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ADVANCED TECHNIQUES FOR IMPROVING
LASER OPTICAL SURFACES

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Raytheon Company

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all polishing techniques began. Acceptable conventional polishing techniques for polycrystalline calcium fluoride and zinc selenide were developed, and preliminary grinding steps of the process were identified as requiring further study. Bowl-feed "superpolishing" was shown to improve the surface quality of conventionally polished zinc selenide and calcium fluoride substantially. Zinc sulfide, a candidate infrared-transparent or abrasive material, was used successfully to produce a rough conventional polish on a potassium chloride single crystal.

Surface relief produced by variations of polishing rate with orientation of the crystallites in the polycrystalline materials was shown to limit the utility of ion-beam polishing to the removal of surface layers significantly thinner than one micrometer.

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TECHNICAL 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 is a 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 will be developed for single crystal and polycrystalline potassium chloride and calcium fluoride, and polycrystalline zinc selenide. A new class of abrasives which are transparent to infrared laser radiation will be studied. Surfaces generated during the study will be characterized by optical microscopy, scanning electron microscopy, transmission electron microscopy of surface replicas, light scattering measurements, and ultimately by laser damage studies.

During the first six months of the program, acceptable conventional polishing techniques for zinc selenide and calcium fluoride were developed. Major defects in these conventionally-polished materials were shown to be produced by cleavage during the grinding steps, which are being studied further. A rough conventional polish was produced on potassium chloride using a zinc sulfide abrasive, which would not absorb 10.6 micrometer radiation significantly if left embedded in the surface.

Bowl-feed "superpolishing" of calcium fluoride and zinc selenide was initiated. Measurements of light scattering from bowl-feed and conventionally-polished specimens demonstrated a factor of three improvement for bowl-feed polished zinc selenide and an order of

magnitude improvement for calcium fluoride. Significantly higher quality surfaces should be obtainable when the preliminary grinding steps are improved.

Ion beam polishing experiments demonstrated that when layers on the order of one micrometer thick are removed, surface relief produced by differential removal rates for the variously-oriented crystallites in polycrystalline specimens of all three materials is a significant problem. The surface relief produced appears to be less for ion beams incident at 84 degrees from the sample normals than for beams incident at 60 degrees. Nevertheless, ion beam polishing may serve these materials well as a final cleaning step prior to optical film deposition.

Chemical-mechanical polishing of polycrystalline calcium fluoride and zinc selenide using Syton, an alkaline colloidal silica suspension, also produced surface relief by differential grain etching. A 0.1 percent solution of bromine in methanol used as a chemical-mechanical polish removed smaller scratches from a zinc selenide specimen while producing some grain relief, but the process is difficult to control. Several reagents were used to etch polycrystalline potassium chloride, all of which etched nonuniformly.

Surface characterization techniques were compared. Normarski interference was adopted as the optical microscopic technique of choice. Scanning electron microscopic imaging of highly polished surfaces was shown to be inferior to interference (optical) microscopy at low magnifications and transmission electron microscopy of surface replicas at high magnifications. The scanning electron microscope was used to characterize abrasive powders and to identify microporosity as the most probable native defect in chemical vapor deposited zinc selenide. The equipment used for measuring light scattering from bowl-feed and conventionally polished surfaces was assembled.

The program will continue with major emphasis being placed on improving the preliminary grinding procedures, optimizing bowl-feed polishing of calcium fluoride and zinc selenide, developing chemical

polishes for all materials, and transparent abrasives for potassium chloride. Polishing procedures will be adapted to larger, 6-inch diameter initially, sample sizes, and laser damage studies will begin.

PREFACE

This program is a study of surface finishing techniques considered to be capable of improving the surface quality of laser optical materials. Research in this area has become necessary as a result of increasing interest in high power laser systems. Optical components of such laser systems must have essentially defect-free surfaces because surface defects which would be acceptable on conventional optical elements may act as sites for laser damage at power densities well below the operating power of high power systems. This is an eighteen-month program, during which a variety of polishing techniques including chemical and chemical-mechanical polishing, ion-beam polishing and bowl-feed and continuously recycled abrasive "superpolishing" will be evaluated as finishing techniques for three important laser optical materials; zinc selenide, calcium fluoride, and potassium chloride. Surfaces generated during the study will be characterized by optical and electron microscopy, light scattering measurements, and ultimately by laser damage studies.

This report details work performed in the first six months of the program during which time preliminary experimentation in all the program areas began, and techniques for conventionally-polishing calcium fluoride and zinc selenide were developed.

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1.0 INTRODUCTION

The goal of this project is to develop techniques which will produce the highest possible laser damage thresholds on surfaces of optical components in lasers operating in the 3-5 and 10.6 micrometer spectral ranges. Until the advent of high power lasers, the important criteria for laser optical component surfaces, were the absence of major light-scattering scratches together with accurate fabrication of the optical figure. Surfaces required to transmit high energy densities have additional constraints. They must be free of embedded particles of absorbing material, polishing abrasives, and free of field-concentrating features such as pores and microcracks, perhaps as small as 100 angstroms.¹ Altogether the conditions now being imposed upon laser component surfaces are not unlike those which exist for substrates used for epitaxial deposition in semiconductor and bubble domain memory technologies. However, the additional constraint of optical flatness (considering the relative softness of the important optical materials), makes the problem a difficult one. Historically, preparation techniques have been developed to produce either optically-figured surfaces or damage-free surfaces.

The double constraint of optical figure and surface perfection makes it likely that the techniques sought will require some form of abrasive polishing to establish the figure while producing the least possible surface damage, followed by a treatment to remove the surface damage and remnant abrasive particles. Chemical etching, chemical-mechanical polishing, and ion-beam polishing are candidate processes for the latter step. Techniques such as bowl-feed and continuously-recycled abrasive polishing, in which the finest abrasive particles are continuously fed to the workpieces, produce the most nearly perfect abrasively-polished surfaces and will be developed as the final abrasive polishing step. All preceding treatments contribute to the final surface character, however, and their importance cannot be overlooked.

Since it is most probable that an optimum surface preparation technique will be particular only to one material or at best to a class of materials (alkaline earth halides, for example), this project considers the surface finishing of three materials: zinc selenide, calcium fluoride, and potassium chloride. These materials not only represent three material classes, but are themselves important laser optical materials. Further, although single crystals of potassium chloride and calcium fluoride will be studied, polycrystalline specimens are being emphasized; high strength or large-area components will most likely be polycrystalline.

Embedded abrasive particles can reasonably be considered to be a universal remnant feature of abrasive polishing. If they absorb the radiation incident upon high power laser optical components, they become preferential sites for laser damage. Aluminum oxide, a most common and useful abrasive material, is quite opaque to 10.6 micrometer radiation. During the course of this project, the utility of zinc sulfide as an abrasive, in pure and solid solution hardened forms, will be determined. It is harder than both potassium chloride and zinc selenide, and should not absorb significantly.

Polished surfaces are inspected and characterized by a variety of direct techniques including optical microscopy and scanning electron microscopy and by indirect methods such as transmission electron microscopy of surface replicas and surface light scattering measurements. Ultimately, laser damage measurements will be made to compare the most promising preparation methods.

Itek Corporation, Lexington, Mass., has been funded as a subcontractor to this project to study the superpolishing of zinc selenide, in a parallel effort. Their considerable experience with bowl-feed and recycled abrasive polishing as well as the finishing of large-scale optical components should prove to be an asset to the effort.

Finally, effective optical finishing techniques have historically been regarded as proprietary art by their processors. The open distribution of the results is an important aspect of this investigation.

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 with a filtered, deionized water supply, a laminar-flow workbench, and a Nikon Apophot microscope equipped for Nomarski interference microscopy.

The other laboratories are an optical evaluation facility, which contains an apparatus for measuring surface and bulk light scattering and a laser calorimeter for absorption measurements, and a thin film deposition laboratory.

During the first six months of the program, experimental work emphasized conventional polishing of the test materials. Characterization methods were compared, and an evaluation of ion beam polishing was initiated. Bowl-feed polishing experiments began at Raytheon, while Itek Corporation, performing under subcontract, began work leading to an evaluation of continuously recycled abrasive polishing of zinc selenide. Preliminary chemical and chemical-mechanical polishing experiments were done, and a first attempt to use zinc sulfide as an abrasive material for potassium chloride was made.



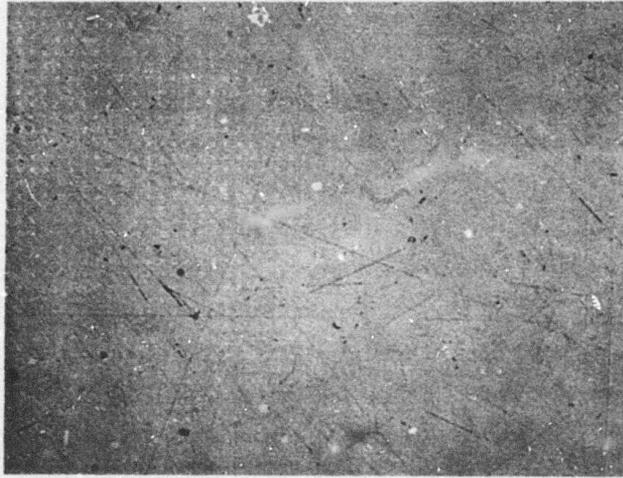
Fig. 1 Raytheon Optical Polishing Facility.

2.2 Surface Evaluation

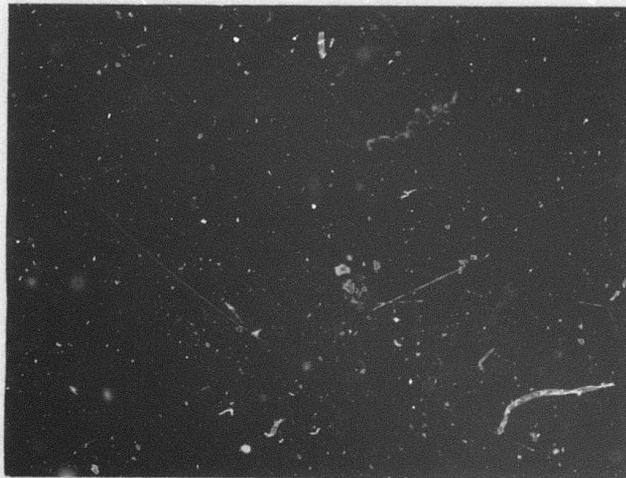
2.2.1 Optical microscopy

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 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. Finally, substantial differences may exist among surfaces which are too highly polished to produce optical microscope images.

