

# SPACE DIVISION



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CRYSTALS FOR OPTO-ELECTRONIC DEVICES: THE  
CASE FOR SOLUTION GROWTH Final Report  
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## SPACE PROCESSING OF CRYSTALS FOR OPTO-ELECTRONIC DEVICES — THE CASE FOR SOLUTION GROWTH

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## FOREWORD

This Study for Solution Crystal Growth was managed by Tommy Bannister of NASA-Marshall Space Flight Center as the Contracting Officer's Representative. It was led in the General Electric Company's Space Sciences Laboratory and The Pennsylvania State University by Louis R. McCreight as Program Manager .

The work was performed in a very exemplary manner by Drs. Rustum Roy and L. Eric Cross, Director and Associate Director (respectively) of the Materials Research Laboratory of The Pennsylvania State University and by Drs. Stephen C. Hayden and Barry A. Noval in the Space Sciences Laboratory of the General Electric Company Space Division.

## ABSTRACT

This report describes the results obtained during a six month program aimed at determining the viability of space processing in the 1980's of dielectric-elastic-magnetic single crystals. The results of this program included: identification of some important emerging technologies dependent on dielectric-elastic-magnetic crystals; identification of the impact of intrinsic properties and defects in the single crystals on system performance; determination of a sensible common basis for the many crystals of this class; identification of the benefits of micro-gravity and some initial experimental evidence that these benefits can be realized in space.

Based on this study, it is concluded that advanced computers and optical communications are at a development stage for high demand of dielectric-elastic-magnetic single crystals in the mid-1980's. Their high unit cost and promise for significantly increased perfection by growth in space justifies pursuit of space processing. No dominate compound presently exists, but it is concluded that the important compounds will most certainly be grown from a solvent. Preparation for space processing in the 1980's should then emphasize crystal growth in a solvent.

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## 1. INTRODUCTION

Technology has been advancing at an ever increasing rate in our already highly technological society. The recent availability of the microgravity environment of space offers an excellent opportunity for providing significant improvements in the crystals used in future computers and optical communications. In particular, the promise for large improvements in synthetically grown single crystals may well lead to economic viability of emerging technologies as well as possibilities for other new applications and technologies.

NASA has for some time recognized the importance of the impact of single crystals in technology and has flown a number of crystal growth experiments on Apollo, Skylab and ASTP<sup>(1)</sup>. These early crystal growth experiments have logically placed an emphasis on simple crystal systems. The results of flight experiments to date have shown excellent promise and should prompt a closer look at the opportunities for more complex, and more valuable, compound materials.

Many technologies are dependent on single crystal materials to varying degrees. Each of these must compete for flight time in space to demonstrate new economically viable concepts for space processing. This demands very careful consideration for each candidate process. However, the present pause in space flight activity until the shuttle in 1980 gives some time to make wise decisions. It is our conclusion that for economic viability of



space processing, crystal growth programs must clearly aim to those materials which will be the basis of the new device markets of the mid-1980's and beyond.

With the rapidly collapsing time scale between initial device conception and large scale exploitation, this clearly means that the programs should aim for those areas where new device concepts are presently appearing in the greatest number. For example, consider the time frame for the recent development of magnetic bubble memories. The pioneering paper by Bobeck on the exploitation of magnetic bubble domains for memory devices appeared in 1967<sup>(2)</sup>. Experimental magnetic bubble memory systems have recently been assembled and tested and are presently in need of improved single crystal magnetic films and substrates for widespread use<sup>(3)</sup>.

In this context, the 1950's through the 1970's was an era of exploiting electron transport properties of materials, in particular, semiconductors. Looking ahead, the present through the 1980's will be an era of exploiting lattice and spin instabilities of single crystals. The primary driving force has been the availability of intense coherent visible and infrared electromagnetic radiation of the laser. The laser has made feasible the exploitation of second order, nonlinear properties of single crystals. By their very nature, these nonlinear effects come from the lack of symmetry and instabilities in the crystal lattice or structures via a reaction with external electric, magnetic or stress fields.

Because of the different natures of electron transport and lattice and spin instability properties, it is not surprising that the types and demands on the crystals are considerably different. The new nonlinear dielectric-elastic-magnetic crystals have much more sophisticated structures of complex composition. Although high chemical purity is generally not required, extremely high structural perfection is vital to most applications. These two considerations are the primary distinctions from semiconductors.

The purpose of the investigation reported here is to take an in-depth look at the current and emerging dielectric-elastic-magnetic crystals. Considered are their 1980's applications and the demands on intrinsic properties and structural perfection in the light of space processing. A logical basis and sensible justification for pursuing space processing is presented. The results of some initial ground based solution growth studies on triglycine sulfate (TGS) is also presented as a starting point for the development of space processing techniques for many of the important emerging compounds.

## 2.0 APPLICATIONS - NEAR AND FAR FUTURE

Since the invention of the laser in 1959, a vigorous expansion of research and development in optics has occurred. Not only did pre-laser fields such as inelastic light scattering and holography experience greatly increased research activity, but entirely new fields such as the nonlinear optics have emerged as well.

The laser has certainly been a prime driving force for many new technologies. Just as the success of semiconductors relies on optimizing the coupling to the radio and microwave frequencies, technologies utilizing laser radiation depend on optimum coupling to visible and infrared electromagnetic waves. In the case of semiconductors, the electronic transport properties of crystals was exploited for optimum coupling. However, it is instabilities in the lattice and spin wave properties that must be exploited for optimum coupling to laser radiation. This area of device exploitation has only recently begun to receive a great deal of attention. With the collapsing time scale from device conception to widespread use, it is our belief that the new important technologies will utilize the dielectric-elastic-magnetic class of materials. Table 1 summarizes the era of conception to utilization for semiconductors and dielectric-elastic-magnetic crystals.

In this section several emerging technologies which utilize lattice and spin wave crystals are considered. Two, advanced computers and optical communications, are discussed in detail.

TABLE 1

THE BASIS FOR NEW DEVICES OF THE 1980's

<u>Basis</u>	<u>1950 to 1970</u>	<u>1980 to —</u>
Driving Force	Solid State Electronics	Laser
Property Exploited	Electronic Transport	Lattice and Spin Waves
Optimum Coupling	Radio and Microwave Frequencies	Visible and Infrared Frequencies
Utilization	Semiconductors	Optical, Elastic and Magnetic Effects

## 2.1 Computers

Because of their potential for significant improvements in information density and access time, optical memories are a leading contender for the next generation of mass storage devices. The replacement of magnetic disks and tapes used in present day computer systems by optical memories would result in a large saving of space and substantial decrease of information reading and writing time between the core processing and information storage areas.

Magnetic disk devices have present densities of approximately  $10^6$  bits/in<sup>2</sup> with realizable capacities of  $10^9$  bits per system. Magnetic bubble memory densities of  $10^8$  bits/in<sup>2</sup> have been demonstrated in the laboratory <sup>(4)</sup>. Holographic memories, which are in an earlier stage of development, have shown promise for densities of  $10^9$  bits/in<sup>2</sup> with capacities of  $10^{12}$  bits. The decrease in access time will be realized because these new memories can utilize non-mechanical addressing means.

### 2.1.1 Magnetic Bubble Memories

Magnetic bubble memories are similar to magnetic disk memories in that in both cases information is stored as magnetization states in a thin magnetic film. However, in a disk memory, the film is moved mechanically under read-write heads in one direction. In a bubble memory, the information bits, or bubbles, are moved in two dimensions by

magnetic fields while the film is stationary. As an additional advantage, operations such as bubble generation, replication, annihilation, and switching, can be performed on a bubble via manipulation of the external magnetic field without reading and writing operations. For example, several loop schemes have been devised using these operations to decrease access time.

Figure 1 shows schematically a simple magnet bubble memory chip. The sensing is accomplished by either the magneto-optic, magnetoresistive or Hall effect. Magnetic bubbles are really small cylindrical magnetic domain whose magnetization is reverse to the rest of the thin magnetic layer.

The restrictions on the magnetic film are severe as shown in Table 2. It is noted that very low defect densities are required. This includes any defects which interfere with the motion of the bubble such as twin planes, grain boundaries, surface scratches and pits, inclusions, dislocations and growth striations. This places additional requirements on the nonmagnetic substrate which supports the film. Not only must the lattice spacing match be close for epitaxy, but the substrate must also be defect free since any defects in the substrate will generally be reproduced in the film.

Magnetic bubble memories have reached an operation stage. The characteristics of a memory developed recently at Bell Telephone Laboratory is given in Table 3<sup>(5)</sup>. Future prospects call for bit densities

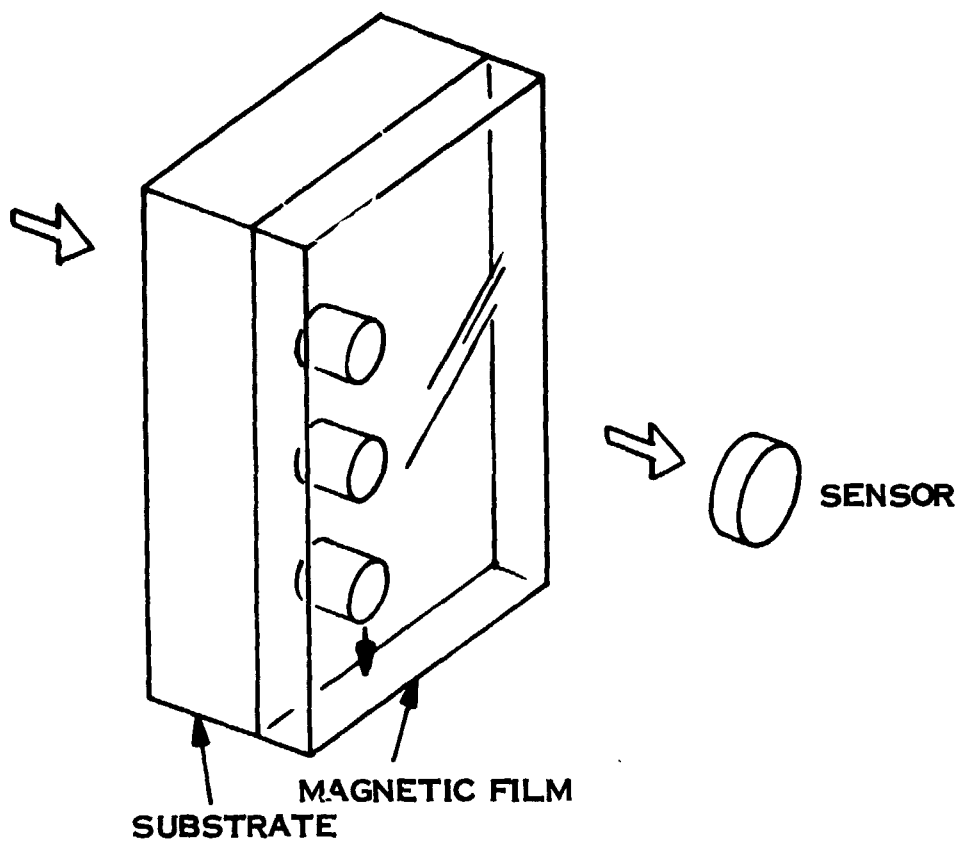


Figure 1. A Schematic Representation of a Magnetic Bubble Memory

TABLE 2

RESTRICTIONS ON MAGNETIC FILMS FOR BUBBLE MEMORY APPLICATIONS\*

Material Property	Specification	Related Device Operating Characteristics
Film Thickness	$3.5 \mu\text{m}^{(a)}$	Bit Size
Bubble Diameter	$6 \mu\text{m}$ : (bias field be paid out	Bit Density
Bubble Ellipticity	$< 0.2$	A compromise between Drive Field Power Requirements, Ease of Detection and Bubble Size and Stability
Characteristic Length	$0.8 \mu\text{m}$	
Saturation Magnetization	150 grams (a)	
Anisotropy Field	$> 2 \times (4\pi M_s)$	
Mobility	$< 200 \text{ cm/Oe}\cdot\text{sec}$	Data Rate
Coercive Force	0.3 Oe	Operating Stability over $50^\circ\text{C}$ temp. range.
Temperature Coefficient of Characteristic Length	$0.01 \mu\text{m}/^\circ\text{K}$	
Density of Crystal Defects which affect Magnetic Properties	$< 5/\text{cm}^2$	Defect Free Diced Garnet Chips
Usable Defect Free Area	$> 25 \text{ mm}^2$	

(a) Film thickness, characteristic length and magnetization to have  $\pm 1\%$  variation over the surface in a given run and to be reproducible to within 5% from run to run.

\* From R. Hiskes, Hewlett-Packard Laboratories, Palo Alto, Calif.



TABLE 3

PRESENT STATE OF MAGNETIC BUBBLE MEMORIES\*

28 chips x 16,448 bits/chip     $4.6 \times 10^5$  bits capacity

Access Time:            2.7 msec.

Read Error:             $< 1.6 \times 10^{-12}$

Read-Write Cycle:    5.15 msec

Error Free Propagation:  $> 8.4 \times 10^{15}$  bubble cycles

Applications:            Repetary dialer  
                              Voice message recorders  
                              Mass storage for electronic switching

\* From Reference 5.

of  $10^8$  to  $10^{10}$  bits/in<sup>2</sup> with cycle rates of  $10^6$  to  $10^7$  bits/sec. Whether or not these predictions are realized will depend to a great extent on further improvements in the substrate and magnetic film. For economic viability, these must be grown and fabricated with high yield rates.

### 2.1.2 Optical Memories

It is expected that when magnetic memory technology reaches its limit in the early 1980's, optical storage should be a competitive contender for the next generation data storage. Utilizing coherent laser radiation and diffraction limited optics, bit packing densities exceeding  $10^9$  bits/in<sup>2</sup> are expected. Combined with optical beam inertialess addressing and parallel processing, data rates in excess of  $10^9$  bits/sec. are theoretically possible. With full utilization of these capabilities, one can envisage a computer with the magnetic tapes and disks and the ferrite or semiconductor core replaced by a main frame optical memory. In principle, it is possible with such a memory to transfer its entire contents in or out of storage on the order of one microsecond.

Two types of optical memories have been shown to be technically feasible. Bit-by-bit permanent memories are now commercially available; for example, the Unicon 690 system developed by Precision Instruments. However, realization of the full potential of optical memories will be realized only in three-dimensional holographic storage.

