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NASA Contractor Report 3370

A Study of Crystal Growth by Solution Technique

R. B. Lal

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A Study of Crystal Growth by Solution Technique

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FOREWORD

This report deals with work done under NASA Grant NSG-8033 to the Alabama A&M University (AAMU) in Huntsville, Alabama. The work reported here was done under the technical supervision of Mr. Charles Schafer of NASA/MSFC, Fluid Dynamics Branch, Atmospheric Sciences Division, Space Sciences Laboratory, and his cooperation and comments are gratefully acknowledged.

The author thanks the NASA Office of University Affairs for the award of this grant which evolved into a flight experiment for the SL 3 Mission. The author also thanks Dr. Leon Frazier, Dr. Bessie W. Jones, and Dr. M. G. George (all of AAMU) for their continued interest and support during the progress of this work.

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I. INTRODUCTION

The promise shown by the results of Skylab I and II and the ASTP experiments,[1,2] on materials science are in confirmation of the possibility of processing of materials in space on a routine basis. These results have logically placed an emphasis on simple crystal systems. The results of different flight experiments on various missions have shown excellent promise and have prompted a closer look at the opportunities for more complex and more valuable compound materials.

The NASA materials processing in space (MPS) program is intended to develop applications of space flights in materials science and technology, including both research and manufacturing activities. Its initial goal is to demonstrate the value of space for materials work by achieving significant scientific results and/or developing specific useful materials and products.

Many technologies are dependent on single crystal materials to varying degree. The materials can be processed for making efficient semi-conductors for use in the field of communications, materials which will make better superconductors for control and distribution of energy, materials for energy conversion devices, materials for various kinds of detectors, and materials for non-linear optical devices. The eventual processing of materials in space is likely to become a major reality with the operational space shuttle in the 80's.

The advantages of weightless environment for materials processing include: a) absence of buoyant convection, b) absence of density segregation, c) absence of sagging, and d) opportunities of containerless processing. With regard to the growth of crystals, the primary advantage is the absence of buoyant convection. A growing crystal extracts materials from and/or releases heat into the surrounding fluid, thereby lowering the fluid's density. So on earth under 1-g conditions, a growing crystal is surrounded by a rising convection current. In most cases, this convection is unstable and gives rise to growth rate instabilities which cause impurity distribution fluctuations and defects such as fluid inclusions.[3-7]

It would, therefore, be expected that crystals grown in low-gravity environment would be more uniform in composition and have fewer defects than their one-g counterparts.

II. OBJECTIVES

The objective of this investigation is to study the mechanism of crystal growth by the solution technique with special reference to materials for electro-optical devices.

During this investigation, a flight experiment entitled, "Solution Growth of Crystals in O-Gravity," was proposed to NASA. The proposal was accepted by NASA in September 1977, and the experiment is now approved for flight on the SL-3 mission under a separate NASA contract.

III. BACKGROUND

In recent years, new applications for non-linear optical devices have been found for ferroelectric single crystals such as Triglycine Sulfate (TGS) $(NH_2CH_2COOH)_3 H_2SO_4$, crystals of iodate family and others. Single crystals of TGS may be used for infra-red image parametric up-conversion due to their phase match ability and for image tubes for television displays of thermal scenes using their large pyroelectric effect. There is, also, an increasing interest in detectors requiring less cooling or no cooling at all, even if they have low performance, which may lead to systems with greater cost-effectiveness. However, the undisturbed operation of these devices and techniques requires single crystals of high optical quality, i.e., of high purity, high homogeneity concerning the physical properties, low density of structural defects and free from inclusions and strains. The long-duration orbital flights in the space shuttle era will definitely allow growth of these crystals using solution technique.

