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(Period: January 1, 1993 till December 31, 1993)

on

Direct Observation of Crystal growth from solution using Optical investigation of a growing crystal face

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Submitted to

Lewis Research Center

National Aeronautics and Space Administration

21000 Brookpark Road

Cleveland, Ohio 44135

by

Department of Physics

Alabama Agricultural and Mechanical University

P.O. Box 71

Normal, Alabama 35762

February 1994

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OBSERVATION OF CRYSTAL GROWTH FROM
SOLUTION USING OPTICAL
INVESTIGATION OF A GROWING CRYSTAL
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Abstract

This report is the first annual technical report for the period January 1, 1993 till December 31, 1993 for the NASA grant NAG3-1429, entitled, "Direct observation of crystal growth from solution using Optical Investigation of a growing crystal Face." Mr. Thomas Glasgow, processing Science and Technology Branch, NASA/Lewis Research Center is the technical Monitor.

The work on the project did not start till June 1, 1993 due to the non-availability of the required personnel. Professor Ravindra Lal is the principal investigator of the project. Dr. B.R. Reddy is working as a research faculty member on the project, and Yongkee Kim as graduate student.

This report describes the progress of the work during the period June 1, 1993 till the end of 1993. Significant progress has been made for testing various optical diagnostic techniques for monitoring crystal growth from solution. Some of the techniques that are being tested are: (1) Optical heterodyne detection technique, in which changes in phase are measured as a function of time/crystal growth; (2) a conventional interferometric technique, in which a fringe brightness is measured as a function of crystal growth/time; (3) a Mach-Zehnder interferometric technique in which a fringe brightness is measured as a function of time to obtain information on concentration changes.

During the second year it will be decided to incorporate the best interferometric technique along with the ellipsometric technique, to obtain real time in-situ growth rate measurements. A laboratory mock-up of the

first two techniques have been made and tested.

Discussions about the work have been made with Dr. James Trolinger of Metrolaser, Irvine, CA and Prof. R. Azzam of the University of New Orleans and with Mr. Thomas Glasgow of NASA/Lewis Research center.

I. Introduction

Most of the time crystal growers are interested in estimating the crystal growth rate and its dependence on the growing face, concentration gradients in the neighborhood of the growing material, and finally the presence of interface, if any, between the new crystal and the seed. Recently there has been some effort to understand the interface, though there is no clear cut understanding about it. In this project our aim is to understand these parameters. For this purpose different techniques may be employed. We are interested in the development of nondestructive and noncontact optical techniques for real-time in-situ monitoring of crystal growth. For crystal growth rate measurement a variety of interferometric techniques can be used ranging from very inexpensive techniques to highly sophisticated techniques. The proposed technique should be feasible, provide accurate estimation of crystal growth parameters and be suitable for microgravity experiments. We pursued several techniques and decided to use the following techniques: (1) Optical heterodyne detection technique, in which a phase change is measured as a function of time/crystal growth; (2) An interferometric technique in which a fringe brightness is measured as a function of crystal growth/time; (3) Mach-Zehnder interferometer technique in which fringe brightness is measured as a function of time to obtain

information on concentration changes; and (4) Ellipsometric technique, which also gives information on the growth rate. In order to implement any of these techniques the crystal/material under study has to reflect some light at least.

II Optical Diagnostics for Crystal growth

II. A.1 Optical Heterodyne Detection

Typical frequency of an optical radiation, say HeNe laser is $\sim 10^{14}$ Hz. When such a radiation falls on a detector it does not respond to the fast oscillations, instead, its output is a dc signal proportional to the intensity of light. However, when two optical frequencies (with a frequency difference of ~ 1.5 MHz) fall on a detector, its output is a dc signal proportional to the intensity of light plus a radio frequency (rf) signal (1.5 MHz). If the pathlength for one of the optical beams varies then the phase of the resulting rf signal varies. Therefore, in this technique, phase change is measured as a function of crystal growth. This technique has been used in several applications for length measurement¹, surface roughness measurement² etc.,.

A block diagram of the experimental setup is shown in Fig.1. A Hewlett-Packard (HP 5501A) two-frequency Zeeman laser is used. Its two optical frequency components are separated by ~ 1.5 MHz. The two frequencies are collinear, but orthogonally polarized. Its wavelength stability is ± 0.5 parts per million. About 5% of the beam is separated and detected by a HP receiver (HP 10780B) which has a built in rf amplifier, whose output is an rf signal at 1.5 MHz, which is hereafter called the

reference signal. The other part of the beam is routed to the crystal growth chamber through a polarizing beam splitter (PBS). The PBS reflects one polarization component and transmits the other orthogonally polarized component. Both the components pass through separate $\lambda/4$ plates and travel to the crystal under growth and a plane mirror respectively as shown in Fig.1. The retroreflected components are recombined by the PBS and exit to another HP receiver. The two components travel approximately equal distances. The receiver output is an rf signal at 1.5 MHz (hereafter called (growth signal)), whose phase varies as the crystal grows in time, because the total pathlength of one frequency component is changing. The change in phase is measured by comparing the phase of the growth signal (rf) with that of the reference rf signal. For this purpose, the two rf signals are given to the two inputs of a phase meter (HP 3575A) whose output is a dc signal (volts) that is proportional to the phase difference between the two inputs. The detector output is given by,

$$I_1(\text{ref}) = 2[1 + \cos(\phi_1 + \Delta\omega t)], \quad (1)$$

where $\Delta\omega = \omega_1 - \omega_2 = 1.5 \text{ MHz}$ and $\phi = k_1 Z_1 - k_2 Z_2$; where k and Z are the wave vector and pathlength of the either frequency component. However, the receiver has a built in rf amplifier whose output is given by,

$$I_1(\text{ref}) = A_1 \cos(\phi_1 + \Delta\omega t). \quad (2)$$

Similarly, the output of the second receiver (growth signal) is given by

$$I_2(\text{growth}) = A_2 \cos(\phi_2 + \Delta\omega t). \quad (3)$$

As the crystal is growing, the pathlength of the beam changes and hence the phase factor ϕ_2 also changes. The change in phase difference $\phi_1 - \phi_2$, is

related to the pathlength change/crystal growth.