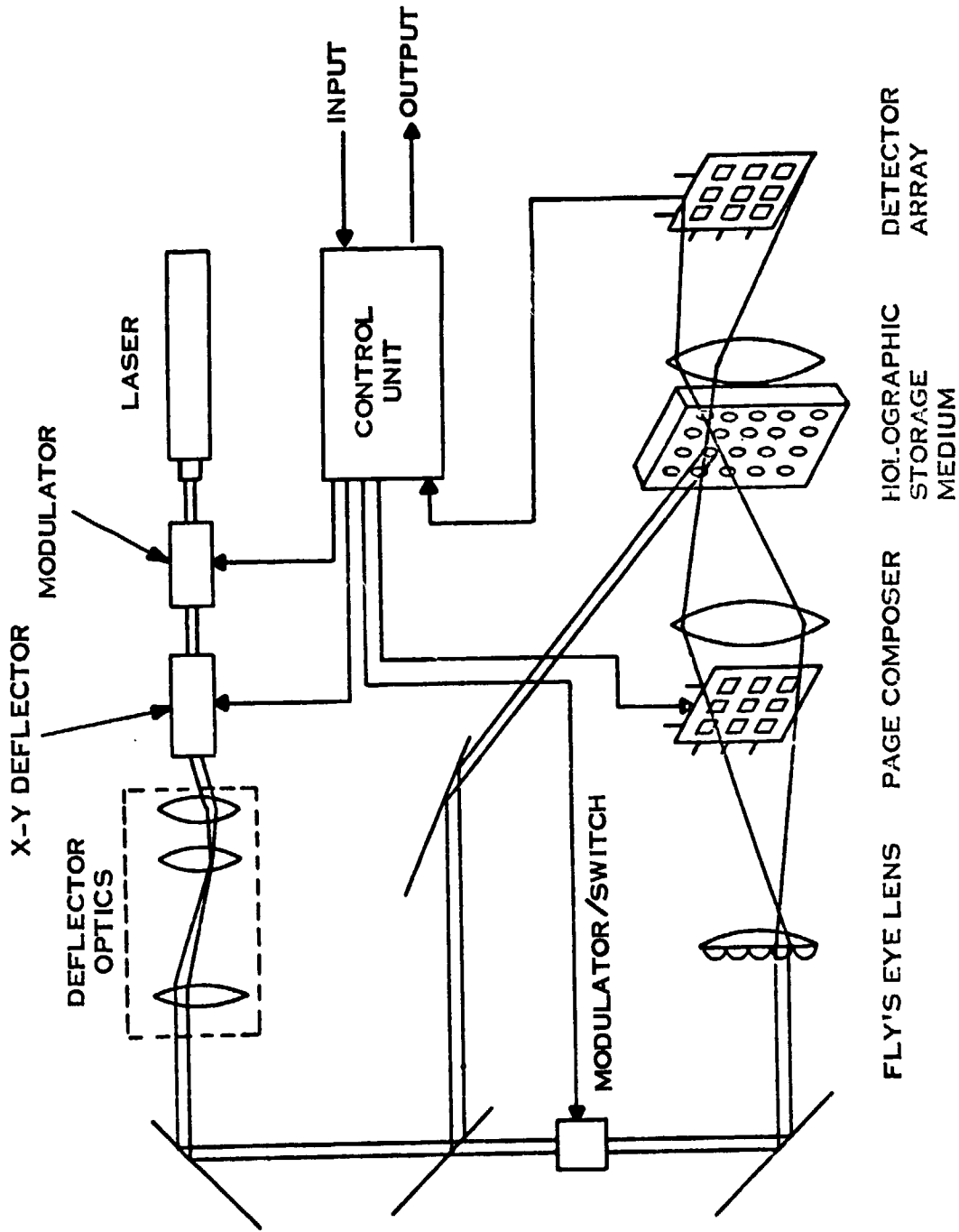


Figure 2. A Schematic Diagram of a Holographic Memory

The holographic memories takes advantage of the coherent nature of laser radiation by recording  $10^4$  to  $10^5$  bit pages as phase holograms. The requirement of the page format increases the system complexity which is balanced against increased capacity. In addition, the redundancy of the hologram allows some tolerance for dust on the recording surface and reduces the diffraction limited restriction on this lens system.

A schematic diagram of the components of a holographic memory system is shown in Figure 2. Before recording, the page is entered and stored in page composer which is an array of X-Y addressed light valves. The location of the page hologram is positioned in a plane in the storage medium by the X-Y deflector, probably of the acoustooptic or perhaps electrooptic type. Different planes are addressed by changing the laser radiation frequency, or, more conveniently, the reference beam incident angle. Intensity modulation and switching of the laser beams is accomplished by electrooptic modulators. Thus, the page composer, X-Y deflector and modulators contain dielectric-elastic-magnetic single crystal components as well as the holographic storage medium.

Holographic systems are more complicated than bit-by-bit memories and are less developed. Several technical difficulties remain to be overcome before they can become competitive with other memory systems. Bit-by-bit memories typically require writing energies of 1 nJ/bit. Thus, for a 1  $\mu$ sec writing time, 1 mW/bit is required, well within the capabilities of

presently available lasers. However, to write a page containing  $10^5$  bits in  $100 \mu$  sec would require a 1 watt pulse. For short (10 nsec) pulses, 10kW peak powers would be required. At the present, a ruby laser would be acceptable except high repetition rates are not possible and the  $1.06 \mu$ m radiation of a Nd:YAG reduces the packing density. In addition, the sensitivity of the storage medium, fixation of the holographic interference fringes and erasure need to be improved. At the present time, it can be concluded that the storage medium and page composer are the primary limiting factors for three-dimensional holographic memories <sup>(6)</sup>.

The primary advantage of holographic memories will be improved performance, very likely with orders of magnitude improvements. Present magnetic disk memories carry price tags in the neighborhood of  $10^{-3}$  cents/bit <sup>(7)</sup>, and thus, are not the dominant cost in the computer system. However, the holographic memory would replace the magnetic tape and core memories as well which would justify a high unit cost and still remain economically competitive.

## 2.2 Optical Communications

One of the most interesting aspects of laser radiation is the enormous bandwidth available by optical communications. In the optical range of approximately  $10^{13}$  to  $10^{15}$  Hz, there are theoretically available  $10^{11}$  channels, each with a width of 10 kHz. Such large capacities are needed to handle the rapidly increasing amount of data being transmitted.

For example, a picture telephone will require a bandwidth approximately 100 times that of the present telephone.

Above the limiting effects of atmosphere, unguided line of sight communication is attractive because of its bandwidth and low power requirements. However, the large demand is on the earth. One of the major difficulties to be overcome here was transmission. Optical fibers with high losses ( $\geq 20$  dB /km) would necessitate closely spaced repeater stations. Presently available 20 to 30 dB/km fibers have been used for short distance, a few km, fiber optical transmission systems now in operation. Such losses would require repeater stations approximately every mile, about the same as conventional cables. However, very low-loss fibers, in the 1 to 4 dB/km range, have been made in the laboratory so there is promise in going significantly further between repeater stations.

There are additional advantages to fiber optical transmission. Even with present modulation/demodulation technology, an optical fiber with an outer diameter of around 0.004 in. can carry over 4000 one-way voice circuits. A conventional coaxial cable with comparable capacity would be approximately three-eighths inches in diameter. In addition, optical fibers are noninductive, relieving interference problems. Therefore, optical communications offers promise as a space saver which is especially important in congested metropolitan areas.

Along with the development of low loss fibers, considerable research has been carried out on a suitable laser light source. In particular, laboratory aluminum gallium arsenide lasers have been in operation for greater than 10,000 hours and the 100,000 hours required for telephone use seems to be achievable. It appears that the utilization of optical communications is rapidly approaching the commercial stage. More recently, fiber optic lasers have been reported. (8,9)

#### 2.2.1 Modulation

However, for full utilization of the enormous available bandwidth, wide band optical modulators will be required to code the information on the laser beam. Current electro- and acousto-optic modulators are severely materials limited. Only a few materials are presently available with sufficient size and optical perfection for optical modulation. These crystals typically have small nonlinear coefficients compared to more desirable materials. However, the growth of bulk crystals with improved properties is often exceedingly difficult and in many cases has not yet been done. For example, the electrooptic coefficient of the widely used potassium dihydrogen phosphate (KDP) has been improved by a factor of approximately three by using its deuterated isomorph (DKDP). However, more difficult crystals to grow, such as strontium barium niobate (SBN), offer an order of magnitude or better improvement.

Another important limiting factor in all bulk wave modulators is dielectric loss. The dielectric loss limits the realizable power that can be applied which, in turn, limits the practical bandwidth. Dielectric loss is a sensitive function of crystal perfection being greatly increased, for example, by inclusion of solvent.

Thus, there is a need for much more perfect crystals of the electro- and acoustooptic type. There are, however, other, more speculative, crystals which may substitute for the electrooptic and acoustooptic type. A class of crystals called secondary ferroics may be utilized as wideband scattering mode intensity modulators. In these crystals, the domains can be modified by two external fields; for example, electric and stress fields. Hence, for a guided wave, an abrupt index change at domain walls may be varied by field or stress index modulation. Secondary ferroics are in an infant stage of research and are mentioned as one possible future modulation technique on the basis of theoretical expectations and not experimental evidence. As new phenomena emerge, similar new possibilities will emerge. Many of these may well lead to improved performance and viability.

### 2.2.2 Switching

Another aspect of optical communications that is a prime candidate for time and space saving is switching. Solid state switching is needed to replace bulky mechanical switching systems.



Magnetic bubble switching systems have been built in the laboratory and offer significantly improved performance. Controlled transfer of data rates exceeding 100,000 bits per second have been found possible <sup>(10)</sup>. The new secondary ferroics also offer switching possibilities by routing of optical signals in the domain structure. Routes can be picked by selective field or stress induced index change. Once again, this represents a speculative use of secondary ferroic crystals.

### 2.3 Other Present and Emerging Applications

There are certainly other areas of application for nonlinear crystals which utilize their dielectric, elastic or magnetic properties. Computers and optical communications have been selected as most promising candidates which by themselves could well justify space processing. Table 4 includes as a summary some of the other areas where a substantial payoff may exist.

Table 4 does not constitute a complete list. However, in the time frame of lattice and spin instability crystals, each listing will most likely be at a materials demand stage in the 1980's. Of course, as this rapidly expanding field evolves, new properties and resulting new applications, will also evolve with their resulting demand for new single crystals.

### 2.4 The Relation of the Crystal to the Application

Two viewpoints are considered when examining the importance of the crystal component with respect to the entire system. First is the relation of the crystal to overall performance. The crystal components of the devices discussed in this section may well determine widespread application

**Table 4. Areas of Device Applications for Dielectric-Elastic-Magnetic Crystals**

<u>Area</u>	<u>Classification</u>	<u>Applications</u>
Computers	Magnetic	Bubble Domains - Memory and logic
	Optical	Holographic storage-memory Page composers Beam deflectors
Communications	Optical	Electro-elasto-magneto-optic modulation Optical switching Signal processing Display
Microwave Acoustics	Elastic	Surface wave amplifiers, delay lines; autocorrelators, signal convoluters.
Ultrasonics	Elastic	Piezoelectric generators, detectors, imaging and display for NDT and biomedical applications, Acoustic holography.
I.R. Detection	Optical	Pyroelectric and Pyromagnetic thermal detection and imaging.
Lasers	Optical	Host crystals, fiber optic lasers, window materials, window coatings.

of the system or even be vital to operation at all. For example, the inability to satisfactorily modulate a laser beam with sufficient bandwidth would greatly degrade an optical communication system. Without a suitable storage medium, three-dimensional holographic memories cannot be realized.

Although the crystal components are usually vital for improved performance or operation, they typically constitute a small fraction of the total system. For example, the mass memory of a large computer is only one of many necessary components.

In terms of the emerging technologies then, single crystal components will be of critical importance and often justify very high single unit costs without greatly effecting the total cost of the system. This is in contrast to the low cost, high volume semiconductor market.

### 3.0 MATERIALS FOR THE EMERGING TECHNOLOGIES

The previous section contained a look at some important emerging technologies and the role of dielectric-elastic-magnetic crystals in them. In this section, some of the crystals themselves are identified, the demands placed upon them are considered and their growth is discussed.

#### 3.1 Present Materials

The present materials are categorized according to the applications of Table 4. The list is certainly not complete but is representative. It contains materials currently commercially available as well as some promising ones well into the research stage.

The most promising magnetic bubble materials are garnets. They possess the preferred combination of properties such as attainable bubble diameter, magnetization and uniaxial anisotropy as opposed to ferrites and other candidates<sup>(11)</sup>. Several of the more useful garnet compositions for both the magnetic film and nonmagnetic substrate are listed in Table 5. Simple garnets are cubic and thus isotropic with respect to their magnetic properties. The small deviations from cubic symmetry are "engineered in" by multiple element substitutions yielding complex solid solution garnets. However, the lattice match with the substrate garnet remains critical to insure film integrity. Nearly all of the complex garnets do not melt congruently and must be grown or epitaxially grown in a solvent. These garnets are enclosed in the boxes in Table 5.

Table 5. Magnetic Bubble Domain Materials

<u>Substrate Crystal</u>	<u>Epitaxial Film</u>
Gd <sub>3</sub> Ga <sub>5</sub> O <sub>12</sub> (GGG)	(EuEr) <sub>3</sub> (FeGa) <sub>5</sub> O <sub>12</sub> (YGdYb) <sub>3</sub> (FeAl) <sub>5</sub> O <sub>12</sub> (YEuGdTb) <sub>3</sub> (FeAl) <sub>5</sub> O <sub>12</sub> (EuGd) <sub>3</sub> (FeAl) <sub>5</sub> O <sub>12</sub> (YEu) <sub>3</sub> (FeAl) <sub>5</sub> O <sub>12</sub> (GdYTb) <sub>3</sub> (FeGa) <sub>5</sub> O <sub>12</sub> (FeGa) <sub>5</sub> O <sub>12</sub> (TGd) <sub>3</sub> (FeGa) <sub>5</sub> O <sub>12</sub> (YEuGd) <sub>3</sub> (FeGa) <sub>5</sub> O <sub>12</sub>
(DyGd) <sub>3</sub> Ga <sub>5</sub> O <sub>12</sub>	(Y <sub>3</sub> )(FeGa) <sub>5</sub> O <sub>12</sub> Er <sub>3</sub> (FeGa) <sub>5</sub> O <sub>12</sub>

Table 6. Optical Computer Memory Crystals

<u>Device</u>	<u>Crystal</u>
Holographic Storage Medium	LiNbO <sub>3</sub> LiTaO <sub>3</sub> Ba <sub>2</sub> NaNbO <sub>15</sub> Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub> IGS + isomorphs
Page Composers	Gd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> Ba <sub>x</sub> Sr <sub>1-x</sub> Nb <sub>2</sub> O <sub>6</sub> (SBN) Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub>
Beam Deflectors	LiNbO <sub>3</sub> LiTaO <sub>3</sub> d-TeO <sub>2</sub> (paratellurite) KH <sub>2</sub> P <sub>4</sub> O <sub>14</sub> (KDP) + isomorphs

Table 6 lists some crystals for optical computer memory devices. Again, the crystals enclosed in boxes must be grown in a solvent because they melt incongruently. Lithium Niobate ( $\text{LiNbO}_3$ ) and especially SBN ( $\text{Ba}_4\text{Sr}_{1-x}\text{Nb}_2\text{O}_6$ ) melt very nearly congruently but growth is complicated by the formation of striations. Growth in a solvent may diminish this difficulty. KDP, TGS and isomorphs are grown in a aqueous solvent since they decompose before melting.