Midway through this report period, a Nikon Apophot microscope equipped for Nomarski interference microscopy became available for use on the project. A Wild M-12 bright field-dark field microscope had been used previously. 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 microscope was used exclusively.



a. Wild Microscope, Bright Field 183X



b. Wild Microscopy, Dark Field 183X

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

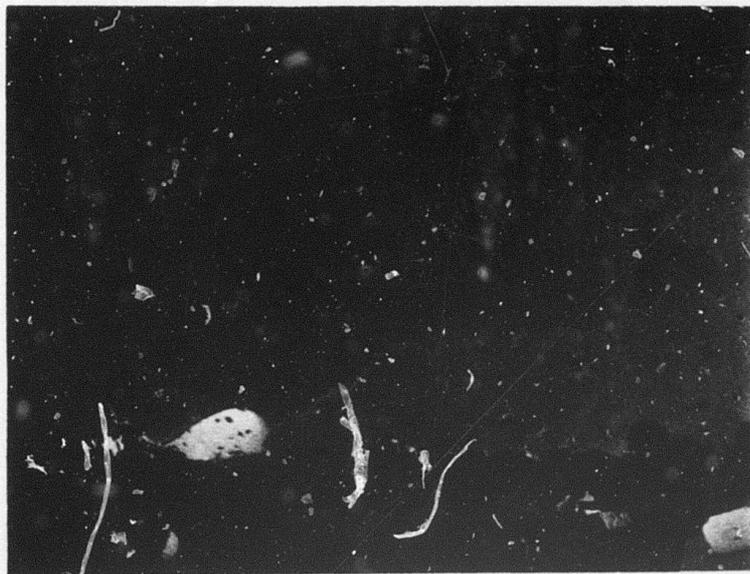


c. Nikon Microscope, Nomarski Interference 187X

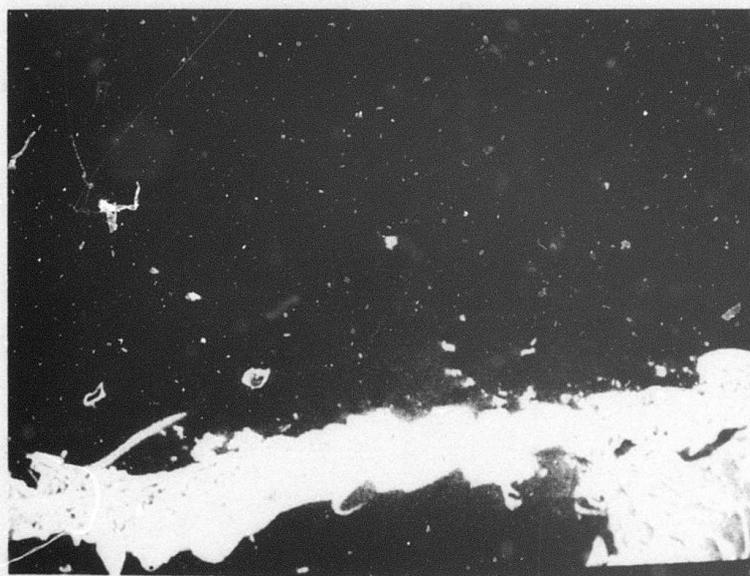
2.2.2 Scanning electron microscopy

As its name implies, 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. 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 2.3.2. 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. Examples of these features are given in paragraphs 2.4.1 and 2.5. It is also a useful tool for the study of abrasive powders. Figure 5 is a photomicrograph of Barnesite No. 85 abrasive, a powder containing two particle types. Four attempts to remove the larger particles by sedimentation had been made, and the photograph demonstrated that the process was incomplete. The SEM will figure prominently in a



a. Optical Microscope (Nomarski) 186X



b. Scanning Electron Microscope. 200X

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

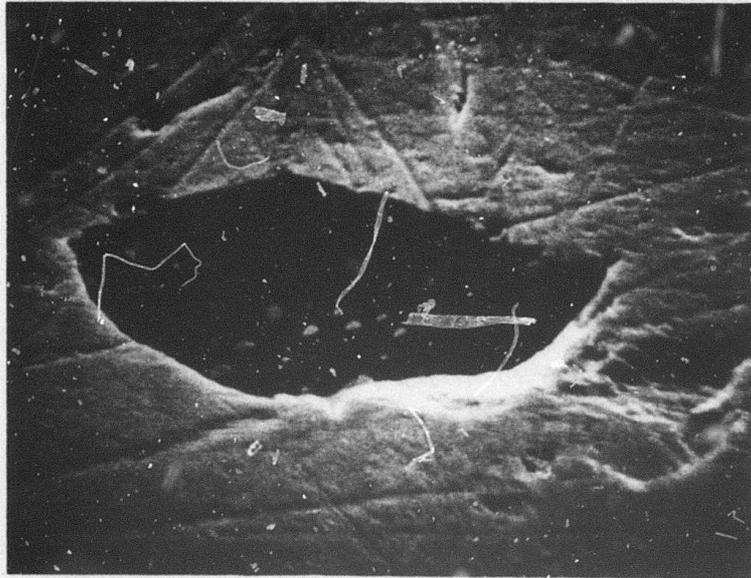


Fig. 4 Scanning Electron Micrograph of Rough Polished Zinc Selenide Specimen. 5000X

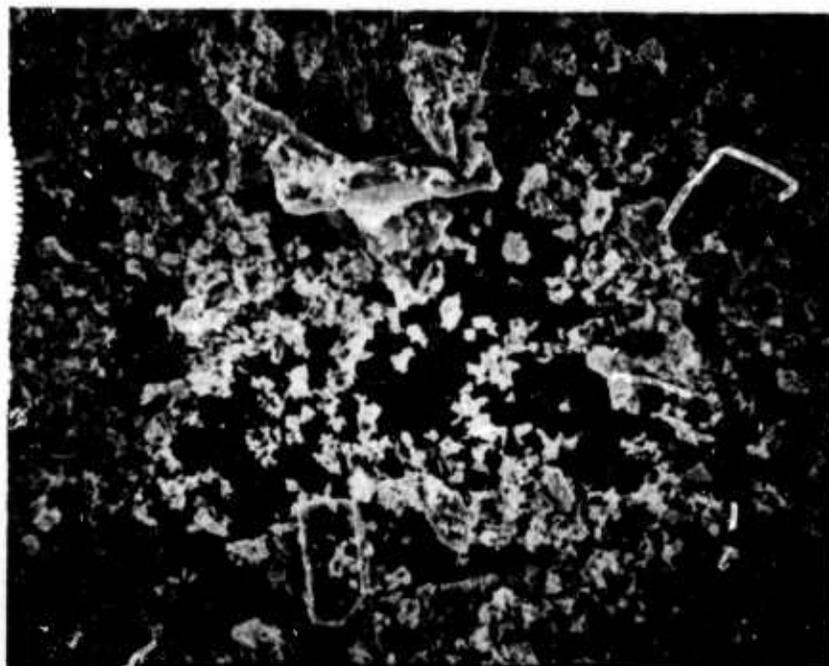


Fig. 5 Scanning Electron Micrograph of Sedimented
Barnesite. 1000X

systematic study of the composition, particle size and shape, and infra-red absorptive properties of various abrasives, to be included in the next report.

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.

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 angles away from a directly transmitted beam incident upon it, or a specularly-reflected beam from it. Differences in surface textures involving defects on the order of 1000 angstroms in size should be detectable by scattering measurements.

* Work performed at Itek Corporation.



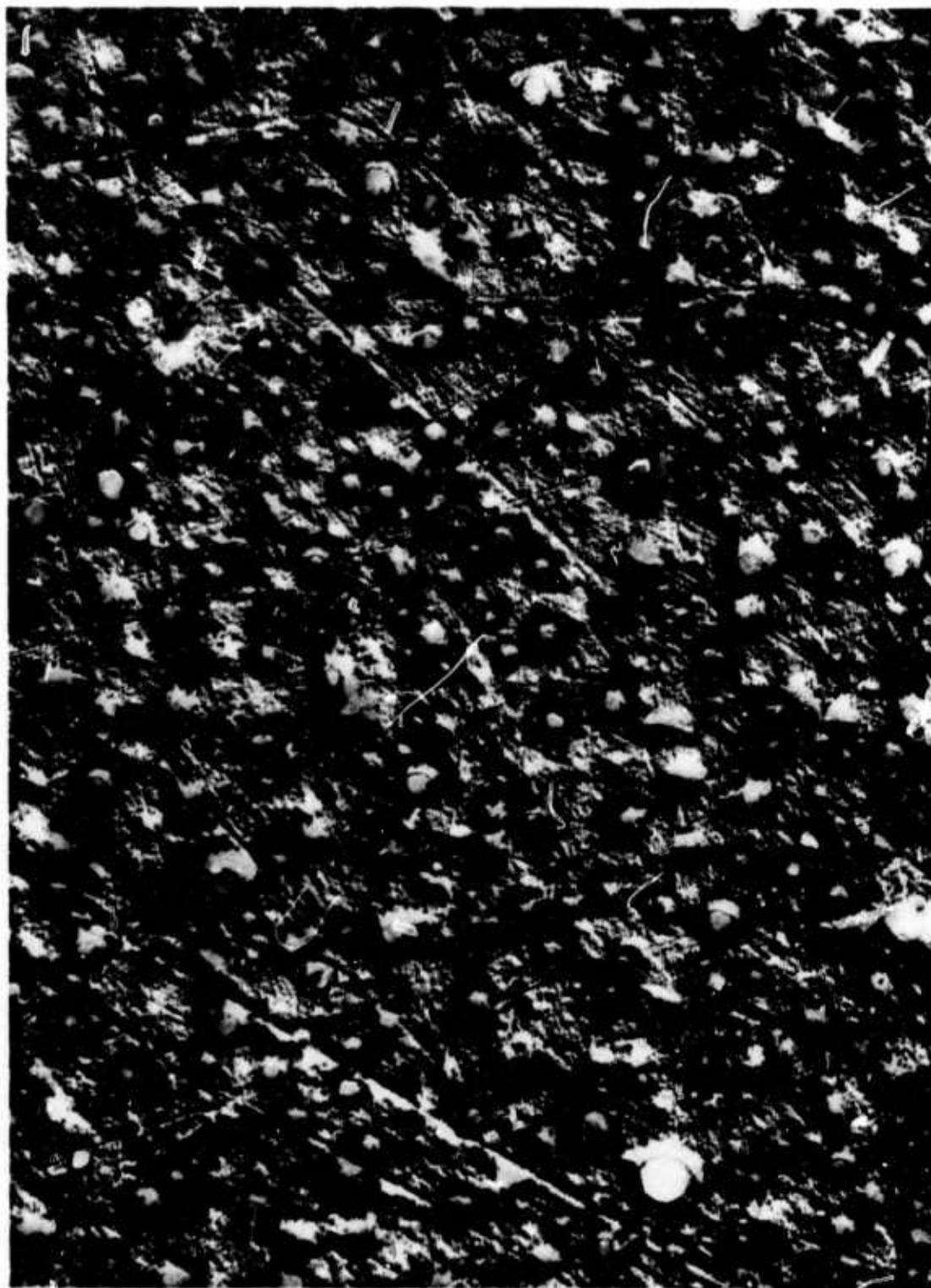
a. Polished One Hours, Linde-B Abrasive

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



a. Polished One Hours, Linde-B Abrasive

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



b. Polished Two Hours, Linde-B Abrasive

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

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

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

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,

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

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. Scattering measurements have begun at Itek Corporation using an apparatus which reports measurements as scatter relative to a matte MgCO_3 surface rather than to the specular beam. The two instruments will be put on a common basis so that comparative measurements can be made.

