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FINAL PROJECT REPORT

"Growth of Lead Tin Telluride Crystals in Gels"

NAG-1-498

by

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(NASA-CR-181258) GROWTH OF LEAD TIN  
TELLURIDE CRYSTALS IN GELS Final Project  
Report (Longwood Coll.) 15 p Avail: NTIS  
EC A02/MF A01 CACL 20L

N87-27543

Unclas  
G3/76 0093182

31 May 1986

## I. Purpose:

Lead tin telluride (LTT) is a compound semiconductor that has properties suitable for use as an infrared detector in wide area arrays. Another similar compound semiconductor, mercury cadmium telluride (MCT), is being used commercially for that purpose. For suitable commercial utilization of such compound materials it is important that they have uniform compositions. In the growth methods such as the Bridgman one, convection exists in these materials, and this leads to compositional inhomogeneities. Because MCT must be grown using high vapor pressures of mercury, LTT is a much safer substance to use to study such flows. LTT thus finds use as a model compound to investigate the processes that occur during crystallization of such compound materials.

In an effort to suppress the convection that leads to compositional inhomogeneities, LTT has been grown in space on the Space Shuttle in October of 1985.

An alternative method to suppress convection is to grow the crystals on earth in a medium that does not allow macroscopic flows. Such a material is a gel and is the subject of this study and report.

## II. Experimental Methods:

Growing crystals in gels is a technique that has been used since the end of the last century. A review of this technique has been given in a 1970 book by H. Henisch.<sup>1</sup> The

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<sup>1</sup>Henisch, Heinz K., Crystal Growth in Gels, The Pennsylvania State University Press, University Park, Pennsylvania, USA. 1970 (#271-00104-6).

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advantage of using a gel as the growth medium for crystals is that microscopic flow is possible thus allowing crystal formation, but macroscopic, fluid flow is retarded because of the increased viscosity of the medium.

This project began with the techniques that have been described in the literature for growing crystals in gels. These methods were tested first to see how suitable they would be for LTT and second to see what modifications in materials and techniques would be needed. This section of the report describes the development of methods to be used with LTT.

There are a number of gels that would be candidates for use in this study. Even strawberry jam has been used to grow crystals, but such a gel is neither reproducible nor generally accepted by the scientific community. Three more generally accepted gels were evaluated for use in this study--gelatin, agar, and silica. The first two, gelatin and agar, were not used because they are of biological origin and subject to some compositional variations. They tend to have variable trace amounts of impurities depending upon sources

and suppliers. A more serious property is the ability of these to serve as a medium for biological growth. Although without nutrients required for growth and with lead, tin, and telluride ions present, it would be highly unlikely that bacteria would grow even on these gels. With time available only to use one gel medium, the silica gel was selected. It is a highly refined, inorganic medium that forms a loosely cross-linked polymer when it gels.

The standard methods used to prepare the silicate gels were tested.<sup>2</sup> The standard method was sensitive to

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<sup>2</sup>Henisch, ibid., p. 22.

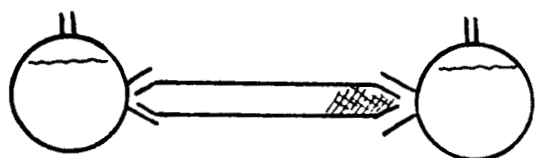
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laboratory conditions such as relative humidity and temperature. The gel that resulted did not have a reproducible gelation time, and it was cloudy. This translucent gel made it difficult to observe crystals as they formed and grew in the gels. Consequently, a method was developed to clarify the gel. This method involved the use of a cation exchange resin to replace most of the sodium ions with potassium ions. This "polishing" procedure resulted in gels that were significantly more transparent.

To make the gelation times more reproducible, it was discovered that these times were rendered more reproducible if all solutions were degassed by being prepared with boiled and cooled distilled water. The methods of clarifying the gels and using degassed water are explained in detail in a publication that resulted from this project.<sup>3</sup>

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Barber, Patrick G. and Norman R. Simpson, "A Clarified Gel  
for Crystal Growth." Journal of Crystal Growth 73  
(1985), 400-402.  
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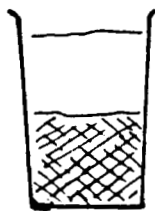
With a reproducible, clarified silica gel available for use, the geometry of crystal growth was studied next so that a suitable one could be selected. Again the classical methods were tried first. Five geometries were investigated--the double bulb, testtube, open tube, beaker, and petri dish geometries. These are illustrated in Figure 1.



