterized by scratches on a background of small, irregular digs or pits which were approximately the same size as the abrasive material (a few micrometers in diameter). Figure 32a is a micrograph of a typical zinc sulfide surface on potassium chloride. The rate of stock removal was typically between two and six micrometers per hour for all sulfide materials. No statistically significant correlation between gallium doping level and rate of removal or surface quality could be made.

In one instance, a surface comparable to the best polishes obtained by conventional polishing with aluminum oxide was obtained. This surface, shown in Fig. 32b was produced with annealed zinc sulfide containing two atomic percent gallium. The samples were polished for one hour during which time approximately four micrometers of stock were removed. Attempts to repeat the experiment were unsuccessful.



2 Microns

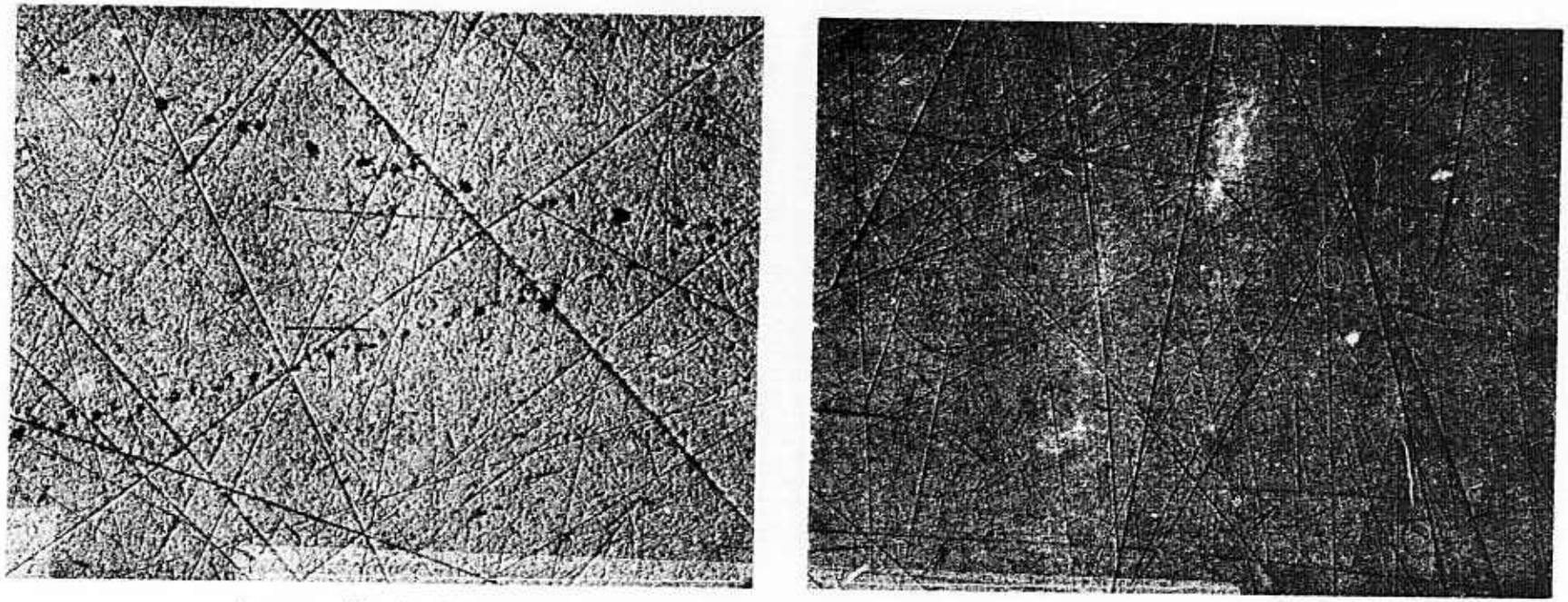
As Precipitated



2 Microns

After Heat Treatment

Fig. 31 Precipitated Zinc Selenide Abrasives. 5000×



a) Typical Surface 187×

b) Best Transparent Abrasive 187× Polished Surface

Fig. 32 Microstructures Produced by Zinc Sulfide Polishing of Potassium Chloride.

Since surfaces produced by the roughly spherical precipitates may have been in part caused by the particle shapes, zinc sulfide powders containing more angular particles were produced by grinding chemically vapor-deposited material in a ball mill. The coarsest fraction of the particles were removed from the powder by the sedimentation and the remaining fine fraction used as an abrasive. This angular, ground abrasive produced surfaces on KCl which were qualitatively similar to the more spherical precipitated material. We concluded that while some improvement of the surfaces produced by transparent ZnS abrasives could be made by continuing our efforts, the advantages offered by the technique were substantially decreased by advances being made in chemical polishing techniques. Transparent abrasive efforts were terminated during the fourth quarter in order to permit more effort to be applied to chemical polishing experiments.

2.4 Chemical Treatments

2.4.1 Specimen cleaning

The surfaces produced by abrasive polishing typically retain some residues of abrasive and mounting wax which must be removed completely from any high power laser components. During the course of this project, we found it necessary to adopt many of the techniques used by the semiconductor industry in order to produce surfaces which were essentially free of microscopically observable residues. The samples investigated here were at most two inches in diameter. Cleaning them so that no particulate residue could be observed in the optical microscope required painstaking and repeated application of the cleaning techniques. Larger components will be correspondingly more difficult to clean. Note that even a single piece of absorbing residue which remains on the component surface and is buried beneath the antireflection coating may destroy the irradiated component. Following is a summary of the techniques used to clean the polished specimens. Chemical polishing is treated in the next paragraph.

TABLE XI

CLEANING PROCEDURES FOR LASER OPTICAL SURFACES

1. Trichloroethylene Rinse (ZnSe, CaF_2) - done in order to remove residual mounting wax. ZnSe may be boiled in trichloroethylene, two-inch pieces of relatively strain-free CaF_2 may be heated to ~50°C without difficulty and removed to a second clean, heated batch which is allowed to cool. Larger CaF_2 pieces and all SrF_2 and BaF_2 should be treated more cautiously to avoid thermal shock.

2. Water Wash (ZnSe, CaF_2) - done in order to remove abrasive residues. We recommend washing the polished specimens in warm detergent solution, wiping gently with

cotton balls or cotton diaper material. Ultrasonic agitation does not completely remove residues. We have used a nylon bristle electric toothbrush (a technique borrowed from silicon processing) to clean both selenide and fluoride specimens without generating microscopically detectable scratches, but the technique requires a light touch.

3. Water Rinse - at this point, we begin using filtered rinses. The water is obtained from a Millipore "Super Q" water supply which produced 18 megohm resistivity water passed through a 0.45 μm pore size filter. This and the next step may be done in an ultrasonic cleaner.

4. Isopropanol Rinse - the isopropanol is filtered through a 0.22 μm pore size filter prior to its use on the cleaned surface. We have found particulate contamination, even in nominal Electronic Grade Solvents.

5. Isopropanol Spray - a spray gun is used to play a jet of isopropanol (0.22 μm filtered) onto the specimen. The jet is broken into a spray by streams of nitrogen (also filtered).

6. Freon Degrease - The cleaned specimens are suspended above boiling Freon 113 in a vapor degreaser until the obvious Freon reflux ceases. The Freon is also filtered through 0.22 μm pore size filters since particulate matter which contaminates the as-shipped solvent may become air borne as the solvent bubbles burst during boiling.

Sample holders in the form of tweezers containing an opening just smaller than the piece being cleaned are cut from 1/8 in. thick teflon sheet. At Step 3, the piece to be cleaned is mounted in the holder and subsequently handled only by the holder.

Potassium chloride specimens are cleaned by steps 4 - 6 of the process. The ultrasonic cleaner is used in Step 4. Potassium chloride is too soft to be scrubbed; a clean politex pad, moistened with isopropanol has been used to attempt to clean as much abrasive as possible from the polished surfaces. Samples used for transmission were polished by hand and not wax mounted.

Triacetin, the slurry medium used for KCl on wax laps is the most viscous liquid used during the project. To investigate the efficiency with which it (and remnant beeswax) is removed from potassium chloride, the series of calorimetric absorption measurements summarized in Table XII was performed on a one-inch square by four-millimeters thick single crystal from Optovac.

Cleaning in this instance was performed by immersing the sample in ultrasonically agitated isopropanol for 15 seconds, spraying in isopropanol, immersing the sample in boiling Freon 113 for 30 seconds, and drying it in the Freon vapors.

The calorimeter is sensitive to about one part in 10^4, so the difference between the etched samples and the one polished without abrasive cannot be considered to be significant. When the abrasive is used, however, absorbing residues remain. Finally, Step 5 demonstrates the importance of using clean solvents to clean the specimens.

In a related set of experiments, the infrared absorption spectrum of triacetin was obtained by attenuated total reflection (ATR) spectroscopy. This experimental apparatus, manufactured by the Harrick Company, sends the sample beam of a Perkin-Elmer Model 457 spectrometer through a sample as shown in Fig. 33. The multiple reflections of the beam accentuate absorptions caused by compounds on the sample surface. The triacetin spectrum, Fig. 34a, was obtained by allowing a one percent solution of triacetin in isopropanol to dry on a potassium chloride ATR plate. Note that several triacetin absorptions occur in the important wavelength range between 9 and 10.6 micrometers. The cleaning procedure described above does appear to clean triacetin from highly polished potassium chloride surfaces (Fig. 34b). The absorption at 4.25 and the "noise" between 5 and 7 micrometers are caused by carbon dioxide and water vapor in the laboratory atmosphere.

TABLE XII

CALORIMETRIC MEASUREMENTS OF POTASSIUM CHLORIDE CLEANING

Treatment	Fraction Absorbed	Apparent Absorption Coefficient
1. Chemical polish, Concentrated HCl Clean	0.00077	0.00193
2. Hand-held polish Beeswax lap and Triacetin. No abrasive Clean	0.00080	0.00199
3. As step 2, but using Type A-alumina abrasive. Clean	0.00094 - 0.00099	0.00235 - 0.00247
4. Chemical Polish, Concentrated HCl Clean	0.00077	0.00193
5. As step 2, but washing in solvents used for previous washing steps.	0.00137 - 0.00149	0.00342 - 0.00374

Finally, the use of a strippable coating to protect potassium chloride surfaces was studied calorimetrically. Opticoat* was applied to the large faces of a one-inch square Optovac single crystal plate, similar to the one used for the etching study, allowed to cure overnight and stripped. This treatment raised the fraction absorbed from 8×10^{-4} to 10×10^{-3}. The increased absorption was removed when the KCl specimen was washed by steps 4-6 of Table XI.

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*Obtained from Spawr Optical, Corona, Calif.

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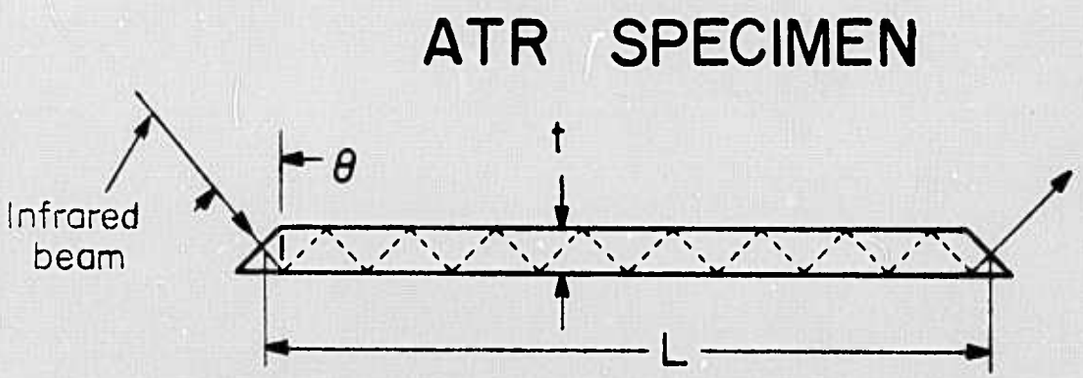
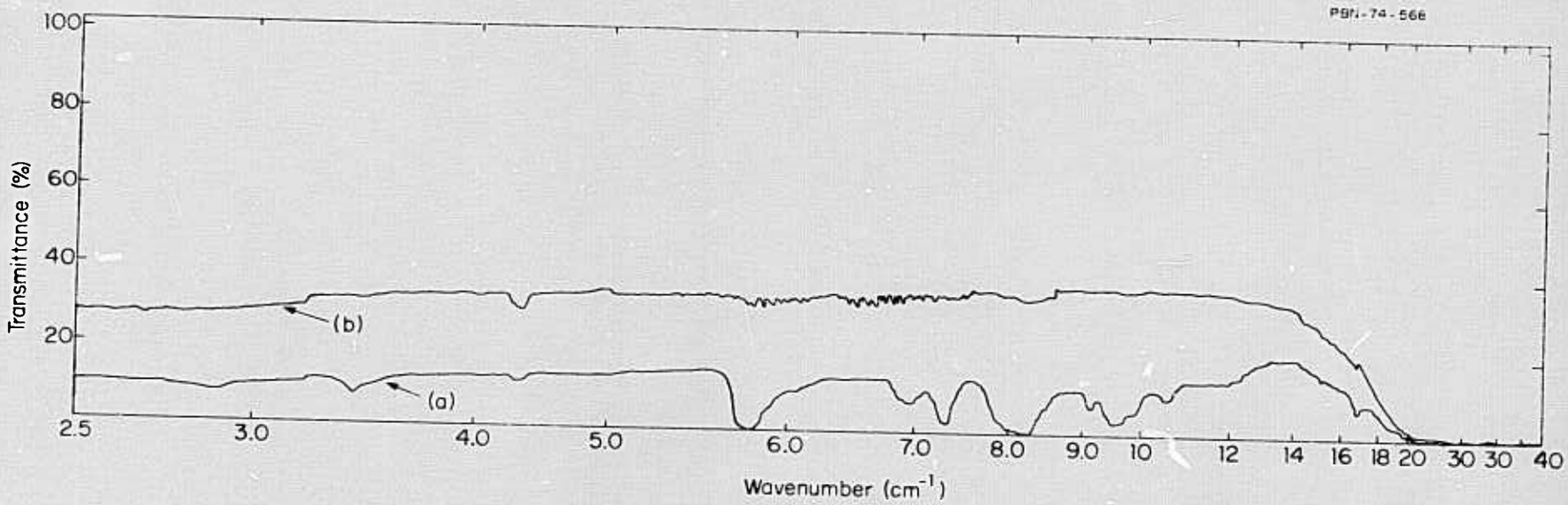


Fig. 33 Attenuated Total Reflection Spectroscopy Sample – Schematic.



a) Triacetin-contaminated specimen
b) Cleaned specimen

Fig. 34 Attenuated Total Reflection Infrared Spectra of Triacetin-Contaminated and Cleaned Potassium Chloride.

