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DEVELOPMENT OF NEW TECHNIQUES FOR THE
CHARACTERIZATION OF CRYSTALS AND THEIR
GROWTH SOLUTIONS

CENTER DIRECTOR'S DISCRETIONARY FUND FINAL REPORT

By Roger L. Kroes and Donald A. Reiss

Space Science Laboratory
Science and Engineering Directorate

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16. ABSTRACT The solubility measurement system and the laser scattering microscope system were designed, built, and utilized for the study of crystal growth solutions and crystal characterization measurements. With these instruments we have been able to make solubility measurements and crystal defect maps for a number of new materials. In some cases, where there have been published solubility data (i.e., TGS), we have been able to make more accurate measurements and resolve discrepancies in the published data. The design of these instruments is presented along with a description of their use and some typical data generated using them.					
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TECHNICAL MEMORANDUM

DEVELOPMENT OF NEW TECHNIQUES FOR THE CHARACTERIZATION OF CRYSTALS AND THEIR GROWTH SOLUTIONS Center Director's Discretionary Fund Final Report

INTRODUCTION

In order to carry out an exacting program in solution crystal growth along with analysis of the growth process applying mathematical models, it is necessary to be able to accurately determine the solubility curves for the materials of interest. It is also important to be able to characterize the degree of perfection of the crystals produced in order to properly optimize the growth parameters. The purpose of this project is to expand the in-house solution crystal growth and characterization capability in the Space Science Laboratory at MSFC. An investigation of the growth of triglycine sulfate (TGS) has been conducted at MSFC over the past 10 years. This work culminated in the flight of the Fluid Experiment System (FES) on Spacelab 3. Two ferroelectric crystals of TGS were successfully grown in the FES on this flight. With the conclusion of the post-flight analysis, the solution crystal growth and characterization program at MSFC is being extended by the addition of new growth and characterization systems and the investigation of new materials, with emphasis on electro-optical materials.

This paper describes two new and unique systems which were designed and developed under this program for the characterization of crystal growth solutions and for the mapping of defects in transparent solution grown crystals. These systems are the solubility measurement system and the laser scattering microscope. Both systems have been brought into operation in our laboratory and are described along with some of the experimental results they have produced.

SOLUBILITY DETERMINATION

One of the most fundamental aspects of solution crystal growth is the determination of the solubility curve. It is a plot of the equilibrium concentrations of the growth solution as a function of temperature. The equilibrium concentration at any given temperature is the concentration at which no net growth or dissolution occurs. A knowledge of the solubility

curve is essential if the researcher is to control the growth process with precision.

The solubility curve cannot normally be calculated from fundamental solution parameters and must be obtained experimentally. The data points are often fitted to a temperature dependence curve. Two equations commonly used to express this temperature dependence of concentration are:

$$c = A + BT + CT^2 + \dots \quad (1)$$

where c = concentration expressed in mass of solute per given mass of solvent, and T is temperature in degrees centigrade. A, B, C are constants and can be found in the literature for many common substances.

$$\log x = a/T + b \quad (2)$$

where x is the mole fraction of non-solvated solute in solution, T is the temperature in degree K, a and b are constants.

The latter equation has the advantage that a plot of $\log x$ versus $1/T$ gives a straight line plot.

The solubility measurement apparatus is shown in Figure 1. It consists of a temperature-controlled water bath, a test cell containing a small crystal immersed in its growth solution, and an optical system consisting of a laser with a beam expander, collimating lens, and an image screen. The bath temperature can be controlled to 0.01°C and has an operating range of 0 to 100°C . The test cell has a volume capacity of approximately 150 ml. It has been built with thin-walled glass for efficient heat transfer giving quicker response to temperature adjustments. It also contains a feed-through for a separate temperature sensor so that any differences in temperature between its interior and that of the water bath can be recorded.

Initially the concentration of the solution to be tested is made to an arbitrary or estimated value. The cell is filled with the solution, and a small crystal of the material mounted on the end of a glass rod is inserted into the cell. A thermal sensor is also inserted and sealed into the test cell. The test cell is then placed in the preheated water bath and the optical system turned on. With the crystal suspended in the solution and an arbitrary temperature set, the crystal will either be in a growth or dissolution mode.