a. Double Bulb



b. Testtube



c. Beaker



d. Petri Dish



e. Open tube

Figure 1: Crystal Growth Geometries

Geometries b, c, d, and e are basically the same. One of the ions subsequently used in the crystal is first incorporated into the gel. This is simply done by using a solution of the ion in place of the distilled water in the recipe for preparing the gel. The subsequent concentration is most important, so that care must be exercised in preparing the aqueous concentrations that are then diluted. These geometries did not have flexibility, but they were simple and did allow for rapid testing of several solution concentrations or conditions. This was especially true of the petri dish method, which by using disposable dishes divided into three sections, allowed three different ion concentrations in gels to be tested at one time for the extent and size of nucleation.

The geometries b, c, d, and e were thus used for preliminary scans of concentrations and conditions. Geometry a, the double bulb, was selected for actual growth conditions, since it allowed for both greater flexibility and control over growth and solution conditions. Subsequently, advantage of this was taken in developing an electrochemical procedure.

To aid in the development of the methods and to test them, use was made of a simpler and safer test crystal system. Lead sulfide crystals were used as the test system. At the time that the methods were ready to be tested the Principal Investigator was invited to spend a year working at NASA-Langley Research Center. Consequently, a student, Norman Simpson, was left at Longwood College to conduct these tests. Although the PI was only a three hour's drive away

and although communications were made by telephone and occasionally in person on weekends, it was decided not to leave a student alone to undertake research using a substance, telluride, with which he was unfamiliar. This was especially true considering the potential toxic hazards from hydrogen telluride. Consequently, the student tested the gels, geometries, and methods using lead sulfide. He had worked with sulfides before, and he was aware of the precautions that had to be taken. Using the clarified gel and mainly geometries d (Petri Dish) and e (Open Tube), he scanned series of concentrations of lead and sulfide ions observing those that gave the most suitable crystal nucleation in the gel. His results are summarized in Figure 2.

