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13. ABSTRACT

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During the investigation, crystal growth was scaled to produce ingots 5 cm in diameter and up to 12 cm in length which yielded large single crystals allowing modulator rods of optimum orientation up to 5 cm in length by 5 mm on edge to be fabricated. Changes in tube geometry provided single crystal starts for all ingots. A general improvement in materials purity and handling and processing improved the over-all quality. The optical absorption coefficient at 10.6 μm was seen to improve from 0.006 cm^{-1} to 0.0015 cm^{-1} for best samples; typically current samples average 0.002 to 0.003 cm^{-1}. Studies of oxygen contamination indicated that small amounts of oxygen (< 50 ppma) have no observable effect on 10.6 μm absorption. However, large amounts (>100 ppma) have extremely deleterious effects on the crystal quality, and hence, adverse effects on the optical transmission. Experimental evidence indicates that useful and superior infrared modulator devices can be fabricated using CdTe as the active crystal.

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Infrared Window						
Electro-Optic Coefficient						
10.6 μm Absorption Coefficient						

I-B

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a division of hughes aircraft company

CADMIUM TELLURIDE MODULATOR MATERIAL

Final Technical Report
Contract N00014-70-C-0303
Project NR 039-106/2-24-70

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September 1972

Prepared for
DEPARTMENT OF THE NAVY
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Metallurgy Program
Arlington, Virginia

I-C

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FOREWORD

This report constitutes the Final Report on work performed by personnel of the Hughes Research Laboratories Division of Hughes Aircraft Company under Office of Naval Research Contract N00014-70-C-0303, Project NR 039-106/2-24-70, during the period 1 May 1970 through 30 April 1972.

The project was directed by Dr. A.L. Gentile and monitored by Dr. A.M. Diness, Metallurgy Program, Office of Naval Research. Experimental work in materials preparation and crystal growth was performed by Mr. N.R. Kyle; evaluation of the material was carried out by Mr. J.E. Kiefer, both Members of the Technical Staff at Hughes Research Laboratories.

ABSTRACT

The program sponsored by the Office of Naval Research involved the investigation of CdTe single-crystal growth by means of variation of crystal growth parameters, including growth rate, thermal gradient at the melting point, quench rate, and materials preparation and handling with the primary objective of optimizing heat transfer to obtain optimum monocrystalline properties for application as an infrared modulator device. Post-growth annealing techniques were also investigated. Measurements on the CdTe crystals were performed primarily as part of an internally supported Hughes Aircraft Company program; the materials study is sponsored by the Office of Naval Research. The research consisted of selection and purification of starting materials, optimization of crystal growth parameters, investigation of post-growth heat treatment, and study of the effects of oxygen contamination on materials properties for optimizing CdTe single crystal material for use in infrared electro-optic devices.

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I. INTRODUCTION AND SUMMARY

The full capabilities of 10.6 μm CO_2 lasers in communication and radar systems can be realized only by improving performance of electro-optic devices. The power output of CO_2 lasers is now adequate for many communication and radar applications, and additional research in new and improved materials with inherently better characteristics will lead to improved electro-optic device performance. As the result of a number of years of research on II-VI compounds, including current cadmium telluride (CdTe) investigations supported by Office of Naval Research Contract N00014-70-C-0303, personnel at Hughes Research Laboratories have developed the capability of growing large single crystals of CdTe with improved properties for application as an electro-optic modulator.

Evaluation of these crystals as a basis for 10.6 μm electro-optic modulator devices, indicates many properties in which such a device would be superior to one based on gallium arsenide (GaAs). An important example is the value of $n_0^3 \cdot r_{41}$, the most important electro-optic parameter, which has been measured as approximately 10×10^{-11} m/V for CdTe; the comparable value for GaAs is 5.8×10^{-11} m/V. The lowest absorption coefficient for our CdTe measured during the course of this investigation is 0.0015 cm^{-1}, a value that makes CdTe desirable for application as a high power infrared laser window.

This program was initiated in order to accelerate the development of CdTe crystals with the desired characteristics to exploit their use in the modulation of infrared radiation. Crystals have been grown of sufficient size to be fabricated as modulators and used in a device. Single crystal rods up to 5 mm x 5 mm x 5 cm have been fabricated. A change in crucible geometry has enabled all crystal growth runs to have single crystal starts, indicating promise of eventual achievement of single crystal ingots.

During the course of this program, a parallel effort was undertaken to develop CdTe as a high power infrared laser window. This project was sponsored by the Air Force under Contract F33615-71-C-1778, monitored by the Air Force Materials Laboratory, WPAFB, Ohio. The window project called for scale-up to 5 cm diameter ingots. The noticeably larger single crystals obtained in this size led to the installation of an additional large bore furnace for growth of 5 cm diameter single crystal CdTe ingots primarily for modulator applications. A distinct advantage from the larger diameter is incurred when the single crystal is oriented for maximum modulation efficiency. The scale-up, however, introduced additional problems, some of which were solved during the course of the two programs. However, programs concerning growth of large single crystals, e.g., the ONR Modulator Materials Study, requires the use of thin-walled tubing which increases the probability of loss of runs. In addition, the standard quench technique used to obtain high resistivity (low absorption) material was found to be inadequate for the large ingots; cooling was too slow to freeze-in the high temperature equilibrium. This led to the development of a thermal annealing process which allows slow cooling under a controlled variable overpressure of cadmium.

During this investigation, we also introduced a necked-down tip to the crystal growing tube which successfully gave single crystal starts to all runs, significantly increasing the single crystal yield. Modulator rods up to 5 cm in length were cut from single crystal material. In general, an improvement in the over-all technique which was made possible by this program sponsored by the Office of Naval Research, together with the use of higher purity starting materials, the use of higher purity (synthetic) fused silica ware, the improvement of clean room facilities and greater care in materials handling, have been responsible for the improvement shown in CdTe modulator materials during the period of this study. Prime among the improvements are

- 10.6 μm absorption coefficient from 0.006 to 0.0015 cm^{-1}
- Increase in single crystal size yielding modulators up to 5 cm in length.

II. CADMIUM TELLURIDE CRYSTAL GROWTH

A. Phase Equilibrium Considerations

Cadmium telluride tends to undergo stoichiometric variations[1] in the growth and cooling procedure; these variations are factors in the determination of what the electrical properties, especially conductivity and type of conduction, will be.

A look at an expanded phase diagram in the region of interest, i.e., the existence region (Fig. 1), shows that the maximum melting point of cadmium telluride is not the stoichiometric composition; the composition of the maximum melting point varies with the constituent pressure above the melt. If a certain vapor pressure of the component (e.g., Cd) is maintained above the melt, the system has a tendency to grow at the composition corresponding to the applied vapor pressure. As solidification proceeds, the segregation process tends to make the melt more and more concentrated with regard to the component present in excess. However, as this occurs the liquid is no longer in equilibrium with the vapor; a reaction between vapor and melt sets in until equilibrium is again reached. The end result is dependent on the rate at which the composiiton changes as a consequence of the segregation, compared with the rate at which atoms are transferred between the melt and the vapor. A steady state eventually will be reached in which the crystals will attain a composition between the maximum melting composition (e.g., A for $P_{Cd} = 0.8$ in Fig. 1) and the stoichiometric composition.

In the Modified Bridgman Technique these conditions (e.g., composition, component overpressure) can be altered to produce CdTe that is stoichiometric, cadmium-rich, or tellurium-rich.

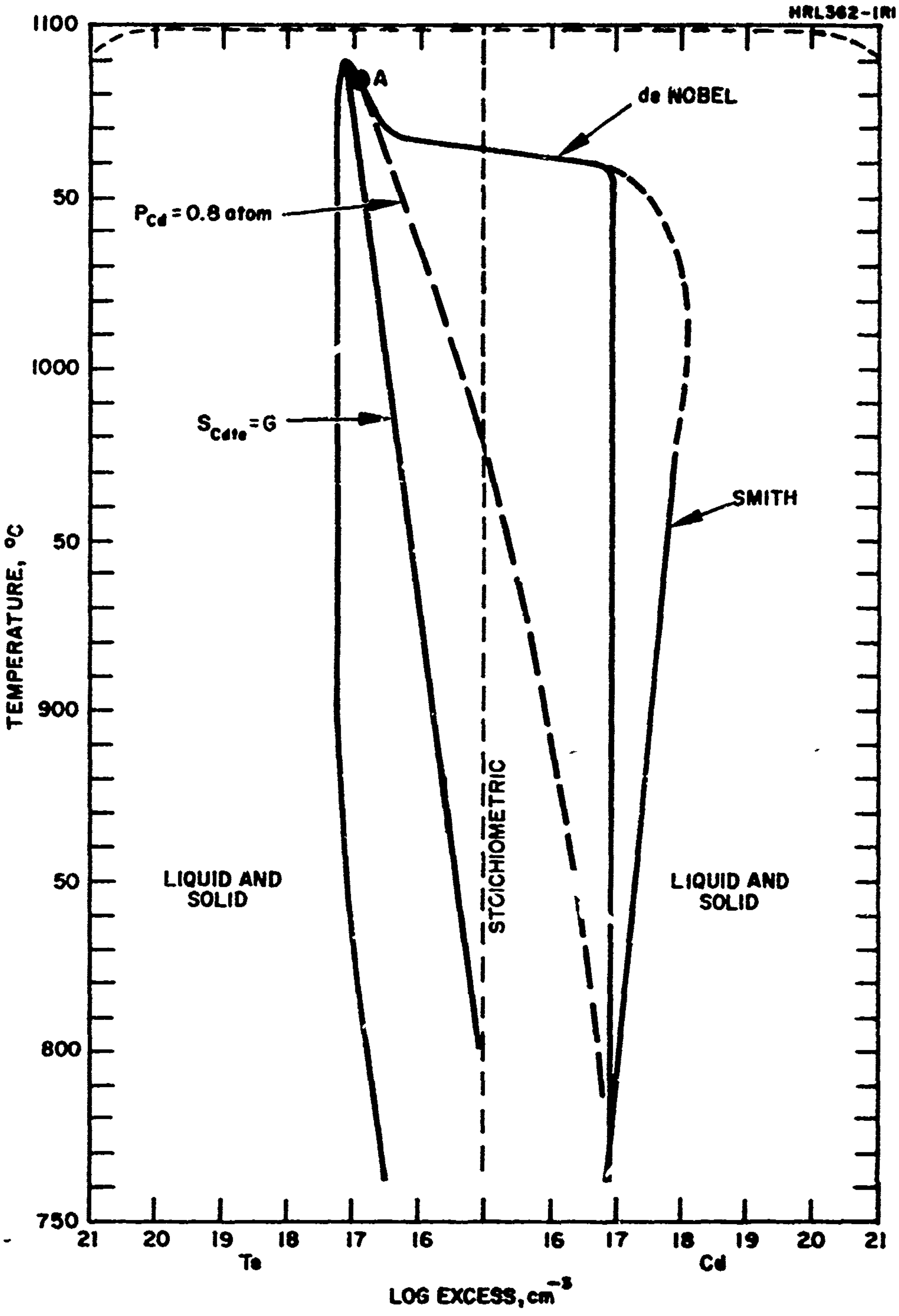

Fig. 1. Expanded Phase Diagram of CdTe.