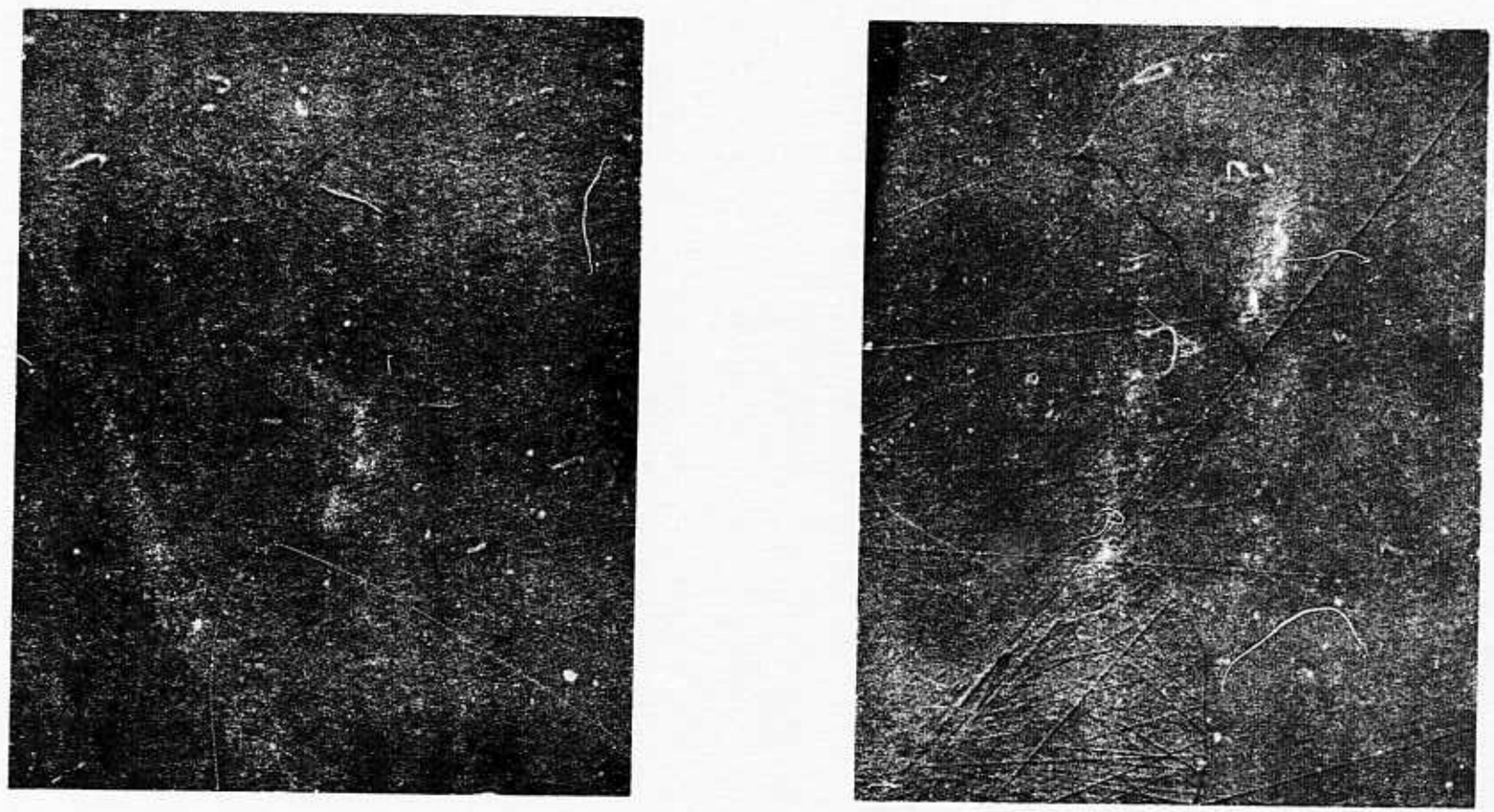
2.4.2 Chemical polishing

2.4.2.1 Calcium fluoride

Calcium fluoride surfaces which are very nearly defect-free to the Nomarski microscope may be prepared by conventional abrasive techniques and improved by bowl-feed or diamond abrasive polishing. Further, the alumina abrasive used to produce these surfaces is essentially transparent to radiation for which high power fluoride optics might be used. The polishing and cleaning steps described above will produce surfaces which absorb only $1\text{-}3 \times 10^{-5}$ of the incident 5.25 micrometer radiation. In this case, the important function for a chemical polish to perform is the removal of surface defects which might otherwise act as extrinsic laser or mechanical breakdown sites. The mechanical strength of cast calcium fluoride has been shown to be strongly influenced by the surface finish, and chemical polishing has been shown to improve strength of conventionally polished material.[5]

A one-molar aqueous solution of ammonium chloride was used as a chemical-mechanical polish for single and polycrystalline calcium fluoride. Polishing was done on a pitch lap immersed in the solution. The solution did not produce any weight loss on specimens simply immersed in it; an insoluble reaction product which must be removed by the action of the lap appears to be formed.

Microstructures produced by an ammonium chloride etch-polish of polycrystalline material are summarized in Fig. 35. One hour of polishing substantially improves the original rather poorly polished 'A'-alumina surface. Some grain relief is produced and the extent of the scratch removal may be seen to depend upon the grain orientation. Continuation of the procedure for a total of two and a half hours removes all but the deepest scratches (Fig. 35c), but it accentuates the grain boundaries and causes pitting on one grain orientation. In a parallel experiment, a block of six single crystal slices was polished for two hours in the chloride solution. Three of the slices were oriented approximately five degrees from the (100) plane; the other three were a "random"



a) Original Surface.

b) After One Hour

Fig. 35 Microstructures Produced by Chemical Polishing of Polycrystalline Calcium Fluoride - Ammonium Chloride Etch. 187×

c) After 2.5 Hours, Note Deep Scratches and Grain Boundaries.

d) After 2.5 Hours, Note Subgrain Boundaries and Surface Pitting.

Figure 35 (Cont'd)

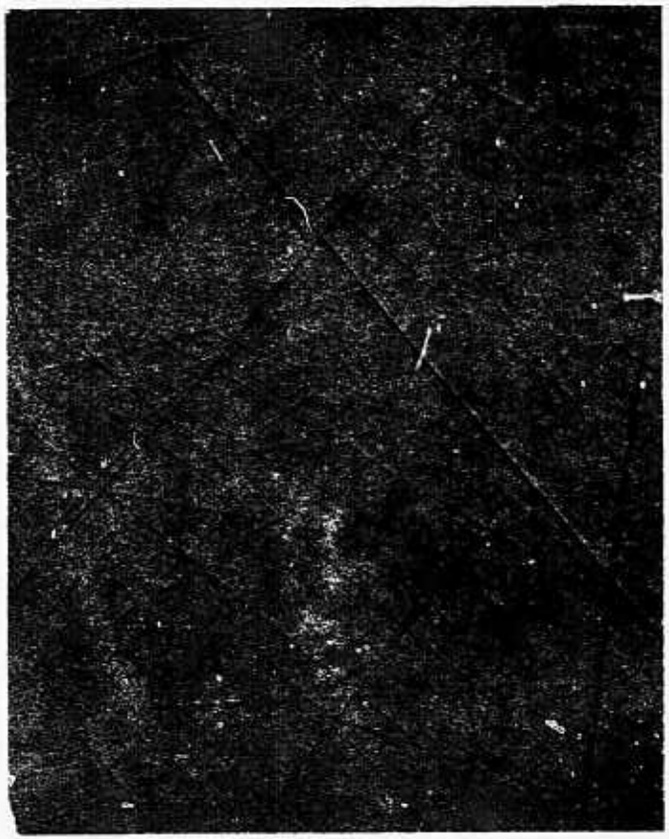
orientation – not close to any simple crystal plane. The "random" slices polished to a surface which was defect-free in the Nomarski microscope while the near (100) slices retained some scratches (Fig. 36).

Variations of the solution concentrations and additions of EDTA (to increase the reactivity by complexing the calcium ion) did not affect the non-uniform polishing behavior of ammonium chloride. The solution does, however produce excellent polishing action on some orientations and should be used as a point of departure for further work in the area. The acid solutions which have been reported for the alkaline earth fluorides all tend to behave as dislocation etches.

2.4.2.2 Zinc selenide

The chemical reactions used to etch zinc selenide are all oxidation-reduction reactions in which the selenium anion is oxidized to some higher valence state in which it may form a hydrous insoluble selenium oxide or (in principle) the more soluble selenate ion. The crystal structure of the II - VI (and III - V) compounds is such that the various crystalline faces are quite different chemically and different chemical polishing solutions and dislocation etches are recommended for the various orientations of member compounds.[6] The solutions listed in Table XIII were used as chemical polishes for zinc selenide during the program. All, being oxidizing solutions, etched the material. As the comments of the preceding paragraph indicate, all etched nonuniformly and eventually revealed the polycrystalline microstructure of the material (Fig. 37).

Of the polishing solutions listed in Table XIII, the alkaline ferricyanide solution (first reported by Hughes Research Labs[7]) was the most useful. Used on a pitch lap for two minutes, it removes remnant scratches and produces some grain relief. Itek Corporation experienced some difficulty in stopping the etch uniformly and began removing the workpiece to a second water-flooded lap. Since this procedure might prove difficult to manage with large pieces, we have used various dilutions of the etch to slow and control

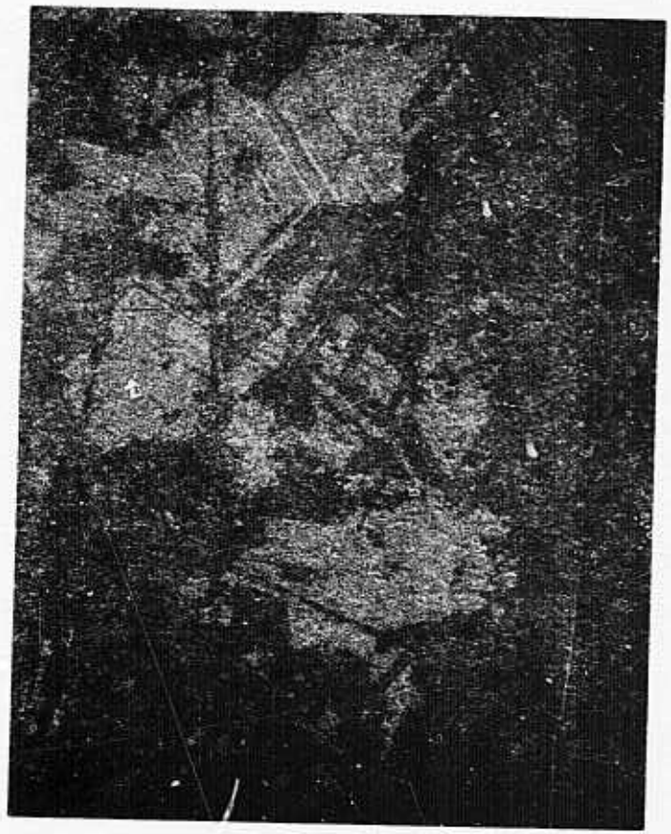


a) Near (100) Surface Orientation
Scratches are Probably Exposed
Subsurface Damage. 378×

b) "Random" Surface Orientation
Defect is a Remnant of Abrasive
Polishing. 378×

Fig. 36 Microstructures Produced by Chemical Polishing of Single Crystal Calcium Fluoride - Ammonium Chloride Etch; Polishing Time, 2.5 Hours.

a) Politex "Supreme" Pad



b) Pellon Pan-W Pad

Fig. 37 Chemically Polished Zinc Selnide Surfaces Produced by Various Lap Surfaces. 187X

its action. Samples were polished on Politex pads saturated with the etchant, rotating at 30 rpm. A comparison of the Politex material with two Pellon materials, XP-500 and Pan W* had established its superiority.

TABLE XIII

OXIDIZING AGENTS FOR CHEMICAL POLISHING ZINC SELENIDE

Compound	pH	Concentration	Comments
Potassium Permanganate	acidic	Saturated Solution	Adherent MnO_2 residue Poor Polish
Potassium Dichromate	acidic	Saturated Solution	Unidentified residue forms slowly, usable as polish
Potassium Ferricyanide	alkaline	1 molar	Residue not adherent, usable as polish
Sodium Hypochlorite	alkaline	5 percent	Surface pitting, adherent residue, attacks pitch lap
Bromine in Methanol		0.1-1 percent	Polishes well at 0.2-0.5 percent, rate difficult to control

The etching rate was shown to decrease roughly in proportion to the dilution of the ferricyanide. For our purposes, a 1:1 dilution of the etch with water and a three-minute etching time have been chosen to be standard. Figure 38 shows the surface absorption improvement which is obtained by chemical polishing of a mechanically polished ZnSe surface. Specimens which had been polished together were chemically polished and cleaned. The surface absorption decreased from approximately 5×10^{-4} per surface to 4×10^{-4} per surface. Surface absorptions on the order of 2.5×10^{-4} have been obtained by ferricyanide chemical polishing.

* From Pellon Corp.