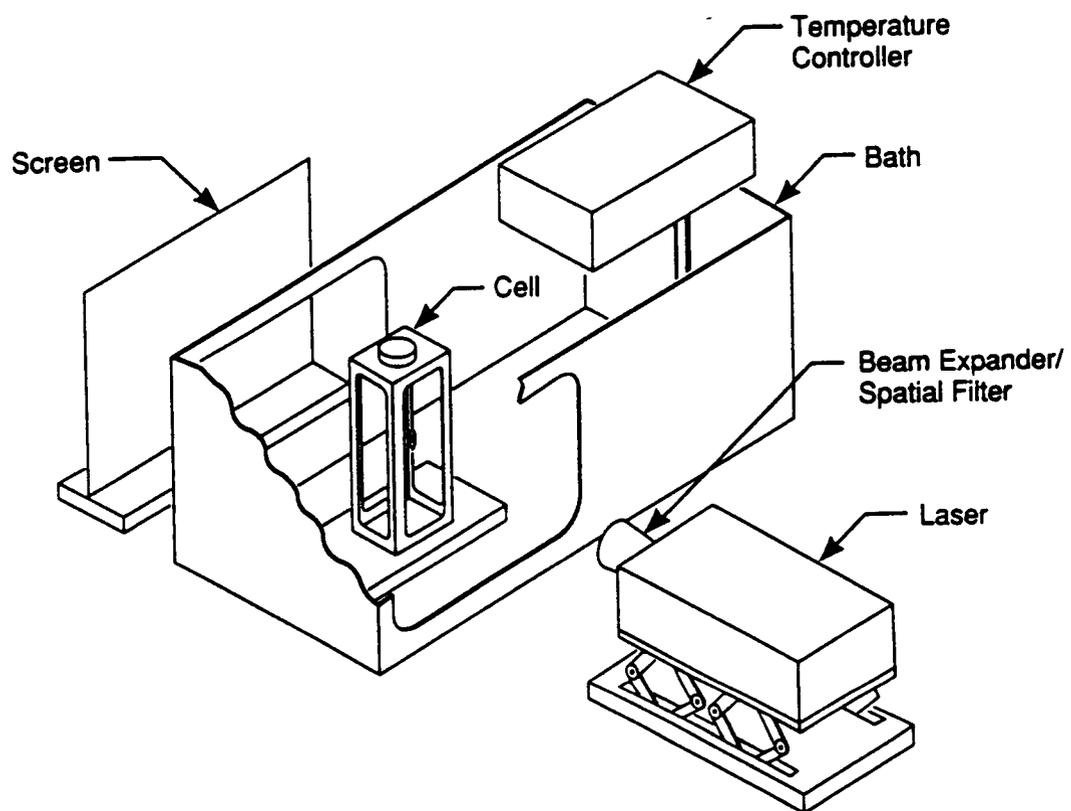


Figure 1. Solubility measurement system.

This will produce a concentration depletion or enhancement region surrounding the crystal. If the crystal is growing, this depletion region, which is less dense than the surrounding solution, will rise to the surface as a growth plume and be clearly visible in the shadowgraph image projected on the screen by the collimated laser beam. Similarly if the crystal is dissolving, a dissolution plume falling from the crystal will clearly be visible in the shadowgraph image on the screen. Then the temperature of the bath can be adjusted to slowly bring the crystal and its solution into equilibrium, and this will be confirmed by the absence of a growth or dissolution plume in the shadowgraph image.

This is a very sensitive process and gives an equilibrium temperature with a very high degree of accuracy. The concentration of the solution can be changed and the process repeated in order to get the equilibrium temperatures over an extended range of concentrations. The equilibrium temperatures are then plotted versus the corresponding solution concentrations and the solubility curve generated. Figure 2 shows the shadowgraph image of a growing crystal with its associated growth plume rising toward the surface. This apparatus has been used by the authors to generate solubility curves for a number of materials of interest and also to remeasure some previously known data in order to get increased accuracy. Figures 3 through 8 show the measured solubility curves for a number of different materials of interest. The high degree of accuracy obtained by this method has enabled the authors to control the growth process of crystals with greater precision, producing consistently better results.

LASER SCATTERING MICROSCOPE

In any crystal growth study it is imperative to be able to properly evaluate the quality of the crystals produced and to use this comparison to evaluate different growth techniques or different values for growth parameters in order to optimize a system or process. No single technique is good for all crystals. Electrical, structural, chemical, or optical properties are all measured differently. Some of these techniques require cutting, shaping, modifying, or destroying the crystal to get the desired measurement.

In solution crystal growth many crystals of interest are optically transparent, and their most prevalent growth

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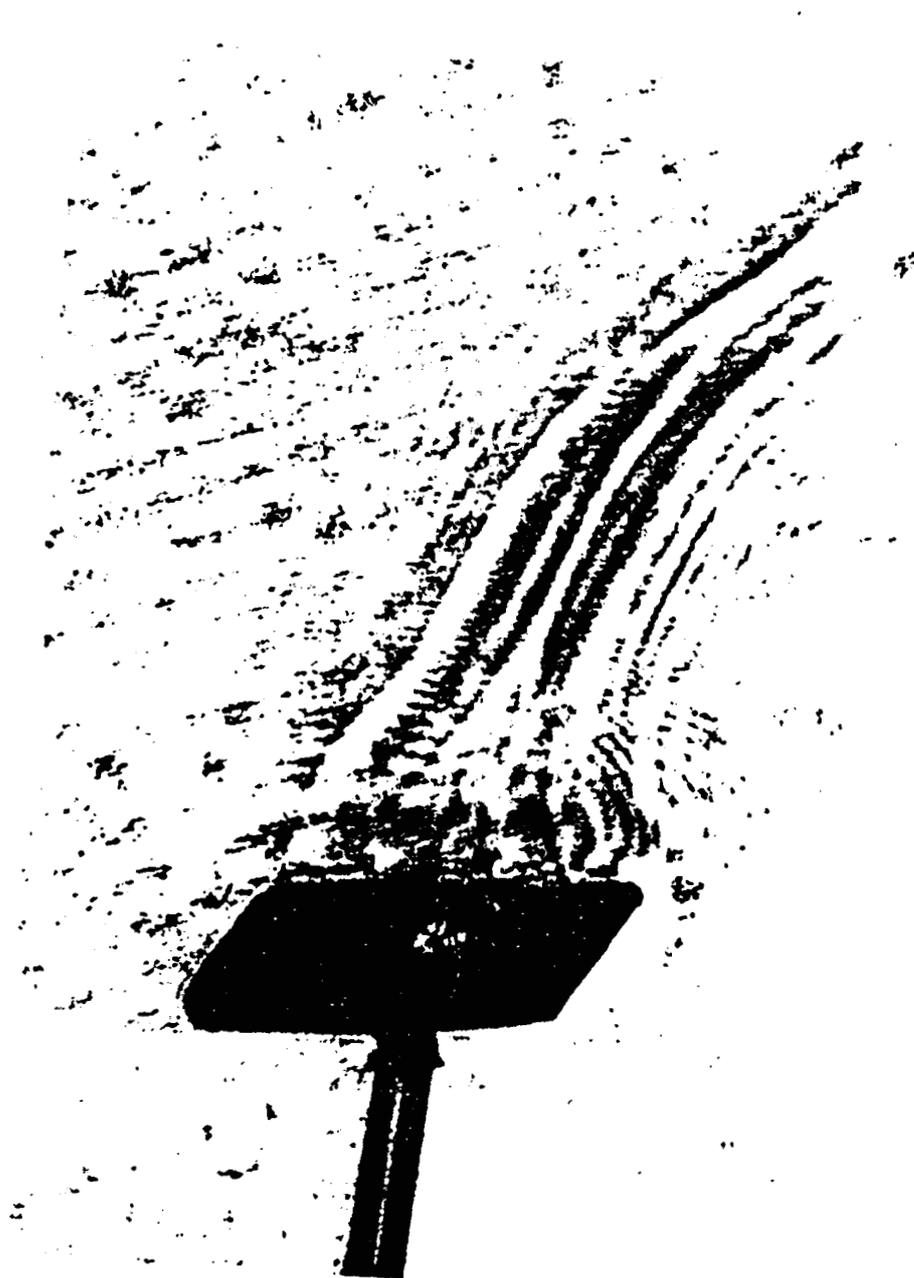