Samples of bowl-feed polished calcium fluoride and zinc selenide prepared at Raytheon were compared with their conventionally-polished

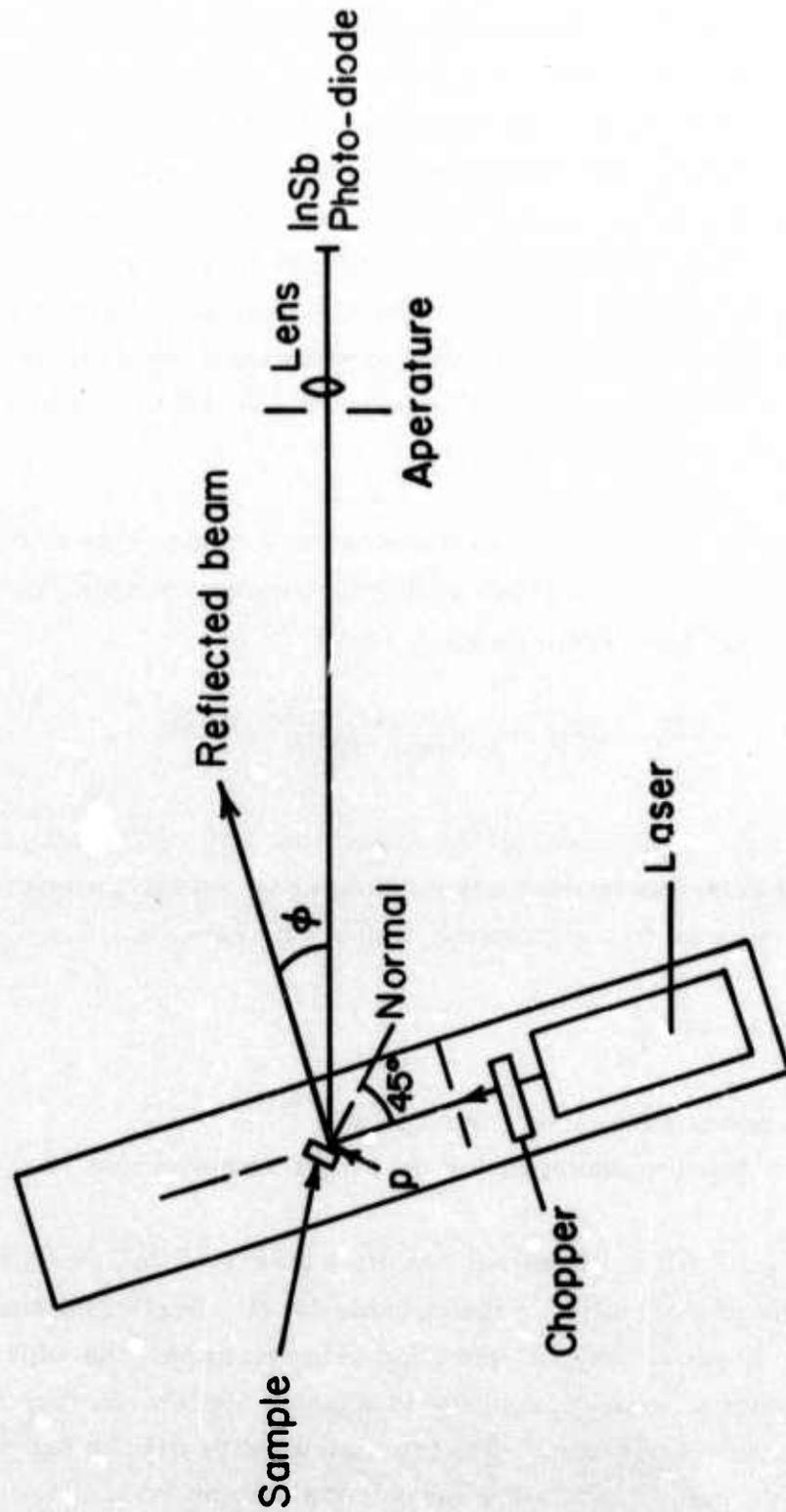


Fig. 7 Scatter Measurement Apparatus - Schematic.

predecessors. Itek Corporation compared conventionally polished zinc selenide with samples prepared by a bowl-feed variation. Results are discussed in Sec. 2.3.2.

2.3 Abrasive Polishing

2.3.1 Conventional polishing

Materials to be superpolished by any technique must first receive the best possible conventional optical polish. Conventional polishing 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. At present, optical figures are 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. A non-contact interferometer is under construction.

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 is 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. We will eventually attempt to apply the abrasives as metered flows of

pumped, characterized slurries. Abrasive choice is best made by experiment. Relatively soft abrasives are frequently used to polish soft materials, although in many cases harder abrasives may work as well.

Samples used for the polishing experiments are listed in Table 1. During the report period, polishing trials using the combinations of parameters summarized in Tables 2, 3, and 4 were performed. Parameters of choice, where found, are noted in the tables and are discussed below.

2.3.1.1 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. 8, 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. 9, an optical micrograph of a bowl-feed polished calcium fluoride specimen.

TABLE 1

SAMPLES USED FOR POLISHING EXPERIMENTS

<u>Material</u>	<u>Dimensions</u>	<u>Grain Size</u>	<u>Fabrication</u>
ZnSe	1.5 in. dia. disc 4 mm thick	50-150 μm	Chem. Vap. Deposit, Raytheon
ZnSe	0.5 in. dia. disc	50-150 μm	Chem. Vap. Deposit, Raytheon
CaF ₂	Irregular, 1 in. square \times 4 mm	1-3 millimeter	Optovac Single Crystal, Hot forged at Raytheon
KCl	Irregular, average 1 in. square \times 4 mm	1-3 millimeter	Optovac Single Crystal, Hot forged at Raytheon

TABLE 2

ABRASIVES USED FOR CONVENTIONAL POLISHING

<u>Abrasive</u>	<u>Compositions</u>	<u>Particle Size (Micro-meters)</u>	<u>Materials Polished</u>			<u>Comments</u>
			<u>ZnSe</u>	<u>CaF₂</u>	<u>KCl</u>	
Diamond	Carbon	3	X			} Scratched Surface
Diamond	Carbon	1	X			
Diamond	Carbon	0.25	X			
Microgrits	Al ₂ O ₃	30	X	X	X	} Grinding Compounds See grinding discussion
Microgrits	Al ₂ O ₃	12	X	X	X	
Microgrits	Al ₂ O ₃	9	X	X	X	
Microgrits	Al ₂ O ₃	5	X	X	X	
"C"-Alumina	Al ₂ O ₃ *	1.0	X	X	X	Rough Polish
"A"-Alumina	Al ₂ O ₃ *	0.3	X	X	X	Intermediate Polish
"B"-Alumina	Al ₂ O 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 Linc-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 3

LAP MATERIALS USED FOR CONVENTIONAL POLISHING

<u>Material</u>	<u>Function</u>	<u>Comments</u>
Cast Iron	Grinding all materials	
Glass	Grinding all materials	
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 0.25 μm diamond paste	Produced badly scratched surface
Swedish Pitch [*]	Polishing ZnSe, CaF ₂	Inferior to softened variety (below)
Swedish Pitch no. 73-3 softened by addition of 1 drop linseed oil per 13 grams pitch	Polishing ZnSe, CaF ₂	Produced highest quality surfaces (Raytheon)
Soft Cycad (pitch) ^{**}	Polishing ZnSe	Produced highest quality ZnSe surfaces (Itek)

* Obtained from Universal Shellac and Supply Company.

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

TABLE 4

SLURRY VEHICLES USED FOR CONVENTIONAL POLISHING

	Materials Polished			<u>Comments</u>
	<u>ZnSe</u>	<u>CaF₂</u>	<u>KCl</u>	
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

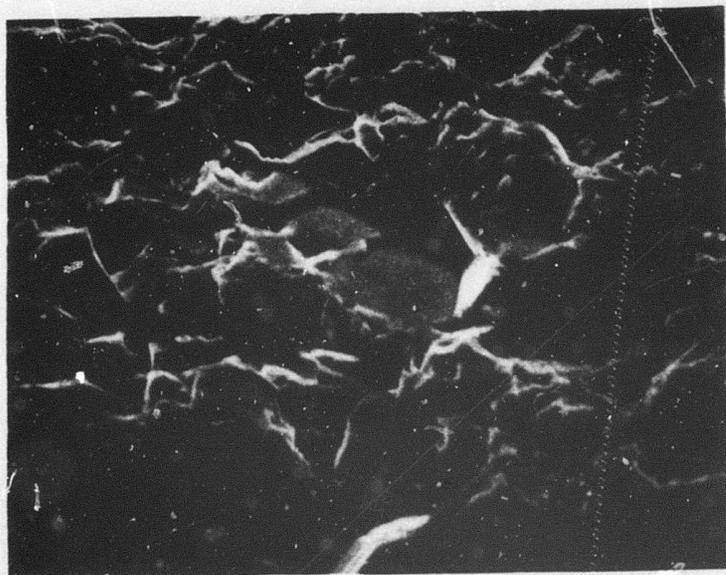


Fig. 8 Scanning Electron Micrograph of Cleavage
Produced During Grinding of Zinc Selenide.
3000X

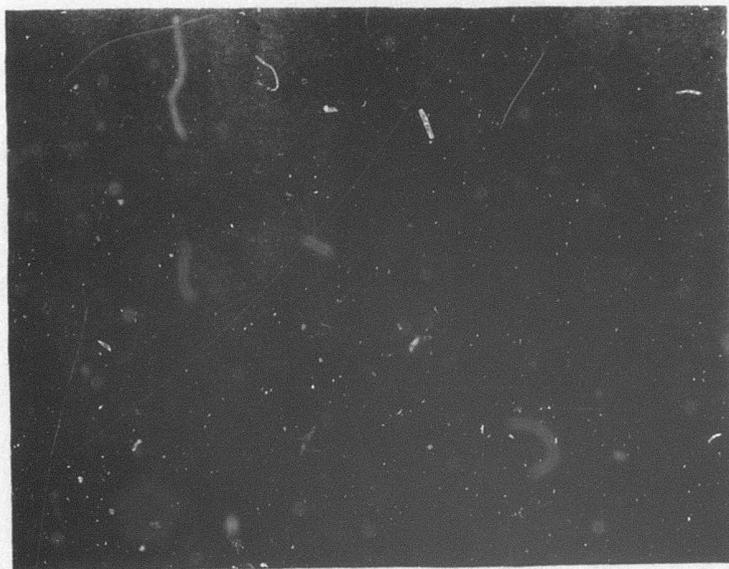


Fig. 9

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

Variations of pit densities, frequently found among similarly-polished specimens, are probably caused by differences in incipient subsurface cleavage damage. To optimize the grinding procedure, the depth of the initial subsurface damage and the stage at which the depth of grinding-induced cleavage damage falls below the grain size must be determined. This aspect of the conventional polishing of calcium fluoride and zinc selenide is being emphasized.

2.3.1.2 Zinc selenide

Parallel studies of conventional polishing of zinc selenide were conducted at Raytheon and Itek Corporation. Both studies reached substantially the same conclusions - which must attest either to the broad applicability of the process or the equality of skill among the opticians. Soft pitch laps, alumina abrasives, and a slurry which contains equal parts of water and ethylene glycol produced the best surfaces. The soft Cycad pitch used by Itek is similar in hardness to the Swedish Pitch, softened by linseed oil addition used at Raytheon. A typical polishing run for zinc selenide is summarized in Table 5. Material removal is measured by a dial gauge, which can be estimated to 0.003 millimeters, mounted above a flat, machined surface. Typical surfaces produced by the steps in the process are shown in Fig. 10.

Alumina abrasives, are absorbers of 10.6 micrometer radiation, and in principle, should be avoided if possible. They do, however, produce vastly superior surfaces which could be used for optical components if residual abrasive particles proved to be either not harmful or removable by very light chemical-mechanical or ion-beam polishing. This point is considered again at the end of paragraph 2.3.2.1.