For a change in growth of Δl the pathlength travelled by one of the beams changes by $\Delta Z = 2 \Delta l$. A pathlength change of λ (for a crystal growth of $\lambda/2$) corresponds to a phase change of 2π . Therefore, the measured phase difference is related to the material growth as, $\Delta\theta = \phi_1 - \phi_2 = 4\pi \cdot \Delta l / \lambda$. So, when the material grows by $1\text{\AA}$ the measured phase changes by $\sim 0.1^\circ$, which is the resolution of the phase meter. Hence this technique is suitable for the measurement of growth rates as low as $1\text{\AA}$.

For a proof of the concept we have demonstrated this technique using the setup shown in Fig. 2. Here, instead of a growing crystal, a moving mirror is used in its place. The mirror was translated using a micrometer. Even for a slight movement of the micrometer (that corresponds to thousands of Ångstroms) the measured phase difference jumped from one value to the other as expected for that type of coarse movement. A slow and continuous motion is not possible with a micrometer. However, this is a very sensitive technique to monitor small changes in length. In fact this technique was used to measure surface roughness of coated mirrors, $\sim \text{\AA}$. Typically, TGS crystal grows at the rate of 1 mm/day ($\sim 10^2 \text{ \AA/sec}$). Hence this technique is very accurate to measure such growth rates. At the same time this is a noncontact, nondestructive technique and is useful for in-situ crystal growth rate measurement. It is important to note that the distance of the moving mirror (or growing crystal) may not be known. Interferometers measure changes in position of a mirror with respect to the other.

II.A.2 Crystal growth setup

The crystal growth chamber is a double walled cylindrical unit with a capacity of 1.8 liters. Saturated solution of TGS is prepared at 25°C by dissolving appropriate quantity of TGS in distilled water (313 grams/liter). About 1.5 liters of the solution was poured into the chamber. Its temperature is maintained steady, by circulating water through the outer jacket of the chamber using a temperature controlled circulator. The seed crystal is glued to the cold finger (sting) of the sting whose temperature is controlled thermoelectrically.³ A schematic diagram of the sting is shown in Fig.3. The temperature of the solution and the cold finger are measured with a YSI 400 series probes and a thermistor thermometer. The sting is thermoelectrically cooled (using a Marlow industries module Model# MI1022T-01AC) to a lower temperature (~24°C) by passing a current ~0.1 Ampere at 1.5 Volts through the device ($V_{\max} = 3.5$ Volts and $I_{\max} = 1.8$ Amps).

Light enters the crystal growth chamber from the bottom and is retroreflected by the front surface of the material. Since, the material is highly transparent in the visible region, reflection from the back surface has to be suppressed. This can be done by either of the following methods. Usually rear surface reflection is eliminated by making a wedge out of the crystal. That means, the rear surface makes a small angle with the front surface which is plane parallel. However, to implement this in our case, cold finger of the sting needs to be at the same angle as the material surface. In general that approach is tedious and time consuming. However, we could successfully eliminate the rear surface reflection by coating it

with a black paint that is insoluble in water.

The maximum power that is available from a commercial Zeeman laser is about 1 mW. However, the in house laser output (that is employed now) is about 0.25 mW. Under crystal growth conditions, the reflected light from the front surface is visible to the naked eye but did not exceed the threshold level of the HP receiver. For this purpose we are planning to make one or more of the following changes

- (1) To replace the existing HP-receivers with photomultiplier tubes whose output is given to rf amplifiers.
- (2) To buy a new 1 mW two-frequency Zeeman laser
- (3) Select materials of high reflectivity which are also useful for microgravity crystal growth experiments.
- (4) To use a high power single frequency laser with Bragg cells as described below.

II.A.3 Heterodyne detection technique with an Ar^+ laser

Weak Zeeman lasers are convenient when the surface reflectivity is high, e.g., metallic films. In general some of the solutions may absorb light also. In those cases it is advantageous to resort to high power single frequency lasers (diode laser/ Ar^+ laser or a HeNe laser). The laser output is split into two parts as shown in Fig.4. A portion of the beam passes through a Bragg cell, whose output is modulated at say, 41 MHz and the other part is modulated at say 40 MHz which transmits through a $\lambda/2$ plate. On exit its polarization is rotated by 90° . The two parts are then combined with a PBS to get collinear beams but orthogonally polarized. Such a two frequency

laser can be used in optical heterodyne detection experiments as in Fig.1. Similar experimental configuration was successfully implemented in heterodyne detection experiments also.⁴