IV. CRYSTAL GROWTH FROM SOLUTION

Crystal growth from solutions is simple in principle and has many applications. The technique is particularly useful for growth of materials which have high vapor pressure or decompose irreversibly at the melting point. Crystals will be grown from solution if the solution is supersaturated, i.e. it contains more solute than it can hold in equilibrium with the solid. The growth methods[8], are based on solvent used, because the equipment, range application, problems and approach are to a large extent determined by the choice of the solvent. However, the more fundamental delineation of the methods could be made on the basis of the methods of producing supersaturation. The growth methods can be divided on this basis.

1. Isothermal methods (constant temperature methods)
   - A. Solvent evaporation or solvent concentration change (mainly used in aqueous and molten salt growth)
   - B. Temperature differential (mainly used in hydrothermal, aqueous and molten salt growth; also includes temperature-gradient zone melting when the gradient is moved through the sample).
   - C. Chemical or electrochemical reaction (mainly used in aqueous growth)
2. Non-isothermal methods (temperature variation methods)
   - A. Slow cooling (mainly used in aqueous, liquid metal solvent, and molten-salt growth)
   - B. Temperature-gradient zone melting (when the gradient is imposed over the whole sample).

IV. 1. Advantages of Growth from Solution

In general solution growth can be accomplished at temperatures considerably below the melting point of the material, and the use of lower temperature alleviates many of the problems associated with the melt growth process.

The main advantages are listed below.

1) The most important advantage of crystal growth from solution is the control that it provides over the temperature of growth. This makes it possible to grow crystals that are unstable at their melting points or that exist in several crystal forms depending upon temperature.

2) A second advantage is the control of viscosity, thus permitting crystals that tend to form glasses when cooled from melts to be grown.

3) Crystals grown from solution usually have well-defined faces as compared with those from melts.

4) It avoids strains, reduces vacancy concentration, and sometime reduces dislocations and low angle grain boundaries associated with high temperature growth.

5) Solution growth or low temperature growth is experimentally more convenient. Higher temperature processes are often more demanding on equipment and difficult to control, and harder to keep clean so that products are pure.

Solution growth has had its main success in the preparation of bulk crystals.

There are some disadvantages of a polycomponent growth and they are enumerated below.

1) The additional component will be contaminant and will have solid stability in the grown crystal.

2) Elimination of the additional component at the growing interface will set an upper limit on rate of growth. Diffusion will be important in this process. This may be an advantage in low-gravity and will be a dominant factor.

3) Because of the concentration gradient at the growing interface, constitutional supercooling will often occur; facets effects, cellular growth and dendritic growth can thus be problems.

The process of crystallization involves simultaneous mass and heat transport between the crystal surface and the surrounding fluid. In almost all cases, this causes a reduction in the density of the fluid. So a growing crystal is usually surrounded by a rising convection current. Chen et al.[9] have demonstrated this in a recent paper. Janssen-van Rosmalen et al.[10] have demonstrated the influence of hydrodynamic environment on the growth and formation of liquid inclusions in large KDP crystals grown by solution technique. It was proposed that veils of liquid inclusions are not a result of starvation in the laminar boundary layer, as suggested earlier, but of depletion in the closed wake at the rear. Growing crystals from a fluid phase under normal gravity conditions involves coupling of the gravitational field with density variations in the fluid, resulting in the generation of convection currents. The spatial and temporal density variations in the fluid media are due to thermal and solutal variations.

Nearly all crystal growth processes involve both a solid and a fluid component. Since internal binding forces in solids are much larger than 1-g forces, only the properties of the fluid are expected to be significantly influenced by gravity. In the liquid state, intrinsic forces such as cohesion or surface tension are of the same order as 1-g forces, and the familiar properties of liquids are the result of the interaction of intermolecular forces and the gravitational forces. If the gravitational forces are reduced considerably, the behavior of fluids will be determined by molecular forces alone. Thus, the environment of the orbital space-lab will have significant influence on the fluid behavior which is expected to affect the crystal growth process. In the absence of convection, diffusion will be much more significant for the mass transport process.

The process of crystallization from solutions represents a typical phase transition in a condensed system. This process is influenced by the creation and structure of the supersaturated solution. The proper crystal growth on the seed inserted into a supersaturated solution is influenced by various factors.

