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INVESTIGATION OF THE GROWTH OF
OPTICAL CRYSTALS

FINAL REPORT

SOLID STATE MATERIALS CORP.

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INVESTIGATION OF THE GROWTH OF OPTICAL CRYSTALS

FINAL REPORT

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I. INTRODUCTION

The experimental work performed under this contract was aimed at developing techniques capable of growing optical quality crystals for solid state LASER applications. The scope of this program was confined to the growth of doped crystals, and in particular to Al_2O_3, CaF_2, BaF_2, $PbMoO_4$, and $CaWO_4$. A lack of evaluation data hampered efforts to evolve improved growth procedures throughout the program. To partially remedy this situation, data obtained on similar crystals grown under Company sponsored programs are included in an attempt to point the direction of future programs.

II. CRYSTAL GROWTH

The methods employed for each class of material are described below. As most of the effort was confined to the growth of ruby, it will be discussed first.

A. RUBY GROWTH

The Verneuil method was used exclusively for the growth of chromium doped sapphire (ruby). The equipment used throughout the program was provided by the Air Force. Certain modifications in the equipment, or procedures, were found desirable and are described in the following paragraphs.

Powders were initially prepared by calcining $AlNH_4(SO_4)_2 \cdot 12H_2O$ and the desired fraction of $Cr_2(SO_4)_3 \cdot 18H_2O$ for 2 hours at 1000°C. Boules prepared from such powder frequently contain bubbles. For this reason the calcining cycle was changed to 3 hours at 1050°C (temperatures above 1050°C produce some sintering with an adverse effect upon the particle size and shape distributions). This treatment was found to reproducibly yield clear, void-free boules.

The following modifications were made to the Verneuil apparatus during the course of the program.

MODIFICATION	RESULT
1. Eliminate taper on the lower end of the outer sleeve.	Broadened flame and improved the temperature control.
2. Doubled the cross sectional area of the hydrogen nozzle (increased the number of 1/16 inch diameter jets from 6 to 12).	Improved the radial temperature distribution in the furnace.
3. Designed a special tool to provide a smooth and constant inner nozzle.	Eliminated powder hang-ups in the nozzle.
4. Changed the design of the alumina blocks, both to improve the thermal lagging and increase the overall length.	Allowed the length of the boule to be increased from 1 7/8 to 3 1/4 inches.
5. Employed standard size seed rods in order to use alumina tubing as the seed holder.	Greatly simplified the alignment problem and eliminated the need for frequent machining of inconel seed holders.

With these modifications, a total of 125 boules were prepared containing between 0.03 and 20.0 mole per cent Cr_2O_3 in the feed powder. Most of these crystals were grown on 60° seeds, although some 0 and 90 degree seeds were employed. Boules 2 1/4" x 1/2" diameter were considered satisfactory. A complete description of the crystal compositions and growth procedures is given in the laboratory notebooks submitted to the Contract Monitor.

All of the crystals were shipped to the Linde Division of Union Carbide for a strain relieving anneal. Since the completion of the contract Solid State Materials Corp. has installed a gas fired annealing furnace for Al_2O_3 crystals.

One of the objects of this program was to provide information on the loss of chromium during the growth process. After the program was well underway it became evident from work done at other laboratories that rubies grown in either the 0 or 90 degree orientations were superior as optical masers, and in fact the 90 degree orientation is to be preferred. This is a result of anisotropy in both the absorption and emission of the chromium ion in the sapphire host. This phenomenon has been reviewed by S. J. Sage (Appl. Optics, 1, 173, 1962).

As the segregation coefficient for chromium in Al_2O_3 may also be anisotropic it is advisable to check a few compositions of 90 degree crystals with the data now available on 60 degree crystals. Also segregation pipes have been observed in 60 degree crystals which may be related to growth rate. The existance of such defects in 90 degree crystals should be investigated.

B. <u>FLUORIDES</u>

Samples of both CaF_2 and BaF_2 were grown in a resistance heated, inert atmosphere furnace. Both samarium and uranium dopings were made. The samarium was added to the charge as Sm_2O_3 and the uranium as U_3O_8. The latter oxide was chosen because of its ease of preparation from the various uranyl compounds available which were deemed unsatisfactory because of the oxygen containing decomposition products.

By carefully purging the furnace chamber, optically clear, doped crystals could be grown. Although the barium compound was more reactive, both BaF_2 and CaF_2 would become opaque on cooling if any trace of oxygen was present in the system. Higher oxygen concentrations would cause a slag to form on the surface of the melt which prevented the growth of any single crystals.