II.B. Conventional interferometry

Crystal growth rate can also be measured using a conventional interferometric technique which is being implemented in our laboratory. Whenever a transparent material is exposed to light, reflection occurs from the front and back surfaces of the material (Fig.5). The two reflected beams interfere to produce a fringe pattern. We have observed the interference pattern in the reflected light from a TGS crystal. As the crystal grows its thickness varies and hence, the intensity of the fringe varies. Therefore, the signal appears like a moving fringe pattern. We are getting a crystal growth chamber fabricated for this purpose. At the fringe pattern a screen is introduced with a hole (Fig.5). A detector is installed behind the hole whose output is given to an amplifier and a chart recorder. When the reflected beams are in phase at the hole, the fringe is bright and when they are out of phase the fringe is dark. However, when the crystal is growing the phase difference between the beams vary continuously and hence the detector output is oscillatory as a function of time. This will also give an estimate of the growth rate. However, this technique is not as accurate as the heterodyne detection technique but is very inexpensive. This technique has been successfully employed for dissolution rate measurement⁵ of polymers. It was also found from dissolution measurements that an interface layer exists between the material and the solution. In our modified design the

crystal growth chamber has two horizontal ports for light entrance and exit. The crystal seed is attached to the side of the sting. The rear surface of the seed is not coated for this experiment. For light detection we are using a PIN diode followed by an amplifier and a strip-chart recorder. For a material that grows at the rate of 1mm/day ($\sim 116 \text{ \AA/sec}$) the amplifier output exhibits oscillatory behavior with a period of $\sim 27 \text{ sec}$ (for a growth/change in thickness of $\lambda/2$) at HeNe laser wavelength and for near normal incidence. We have different configurations for this technique as shown in Figs. 5(a) & 5(b). For opaque materials only the top surface reflects. In that case one can use an experimental configuration similar to that of Michaelson's interferometer, Fig. 5(b). The light from the two paths add or cancel depending on whether the two beams are in phase or out of phase.

II.C. Mach-Zehnder interferometer

For the measurement of concentration gradients we are proposing to use Mach-Zehnder type of interferometric configuration as shown in Fig. 6. In this configuration, the laser beam is split into two parts by a beam splitter and then reflected by pentaprisms (or a pair of mirrors), P. The use of mirror-pair or pentaprism simplifies the alignment and adjusts the pathlengths of the two beams nearly equal. One component passes through the crystal growth chamber beneath the crystal and after exit interferes with the other component producing a fringe pattern on a screen when expanded with a lens. The detector measures the intensity of one fringe as a function of time/crystal growth. When the crystal grows/dissolves in time the concentration in the vicinity of the crystal will be different from the rest

of the chamber. As the concentration varies, the effective pathlength of the beam varies causing the intensity of the fringe measured by the detector to vary. The detector output is going to be oscillatory whose period depends on how fast the concentration of the solution/effective pathlength of the beam varies. To get information on how the concentration is varying around the crystal (spatial variation) one has to use an expanded beam and a two dimensional array detector/camera (CCD) has to be used to record the whole fringe pattern.

II.D. Ellipsometry

A linearly polarized light becomes elliptically polarized on reflection. In ellipsometry, the reflectivities of the p- and s- polarized components and the phase difference between them are measured. From these measurements, its refractive index, absorption coefficient, film thickness and composition are deduced. In fact, in microelectronic industry, the layer thickness is accurately measured using ellipsometry. Ellipsometry measurements can be made at a fixed angle and multiple wavelengths or at variable angle of incidence and multiple wavelengths. The latter provides additional information and is more accurate in predicting the structure model. Ellipsometric measurements can also be made in nulling-mode configuration or by polarization modulation technique. The former is very slow and the latter is much faster and is suitable for fast growth changes.

We intend to compare the value of the crystal thickness obtained from ellipsometry and other optical techniques. Information from all these techniques will be combined to obtain information about the growth process,

and the presence of interface layer if any, between the crystal and the seed. Ellipsometric technique has been earlier used by Tronin,⁶ for crystal growth rate measurements.

III. Adaptability of these techniques to microgravity experiments

It is possible to miniaturize these experiments for crystal growth in space. A typical interferometric technique that can be easily modified for space growth applications is shown in Fig 7. For this setup, a diode laser, PBS, quarter wave plate, detector and a memory device for data storage are needed. All of these can be assembled in a small module which can be operated with minimum training. The data from the memory device can be retrieved later for analysis. Similarly, the heterodyne detection setup can be modified too for space experiments on space shuttle or later on the space station module.

These techniques are applicable not only for crystal growth but for any other experiment that involves precision growth rate measurements, say, quantum wells, metallic films and any other material growth.

IV. References

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- (4) N.A. Massie et al, Appl.Optics 18, 1797 (1979).
- (5) K.L. Saenger and H.M. Tong, Polymer Engineering and Science 31, 432 (1991).
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V. Figure captions

Fig.1 Block diagram of the Optical Heterodyne detection setup for crystal growth.

Fig.2 Conceptual diagram of the heterodyne detection technique that was demonstrated with a moving mirror in place of a growing crystal.