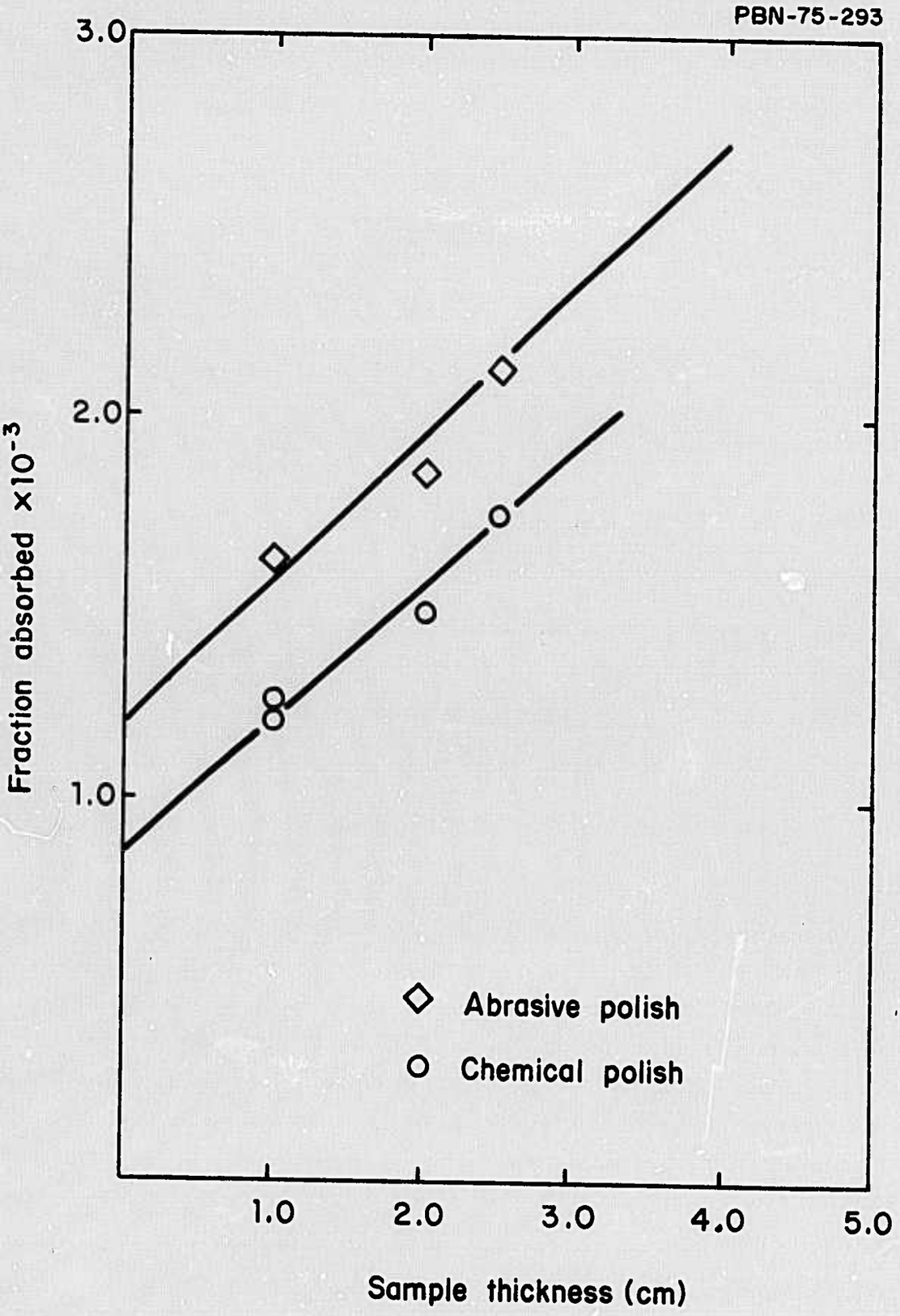


Fig. 38 Effect of Chemical Polishing on the Absorptivity of Zinc Selenide.

2.4.2.3 Potassium chloride

Of the materials being studied for use as high power laser windows, none requires a chemical polish more than potassium chloride. It is best polished by absorbing alumina abrasives which cannot be loosened by brushing because of the softness of the halide. Embedded abrasives, surface scratches, and surface plastic deformation are exacerbated by the softness as well. Concentrated hydrochloric acid[8] and acetic acid[9] have been reported as chemical polishes, initially for single crystal material. This section considers their application chiefly to two polycrystalline forms of KCl which are high power window candidates. Some single crystal specimens are also included. These are in the form of 25 millimeter diameter by 5 millimeter thick discs, obtained from Harshaw Chemical Co.

The polycrystalline material included fusion cast specimens fabricated at Raytheon Research Division and hot forged material produced by the Honeywell Ceramics Center. Both material types were fabricated into specimens with the shape shown in Fig. 39. Figure 39 summarized the compositions and grain sizes of the specimens and places their preferred orientations with respect to the sample shapes. Note that this sample arrangement permits the simultaneous determination of the etching character of several crystalline orientations.

The cast material has a strong texture. That is, the individual grains grew preferentially in the <100> direction, but at all rotations about the growth axis. The top face of the specimen has crystal surfaces which are typically within ten degrees of (100) planes. Vertical sides contain orientations which lie in the zone normal to the <100> direction. The beveled edge is ground at 45 degrees to the top and contains all orientations which intersect the <100> direction at that angle. The beveled surface thus may contain a fortuitous (110) plane along with less simple orientations.

The forged piece retained a strong remanent orientation from its single crystal precursor. The top surface was essentially a (110) plane

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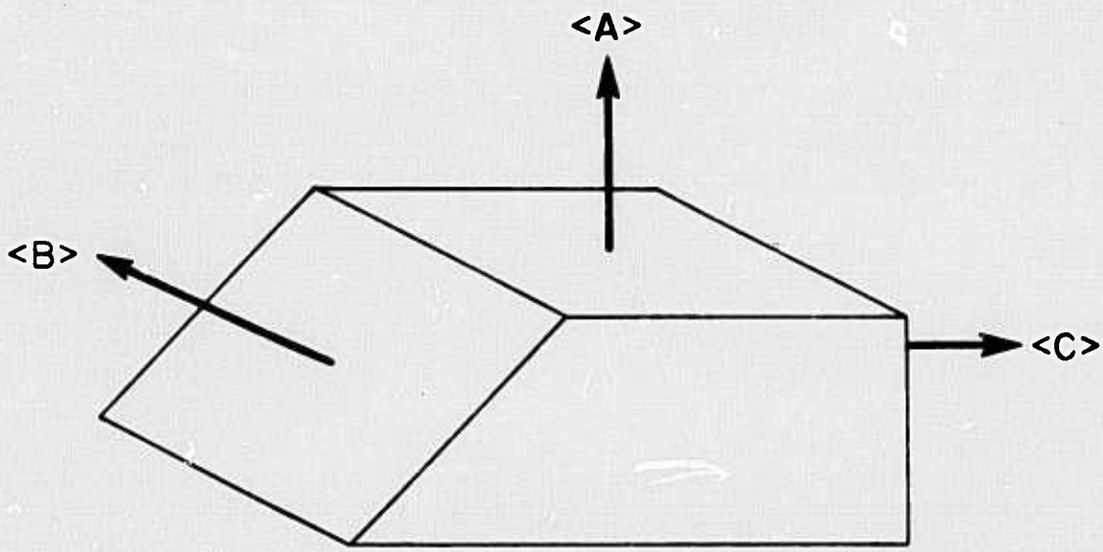

CAST MATERIAL (Raytheon)	HOT FORGED MATERIAL (Honeywell)
100 ppm Sr^{++}	100 ppm Eu^{++}
1 cm grain size	~7-25 μm grain size
<A> - Predominantly 100	<A> = <110>
<B> - 110 + Others	<B> = <100>
<C> - (100) Zone	<C> = <110>

Fig. 39 Specimens Used for Chemical Polishing Experiments.

and the vertical and beveled surfaces (110) and (100) planes respectively. An X-ray rocking curve of the (310) diffraction reflections of the specimen had a full width at half maximum intensity of approximately two degrees. This indicates that typical subgrain misorientations in the specimen are on that order.

Etching was performed with the solutions at room temperature (the optical surface laboratory is kept at 75°F and 35-45 percent relative humidity) by immersing the samples and gently agitating by hand for the required period. Etched specimens were immersed in isopropanol, rinsed in warm Freon 113, and dried in the Freon vapors. Etch rates were determined using the single crystal discs obtained from Harshaw by weighing the specimens before and after the etching and calculating the thickness removed from the weight loss, material density and specimen area.

Solutions used as chemical polishes during the study were prepared from electronic grade hydrochloric acid,* acetic acid, and isopropanol and reagent grade triacetin (triacetic glycol). Compositions are reported as volume percent or ratios by volume. Triacetin was chosen as a second component for the etches because it does not attack potassium chloride surfaces. Isopropanol is only weakly corrosive.

Specimens were polished prior to etching primarily either on paraffin laps using triacetin-based alumina slurries or on cloth (bed sheet) laps in isopropanol-alumina slurries. Toward the end of the experiments, some surfaces were polished on Politex laps using 0.25 μm diamond abrasives.

When evidence of a relationship between polishing technique and etch behavior developed, a series of disc-shaped cast specimens, approximately one inch diameter, was polished by the first technique on one side and the second on the other so that the behavior could be compared on single specimens. After mechanical polishing, specimens were washed in a jet of isopropanol, rinsed ultrasonically in isopropanol, rinsed in a second isopropanol bath, rinsed in warm Freon 113, and dried in the Freon vapors.

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* Electronic grade acids were occasionally found to contain particulate contamination. Since these were inconvenient to filter in large quantity, the procedure of filtering small samples from each fresh bottle and examining the filter membrane for contamination was used.

In order to determine the ability of the cleaning procedure to remove the absorbing triacetin from specimen surfaces, the experiments summarized in Fig. 40 were performed. A single crystal KCl slab 2.5 centimeters square by 4 millimeters thick was etched for one minute in concentrated hydrochloric acid and rinsed in isopropanol and Freon as described above. The absorption of the sample at 10.6 micrometers, measured calorimetrically, appears as the dashed horizontal line in the figure. This absorption level is taken to represent the sample with the cleanest obtainable surfaces. Both sides of the sample were then polished on a paraffin lap using alumina and triacetin. The absorption of the sample after this treatment is the data point on the ordinate of the figure. The polishing operation produced a factor of three increase. Absorption measurements made after the indicated material removal using an etch containing 50 percent triacetin are given. The absorption is seen to drop back to the minimum level after the removal of approximately two microns from the surface. The important conclusion to be drawn from this experiment is that triacetin-containing etches can be removed from etched surfaces, at least insofar as can be determined calorimetrically. Triacetin containing slurries, however, cannot be removed completely by washing and must be etched away.

The diamond-shaped point in the figure corresponds to an absorption measurement made after a single washing attempt. The circled point below it was obtained by a second washing. Further conclusions to be drawn, therefore, are that detectable absorbing residues may in fact be removed by the removal of less than two micrometer thick surface layers and that washing procedures must be verified by experiments at their present state of sophistication.

The surfaces produced by abrasive polishing of KCl should be reviewed in the context of the above results. Of the surfaces produced and examined during the course of this study, only the Harshaw polishes could be etched to produce featureless surfaces by the removal of as little as two micrometer thick surface layers. Rougher surfaces require the removal of as much as ten micrometers in order to eliminate scratch remnants, although scratches are significantly broadened and probably no longer

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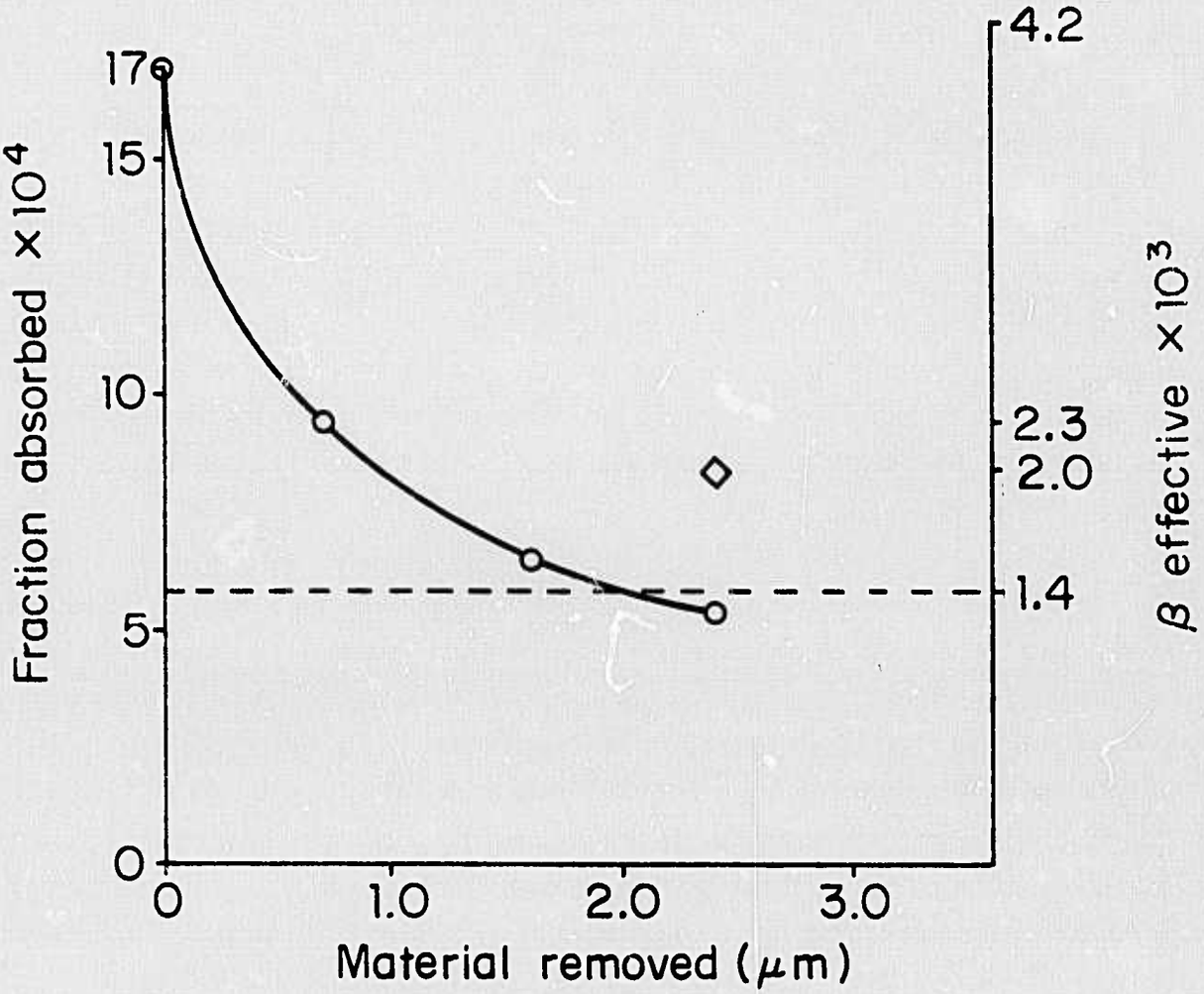