Figure 2. Shadowgraph of growing TGS crystal.

Solubility of TGS in water

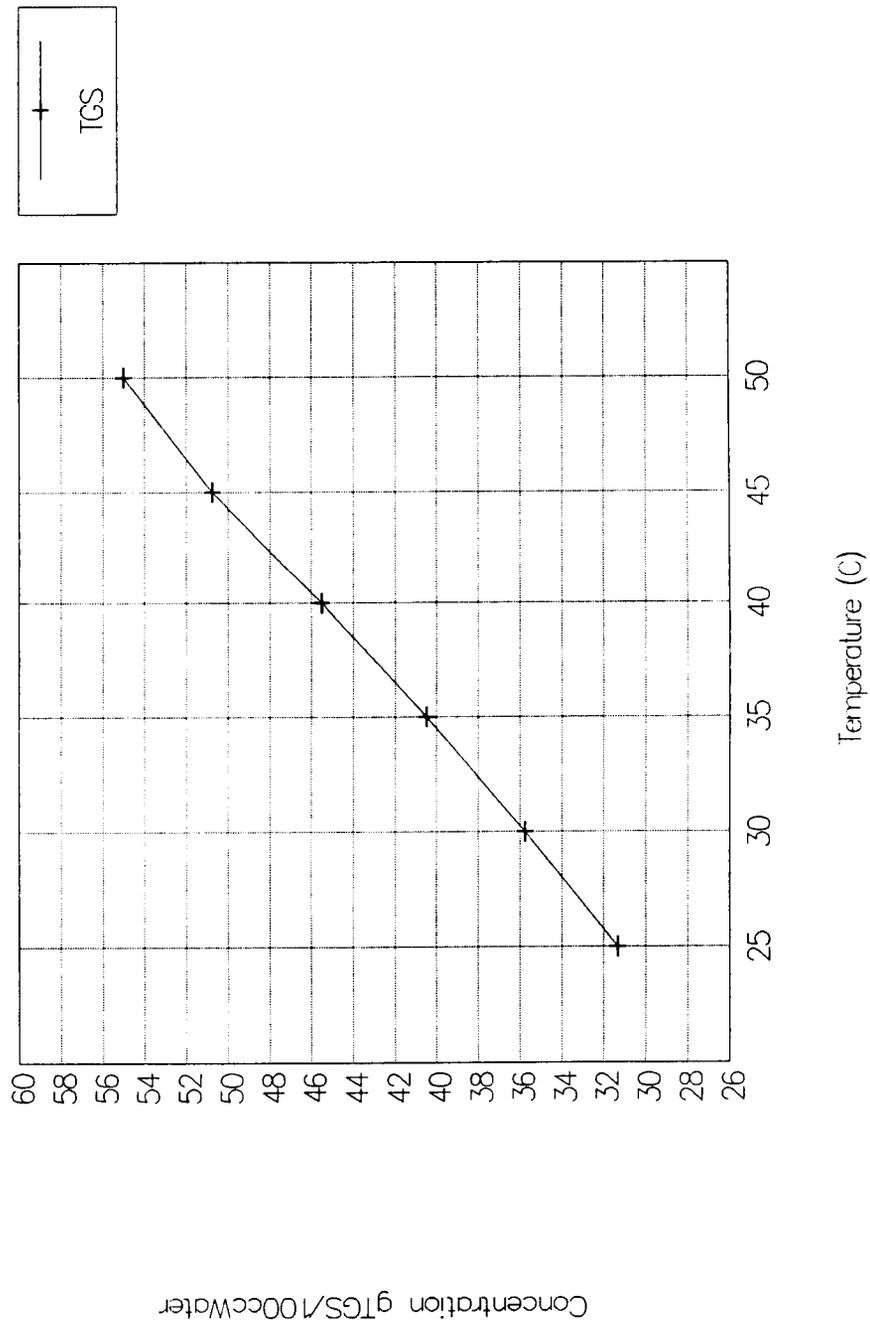


Figure 3. Solubility of TGS in water.