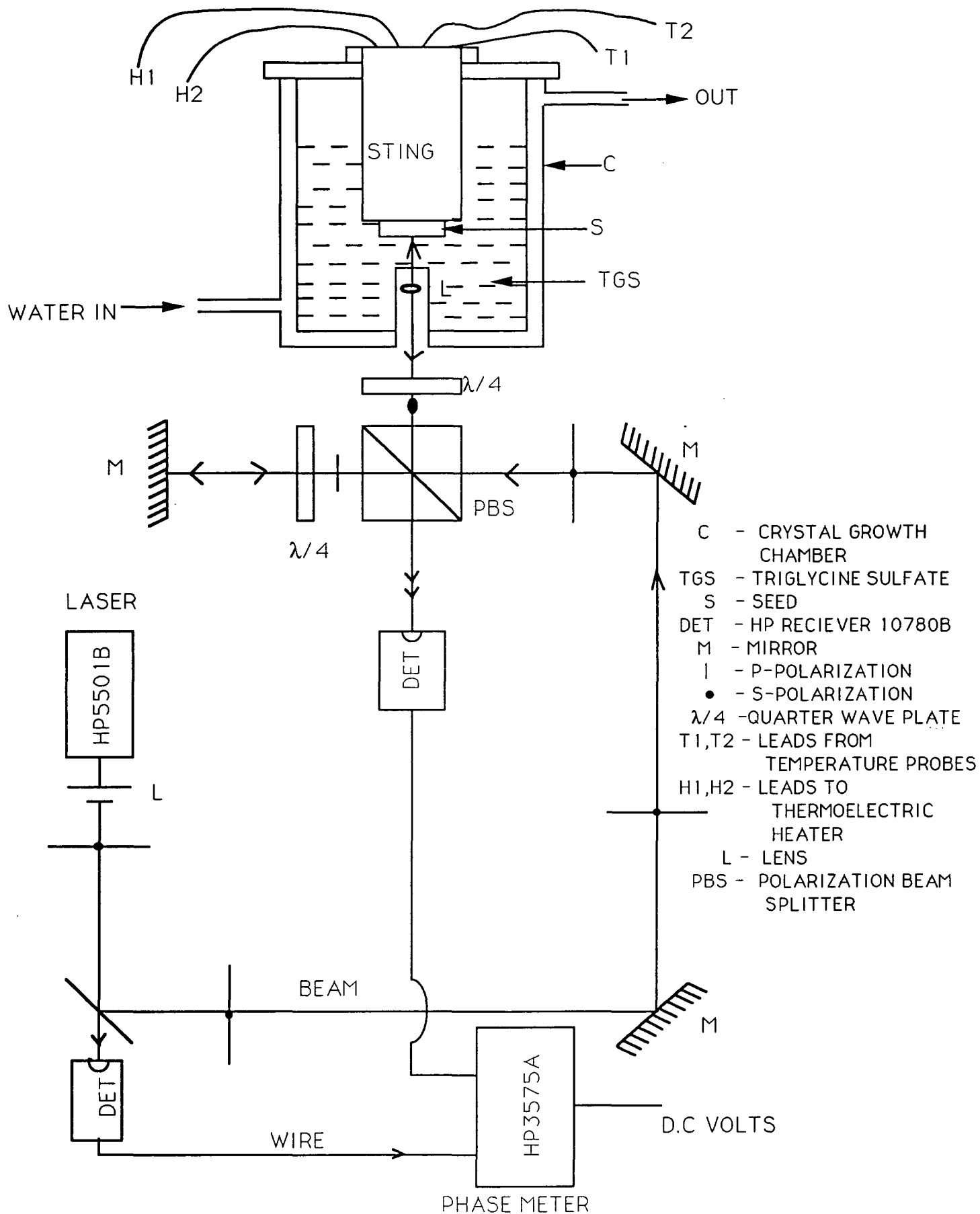
Fig.3 Detailed representative diagram of the crystal growth Sting.

Fig.4 Diagram for the generation of two optical frequencies ($\Delta f=1$ MHz) with orthogonal polarization, from a single frequency linearly polarized beam.

Fig.5 Schematic of the conventional interferometric technique for crystal growth measurement (a) transparent crystals and (b) opaque crystals.

Fig.6 Mach-Zehnder interferometer configuration for the measurement of concentration changes.

Fig.7 Modified configuration of the interferometric technique for space grown materials.