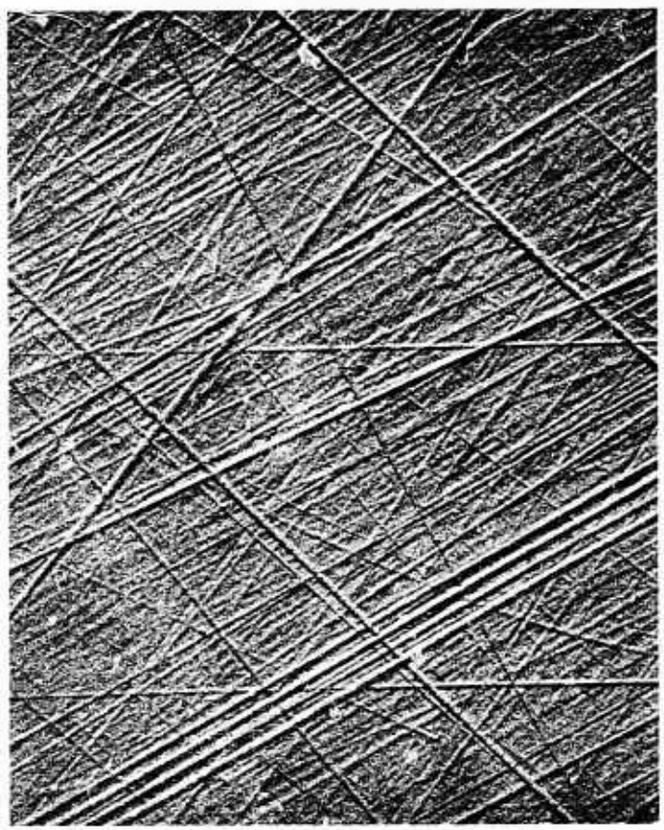
Fig. 40 Absorptivity vs Material Removal for Chemically Polished Potassium Chloride.

potential Bloembergen cracks after two micrometers have been removed from coarser surfaces (Fig. 41a). The Harshaw polishing technique produces subsurface mechanical damage (as do all others) as shown by Fig. 41b. This surface was produced by etching away approximately one micrometer from a nearly featureless Harshaw surface using a very gentle hydrochloric-acetic acid-triacetin etch which etches damaged areas nonuniformly.

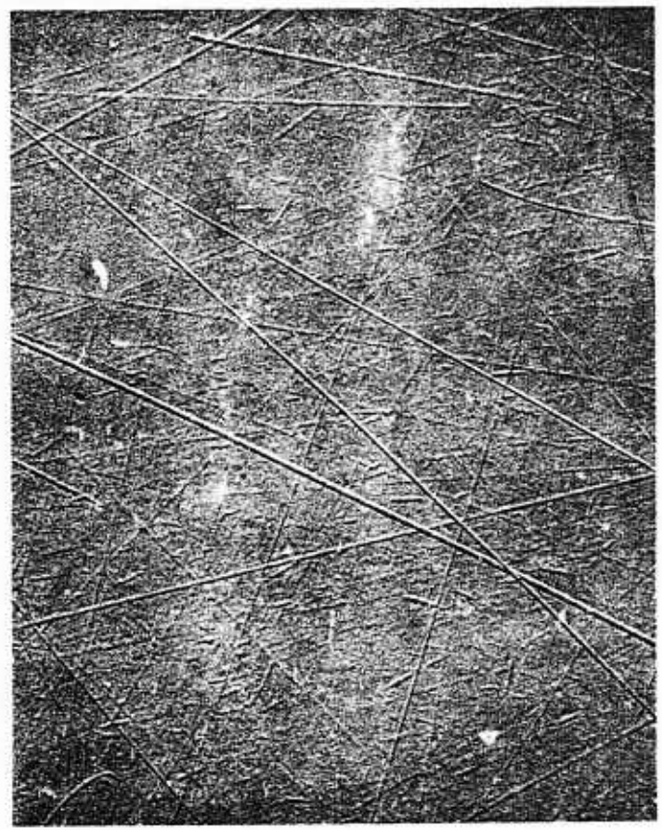
The results of the etching rate study are summarized in Fig. 42. Triacetin and isopropanol produce similar rate-composition behavior in binary and ternary (with acetic acid) solutions. The etching rates fall to approximately one micrometer per minute at 66 percent HCl, 33 percent "inert" component. Etch rates for acetic-hydrochloric acid mixtures fall off more slowly with composition. Concentrated HCl by itself etches at approximately 10 micrometers per minute. This rate was considered to be too rapid to control effectively, which observation lead to these attempts to produce slower more easily controlled etching.

The ideal chemical polishing agent transforms a scratched, contaminated, mechanically worked surface into a featureless, atomically smooth and perfect surface. To do so on polycrystalline specimens, the etch must have several properties which are not characteristic of most corrosive liquids. To avoid producing etched microstructures, it must etch all exposed orientations at approximately the same rate. At the same time, it must preferentially remove scratches from the surface, a process which requires a measure of nonuniformity in etching behavior. Further, the desired smooth surface will only be produced in the absence of preferential etching behavior associated with such discontinuities in the structure as grain boundaries and dislocations.

Of the two etchants, hydrochloric acid produced the more generally uniform surfaces, especially on the cast specimens. Acetic acid containing etches could be made to produce most of the unwanted surface features. As indicated in Fig. 43, acetic acid will produce dislocation etch pits on appropriate grain orientations, and a variety of surface facetting patterns which also depend upon grain orientations. Generally speaking, orientations not



a) Specimen Prepared on Paraffin Lap - 2 Micrometers Removed.



b) Commercially Polished - 1 Micrometer Removed.

Fig. 41 Microstructures of Chemically Polished Potassium Chloride.

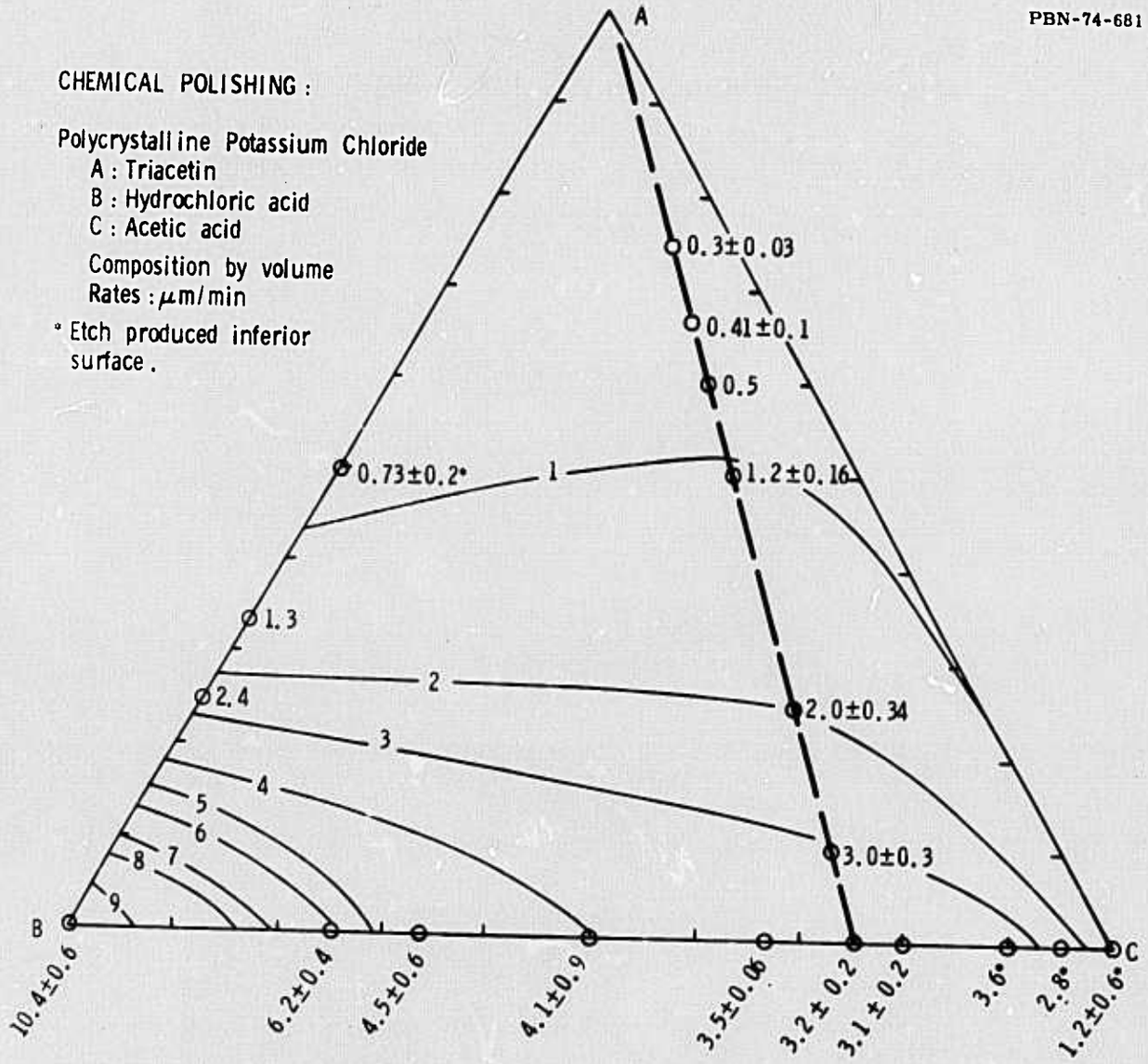
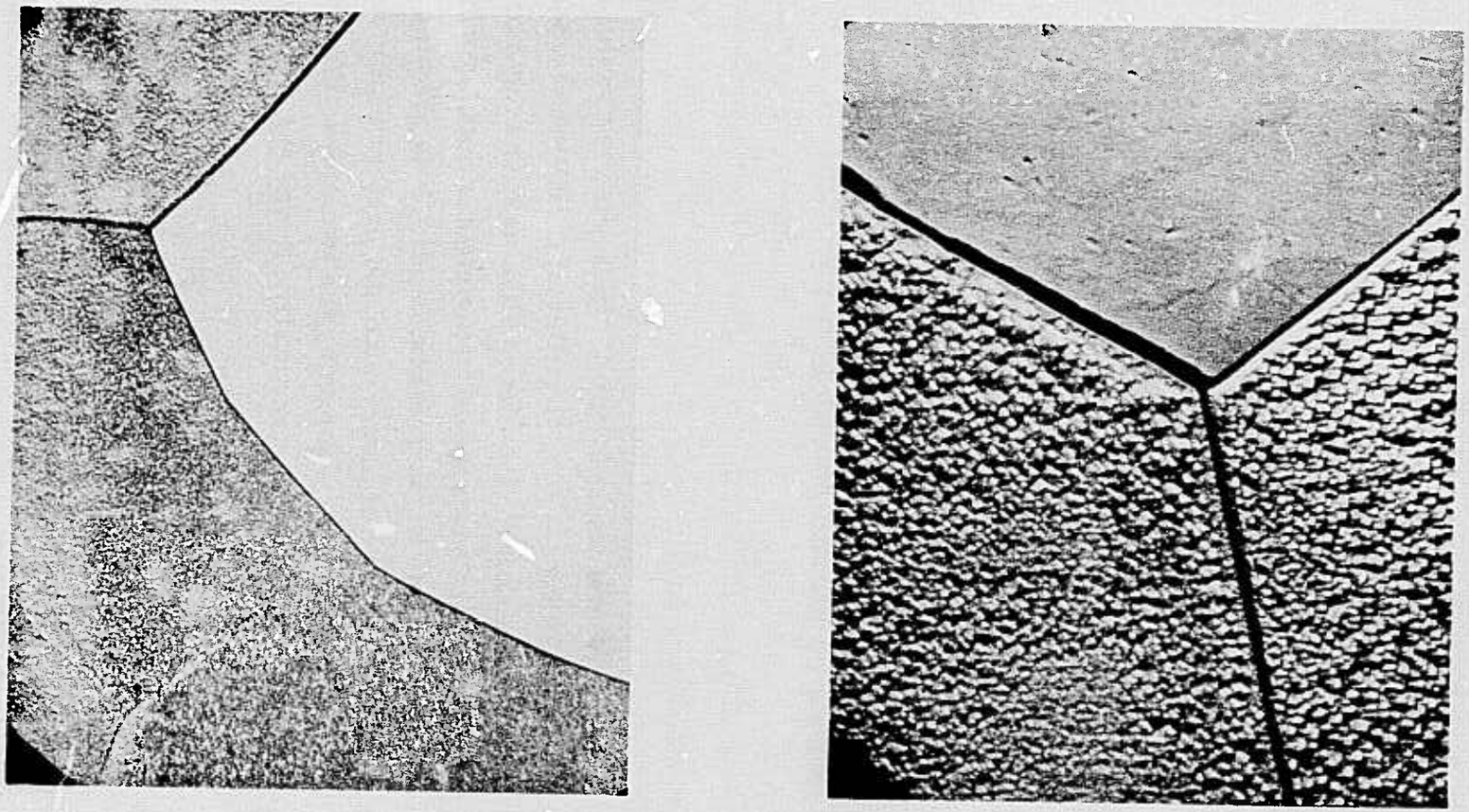


Fig. 42 Etch Rate vs Composition for Potassium Chloride Chemical Polishes.

far removed from (100) planes are the most susceptable to the preferential etching phenomena. On the beveled cast specimen for example, the top surface (which contains mostly near (100) surfaces) frequently becomes "fogged" from surface facetting while the beveled surface (which contains mostly non-simple orientations) etches smoothly. The <C> face of the cast specimen (Fig. 39) contained some especially smooth grains after acetic acid etching. Orientations of two of these were determined by X-ray diffraction (Laue back reflection) to be between 15 and 20 degrees away from the (100) towards a (110) plane.