(a) the degree of supersaturation, which determines the rate and also the mechanism of growth.

(b) the hydrodynamic conditions in the solution, specially at higher degrees of supersaturation, which influences the transfer of the material from the solution to the crystal through the diffusion layer.

(c) the temperature of crystallization.

(d) the quality of the seed used and the chemical purity of the solution.

(e) Another problem in the growth of large, high-quality single crystals is the strain induced during growth by the method used in holding the original seed. This is specially evident in solution crystal growth where strain induces optical inhomogeneities, cracks and regions of non-uniform growth rates. Recently, Loiacono et al.[11] have used a cylindrical seed method to the solution growth of large single crystals of TGS. The method permits the strain-free mounting of oriented seed crystals.

(f) finally even the manipulation with the crystal as grown (taking the crystal out of equipment, etc.) can strongly influence its properties.

To investigate the crystallization conditions of TGS in view of growing environment, a crystallizer is required which can be used for growing crystals in absence or with a minimum mechanical disturbance in the growing solution.

Growth of crystals on earth is always accompanied by gravity-driven convection currents as well as diffusion fronts.

IV. 2. Effect of Impurity Adsorption on Kinetics of Crystal Growth From Solution.

Recently it has been reported by Davey[12], that a presence of a third component can often have dramatic effects on the crystal growth kinetics (third component may be an impurity). Adsorption of impurities onto the crystal faces changes the relative surface free energies of the faces and may block sites essential to the incorporation of new solute into the crystal lattice. These effects may result in changes in growth kinetics and, hence, habit modification of the crystalline phase.

From the studies of Davey (loc. cit) it seems worth noting the following points in relation to the mechanism of growth rate reduction by impurity adsorption.

a) Impurity adsorption results in the blocking of key sites on the crystal surface.

b) Impurities which bear a structural resemblence to the crystallizing component may be most effective in kink and step sites, while impurities which are structurally dissimilar to the crystallizing component may be limited to ledge sites.

The following requirements of an experimental study may be elucidated.

1. Substantiation of growth mechanism for pure solution.

2. Measurement of growth rate as a function of impurity concentration at a fixed supersaturation.

3. Observation of step systems on faces growing in pure and impure solutions.

4. Measurement of adsorption isotherm of the impurity onto the crystal faces under consideration.

5. The selection of experimental system in which the structural nature of the impurity in solution is known.

The experimental data should then be correlated with different available models of crystal growth in solution.

IV. 3. Uncertainties Regarding Crystal Growth in Low-Gravity Environment

For a detailed study of the crystal growth processes in low-gravity environment, uncertainties about residual, transient and non-buoyant convection present and their effect on impurity distribution and the formation of defects in the crystal must be considered. Another area of uncertainty is caused by our poor understanding of the basic mechanisms of crystallization.[13-14] Choices between competing theories depend on accurate measurements of growth rate as a function of the adjacent thermal and concentration gradients and on interface kinetics terms. All these measurements, when perfomed on earth in one-g, are distorted by the effects of convection. Measurement of such data in a fluid in a solution growth experiment will be extremely beneficial to the crystal growth theorists.

Also, the effect of low-frequency g-levels on the crystal quality is a very important parameter. Displacements produced by low-frequency (<10 Hz) g-levels are most harmful to solution crystal growth and must be accounted very carefully.