OPTICAL HETERODYNE DETECTION EXPERIMENTAL CONFIGURATION

FIG 1

CONCEPTUAL DIAGRAM - HETRODYNE DETECTION OF CRYSTAL GROWTH DEMONSTRATION

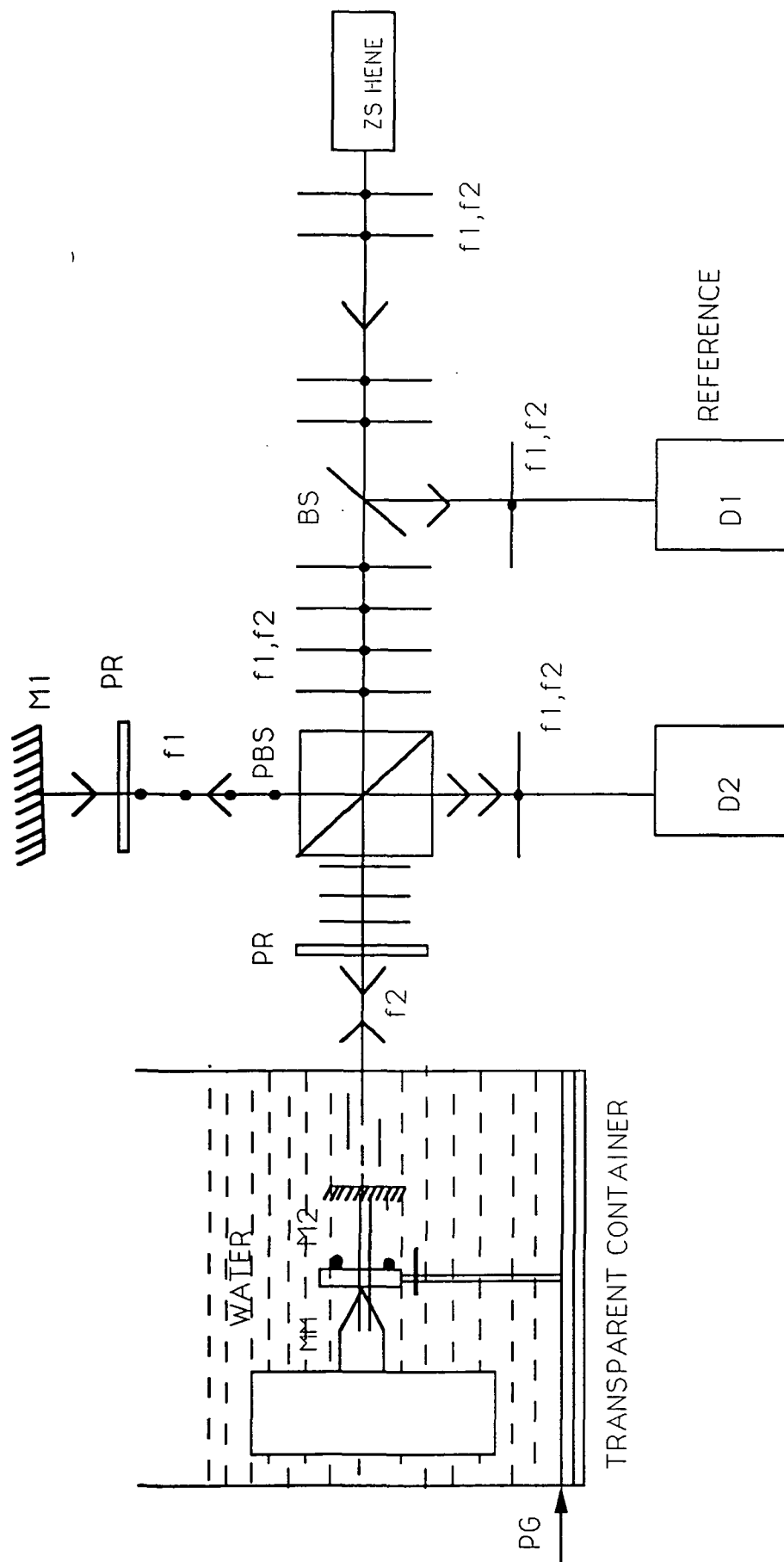


FIG 2

PG - PLEXIGLASS SHEET

MM - MICROMETER

M1, M2 - MIRRORS

PR - POLARIZATION ROTATOR ($\lambda/4$)