LAP solubility in water

L-Arginine Phosphate Monohydrate

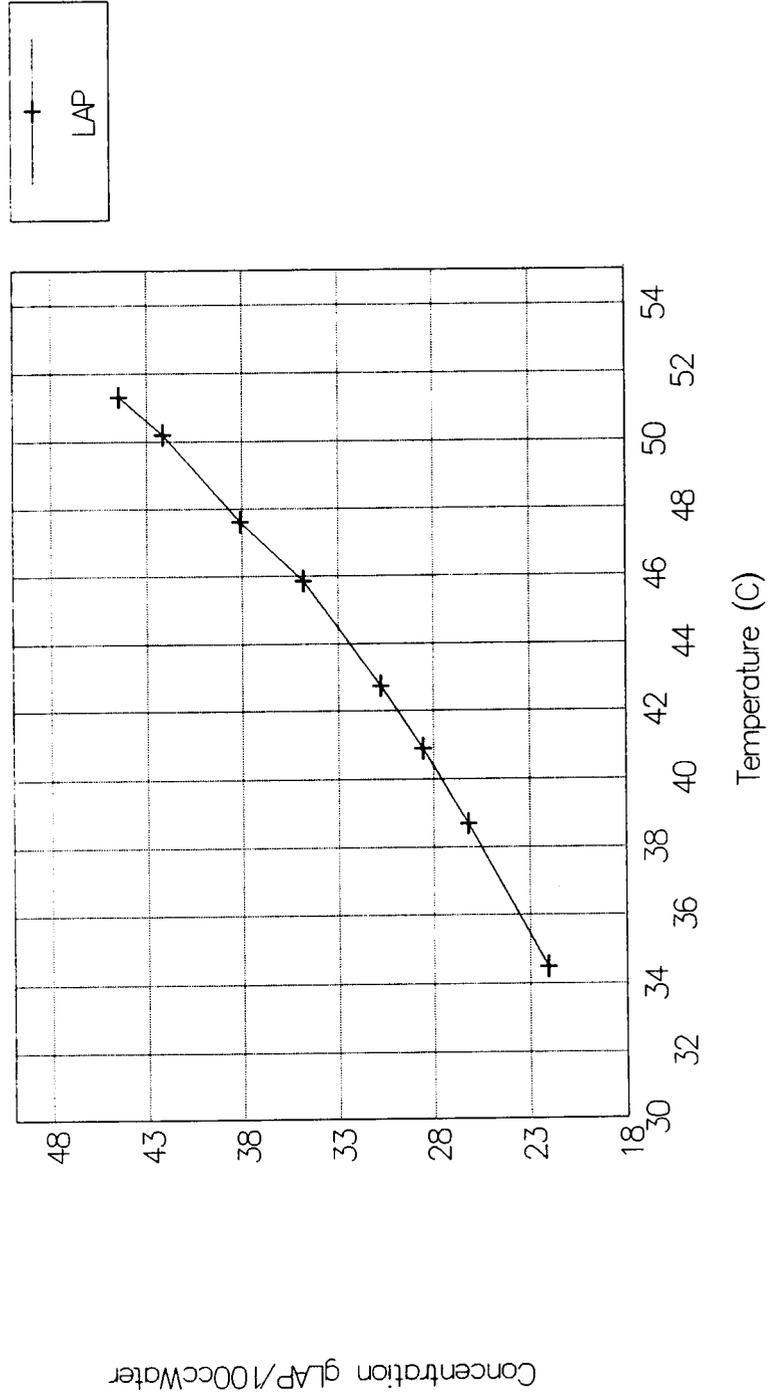


Figure 4. Solubility of LAP in water.