In Table 7 are listed crystals for optical communication components. Once again, those crystals enclosed in boxes must be grown for a solvent.

Table 8 lists several important crystals for other promising applications.  $\alpha\text{-SiO}_2$  and  $\text{AlPO}_4$  are enclosed in boxes since they are grown hydrothermally.

A summary of the growth techniques for the compounds listed in Tables 5 through 8 are given in Table 9. Included are the melting temperatures and the approximate range of growth temperatures in a solvent when available. It should be noted that for crystals which have been grown both from the melt and a solvent, such as YAG, the growth temperature from the solvent is lower. Most of the crystals can be grown in a solvent below  $1200^\circ\text{C}$ .

### 3.2 New Demands on the Crystals

The demands on the single crystals can be separated into two categories. First, crystalline perfection is considered in terms of its

Table 7. Optical Communication Crystals

<u>Device</u>	<u>Crystal</u>
Electrooptic Modulators	LiNbO <sub>3</sub>
	LiTaO <sub>3</sub>
	Gd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>
	SBN
	Ba <sub>2</sub> NaNb <sub>5</sub> O <sub>15</sub> type
	KDP + isomorphs
	BaTiO K(NbTa)O <sub>3</sub>
Acoustooptic Modulators	LiNbO <sub>3</sub>
	LiTaO <sub>3</sub>
	Paratellurite
	PbMoO <sub>4</sub>
	CaMoO <sub>4</sub>
Optical Switches	LiNbO <sub>3</sub>
	LiTaO <sub>3</sub>
	Gd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>
Fiber Optic Lasers	LiNdP <sub>4</sub> O <sub>12</sub>
	Nd <sub>0.5</sub> La <sub>0.5</sub> P <sub>5</sub> O <sub>14</sub>

Table 8. Crystals for Other Applications

<u>Application</u>	<u>Crystals</u>
Microwave Acoustics	LiNbO <sub>3</sub> LiTaO <sub>3</sub> <span style="border: 1px solid black; padding: 2px;">α-SiO<sub>2</sub> AlPO<sub>4</sub></span>
Ultrasonics	LiNbO <sub>3</sub> LiTaO <sub>3</sub> <span style="border: 1px solid black; padding: 2px;">BaTiO<sub>3</sub> Pb<sub>2</sub>KNb<sub>5</sub>O<sub>15</sub> Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> α-SiO<sub>2</sub></span>
IR Detectors	LiNbO <sub>3</sub> LiTaO <sub>3</sub> Pb <sub>5</sub> Ge <sub>3</sub> O <sub>11</sub> <span style="border: 1px solid black; padding: 2px;">SBN BaTiO<sub>3</sub> TGS + isomorphs</span>
Optical Laser Hosts	Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> (YAG) Gd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> PbMoO <sub>4</sub> CaMoO <sub>4</sub>



TABLE 9

GROWTH METHODS FOR SELECTED DIELECTRIC-ELASTIC-MAGNET  
CRYSTALS

Material	Growth Method	T <sub>melt</sub> (°C)	Solvent	T <sub>growth</sub> (°C)
GGG	Czochralski	1700	PbO + Ga <sub>2</sub> O <sub>3</sub> rich	1250
Rare Earth Garnets	Flux	1700 to 1750	BaO + B <sub>2</sub> O <sub>3</sub> or BaO + B <sub>2</sub> O <sub>3</sub> + BaF <sub>2</sub>	800 to 1200
KDP & Isomorphs	Aqueous Solution	Decomp.	H <sub>2</sub> O	~T room
TGS & Isomorphs	Aqueous Solution	Decomp.	H <sub>2</sub> O	30 to 70
LiNbO <sub>3</sub>	Czochralski	1650		
BaTiO <sub>3</sub>	Flux	1618	KF or TiO <sub>2</sub> rich	1200  1350
K(Nb, Ta)O <sub>3</sub>	Flux	~1300	K <sub>2</sub> CO <sub>3</sub>	1100
SBN	Czochralski	~1500		
Ba <sub>2</sub> NaNb <sub>5</sub> O <sub>15</sub>	Czochralski	1429		
Gd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	Czochralski	1170		
α-TeO <sub>2</sub>	Czochralski	733		
PbMoO <sub>4</sub>	Czochralski	1430		
LiNdP <sub>4</sub> O <sub>12</sub>	Flux	-	Li <sub>2</sub> CO <sub>3</sub> rich + NH <sub>4</sub> N <sub>2</sub> P <sub>4</sub> O <sub>4</sub>	700 +0 950 400 +0 750

Table 9 - Growth Methods for Selected Dielectric-Elastic-Magnet Crystals  
(continued)

Material	Growth Method	T melt (°C)	Solvent	T growth (°C)
$\text{Nd}_{0.5}\text{La}_{0.5}\text{P}_5\text{O}_{14}$	Flux		$\text{H}_3\text{P}_4$	400 to 750
$\alpha\text{-SiO}_2$	Hydrothermal	~1600		
$\text{AlPO}_4$	Hydrothermal	>1500		
$\text{Pb}_2\text{KNb}_5\text{O}_{15}$	Czochralski Flux	1300	off stoichiometry ?	?
$\text{Sr}_2\text{Nb}_2\text{O}_7$	Float Zone	~2000		
$\text{Pb}_5\text{Ge}_3\text{O}_{11}$	Czochralski	738		
YAG	Czochralski	1970		
	Flux	-	$\text{PbO} + \text{B}_2\text{O}_3$	1250
	Flux	-	$\text{PbO} + \text{B}_2\text{O}_3 + \text{PbF}_2$	1300
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	Flux	-	$\text{Bi}_2\text{O}_3$ rich	1200

effects on device performance. Second, the required intrinsic properties of the crystal are considered in terms of the often required improved performance.

### 3.2.1 Crystal Perfection

The use of intense, coherent visible or near infrared laser radiation places a number of demands on crystal perfection. Three mechanisms are particularly detrimental to device performance which are related to crystalline perfection; absorption, scattering and nonuniformities.

Absorption irreversibly depletes the optical beam and causes heating of the crystal. Applications often demand the crystal be operated at or near a critical temperature point. It is particularly bothersome, for example, when utilizing intense beams for harmonic generation. Efficient harmonic generation depends on the fundamental and harmonic rays remaining in phase; i.e., their indices of refraction remain equal. Heating of the crystal changes the indices of refraction and, hence, the phase matching.

Absorption bands and edges that occur at lattice and electronic resonances are intrinsic properties of the material. Additional absorption may be added by the inclusion of impurities such as the solvent used in solution growth. Such inclusions are one of the major problems in growth from a solvent.

Usually a more serious problem is scattering. The wavelength of visible light can scatter off small defects, in the neighborhood of 0.5 micron or less. The list of scattering defects is extensive. It includes inclusions of solvent or veils, which are clusters of inclusions, voids and inhomogeneities. Grain boundaries which are noncrystalline walls separating crystal sections with different orientations, and dislocations which are surfaces over which slip has occurred can also cause scattering. Also included are twin boundaries which are surfaces separating two regions of the crystal which are mirror images of each other and the walls between electric, elastic or magnetic domains. The TGS crystal shown in Figure 3 demonstrates light scattered from a veil.

Compositional variations constitute a major problem in the growth of complex dielectric-elastic-magnetic single crystals. Nonuniformities of composition correspond to index of refraction gradients which can also cause scattering. Many of the applications such as electrooptic modulation rely on precise external control of the index of refraction so that index uniformity is critical.

Structural defects are also important for other parameters. As was mentioned earlier, high dielectric losses limit modulation bandwidth. Dielectric losses are especially sensitive to inclusions in the crystal. Strained crystal lattices can contribute sometimes undesirable internal fields and index inhomogeneities.



Figure 3. Veiled TGS Crystal

### 3.2.2 Intrinsic Properties

The dielectric-elastic-magnetic single crystals considered in this report all rely on anisotropic structure. The anisotropy may be natural or may be induced by external fields, via a nonlinear effect. As a consequence, high symmetry crystal systems do not possess the required properties and the usable materials necessarily have more sophisticated structure and complex compositions. As an example, Figure 4 shows models of the structure of silicon and garnet, both of which are cubic. However, it is clear that the composition and bonding in the garnet is much more complicated.

The origins of the nonlinear effects is not always well understood but it can be related to lattice or spin instabilities. For example, in KDP, the hydrogen bonds to the phosphate groups are responsible in a complicated way for the second order effects. As the transition temperature, a region of large instabilities, is approached the magnitude of these effects is greatly enhanced. The mechanism differs for different classes of compounds, but suitable instabilities are required. It is this need to tailor suitable instabilities in lattice or spin systems that mandates complex compositions and structures.

The complexity of structure and composition implies high anisodesmity or spatially nonuniform bonding energies. It is this anisodesmity and high structural perfection requirement that distinguish

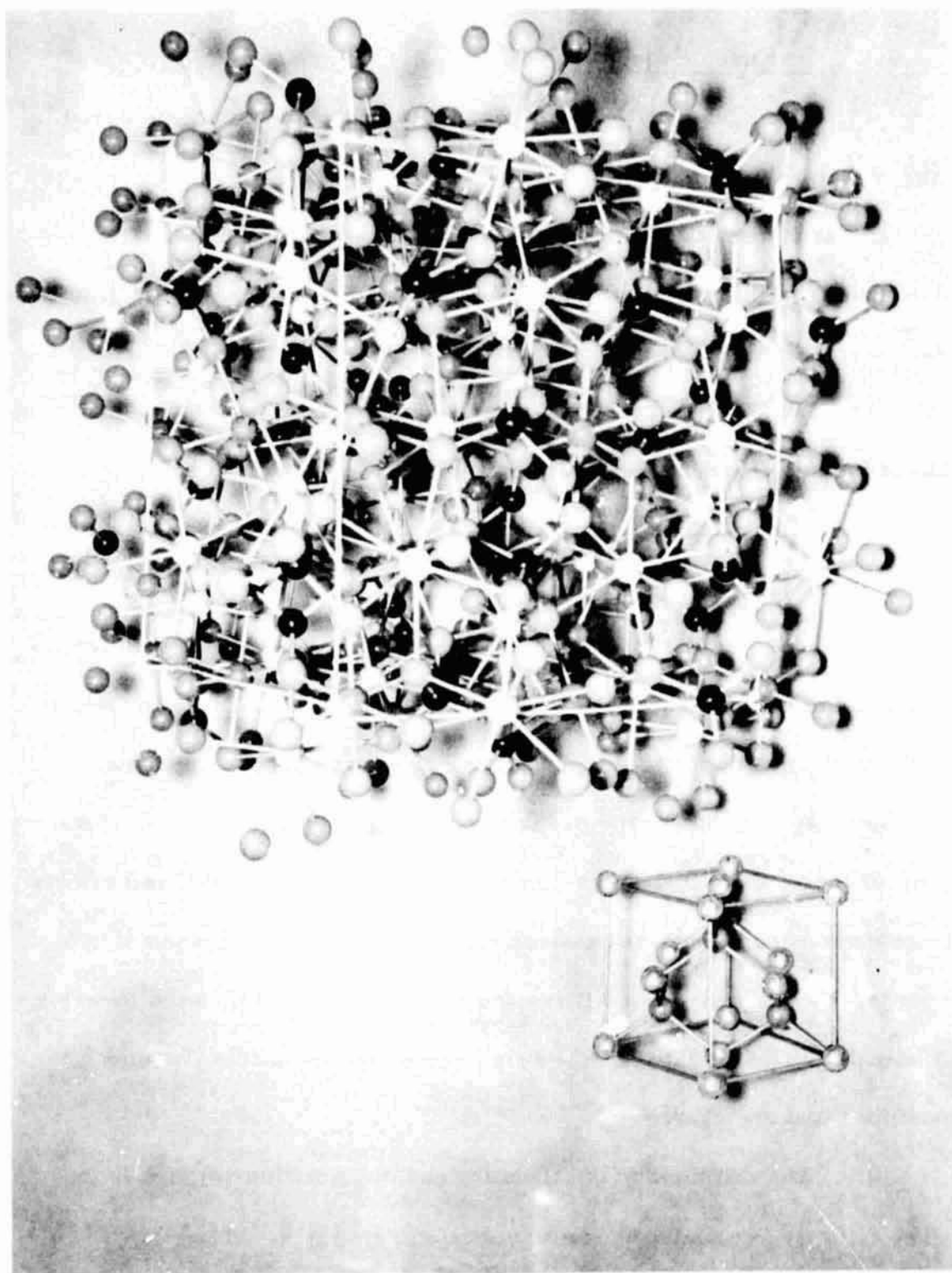


Figure 4. Models of the Crystal Structures of Silicon and Garnet

the dielectric-elastic-magnetic crystals from the electron transport crystals such as semiconductors. Table 10 summarizes the comparison.

### 3.3 Crystal Growth

Essentially all synthetic crystals are grown by a liquid-solid or vapor-solid reaction. Vapor growth techniques are usually limited to films and small crystals and are not well suited to bulk crystals, especially on a production basis. The liquid solid reaction must be further divided for all but elemental materials. To grow a crystal from the melt, the compound must melt congruently; that is, the solid and the liquid must have the same composition. Melt growth is clearly impossible if the compound decomposes before melting and usually not possible if the grown crystal undergoes a major phase transition between the melting temperature and ambient. The growth methods available are summarized in Table 11, and those applicable to dielectric-elastic-magnetic crystals indicated by asterisks.

Table 10. Comparison of Electron Transport and Lattice-Spin Instabilities Crystals

1950-1970	1980 →
<u>Electron Transport Properties</u>	<u>Lattice Wave-Spin Wave Properties</u>
Simple Structures	Complex Structures
Elemental or Binary Compositions	Complex Compositions
Extreme Chemical Purity Required	Less Critical Chemical Purity
Less Critical Structural Perfection	Extreme Critical Structural Perfections



Many present day crystals, as was indicated in Section 3.1, have been grown from the melt by the Czochralski technique. Others either because they melt incongruently, for example, bismuth titanate, or decompose before melting, for example, KDP and TGS, must be grown in a solvent.

