

UBSIR 74-507

AFML-TR-74-56

MERCUROUS CHLORIDE POLARIZER MATERIAL

TECHNICAL REPORT AFML-TR-74-56

1 JUNE 1974

Approved for public release; distribution unlimited.

**AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433**

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This technical report has been reviewed and is approved for publication.

Vincent L. Donlan

Vincent L. Donlan
Project Engineer

FOR THE COMMANDER

for Paul W. Elder, Maj USAF

William Goldberg, Lt. Col., USAF
Chief, Laser and Optical Materials Branch
Air Force Materials Laboratory

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFML-TR-74-56	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Mercurous Chloride Polarizer Material		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report 15 June 73 - 15 Dec 73
		6. PERFORMING ORG. REPORT NUMBER NBSIR 74-507
7. AUTHOR(s) Richard Forman, William S. Brower, Harry S. Parker		8. CONTRACT OR GRANT NUMBER(s) F33615-73-M-6752
9. PERFORMING ORGANIZATION NAME AND ADDRESS National Bureau of Standards Washington DC 20234		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS PE61101F JO# ILIR0040
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Materials Laboratory Air Force Systems Command Wright-Patterson AFB, OH 45433		12. REPORT DATE 1 April 1974
		13. NUMBER OF PAGES 25
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) mercurous chloride; polarizer material; visible; infrared		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This contract report covers a feasibility study on the potential use of mercurous chloride crystals for construction of prism polarizers, primarily for the infrared region of the spectrum. In particular, the research has consisted of crystal growth from the vapor phase and optical characterization of the absorption, dichroism, and birefringence. Crystal growth has been performed in quartz or Vycor ampoules sealed off under a pressure of 10^{-5} torr or better. Crystals are grown in a vertical modified Bridgman furnace by vapor transport. Repeated regrowth has been		

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

found to produce a continuous improvement in clarity, the best samples being virtually colorless. The growth rates used of 2 mm/day in tubes of 17 mm inside diameter have been found to be satisfactory for producing the crystals used to date, but strain patterns and a tendency to polycrystallinity indicate that slower growth rates should be attempted. Conditions for growth have not yet been optimized, but reasonably good growing conditions have been delineated.

Single crystal samples have been oriented by Laue back-reflection techniques and measurements made of optical absorption, dichroism, and birefringence. Proper sample handling procedures have been determined to minimize thermal shock and thermal etching. The index of refraction has been measured at selected wavelengths, and calorimetric absorption studies have been performed at AFML on some of the samples produced.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

FOREWORD

This report covers work performed under Delivery Order F33615-73-M-6752 and covers the period 15 June 1973 to 15 December 1973. Vincent L. Donlan, AFML/LPL, Wright-Patterson AFB, Ohio 45433, was the project engineer.

This research was sponsored by AFML Laboratory Director's Funds.

TABLE OF CONTENTS

SECTION	PAGE
I. Introduction	1
II. Research Conducted	3
A. Crystal Growth	3
B. Sample Preparation	10
C. Optical Properties	19
III. Suggestions for Further Developmental Work . .	22
A. Crystal Growth	22
B. Chemical and Physical Properties	23
IV. References	25

MERCUROUS CHLORIDE POLARIZER MATERIAL

I. Introduction

The purpose of this research was to determine whether mercurous chloride was a suitable material for construction of prism polarizers for the infrared region of the spectrum. At the present time, polarizers suitable for use with high power lasers in the infrared region of the spectrum either do not exist or are of limited utility. This statement should properly be qualified, as Rochon or Wollaston prisms could be fabricated from a number of materials. These types of prism polarizers suffer from the problem that the ordinary and extraordinary rays both emerge from the same surface with only a small angular displacement between them. Extant infrared polarizers are not easily applied to all experiments.

The first type utilizes Brewster angle reflection to remove one of the beams. This is the principle used in the pile-of-plates polarizer, where the transmitted beam through the stack is used. By utilizing materials with high index of refraction, such as silicon or germanium, polarizers can be made to operate from the reflected beam. In general, with polarizers which utilize Brewster angle reflection, a number of optical surfaces are used at reasonably large angles of incidence. To obtain a high quality output beam, all of these optical surfaces must be of very high optical quality, which is usually difficult to achieve.

The second method of producing polarized infrared light, which can be used if power densities are low enough, is the so-called wire-grid polarizer. In this case, the polarized light is produced by an essentially transmission-type diffraction grating. In order to obtain a high degree of polarization, the spacing of the grating must be small compared to the wavelength of the light. This means that the grating spacing must be exceedingly small (~ 3000 lines/mm). Gratings with these fine spacings have relatively poor optical quality at the present time. In addition, the thin metallic "wires" which comprise the grating can only handle relatively small amounts of incident power without destruction of the wires.

The most favorable method for producing polarized laser beams would be to use a Glan-type prism polarizer in which one polarization appears as a beam at $\sim 90^\circ$ to the incident beam while the other is transmitted directly through. Generally, an absorbing material is placed to absorb the $\sim 90^\circ$ reflected beam. To produce polarizers of this type, one uses uniaxial crystals with substantial birefringences. At the present time, the only material which has proved practical in prism polarizers of this type has been calcite. Due to lattice absorption, calcite polarizing prisms are not usable beyond $2.3 \mu\text{m}$ in the infrared.

A further problem exists in producing laser quality prisms for the near infrared from calcite, and that is the availability of single-crystal calcite. All calcite prisms produced to date have been made from the naturally occurring mineral. The known deposits of this mineral are now almost exhausted of materials of laser quality, and large efforts have been devoted to producing the material artificially. To date, to our knowledge, this effort has had extremely limited success with only very small crystals produced.

With the above considerations in view, we undertook to examine the literature for other promising uniaxial crystals with sufficient birefringence to make possible the manufacture of Glan-type polarizers. After a literature search, we decided that mercurous chloride appeared to be a good candidate, though there was a paucity of data on its physical properties. The birefringence was enormous, the powdered material was reported to be yellowish-white, and it was composed of heavy-enough atoms to expect transmission in the infrared to wavelengths at least the vicinity of the important CO₂ laser at 10.6 μm . A hazardous method of crystal growth has also been reported in 1970 which was related to the method we had used earlier for the growth of ammonium chloride from the vapor phase.

Small single-crystal samples were produced in our laboratory by a vapor growth technique and the optical transmission range was measured. These measurements showed that the material was transparent from 0.4 μm to $\sim 16 \mu\text{m}$ with no absorption bands visible within these limits. At this point, the contract was initiated. Its objectives were, first, to develop techniques of crystal growth, hopefully suitable for scaling up to larger size crystals, and secondly, to characterize the optical properties of pure samples, including measurement of the index of refraction.