Urea solubility in water

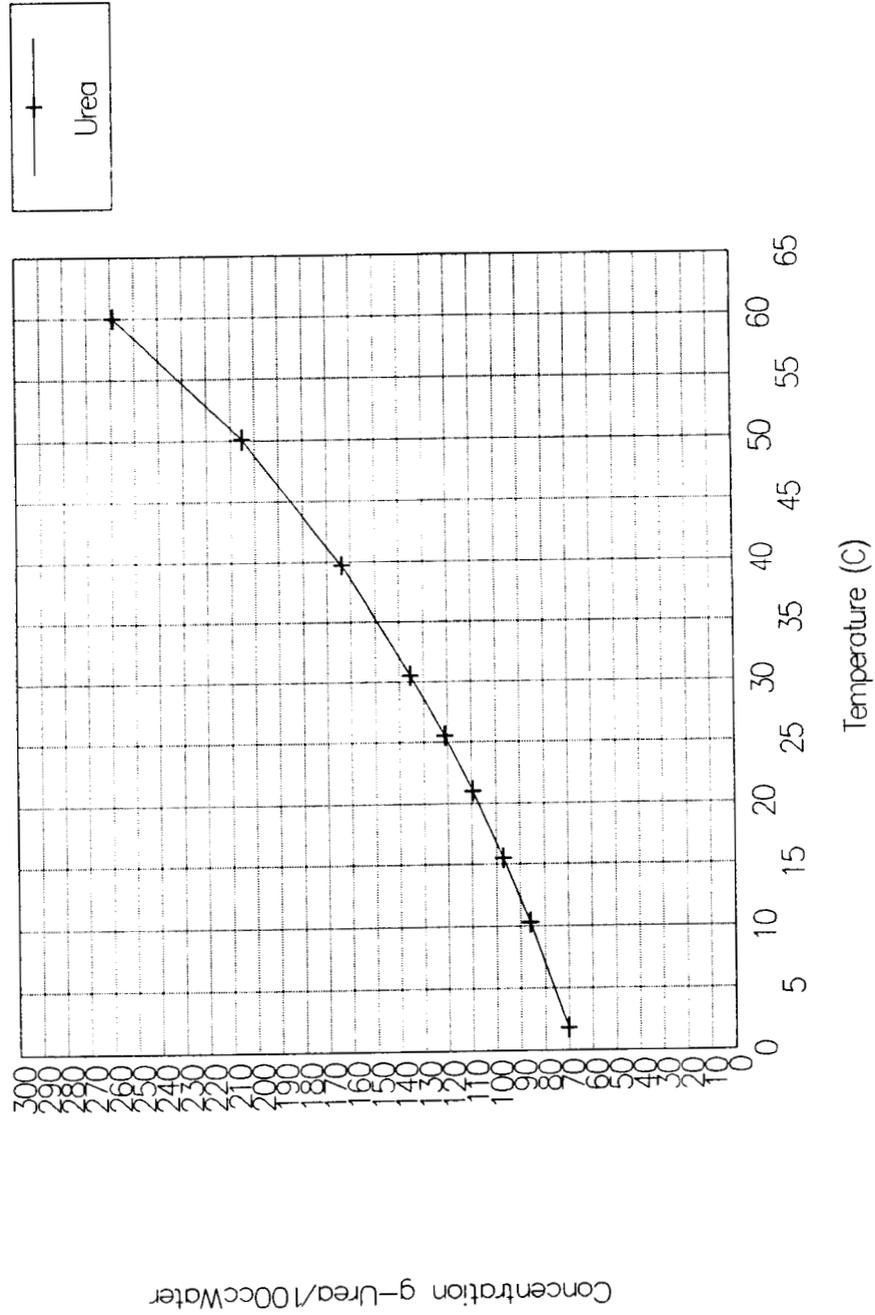


Figure 5. Solubility of urea in water.

Urea solubility in ethanol

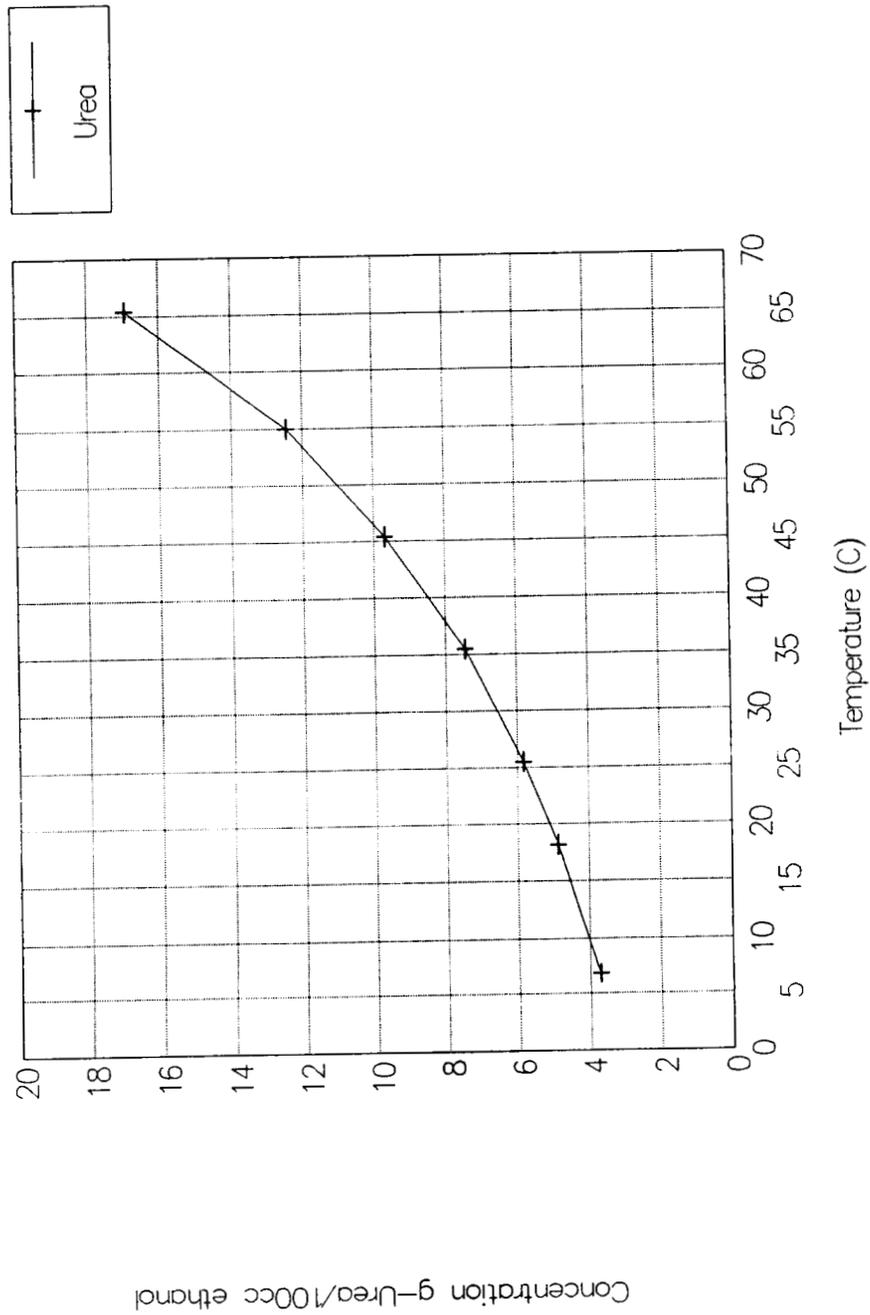


Figure 6. Solubility of urea in ethanol.