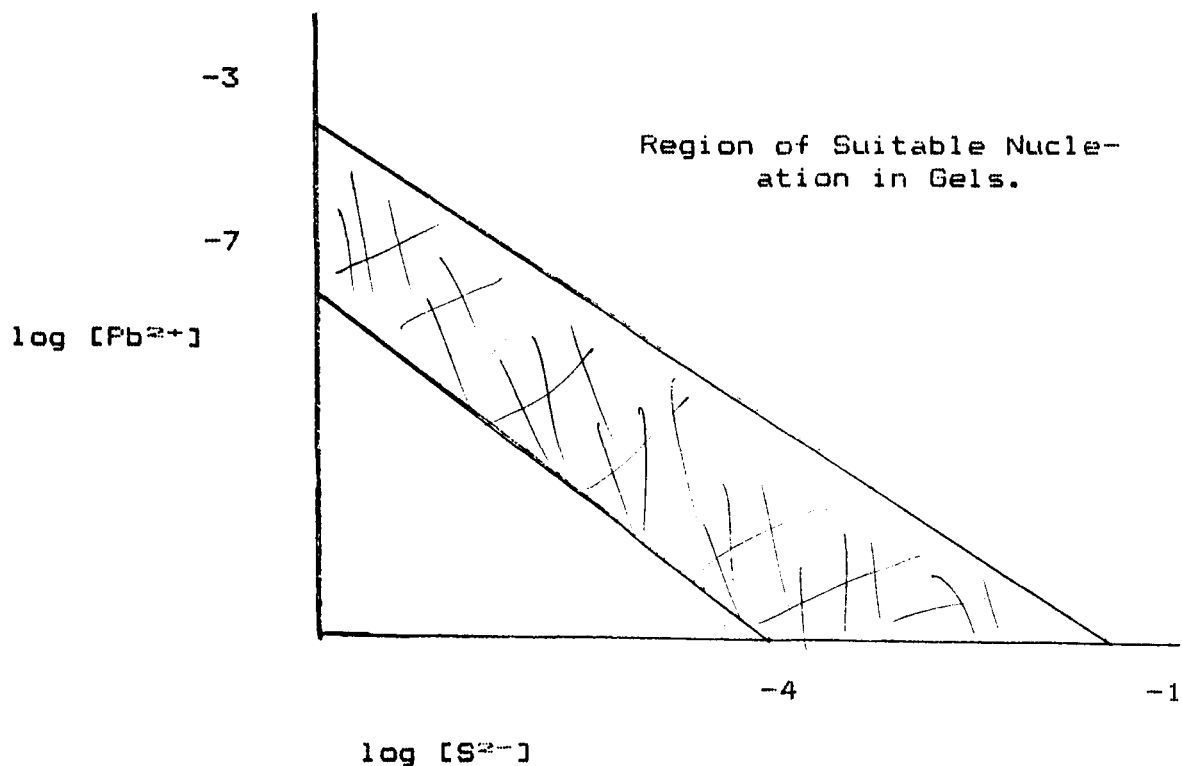


Figure 2: Lead and Sulfide Ion Concentrations Leading to Nucleation in Gels.

Upon the return of the PI, the concentration data collected from the preliminary studies using lead sulfide were used by the PI and another student, James Coleman, to develop techniques using lead telluride and geometry a (Double Bulb).

### III. Theoretical Considerations:

Because the use of gels is designed to reduce the extent of convection, the possible roles that this fluid flow could have in crystal habit formation were considered. Non-spherical particles will orient in a fluid flow and this orientation will be governed by the moments of momenta of particles. These considerations culminated in a NASA Contractor's Report #3907.

Because such considerations of orientation in fluid flows are important in other, commercially important crystal growth system, the technologically significant consequences of this orientation were summarized in a NASA Tech Brief. Specifically, the habits of the crystals of Gallium Arsenide grown in MOCVD systems may be selected by using reagents having suitable interatomic spacings and molecular momenta.



#### IV. Results:

The double bulb technique was used in two groups of experiments. Because of the difficulty of obtaining and keeping telluride ion ( $\text{Te}^{2-}$ ) in aqueous solutions in the presence of oxygen, the telluride ion was developed in situ in two ways.

The lead ion solution was made and put in bulb A of the double bulb illustrated in Figure 3. The solution

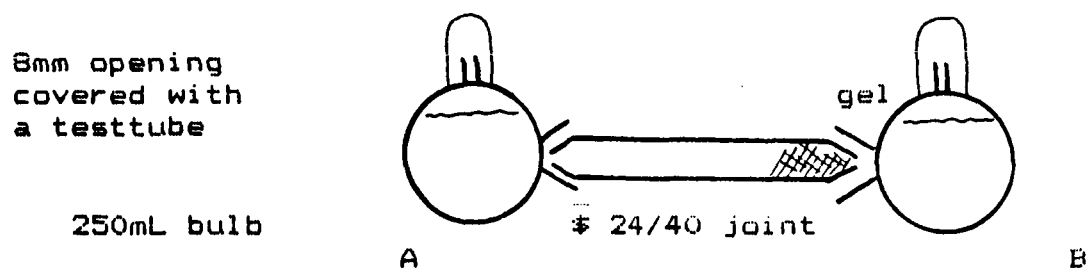


Figure 3: Details of the Double Bulb Apparatus

that would develop the telluride ion was placed in bulb B.

The first reagent used to develop telluride was sodium tellurite,  $\text{Na}_2\text{TeO}_3$ . This solution was reduced in two ways using hydrazine and sodium borohydride. The borohydride immediately reduced the telluride to a black precipitate of tellurium metal; and the hydrazine solution did the same, but it did so more slowly taking several hours. To retard this reduction process, a new method was developed to slowly release the reagents into the solutions by incorporating the reagents in gel filled tubes. When the hydrazine doped gel was squeezed out of the tube into the tellurite solution in bulb B, the solution was slowly reduced to give an orange colored solution typical of polytelluride ion.<sup>4</sup> Crystals

developed in bulb B, and analysis by x-ray fluorescence and

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\*Yost, Don M. and Horace Russel, Jr., Systematic Inorganic Chemistry Prentice-Hall, Inc., New York, 1946. p. 293.  
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powder diffraction indicated that these crystals were crystals are attached in the appendix.

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\*Analyses were done by Mr. Richard Simchik at NASA-LaRC.  
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This technique of slow-release of reagents has applications as a safer way to carry chemicals into space. Consequently, a NASA Tech Brief was submitted for this.

Even with the slow release of reagent from gel tubes, the tellurite solution would not be reduced to telluride. Consequently, an electrochemical method was developed to generate the telluride ion in situ in bulb B. The double bulb apparatus was modified as shown in Figure 4.