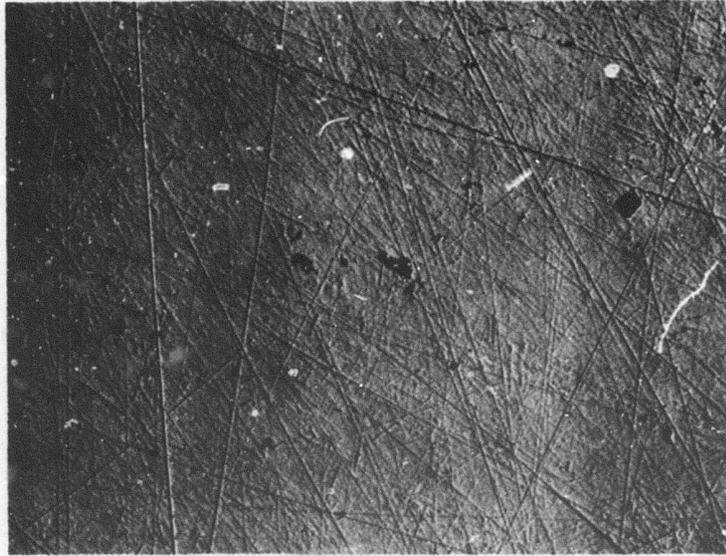
2.3.1.3 Calcium fluoride

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. A typical calcium fluoride polishing run is summarized in Table 6.

TABLE 5

TYPICAL POLISHING RUN FOR ZINC SELENIDE

Operation	Abrasive	Slurry	Lap	Time	Material Removed (μm)	Removal Rate ($\mu\text{m}/\text{min}$)
Grind	9 μm alumina	H ₂ O	Cast Iron	10 min	70	7
Grind	5 μm alumina	H ₂ O	Cast Iron	10 min	30	3
Polish	"C" - Alumina	H ₂ O/glycol	Softened Pitch	1 hour	10	0.16
Polish	"A" - Alumina	H ₂ O/glycol	Softened Pitch	1 hour	5	0.06
Polish (Bowl-Feed)	"B" - Alumina	H ₂ O	Softened Pitch	4 3/4 hours	8	0.03



b. Type A-Alumina Abrasive. 187X

Fig. 10 Surfaces Produced During Conventional Polishing of Zinc Selenide.



c. Type B-Alumina Abrasive. 187X

TABLE 6

TYPICAL POLISHING RUN FOR CALCIUM FLUORIDE

Operation	Abrasive	Slurry	Lap	Time	Material Removed (μm)	Removal Rate $\mu\text{m}/\text{min}$
Grind	5 μm alumina	H ₂ O	Cast Iron	20 min	30	1.5
Polish	"C" -Alumina	H ₂ O/glycol 1:1	Softened Pitch	1.3 hrs	9	0.12
Polish	"A" -Alumina	H ₂ O/glycol 1:1	Softened Pitch	1 hr	6	0.1
Polish	"B" -Alumina	H ₂ O/glycol 1:1	Softened Pitch	0.75 hr	3	0.06
Polish (Bowl-Feed)	"B" -Alumina	H ₂ O/glycol 1:1	Softened Pitch	2.75 hr	Not detect- able	Not detectable

2.3.1.4 Potassium chloride

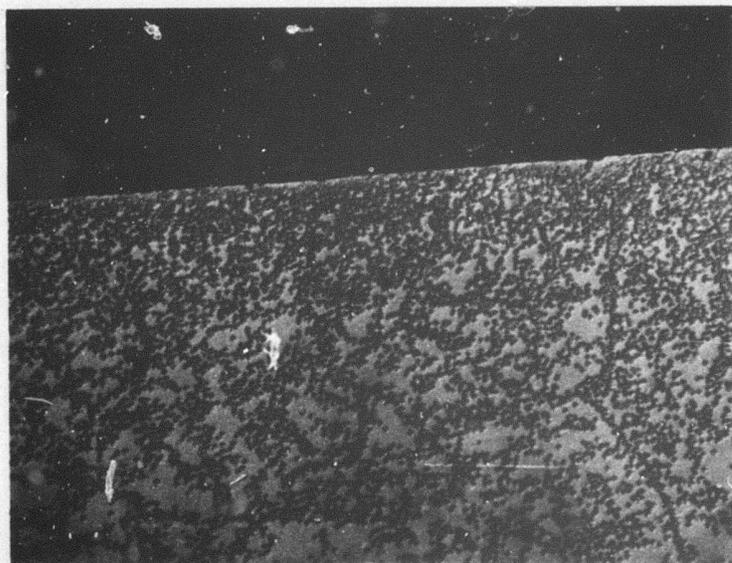
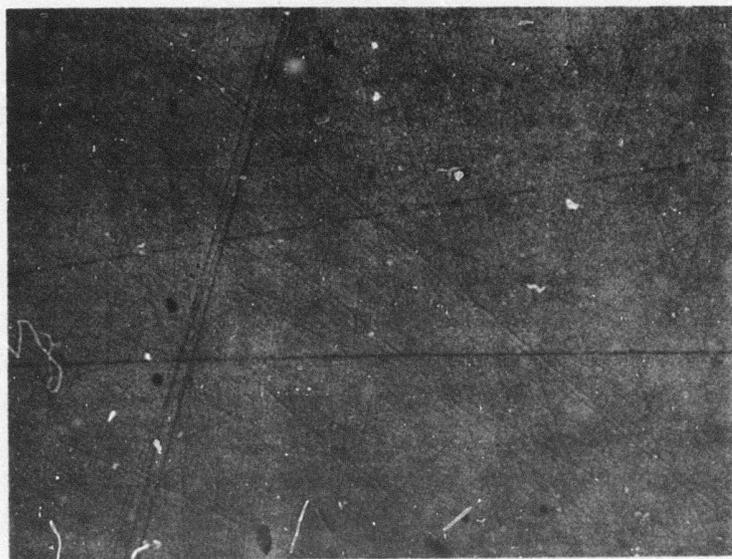
Potassium chloride is by far the softest of the test materials and is the most difficult to polish. The better commercially-available abrasively polished potassium chloride single crystals are covered with fine scratches (Fig. 11a), and the high-speed buffing step with which the polishing is commonly concluded introduces subsurface damage and probably buries any residual abrasive particles. Figure 11b is a micrograph of a cleaved portion of the crystal shown in Fig. 11a, etched to reveal the higher dislocation density, an indication of damage, near the surface. Smooth surfaces may be produced by chemical polishing (at a considerable sacrifice of the optical figure), while abrasively-polished potassium chloride surfaces, although flat, apparently contain significant quantities of embedded abrasives. Some form of chemical polishing will probably be used eventually as a final step for potassium chloride finishing. Since the chemical technique must remove as little material as possible to preserve the optical figure, it must be applied to the best possible abrasively polished surface.

During the report period, alumina abrasives, tin oxide, and zinc sulfide (1 μm particle size) were used to polish potassium chloride. The buffing step was eliminated, and the procedure of cleaning the samples ultrasonically in propanol was adopted. This cleaning procedure etches the sample surfaces slightly and reveals grain boundaries in polycrystalline potassium chloride (Fig. 12), but it is the least damaging procedure developed at this time. Other solvents used are summarized in Table 7; all etched the surfaces more severely than propanol.

TABLE 7

SOLVENTS USED TO CLEAN KCl SPECIMENS

Methanol	Amyl Alcohol
Ethanol	Trichloroethylene
Propanol	Acetone



b. Dislocation Etched Cleavage Surface, 187X.

Fig. 11 Commercially Polished Potassium Chloride Single Crystal (Janos Optical Co., Newfane, Vermont).



Fig. 12 Grain Boundary Etching Produced by Propanol Cleaning of Polycrystalline Potassium Chloride. 187X

Specimens were polished by hand, on stationary beeswax and paraffin laps. It is more difficult to avoid digging specimen edges into the paraffin laps, but easier to control the figure. Beeswax laps may be used with continuous rotation.

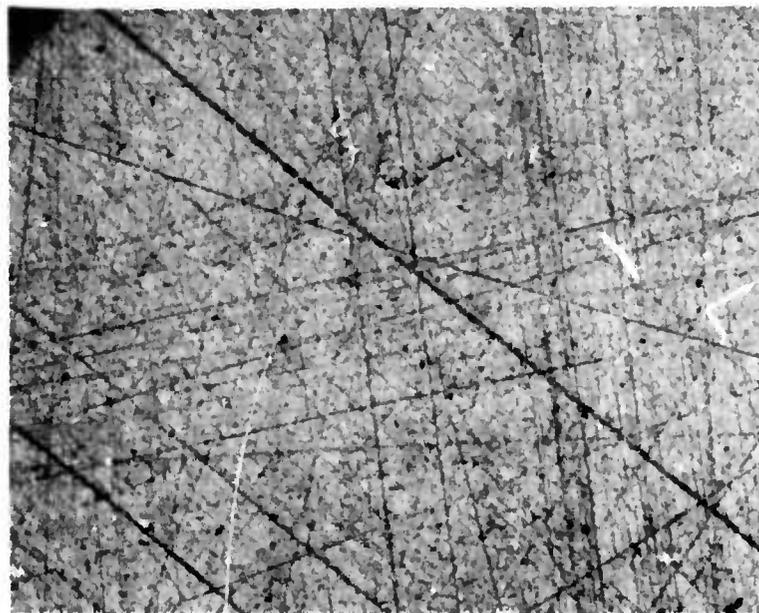
None of the abrasives used have produced high-quality surfaces. Tin oxide adhered to the surfaces; attempts to remove it by more extended ultrasonic cleaning etched the surfaces badly. Figure 13 is a comparison of surfaces produced on potassium chloride single crystals by B-alumina (0.06 μm particle size) and zinc sulfide powder (1 μm particle size). While neither micrograph is particularly attractive, both specimens appeared to be reasonably glossy when examined visually. The important observation here is that zinc sulfide, which should present negligible absorption at 10.6 micrometers when present as an embedded abrasive, can be used to produce a rough polish on potassium chloride which is at least comparable to that produced by a conventional, absorptive abrasive. Attempts to extend the concept both to finer polishing and to grinding will be emphasized during the next report period.

2.3.2 Bowl-feed polishing

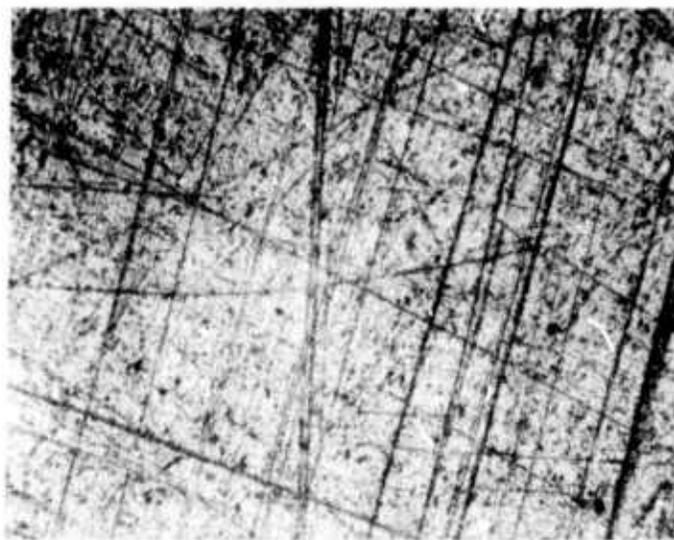
Bowl-feed polishing is a technique widely used for finishing surfaces of fused silica and metal super-reflectors. Surfaces having root mean square deviations from planarity as small as 5 angstroms have been reported.² Figure 14a shows schematically a polishing lap adapted for bowl-feed polishing. The bowl, which rotates with the lap, contains 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. 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. 14b was used by Itek Corporation for their preliminary superpolishing experiments. They have used it successfully in other systems. In this variation,