Urea solubility in isopropanol

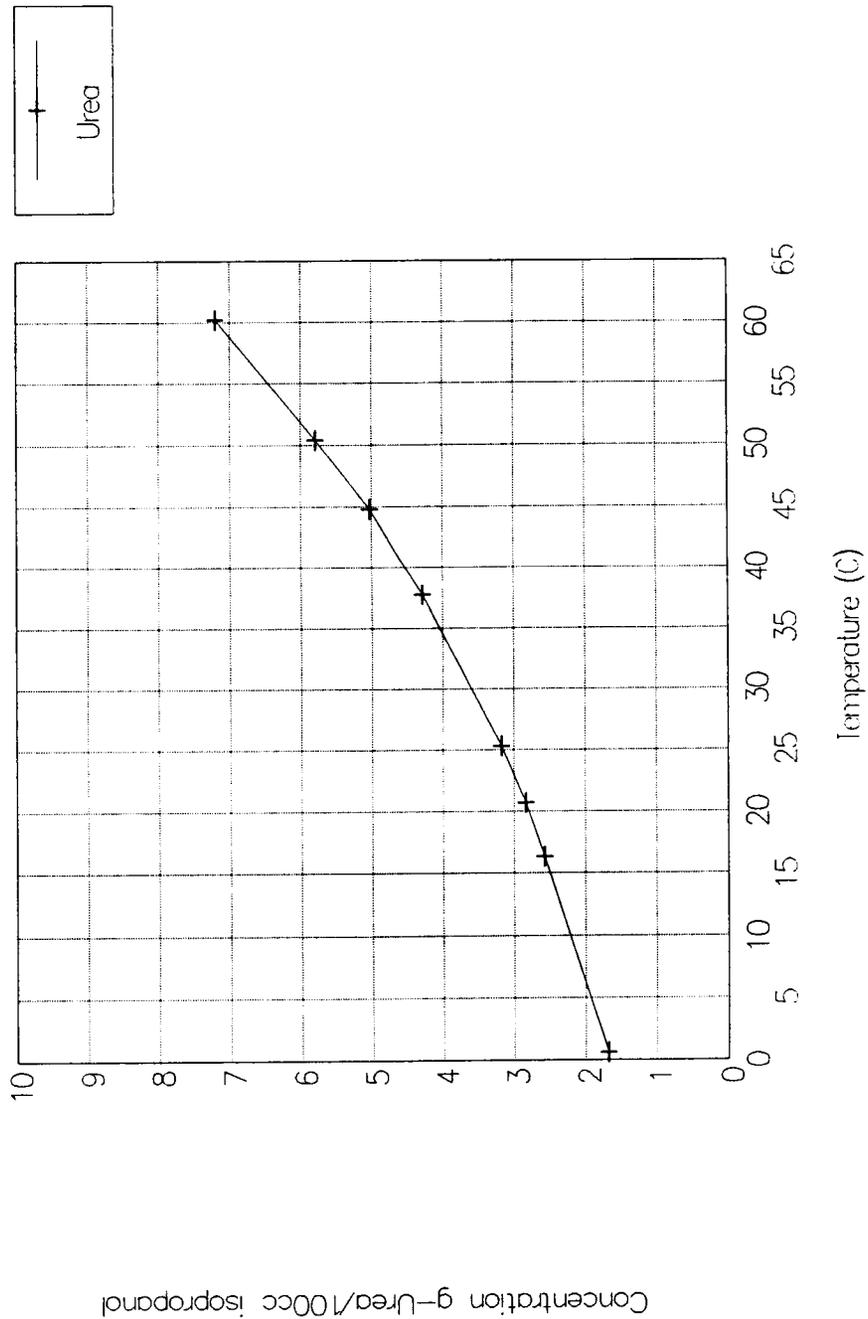


Figure 7. Solubility of urea in isopropanol.