The Modified Bridgman Technique was developed[2] primarily to grow high resistivity material for optical modulators, gamma detectors, and infrared windows. High resistivity material is readily obtained when deep levels in the band are filled with electrons from donor impurities. The addition of a donor to the melt causes the entire tellurium-rich side of the phase diagram (Fig. 2) to yield high resistivity material when rapidly cooled (quenched) to room temperature from elevated temperatures as indicated in the diagram. Obviously, if the material is slowly cooled, it will move into the low resistivity region to the right of the line in Fig. 2, which represents the amount of indium dopant in the crystal. By proper selection of the quench point, high resistivity CdTe is obtained over a range of conditions making extremely critical control of pressure, quench temperature, or donor (e.g., indium) concentration unnecessary. Typical results of this process are shown in Table I. In addition, slowly cooled material (low ρ) within certain size limits, may be thermally annealed after growth and subsequently quenched to yield high resistivity material.

TABLE I

Resistivity as a Function of Growth Conditions

Ingot	Resistivity, Ω-cm	Indium, cm^{-3}	Atmosphere	Pressure, atm
21	10^7	2.4×10^{17}	Cd	1
22	10^7	2.5×10^{17}	Cd	1
24	10^7	2.5×10^{17}	Cd	1
25	10^7	5×10^{17}	Cd	1
01	10^5	1.9×10^{18}	Cd	2.1
37	$10^8 - 10^9$	2.5×10^{17}	Te	0.84
38	10^7	2.5×10^{17}	Te	0.84
35	10^8	1.7×10^{17}	Te	0.5

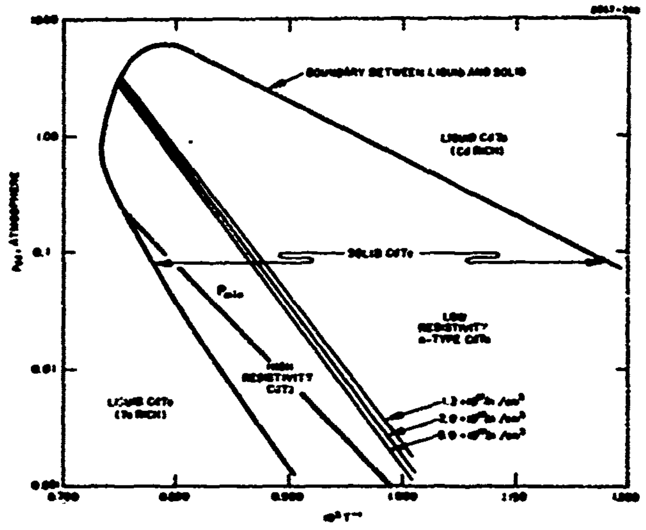

Fig. 2. Dependence of CdTe Melting Point on Cd Pressure.

B. Cadmium Telluride Purification and Preparation Techniques

Purification of the starting material is a very important part of the crystal growing process. Many methods for obtaining pure CdTe have been reported, but much of the early work which involved purification of the elemental constituents by sublimation and zone refining was necessary because high purity cadmium and tellurium could not be obtained commercially. This is no longer the case; the elements can now be obtained with a minimum purity of 99.9999%. Zone refining the compound is not an efficient means of obtaining high purity crystals because the segregation coefficients of most impurities in CdTe are about 0.5 and that of aluminum is actually greater than one. When impurity segregation coefficients are close to unity, many zone passes are necessary to reach a given purity level, and the time required intensifies the problem of contamination by the container. For these reasons, purification of the compound by sublimation was chosen as the most promising technique.

Purification by sublimation is more rapid than zone refining, and less chance of container contamination exists because no melt is involved and the temperatures are low. In addition, the compound recombines stoichiometrically[1] according to the equation

$$CdTe_{(s)} \rightleftarrows Cd_{(g)} + \frac{1}{2} Te_{2(g)} \quad .$$

Therefore, any excess cadmium or tellurium can be segregated because the vapor pressures of cadmium and tellurium are much higher than that of CdTe.

Purification by sublimation is based on a distribution equilibrium between the solid and gas phases. Impurities that are nonvolatile will be effectively segregated, and those that are volatile will be in equilibrium with the sublimate and condensate. Starting with the purest cadmium and tellurium available (at least 99.9999%), the components are reacted to form the compound CdTe and then sublimed to purify it. This is a one-step process which takes place in a closed evacuated tube (Fig. 3). Starting with cadmium and tellurium, near-stoichiometric amounts are placed in a long quartz tube which has been cleaned in electronic grade HF-HNO_3, washed in de-ionized water, and coated with pyrolytic carbon. The de-ionized wash consists of a closed system of circulating de-ionized water which continuously passes through a deionizer. After the tube is loaded, it is sealed off under a vacuum of 10^{-7} Torr.

The tube is initially lowered partially into the furnace until the heat is sufficient to start the reaction of cadmium and tellurium. The reaction is exothermic and proceeds rapidly. When the reaction stops, the tube is then lowered completely into the furnace and withdrawn at 0.25 in./hour.

There is no attempt to clean the material mechanically or chemically. This method reduces contamination by minimizing handling. In addition, the CdTe sublimate is heated in the sublimation tube under a hydrogen atmosphere at 800°C. This is done to remove any oxides, thereby preventing removal of the pyrolytic carbon coating by oxidation. In addition, the material is prevented from sticking to the tube through the reaction of silica with the oxide. It is important that the material does not come in contact with the fused silica container, because the container has been found to be a source

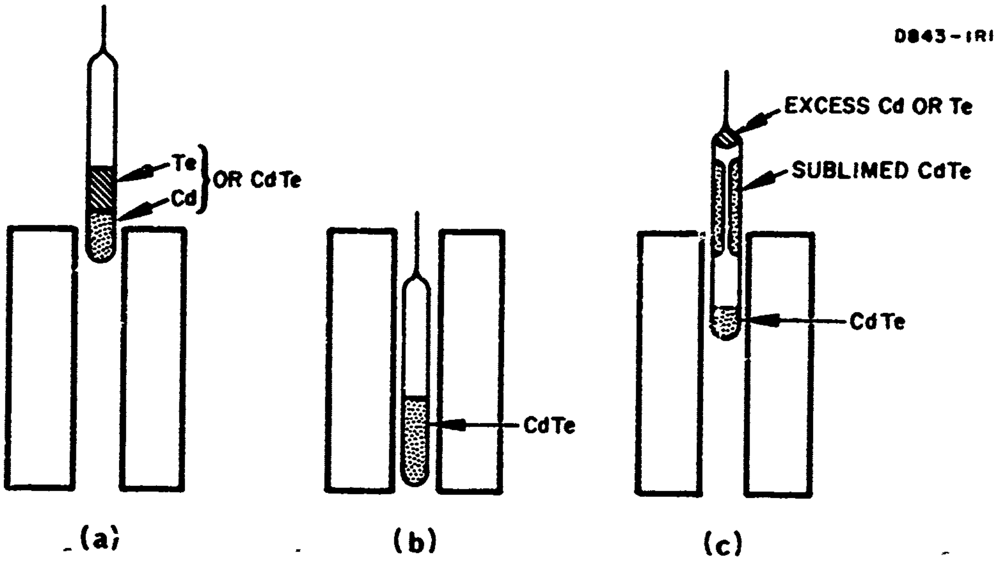

Fig. 3. Preparation and Purification of CdTe.

of contamination. A direct correlation has been found between the impurities in the fused silica tubes and the impurities in CdTe crystals. Consequently, synthetic quartz, which has the lowest impurity content of any available tubing, is used to grow the single crystals.

C. Modified Bridgman Technique

The optimum growth conditions for producing high quality, large single crystals of CdTe are determined by rate of growth, growth temperature, temperature gradient, and rate of cooling of the ingot.

The following general conditions for crystal growth by the Modified Bridgman Technique have been determined as a result of numerous investigations.

- A sharp temperature gradient in the growth zone is necessary for an axial flow of heat. Crystals grown through a shallow gradient are invariably polycrystalline. We currently use a gradient at the melting point of CdTe of 20°C/cm.

- A flat axial profile is required to minimize the radial flow of heat and thermal convection in the melt.

- A slow growth rate is necessary to avoid rapid cooling of the surface, which would result in a concave solid-liquid interface in the direction of growth. (A convex interface in the direction of growth is considered ideal.) The thermal conductivity is the dominant factor determining growth rate. Thus, for materials having low thermal conductivity, the growth rate must be slow. For CdTe, a concave shape was obtained for growth speeds much greater than 0.20 in./hour. In addition, at speeds much greater than 0.20 in./hour the dislocation density increases rapidly. If the crystals are grown very slowly to minimize the dislocation density, the seeds which form initially propagate linearly through the crystal along the growth axis. The speed is then too slow for the fastest growing crystal plane to dominate. As a result, an optimum speed of 0.10 to 0.20 in./hour is used.

- Crystals of approximately 1 in. in diameter minimize radial temperature fluctuations across the ingot because of their large mass.
- The crystal must be rotated if the furnace is not symmetrical. Rotation will smooth out the asymmetry of the furnace and minimize radial fluctuations.
- The solid-liquid interface can become concave if the melt temperature is run well above the melting point of the material. A temperature of 5 to 10°C above the melting point is ideal.
- The pressure of one of the components above the melt as used in the Modified Bridgman Technique also affects the crystallinity. In particular, when the cadmium pressure was much above or below 1 atm, the crystallinity degenerated.
- Six different geometric configurations of quartz crucibles have been tested to determine whether the different methods of crystal nucleation and slopes of the tube had any effect on the crystallinity of the material. Recently one showed a particular advantage for the growth of CdTe.