V. EXPERIMENTAL PROCEDURE*

A low temperature solution growth system for growing TGS was designed and fabricated (fig. 1). The system includes an outside bath 27.5 cm x 27.5 cm x 17.5 cm made out of 0.9 cm plexiglass. The bath is heated with two vertical quartz heaters each of 350 watts. The fluid in the outside bath, which is distilled water, is stirred with two stirrers running at 20 rpm using a.c. synchronous motors. The input to the heaters is controlled using a Fisher proportional temperature controller with an accuracy of $\pm 0.01^{\circ}C$. The actual accuracy of the bath is measured at present only to $\pm 0.1^{\circ}C$ using NBS calibrated thermometers. The growth solution is kept in a 10 x 10 x 10 cm^3 cell made out of 0.6 cm thick plexiglass. The growth cell is surrounded on all sides (except top) by the outside constant temperature bath. The seed crystal is mounted on a specially designed sting which is inserted in the inner cell at a proper time. Details of the sting are given in fig. 2. A stainless steel tube is encapsulated by a plexiglass tube machined to fit the stainless tube. A narrow outer jacket is left between the plexiglass and the stainless tube. A desired flow of high-purity argon gas can be maintained between this narrow jacket. The desired flow of argon gas is monitored through a flow meter.

*This work was done in conjunction with other NASA Contract NAS 8-32945.