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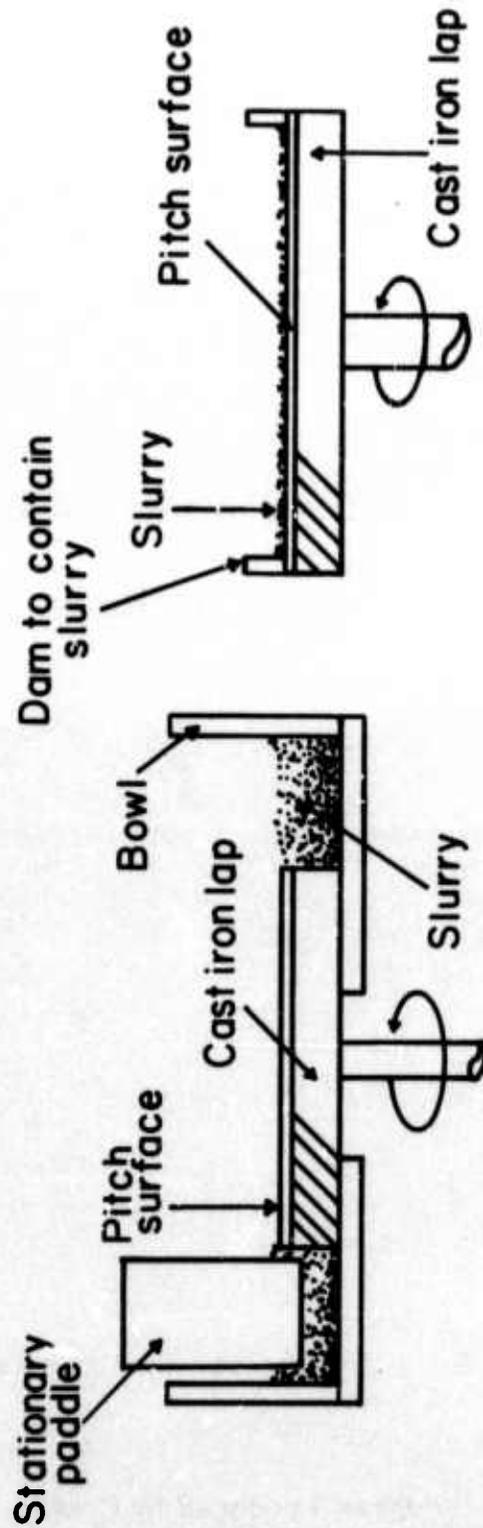


a. B-Alumina Abrasive. 187X



b. Zinc Sulfide Abrasive. 183X

Fig. 13 Surfaces Produced by Conventional and
Transparent Abrasive Polishing of
Potassium Chloride.



a. Used at Raytheon

b. Used at Itek

Fig. 14 Bowl-Feed Polishing Laps - Schematic.

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 experiments were 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. Experiments performed are summarized in Table 8.

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.

The alumina abrasive dramatically improved the surfaces of both calcium fluoride and zinc selenide specimens. Scratches in the zinc selenide surface could be seen in the microscope, but were too fine to photograph clearly. Replicas for electron microscopy have not yet been prepared. The 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 function of abrasive breakdown in the process cannot be determined from the micrographs taken of the abrasive extracted from

TABLE 8

BOWL-FEED POLISHING EXPERIMENTS

Material	Abrasive	Time (hr)	Removal Rate ($\mu\text{m}/\text{min}$)	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 , poly- crystalline	Univ. B (Alumina)	4	None detectable	Surface Improvement
	Barnesite No. 924	3.25	0.01	Degradation
	Tin Oxide	4	NM	Degradation

the bowl after the experiment. The largest particles in a scanning electron micrograph taken of a sample of the final slurry are as large as the largest particles in the as-received abrasive, but the photograph does not contain enough particles to determine the size distribution. Both the surface refinement and the abrasive breakdown must be treated statistically.

The improvement produced by bowl-feed polishing of zinc selenide is demonstrated by the scattering measurements presented in Fig. 15, in which a bowl-feed polished sample is compared with a specimen polished by conventional techniques using the same abrasive type. Both specimens were coated with a 500 angstrom thick aluminum film to eliminate bulk scattering effects. The bowl-feed polished specimen improved by approximately a factor of three at all angles.

Figure 16 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 specimen are associated with surface pits which are probably the result of grinding damage introduced during the earliest processing steps. (Fig. 9) The importance of all the processing steps cannot be overemphasized. As was the case with zinc selenide, no grain boundary relief was produced.

At scattering angles greater than 15 degrees, the calcium fluoride sample, which appeared to be the better one in the microscope, scatters less strongly than the zinc selenide specimen. Whether this correlation will occur generally must be determined by further measurements.

Tin oxide and Barnesite No. 924 abrasives degraded calcium fluoride surfaces during bowl-feed polishing runs. Figure 17 illustrates the scratches and relief polishing produced by Barnesite. Surface structure produced by tin oxide was shown in Fig. 3. These abrasives

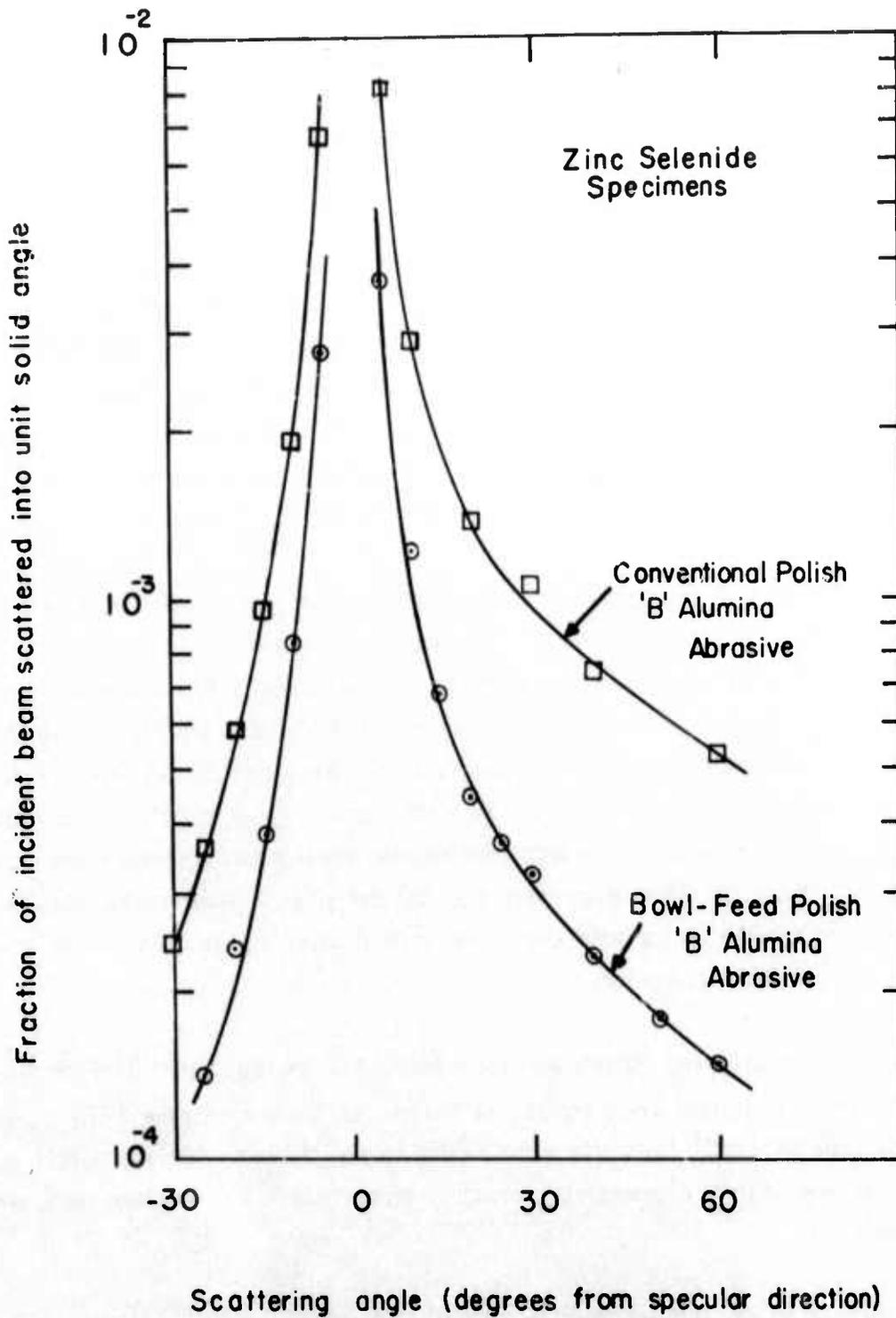


Fig. 15 Fraction of Incident Beam Scattered Into Unit Solid Angle vs Scattering Angle, Zinc Selenide Specimens.

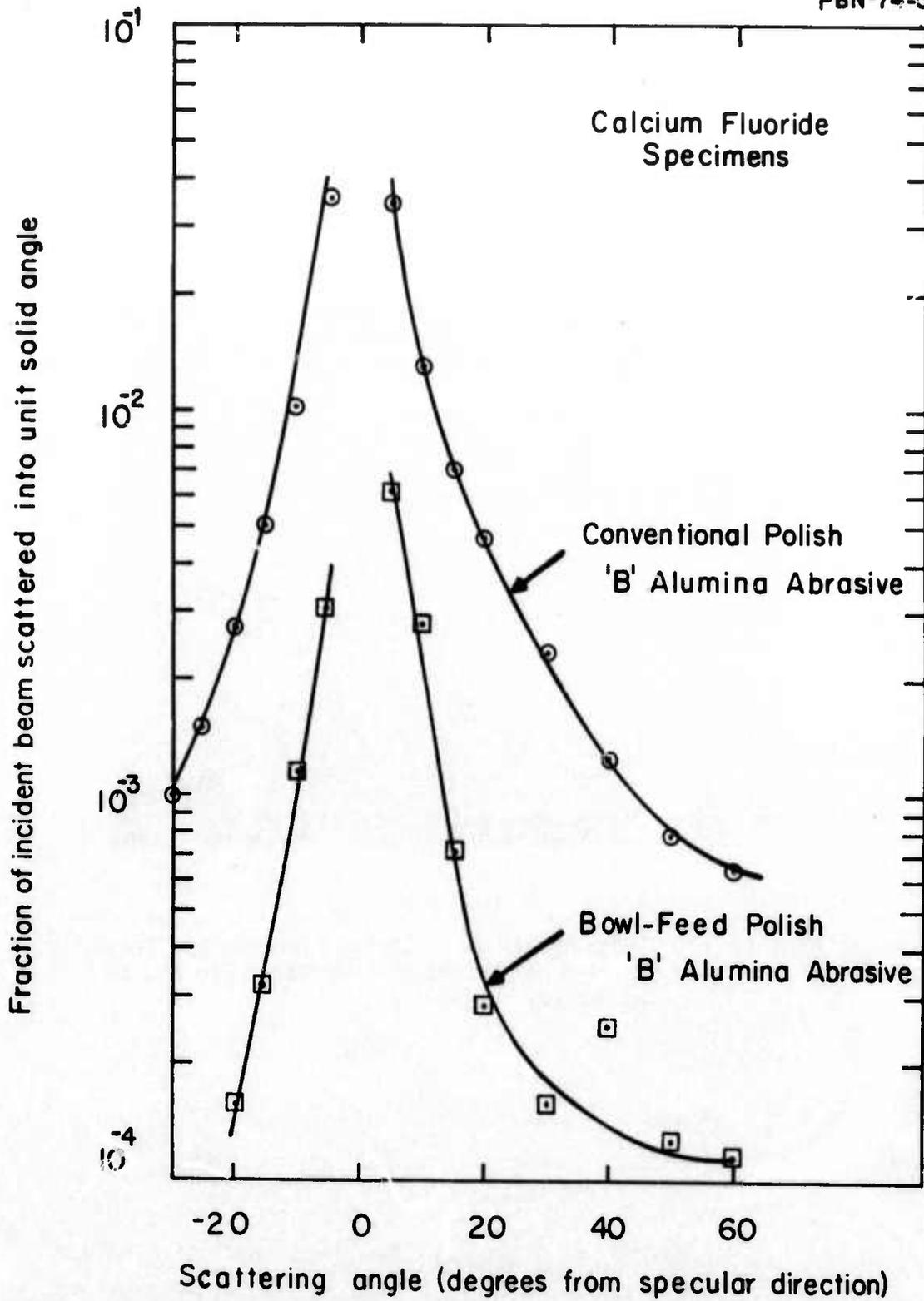


Fig. 16 Fraction of Incident Beam Scattered Into Unit Solid Angle vs Scattering Angle, Calcium Fluoride Specimens.