On the basis of alpha counting experiments and visual inspection, it was found that the normal segregation of uranium in CaF_2 could be overcome by employing a floating crucible, similar to that shown in Figure 1. By placing five-sevenths of the U_3O_8 in the float uniform crystals were obtained. In order to obtain trivalent uranium doping, it was necessary to place the U_3O_8 directly on the graphite crucible. The graphite apparently reduced a considerable fraction of the $U^{5.3+}$ to U^{3+}. If the U_3O_8 were placed on the CaF_2 so that it could not come in direct contact with the crucible, the grown crystal would be a greenish-yellow color, very similar to uranium glass.

Although none of the fluorides grown on this program were annealed, it was found on similar crystals grown at SSM that heating to 1200°C for 18 hours would completely remove the residual stresses. Crystals so annealed can be readily fabricated and show no evidence of a strain pattern when observed between crossed polarizers.

Examination of thin sections of $CaF_2(U^{3+})$ crystals showed them to be very prone to contain precipitate particles. It is quite possible that the large observed variations in threshold power for $CaF_2(U^{3+})$ lasers is due to scatter as well as the type of charge compensation. This work done at SSM was reported by J. B. Schroeder at the Electrochemical Society Meeting in Los Angeles (March 1962).

C. SCHEELITE-STRUCTURED COMPOUNDS

Small crystals of $PbMoO_4$ and $CaWO_4$ were grown from a noble metal crucible heated by direct coupling to an rf generator. Very serious difficulties were encountered because no temperature control equipment was available for the rf generator.

The following remarks are therefore based upon the experience gained at SSM on a controlled rf generator. The apparatus employed at SSM in shown in Figure 2.

Both the molybdates and tungstates are somewhat prone to decompose at their melting points. For this reason a slight excess of MoO_3 (or WO_3) must be added to the melt. With this precaution uniformly doped crystals, free of scatter centers may be grown by pulling up to half the melt at less than 1/4 inch/hour (see Figure 3). The Scheelite-structured compounds, like the fluorides, are highly strained and frangible in the as-grown condition. Annealing for 18 hours at 1300°C relieves the residual strains. Low threshold Maser action has been consistently observed in confocal rods fabricated from such crystals.

Since the termination of the experimental work on $CaWO_4$ and related compounds, SSM has perfected production techniques which are capable of producing rods up to 6" x 3/8" diameter containing charge compensated rare earth dopings. The loss through scattering is on the order of 0.6%/cm and the threshold is between 5 and 12 joules depending upon the pumping geometry. With such crystals commercially available, future development should be aimed at producing larger $CaWO_4$ crystals for high power applications or completely different materials.