In summary, the objectives of the contract have been achieved. A technique of crystal growth has been found which should allow boules of several centimeters diameter by tens of centimeters in length to be produced. Further, optical absorption at 10.6 μm in these crystals has been found to be less than 0.02 cm^{-1} ; a thorough evaluation of the effects of impurities could significantly lower this value. Measurements of index of refraction have demonstrated feasibility of construction of Glan-type prism polarizers with transmission from 0.4 μm to greater than 10.6 μm .

By way of comparison with other potential artificial materials for polarizers, mercurous chloride appears to have many advantages. Crystal growth occurs at low temperatures from the vapor phase, a method which is expected to produce material of high purity and high optical quality. No obvious stoichiometry problems have been encountered, in sharp contrast to many chalcogenide materials which

could be possible candidates. Further, the crystals appear to be quite inert when pure, and are capable of holding a good optical finish. The indices of refraction are relatively low for infrared materials, which is favorable for dielectric coatings to reduce reflection losses. Optical transmission over the entire visible region of the spectrum is especially useful as mercurous chloride optical elements could easily be examined, for homogeneity for example, at high sensitivity in an interferometer operating in the visible region; many infrared materials can be examined only in the infrared region of the spectrum, and apparatus for such examinations are not generally available.

There appear to be no obstacles to production of laser quality polarizing prisms from mercurous chloride crystals. Over their transparency region they should be superior to prisms made from other known materials, as the higher birefringence means that the finished prisms will have very large acceptance angles. Further work is, of course, required to make this promise a reality.

II. Research Conducted

A. Crystal Growth

As mercurous chloride sublimes easily, numerous experimenters have reported on the growth of millimeter-sized crystals by this technique. Only one literature reference exists which is devoted primarily to crystal growth, the paper of 1970 by Barta. He reports the growth of mm-size crystals from sealed ampoules. He determined that, for his method, optimal growth occurred at a temperature of 480°C, which corresponded to a pressure of 15 atm. inside the growth tube. Growth by this technique then was obviously not simply scalable up to larger sizes as the ampoules would burst under the high pressure developed.

We had encountered a similar situation in some of our earlier work in the growth of single-crystal ammonium chloride. In this earlier work, we had resorted to vapor transport in a Bridgman-type apparatus to somewhat reduce the growth temperatures and pressures required. Three different geometries have been attempted for mercurous chloride growth as well as several different furnace profiles.

All of the crystal growth has been performed using commercial powdered materials for the starting charge. We have examined the products of a number of manufacturers with the results summarized in Table I. In each case, the as-received material was sealed in a Vycor* tube evacuated to pressures of less than 10^{-5} torr and then rapidly sublimed to the top of the tube in a vertical gradient furnace with the hot zone at 350°C and the cooler top at 340°C. The fibrous mass at the top was then used for a slow controlled growth run to produce a single crystal. As the table indicates, best results were obtained from the materials supplied by Cerac/Pure*. Chemical analysis of the final grown crystals has not been performed.

Table I. Typical analyses of as-received mercurous chloride powder from various suppliers.

Element	1	2	3	4	5	6	7	8
Ag	.0001-.001	-	-	.001 -.01	.001 -.01	-	-	-
Al	-	-	-	-	.003 -.03	.001 -.01	-	-
Ca	.0001-.001	.0001-.001	.0001-.001	.0001-.001	-	.0001-.001	.0001-.001	.001 -.01
Cu	.0001-.001	.0001-.001	.0001-.001	.0001-.001	.0001-.001	.0001-.001	.0001-.001	.0001-.001
Fe	< .001	< .001	< .001	< .001	< .001	< .001	< .001	< .001
Hg	> 10.0	> 10.0	> 10.0	> 10.0	> 10.0	> 10.0	> 10.0	> 10.0
Mg	.0001-.001	.0001-.001	.0001-.001	.0001-.001	.0003-.003	.0001-.001	-	.0001-.001
Si	.0003-.003	.0003-.003	.0003-.003	.0003-.003	.001 -.01	.0003-.003	.0003-.003	.0003-.003

Note: >, greater than; <, less than; values given in weight percent.

Using the prepurified starting material described above as a charge, final growth was performed in highly evacuated, specially prepared ampoules. In figure 1, we show the ampoule geometry used for the early experiments. These ampoules were charged as shown in the figure and then lowered out of the furnace shown in figure 2 at a rate of approximately 2 mm/day. The geometry of this furnace was such that the sample could not be viewed during growth, but from variation of temperature and pulling rates the optimal growth conditions were found to be 2 mm/day or less through a temperature gradient of 10 to 15°C. The larger sample tubes shown in figure 3 were then prepared and the same furnace used for growth runs with these tubes. With these larger tubes the optimal conditions for growth were found to be 1.5 mm/day with a 15°C gradient.

A persistent difficulty, which we were never able to correct, was found in using ampoules of this shape, and, along with other factors, led us to abandon this geometry. In every case, we found that the crystals became entrapped in the lower portion of the growth tube in the region of the ring seal. While this appears to be a simple glassblowing problem, requiring an expanding taper at this point, our glass shop was not successful in this endeavor. Further difficulties were encountered with charge material occasionally getting into the growth zone during filling and with restrictions imposed on the thermal profiles of the oven by the geometry of the ampoule.

Notwithstanding all of the above, this method produced high quality boules, often with well developed vapor growth faces on the tops of the boules. While the samples produced in the small ampoules were relatively strain free, the larger size boules were quite strained, probably because of a lack of annealing after growth. The growth geometry used did not automatically produce annealing, and before the annealing problem became obvious, a change in growth geometry was initiated.

Several generations of ovens were manufactured to perform the crystal growth in an inverted Bridgman geometry. The last design is the only one shown and is described by figure 4(a). In this oven, crystal growth occurs by moving the tube upward through the furnace. The furnace has been designed so that the hot zone is uniform with a temperature of 390°C with an abrupt gradient of 10°C in going to the lower temperature top zone followed by a relatively long top zone to provide annealing. Actual growth conditions in the tube correspond to pressures of approximately 1.2 atm. so that no problem in scale-up is anticipated. Growth rates of 2 mm/day have been successful, requiring growth runs of approximately two weeks for a charge of 50-60 gms. The furnace temperature profile is shown in figure 4(b).