The Czochralski melt techniques and low temperature solvent methods such as aqueous solution growth have received considerable attention and many bulk crystals have been grown by these methods. On the other hand, high temperature solvent (flux) techniques have received considerably less attention primarily due to experimental difficulties. Seeded growth is usually required to obtain large crystals with some control over orientation, growth rate and perfection. Much more elaborate equipment is needed for seeding and stirring a high temperature flux which leads to much of the experimental difficulty.

TABLE 11. GROWTH METHODS AVAILABLE

	Vapor	Melt	Solvent
<b>Example</b>	CVD Sputtering	Czochralski Bridgeman	Flux Aqueous Solution
<b>Congruent</b>	Yes (a)	Yes* (b)	Yes*
<b>Incongruent</b>	?	No	Yes*

Notes: (a) Example is Skylab Experiment M556, Vapor Growth of IV-VI Compounds, Professor Wiedemeier.  
 (b) Example is Skylab Experiment M562, Indium Antimonide Crystals, Professor Gatos.  
 \* Methods for growth of dielectric-elastic-magnetic crystals.

However, even for congruently melting compounds, Czochralski growth is often not satisfactory for the growth of high perfection crystals. For most compounds, a solid solution region exists delineated by liquidus-solidus lines in the phase diagram. The degree of congruency is a function of the narrowness of the solid solution region. In order to grow the stoichiometric compound, the melt is enriched with the lower melting end member. The composition of the solid compound is then a critical function of the solidification temperature. Temperature fluctuations across the growing face will yield composition nonuniformities normal to the growth direction while temporal temperature differences yield different compositions along the growth axis. Phase separation in the melt will also lead to compositional gradients in the solid. Periodic compositional variations, known as striations, result in refractive index inhomogeneities which are highly detrimental to many applications.

When the solid solution region is appreciable, Czochralski growth is essentially growth from a solvent which is the lower melting point end member. In both cases, convection related temperature variations lead to refractive index nonuniformities.

Stirring of melts and low temperature solutions have been widely used to "smooth out" composition gradients. However, even with precise control of temperature and heat flow, short term temperature fluctuations caused by nonuniform thermal convection nearly always exist<sup>(12-15)</sup>.

It has been shown that usable stirring rates are usually not sufficient to override these random convective effects<sup>(13)</sup>.

Temperature and compositional gradients lead to nonuniform growth rates across the interface. Nonuniform growth rates are often the cause of defects such as grain boundaries, strains and inclusions. Inclusions, for example, are formed when projections caused by different rates on a growing face coalesce and trap small bubbles of the solvent.

Thus the Czochralski method is not always satisfactory, especially for the more complex compounds. In addition, it is reasonable to expect that the more complex compounds of the future will not melt congruently. This can intuitively be seen by considering the increase in anisodesmity with increasing complexity. With large differences in the bonding energies, the solid-liquid transformation may well take place by dissolution into "pieces" of the original compounds not having the solid's composition.

It is concluded then that for dielectric-elastic-magnetic single crystal growth, the possible benefits of space processing must be investigated in terms of Czochralski growth and, to a greater extent, solvent growth. It is reasonable to expect that growth from a solvent will become increasingly important for future materials. The kinetics at the liquid-solid interface are of utmost importance. In both cases, a stable interface region is required to:

- (1) eliminate compositional gradients, and
- (2) to insure uniform growth rates.

#### 4.0 ADVANTAGES OF MICRO-GRAVITY PROCESSING

The micro-gravity environment of space is believed to offer considerable promise for substantial increases in crystal perfection. The benefits for the solvent and, to a lesser extent, melt methods discussed in Section 3.3 are considered along with possibilities for some other related methods.

##### 4.1 "Normal" Solvent Growth

As was stated earlier, essentially quiescent conditions at the growth interface are highly desirable for the growth of high perfection crystals. Under these conditions, the growth of the bulk crystals needed for device applications proceeds at a slow rate. However, if the need for stirring is eliminated, the complexity of the apparatus is greatly decreased. Table 12 gives a comparison of growth from the melt and in a solvent in terms of flight requirements.

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Table 12. Comparison of Melt and Solvent Growth Parameters  
for Space Processing

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Growth Method	Time Requirements	Energy Requirements	Apparatus Complexity	Structural Perfection
Melt	1 day	High	High	Low
Solvent	10-100 day <sup>(a)</sup>	Low	Low	High

Note (a): Shorter growth times may be possible but with a decrease in perfection.

---

It is clear that solvent growth will require long duration flights for the actual production of bulk crystals. The energy and apparatus requirements will no doubt be well within the limits of planned flights in the 1980's.

The principle advantage is the relief of convective conditions at the growth interfaces. This should allow close control of composition and growth rate uniformity at the diffusion controlled interface. The expected result is much higher structural perfection.

The increase in stability at the interface without convection should allow growth at higher supersaturations of solute in solvent. Then perfections comparable with crystals grown on earth may be obtained at higher growth rates.

Without the necessity for stirring, more control over morphology can be reasonably expected by using orientated and preshaped seeds. This would be especially favorable for the plate morphologies needed in many applications, and the need to obtain high perfection surfaces free from polishing streaks, scratches and pits.

Little is presently known about the kinetics at the growth interface. By eliminating the masking effects of gravity crystal growth in space offers the additional promise of a better understanding of the liquid-solid interface. A better understanding of interface kinetics would contribute to improvements in growth methods on earth that may otherwise arrived much further in the future.

It is reasonable to expect then that relief of convection at the interface by growth in a micro-gravity environment would lead to the following benefits for the growth of dielectric-elastic-magnetic crystals.

- 1) Higher Perfection
- 2) Higher Growth Rates for Crystals of Equivalent one-g Perfection
- 3) Morphology Control
- 4) Better understanding of Liquid-Solid interface.

#### 4.2 Other Possibilities

Other, more speculative, possible benefits of the micro-gravity environment of space can be envisioned. Three which seem reasonable are considered here.

One of the first suggested crystal growth methods for space was float zone refining<sup>(16)</sup>. The existence of larger, more stable liquid zones would allow growth of larger diameter crystals such as silicon. The same benefits would apply to a travelling solvent technique for the growth and purification of solvent grown crystals.

Without gravity, it may also be possible to grow very uniform thickness films by liquid phase epitaxy. Thin uniform garnet films are required for magnetic bubble memories, for example.

Another intriguing prospect is generating controlled special low level gravity fields. For example, a cylindrically symmetric gravitational field

could be generated by rotating a crucible without a component of the earth's gravitational field. Such small fields could be used to sweep spurious growth nuclei away from a seed in the center of the cylinder to a hotter region near the walls for remelting.

## 5.0 EXPERIMENTAL INVESTIGATION OF SOLUTION GROWN TGS

Experimental data on the effects of convection in solvent growth systems is essentially absent. The experimental portion of this investigation was initiated in order to obtain an estimate of the benefits of a micro-gravity environment for crystal growth from a solvent. An evaluation of perfection in terms of dislocation etch pit densities and dielectric loss was made under three different growth conditions.

Isothermal growth by means of controlled evaporation without stirring was chosen as the best means of simulating low convection growth on earth. A determination of optimum evaporation and growth rates was made. These conditions were then used for high convection growth experiments. High convection growth, again by controlled evaporation, was facilitated by introducing thermal gradients. A small 2 liter capacity rotary crystallizer was used to grow crystals representing those presently commercially available.

TGS was chosen as the model system for several reasons. TGS is grown from an aqueous solution at low temperatures (40 to 50°C) which eliminates experimental problems associated with high temperature melts. The aqueous solution is transparent so that growth could be seen and photographed. The growth conditions and parameters are reasonably well known, eliminating the need for much preparative work. In addition, TGS is currently an important pyroelectric material.



## 5.1 Growth Procedures

### 5.1.1 Starting Materials

Earlier studies have shown the importance of limiting impurity concentrations in TGS<sup>(17)</sup>. Therefore, a great deal of care was exercised in the preparation of saturated solutions. Only high resistivity water was used and the TGS was recrystallized three times before being used in a growth solution. Both commercially available TGS powder (from Eastman Kodak Co.) and TGS synthesized from glycine and sulphuric acid in the stoichiometric ratio were used.

### 5.1.2 Low Convection Growth Cell

For isothermal crystal growth under low convection conditions a 40 liter glass tank equipped with a mercury switch thermal regulator, 400 watt quartz immersion heater and a mechanical stirrer was employed. The bath temperature was 40°C and control was better than 0.1°C. Rectangular glass tubes, 6 inches in length of 1 inch square cross section containing growth solution and seed were inserted into openings in the fiber glass board cover and immersed to a depth which exceeded the solution level in the tubes. A photograph of the system is shown in Figure 5.

### 5.1.3 High Convection Growth Cell

For growth by controlled evaporation under conditions of high convection, a cell was designed and built which consisted of a rectangular 2 inch square glass container, 6 inches in length, sandwiched between

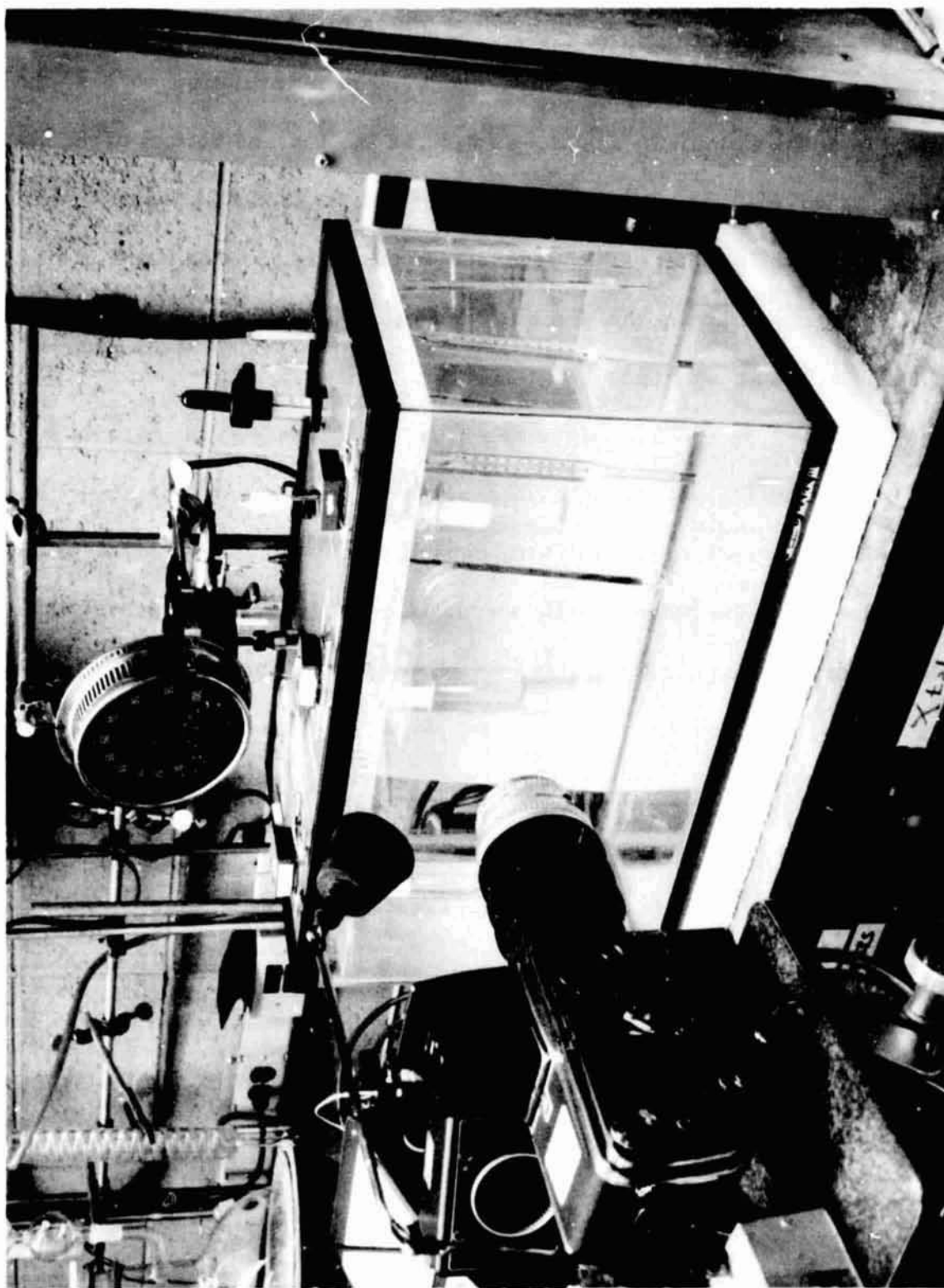


Figure 5. Low Convection Growth Cell

aluminum blocks of similar dimensions which had provisions for incorporating cartridge heaters and thermistor sensors. Foam insulation covered the outside of the aluminum blocks, as well as the top and bottom of the glass tube. Two 1/16 inch thick glass plates were positioned in front of and behind the glass container in recesses in the foam so as to function similar to a thermopane and at the same time afforded unrestricted visibility for filming of the growth process.

In addition to the two cartridge heaters in the aluminum blocks, an additional pancake heater was located beneath the glass vessel. An RFL temperature control with capability of  $\pm 0.05^{\circ}\text{C}$  control was used with the cartridge heaters while a constant voltage transformer controlled the power to the pancake heater. A photograph of the high convection cell is shown in Figure 6.

#### 5.1.4 Rotary Crystallizer

Seeded growth of TGS was also carried out in a rotary crystallizer in order to obtain single crystals representative of those commercially available. In the rotator, stirring is utilized to keep fresh nutrient at the growth interface and to overcome convective effects. These crystals served for comparison purposes when characterizing the types and density of defects obtained during growth under different sets of convective conditions.