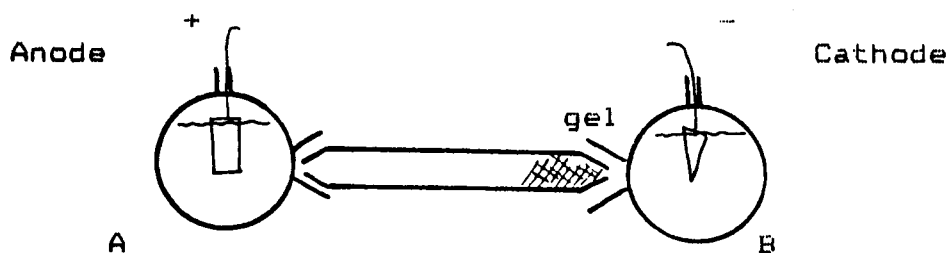
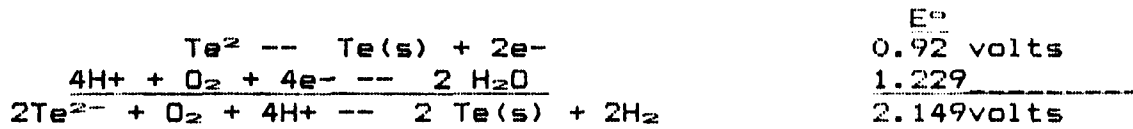


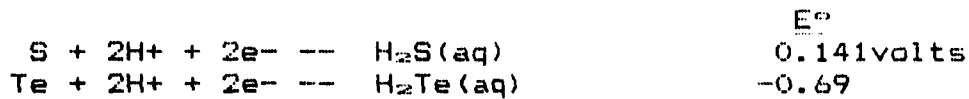
Figure 4: Double Bulb Modified for Electrochemical Production of Telluride In Situ

The electrochemical preparation of telluride ion in situ did prepare the desired ion. The oxygen in the aqueous solution and in the apparatus, however, caused the telluride

to be oxidized back up to the black tellurium metal. In the aerobic environment it was not possible to keep the tellurium as the minus-two ion in sufficient concentration to enable crystals to grow. The following thermodynamics data substantiates this conclusion:



The sulfide ion of the test solutions used to develop the methods does not suffer this tendency to react as readily with oxygen as shown by the following thermodynamic data:



These data indicate that the equilibrium favors the formation of  $\text{H}_2\text{S(aq)}$ , while in the tellurium case the metal is favored. Thus, it was not possible to develop and to maintain a sufficient telluride ion concentration to force the growth of crystals of lead telluride in the gel.

## V. Conclusion:

Improved gels and several geometries were investigated for use in growing crystals. These worked for lead sulfide test crystals, but it proved impossible to obtain and to maintain a sufficiently concentrated telluride ion solution to successfully grow lead telluride crystals. It appears as if oxygen in the solution is capable of oxidizing the telluride ion up to tellurium metal.

The method may still be successfully but only if precautions are taken to eliminate dissolved oxygen from the gels and aqueous solutions and to maintain a suitable concentration of telluride,  $\text{Te}^{2-}(\text{aq})$ .

## VI. Papers:

This project resulted in the following publications, NASA Tech Briefs, Patent Proposals, and presentations at scientific meetings:

Journal of Crystal Growth 73, 400-402 - Numerous reprint requests received mainly from East and West Europe.

NASA Rep. #3904

Tech Brief and Patent Possibility Application -  
Gel Clarification Process LAR-13476-1-CU

Tech Brief and Patent Possibility Application - Slow  
Release LAR-13607

Tech Brief and Patent Possibility Application - Gel  
support for electrochemical crystal growth  
LAR-13608

Tech Brief and Patent Possibility Application -  
Pre-crystalline aggregates for GaAs and other  
substances LAR-13606

**Presentations:**

1. MRS (Europe), Strasbourg, FR, May 1985
2. American Chemical Society, National Meeting, NYC, March 1986

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Appendix 1

Crystals of tellurium dioxide grown in this project.



86-1573  
Dull "B" Te  
50X



86-1573  
Dull "B" Te  
25X  
2.3/10

## Appendix 2

Undergraduate students at Longwood College who have worked on this Project while supported by NASA:

Dawn Adams - still an undergraduate  
James Coleman - 1986 graduate  
Judy Phillips - U. of Florida graduate school  
Norman Simpson - employee NIH, Washington, D.C.