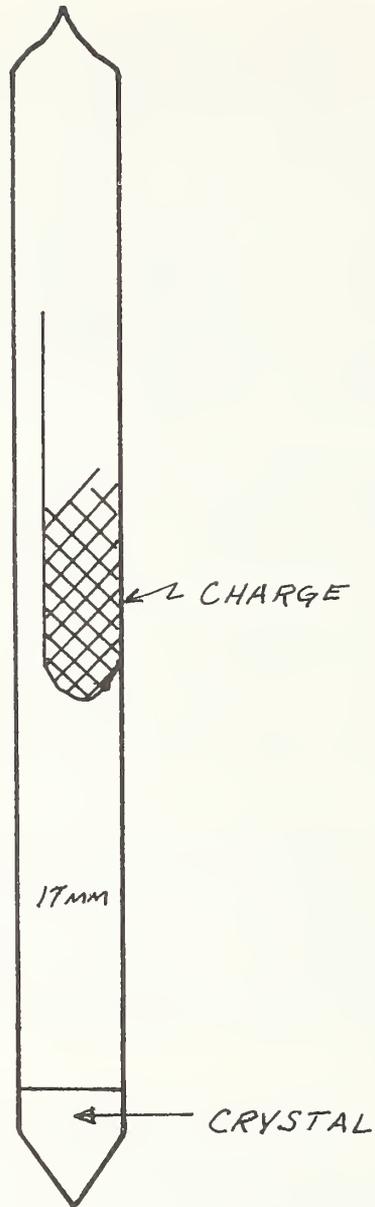


Fig. 1. Early crystal growth ampoule geometry. Material is transported from upper container to bottom of tube as ampoule passes through temperature gradient.

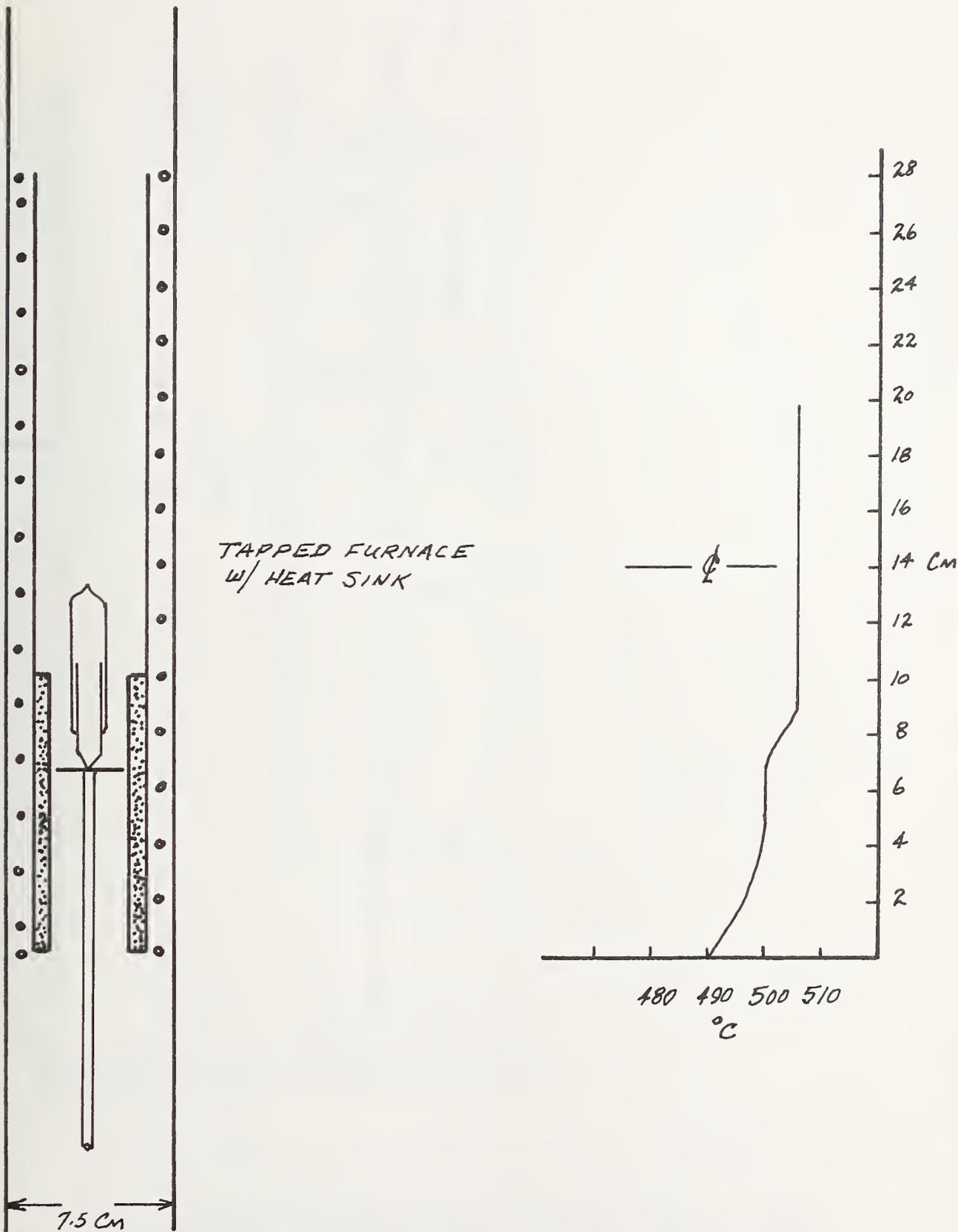


Fig. 2. Improved early furnace design showing temperature profile.