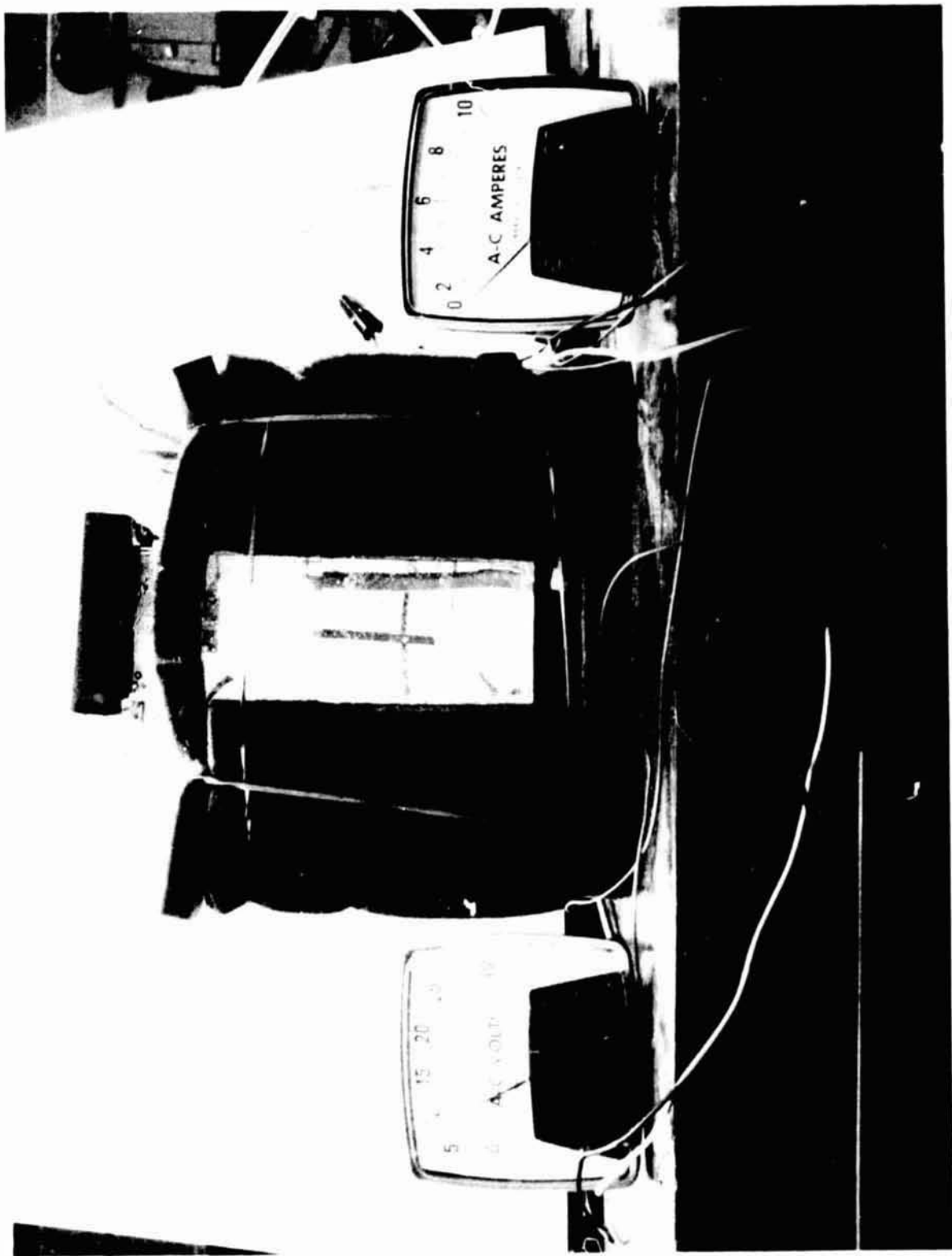


Figure 6. High Convection Growth Cell

The crystallizer consisted of a large capacity outer container and an inner 2 liter capacity growth jar which contained the growth solution as well as the suspended (010) oriented cylindrical seed attached to a lucite support. Paddles and the seed suspended from the cover rotated at about 15 rpm. The direction of rotation was reversed every two minutes to approximate uniform flow over the faceted crystal faces. Mercury thermo-regulators maintained temperature control of  $\pm 0.005^{\circ}\text{C}$ . Slow cooling from  $45^{\circ}\text{C}$  was employed with an initial cooling rate of  $0.05^{\circ}\text{C}$  per day which was increased gradually to a maximum of  $1^{\circ}\text{C}$  per day by following a compound growth law for the mass of the crystal.

Under these conditions, approximately 5 gms/liter/ $^{\circ}\text{C}$  of TGS can be deposited. Hence, in the rotator described here approximately 30 gms of TGS can be grown in one month. The larger capacity ( $\sim 10$  liter) commercial apparatus can grow approximately 150 gms in one month. The two liter rotary crystallizer is shown in Figure 7.

#### 5.1.5 Solution Preparation and Growth

Saturated solutions at  $40^{\circ}\text{C}$  were prepared from triply recrystallized TGS employing the solubility curve of Konstantinova<sup>(18)</sup>. All solutions were permitted to equilibrate for several hours.

In order to limit the onset of spurious nucleation during growth, all growth vessels were thoroughly cleaned and kept free of dust and other particulate matter. Seeds were rinsed in high purity water

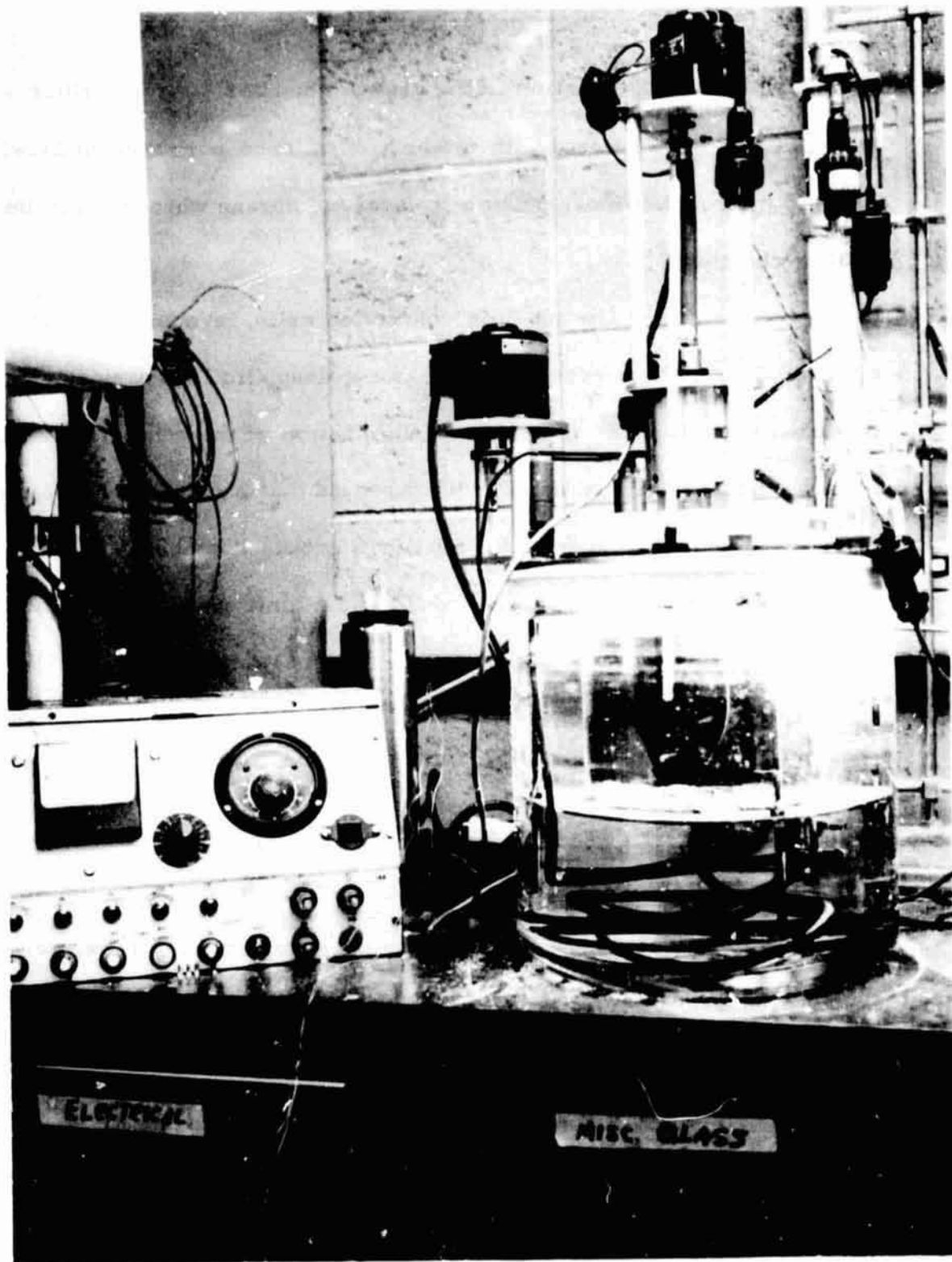


Figure 7. Rotary Crystallizer

immediately before insertion in the growth chamber. As a further precaution, all solutions were filtered with either a 30 micron pore size sintered filter or 0.45 micron Millipore polymeric filter membrane when pumped into the growth chamber.

In the low and high convection cells, evaporation was controlled by PVC porous covers. The hydrophilic 1000 Å<sup>o</sup> pore size cover was used since it protects against contamination of the solution from all but the most minute dust particles. It was found that a great deal of care must be taken to seal the cover on the top of the growth chamber. Very snugly fitting molded RTV covers were found to best limit evaporation around the seal. Evaporation rates were controlled by masking areas of the PVC cover with adhesive tape.

## 5.2 Growth Experiments

### 5.2.1 Low Convection Growth

A total of eleven growth runs were made in the low convection growth cell. The initial eight runs were used to establish cover area and evaporation rate regimes for successful growth. The final three runs, each with three separate growth chambers, were made to find ideal evaporation and growth rate conditions.

Growth rate is directly related to evaporation rate. In order to use equivalent growth rates in the low and high convection cells, evaporation rates were first determined as a function of porous cover areas. In initial experiments, evaporation from around the cover was often found

to be the dominating factor. By using snugly fitting molded RTV covers, reasonably predictable evaporation rates could be obtained. Evaporation rates for the final three low convection runs (T-9, T-10 and T-11) as functions of porous cover area are shown in Figure 8. Approximately a linear relationship shows that the slopes are reasonably constant, within experiment error, as shown in Table 13.

Table 13. Evaporation Rate per Unit Area

<u>Growth Run</u>	<u>Rate/Area (cc/hr/cm<sup>2</sup>)</u>
T-9	0.012
T-10	0.013
T-11	0.011

However, the intercept is not constant indicating evaporation around the cover is still important. In Run T-11, which has the smallest intercept value, epoxy cement was used to seal the edges of the PVC cover to the RTV molding.

In order to correlate growth rate as a function of evaporation rate, the change in the growing crystal linear dimensions as a function of time was also measured. Growth rate is a function of crystallographic direction. Growth rates for different directions were measured by Novotny and Moravec and found to be linear<sup>(19)</sup>. The growth rates measured for runs T-9, T-10 and T-11, are shown in Figures 9-11 respectively. The observed growth rates are not linear throughout growth but exhibit two and often three linear regions.