AlK_S04 solubility in water
hydrated salt

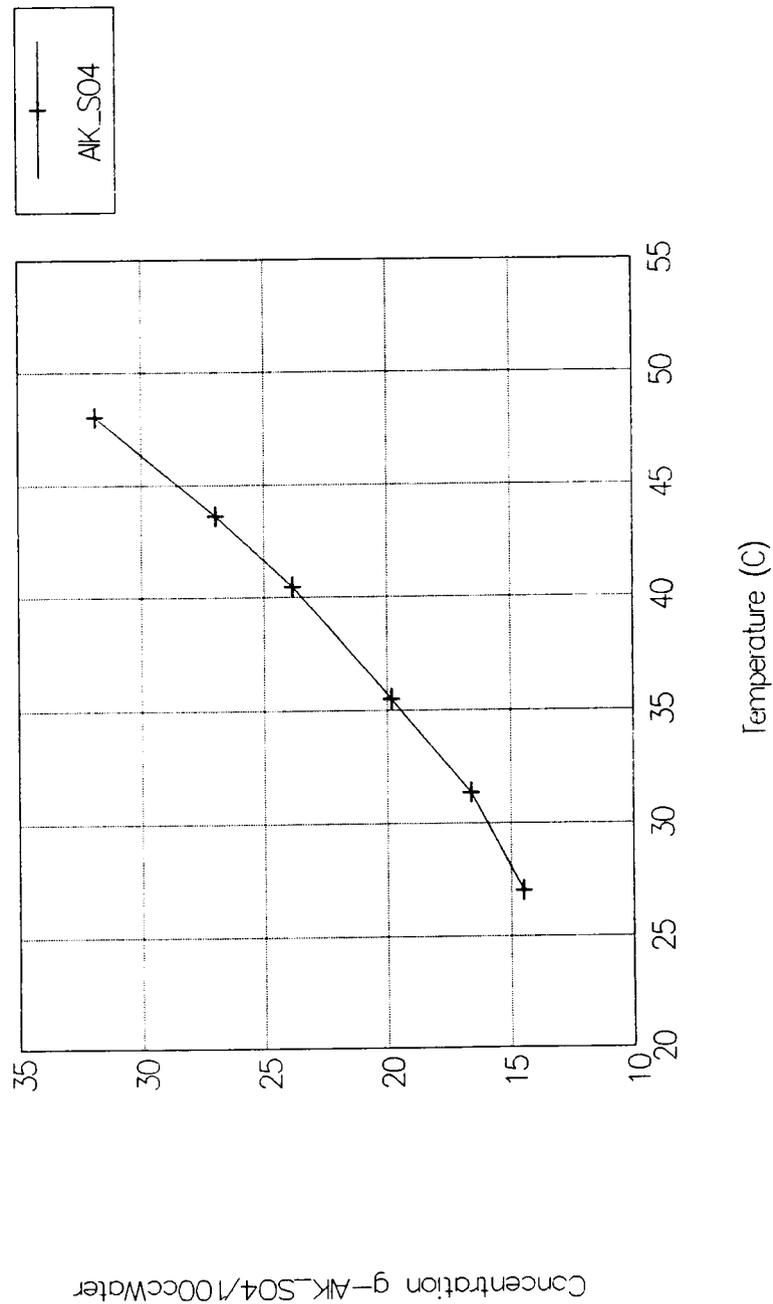


Figure 8. Solubility of Al alum in water.

defects are small voids or inclusions. In such crystals these defects act as light scattering centers. The laser scattering microscope was designed and built to detect, measure, and map in three dimensions these light scattering centers. A particular advantage to using this instrument is the fact that it is a non-destructive test procedure which leaves the crystal available for other test procedures and for fabrication for device applications. It is a particularly useful method for mapping regions in the crystal of exceptionally high quality which can be cut out of an otherwise mediocre quality crystal and used in applications requiring a high degree of uniformity and perfection. The fact that this instrument is only applicable to transparent materials is not as limiting as it might first appear since optically transparent, solution-grown crystals form a large class of the technically interesting crystals.

Figure 9 is a schematic of the laser scattering microscope. It consists of a laser optical system, sample stage, microscope, electronic detection and control system, and computer system for data acquisition and analysis. A sample crystal is mounted in the sample chamber which is then filled with a silicone fluid made to match the index of refraction of the crystal.

The presence of this index matching fluid greatly reduces light scattering from the crystal surface at the points where the laser beam enters and exits. In this way we are able to detect growth defects very close to the surface without their presence being masked by scattered light from the surface. The light incident on the crystal comes from a 10 mW helium-neon laser which after passing through a chopper is focused down to a very narrow beam before entering the crystal. Next, crystal and laser beam are aligned with respect to the microscope. Light scattered from defects in the crystal is focused by the microscope on a photo detector whose signal is fed to the lock-in amplifier which is synchronized with the chopper wheel to reduce background noise. The output of the lock-in amplifier is fed to the data acquisition system which consists of an IBM model 30 PC computer and specially designed software.

Three-dimensional maps of the defect structure in the crystal are made by stacking a series of two-dimension maps gotten by scanning a given plane in the crystal using the programmed X-Y moveable sample stage. This scanning is done in preselected steps of about 20 microns over an adjustable range along the X and Y axis of the crystal. The scanning of