Because CdTe readily dissociates at high temperatures, growth from the melt requires a closed system. Although an ordinary Bridgman method of growth in a closed system can be used, there is little control over the electrical parameters and composition of the crystal. If the melt is off stoichiometry, the composition of the melt changes continuously as solidification takes place, thus changing the composition and resistivity of the solid as it grows.

Crystal growth of CdTe was pursued by the Modified Bridgman Technique. The main advantage of this technique is that the composition of the melt can be controlled. It also offers the advantages of uniformity of ingot size and greater uniformity of impurities in the direction transverse to the direction of growth. The growth tube is elongated (Fig. 4) so that cadmium or tellurium can be placed in a reservoir high in the tube, where vapor pressure can be controlled by a second furnace operating significantly below the temperature of the crystal furnace. Crystals of CdTe can be grown stoichiometrically, cadmium-rich, or tellurium-rich, by changing the pressure of one of the components. In practice, the Modified Bridgman tubes, made of synthetic quartz, are cleaned and coated with pyrolytic carbon. The sublimate is loaded into the tube and hydrogen treated at 800°C to remove the oxides. Cadmium is placed within the reservoir of the tube, the tube is sealed under a vacuum of 10^{-8} Torr, and lowered through the crystal growth furnace. When CdTe is prepared at specified temperatures, with appropriate overpressures of its components and with $10^{17}/cm^3$ indium atoms or other suitable n-type dopants, the resulting material is high resistivity. The region specifying these conditions is presented in Fig. 2. As shown in the figure, indium-doped CdTe grown at a pressure of 1 atm should have high resistivity if it is quenched rapidly to room temperature from a temperature of 900°C or higher. Since the ultimate resistivity is also influenced by quench rate, profile of the lower furnace, and rate of crystal growth, these factors must be controlled to optimize the as-grown crystal.

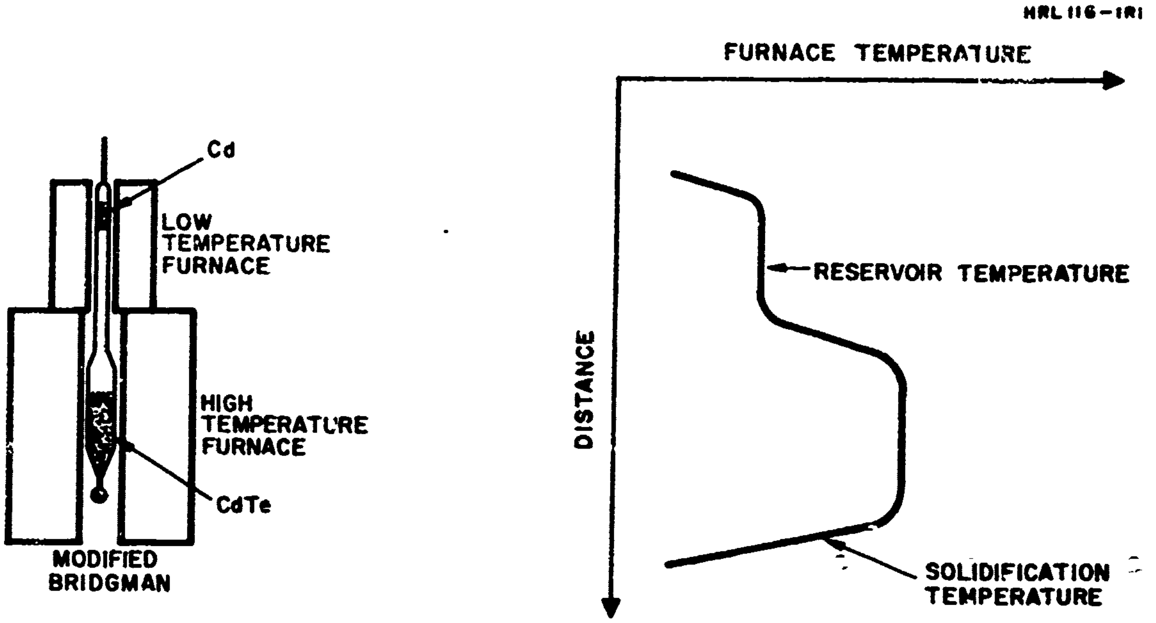

Fig. 4. Schematic of Apparatus for Crystal Growth.

The platinum-wound Modified Bridgman furnaces which satisfy the temperature profile conditions shown in Fig. 4 are illustrated in Fig. 5. A portion of typical boules of single crystal CdTe grown in this equipment is shown in Fig. 6.

Several modifications of the Modified Bridgman Technique were accomplished during the course of this study which added to improved materials for use as modulators.

The crucible, which was developed for the growth of large ingots (5 cm diameter) of CdTe and which would yield the largest single crystals, consisted of an inner crucible of high purity synthetic fused silica (Suprasil) clad on the outside with regular fused silica (Amersil) and has a total wall thickness of approximately one millimeter. This is necessary because of the lower softening point of the synthetic fused silica (below the usually quoted 1200°C) because of the high OH^- content residual from the hydrothermal growth process. The softening point of synthetic quartz containers was variable and frequently observed to be close to the melting point of CdTe. The synthetic fused silica is significantly purer than the other grades, and therefore is necessary as an internal liner close to the melt (separated by a pyrolytic carbon layer). The thin wall has been proved to be required for maximum single crystal yield because of the greater ease of heat removal. In addition, a large conductive metal heat sink on the nose of the crystal greatly assists in the axial removal of heat; this was incorporated into the lowering mechanism of the growth furnace apparatus Growth parameters including lowering rate and thermal gradient were adjusted to yield maximum monocrystallinity. Most runs were slowly cooled and allowed to run out of the bottom of the furnace before removal. Although this technique yielded some of the largest single crystals of CdTe yet reported (see Fig. 6), problems persisted which resulted in cracking of the ampoule before

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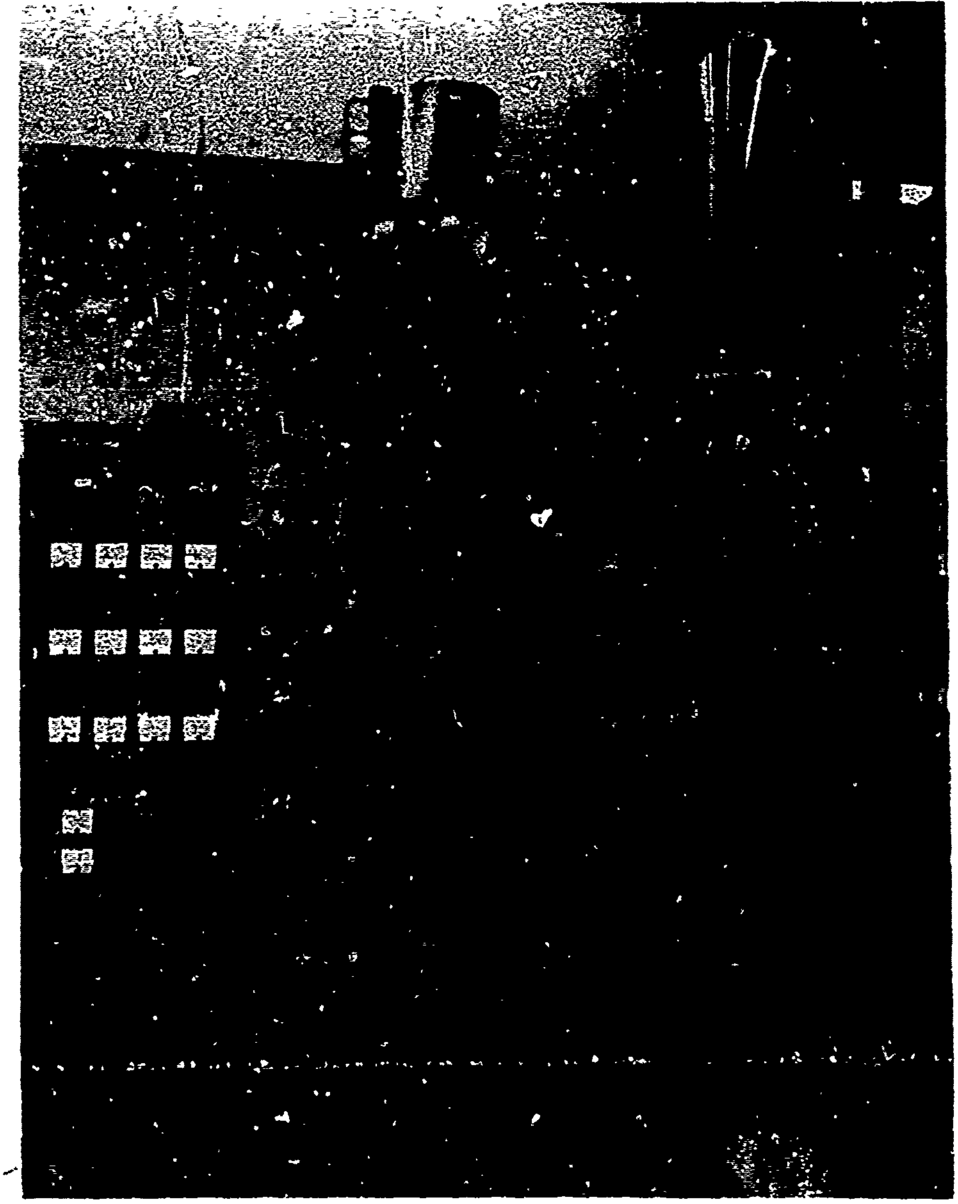

Fig. 5. Modified Bridgman Growth Furnaces.