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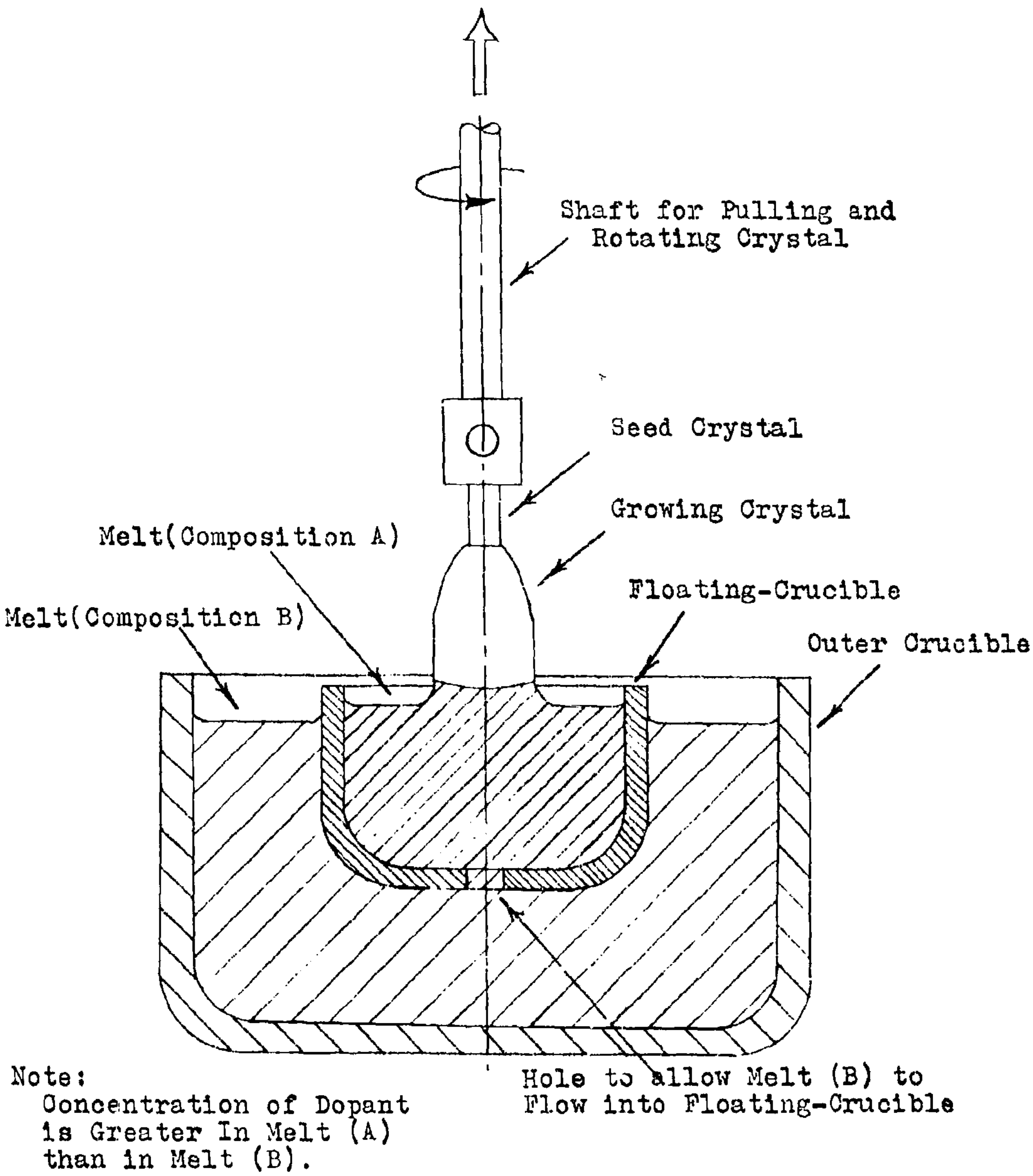
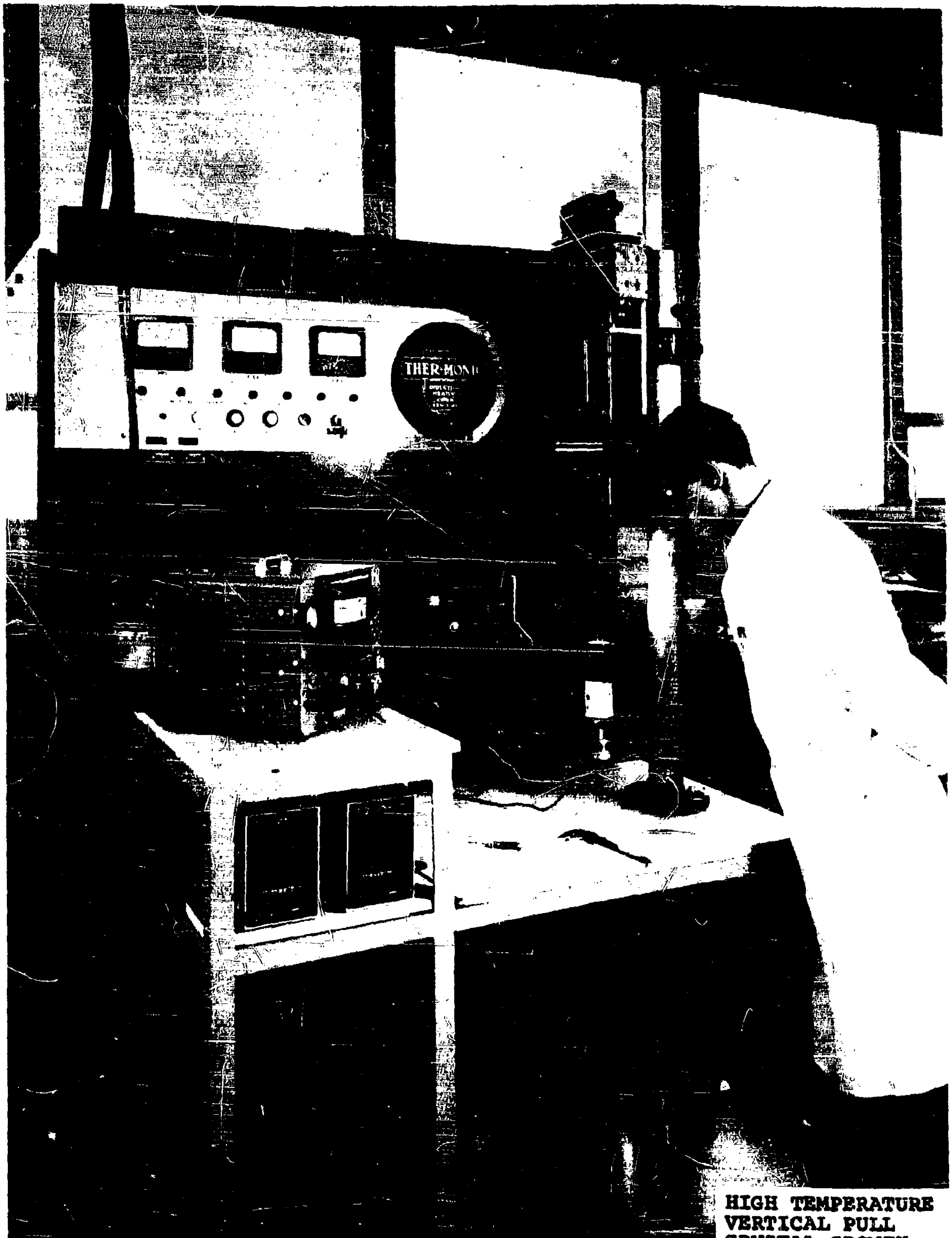
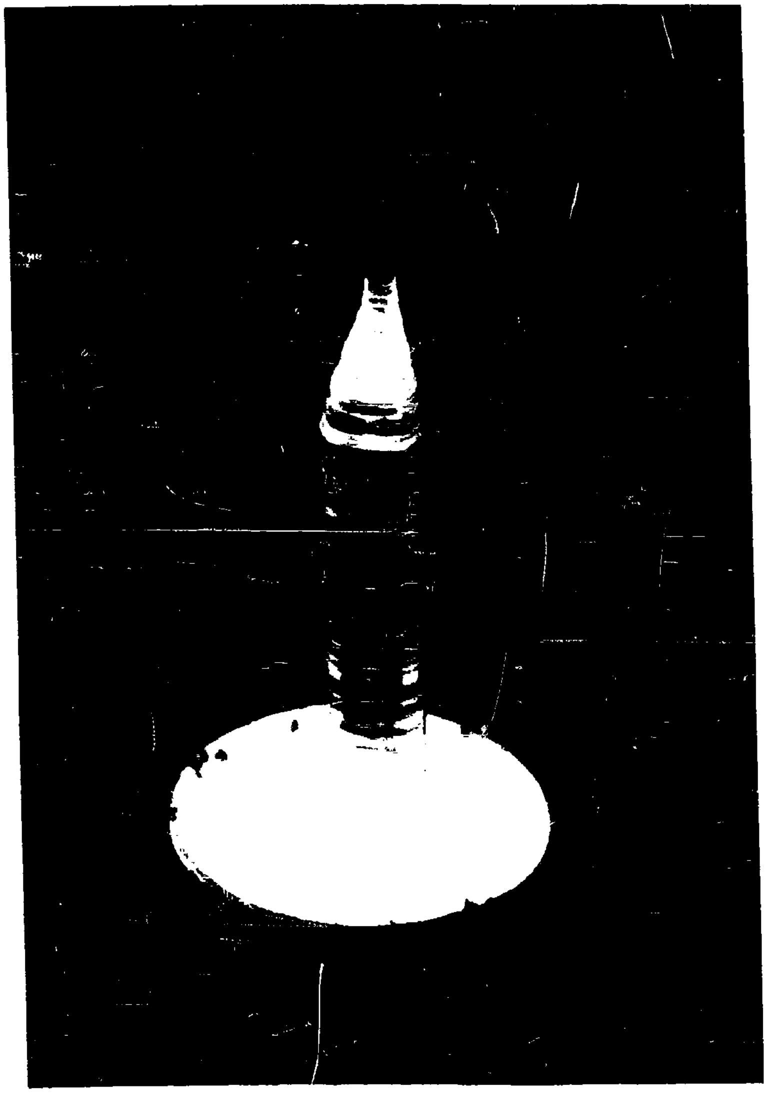


Schematic Cross-Section of Floating-Crucible Modification used with the Vertical-Pull Technique



HIGH TEMPERATURE
VERTICAL PULL
CRYSTAL GROWTH



A SINGLE CRYSTAL OF CALCIUM TUNGSTATE
BEING PULLED FROM A MELT
(ACTUAL SIZE)

UNCLASSIFIED

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