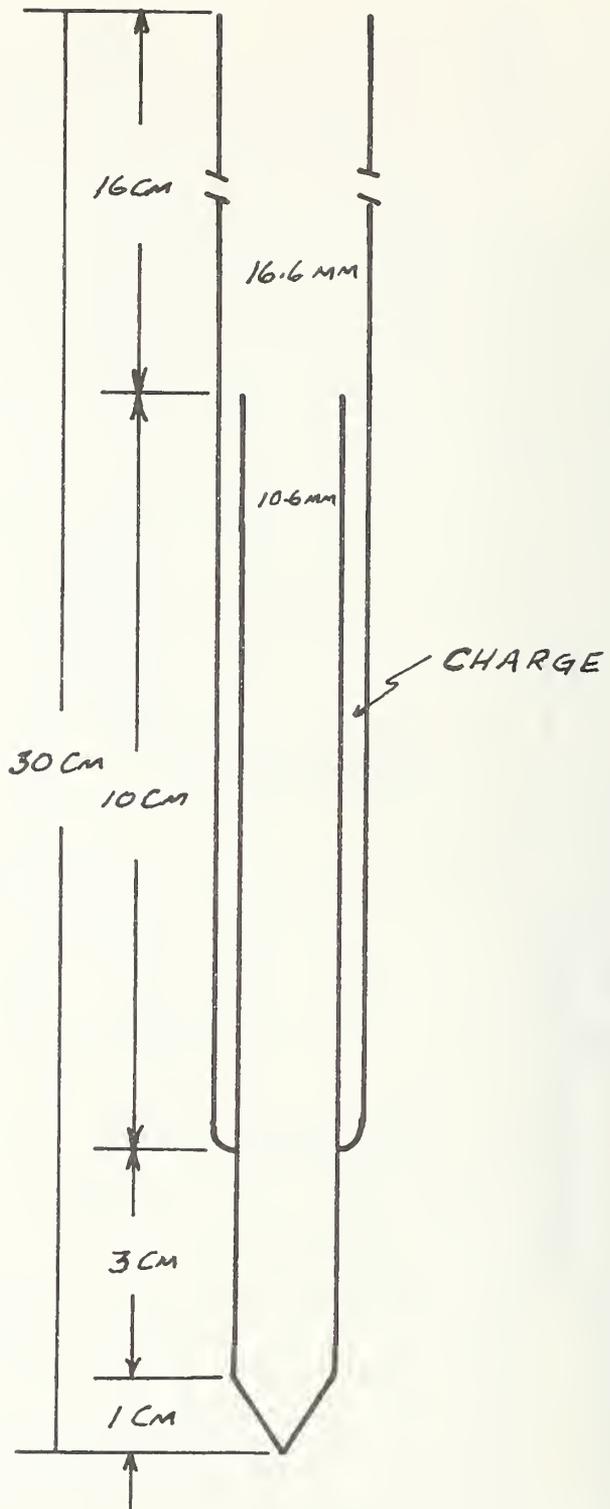
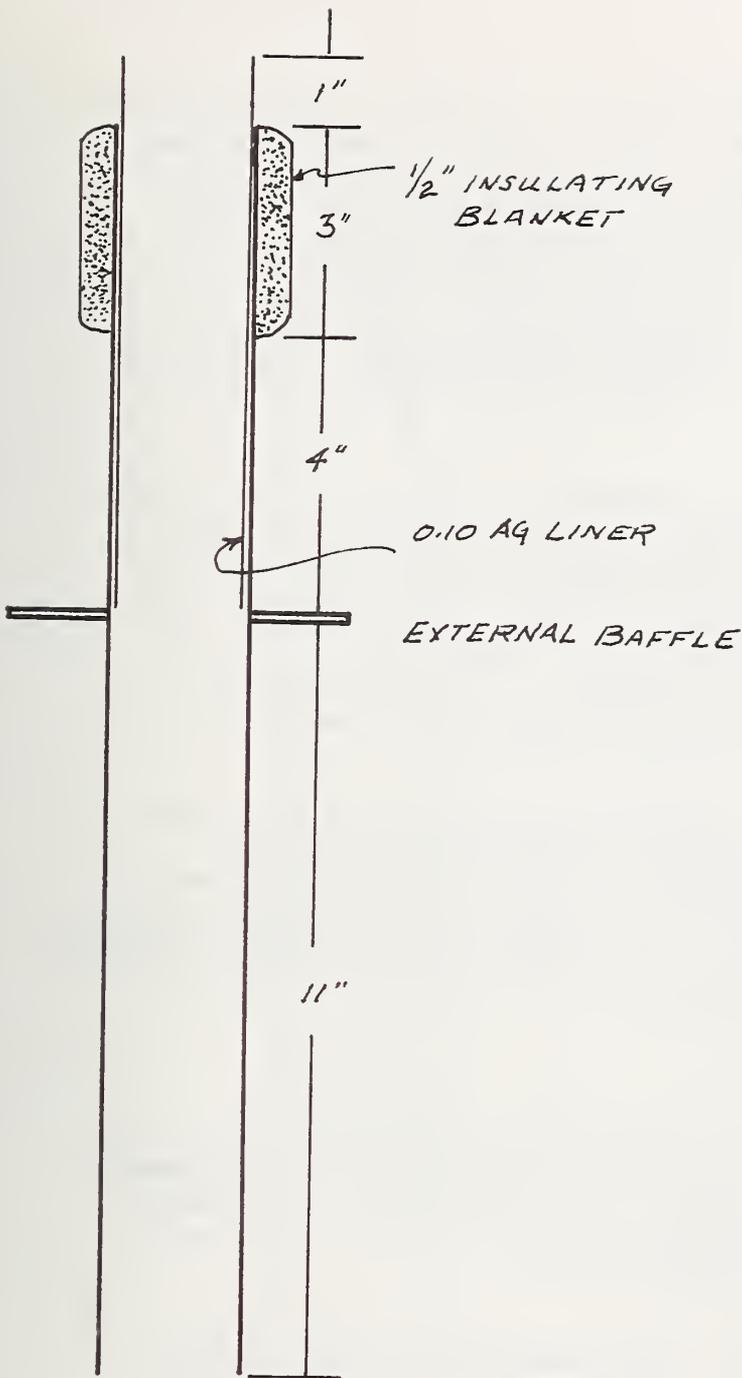


Fig. 3. Larger improved growth tubes used with the furnace of Fig. 2.



25mm ID VYCORTUBE
 UNIFORMLY WOUND 8 TURNS/IN
 18 GA. NICHROME

FIG 4a

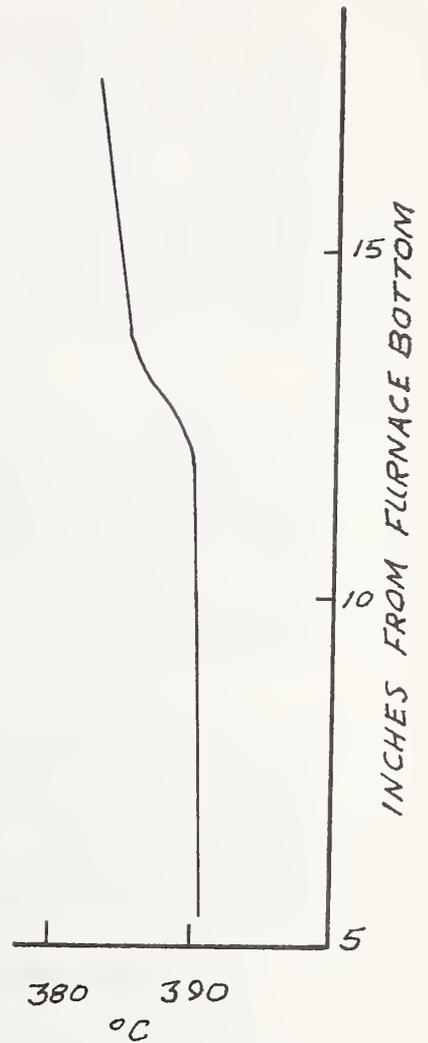


FIG 4b

Fig. 4. (a) Final furnace design for lower temperature growth (Bridgman). (b) Temperature profile of final furnace.