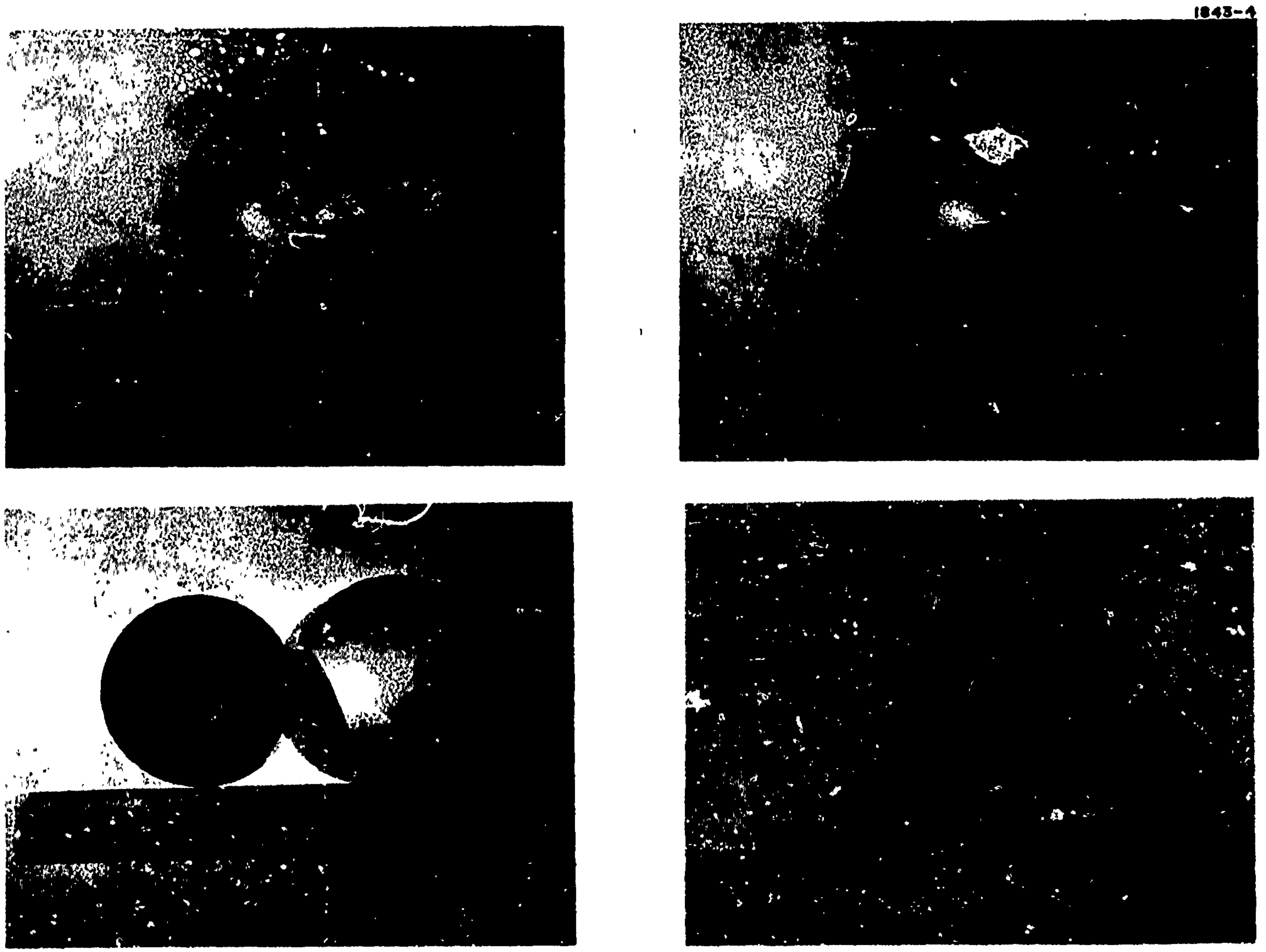

Fig. 6. CdTe Sample 226, 5 cm Diameter Ingot.

sufficiently low temperatures were achieved and sometimes resulted in explosion. In addition, slowly cooled crystals required longer annealing times. Too often, single crystals of large sizes showed extensive cracking. Several causes observed for these results were (1) keying of the CdTe or cadmium coating (deposited over the ingot after or during solidification) to the walls of the crucible where the carbon coating was porous or somehow removed, (2) differential contraction (expansion) of a solidified ingot which sets in a sharp thermal gradient, and (3) deposition of large amounts of metallic cadmium onto the ingot by condensation of the excess cadmium from above. At the present time, large single crystals can be grown from which modulator rods as long as 5 cm x 5 mm x 5 mm can be cut. However, the problems have not yet been entirely solved.

D. Thermal Annealing

In the process of quenching under an atmosphere of one of the components, it is assumed that the atomic positions of vacancies and foreign atoms remain unchanged while the electrons and holes are free to redistribute themselves over the energy levels in the crystal. Consequently, quenching under a high cadmium pressure would introduce cadmium interstitials as the dominant donor. As the cadmium pressure is lowered, the concentration of cadmium interstitials decreases and the donor impurity (indium) becomes the dominant electron supplier. Further reduction in cadmium vapor pressure eventually results in a tellurium-rich crystal in which the dominant defects are cadmium vacancies rather than interstitials. The cadmium vacancy is an electron acceptor. When enough of these have been introduced so that all the electrons from the donor impurity are captured in the quenching process the n-type region of conductivity ends. The imperfections which trap electrons are thought to be cadmium vacancies with a single negative electrical charge (V'_{Cd}).

As the cadmium pressure is lowered further, the V''_{Cd} (cadmium vacancy with effective charge of -2) functions as a trap for the holes during the quenching process. The ionization energy of these V''_{Cd} levels is too large to give appreciable conduction at room temperature. It is not clear whether these deep-lying energy levels consist of a double negatively charged cadmium vacancy or associates of cadmium vacancies with donors[1]; however, the result is that the transition from n- to p-type material takes place over a wide range of atmospheres in which the crystal has an extremely high resistance. The pressure range yielding low resistivity p-type conductivity is never reached.

If the cooling takes place slowly or if the quench occurs at too low a temperature, vacancies are able to diffuse away and the deep acceptor centers are not present; the Fermi level is no longer pinned near the center of the forbidden energy zone, and the lower resistivity material is formed. This is in good agreement with the phase diagram (Fig. 2) which shows, for example, that indium doped CdTe grown at a pressure of one atmosphere should have high resistivity if it is quenched rapidly from 1000°C to room temperature. The temperature range from which a crystal may be quenched to room temperature and have high resistivity i e., no free carrier absorption, has an upper limit which is the melting point of CdTe at the cadmium pressure being used (the left boundary of the solidus region in Fig. 2 and a lower limit determined by the shallow donor concentration in the crystal (one of the diagonal lines corresponding to different indium concentrations in Fig. 2.

Typical optical transmission curves before and after the thermal anneal procedure are shown in Fig. 7.

When the ingot size was increased to a 5 cm diameter and the total weight of CdTe exceeded 500 grams, we observed that quenching became impossible because of the large mass and relatively poor thermal conductivity of the material. A technique was initiated which involved slowly cooling the crystal with accompanying lowering of the overpressure as illustrated by the dotted line in Fig. 8,* remaining in the high resistivity region to a temperature where diffusion processes become sluggish. This annealing procedure can also assist in reducing any thermal strain that may have been present due to growth conditions; certainly it cannot introduce any additional strain in the ingot. This technique is still in the experimental stage and as such is not entirely reproducible. Initially, excellent results have been obtained. At the present time, however, modulator rods are cut from the ingots and heat treated by the standard quench technique.

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*The circle designated with number 1 is the area of thermal anneal used both prior to quenching or subsequent to slow cooling techniques.

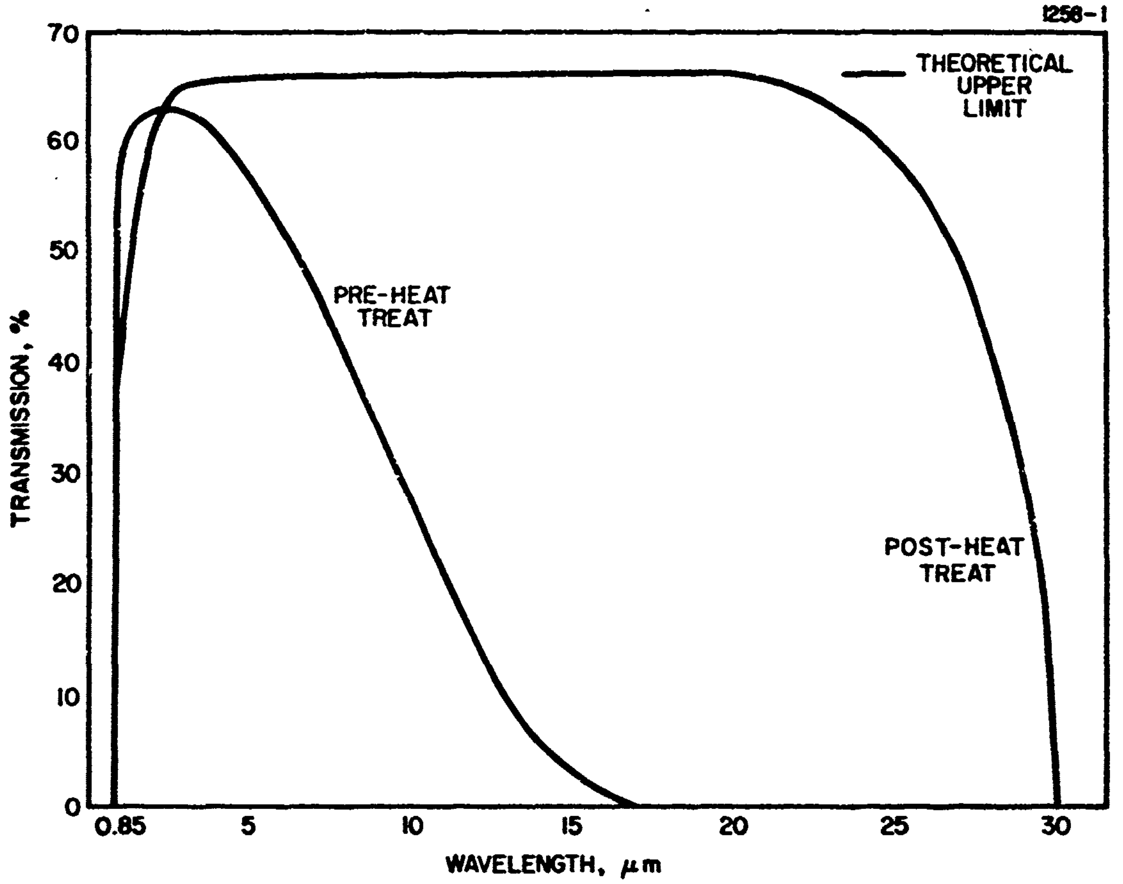

Fig. 7. Transmission Spectrum of CdTe Sample Before and After Heat Treatment.