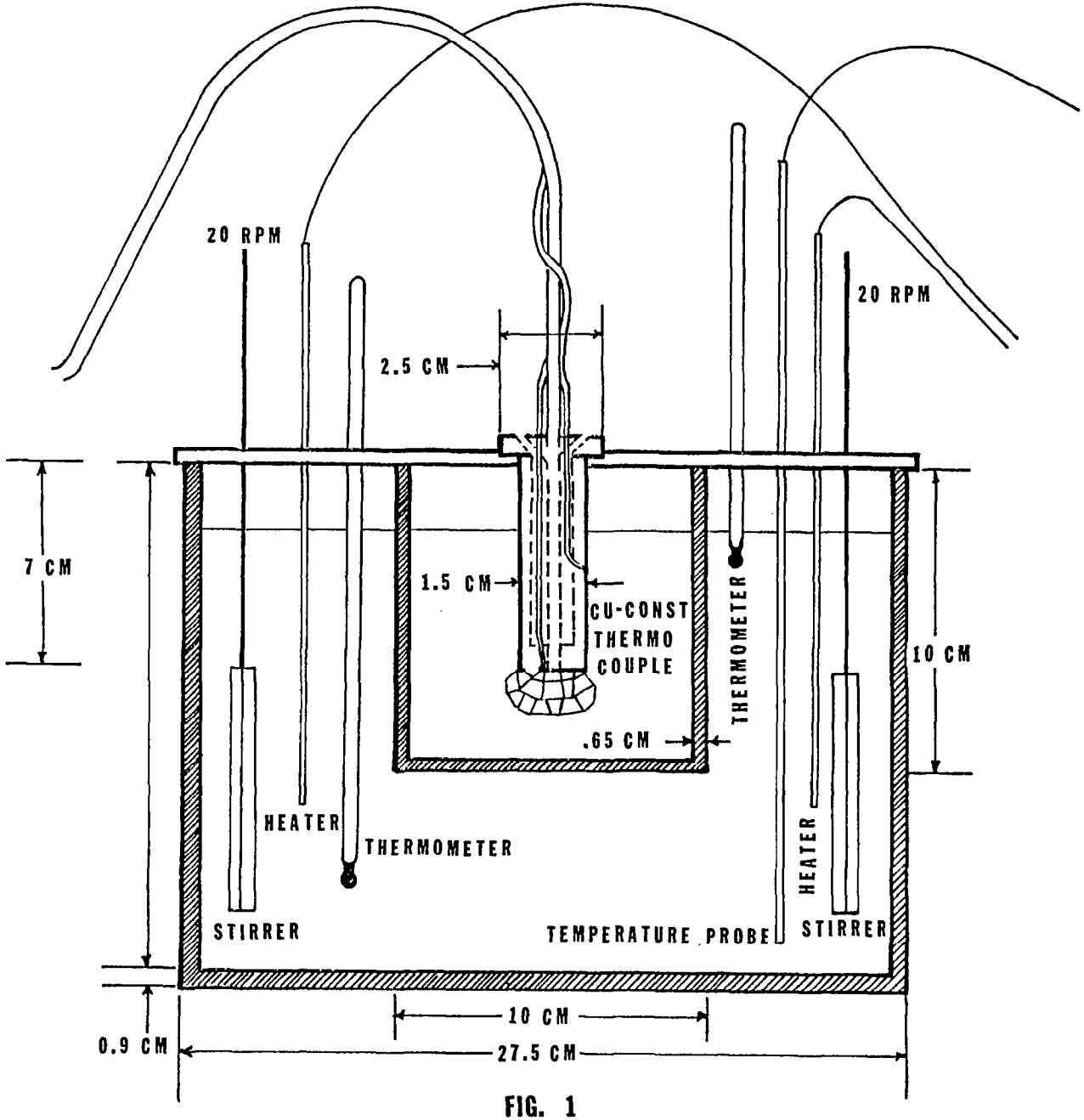

FIG. 1
SOLUTION CRYSTAL GROWTH SYSTEM

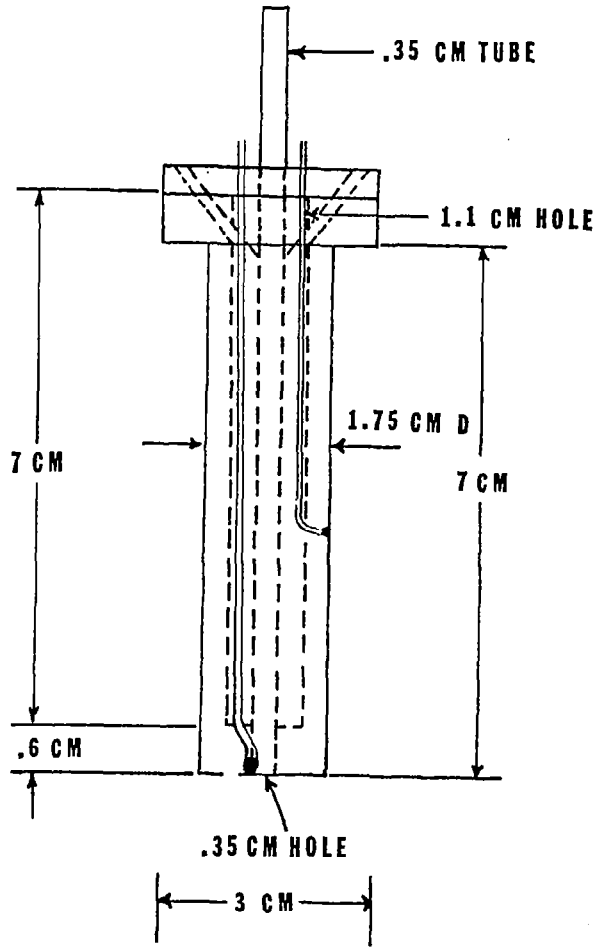

FIG. 2

DESIGN OF STING

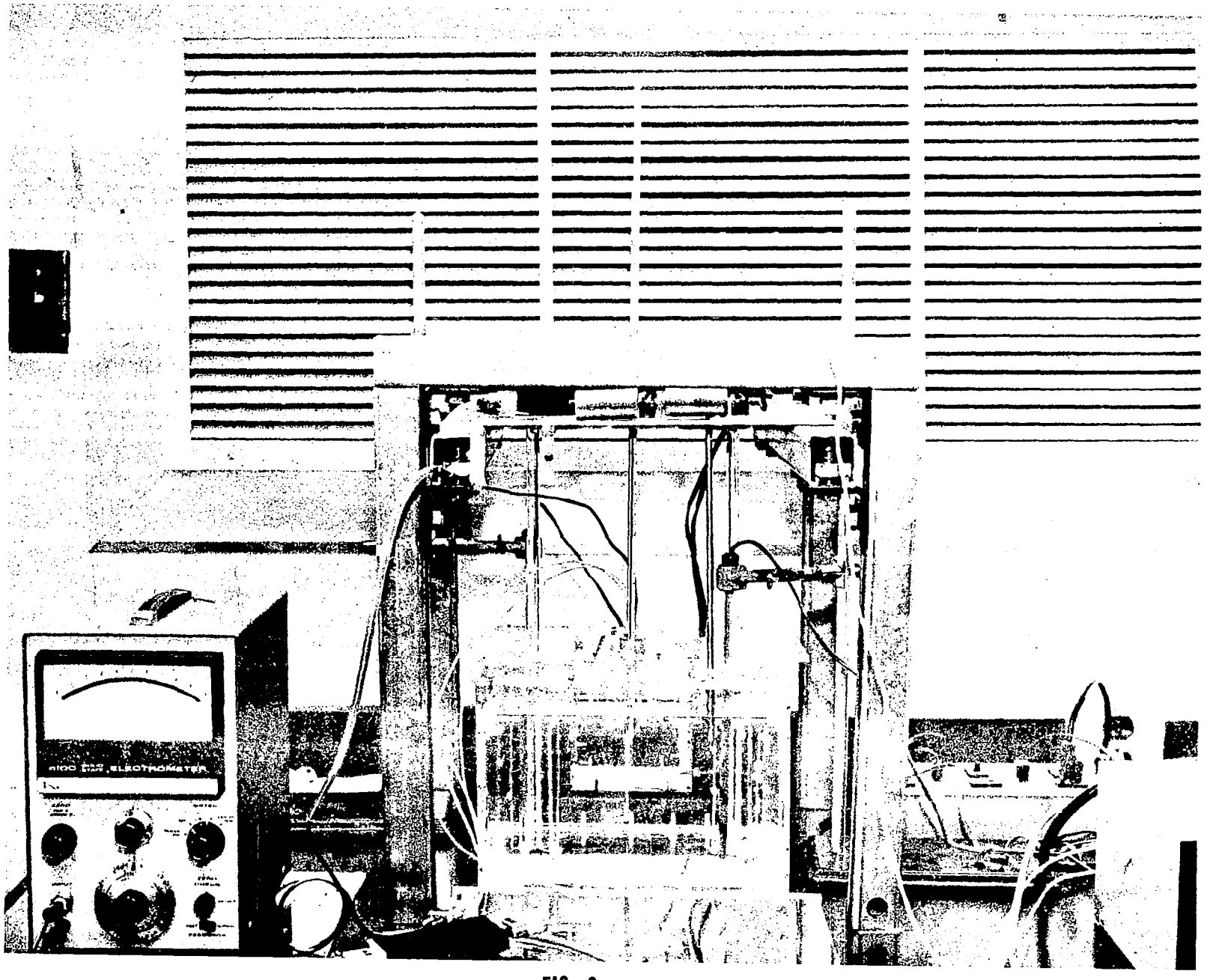

FIG. 3

This serves the purpose of cooling the sting and the seed crystal. The seed crystal is mounted using RTV silicone adhesive at the end of the stainless tube which barely projects out of the plexiglass rod. Two copper-constantan thermocouples have been installed in the sting. One is behind the seed crystal inside the rod and the other on the outside wall of the sting mounted flush to the surface of the sting. The emf of the two thermocouples is measured using a Keithley 610C electrometer. Omega company copper-constantan 0°C temperature compensator is used for 0°C reference junction.

The inner growth cell is tightly covered with a plexiglass cover to avoid any appreciable loss of liquid due to evaporation.

An overall picture of the experimental setup is given in fig. 3.

V. 1. Test of Thermal Stability of the System

The thermal stability of the growth system was tested for a desired set temperature (between 30°C - 50°C) over a period of 8-12 hours. The stability of the cell temperature greatly depends upon the stirring provided to the outside bath. In the initial run, commercially available Fisher Scientific stirrers were used. It was found that there was a large variation of temperature (±4°C) between the lowest and the top level of the water in the outside bath. The design of the stirrers was modified so that they can stir about 4" of vertical depth of water below the top surface. The bath temperature was then maintained within less than ±0.1°C between different layers of water all around the growth cell. The growth cell was also tested for cool-down and heat-up rates. The outside bath can be brought to a desired temperature within ±0.1°C in a period of 20 minutes. Due to the poor conduction of plexiglass, the inner cell takes about 2 hours to reach a steady-state temperature, which was found to be 1°C below the outside bath for a particular cell.