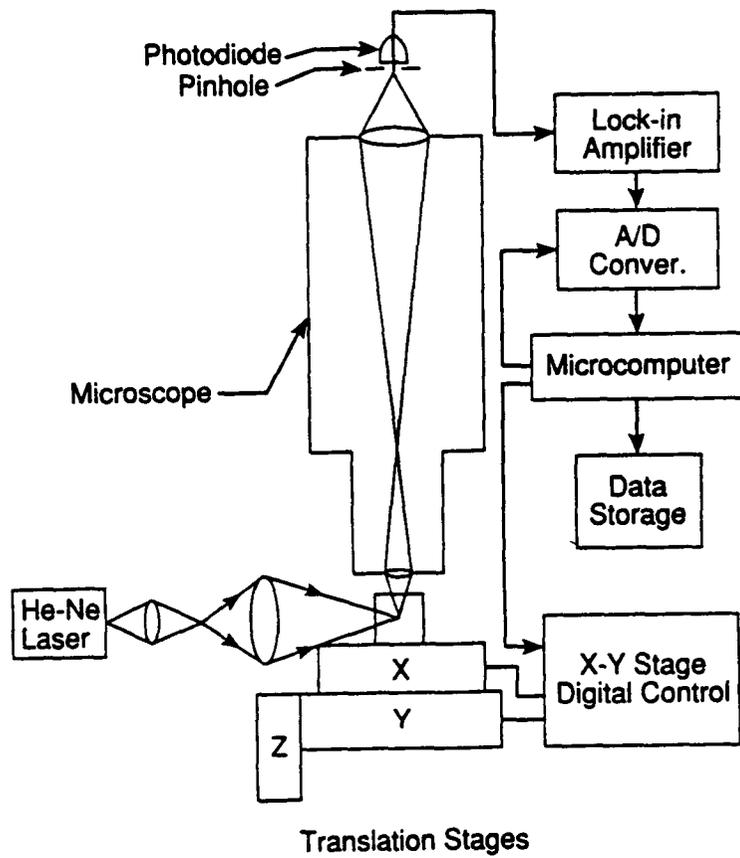


Figure 9. Schematic of laser scattering microscope.

the crystal and the measurement of scattered light intensity at each step is coordinated by the data acquisition system and directed by a software program specially written for this instrument. A graph of the data can be displayed either on the computer screen or a hard copy made on the HP plotter. Figure 10 shows a plot of the positions and intensities of scattered light from a fixed plane in a TGS crystal. The intensity of the scattered light is proportional to the defect size. In this way the laser scattering microscope produces a highly accurate mapping of relative sizes and positions of defects in solution-grown crystals.

CONCLUSION

The solubility measurement system and the laser scattering microscope have significantly increased the capabilities of our solution crystal growth effort. The increased accuracy of solubility data enables us to control crystal growth processes to a higher degree of precision and also to better compare experimental growth rate data with theory by having more accurate data. The laser scattering microscope has added to our crystal characterization capability with its unique defect mapping ability. Since this is a nondestructive procedure it leaves the crystal free for other subsequent applications. We are in the process of extending our use of this instrument to include a number of new materials of interest.

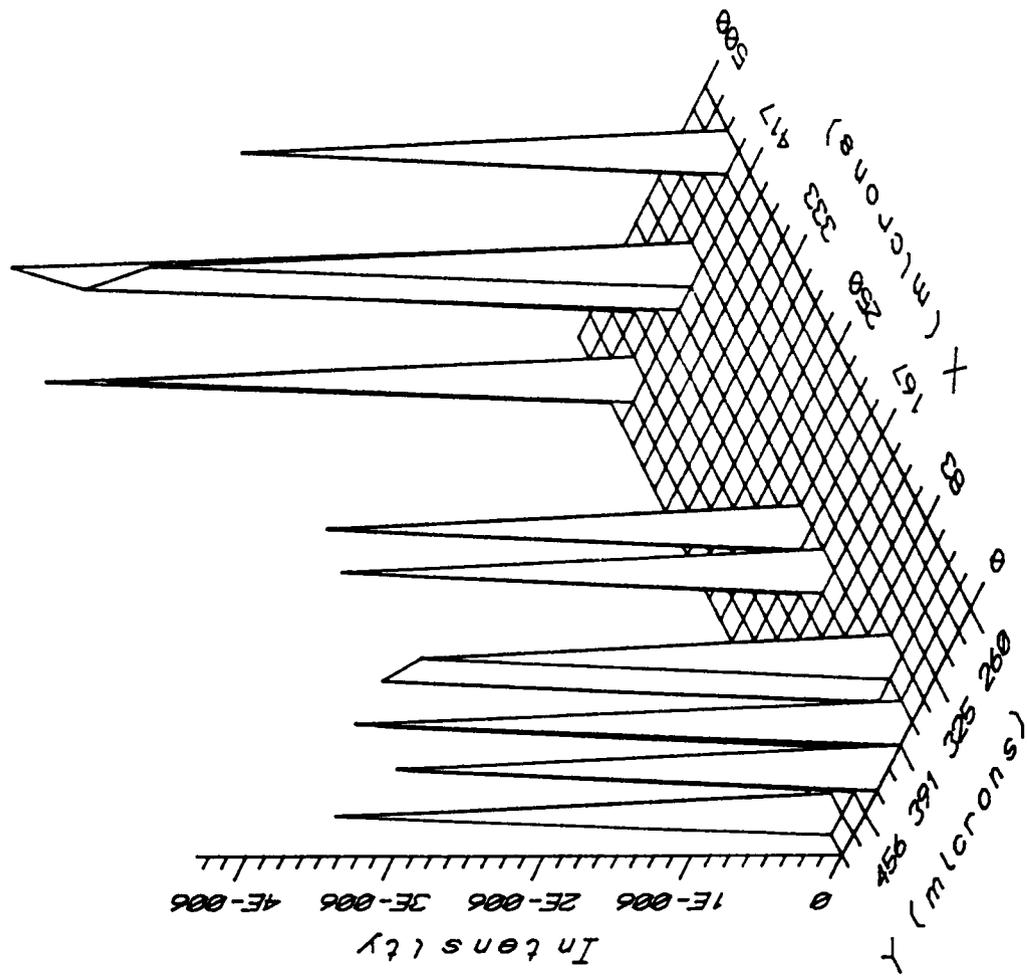


Figure 10. Light scattered from TGS crystal.

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APPROVAL

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The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.



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Space Science Laboratory