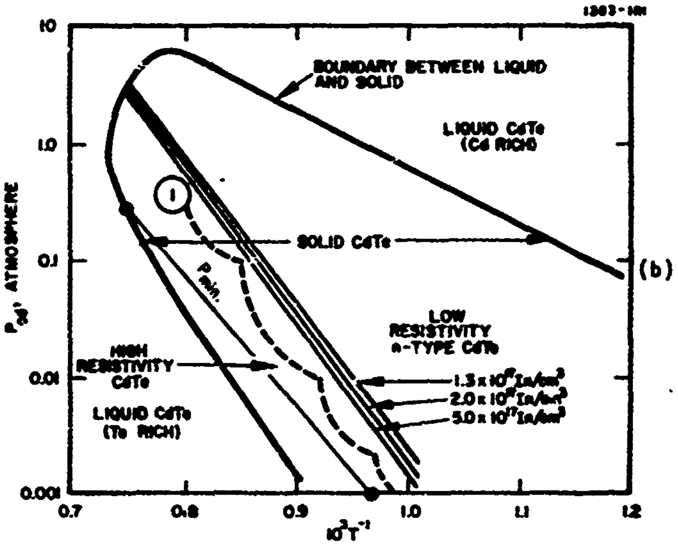

Fig. 8. CdTe Pressure-Temperature Equilibrium Relationships.

III. CADMIUM TELLURIDE CRYSTAL EVALUATION

A. Measurement of Electro-Optic Coefficient

The most efficient means by which the electro-optic coefficient of a material such as CdTe may be measured, utilizes a sample of the material in the form of a rectangular bar with the end faces and two opposing sides parallel to crystalline (110) planes. The end faces are optically polished to allow passage of a light beam, and the (110) plane sides are electroded to provide for the electric driving field across the crystal.

In its simplest form, the measurement is made by allowing the polarized output beam of a suitable laser to pass axially through the sample, through a crossed analyzer, and onto a detector where the intensity of the transmitted light can be measured. A known dc voltage is then applied to the crystal, and the intensity of the transmitted light is measured as a function of the applied voltage. When an element with birefringence Γ radians is placed between crossed polarizers with the induced axes of the element $\pi/4$ from the polarizer axes, the ratio of transmitted to incident light intensity is given by

$$I/I_o = \sin^2 (\Gamma/2) \quad . \qquad (1)$$

For this crystalline orientation, the birefringence or phase retardation as a function of driving voltage V is

$$\Gamma = \frac{2\pi}{\lambda} n_o^3 r_{41} \left(\frac{L}{d}\right) V \text{ radians}, \qquad (2)$$

where λ is the free space wavelength of the incident radiation, n_o is the refractive index, r_{41} is the electro-optic

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coefficient, L is the length, and d is the thickness of the sample. Combining the two equations and solving for r_{41},

$$r_{41} = \frac{\lambda}{2\pi n_o^3 V} \left(\frac{d}{L}\right) \sin^{-1} 2 \sqrt{\frac{I}{I_o}} \ , \qquad (3)$$

which yields the unclamped electro-optic coefficient.

To measure r_{41} with an ac signal (e.g., to find the clamped or high-frequency value of r_{41}, a quarter-wave plate with axes parallel to the induced axes of the sample is placed in series optically with the sample, and a sinusoidal signal with peak voltage V_o and frequency F_m is applied to the sample. The above equations are then modified as follows.

$$I/I_o = \sin^2\left(\frac{\Gamma}{2} + \frac{\pi}{4}\right) = \frac{1}{2} \sin\ (1 + \Gamma) \qquad (4)$$

$$\Gamma = \frac{2\pi}{\lambda}\, n_o^3\, r_{41} \left(\frac{L}{d}\right) V_o \sin\ (2\pi\ F_m t) \ . \qquad (5)$$

Thus,

$$\left.\frac{I}{I_o}\right|_{max} - \left.\frac{I}{I_o}\right|_{min} = \sin\left[\frac{2\pi}{\lambda}\, n_o^3\, r_{41} \left(\frac{L}{d}\right) V_o\right] \ , \qquad (6)$$

or for small signals

$$r_{41} \sim \frac{\Delta I}{I_o}\ \frac{\lambda}{2\pi n_o^3 V_o} \left(\frac{d}{L}\right) \ , \qquad (7)$$

The apparatus for these measurements is illustrated schematically in Fig. 9 and a photograph of our test station is shown in Fig. 10.

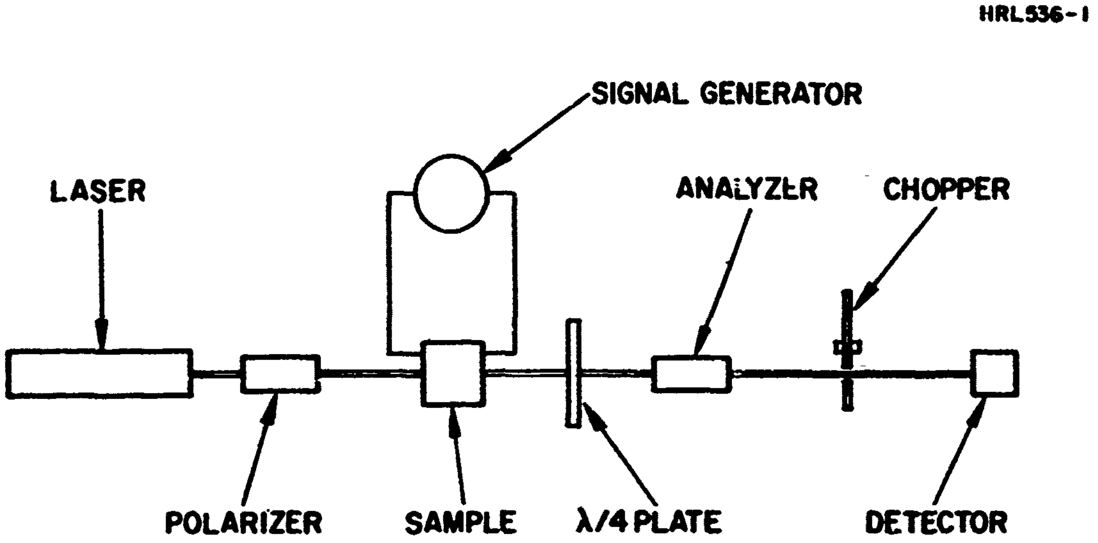

Fig. 9. Electro-Optic Evaluation Apparatus Diagram.

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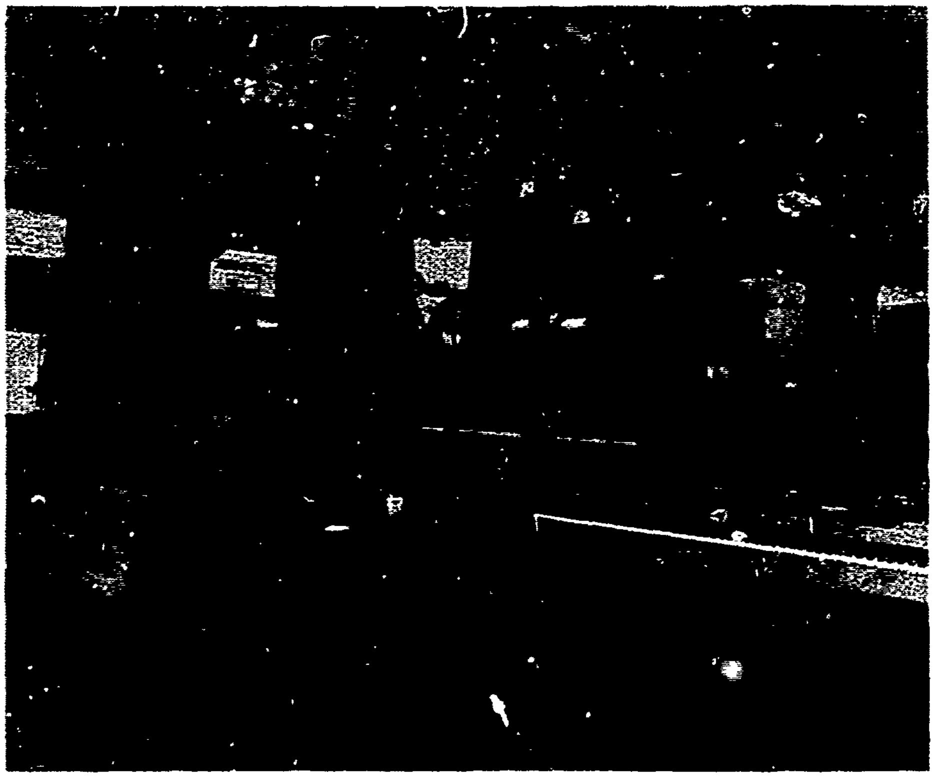

Fig.10. Electro-Optic Evaluation Apparatus.

B. Optical Absorption Measurements

The calorimetric technique is the most common method of measuring the optical absorption coefficient of materials at 10.6 μm. Basically, this method involves radiating a sample of the material to be measured with a known amount of energy from a CO_2 laser and measuring the resultant temperature rise of the sample. From the mass and specific heat of the material and the power absorbed, the absorption coefficient of the material may then be calculated.

The power absorbed in a medium of length ℓ and having nominally plane, parallel faces is given by

$$P_a = \frac{(1-R)(1-e^{-\alpha\ell})}{(1-Re^{-\alpha\ell})} P_i \ , \tag{8}$$

where R is the reflection coefficient at normal incidence, P_i is the normally incident power, and α is the absorption coefficient. For the product $(\alpha\ell)$ much less than unity, the relation for the power absorbed simplifies to

$$P_a = \alpha\ell \, P_i \ , \tag{9}$$

independent of the reflection coefficient. The power absorbed is found calorimetrically by analysis of the sample's transient thermal response to the incident power.