Two differently shaped ampoules have been used for crystal growth in the inverted Bridgman furnace and are shown in figures 5(a) and 5(b). Most of the crystal growth runs were made in the 5(a) geometry, but near the end of the contract we switched to the 5(b) geometry to attempt to avoid the small-angle grain boundaries found in many samples. In this geometry, the narrow neck should select out one crystallite from the initial starting growth for a seed for the final large growth section. This technique has proved successful in the initial runs, but there is an indication that somewhat slower growth rates would be more favorable. Typical finished boules are shown in figures 6 and 7.

In all of the growth runs, a residue has remained at the bottom of the tube. If the same material is multiply regrown, the amount of residue continuously decreases from run to run and the finished crystals become progressively less yellow, with two regrowths being sufficient to produce material which is completely colorless. The first residue occasionally contains free mercury, but the major portion of the residue is a black fluffy material. The black residue is amorphous to X ray, and a qualitative analysis performed on this residue showed the presence of iron and silver.

In conclusion, a crystal growth technique has been developed which is suitable for scaling up for production of large size boules. No quantitative measurements of impurities have yet been attempted. Further work should be performed to optimize the crystal growth conditions. In addition, there should be quantitative consideration of the impurity problems and strategies developed to lower the effects of any undesirable impurities.

B. Sample Preparation

Samples are removed from the fused silica ampoules by scratching and breaking the glass far away from the grown crystal and the samples then simply shaken out of the tube. In the case where the geometry of figure 5(b) was used, a second break is made in the lower neck and both crystal and glass are cracked off here.

Examination of the crystals by eye is performed next to see whether any cracks are present. This examination is quite deceptive as small cracks near the surface often appear to go deep into the crystal due to the large index of refraction of the material. Inspection of the boules between crossed polarizers is generally worthless because of the curved surfaces.

The next step in sample preparation is X-ray orientation of the samples. Our technique has been to use back-reflection Laue photographs. From numerous disheartening experiences, we have found that, in handling the whole boules, great care must be taken during heating and cooling.

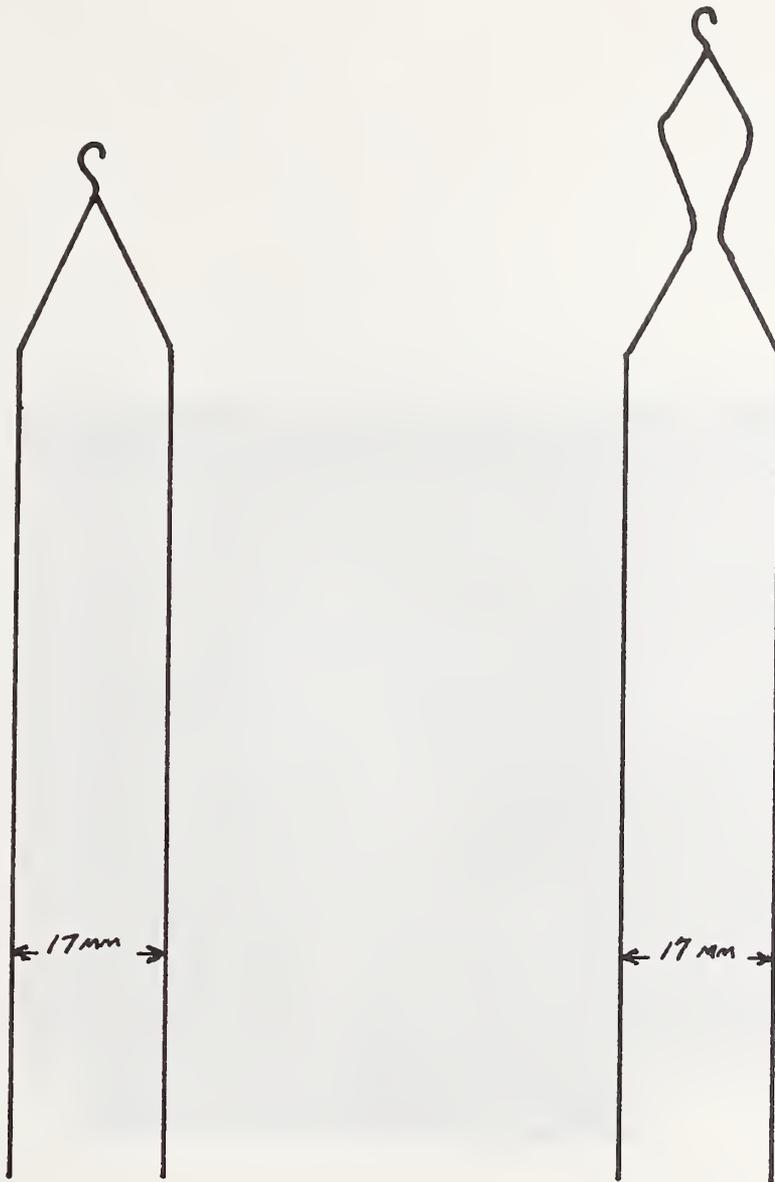


FIG 5a

FIG 5b

Fig. 5. (a) Early inverted Bridgman furnace ampoules.
(b) Final ampoule design for seed selecting growth.



Fig. 6. Early boule of diameter approximately 17 mm grown in tube of type 5(a).