The microstructures produced in Fig. 43 were obtained on a surface which had previously been etched for two minutes in concentrated hydrochloric acid (to remove twenty micrometers of material from the mechanically-polished surface). This was taken as an approximation of an equilibrium surface. In this instance, the surface features were developed by removing a two-micrometer thick layer in undiluted acetic acid. The effect could readily be produced in all etches containing more than approximately 40 percent acetic acid and the tendency toward nonuniform effects increased with increasing acetic acid content. The mechanical polishing technique used to produce a surface also influenced the tendency of that surface to etch nonuniformly. This is because acetic acid tends to remove cold worked surface layers uniformly and etch more nearly equilibrium surfaces nonuniformly. Thus when the various surface types are etched with acetic acid, the "equilibrium" HCl-etched surface becomes facetted almost immediately, the cloth polish next and the more severe paraffin lap finish is least susceptable to the effects because its plastically deformed layer extends to the greatest depth. It is possible to produce uniform etching on one face of a specimen and preferential etching on the opposite face at the same time by polishing the two sides differently. In all cases when only one side etched preferentially, it was the cloth-polished side.

The binary HCl-triacetin and HCl-isopropanol mixtures produce more uniform surfaces in cast potassium chloride. At etching rates below approximately three micrometers per minute, the isopropanol-based etches have a greater tendency toward nonuniform etching characterized by a "pock marked" surface. Both etches may be removed from the surfaces by washing but surfaces treated by triacetin-based etches should be very thoroughly washed.



a) Clear and "fogged" Surfaces, 93×.

b) Surface Facetting on Near (100) Surfaces, 720×.

Fig. 43 Microstructures of Chemically Polished Cast Potassium Chloride - Acetic Acid Etchants.

Microscopic examinations of hot forged specimens reveals that hydrochloric acid and the binary etches produce deep grooves at the subgrain boundaries. This feature is illustrated in Fig. 44. Subgrain boundaries can be seen after the removal of only one micrometer and are clearly visible after 4.5 micrometers have been removed from the original surface. In a separate experiment, the subgrain boundary grooves were shown to be more than 3200 Å deep by ion beam polishing away a layer of that thickness (under conditions which would not attack the grain boundaries) without removing the surface grooves completely.

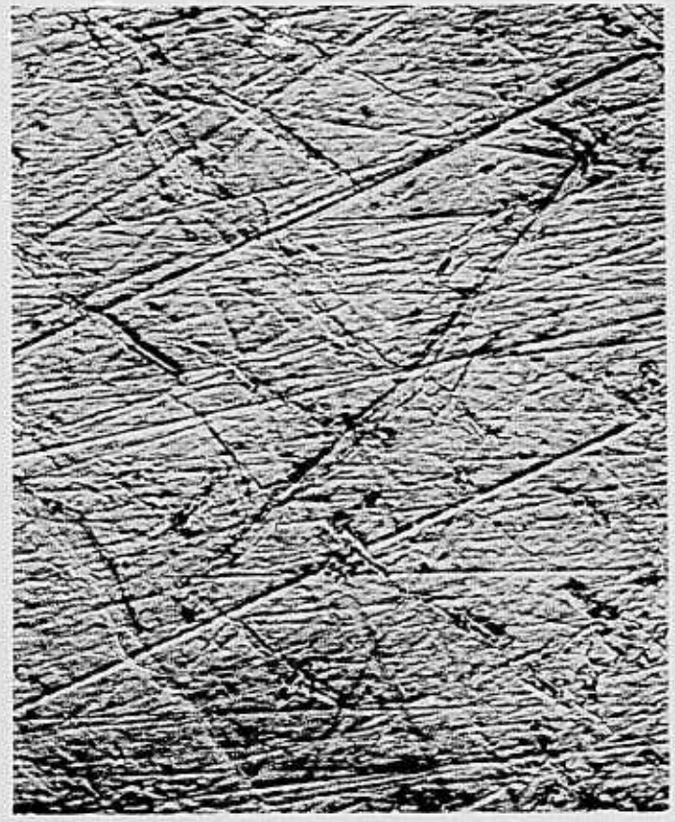
Subgrain boundary grooves are produced on both the nominal (100) and (110) faces of the forged material as well as on intermediate faces produced by additional bevels ground on one specimen. These grooves will contribute to scatter from HCl-etched surfaces and could in principle act as sites for preferential laser damage.

Acetic acid etches produced the nonuniform surfaces shown in Fig. 45 on the (100) and (110) faces of the forged material. Again the subgrain boundary grooves are produced. Figure 46 details the etching behavior of a surface which was ground to be 16 degrees away from the (100) toward the (110) in a hot forged specimen. This orientation was chosen to correspond with one of the most uniform areas of the acetic acid etched cast specimens. In this case, subgrain boundary grooves are not produced, but acetic acid is a less effective scratch remover than hydrochloric acid. Mixtures of hydrochloric and acetic acid were used to etch this orientation in an attempt to improve the scratch removal capability of the acetic acid without inordinately etching the grain boundaries. It was found that as little as two percent of HCl in acetic acid was sufficient to produce grain boundary grooving.

Experiments carried out at the Honeywell Ceramics Center have indicated that atmospheric water vapor can have a deleterious effect on the etching behavior of acetic acid containing etches.[10] Our experiments have been carried out at a relative humidity of approximately 35 percent using freshly opened bottles of acetic acid. Moving the experiments into a dry box flushed with the boil-off gas from our liquid nitrogen and supply did not change the surface morphologies produced.

Fig. 44 Subgrain Boundary Grooves in Hydrochloric Acid Polished Hot Forged Potassium Chloride, (110) Face.

a) (100) Face



b) (110) Face

Fig. 45 Microstructures of Acetic Acid Polished Hot Forged Potassium Chloride. 6 micrometers removed by etch.

a) 4 Micrometers Removed. 187×

b) 10 Micrometer Removed. 374× Subgrain relief is not associated with groove. Some dislocation etch pits present.

Fig. 46 Microstructures of Oriented Hot Forged Potassium Chloride. Sample Surface 16 Degrees from (100) Toward (110).

2.4.2.3.1 Summary, potassium chloride chemical polishing

Summarizing, chemical polishing will be required for KCl surfaces. These experiments define some characteristics of the most commonly used etchants which must be considered.

1. Hydrochloric acid containing etchants are excellent chemical polishes and remove scratches rapidly from all orientations. They also produce rather deep grooves at subgrain boundaries in all orientations of hot forged material and grain boundary grooves in cast material. These grooves may act as laser damage sites or defect centers for protective or antireflection coatings; they will be surface radiation scattering sites.

2. At most, two micrometers of material must be removed from mechanically polished surfaces in order to remove all calorimetrically detectable surface residues.

3. Additions of twenty volume percent of either triacetin or isopropanol to concentrated HCl produces an etchant which will remove the requisite layer in approximately one minute. This facilitates stopping the reaction and removing the etchant solution uniformly.

4. Acetic acid containing etches may be used to remove material from some orientations of forged KCl without preferentially etching subgrain boundaries. In our experiments, these surfaces could not be made as smooth overall as HCl-produced surfaces and would be recommended only if the grooves in the HCl-produced surfaces were demonstrated to be deleterious. Acetic acid would not be usable with cast material. In order to etch hot forged material using acetic acid without producing subgrain boundary grooves, the window surface would have to be ground by mechanical means to a non-simple orientation such as the 16 degrees from the (100) reported above.

2.4.2.4 Syton polishing

Syton* is an alkaline colloidal suspension of hydrous silica. It has been used in the past to good advantage to polish single crystal wafers of silicon and gadolinium gallium garnet (a substrate for magnetic bubble domain films). It was used as a potential chemical-mechanical polish for both zinc selenide and calcium fluoride during this project and found to produce unacceptably severe relief polishing on both materials.

The relief polishing appears, at least on calcium fluoride surfaces, to be caused by both the chemical and mechanical actions of the solution. Grain boundary relief in Syton-polished calcium fluoride is diminished but not eliminated by neutralization of the solution. The neutralized solution apparently polishes in a manner similar to the very fine Alon fumed alumina discussed in paragraph 2.3.4.

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* Trademark, Monsanto Corp.

2.5 Laser Damage Experiments

When subgrain boundary grooving proved to be an unavoidable feature of HCl-etched hot forged KCl, a series of laser damage experiments was initiated to determine whether the grooves could be shown to behave as preferential laser damage sites. The experiments were performed at 10.6 micrometers using a CO_2 TEA laser located at the Air Force Cambridge Research Laboratories.* The laser was originally built at Raytheon and is described in the reports of Contract Number F19628-78-C-0127.

For these experiments, the laser was focussed onto the front surfaces of the specimens by a 3.8 centimeter focal length germanium lens. The sample was aligned normally to the beam by autocollimation using a He-Ne laser and was placed in the center of the depth of field of the lens (calculated to be 1.62 mn) by determining the minimum damaging energy of a KCl specimen as a function of position several times and averaging the positions of the lowest values obtained in each of the trials.

The laser output was restricted to TEM_{00} by means of an aperture in the laser cavity. The pulse width was 115 nanoseconds and the output energy, as measured with a Scientech Model 362 energy meter was on the order of 50 millijoules. The actual pulse energy was determined before and after each series of damage experiments. The laser beam had the Gaussian distribution shown in Fig. 47; the focussed beam diameter was calculated to be 108 micrometers.

The experimental arrangement used for the damage studies is shown in Fig. 48. During the experiments, the electrical input to the laser was kept constant in order to maintain a constant output pulse shape and beam profile. The laser output energy was attenuated externally by means of calibrated calcium fluoride and barium fluoride attenuators.

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* We gratefully acknowledge the assistance of Mr. R. Bradbury of AFCRL during the laser damage experiments.

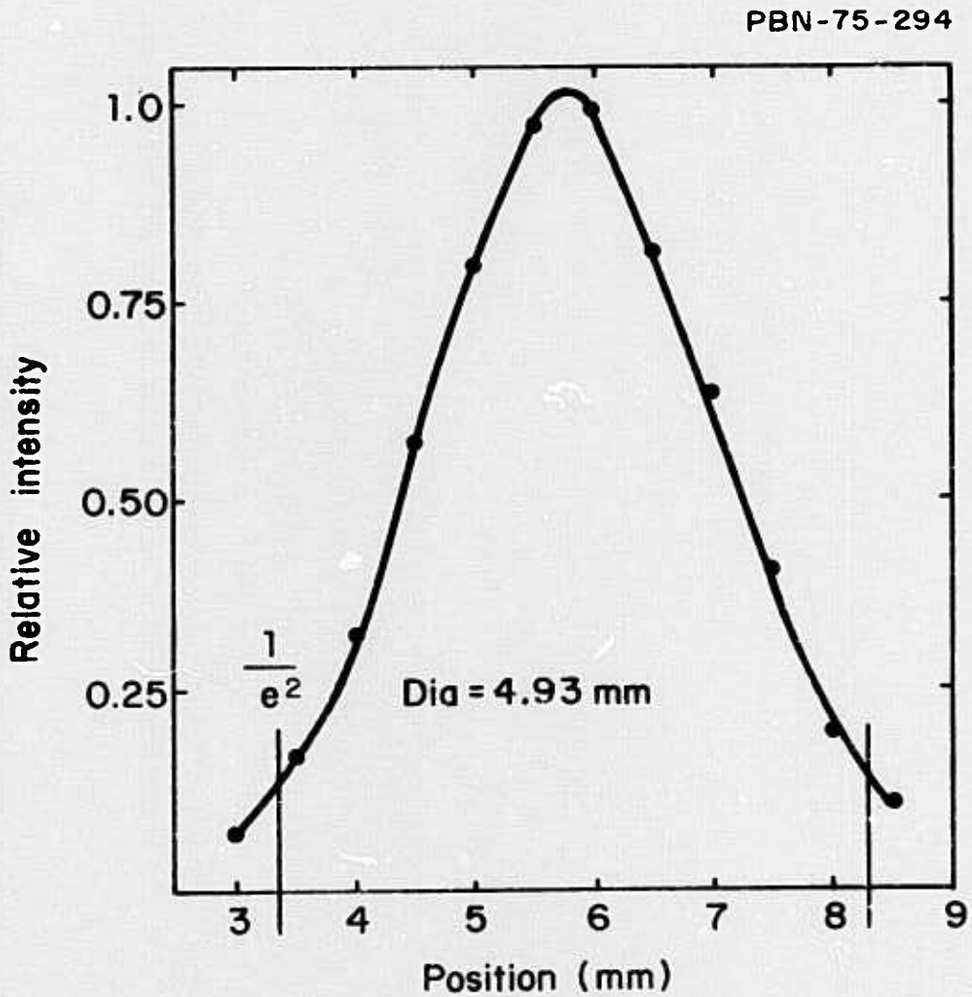

Fig. 47 Intensity Distribution of CO_2 Laser Beam.