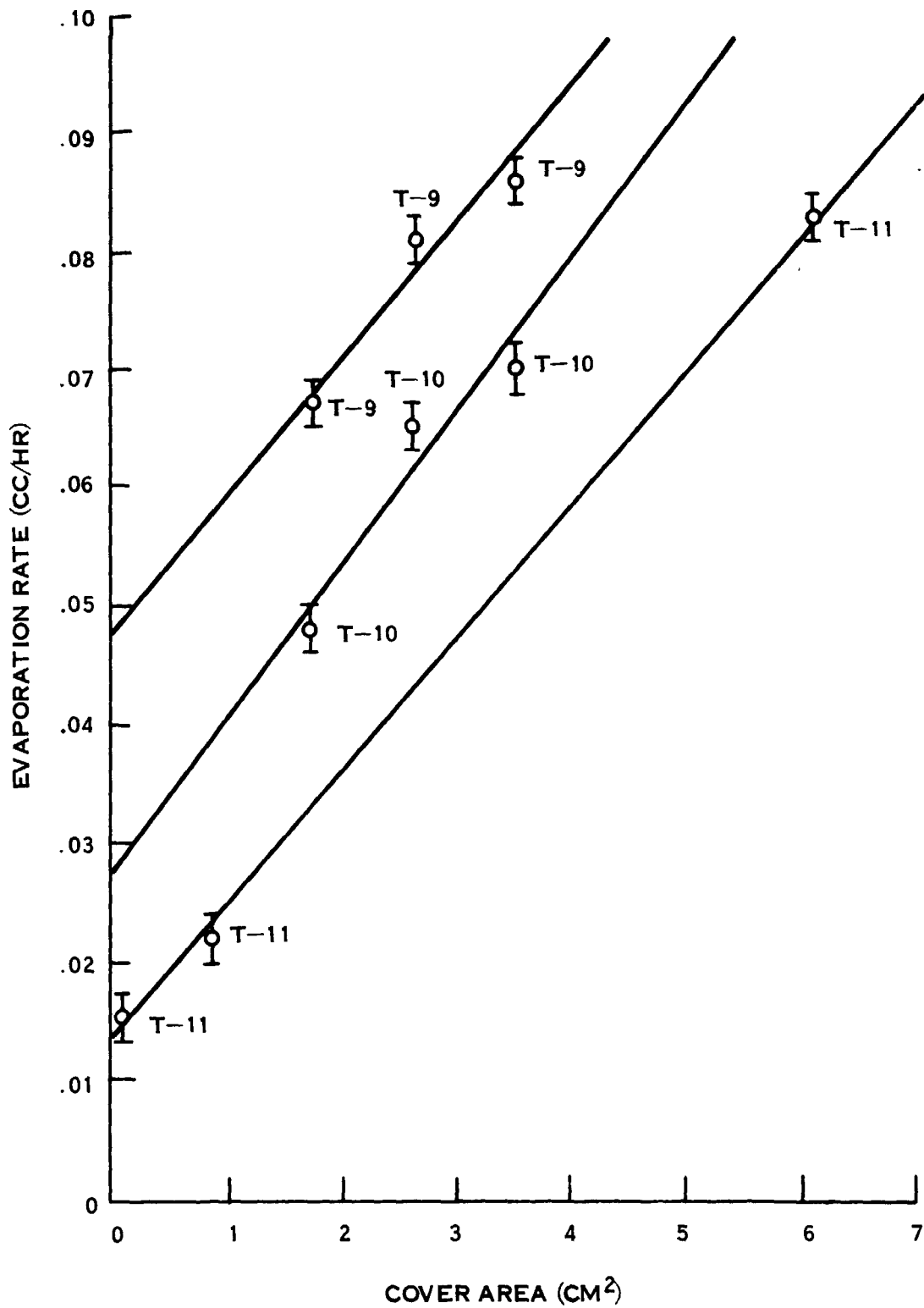


Figure 8. Evaporation Rate vs. Cover Area

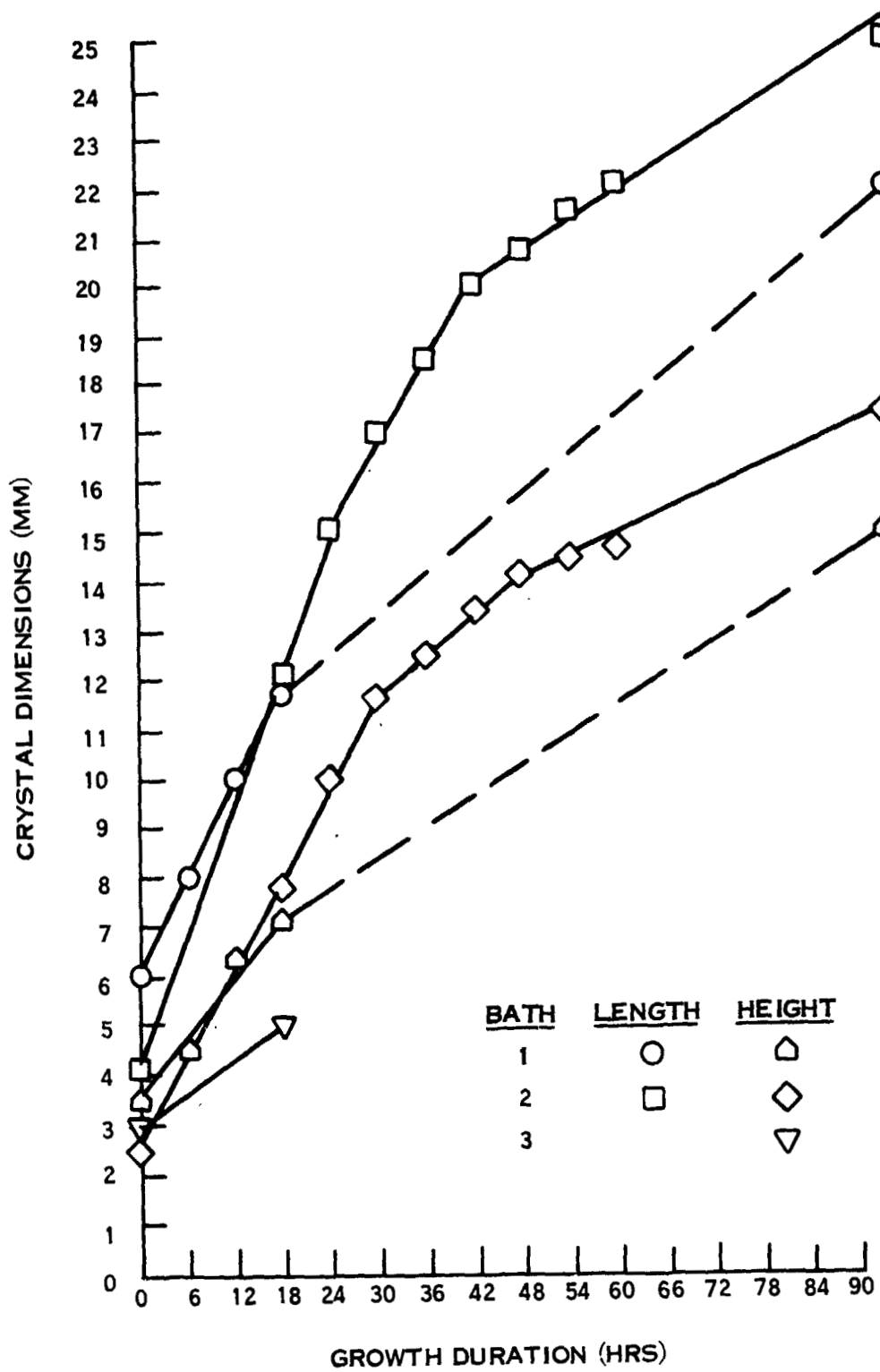


Figure 9. Crystal Dimensions vs. Time of Growth for T-9

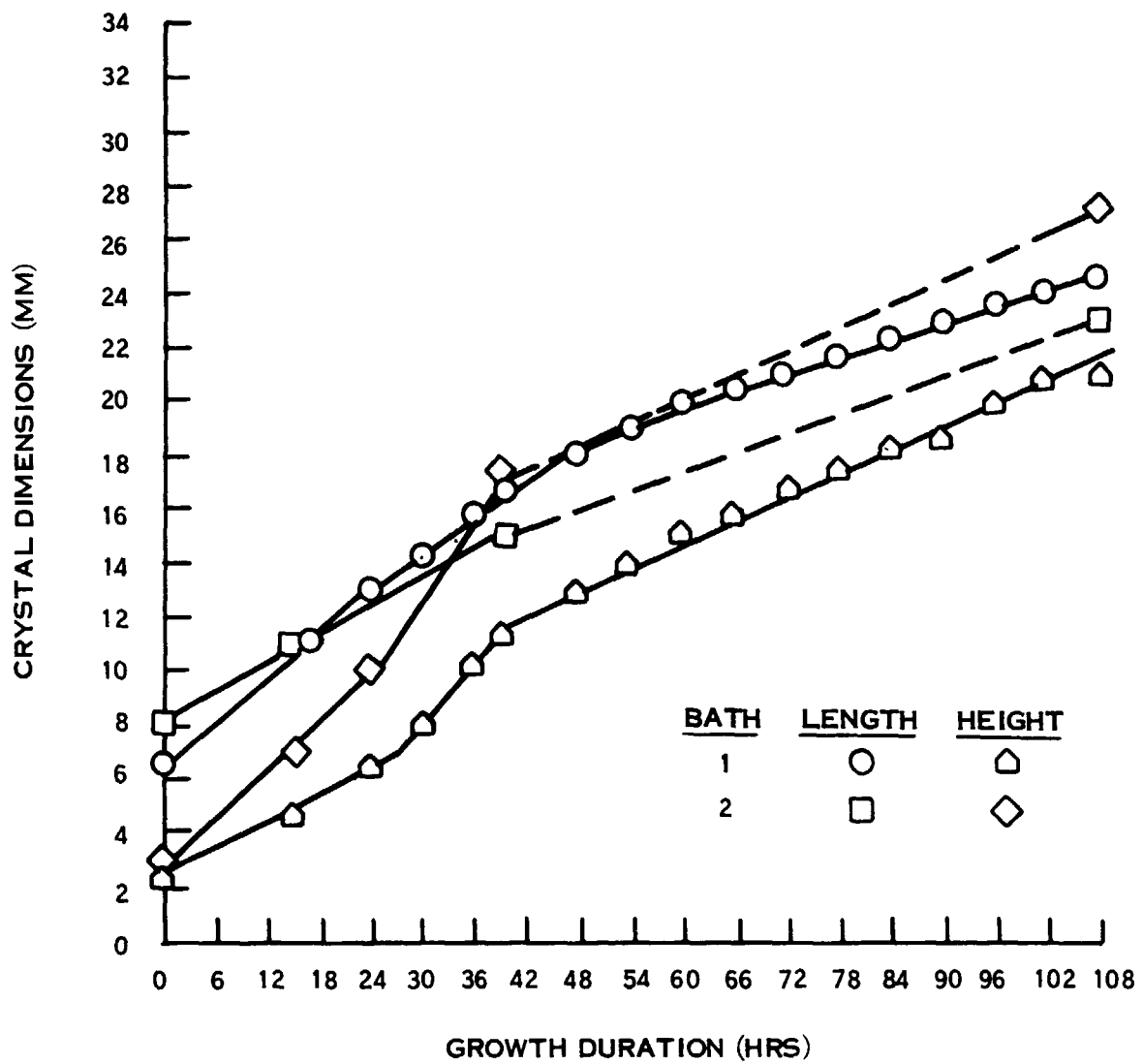


Figure 10. Crystal Dimensions vs. Time of Growth for T-10

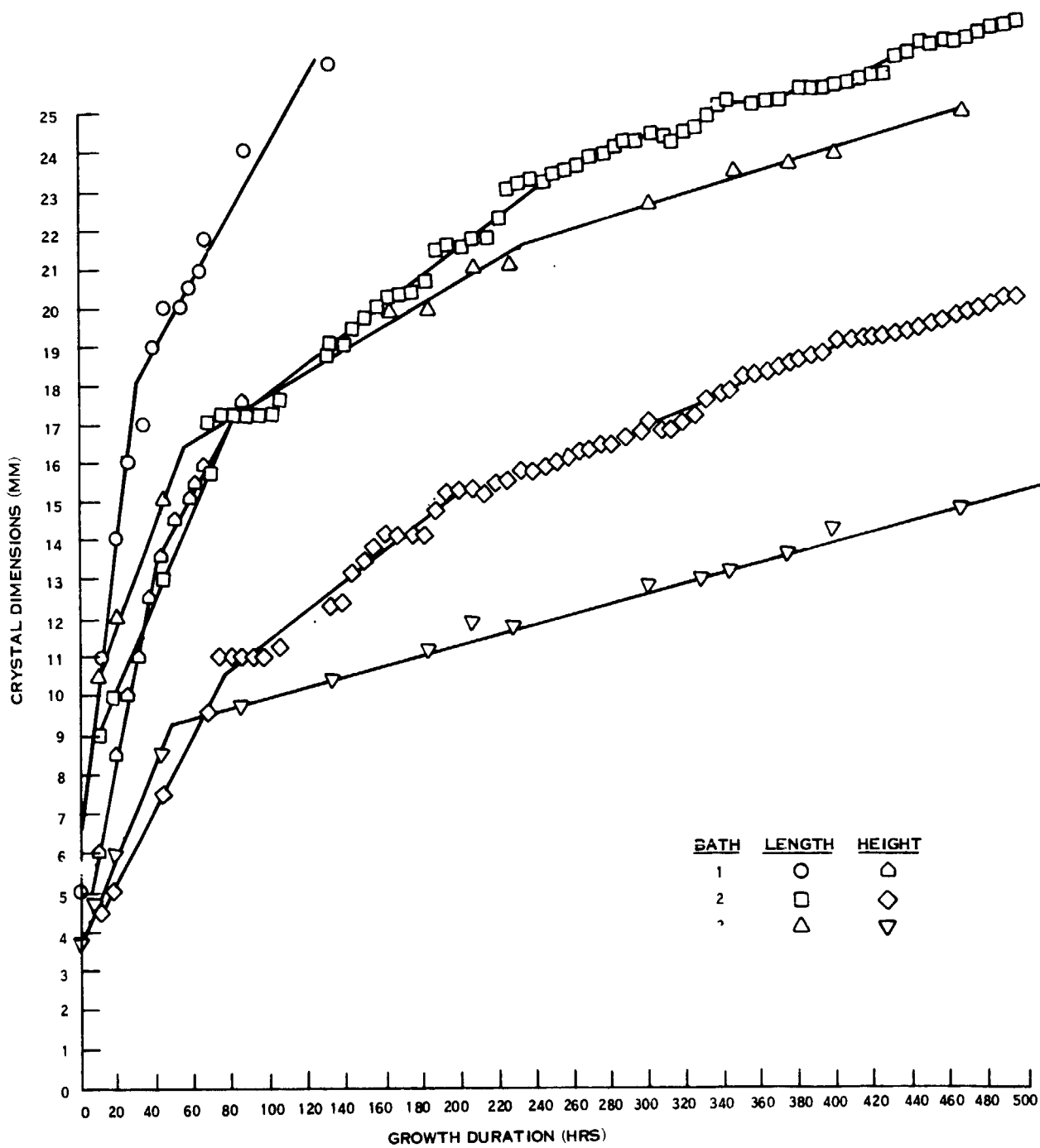


Figure 11. Crystal Dimensions vs. Time of Growth for T-11

There are several factors which may account for this behavior. Growth rate is influenced by the perfection and orientation of the seed, the degree of supersaturation which in turn is a function of temperature and concentration, amount of spurious growth, impurity concentrations and the proximity of the growth cell walls with respect to the growing crystal.

The seed crystals employed were small platelets, usually not exceeding a few mm on a side which had nucleated and grew at the bottom of the growth container of previous growth runs. They were of fairly good quality, generally free of veils but showed some evidence of hopper growth. No attempt was made to orient the seeds except for T-10 where the (010) direction was vertical.

Supersaturation was another variable which proved difficult to control closely. Growth solutions were initially saturated at 40°C in all cases and then heated to 50°C prior to filtering so as to avoid plugging. Due to the onset of spurious nucleation which occurred in nearly half of the growth runs despite stringent precautions, reheating of the solution at an elevated temperature was necessary. This resulted in additional solvent evaporation and an undetermined increase in supersaturation. It is believed that the initial high supersaturation accounts for the initially large growth rates.

Spuriously nucleated crystals which usually grow at the bottom of the container compete for nutrient material. This acts to slow down growth on the seed. The effect should be more pronounced as growth proceeds because of the larger area of the spurious crystals. There was no correlation, however, of spurious nucleation and the change in growth rate.

Without further investigation, the best estimate is that the proximity of container walls accounts for the final small growth rate region. To examine the effect on growth rate of the proximity of surrounding container walls to the crystal, note was taken of the crystal dimensions at the point where there was a change in slope from the middle to final growth stage. It was found in all cases that the crystal to wall separation was less than 5 mm. For the unstirred solution with growth proceeding under conditions of minimal convection, the diffusion boundary layer should exceed 1 cm in width. Therefore, the walls should be located within the boundary layer and thereby affect the diffusion of nutrient to the crystal faces. This explanation is not as obvious for discontinuous changes in height dimensions since the mechanisms relating height and width are not as clear.

A summary of the data for low convection cell growth runs T-9 through T-11 is given in Table 14. Figure 12 is a photograph of crystal T-11.