Consider a sample having no constraints on the temperature at its boundaries and subject to heat losses to the environment alone. The heat losses increase as the temperature difference ΔT between the sample and the environment increases. The rate of heat loss P_L at a specific temperature difference $(\Delta T = \Delta)$ is given by

$$P_L\Big|_{\Delta T = \Delta} = -C_p M \frac{d(\Delta T)}{dt}\Big|_{\Delta T = \Delta} \ , \tag{10}$$

where C_p is the sample heat capacity, M the ~~sample~~ mass, and $d(\Delta T)/dt$ the instantaneous change in sample temperature with respect to time.

If power is incident on a sample, its temperature rise is influenced by the absorbed power and also by the power lost to the environment. The instantaneous change in sample temperature at $\Delta T = \Delta$ in this case is given by

$$\left.\frac{d(\Delta T)}{dt}\right|_{\substack{\Delta T=\Delta \\ P_i \neq 0}} = \frac{1}{C_p M} \left(P_a - P_L\right)\Big|_{\Delta T=\Delta} \quad . \tag{11}$$

Combining eqs. (9), (10), and (11), and solving for α results in the relation,

$$\alpha(\Delta T)\Big|_{\Delta T=\Delta} = \frac{C_p M}{\ell P_i} \left[\left.\frac{d(\Delta T)}{dt}\right|_{\substack{\Delta T=\Delta \\ P_i \neq 0}} - \left.\frac{d(\Delta T)}{dt}\right|_{\Delta T=\Delta} \right] . \tag{12}$$

Equation (12) implies that the absorption coefficient α, which may be temperature dependent, can be found experimentally by analysis of transient thermal response of a sample during and after laser irradiation. A typical transient response of a sample having temperature independent absorption is shown in Fig. 11. The sample is initially at equilibrium with the environment ($\Delta T=0$). During laser irradiation, the slope

$$\left.\frac{d(\Delta T)}{dt}\right|_{\substack{\Delta T=\Delta \\ P_i \neq 0}} \tag{13}$$

is measured at a particular departure from equilibrium $\Delta T = \Delta$. As the sample returns to equilibrium, the slope

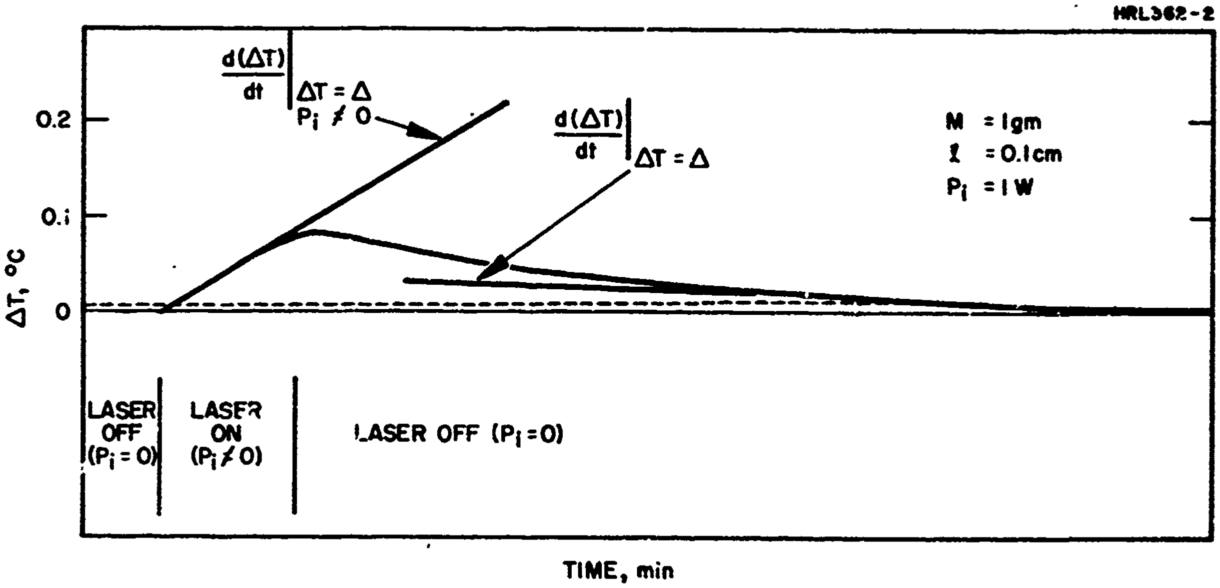

Fig. 11. Typical Transient Thermal Response for Temperature Independent Absorption.

$$\left.\frac{d(\Delta T)}{dt}\right|_{\Delta T=\Delta} \qquad (14)$$

is measured at the same departure from equilibrium. The absorption coefficient is found by substitution of these values into eq. (12).

The calorimeter is illustrated schematically in Fig. 12 and a photograph of the actual device using a CO_2 laser as the source is shown in Fig. 13. We have used both CO_2 (10.6 μm) and Nd:YAG (1.06 μm) as source illuminators for this calorimeter. A close-up view of the sample holder is shown in Fig. 14.

C. Modulator-Related Properties of CdTe

Several of the important modulator-related properties of Modified Bridgman-grown CdTe have been measured. The properties measured at Hughes Research Laboratories include the refractive index, hardness, the electro-optic coefficient, the optical absorption coefficient, the loss tangent at 1 GHz, the specific heat, and the temperature coefficient of the refractive index. The value given for thermal conductivity was determined on our sample from a commercial source using the Colora Thermoconductometer.* Values of the properties measured are given in Table II. For completeness, the values of other important properties from the literature are also included. Where applicable, the values given correspond to data taken at 10.6 μm. Results of the absorption measurements on thermally annealed samples show the lowest value for single crystal material to be $\alpha = 0.0015\ \text{cm}^{-1}$. Actual bulk values

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*Measurement performed by Ablestik Adhesive Company, Gardena, California.

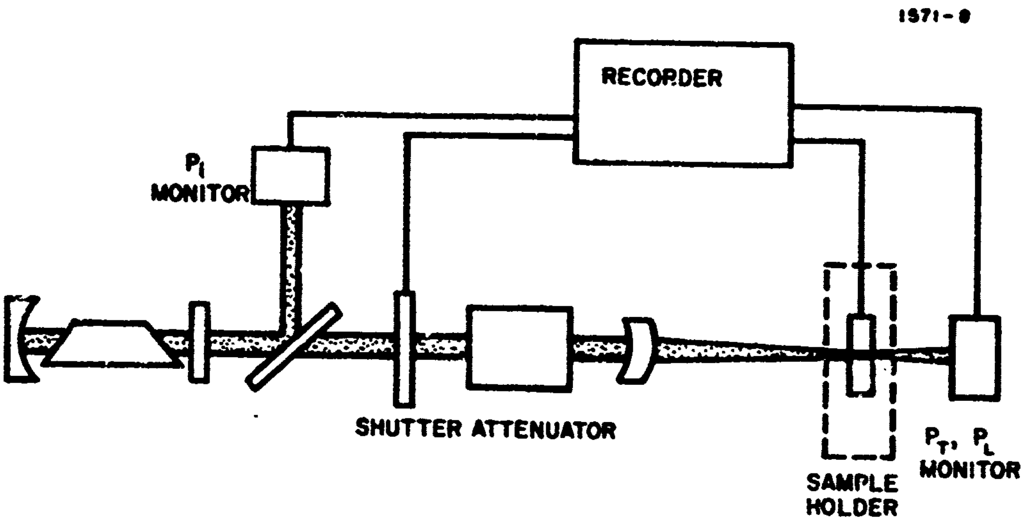

Fig. 12. Laser Calorimeter Schematic.

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Fig. 13. Laser Calorimeter.

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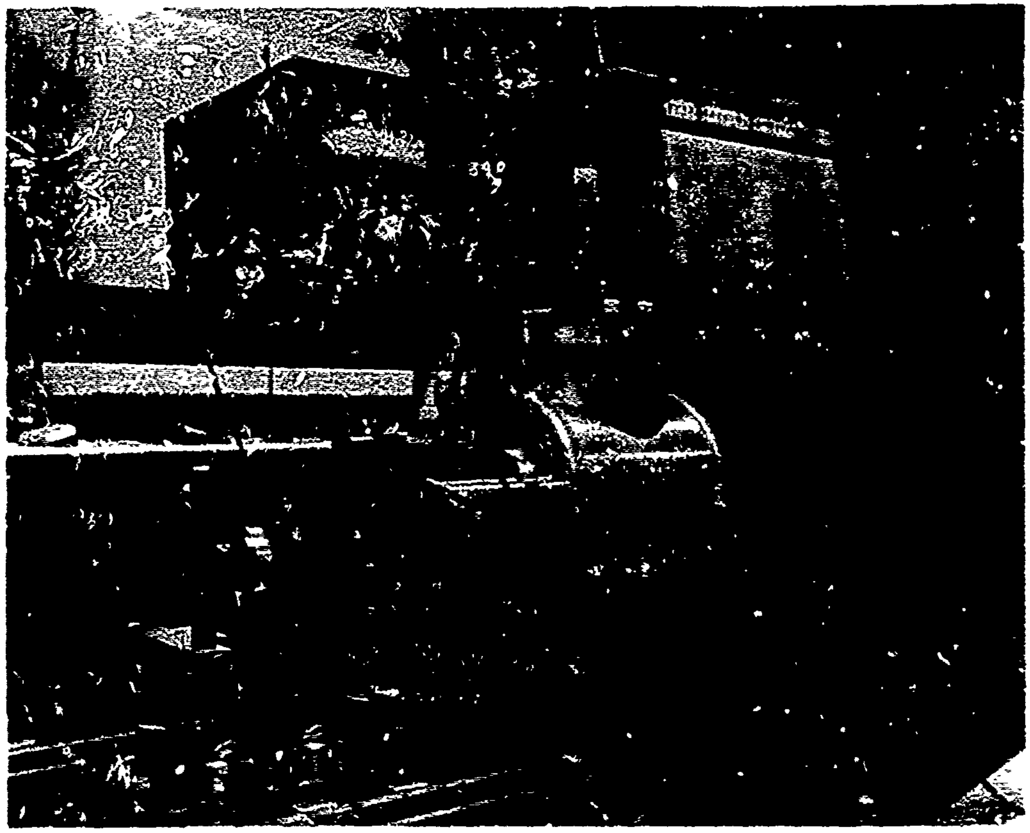

Fig. 14. Optical Calorimeter Sample Holder.

may be less than this measured value as discussed in recent work as by Shiozawa, et al.[3] Currently, single crystal CdTe averages 0.002 to 0.003 cm^{-1}. The method of measurement of α, the absorption coefficient is discussed in a previous section.