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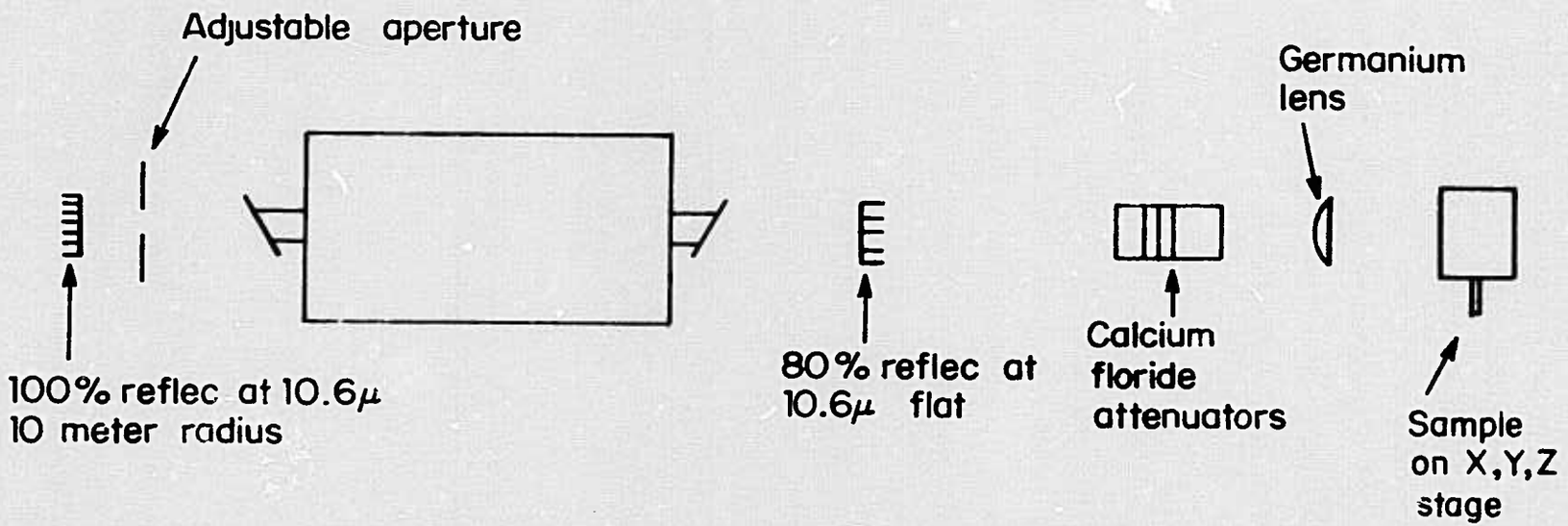

Fig. 48 Apparatus for Laser Damage Experiments - Schematic.

Disc-shaped (40 millimeters diameter by 10 millimeters thick) specimens of hot forged KCl containing approximately 100 ppm of divalent europium* were polished on paraffin laps using A-type alumina and triacetin, etched for one minute in concentrated hydrochloric acid to remove approximately 10 micrometers from the surfaces; rinsed in a bath and filtered spray of isopropanol, immersed in Freon vapors, and allowed to dry in a clean hood. Specimens were stored in glass containers which were placed in a dessicator for transport from Raytheon to AFCRL.

Specimens were located in the previously positioned specimen holder and a fiduciary mark (a large damage spot) was placed near one edge. Subsequent damage spots were located with respect to the original spot by means of indexed specimen translations. At the conclusion of the tests, specimens were examined by Nomarski microscopy at Raytheon.

Results of a series of damage experiments are summarized in Table XIV.

TABLE XIV

10.6 μm SURFACE DAMAGE OF HONEYWELL HOT FORGED, STRENGTHENED KCl

Power Density (GW/cm^2)	No. Shots	Percent Causing Damage
0.3	4	25
0.6	8	12.75
0.7	12	67
1.1	18	55
1.6	8	87.5

Damage was judged to have occurred when the shot was accompanied by a visible spark. These sites later correlated well with sites observed in the Nomarski interference microscope.

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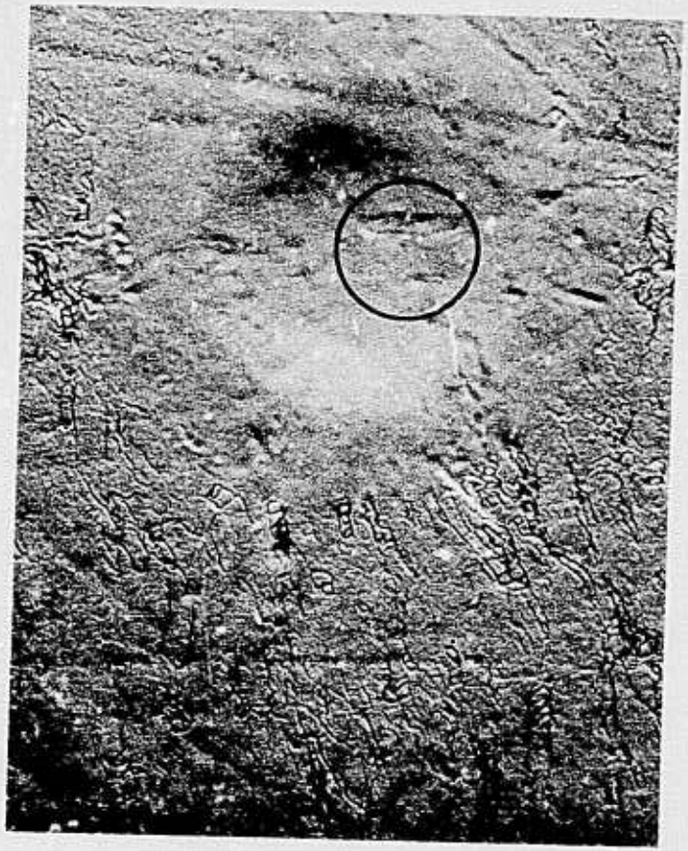
* Obtained from Honeywell Ceramics Center, Minneapolis, Minn.

Damage occurs over the entire measured range of 0.3 to 1.6 GW/cm^2 with the fifty percent probability of damage occurring just below one GW/cm^2. This is comparable to the lower end of the range of surface breakdown thresholds reported for HCl-etched RAP processed single crystals and a factor of three below those of undoped hot forged material.[11] An absorption coefficient of $3.5 \pm 0.8 \times 10^{-4}$ cm^{-1} was measured calorimetrically at 10.6 μm for the specimen on the basis of three determinations taken at different points. This is comparable to absorptivities reported for undoped RAP forgings.

Typical damage sites appear in Fig. 49. Damage site morphology was not very dependent upon the laser intensity at which breakdown occurred, probably because in all cases the breakdown was produced by surface contamination and not by intrinsic processes. Figure 49a corresponds to damage at 0.7 GW/cm^2; 49b and 49c to damage at 1.1 GW/cm^2. In 49c, the damage appears to have been initiated at an absorbing particle which in turn produced enough bulk heating to produce cleavage on cooling. Few sites had associated cleavage. Figure 49a contains some more or less intact remnants of the subgrain boundary grooving within the central area of the damage spot (circled area) which corresponds well in diameter with the calculated beam diameter. This damage occurred at 0.7 GW/cm^2. The field concentration at the grain boundary groove tips should provide approximately a factor of five enhancement of the intensity to roughly 3.5 GW/cm^2.[1] Higher energy damage sites are deep enough to remove groove remnants (Fig. 49 b) so no morphology correlations can be made. The one site which survived a 1.6 GW/cm^2 slot was very carefully searched microscopically for evidence of changes in groove appearance and none was found. In this case, the field concentration should have produced an effective 8 GW/cm^2 at the groove tips, which is comparable to the highest reported bulk levels.[11]

In summary, the absolute breakdown levels produced during these experiments were apparently determined by surface contamination introduced between etching and testing of the specimens. Nevertheless, the levels compare with the lower end of the range reported for other



a) 0.7 GW/cm^2, Grain Boundary Remnants in Damage Spot

b) 1.1 GW/cm^2

Fig. 49 Laser Damage on HCl-Polished Hot-Forged Potassium Chloride Surfaces. 378X

c) 1.1 GW/cm^2, with Associated Cleavage Damage

Fig. 49 (Cont'd)

chemically polished specimens. No evidence that the subgrain boundary grooves produced preferential breakdown was found. Note that filling the grooves with the high index component of an antireflection coating should lessen its influence as a field concentrator. Note further, however, that such defects may be difficult to coat uniformly and so act as defect sites in thin film coatings on the etched pieces.

A second series of damage experiments which was planned could not be carried out because the laser power supply became too unstable to produce characterizable pulses of sufficient energy. Replacement condensers for the power supply could not have been delivered until well after the expiration of this project. In this series, for which specimens were prepared, two modifications were to have been made. First, the etching and specimen cleaning were to have been carried out at AFCRL. Reagents and a portable clean hood had been assembled. Second, the damage behavior of HCl and acetic acid-etched surfaces were to have been compared. For these experiments, bevels oriented 16 degrees from (100) planes had been ground and polished on hot forged specimens to provide surfaces which could be etched with acetic acid and not exhibit subgrain boundary grooving. We recommend that this comparison be made in the future and that the study be expanded to include comparisons of coated specimens which were first chemically polished by the two techniques.

2.6 Ion Beam Polishing

Ion bombardment has been used for some time to remove atoms from solid surfaces, principally for deposition of thin films of the atoms so removed (sputtering). More recently[12,13] it has been shown that with sufficient control, the process may be used to considerable advantage as a surface preparation technique. Removal of surface scratches and generation of aspheric surface figures have been reported. The observation of improved laser damage threshold in sapphire[14] and lowered 10.6 micrometer absorptivity in copper (after annealing)[15] are particularly significant for high power laser applications. Ion beam polishing may be considered as a candidate for final surface finishing treatments,

during which some surface figuring could be produced by computer control of the ion beam position or simply as a final cleaning step prior to antireflection coating deposition. Since it is carried out in vacuum, polishing/cleaning could be carried out in the deposition chamber immediately prior to coating deposition, providing a particularly clean substrate surface to maximize coating adhesion.

The materials considered in this study are polycrystalline ionic compounds. As such, they may be particularly degraded by two aspects of the ion polishing process. Both are related to the fact that the fundamental process by which energy is transferred from the bombarding ions to the substrate is by momentum transfer.

For all materials, the sputtering yield (number of substrate atoms ejected per incident bombarding ion) and its variation with the substrate and process parameters determines the surface microstructure generated by ion polishing. For the noble gas elements which are of practical importance for ion polishing, sputtering yields increase with the mass of the bombarding ion, with the accelerating voltage* and increasing angle of incidence to approximately 60°.

The polishing action obtained at oblique incidence may be understood as a combination of preferential sputtering of flat portions of the surface, shielding of scratch and groove bottoms, and perhaps preferential removal of some asperities which may eject atoms into more than 2π steradians. When mechanically polished specimens are ion polished, the initial effort may roughen and pit the surface. This effect is probably caused by the removal of grains of partially embedded abrasives and also of severely plastically deformed surface material.

Polycrystalline specimens such as those considered here tend to be preferentially etched by the ion beam because the sputtering yield (polishing rate) of a crystalline material is also a function of the crystal face being sputtered. For copper being sputtered by 1 keV argon ions, this ratio of yields from (111) and (110) faces is approximately 3:1.[16]

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* Below approximately 10 keV. At higher potentials, implantation becomes significant.

The ratio decreases with decreasing ion energy. In this section, we discuss the rate at which grain boundary relief is produced by ion beam polishing of the study materials.

Second, since the ion beam sputters the surface atoms away by rupturing chemical bonds, sputtering yields for the individual components of chemical compounds may not be equal. This effect may produce a surface region which differs from the bulk in composition as well as in crystallographic perfection. This layer may have different absorptive properties than the bulk and perhaps different chemical reactivity as well.

Two ion polishing units were used during the course of the project. The first, located at Ion Optics, Winchester, Mass., is a cylindrical vacuum chamber three feet in diameter and four feet long, pumped by a Freon-trapped diffusion pump. The chamber contains a 24-inch diameter rotating table which supports the samples. An argon ion beam from a duo-plasmatron source is focussed onto the table surface. Beam diameter at normal incidence is approximately one centimeter. At oblique incidence, it becomes elliptical, the minor axis remaining one centimeter. In these experiments, a 10 kilovolt accelerating potential, 1 milliampere beam was used. Lower energies are inconvenient on this equipment.

The second unit, located at Raytheon, is a Veeco Microetch apparatus which consists of a diffusion-pumped vacuum system in which a three-inch diameter neutralized argon ion beam is directed, as shown schematically in Fig. 50a, onto a sample holder which can be tilted with respect to the argon ion beam and rotated about an axis normal to its surface. In these experiments, an accelerating potential of 500 volts and beam current density of 0.95 milliamperes per square centimeter were used. This represents a much gentler application of the technique than was available in the larger unit.