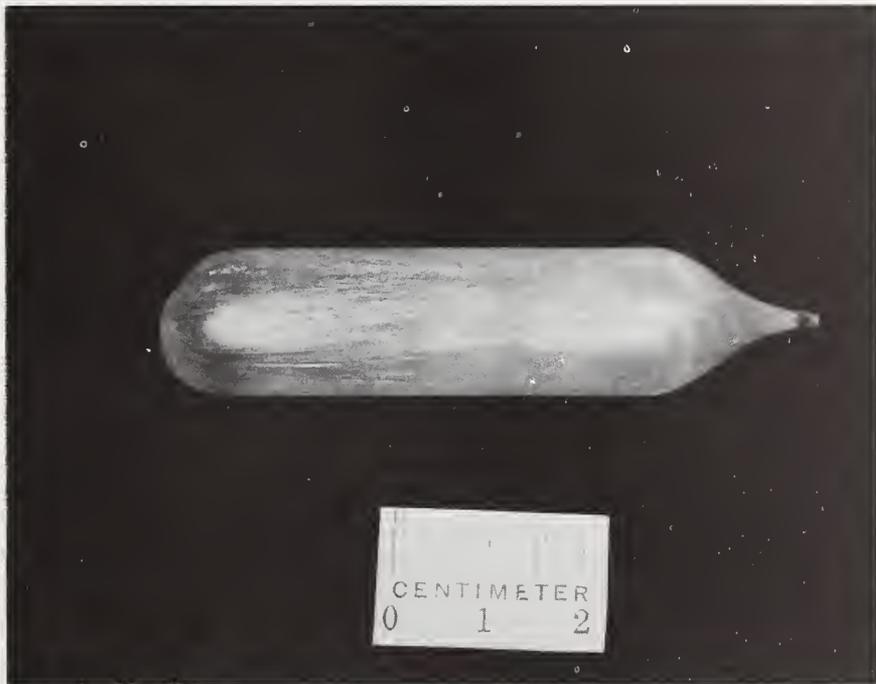


Fig. 7. Late boule grown in tube of tube 5(b) dimensions as shown on photograph.

Our technique had been to place the boule on top of a brass X-ray goniometer sample holder, whose surface was covered with glass, on a cold "hot-plate" and then heat the hot-plate and glue the sample using glycol phthalate. Invariably this technique produced cracked boules. While it is possible that the cracking was caused by the presence of small-angle grain boundaries in the crystals, the unevenness of heating was clearly undesirable. We finally arrived at the method of placing the sample and holder in the center of a large cold oven and slowly (~ 1 hour) bringing the temperature up to $\sim 100^\circ\text{C}$; the oven was then shut off, the door opened, and the mounted sample allowed to cool slowly in the oven (~ 2 hours). The sample was then mounted on the X-ray goniometer.

All of the X-ray pictures were taken with a copper target tube operating at 35 kV and 15 ma at 3 cm distance using Kodak* screen type film with a camera containing a fluorescent screen. A typical photograph for orientation required exposures of 30 minutes. In taking these photographs, it was important not to damage the surface of the crystal, because, with a material as soft as mercurous chloride, this often would greatly degrade the X-ray photograph. The best photographs were obtained from the vapor grown faces. If X-ray photographs had to be taken of cut faces, it was necessary first to heavily etch the surface (see below). When using the screen type film, X-ray fluorescence produced considerable fogging. This problem could be alleviated by reducing the tube voltage to ~ 25 kV and increasing the exposure time to approximately 45 minutes, but generally the fogging was not severe enough to prevent sample orientation.

The X-ray pictures shown in figures 8, 9, and 10 were taken specifically for reproduction and were taken under different conditions. In figure 8, we show the c-axis (001) in an exposure of 60 minutes with screen film. This particular photograph was taken on a vapor grown face, which is in part responsible for its high quality. Figures 9 and 10 were taken on etched cut faces and show the a-axis (100) and (110)-directions, respectively. These photographs were taken with Kodak* Medical No-Screen Film at 25 kV and 15 ma with exposures of approximately two hours. The presence of some broadened spots is not indicative of grain boundaries or strain but is a manifestation of large thermal diffuse scattering. The correctness of the indexing of the X-ray spots has been verified by an X-ray precession photograph of one of the planes. Without the precession pattern, the indexing of the (100) and (110) patterns is somewhat ambiguous.

After the crystals have been oriented, they are cut on the X-ray goniometer. Our early attempts were to cut the samples using a diamond wafering saw with kerosine as a lubricant. This invariably produced fracturing of the samples. We then switched to an abrasive slurry wire saw which was successful but quite slow. Using a 10-mil wire and 600-mesh boron carbide abrasive water-glycerine (1:4) slurry, cutting through the diameter of a boule (17 mm) required



Fig. 8. Laue X-ray photograph of [001] surface.



Fig. 9. Laue X-ray photograph of [100] face.
The direction of the c-axis is as shown.



Fig. 10. Laue X-ray photograph of [110] surface. The direction of the c-axis is as shown.

approximately 20 minutes. Preliminary experiments indicated that a hot platinum wire could be used as a saw but this technique was not pursued.

Cut samples were then mounted on a brass polishing holder using glycol phthalate. With large samples, for safety we have resorted to mounting and dismounting in our oven. With smaller samples, the conventional technique of heating on a hot-plate was satisfactory. Dismounting was accomplished in the same manner as mounting with one change. The temperatures involved for the mounting glue we used were high enough to produce thermal etching of polished surfaces. After trying various coatings for the exposed polished surfaces, we found that glycol phthalate dissolved in acetone provided suitable protection. Most other coatings which we tried were not easily cleaned from the surface later; the material is too soft to allow any rubbing of a polished surface. Soaking of finished samples in clear acetone left the sample apparently perfectly clean.

Because of the possibility of thermal damage during polishing, all of our polishing and grinding has been done with water lubricant. For rough grinding, ordinary 400-grit wet-type silicon carbide or aluminum oxide grinding paper has been very satisfactory. Final polishing was accomplished by use of a water suspension of Linde* A aluminum oxide grinding powder on a standard rotating-lap polishing machine (Uni-pol*, manufactured by Geoscience). Polishing is rapid but we have not examined the possibility that some of the polishing abrasive or iron from the probing ring became imbedded in the sample. No imbedding was visible, however, under a 100-power optical microscope. A very high finish could be obtained in this manner, but we have not attempted to characterize the polish itself.

For measurements such as X-ray measurements from cut surfaces, we have found it necessary to etch the surface to remove damage. We have attempted to use a number of acids as well as solutions of mercuric nitrate. The only successful etch we have found is hot aqua regia. We have not done controlled etching experiments, i.e., weight loss, etc., but slowly boiling aqua regia acts as a good chemical etch. Typical times required for fresh slow boiling aqua regia are 1/2 to 5 minutes depending on the depth of damage required to be removed. Chemically polished samples appear quite shiny to the eye, but the flatness of surfaces has been degraded.

The cracking we have observed upon minor thermal shock could be related to the presence of small-angle grain boundaries in the samples produced to date. These boundaries are only observable by polarized light on polished samples so that in cases where cracks have been produced there is no simple way to determine the cause.