TABLE IV

CdTe Properties

Clamped (high frequency) electro-optic characteristic $n_o^3 r_{41}$	$10 \pm 1 \times 10^{-11}$ m/V
Halfwave voltage $V_\pi \cdot \ell / d$ (10.6 μm)	53 kV
Dielectric constant $\varepsilon/\varepsilon_o$	10
Resistivity	$>10^7$ Ω·cm
Loss tangent (1 GHz)	$<10^{-2}$
Refractive index n_o	2.67
Transmission range	1 to 25 μm
Optical absorption coefficient	0.0015 to 0.003 cm^{-1}
Thermal conductivity	0.0093 cal(sec·cm·°C)$^{-1}$ 120°C
Temperature coefficient of the refractive index (1/n) dn/dt	4.4×10^{-5}°C^{-1}
Linear coefficient of thermal expansion	5.5×10^{-6}°C^{-1}
Hardness	
Moh	2.8
Knoop	47 to 53

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D. Oxygen Contamination Studies

In the investigation of the limiting mechanisms of the absorption coefficient of CdTe, a number of factors, including impurity content, have been analyzed.* However, analysis of impurity content by mass spectrographic and emission spectrographic techniques failed to show any meaningful correlation between impurity levels and the measured absorption coefficient. Even for variations in oxygen content — a contaminant of great suspect for limiting the absorption coefficient — ranging from 0.4 to 22 ppma, no significant deterioration of α (absorption coefficient) was observed (see Table III). In order to determine the role of oxygen as a deleterious impurity to optical transmission at 10.6 µm, we undertook a series of experiments using CdO to dope ingots with known concentrations of oxygen. Although the degree of solubility (segregation coefficient) is unknown for oxygen in CdTe, the concentrations introduced into the melt were 0, 100, 1000, and 10,000 ppma oxygen; 10 ppma oxygen was not used since data indicated little difference could be shown between intentionally doped samples at that level and unintentionally doped ones, i.e., not specifically added oxygen impurity. Crystals were grown, both only oxygen doped and oxygen plus indium doped (2×10^{17} In atoms/cc). Indium is used as the usual dopant to ensure high resistivity, hence good quality after the heat treatment procedure. The ingots were grown by a Bridgman technique, and after being cut and polished were optically evaluated. The results of the investigation are summarized in Table IV. The data contain few conclusions. Samples that were not indium-doped showed poor optical transmission but no free carrier absorption

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*This investigation was supported by the Air Force Materials Laboratory under Contract F33615-71-C-1778.

TABLE III

Oxide Impurity Study of CdTe Crystals

ppma Oxygen[a]	$\alpha^{(b)}$ cm^{-1}	ρ, Ω-cm	Sample
0.4	0.008	6×10^8	214
0.6	0.7	0.99	219[c]
0.9	0.010	6×10^8	208
1.1	0.002	$> 10^7$	176
2.5	0.010	---	191
6.6	---	2.0	204[c]
22.0	0.007	4×10^2	212

[a] Mass spectrographic analysis performed by Bell and Howell, Pasadena, California.

[b] Calorimetric absorption coefficient measurement made at HRL.

[c] Free carrier absorption.

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TABLE IV

CdTe Samples Oxygen and Indium(a) Doped

		10.6 μm Transmission I_T/I_0, %		
Sample	Oxygen, ppma	As Grown	First Heat Treatment	Second Heat Treatment
1-0	0	0	63	56
1-1	100	0	10	24
1-2	1000	0	5	50
1-3	10,000	0	2	17
2-0	0	0	56	--
2-1	100	0	42	--
2-2	1000	0	52	--
2-3	10,000	0	54	--
3-0-N(b)	0	57	--	--
3-0-T(b)	0	51	--	--
1-1-N(c)	100	0	60	--
1-1=T(d)	100	0	64	--

(a) Indium doping ≈ 2 x 10^{17} atoms/cc.

(b) Control sample, no indium doping.

(c) Absorption coefficient, $\alpha = 0.116$ cm^{-1}.

(d) $\alpha = 0.016$ cm^{-1}.

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(see Fig. 15) and could not be further treated in any way. In this figure samples are designated according to the oxygen concentration of the starting materials, i.e., 0 = no intentional oxygen doping, 1 = 100 ppma, 2 = 1000 ppma, and 3 = 10,000 ppma oxygen. Data are shown for two different samples, one designated by prime which contains no indium. Samples both oxygen and indium doped initially showed no transmission at 10.6 μm and were subsequently subjected to thermal anneal. After heat treatment, a sample with no intentional oxygen doping showed a 63% transmission using a calibrated laser beam. Increasing concentrations showed decreasing transmission but the range was so low that the accuracy of the results is questionable. The spectrophotometer traces taken after one heat treatment (see Fig. 16) indicate the possibility of residual free carrier absorption in some of the doped samples. However, a second cut of samples showed nominal transmission using a 10.6 μm laser beam following a first heat treatment. A second heat treatment (see Fig. 17) showed essentially a lack of free carrier absorption in all samples, but extremely poor transmission. The main result of the oxygen study was to show that oxygen contamination at these high levels has extremely deleterious effects on the structural quality of the crystal. Crystals become very brittle and polishing causes excessive pitting of the surfaces. These effects are exhibited by extreme variations in optical transmission caused by scattering. The general crystal bulk was filled with voids (see Fig. 18) and the crystal had a very black appearance similar to soft coal.

The second heat treatment, although carried out under an overpressure of Cd, seemed to have been deleterious to all samples (including undoped or unintentionally doped samples) which may be a result of the existence of an oxygen partial

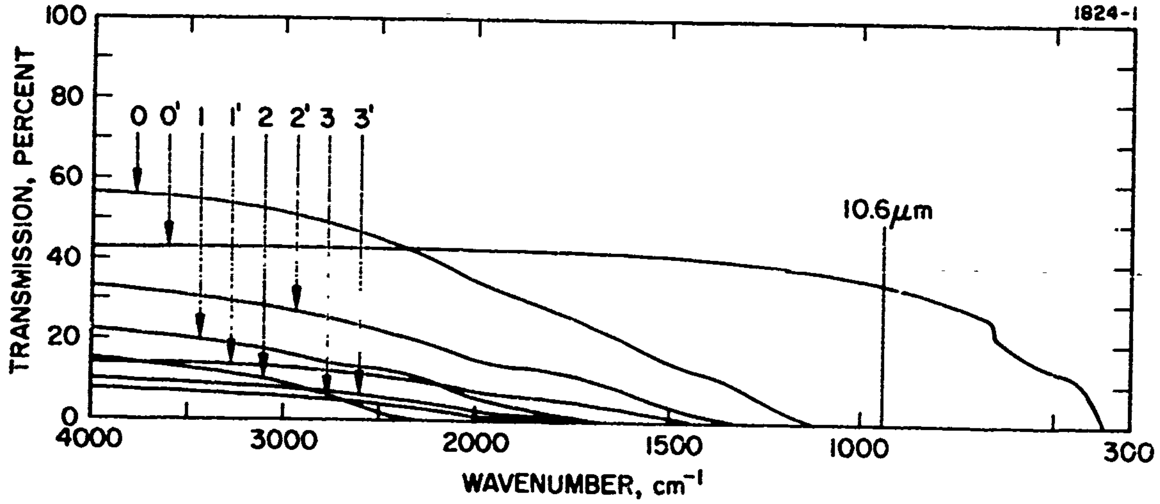

Fig. 15. Infrared Transmission of As-Grown CdTe For Oxygen Contamination Evaluation.

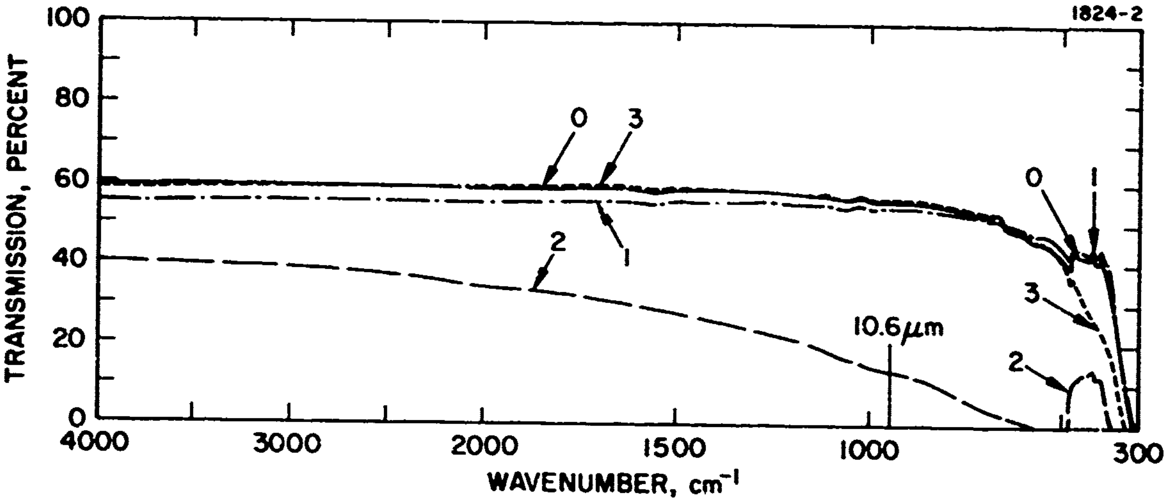

Fig. 16. Indium and Oxygen Doped Samples After First Heat Treat.