V. 2. Growth of TGS Crystals

Initially, seed crystals of TGS were grown by spontaneous nucleation and grown in about 2 or 3% supersaturated solution. Saturated solutions of TGS were prepared from BDH high-purity crystalline Trigylcine sulfate using double-distilled water. Solution is filtered at a temperature of a few degrees centigrade above the saturation temperature. At the present time crystal growth experiments have been performed in the ferroelectric range, which is below the transition temperature of TGS ($T_c \simeq 49^{\circ}C$).

Before the start of the experiment, the outer bath was set at $37^{\circ}C$. The inner cell was filled with 800 ml of $36^{\circ}C$ saturated solution of TGS. The pH of the solution was measured as 2.4 ± 0.1. The cell was left for two hours in the constant temperature bath till its temperature reached a steady value of $36^{\circ}C$. The experiment was initiated by inserting the sting, mounted with a polyhedral seed of TGS using RTV silicone adhesive, in the solution. A slow purge of prepurified Argon at 2 p.s.i. was maintained through the sting. In this initial run no thermocouple was mounted at the tip of the sting so no temperature reading of the tip and the growth solution were recorded during the growth of the crystal. The Argon gas provided a constant cooling of the sting and a constant supersaturation near the seed crystal. The growth process continued for 26 hours. The crystal grew about four times the size of the seed. The total mass deposited in 26 hours was 2.79679 g. This gives an average growth rate of 0.15 mm/hour, but no precise calculation of average mass transfer coefficient ($\bar{k}$) has been made at this time. This growth rate is appreciably faster than required for a laminar growth. In this growth, an under-cooling of $1^{\circ}C$ was maintained on the tip of the sting. At the end

of the experiment the crystal was removed from the growth solution, dried and stored. Due to some inaccuracy in the saturation curve there were some crystallites seen at the bottom of the growth cell.

No evaluation of the grown sample has been done at this time. It is planned that measurement of dielectric constant, specific heat and domain structure studies will be performed. Crystals will be grown at different supersaturation, growth temperatures and by varying the pH of the solution.

V. 3. Evaluation Plan

a) Transitiion Temperature

The transition temperature T_c can be determined for each sample by plotting the temperature variation of the dielectric constant using a General Radio model 1620-AP capacitance measuring assembly.

b) Domain Structure

The dielectric properties of TGS as defined by the electric permittivity ε'' and ε'' and the spontaneous polarization, P_s, depend strongly on the conditions in which the crystals are grown. Crystals grown above the Curie point at a constant temperature and the ones grown below the curie point have been found to show different domain structure.[15] Domain structure will be studied in crystals grown in ferroelectric and paraelectric range.

c) Specific Heat Measurements

The relative perfection of ferroelectric crystals can be assessed by the evaluation of the specific heat (c_p) curve in the vicinity of a phase transition. In particular, the width and displacement of C_p curve at the transition is significant. Crystalline defects and/or gross impurities produce internal electrical fields and stresses which can cause broadening of the C_p curve and a reduction of C_p at the transition.[11]

The specific heat (C_p) for a crystal grown earlier was measured with a Perkin Elmer (DSCI) differential scanning calorimeter.* The measured value of C_p = 0.3155 cal/g°C corresponds to values reported earlier. The precisiion of the instrument was not adequate to detect any changes in C_p for 0.1°C change in temperature. We are trying to improve the sensitivity of measurements.*

*These measurements were made at the Physics Department of the University of Alabama in Huntsville.

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16. ABSTRACT

The purpose of this investigation is to study the mechanism of crystal growth by solution technique. A low-temperature solution crystal growth setup is developed. Crystals of Triglycine Sulfate (TGS) are grown using this arrangement. Some additional tasks were performed toward fabrication of some experiments for future space flights.

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