C. Optical Properties

Measurements have been made at room temperature of the optical absorption of polished single-crystal samples from several different boules. Over the region 0.35 μm to 2.6 μm a Cary* 14R spectrophotometer was used, and over the range 2.5 μm to 25 μm a Perkin-Elmer* 337 grating monochromator was used. The absorption data are presented in figure 11. Substantial dichroism is evident at both ends of the spectrum. The results of the dichroic absorption should be considered preliminary, as the effects of imperfect polarizers as well as possible small misorientation of the crystals have not been considered. With dichroisms as large as observed in this case, corrections undoubtedly will have to be made to the data.

In the transparent region of the spectrum, we have used the spectrum of one of the most colorless boules. The reflection correction used was not calculated from the index of refraction, but represented the apparent reflection loss for two samples of two different thicknesses. That is, the same optical density was observed for two different thickness samples in the transparent region; in general, this type of correction is more satisfactory for high reflectivity materials where surface effects are often significant.

On the samples which were not colorless, no distinct absorption bands were observed. The absorption in these samples could best be characterized as a tail on the ultraviolet absorption edge. This absorption is most likely caused by the same impurity which caused the black residue at the bottom of the growth tubes.

No studies of luminescence were performed on any of these samples, though the literature indicates that a number of luminescent centers are often present in mercurous chloride.

Initial measurements of index of refraction were attempted by measurement of front-to-back interference fringes, but difficulties in producing suitable thin samples led us to perform index measurements by a different technique.

For this preliminary investigation, an accurate knowledge of the index of refraction at all wavelengths was not required, so we decided to make measurements only at important laser wavelengths. A sample was prepared in the form of a 30° prism with the c-axis oriented parallel to the refracting edge of the triangular prism. This geometry was chosen so that both indices of refraction could be measured on a single sample. The sample was placed on a rotation stage and the index measured by the standard technique of minimum deviation.

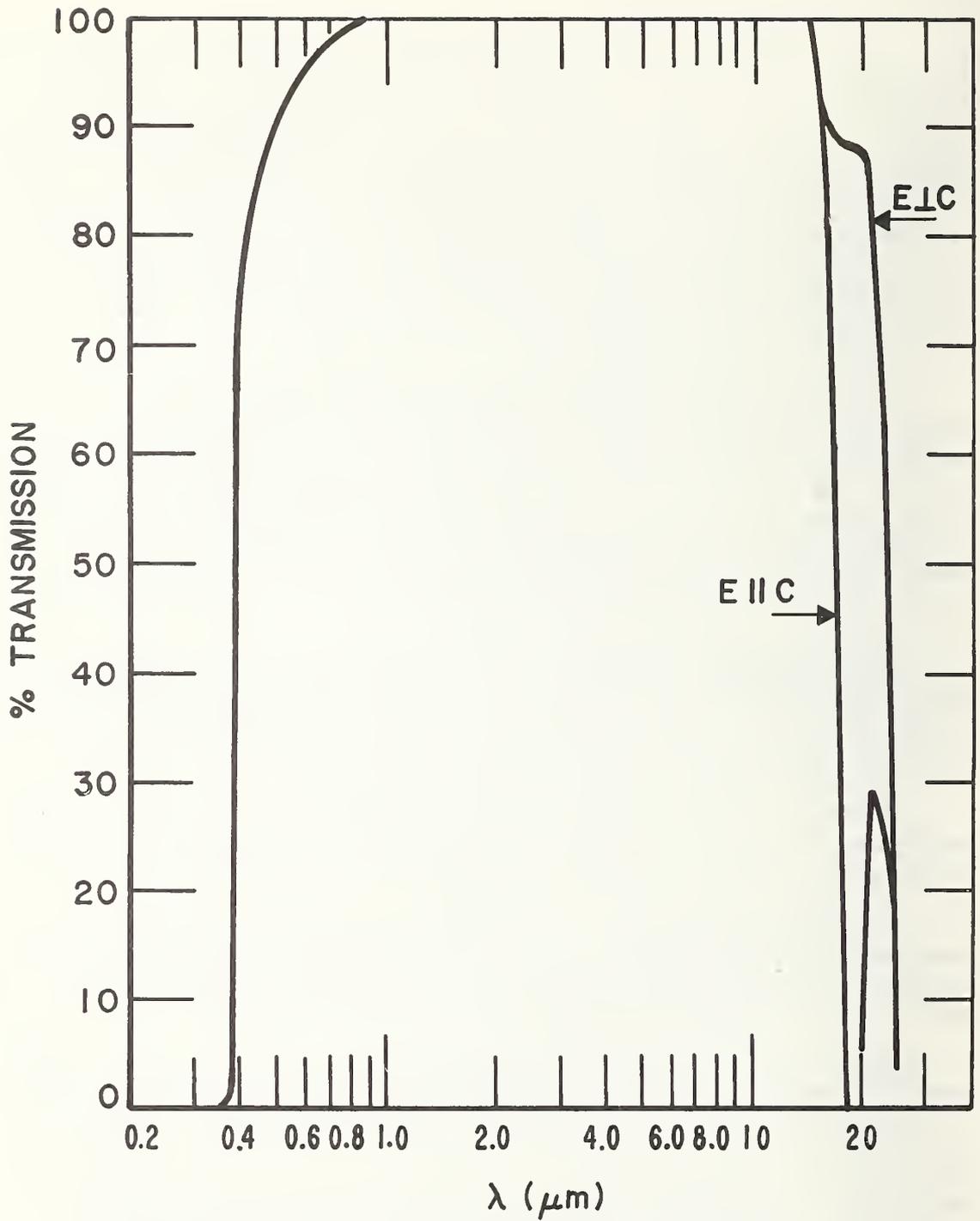


Fig. 11. Absorption data normalized for reflection losses for a 1-mm thick sample of mercurous chloride. The incident light was parallel to a [110] axis.

In our case, we used linearly polarized laser beams polarized at 45° to the c-axis. In this geometry, the light beam is split into two beams of orthogonal polarization upon entering the crystal. A fine adjustment of the alignment of the c-axis of the crystal with the prism rotation axis was made using this geometry. With the incident laser beam polarized at 45° to the c-axis, a linear polarizer was placed between the laser and the crystal. This polarizer was then rotated to 0°, or 90° to the c-axis. When perfect alignment was obtained, extinction was obtained for one of the emergent beams for each polarizer orientation.