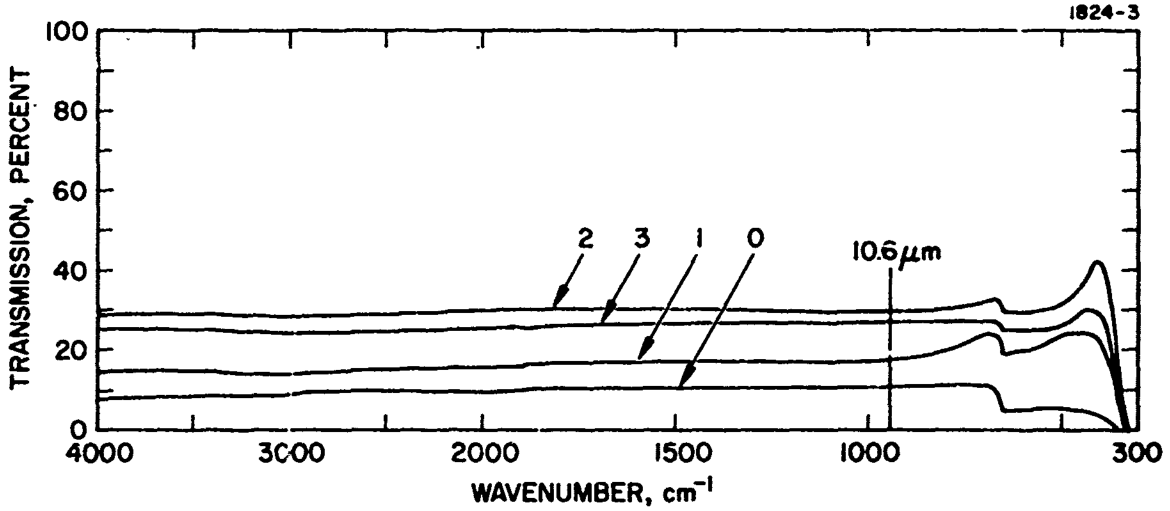

Fig. 17. Indium and Oxygen Doped Samples After Second Heat Treat.

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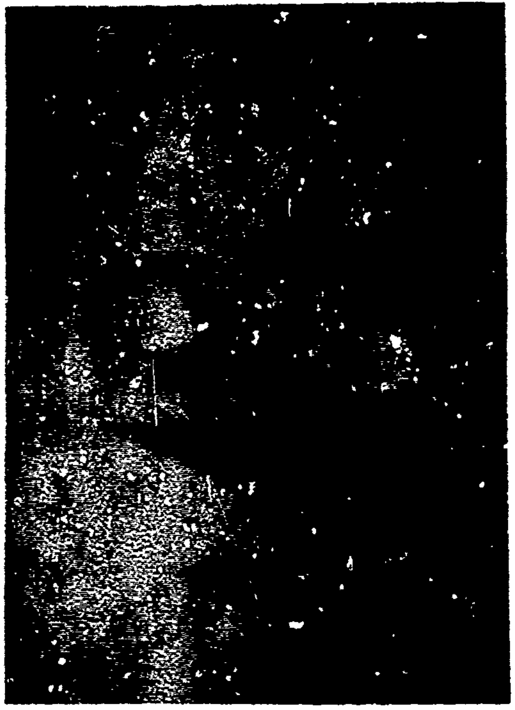

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Fig. 18.
Apparent Voids in Oxygen Doped CdTe.

pressure in transmission of these samples after processing. As anticipated, there are general evidences of variations in oxygen content from nose to tail with the tail of some ingots appearing to have higher transmission and higher resistivity than the nose. However, we feel that an insufficient number of samples was studied and conditions were not adequately reproducible to draw any additional conclusions. Great amounts of oxygen contamination (>100 ppma) obviously must be avoided for high quality optical material as required for the infrared modulator application.

IV. CONCLUSIONS AND RECOMMENDATIONS

Cadmium telluride appears to be the most promising material available for modulation at 10.6 μm because of its low absorption value and high value for the electro-optic parameter $n_o^3 \cdot r_{41}$ which is 10×10^{-11} m/V. In addition, large single crystals are available that are capable of yielding rods as long as 5 cm; because of the relative values of the electro-optic coefficients, this corresponds to a GaAs modulator rod of nearly 10 cm in length. Cadmium telluride is also promising for modulation in the 3 to 5 μm region and may be useful at 1.06 μm. At the present time, an absorption is observed at 1.06 μm, following thermal anneal which is not observed in as-grown (unannealed) material. There is a possibility that this absorption is enhanced by impurity-defect relationships in the annealed material. This is an area in which further work is recommended for understanding the phenomenon and developing CdTe as an electro-optic modulator at that frequency.

A number of CdTe modulators have been fabricated at Hughes Research Laboratories (see Figs. 19 and 20), in addition to CdTe windows and lenses for 10.6 μm communications.* The development of CdTe as the promising modulator material at 10.6 μm has been achieved through the type of investigation sponsored by the Office of Naval Research. In addition, we acknowledge the program support of Hughes Aircraft Company, the Air Force Materials Laboratory, the NASA Langley Research Center, the Atomic Energy Commission, and Advanced Research Projects Agency, which has allowed significant contributions to the knowledge concerning the many applications of cadmium telluride.

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*A portion of this work has been sponsored by NASA Langley Research Center.

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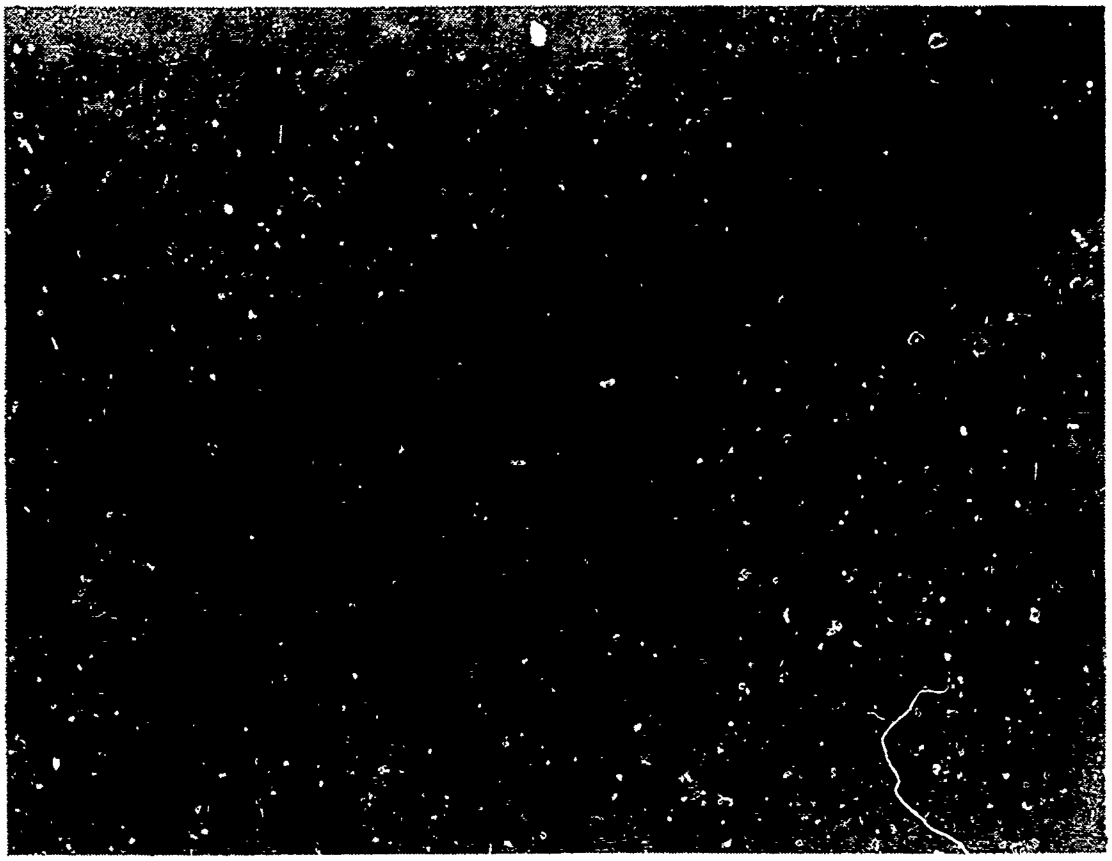

Fig. 19. CdTe Modulator Rod.

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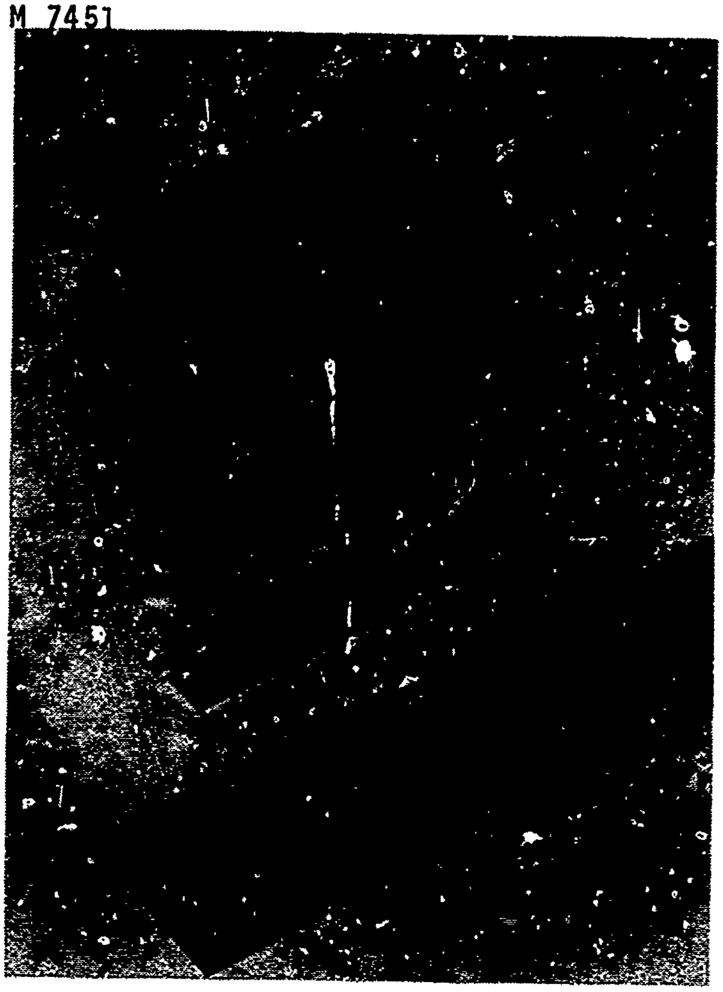

Fig. 20. Intracavity CdTe Modulator.

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