• S - POLARIZATION

| P - POLARIZATION

BS - BEAM SPLITTER

PBS - POLARIZATION BEAM SPLITTER

ZS - ZEEMAN SPLIT HeNe LAYER

$\Delta f = 1.5 \text{ MHz}$; $\lambda = 632.8 \text{ nm}$

D1, D2 - DETECTORS

REFERENCE

D1

D2

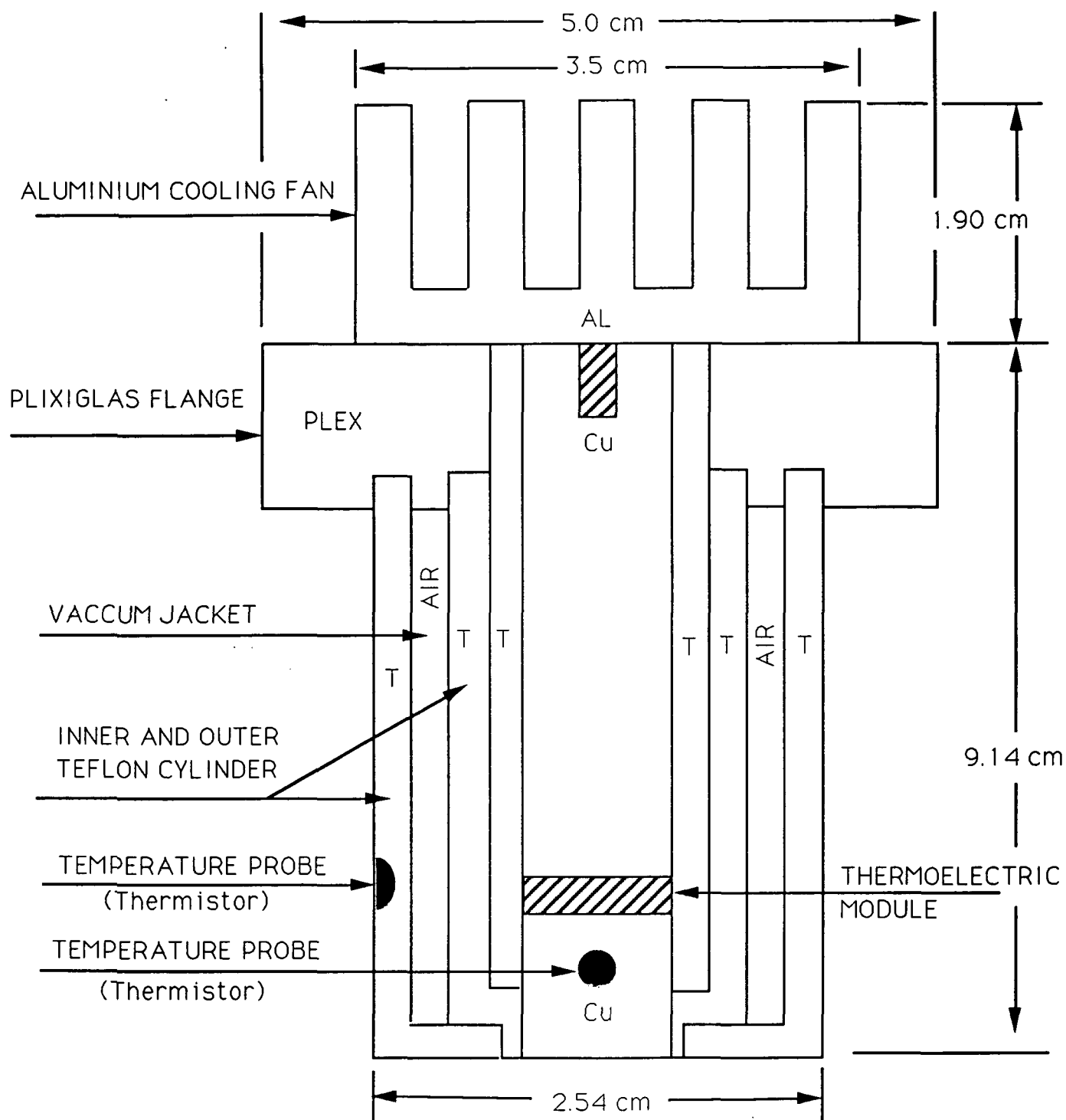
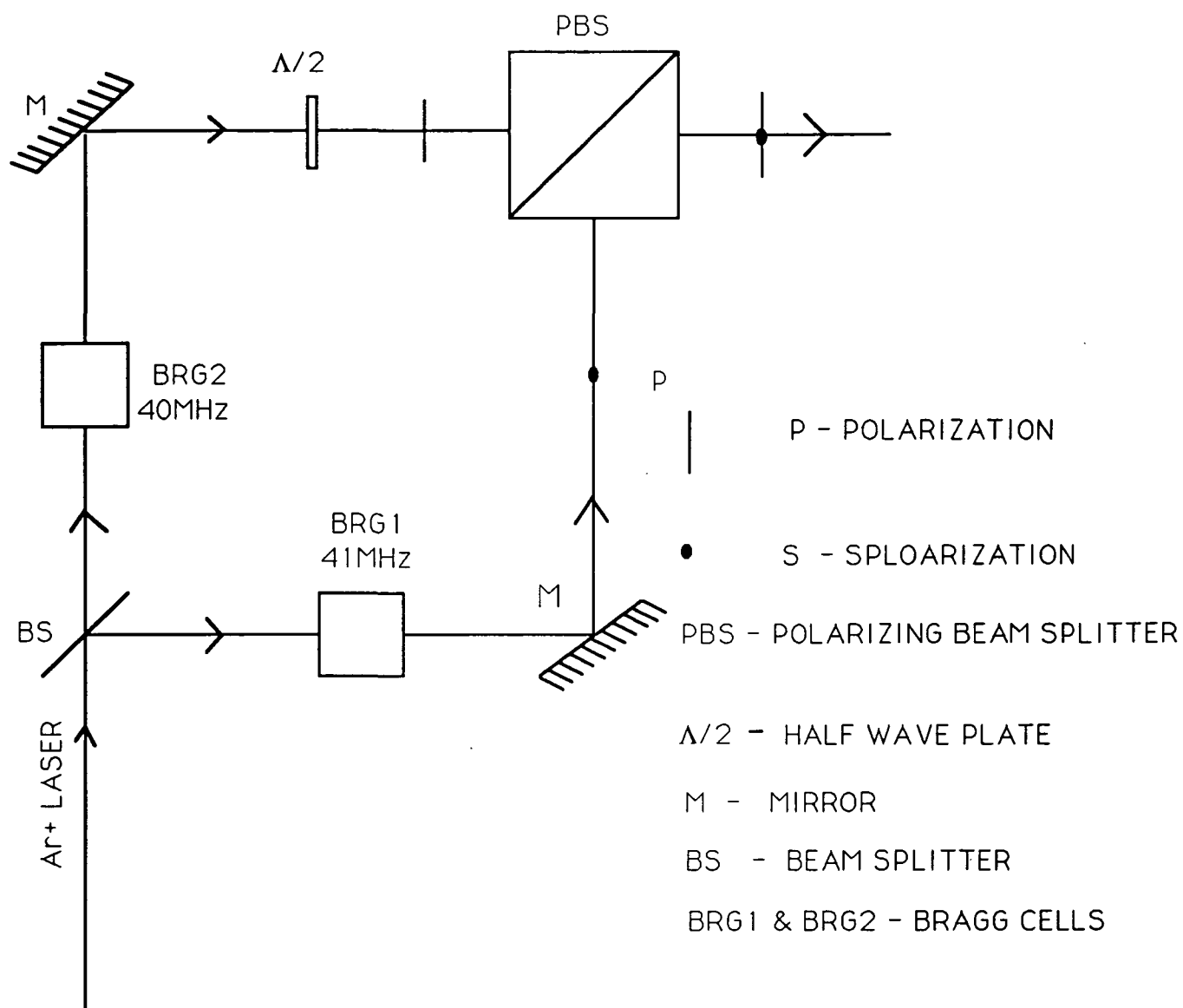