The prism angle was measured using a 632.8 nm He-Ne laser by reflection from both of its faces back upon the laser head. Minimum deviation measurements were then made at 632.8 nm, 1150 nm and 10.6 μm, using two different He-Ne lasers and a CO₂ laser, respectively. For the measurements at 632.8 nm visual detection was employed. At 1150 nm an image converter was employed, and at 10.6 μm, liquid crystal thermal imaging material was used. The results of the measurements are reported in Table II. While the errors are large, further refinement is easily possible. One source of error in these measurements was crystal imperfection which tended to smear out the laser beams. This was most apparent on the extraordinary ray, and care was taken to select a good portion of the crystal for the measurements.

Table II. Indices of refraction and birefringence of mercurous chloride measured at important laser wavelengths.

Wavelength	n_e	n_o	Δn
.6328 μm (He-Ne)	2.65 ± 0.05	2.00 ± 0.02	.65
1.15 μm (He-Ne)	2.47 ± 0.07	1.91 ± 0.03	.56
10.6 μm (CO ₂)	2.45 ± 0.15	1.90 ± 0.07	.55

Further measurements of index are contemplated soon, contingent on preparation of a suitable prism.

Calorimetric absorption measurements at 10.6 μm have been performed at AFML on one sample to date. This was not one of the colorless samples, but nonetheless, absorption was found to be only 0.02 cm⁻¹. Further measurements are contemplated including measurements in polarized light as an aid to determining whether the absorption is intrinsic or extrinsic.

III. Suggestions for Further Developmental Work

A. Crystal Growth

As has been pointed out in the text, the only method of crystal growth used has been in sealed, evacuated ampoules. With the exception of a few growth runs near the end of the contract period, no attempt was made to seed the crystal growth. In all of the growth runs to date, a problem existed in that small-angle grain boundaries were found in most crystals. A simple reduction in growth rate could very well solve this problem, but since it occurred only when growth was carried out in large diameter (~ 17 mm) tubes, optimization of growth rate requires a decision on the size crystals desired. This optimization could probably be carried out best by a commercial contractor who would have a large number of growth furnaces available. As we do not have a large number of growth furnaces at NBS, it would appear inappropriate for this facet of further development to be carried out at NBS.

Other approaches to crystal growth should be attempted, in particular, methods in which seeded growth might be more feasible. Various vapor transport methods are available in addition to the inverted Bridgman methods used in this investigation. An attractive possibility would be transport in gradient furnace using a suitable carrier gas. NBS has previous experience with similar techniques in the production of ultra-high-purity sapphire. The investigation would involve appropriate choice of carrier gas(es) as well as all of the conditions of growth. A reasonable expectation would be that higher purity material could be produced and that improved physical perfection at higher growth rates could be achieved.

An important extension of the work reported here would be to examine the other mercurous halides, all of which are reported to have the same crystal structure as mercurous chloride. On the basis of the index of refraction measurements reported here, and the correspondences which could be drawn from the known reststrahlen bands of these materials, these other mercurous halides also should possess large birefringence. The same crystal growth techniques should be suitable for growth of these compounds, requiring only determination of suitable growth temperatures. The extension of the work to these other isostructural compounds would be useful in that the window regions for each of them would be different, possibly providing a superior polarizer material for certain regions of the spectrum.

The other mercury halides have been much less investigated than the chloride. There also exists the possibility that one of them has a non-centrosymmetric crystal structure, contrary to literature reports, and would be useful as a parametric material. Our observation of a low temperature phase transition in mercurous chloride

makes it unlikely that all of the mercurous halides do have the same structure at room temperature. If a non-centrosymmetric phase does exist, the expected large birefringence would easily allow phase matching to occur and a useful parametric material could result.

If the conditions for growth of the other halides could be determined, an extension envisioned would be the growth of mixed halides by codeposition. This would undoubtedly require a substantial effort, but alloy hardening could occur as is the case in thallos halides, in the production of KRS-5 and KRS-6. While hardening of the material is not required for polarizer use, some toughening would be desirable.

B. Chemical and Physical Properties

Chemical purity of the finished crystals could become important depending upon the particular usage for the material. Crystal growth has demonstrated a segregation of impurities, as judged by boule color, but no quantitative chemical analysis for impurities has been attempted.

In any new material, it is advisable to examine possible impurity effects before considering placing the material in service in a system. In particular, photolysis, photochromism, stability in various atmospheres, luminescence, and possibly the effects of ionizing radiation should be examined. In general, while each of these phenomena could be intrinsic, impurities often tend to catalyze these effects. Conversely, doping studies should be conducted to see if improvement in desired properties can be obtained. These studies are most easily conducted on a small scale as a modification of a crystal growth run.

Further study into the phase transition observed at 181 K is warranted to determine the structure and optical properties of the material in the low temperature phase. If this phase lacks a center of inversion, mercurous chloride could become an important parametric material. These studies could be performed by low temperature X-ray and Raman studies, both of which have been started. The crystals appear to be undamaged by repeated cycling through the transitions, which is an obvious and necessary requisite for the material to be useful in the low temperature phase.

Another study which clearly should be conducted would be the effect of purity on absorption. This study should be conducted in conjunction with other indirect measurements of purity, such as visible absorption and luminescence, as these are often more sensitive than ordinary chemical analysis. Measurements should be performed using a polarized laser beam in the calorimetric studies so as to aid in separation of lattice effects.

Acknowledgments

We would like to thank Deane Horowitz and Albert Feldman of the National Bureau of Standards for their aid in the measurements of refractive index. We would also like to thank G. T. Johnston of AFML for performing measurements of calorimetric absorption at 10.6 μm on our crystals.

*Certain commercial instruments and materials are identified in this report in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the instrument or material identified is necessarily the best available for the purpose.

Selected References

- Barta, V., Kristall u. Technik 5, 541 (1970), (crystal growth).
- Bohun, A., Rozsival, M., and Brabee, F., Phys. Stat. Solidi (b) 45, K85 (1971), (uv absorption).
- Deb, S. K., Phys. Rev. B2, 5003 (1970), (uv absorption).
- Dufet, M. H., Bull. Soc. Franc. Mineral. 21, 90 (1898), (index of refraction).
- Durig, J. R., Lau, K. K., Nagarajan, G., Walker, M., and Bragin, J., J. Chem. Phys. 50, 2130 (1969), (IR and Raman).
- Ejder, E., J. Phys. Chem. Solids 31, 453 (1970), (absorption and luminescence).
- Gmelin's Handbuch der Anorganische Chemie System 34, Vol. B, Sec. 2 (1967), 8th edition (general reference on properties).