In the larger unit, specimens of all three candidate materials were ion beam polished using ion beams incident at 60 degrees and at

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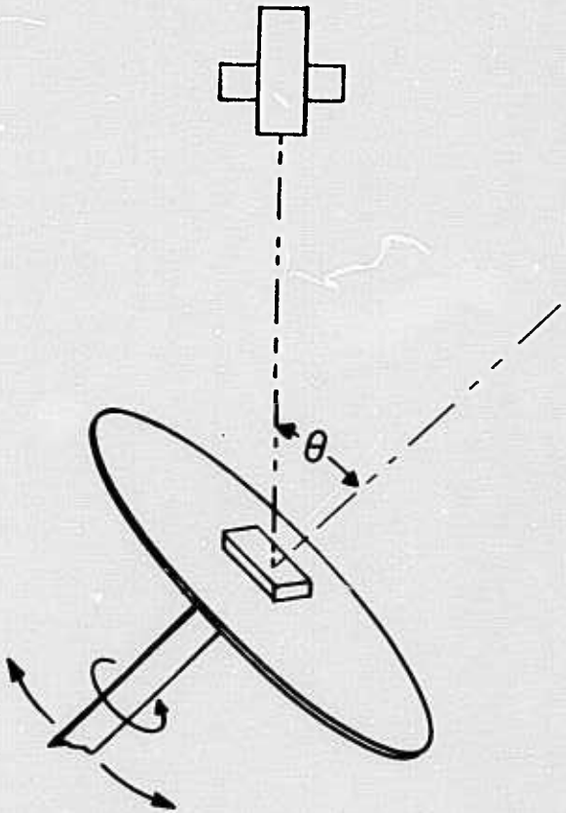
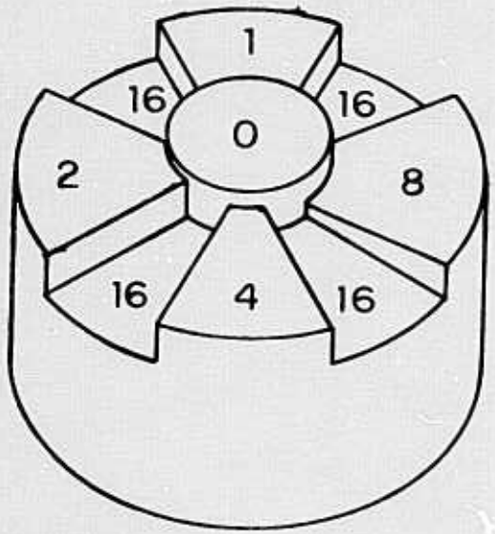
* Work performed at Ion Optics by Mr. John Gale.



a) Veeco unit



b) Polished specimen (numbers represent relative etching times)

Fig. 50 Ion Beam Polishing Apparatus and Etched Sample - Schematic.

84 degrees from the substrate normal (in separate experiments). Polishing was carried out for a time which would have removed approximately one micrometer from typical glass surfaces. Results of these experiments may be summarized as follows:

1) All three polycrystalline materials polished nonuniformly because of orientation-dependent variations in the sputtering rate. Figure 51 is the surface profile, taken with a Dektak* profilometer, of the 60-degree incidence, ion-milled zinc selenide specimen. Note that several sets of surface heights are repeated. As already noted, the etching rate is dependent upon the orientation of the crystal being etched with respect to the ion beam. Repetitions of surface heights reflect repetitions of the total amount of material removed and therefore of crystalline orientations. These repetitions occur frequently in polycrystalline zinc selenide samples because their larger grains commonly contain many twins. The microstructure of this specimen is shown in Fig. 52a. Note that considerably more than the estimated one micrometer of material was removed.

2) The extent of surface roughening decreases with increasing angle of incidence (Fig. 52b shows the results obtained for ZnSe at 84 degrees incidence) and among the study materials in the order potassium chloride, zinc selenide, calcium fluoride.

The Veeco apparatus was used to determine the relief produced by its more appropriate low voltage (500 eV) beam.

Polycrystalline 1.5-inch diameter discs of chemical vapor deposited zinc selenide and hot pressed calcium fluoride (Irtran 3)† were ion polished in separate experiments. Both were bowl-feed polished to nearly scratch-free surfaces prior to the etching. The central portions of the specimen discs were coated with photoresist prior to the etching to provide an unetched reference plane. Etching was then interrupted periodically during the experiment, and each time an additional area

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* Trademark Sloan Instrument Co.

† Trademark Eastman Kodak Co.

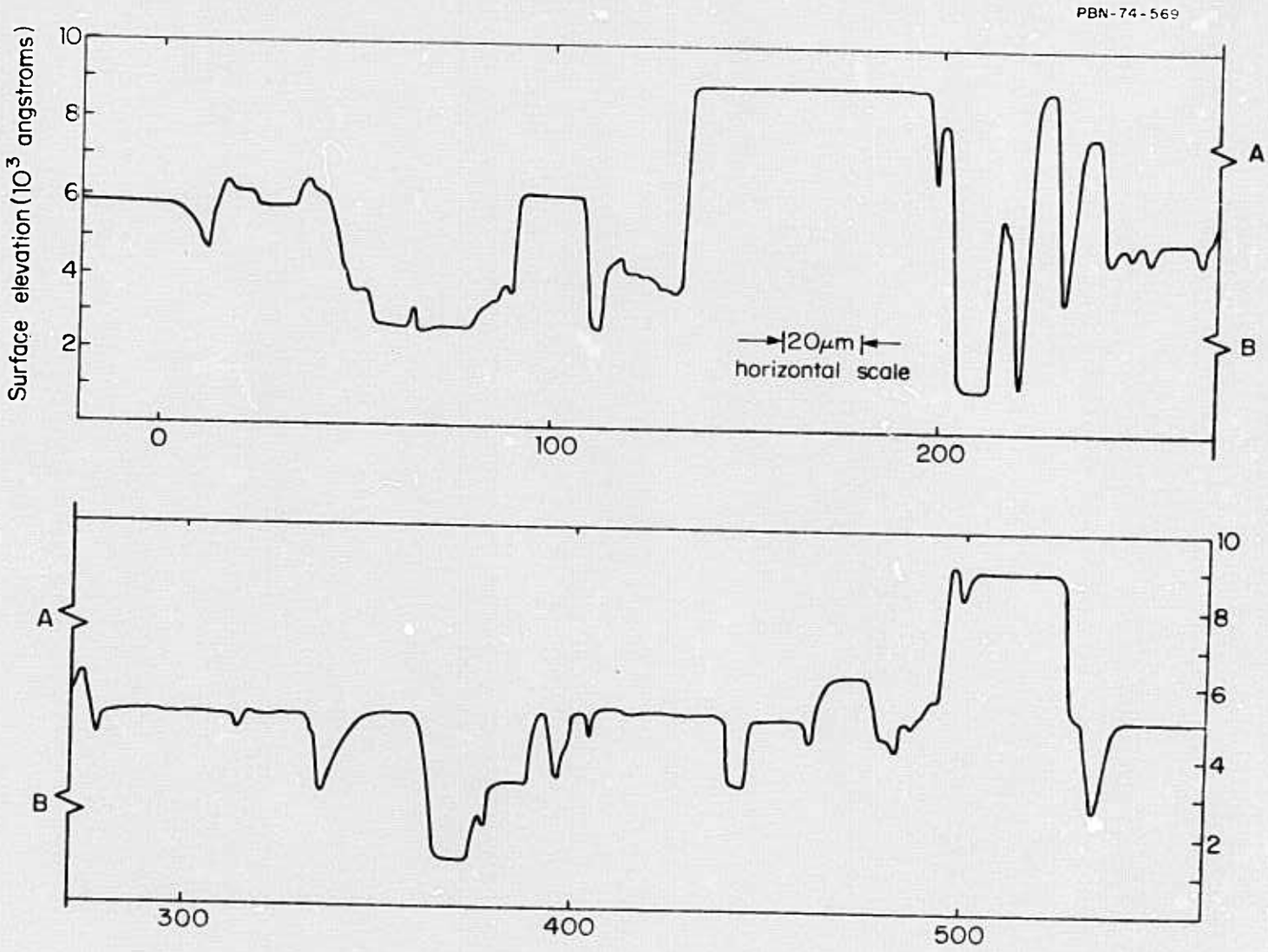
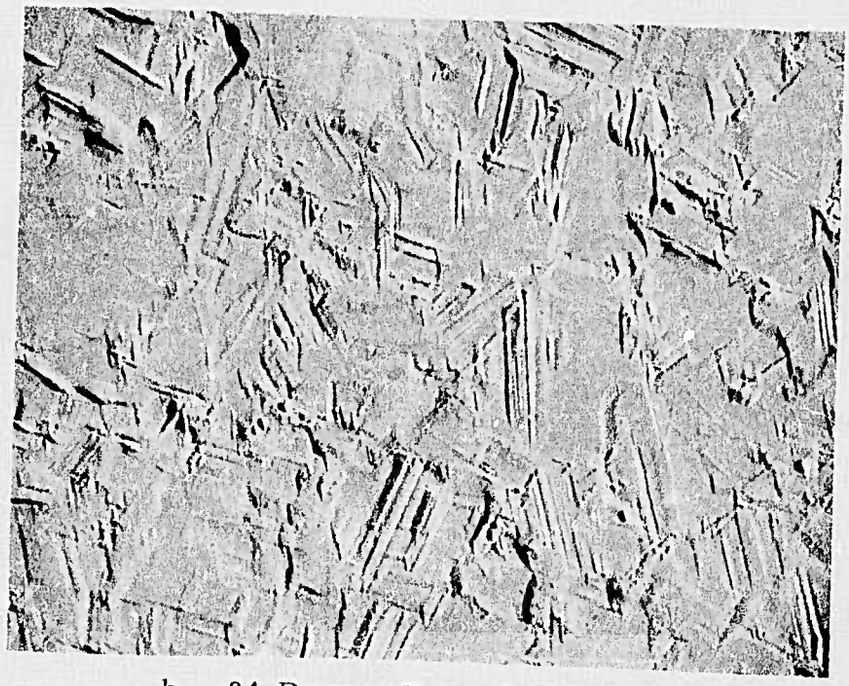


Fig. 51 Surface Profilometer Trace of Ion Beam Polished Zinc Selenide.

a. 60-Degree Beam Incidence. 187X



b. 84-Degree Beam Incidence. 187X

Fig. 52 Ion Beam Polished Zinc Selenide.

on the surface was protected by photoresist. A typical sample produced by the procedure is sketched in Fig. 50b. The material removal and grain relief on the sample were measured with a profilometer, and scattering measurements were made on the zinc selenide specimen. Since the surface of the calcium fluoride specimen contained some flaws (produced by bulk defects) which would have contributed to the intensity of light scattered from the surface, no scattering measurements were made on it.

Results of the profilometer measurements made on the two samples are summarized in Table XV. The surface reliefs reported are the average heights of steps at grain boundaries.

TABLE XV

SURFACE DEVELOPMENT PRODUCED BY ION BEAM POLISHING

Sample	Etch Time (Minutes)	Average Thickness of Material Removed (Angstroms)	Surface Relief (Angstroms)
Zinc Selenide	4	800	~100
	8	1800	100
	16	2300	100 - 300
	32	4200	200 - 800
Calcium Fluoride	6	~600	50 - 100
	8	~1000	NM
	16	1400	NM
	32	3150	250 - 450

As the surface layers are removed from these polycrystalline materials, the average grain boundary step produced is approximately ten percent of the total thickness removed. The variation of step heights was somewhat larger for zinc selenide than for calcium fluoride. Although the etch rates for both materials varied somewhat during the experiments (the power supply for the beam was not well stabilized), the average etch rate for zinc selenide was approximately 30 percent higher than that for calcium fluoride.

Figure 53 is a photomicrograph of the zinc selenide sample, taken to include the unetched portions from which the maximum 4200 angstrom layer of material had been removed. Intermediate surfaces were similar but had less distinct grain boundaries. The etched portion contains fine-scale defects such as scratch traces and pitting which are more distinct than those on the unetched portion, as well as the etched polycrystalline microstructure.

A second example of subsurface damage being revealed by ion beam polishing is given in Fig. 54. In this case, a single crystal of potassium chloride obtained from and polished by the Harshaw Chemical Co. was first chemically polished in hydrochloric acid. Ten micrometers of material were removed, producing a microscopically featureless surface. When a further 4000 angstroms of material were removed by ion beam polishing, the remnant subsurface damage in Fig. 54 was revealed.

The effect of ion milling on the light scattering behavior of the zinc selenide surface is given in Fig. 55. Measurements were made using 6328 angstrom helium-neon laser radiation incident at 45 degrees. The removal of the first two thousand angstroms of material causes an increase of scattering at all angles, probably because both the coarse microstructure relief and the finer polishing-related defects are accentuated. As the etching proceeds, the microstructure relief becomes more pronounced than the finer defects and the low angle scattering increases in intensity more rapidly than the high angle scattering. (Recall that low frequency defects will scatter more strongly at small angles.) After approximately 4000 angstroms have been removed, the scattering between five and ten degrees has increased by a factor of six over the original surface. Some removal of finer defects is indicated by the decrease of the higher angle values relative to less severely etched portions of the specimen.

The scattered intensity increases by approximately fifteen percent at all angles when as much as 2000 angstroms of materials are removed from the selenide surface. Certainly no more than this would need to be removed during any cleaning procedure and a fifteen percent degradation may be taken as a generous upper limit for that produced by ion-beam cleaning.