FIG 3



GENERATION OF ORTHOGONALLY PLANE POLARIZED
 BEAMS($\Delta F = 1\text{MHz}$)
 FROM A SINGLE FREQUENCY AR⁺ LASER

FIG 4

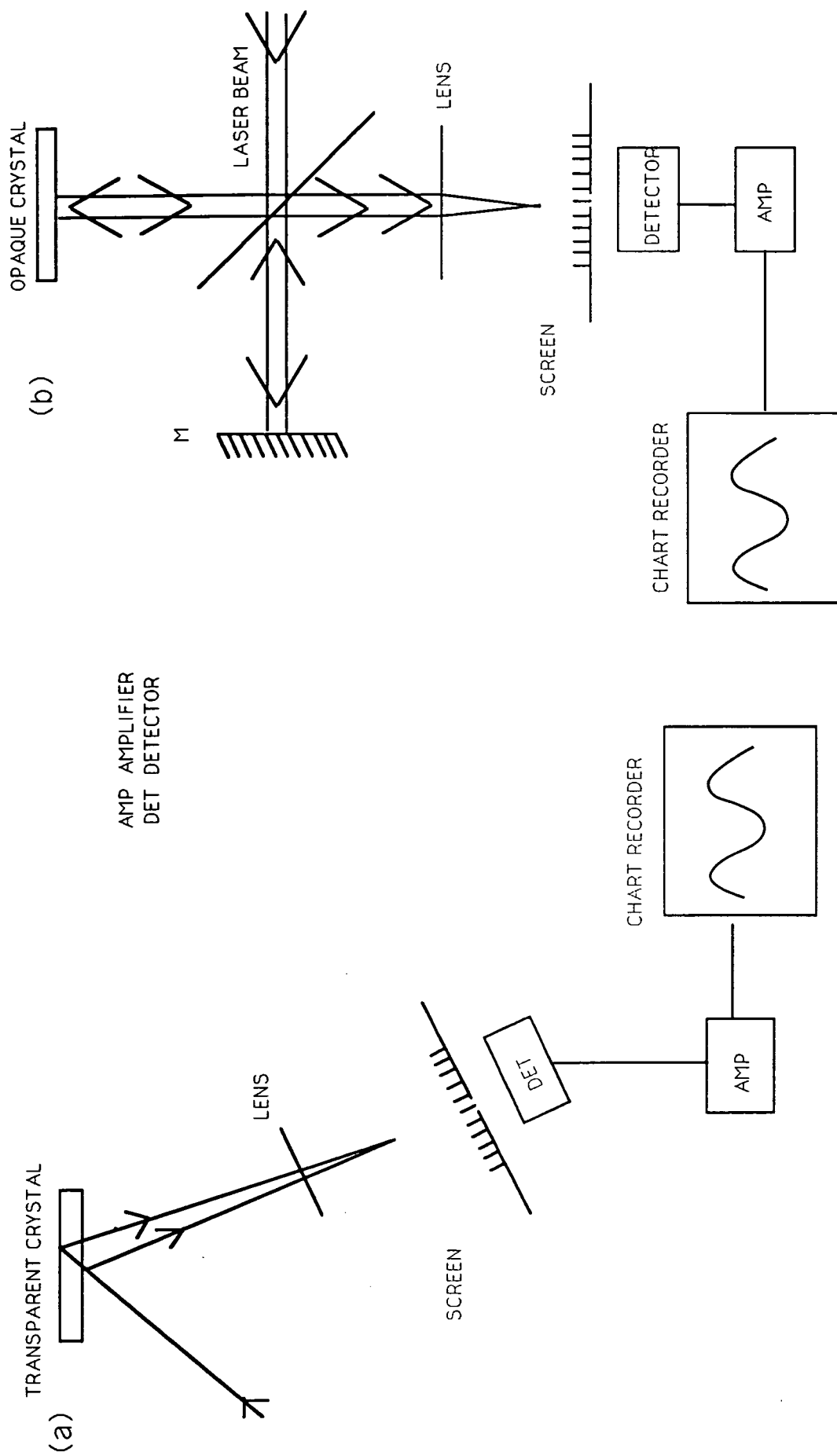


FIG 5

EXPERIMENTAL SETUP FOR INSITU INTERFEROMETRY