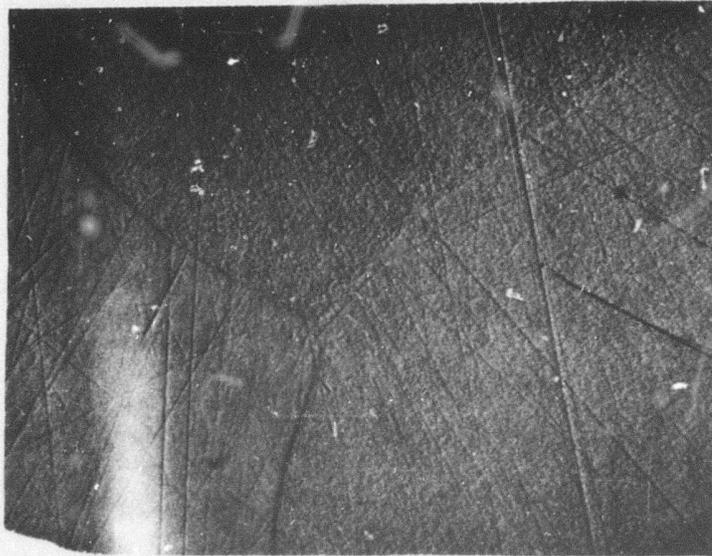


Fig. 17 Polycrystalline Calcium Fluoride Specimen,
Bowl-Feed Polished with Barnesite No. 924
Abrasive. 187X

have smaller particle sizes than the more effective alumina abrasive and are probably more transparent to infrared radiation. To the extent that some abrasive remains on polished surfaces, they would be preferable to alumina.

Itek Corporation has polished a sample of zinc selenide for two hours on the lap shown in Fig. 14b using Linde A abrasive (which is coarser than the abrasive used for bowl-feed polishing at Raytheon). Microscopic examination of the specimens indicated that, while they contained some pits and scratches, the surface quality had improved. Their preliminary scattering results (Fig. 18), however, indicated a slight degradation. The measurements are being repeated at Itek.

2.3.2.1 Conclusions

Bowl-feed polishing of calcium fluoride and zinc selenide has been shown to be an attractive superpolishing technique. Alumina, while not an attractive abrasive choice from an infrared absorption point of view, produces the best surfaces. Attempts to improve the process using alumina are in order; they must include better control of the grinding and rough polishing steps. If residual alumina is shown to be a source of preferential breakdown in bowl-feed polished materials, alternative abrasives will have to be pursued further.

A single laser damage experiment, performed on another project using zinc selenide prepared on this project should be mentioned here.* A 25 centimeter square, 6 millimeter thick zinc selenide sample bowl-feed polished and subsequently chemically polished on one side with a 0.1 percent solution of bromine in methanol was subjected to high 10.6 micrometer power densities in a series of tests performed with the Avco HPL-10 10.6 micrometer laser welder.

This sample withstood an average power of 43 kilowatts per square centimeter for 10 seconds, 250 kilowatts per square centimeter

* Work performed under Contract DAAH01-72-C-0194 by Dr. T. Deutsch of Raytheon Co., together with Dr. D.H. Douglas-Hamilton of Avco ERL.

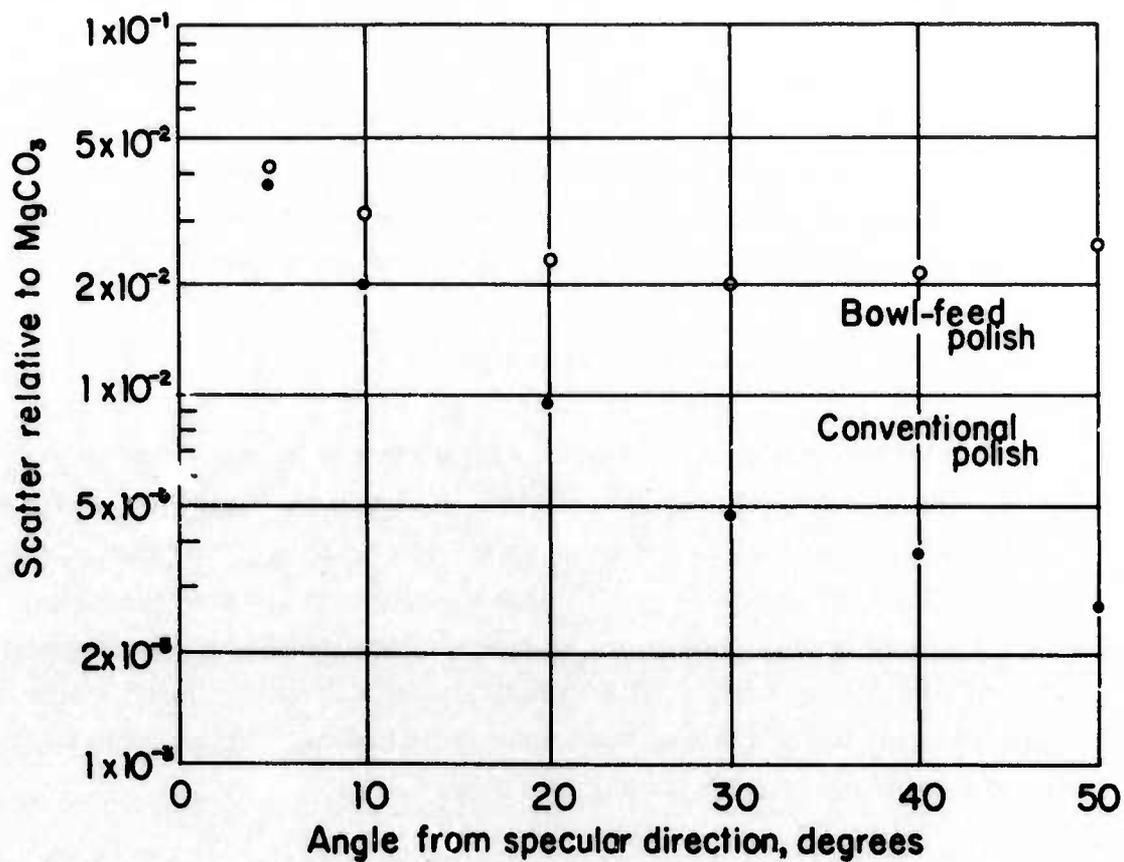


Fig. 18 Scattered Intensity Relative to MgCO₃ Surface vs Scattering Angle, Itek Zinc Selenide Specimens.

for 5 seconds, and failed in 1.4 seconds at power density of 625 kilowatts per square centimeter. Details of the experiment are presented elsewhere.³

Although only a single, preliminary experiment has been performed, it does appear that zinc selenide which has been bowl-feed polished using alumina or an abrasive will pass substantial levels of 10.6 micrometer laser radiation. This result must be pursued further, as must the possibility that embedded alumina will become deleterious after the deposition of an antireflection coating.

2.4 Chemical-Mechanical Polishing

The likelihood that the techniques sought will include some form of chemical etching as a final step has been pointed out above. These methods include chemical polishing, in which the specimens are simply immersed in a suitable solution, and chemical-mechanical polishing, in which the specimens are run on a polishing lap dampened with the corrosive solution which may also contain an abrasive. The moving lap continuously removes reaction products from the specimen and permits the attack to proceed uniformly. Chemical-mechanical polishing is widely used in semiconductor technology to prepare damage-free surfaces on single crystals. When single crystal specimens are polished, the method's most serious deficiency is its tendency to produce convex surfaces which are caused by preferential etching of the edges of the specimens as they are moved through the etchant on the lap surface. This effect can be minimized by proper choice of polishing conditions. Polycrystalline specimens require, in addition, an etchant which will attack all crystallographic orientations uniformly. Nonuniform etching rates produce relief in the surface which cannot be tolerated. In general, the dissolution rate of a crystalline material in a solvent is a function of the crystal's orientation; uniform etchants are the exception rather than the rule among solvents. Our preliminary chemical-mechanical polishing experiments have identified only nonuniform etchants, as detailed below.

2.4.1 Syton polishing

Syton,* an alkaline colloidal suspension of hydrated silica, has been widely used as a chemical-mechanical polishing agent for silicon and gadolinium gallium garnet, a substrate for magnetic bubble domain films. In the former case, it appears to act by alkaline attack of the silicon and removal of the reaction products by the colloidal silica.

Syton polishes polycrystalline calcium fluoride and zinc selenide nonuniformly, producing etched surfaces. In the case of calcium fluoride, the etching preceded significant scratch removal and degraded the surface so efforts to use Syton with calcium fluoride were terminated.

Since the as-received alkaline Syton solution was found to etch zinc selenide too strongly for chemical-mechanical polishing, dilution and acidification were used to slow its action. Dilutions of as much as 10 parts water to one of Syton and neutralization of the solution with acetic acid, however, failed to prevent nonuniform etching of the zinc selenide. Significant grain boundary relief was always produced before the scratches were eliminated. Figure 19 is the microstructure of a zinc selenide specimen polished for 10 hours on a Politex** polishing pad (a synthetic leather material commonly used with Syton) and Syton which had been adjusted to pH7 with acetic acid. The surface is scratch-free, but the grain structure is obvious. This sample was intentionally over-etched to emphasize the bright spots which are "dimples" in the surface. At the highest optical magnifications many of these could be seen to terminate in unresolvable black specks which at first were thought to be second phase inclusions in the zinc selenide.

Since the origin of bulk scattering in zinc selenide is the source of some interest, this sample was examined further in the scanning electron microscope. Figure 20 taken in the SEM at 5000 diameters, shows the feature to be a micropore; this one is approximately two

* Monsanto trademark.

** Geascience trademark.



Fig. 19 Microstructure of Syton-Polished
Zinc Selenide. 183X



Fig. 20 Scanning Electron Micrograph of Pore
Exposed by Syton-Polishing Zinc
Selenide. 5000X

micrometers long and one micrometer wide. The white particles in the photograph are contamination introduced by improper handling of the specimen. Ion beam polishing of zinc selenide (discussed in Sec. 2.5) also produces surface scratches caused by pores, so it appears that these are characteristic of the material used for these specimens and are contributors to its bulk scattering. The material used for this and the ion beam polishing experiments was not high optical quality material; better material should be examined for comparison.