#### 5.2.2 High Convection Growth

TGS growth under high convection conditions was performed in the special growth cell described earlier. From the data for the low

Table 14. Summary of Low Convection Growth Runs T-9, T-10 and T-11

Run	Bath	Evap. Rate (cc/hr)	Cover Area (cm <sup>2</sup> )	Linear Growth Rates						Total Crystal Mass (gms)	Comments
				Initial width height	Middle width height	Final width height	Initial width height	Middle width height	Final width height		
T-9	1	.067	1.75	.24	.16	terminated				2.88	much growth on bottom of cell
T-9	2	.086	3.50	.33	.22	.32	.10	.08	.06	3.30	good growth at end
T-9	3	.081	2.60	.33	.08	terminated				2.98	fast growth. many veils
T-10	1	.048	1.75	not measured	.17	.19	.08	.10		2.61	clear growth near end
T-10	2	.070	3.50	not measured	.14	.32	.09	.11		3.76	
T-10	3	.065	2.62	many small crystals						2.60	
T-11	1	.083	6.05	.31	.19	.07	.07	-	-	5.93	fast growth
T-11	2	.022	0.87	.09	.07	.03	.03	.01	.01	7.14	good growth
T-11	3	.016	0.09	.11	.09	.02	.01	.01	.01	5.76	

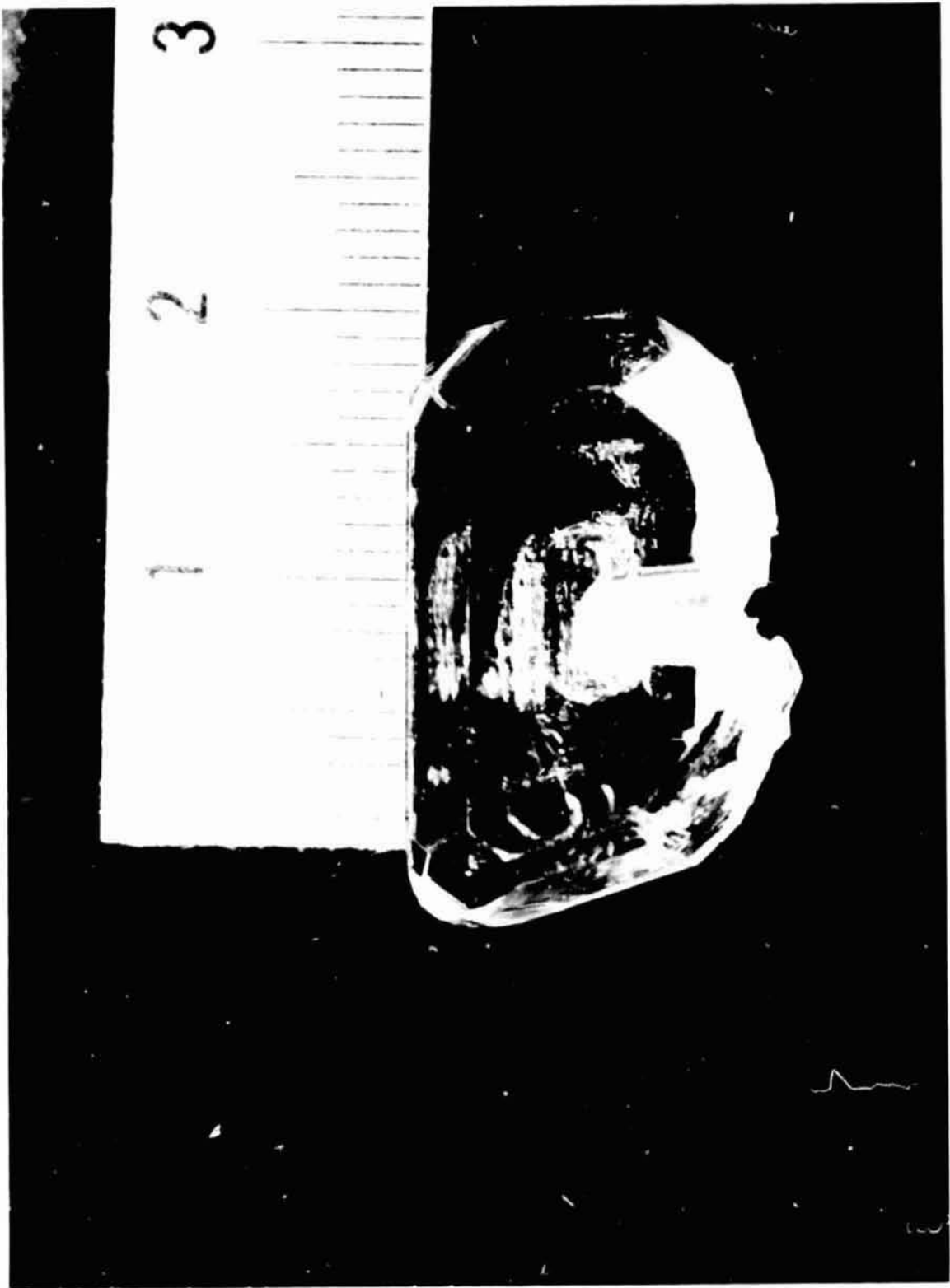


Figure 12. Low Convection Grown Crystal

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convection cell, it was decided that a porous cover area of approximately  $3.4 \text{ cm}^2$  would yield growth rates for optimum perfection.

Thermal gradients were introduced by independently varying the power to either of the side heaters or bottom heater in order to explore the use of various convective conditions during growth. Three temperature gradients were employed. Three temperature profiles are shown in Figure 13a, 13b, and 13c. The largest temperature differences diagonally across the growth cell were  $3.7^\circ\text{C}$ ,  $1.05^\circ\text{C}$  and  $0.8^\circ\text{C}$  respectively.

Five high convection growth runs were made. It was found that only with the smallest gradient (gradient c) were transparent crystals grown. The results of the five growth runs are summarized in Table 15.

Generally, the growth rate had only two linear regions, an initial region corresponding to high supersaturation as in the low convection case and a final region. It is the data from final region that is listed in Table 15. The grown crystals did not come into proximity with the growth vessel walls which may explain the absence of the third linear region. Growth rate data was only obtainable for runs HC-3, HC-4 and HC-5 where growth took place. Plots of linear dimensions versus time for these runs are shown in Figure 14. The photograph of crystal HC-5 in Figure 15 shows very little optically clear area.

The following observations relating to high convection growths were made:

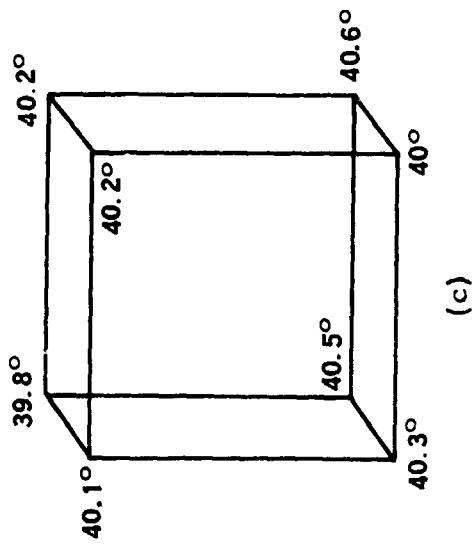
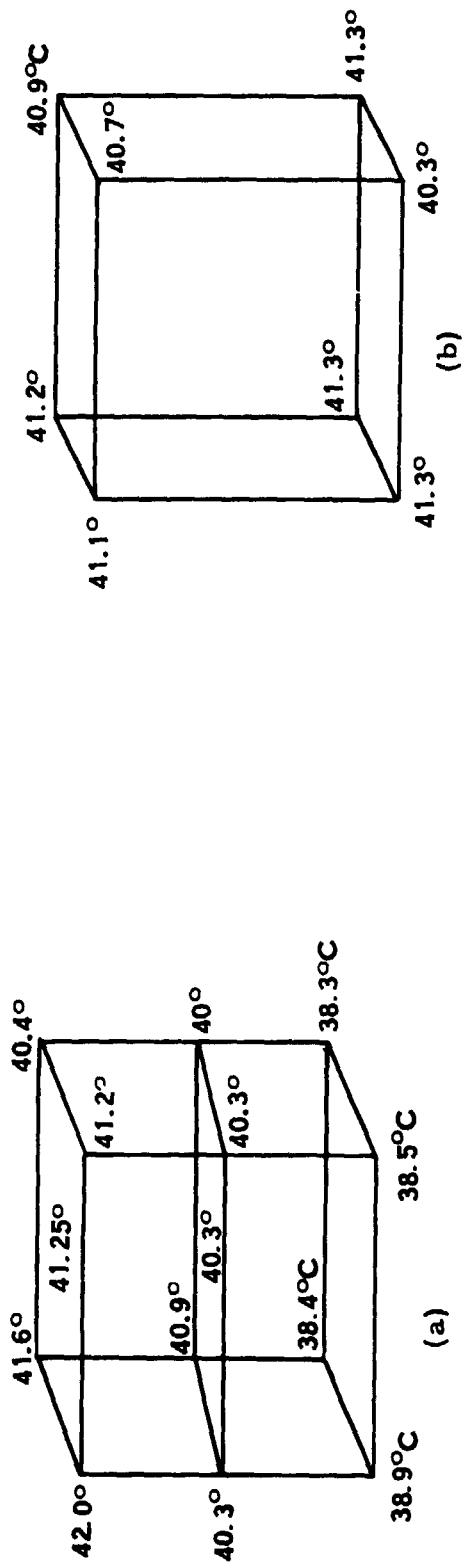


Figure 13. Temperature Profiles During High Convection TGS Growth

Table 15. Summary of Growth Runs in the High Convection Cell

Run	Temp. Grad. Imposed	Duration hours	Meas. Evap. Rate	Meas. (mm/hr)		Crystal Prop.
				Growth Rate l	h	
HC-1	(a)	14 1/4 hr.		-	-	Platelike habit
HC-2	(a)	72 hours	-		-	Seed had fallen off holder .
HC-3	(a)	68 hours	.14	.016	.014	Used 2 seeds - upper dissolved - lower had some growth badly veiled.
HC-4	(b)	133 hours	.14 cc/hr	.054	.031	Initial 2/3 of growth cloudy, last 1/3 clear.
HC-5	(c)	180 hours	.14 cc/hr	.003	.007	Largest growth; had some veiled regions, mostly transparent near the end of growth period.

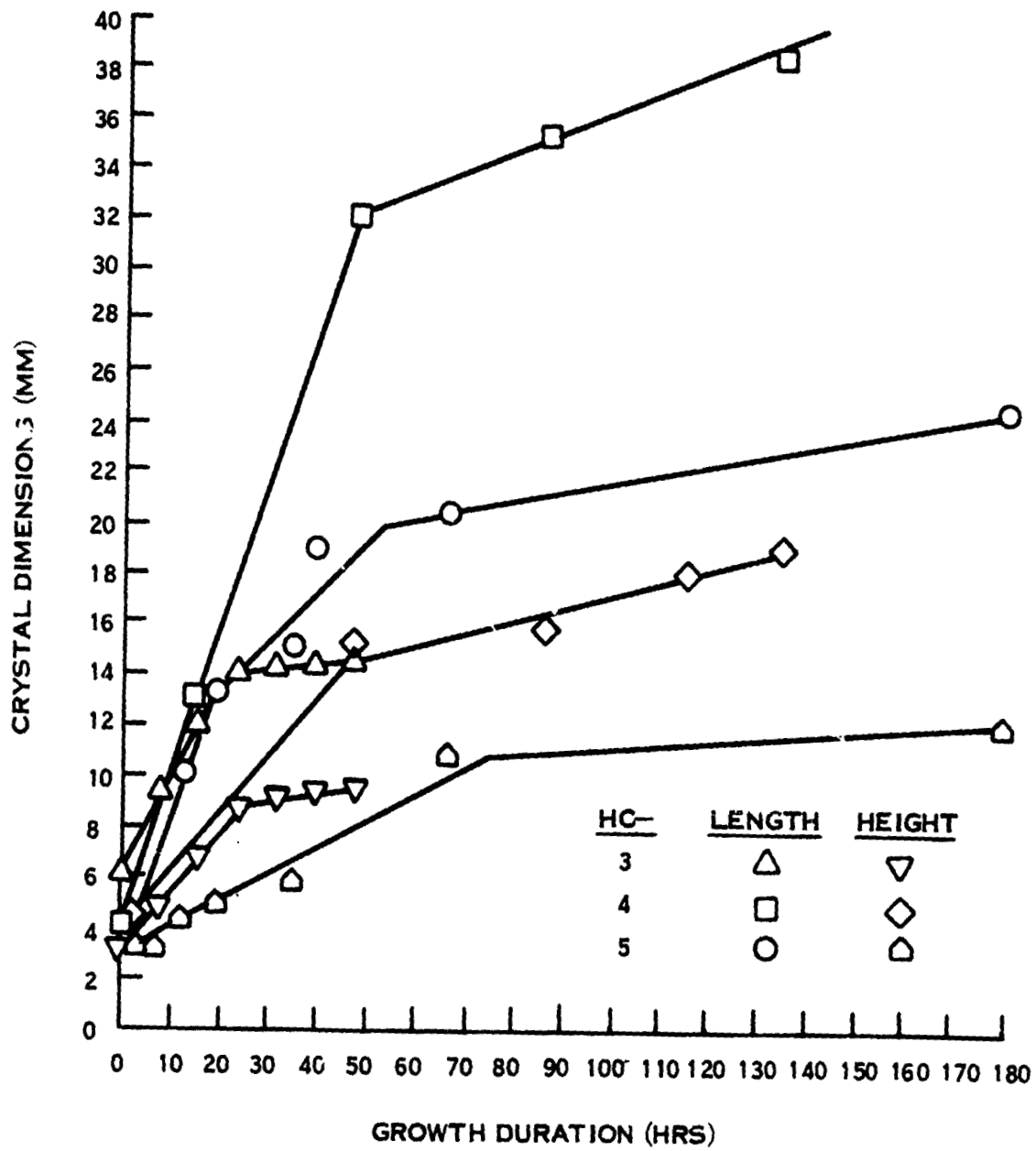


Figure 14. Crystal Dimensions vs. Time of Growth for High Convection Growth



Figure 15. High Convection Grown Crystal - HC-5

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1) Measured evaporation rates are quite reproducible but a wide spread in growth rate data for the latter stages of growth is very evident.

2) Excessive nucleation occurred in all runs to a much greater extent than observed in low convection growth.

3) Marked differences in morphology were observed for high convection grown TGS crystals. Growth is more pronounced in the basal plane at the expense of growth along the vertical direction. The orientation of the basal plane in the HC-5 crystal was  $(10\bar{1})$ .

4) Crystals were not as transparent indicating greater inclusion of solvent.

5) The crystals did not cleave easily indicating poor structural perfection and the surfaces were often not flat.

6) Density gradients in the growth solution are quite large as indicated by a seed near top of solution dissolving while a seed near bottom continued to grow in HC-3.

### 5.2.3 Rotary Crystallizer Growth

The rotary crystallizer was obtained late in the program, so that only two runs were attempted. The first was terminated due to a power failure and a usable specimen was not obtained.

The second crystal grew for a period of two weeks on a (010) oriented cylindrical seed. The temperature cooling rate increased from an initial  $0.05^{\circ}\text{C}/\text{day}$  to  $0.16^{\circ}\text{C}/\text{day}$  at termination. A photograph of this crystal is shown in Figure 16. The crystal exhibited high optical quality except for veils at the seed tip and near the upper faceted faces. In the clear sections there was no visible evidence of  $6328\text{ \AA}$  He-Ne laser radiation scattering in the bulk of the crystal. These sections of the crystal are then representative of commercially available TGS.