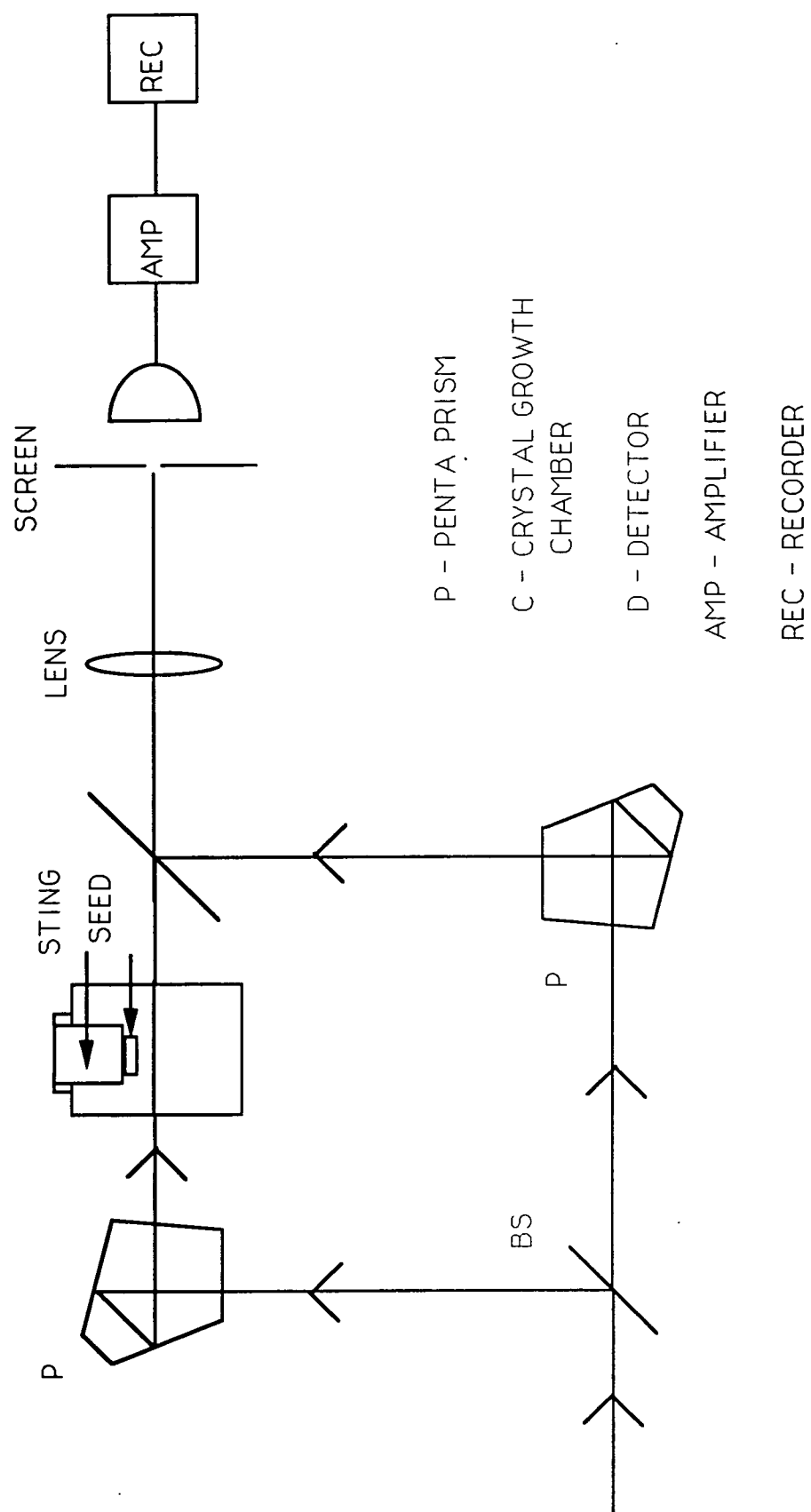
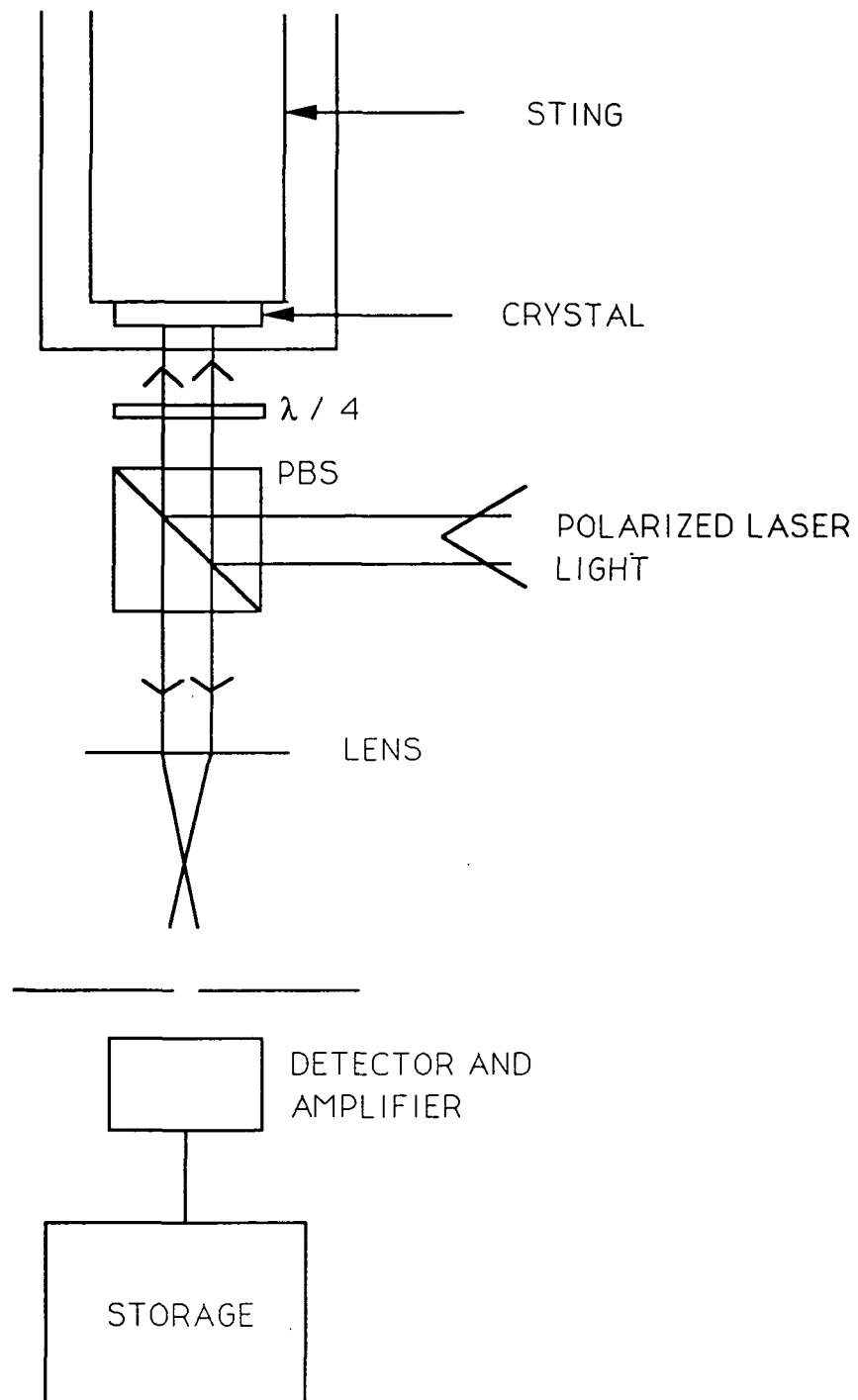


FIG 6

MACH - ZEHNDER INTERFEROMETER CONFIGURATION FOR THE
MEASUREMENT OF CONCENTRATION CHANGES



MODIFIED SETUP FOR CRYSTAL GROWTH RATE
MEASUREMENT IN SPACE

FIG 7