2.4.2 Other chemical-mechanical polishing

The remaining chemical-mechanical polishing experiments performed during the report period are summarized in Table 9.

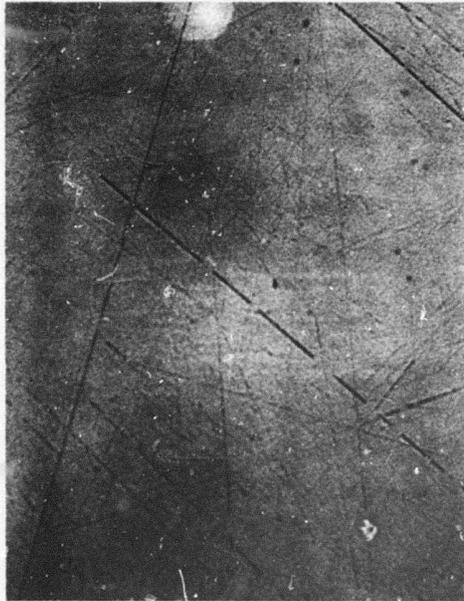
TABLE 9

CHEMICAL-MECHANICAL POLISHING EXPERIMENTS

<u>Material Polished</u>	<u>Etchant</u>	<u>Lap Surface</u>
ZnSe	Br: Methanol	Pellon XP-500
	Conc from 0.05 - 1 percent Br	Politex
	KOH: Ethylene Glycol: H ₂ O	None, used as etch
KCl	Conc HCl	Pellon XP-500
	Methanol	Pellon XP-500
	Ethanol	Pellon XP-500
	Propanol	Pellon XP-500

All solutions etched nonuniformly within two or three minutes except the 0.05 percent bromine-methanol solution used with zinc selenide, which did not react at all. The next higher concentration, 0.1 percent produced the results illustrated in Fig. 21. The sample after a

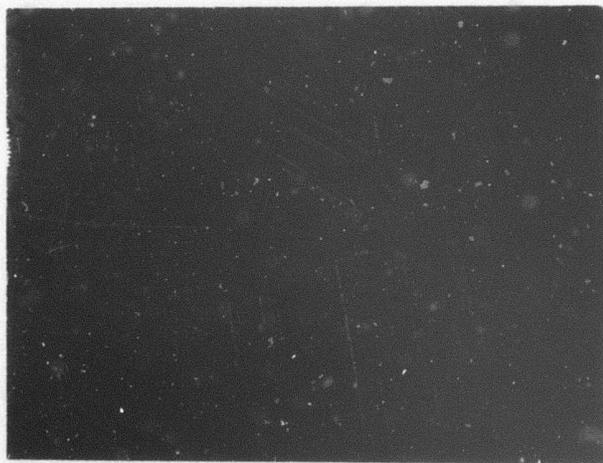
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a. Unetched Specimen



b. After Two Minutes



c. After Four Minutes

Fig. 21

Chemical-Mechanical Polishing Zinc Selenide
by 0.1 Percent Bromine in Methanol Solution.
370X

2-minute chemical polishing (Fig. 21b) has fewer scratches. In the original micrograph however, the microstructure, revealed by nonuniform etching, can be seen faintly. The process is very sensitive to the polishing conditions and is difficult to reproduce. Operator-to-operator variations tend to produce either no etching or beautiful microstructures (Fig. 21c).

A typical chemically-polished polycrystalline potassium chloride surface is shown in Fig. 22. This sample was polished with concentrated hydrochloric acid, a commonly used chemical polish for single crystal potassium chloride. Variations in etch rate and scratch removal are apparent.

2.5 Ion Beam Polishing

The removal of material from solid surfaces by ion bombardment has been shown to be a useful technique for preparation of optical components. It has been used to remove scratches from optical surfaces⁴ and to produce aspheric surfaces in glass. Ion beam polishing of fused silica⁵ and of single crystal sapphire⁶ has been shown to increase their surface laser damage thresholds.

Scratches are removed by an obliquely incident ion beam, as shown in Fig. 23, because the plane surface is removed faster than the scratch wall, which is more nearly normal to the ion beam. Etch rates are typically maximized for beams incident at 60-70 degrees from normal.⁷ Beams incident at 60 degrees have been used successfully to polish fused silica.⁵

The major difficulty to be anticipated when ion beam polishing is used to polish polycrystalline specimens is, as it was with chemical polishing, nonuniform etching of the various crystalline orientations. Again, nonuniform rates are to be expected, the utility of the technique must be determined by experiment.



Fig. 22 **Chemical Polishing of Polycrystalline
Potassium Chloride by Concentrated
Hydrochloric Acid. 370X**

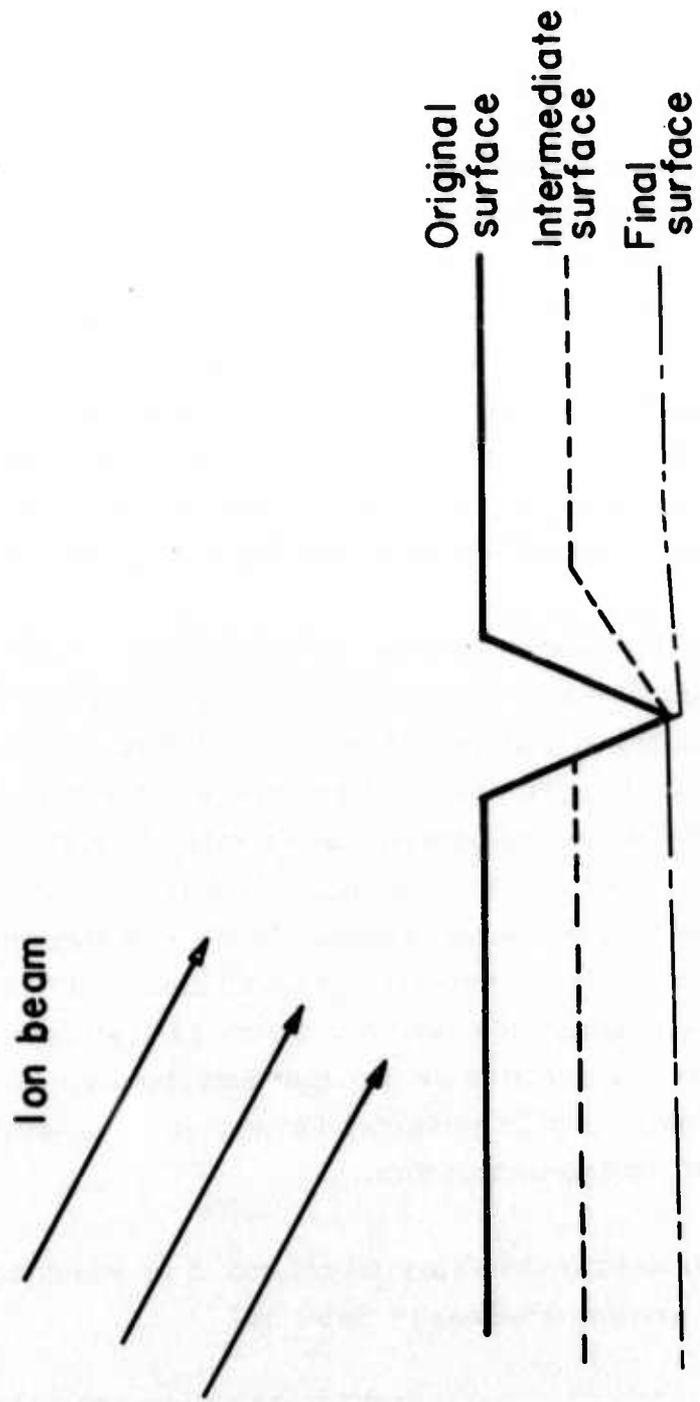


Fig. 23 Scratch Removal by Ion Beam Polishing - Schematic.

To investigate ion beam polishing of the test materials, polycrystalline specimens of zinc selenide, calcium fluoride, and potassium chloride were ion-polished in two experiments conducted at Ion Optics, Winchester, Mass.* Ion beams incident at 60 and 84° from the specimen normals were used.

The equipment used (Ion Optics FM24) 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 duoplasmatron 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 milliamperere beam was used. Lower energies are inconvenient on this equipment.

During the experiment, the rotating table sweeps the samples through the fixed beam. To polish the samples uniformly, the table assembly is periodically stepped forward so that the beam is in effect stepped across the specimens. After one or more complete sweeps, the unit is shut down, the samples are rotated through some angle about their own axes, and the polishing procedure is repeated. This step is necessary because the samples cannot be rotated about their own axes in the equipment. In the experiment performed at 60° incidence the samples were rotated once, by 90°. In the 84° incidence experiment the specimens were rotated by two 120° increments. The gross microstructure of only the zinc selenide, 84° specimen seemed to be effected by the lack of continuous rotation.

Samples used in the experiments and their visual appearance after the polishing are summarized in Table 10.

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

TABLE 10

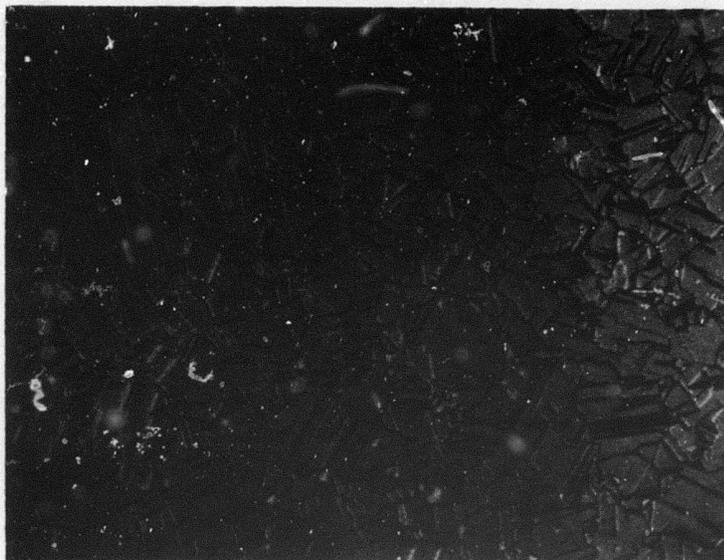
ION MILLING EXPERIMENTS

<u>Angle Of Incidence</u>	<u>Sample</u>	<u>Dimensions</u>	<u>Prior Polishing</u>	<u>Visual Appearance</u>	
				<u>Before Ion Polishing</u>	<u>After Ion Polishing</u>
50°	ZnSe	1½ in. Dia. Disc	Univ. A alumina	highly reflecting	matte
	ZnSe	1½ in. Dia. Disc	Univ. B alumina	highly reflecting	matte
	CaF ₂	1½ × 1 in.	Univ. A alumina	highly reflecting	glossy, but grain boundaries apparent
84°	KCl	1½ × 3/4	Barnesite	matte	matte
	ZnSe	1½ in. Disc	Univ. A alumina	highly reflecting	matte
	CaF ₂	1½ × 1 in.	Univ. A alumina	highly reflecting	matte
	KCl	1½ × 1 in.	Barnesite	matte	matte