### 5.3 Characterization of Convection

Typically in studies to determine the onset of convection for fluids confined in an enclosed rectangular cavity, two-dimensional heat flow is assumed and the aspect ratio, the quotient of cavity height to width, is varied. In this investigation, however, due to time limitations, only one aspect ratio of 1.5:1 was employed and heat conduction occurred over the entire three-dimensional volume.

In order to obtain as quantitative as possible comparison of convection, particle velocities were measured in both the low and high convection cells with gradient  $c$  (Figure 13c). These measurements were made by photographing polystyrene beads approximately 1 mm in diameter suspended in a  $\text{NaClO}_3$  solution. The concentration of the salt was adjusted so that the beads were neutrally buoyant. The measurements from the time lapsed photographs are given in Table 16.



Figure 16. TGS Crystal Grown in Rotary Crystallizer

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Table 16. Particle Velocities in High and Low Convection Cells

	<u>Vertical Velocity</u> (mm/hr.)	<u>Horizontal Velocity</u> (mm/hr.)
Low Convection	0.2	2
High Convection	400	2000

The absolute values of the velocities are not particularly meaningful since the densities and viscosities of the  $\text{NaClO}_3$  and TGS solutions are different. However, the differences of three orders of magnitude are indicative of the different degrees of convection.

The convection flow pattern for gradient b in the high convection cell was also photographed and is shown as Figure 17. This photograph was obtained by suspending fluorescent anthracene particles in the  $\text{NaClO}_3$  solution and illuminating the cell with ultraviolet light.

#### 5.4 Characterization of Perfection

The grown crystals visually exhibiting the highest optical quality were selected from each of the growth methods. These crystals were used for characterization studies. Besides visual inspection, etch pit densities and dielectric loss ( $\tan \delta$ ) were used for perfection characterization.

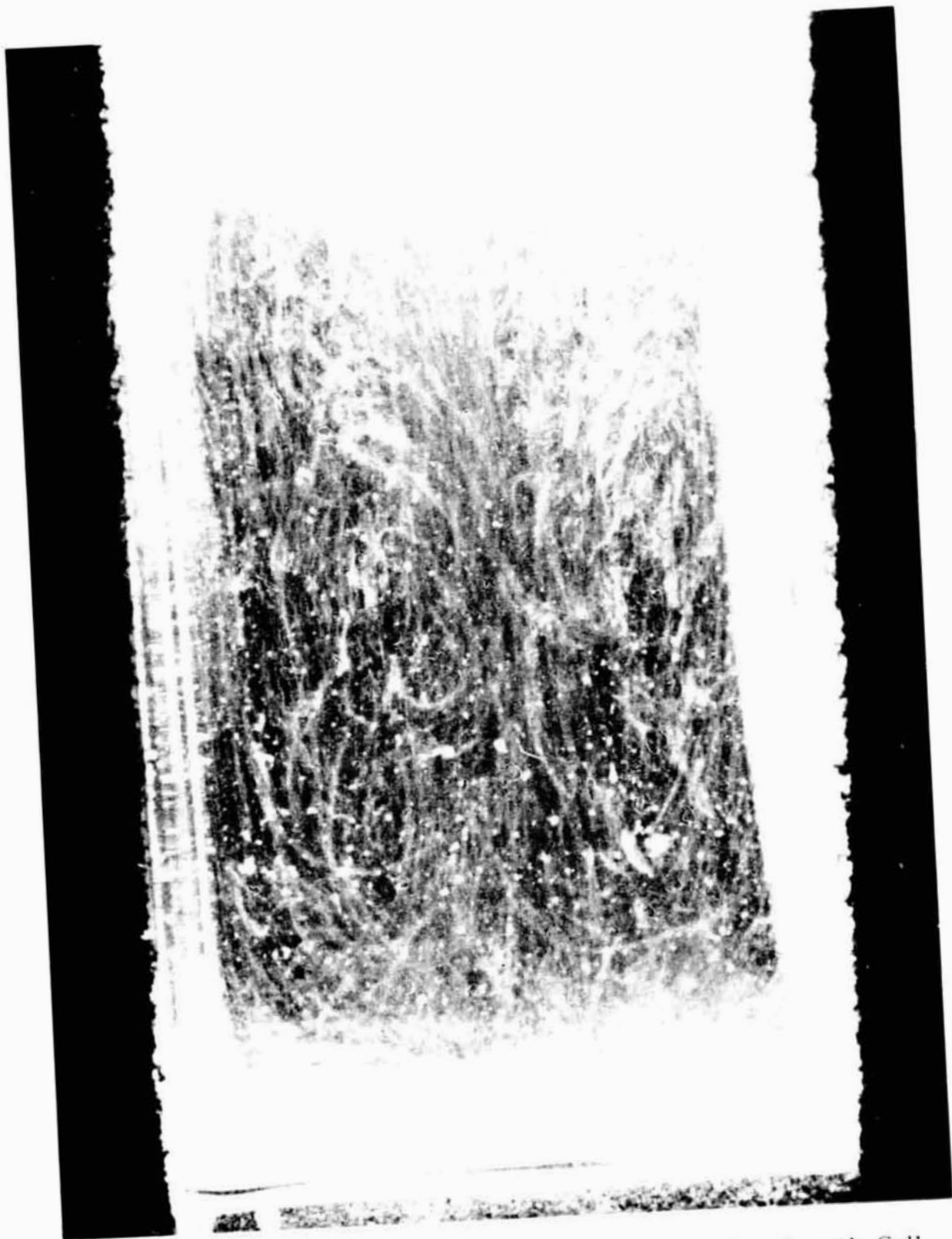
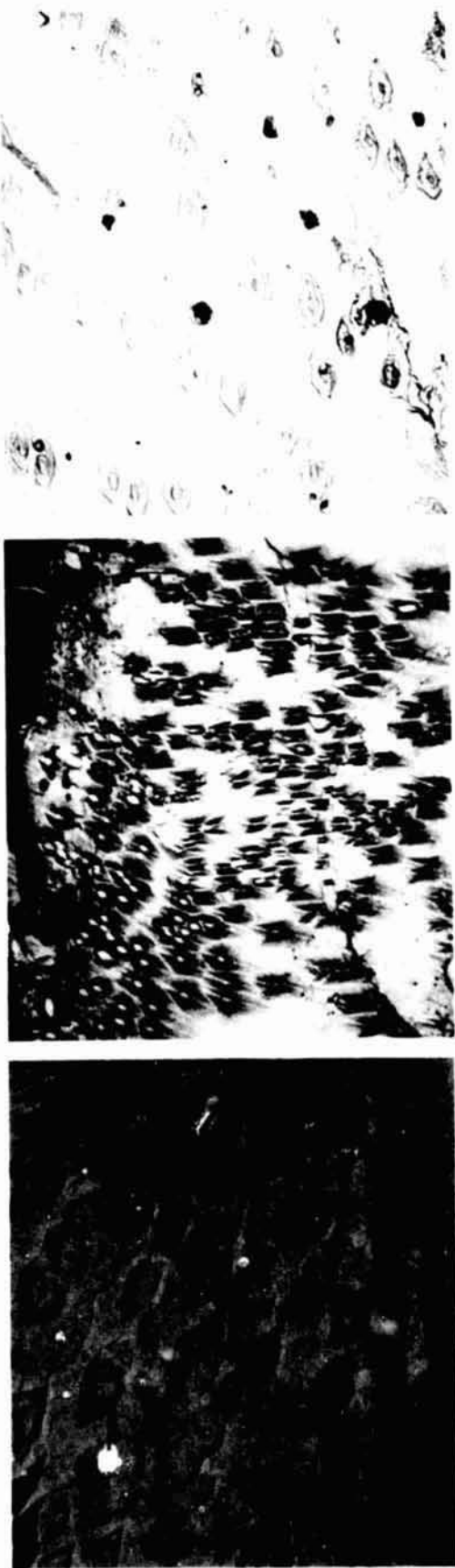


Figure 17. Convection Flow Pattern in High Convection Growth Cell

A selective etching method developed by Kontantinova for revealing the distribution of dislocation sites on cleaved (010) surfaces was used to obtain dislocation densities <sup>(20)</sup>. The etchant composition consisted of glacial acetic acid with an addition of 1.4% water and 0.7% nitric acid.

The dielectric loss was measured using a General Radio Type 1650A impedance bridge. All samples were electroded on the (010) faces and measurements were made in a constant temperature bath at 40°C. Measurements of  $\tan \delta$  are often complicated by the aging of TGS <sup>(21)</sup>. Therefore, all specimens were held at 40°C for one day before measurements were made and small applied fields ( $\sim 1$  v. rms) were used. Under these conditions, reasonably reproducible results were obtained.

The results of the etch pit densities and  $\tan \delta$  measurements are shown in Figure 18. These initial results are significant in that they support the hypothesis that solution growth under low convection conditions will produce crystals of higher perfection. The low convection specimens grown isothermally by controlled evaporation appears to have at least as high of a perfection as the "commercial" TGS crystal grown under forced convection with temperature lowering. The differences in etch pit sizes is due to the different etching times required to reveal pits.



LOW CONVECTION

$1 \times 10^4 \text{ CM}^{-2}$

0.03

HIGH CONVECTION

$8 \times 10^4 \text{ CM}^{-2}$

ETCH PIT DENSITY

0.13

DIELECTRIC LOSS

"COMMERCIAL"

$3 \times 10^4 \text{ CM}^{-2}$

0.09

Figure 18. Comparison of Etch Pit Densities and Dielectric Loss

## 6.0 CONCLUSIONS AND FUTURE DIRECTIONS

### 6.1 Conclusions

It is concluded that a great deal of justification does exist to pursue space processing of dielectric-elastic-magnetic single crystals. They are crystals which will form the basis for components of high intrinsic value for major new device markets in the mid-1980's. In addition, there is evidence that significant improvement in crystal-device performance can be realized by space processing and their growth method is compatible with long duration flights. Essentially four tasks were undertaken in order to reach this conclusion. They are:

- 1) Identify applications for dielectric-elastic-magnetic single crystals, especially in emerging technologies which will be important in the 1980's and beyond.
- 2) Identify important materials, both present and emerging, and the effect of their limitations on application viability.
- 3) Consider what impact the micro-gravity environment of space may have on improvements and relief of crystal limitations.
- 4) Perform some preliminary ground based experiments to see if there is promise for improvements by relief of convective conditions in space.

In terms of these tasks, several conclusions have been reached. High density and rapid access time storage in computers and information coding in optical communications have been identified as two

very promising applications that will extensively use emerging dielectric-elastic-magnetic crystals. Both technologies are in the proper time scale for development into commercial use in the 1980's and beyond. Both are as well, to a large extent, materials limited at the present time. Although the crystals have high unit costs and are extremely critical for performance, they often do not constitute the major cost of the system. This is particularly attractive in terms of space processing payoffs.

This class of materials is presently in the stage of device conception. Their properties are only now beginning to be exploited. It is reasonable to expect that applications other than advanced computers and optical communications will be found in the future and these materials will occupy a dominate role in future technologies.

As opposed to the era of semiconductors which utilize electron transport properties, the emerging dielectric-elastic-magnetic materials utilize lattice and spin instabilities. The need is then to engineer in appropriate instabilities for the device requirements. As a consequence of these instabilities, these new materials have a complicated structure and complex compositions. Because of the high sophistication and varied effects desired, there exists no dominate material such as the semiconductor silicon and it is doubtful if one will exist in the near future.

However, because of symmetry and instability requirements, there are few structural families of cardinal importance. The anisodesmity

that is required for the instabilities further limits growth to essentially the solvent method.

The applications for the dielectric-elastic-magnetic crystals require very high structural perfection. It is important then to consider structural defects in terms of solvent growth. The growth kinetics at the liquid-solid interface are of utmost importance. Slow growth, which is characterized by a stable interface, is required for high perfection.

One of the primary causes of instabilities at the interface is thermal and density gradients due to convection. The relief of convective effects in a micro-gravity environment shows great promise for significant increases in structural perfection. In addition, stable interfaces can support higher supersaturations which offers fast growth rates with equivalent one g perfection.

Morphology control is another promising benefit of micro-gravity. Without the requirement for stirring and utilizing a diffusion controlled interface, specially oriented seed platelets could be used to grow the plate morphologies needed for many applications. Such control could reduce the number of fabrication steps and yield a higher perfection surface.

Although the equilibrium properties of crystal growth are reasonably well understood, little is known about the kinetic details at the interface. The kinetics are often masked by gravity induced effects which

makes experimental observations exceedingly difficult. Thus, space also offers the promise for significant crystal growth research advances.

The preliminary investigation with representative TGS gives experimental evidence that growth in space could offer significant perfection improvements. Measurements of etch pit densities and dielectric loss indicate that the magnitudes of these parameters increase in high convection grown crystals. An extrapolation toward zero-gravity indicates that a significant reduction in these defects can be expected.

#### 6.2 Future Directions

With the present pause in long duration space flight activity, sensible plans can and should be made for the growth of dielectric-elastic-magnetic single crystals in space. The pursuit of a single compound is not justified. On the other hand, since only a few families of crystals are of cardinal importance, pursuit of some representative solvent systems is reasonable.

Growth from a solvent is perhaps the least understood crystal growth technique. Although the equilibrium thermodynamics are generally well understood, the details required to predict growth conditions generally must be empirically determined. In addition, very little is known about the growth kinetics at the liquid-solid interface. Under these considerations, three general directions for immediate future work are presented. First, because of its experimental ease, growth from aqueous



solutions should be continued to further verify and quantify the preliminary results of this program. Aqueous solution growth is the most likely initial candidate for growth in space because its power and thermal requirements are more easily manageable in a spacecraft than higher temperature solvent growth. Secondly, however, ground-based work on the higher temperature solvents should be initiated since a large number of the high potential crystals cannot be grown from a water solution. The solute-solvent systems selected should be representative of as large a group of materials as possible without imposing severe experimental difficulties. The objectives of this work should be primarily two fold: (1) to determine the degree to which understanding gained from aqueous growth can be carried over to higher temperature solvents, and (2) to gain the experience required for the design of a workable spacecraft apparatus. The third area of pursuit is in investigation of the interface kinetics. The results of this work would have far reaching benefits for all liquid-to-solid growth processes. Ground-based investigations would be difficult but the ellipsometric technique, for example, offers promise for significant gains in understanding. Results from using this technique could be incorporated in investigations in space where quiescent interface conditions may offer considerably improved experimental conditions.

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