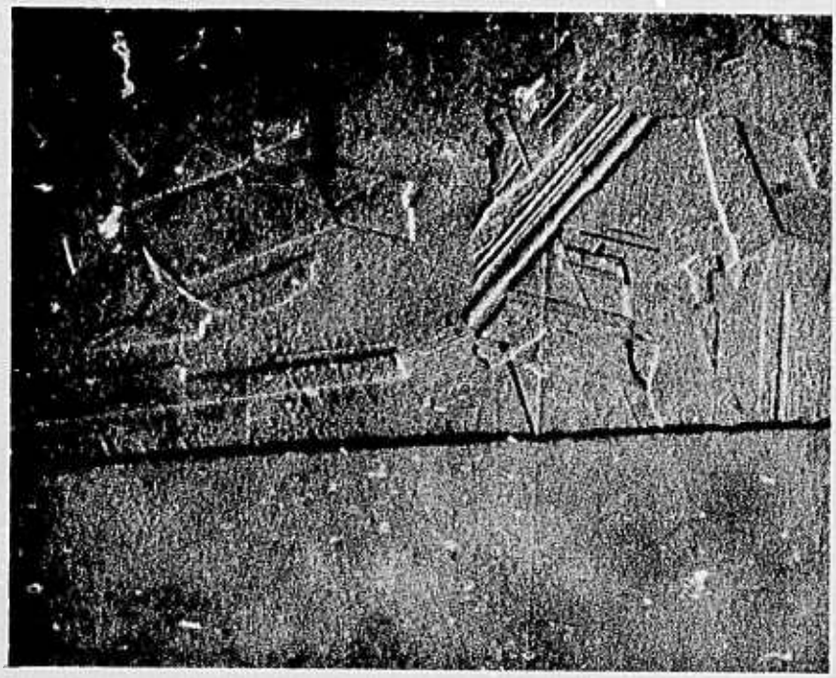


Fig. 53 Microstructure of Ion Beam Polished Zinc Selenide. 766×

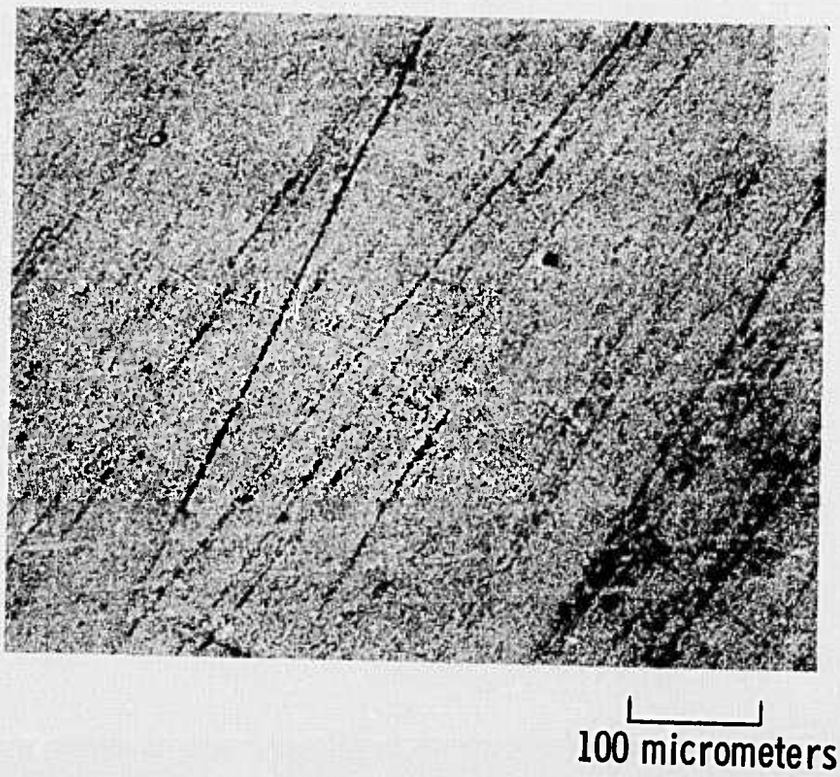


Fig. 54 Ion Beam Polished Potassium Chloride - Subsurface Damage Exposed in Previously Chemically Polished Surface.

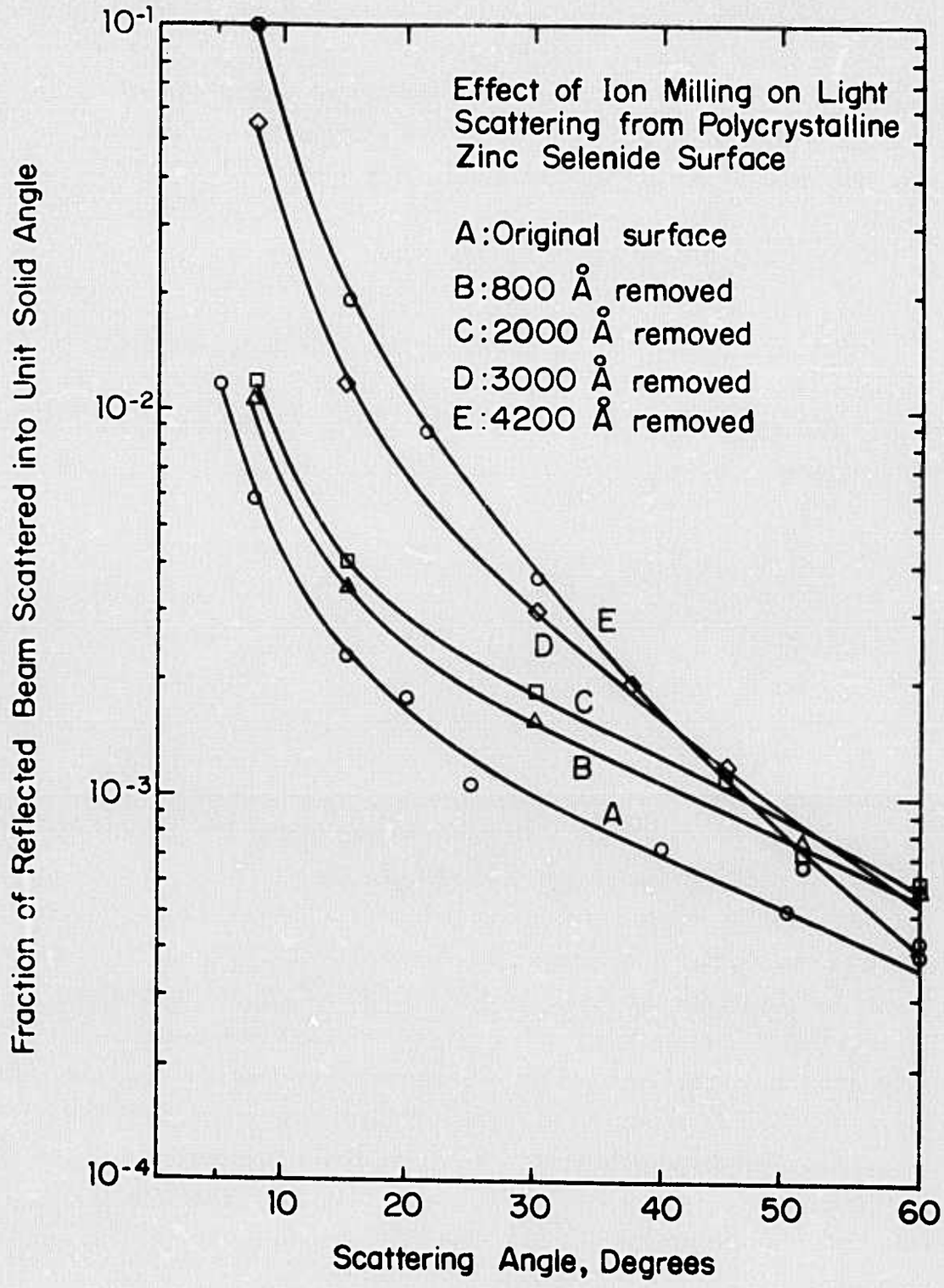


Fig. 55 Light Scattered per Unit Solid Angle vs Scattering Angle - Ion Beam Polished Zinc Selenide Specimens.

The second effect of ion polishing, changes in the infrared absorptivity of the polished specimens was investigated in the Veeco apparatus at Raytheon. Table XVI summarizes results obtained for a Harshaw single crystal disc which was chemically etched, then exposed to two separate ion beam polishing steps.

TABLE XVI

10.6 MICROMETER ABSORPTIVITY OF ION POLISHED KCl

Surface Treatment	Absorption Coefficient (cm^{-1})
30 second HCl etch Isopropanol and Freon Rinses	1.68×10^{-3}
1500 Angstroms removed by 500 eV argon ions	1.58×10^{-3}
3000 Angstroms additionally removed (total of 4500 angstroms)	1.52×10^{-3}

The variation among the absorption coefficients should not be considered to be significant. In these experiments, no increase in absorptivity was produced during the removal of a layer of surface material which was sufficiently thick to contain all surface contaminants. Since argon atoms accelerated through only 500 volts, as these were, would not penetrate the uppermost two or three atomic layers, no detectable absorption increase should have been produced unless an extraordinarily absorbing surface layer were produced. The absorptivity increase which is produced in metal surfaces occurs because the interaction between the specimen and the light is almost totally confined to the disturbed surface layers. Two sets of similar experiments using zinc selenide specimens did not detect a statistically significant increase.

In fact, however, most of the ion polishing experiments did produce absorptivity increases on the polished potassium chloride

specimens. These increases, we believe, were produced by contamination of the surfaces in the ion polishing apparatus by material removed from walls or sample holders during the polishing step. Two observations support this view. First, when potassium chloride specimens were mounted in the chamber, evacuated and stored in the evacuated polishing apparatus for several hours with the ion beam turned off, their absorptivities did not change. Second, on several occasions, the ion polishing of potassium chloride specimens which were masked from the ion beam over half their areas produced absorptivity increases on both masked and exposed areas.

Summarizing, ion polishing of these polycrystalline materials should be considered to be a technique with limited utility. It should be used only to prepare surfaces for thin film deposition by removing the outermost surface layers. Even at that, the technique should be expected to produce some surface roughening by exposing subsurface mechanical damage and grain relief. Contamination of the ion polished surfaces in the vacuum chamber may be encountered and should be sought.

3.0 CONCLUSIONS AND RECOMMENDATIONS

1. Conventional polishing using alumina abrasives followed by diamond polishing on pitch can be used to produce microscopically defect-free surfaces on polycrystalline zinc selenide and calcium fluoride. Diamond polishing is more reliable than bowl-feed superpolishing. It appears to minimize relief polishing effects and be scalable to large polycrystalline pieces. The technique should be extended to larger pieces. Calorimetric absorption characterization of these surfaces, which were developed late in the program, was not done but should be.

2. Chemical polishing of zinc selenide, using the techniques recommended in this report, can reduce surface absorption to $2\text{-}4 \times 10^{-4}$ per surface. Further work to determine whether this is a minimum value should be carried out. Recent advances in the technology used to produce the selenide material have reduced its bulk absorption coefficient from typically $3\text{-}5 \times 10^{-3}$ cm^{-1} to approximately 4×10^{-4} cm^{-1} causing surface absorption to reappear as a major contributor to total absorption.

3. Chemical polishing of polycrystalline CaF_2 should receive further attention. Ammonium salts appear to be capable of true chemical polishing action and should be pursued. The surface absorptivity of the alkaline earth fluorides at the HF and DF laser wavelengths has not been extensively studied. At these wavelengths, the influence of water and solvent absorptions will be substantial. Chemical polishing techniques may be required to produce minimum surface absorptivity.

4. Vacuum annealing has been shown[17] to reduce what is apparently a surface absorption in potassium chloride. The technique should be applied to both zinc selenide and the alkaline earth fluorides and the effects determined calorimetrically at all important laser wavelengths. For these experiments, it would be useful to determine the absorptivity changes in the vacuum chamber because the vacuum anneal could be used as a final preparative step prior to antireflection coating deposition. Note that chemical polishing and vacuum annealing may be used in combination to remove buried abrasives, chemical residues, and mechanically deformed surface layers.

5. No satisfactory abrasive polishing technique for potassium chloride was developed. The best specimens received from Harshaw Chemical Company can be etched free of surface residues and surface scratches by the removal of as little as two micrometers by chemical polishing. Some examples of their surfaces did exhibit relief polishing and all contain subsurface damage which may prove deleterious for very high-power applications. Abrasive polishing of potassium chloride should receive more attention.

6. Mixtures of hydrochloric acid with either isopropanol or triacetic glycol may be used to etch potassium chloride at rates which are slow enough to permit controlled chemical polishing of large components. Hot forged material will exhibit grain boundary grooving at subgrain boundaries. These do not appear to act as preferential laser damage sites, but will contribute to surface scattering and perhaps to defects in antireflection coatings.

7. Acetic acid-based etches may be used to avoid subgrain boundary grooving but those tested removed pits and scratches less effectively than hydrochloric acid-based etched. A chemical polishing solution which combines the best features of the acetic and hydrochloric acid etchants should be developed.

8. Nomarski interference microscopy is the more convenient direct imaging technique for highly polished surfaces. Light scattering measurements, which were used to rank microscopically similar surfaces could be used to characterize developing surfaces and surfaces of large components if suitable replication techniques could be developed.

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APPENDIX 1

STATISTICAL COMPARISON OF MICROSCOPES

Five areas of a sample of zinc selenide were selected at random and photographed at 183 × with bright field and with dark field illumination in a Wild, Model M-12 microscope. The experiment was repeated at 187 × in a Nikon Apophot microscope equipped with a Francon-Yamamoto (their equivalent to Nomarski) interference attachment. Five straight lines were drawn on each photograph; their placements were selected randomly. The number of scratches intersecting each line was counted and reported as number per unit length on the sample (taking magnifications into account. Mean scratch counts and their variances are given in Table A-1.

TABLE A-1

STATISTICAL COMPARISON OF MICROSCOPE TECHNIQUES

Microscope	Scratch Count		
	Mean $\bar{x}$	Variance σ^2	Lines Counted N
Wild, Bright field	33.93	34.80	24
Wild, dark field	36.06	77.60	25
Nikon, Nomarski	42.64	75.40	25

TABLE A-2

RESULTS OF STATISTICAL COMPARISON

Comparison	Difference of Means	Standard Error of Difference	Degrees of Freedom	t	Probability of Chance Occurence
Bright-dark field	2.13	2.32	47	0.92	~1
Bright field-Nomarski	8.71	2.32	47	3.75	< 0.005
Dark field-Nomarski	6.58	2.29	48	2.80	< 0.005

A best estimate of the population variance is given by

$$\hat{\sigma}^2 = \frac{\Sigma n_i \sigma_i^2}{\Sigma n_i - 3} = 65.5$$

A best estimate of the standard error of the difference between any pair of sample means is given by:

$$\hat{\sigma}_{w_{ij}} = \hat{\sigma}\sqrt{\frac{1}{N_i} + \frac{1}{N_j}}$$

The statistical parameter, t, for each pair comparison is given by

$$t = \frac{\text{difference of means}}{\text{standard error of difference}}$$

The number of degrees of freedom for each pair comparison is given by

$$N_{ij} = N_i + N_j - 2$$

And the probability that the value of t computed for each comparison could have occurred by pure chance can be obtained from standard statistical Table A-2.