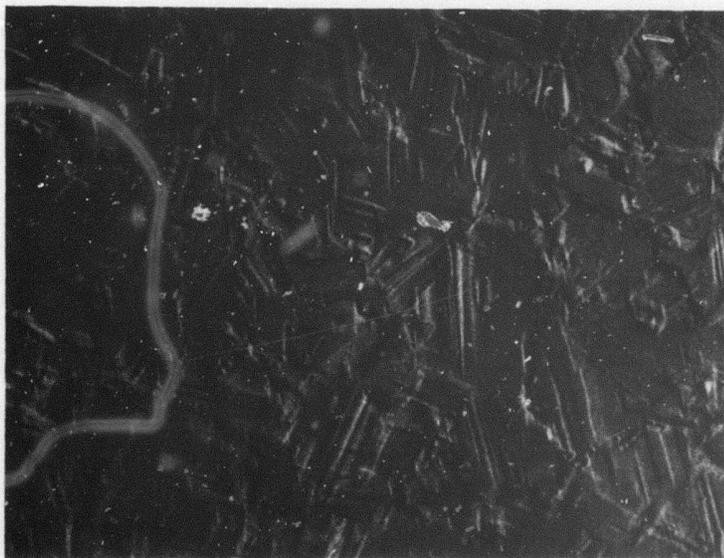
An estimated one micrometer of material was removed from each of the samples except for the poorly polished potassium chloride specimens from which an approximately two micrometer thick layer was removed. A removal rate of 0.55 cubic millimeters per coulomb was assumed at 60° and half that at 84° . These may underestimate the actual rate, but should be correct to within 50 percent. Micrographs of six of the ion-polished specimens appear in Figs. 24-26. The two zinc selenide specimens polished at 60° incidence were essentially identical; only one of them is reproduced here. The polycrystalline grain structure of all the specimens is clearly visible, the relief being greatest for potassium chloride and least for the calcium fluoride specimens. Further, the grain boundary relief is less for the higher (closer to grazing angle of incidence) specimens. This effect is most noticeable with the calcium fluoride specimens (Fig. 25). The specimen etched at the higher angle is photographed at twice the magnification of the other specimen and the grain boundaries are still less distinct. They cannot be seen without the microscope while grains in 60° samples are clearly distinguishable by the unaided eye. Grains in the zinc selenide sample polished at 84° are less distinct than in the other zinc selenide specimens. Unfortunately, until the etch rates are calibrated the lower relief produced at more grazing incidence cannot be attributed to a decrease in the orientation etch rate uniformity. It may simply reflect a lesser material removal.

Scratches remain on all the surfaces, and scratch densities and other etching features are seen to vary from grain to grain. Figure 27 shows scratches and differential grain etching at high magnification on zinc selenide polished at 60 degrees.

The zinc selenide specimen polished at 84° incidence (Fig. 24b) contains, in addition to the grain boundary relief, numerous striations which are oriented at approximately 60° to one another. Recall that this specimen was rotated through two 120° steps during polishing experiments and polished in three steps 120° from each other. At higher magnifications, smaller striae can be seen (Fig. 28). The small striae in Fig. 28 cross broader features at 60° ; many of the smaller



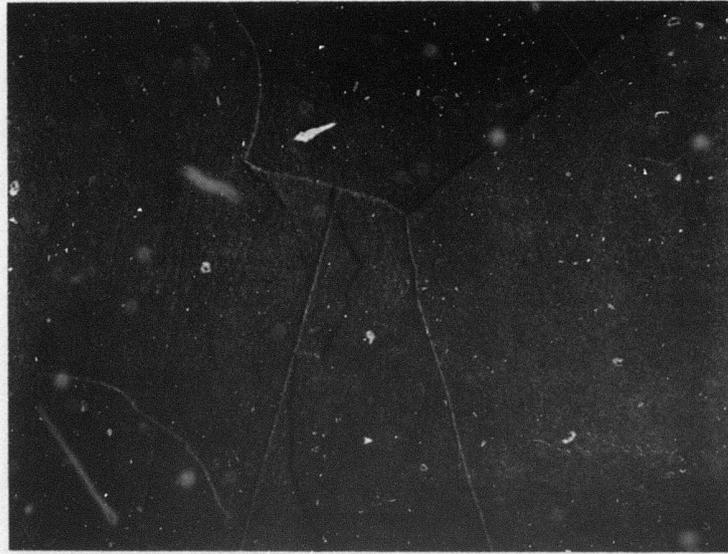
a. 60-Degree Beam Incidence. 187X



b. 84-Degree Beam Incidence. 187X

Fig. 24

Ion Beam Polished Zinc Selenide.

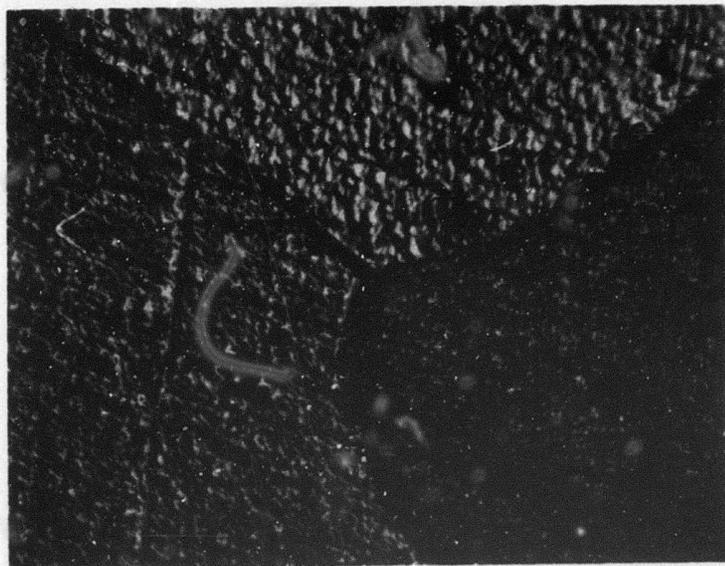


a. 60-Degree Beam Incidence. 378X

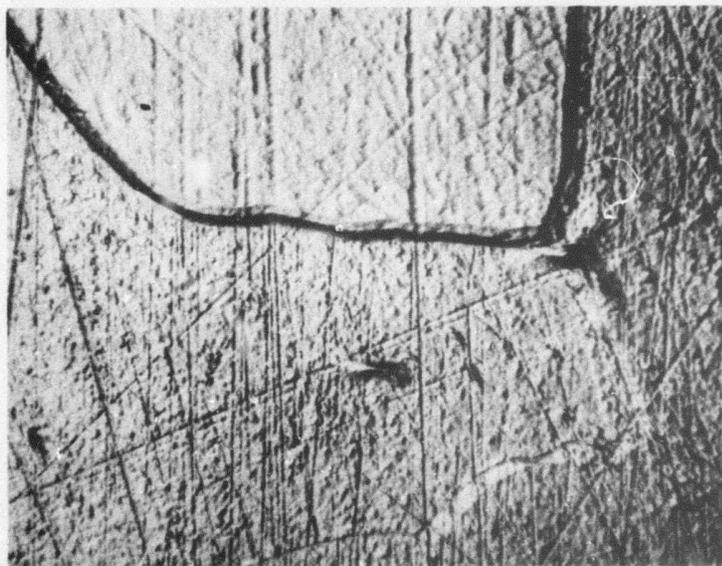


b. 84-Degree Beam Incidence. 187X

Fig. 25 Ion Beam Polished Calcium Fluoride.



a. 60-Degree Beam Incidence. 378X



b. 84-Degree Beam Incidence. 93X

Fig. 26 Ion Beam Polished Potassium Chloride.



Fig. 27 Remnant Scratches on Ion Beam Polished
Zinc Selenide (60° incidence). 766X

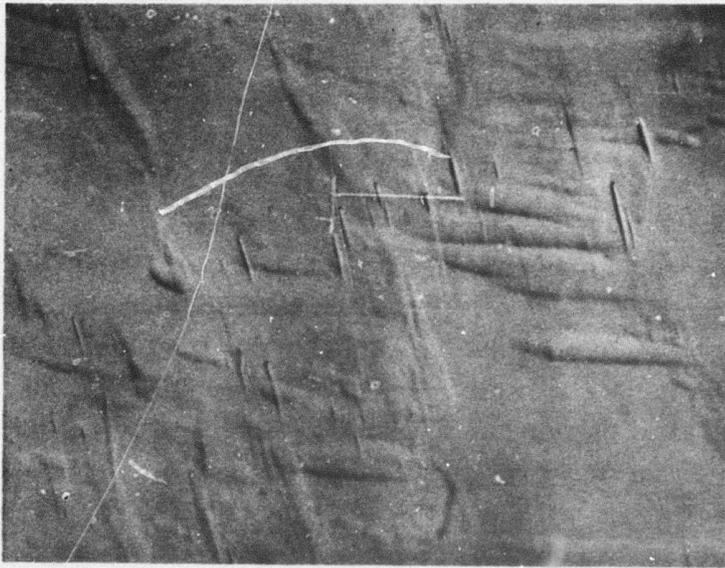


Fig. 28 Striae on Ion Beam Polished Zinc Selenide (84° incidence). 766X

striae contain a black speck at the upper end. The features are too small to be distinguished as ridges or grooves in the optical microscope. Ridges of this sort might be caused by embedded particles of more slowly etched material shielding the zinc selenide behind them from the grazing incidence beam. Grooves, on the other hand, would be produced by small pores on the surface. A scanning electron micrograph of one of the features (Fig. 29) shows it to be a groove caused by a pore, the remnant of which is visible at the left end of the groove. These are evidently the pores in the material which are also revealed by Syton polishing. The broad striae in Fig. 28 are probably remnants of smaller ones produced during one of the first two polishing intervals; the small striae were probably produced during the final interval.

2.5.1 Conclusions

Ion beam polishing produces grain boundary relief without eliminating scratches in the polycrystalline materials studied. It does not appear to be an appropriate technique for surface finishing if material removal on the order of one micrometer is required. It may, however, serve as a final cleaning step prior to optical film deposition if only a few hundred angstroms are removed.

Ion beam polishing of zinc selenide at grazing incidence makes visible pores which are probably present in the bulk material as defects.



Fig. 29 Scanning Electron Micrograph of Ion Beam Polished Zinc Selenide. 7000X

3.0 ACKNOWLEDGMENTS

Experimental work in the polishing laboratory was performed by Messrs. R. Cosgro and F. Taylor. The Itek program was conducted under the supervision of Dr. W.P. Barnes; Ion Beam Polishing was conducted by Mr. John Gale, Ion Optics Company, Winchester, Mass. Surface scatter measurements were done by Dr. T. Kohane, scanning electron microscopy by Dr. O. Guentert. Others participating in the program include Dr. P. Miles and T. Deutsch and Mr. F. Spooner.

4.0 FUTURE PLANS

During the next three months, the program emphasis will be as detailed below:

- a. Surface characterization will be put on a more quantitative basis through expanded use of scattering measurements. Instruments at Itek and Raytheon will be put on a common basis. Surfaces produced by various suppliers will be compared.
- b. Conventional polishing experiments will emphasize the elimination of grinding damage in the specimens.
- c. Superpolishing experiments at Raytheon will emphasize optimization of bowl-feed polishing parameters. Itek will begin continuously-recycled abrasive polishing of zinc selenide.
- d. Precipitation of transparent abrasives will begin, they will be evaluated as abrasives for potassium chloride. Grinding of potassium chloride with transparent abrasives will be explored.
- e. A major effort will be made to develop chemical polishes for all materials.

In approximately three months two new project areas will be added to continuing efforts in the first five areas. These are:

- f. Extension of polishing effects to larger sample sizes. Six-inch diameter specimens of calcium fluoride and zinc selenide will be used to study scale-up problems.
- g. Laser damage experiments will begin.

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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

<u>Comparison</u>	<u>Difference of Means</u>	<u>Standard Error of Difference</u>	<u>Degrees of Freedom</u>	<u>t</u>	<u>Probability of Chance Occurrence</u>
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

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

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.