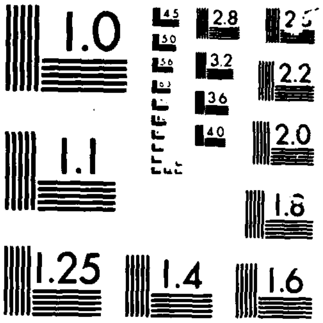
AD-A167 613 INVESTIGATION OF SINGLE CRYSTAL SILICATES FOR BLUE 1/1
TUNABLE LASERS(U) LITTON SYSTEMS INC MORRIS PLAINS NJ
AIRTRON DIV R F BELT ET AL. JAN 86 N00014-85-C-0823
UNCLASSIFIED F/G 20/5 NL



MICROCOPY CHART

Unclassified

(12)

# INVESTIGATION OF SINGLE CRYSTAL SILICATES FOR BLUE TUNABLE LASERS

by

R. F. Belt and J. A. Catalano

Quarterly Report No. 1
September 1, 1985 - November 30, 1985
Contract No. N00014-85-C-0823

Airtron Division
Litton Industries, Inc.
200 E. Hanover Avenue
Morris Plains, N. J. 07950

January, 1986

## NOTICES

Approved for public release; distribution unlimited. This research was sponsored by the Office of Naval Research, Department of the Navy, Physics Program, 800 North Quincy Street, Arlington, Virginia 22217. Qualified requesters may obtain copies of this report from Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314. Destroy this report if no longer needed; do not return to sender.

NOTICES

The findings in this report are not to be construed as an official Department of the Navy position unless designated by other authorized documents.

The citation of trade names or names of manufacturers in this report should not be taken as official Government endorsement or approval of commercial products or services referenced herein.

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder of any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

| | | |
|---|---|---|
| **REPORT DOCUMENTATION PAGE** | | READ INSTRUCTIONS<br>BEFORE COMPLETING FORM |
| 1. REPORT NUMBER | 2. GOVT ACCESSION NO.<br>ADA167613 | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle)<br>Investigation of single crystal silicates for blue tunable lasers | | 5. TYPE OF REPORT & PERIOD COVERED<br>Quarterly No. 1<br>Sept. 1, 1985-Nov. 30, 1985 |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s)<br>R.F. Belt & J.A. Catalano | | 8. CONTRACT OR GRANT NUMBER(s)<br>N00014-85-C-0823 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Airtron Division, Litton Industries<br>200 E. Hanover Ave.<br>Morris Plains, NJ 07950 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS<br>Project 410<br>NR 392-053/4-19-85 |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>Defense Contract Administration Services<br>240 Route 22<br>Springfield, NJ 07081 | | 12. REPORT DATE<br>January, 1986 |
| | | 13. NUMBER OF PAGES<br>iii + 27 |
| 14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)<br>Office of Naval Research<br>Department of the Navy<br>800 No. Quincy Street<br>Arlington, Virginia 22217 | | 15. SECURITY CLASS. (of this report)<br>UNCLASSIFIED |
| | | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release: distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NONE

18. SUPPLEMENTARY NOTES

NONE

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Tunable lasers
Rare earth silicates
Czochralski growth
Laser crystals

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The single crystal growth of rare earth silicates was investigated for the purpose of tunable laser hosts. Silicates of the type $R_2SiO_5$, where R = La, Gd, Y, Lu, were prepared from stoichiometric melts and doped with $Ce^{3+}$ activators. Seed crystals were obtained from crystallized melt sections or by growth on an iridium wire. These seeds were utilized in standard Czochralski type growth to obtain larger single crystals.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Cathodoluminescence experiments on both powders and single crystals showed wavelength shifts with different rare earth ions. The Gd, Y, and mixed crystals of Gd-Y silicates gave good bright emission with $Ce^{3+}$. The emission is broad band and covers the wavelength range of 370-525nm. The peak emission can be centered near 450-460 by other compositions. Larger single crystals for laser hosts are under development.

# TABLE OF CONTENTS

# LIST OF FIGURES AND TABLES

# FOREWORD

This quarterly report describes research efforts on the preparation of single crystal rare earth and other silicate laser hosts. All crystals were doped with $Ce^{3+}$ in an attempt to obtain blue or blue-green lasers which may operate near 450-480nm. The report relates work started in the period of September 1, 1985 up to November 30, 1985. All work was done under a program of Dr. Van O. Nicolai of the Office of Naval Research. It is now continuing under the administrative supervision of Dr. Robert Junker of the Office of Naval Research and technical monitoring of Dr. Leon Esterowitz at the Naval Research Laboratory.

All physical preparations were completed in the laboratories of Airtron Division of Litton Industries, 200 E. Hanover Avenue, Morris Plains, New Jersey, 07950. The program was directed by Dr. Roger F. Belt and Mr. Joseph Catalano served as Senior Staff Scientist. Mr. Gregory Foundos was the technician. Optical tests were performed at the Naval Research Laboratory through the courtesy of Dr. Leon Esterowitz. The X-ray patterns were run by Mr. John Yorston. Cathoduluminescent tests were performed by Dr. John Ings. The report was prepared by Dr. Roger Belt and Mr. Joseph Catalano. It was released for publication in February 1986.

## 1.0 Introduction

It has been a long term goal of the Navy to obtain high efficiency blue or blue-green solid state lasers. One of many approaches for tunable systems involves the luminescent 5d - 4f transitions of $Ce^{3+}$. A major problem has been to find suitable single crystal hosts which have the following features.

1. Chemical and physical properties similar to other good hosts, e.g. $Al_2O_3$, $Y_3Al_5O_{12}$, $YLiF_4$.
2. Ability to incorporate $Ce^{3+}$, $Pr^{3+}$, or other rare earth ions substitutionally.
3. A high band gap of about 6 ev to prevent excited state absorption of $Ce^{3+}$.
4. High radiative lifetime and fluorescent yield of $Ce^{3+}$.
5. The presence of $Ce^{3+}$ in a suitable site and symmetry to luminesce at 450-500nm.

Most of the previous work under this program (1) has been concerned with the perovskite structured host materials such as $LaAlO_3$. This compound is a distorted cubic crystal which leads to a hexagonal or orthorhombic structure. Efforts to obtain the stable cubic form of the crystal have been largely negative. The crystal of pure $LaAlO_3$ gives fluorescence with $Ce^{3+}$ but the presence of twins and a phase transformation prevents good laser crystals from being produced. So far no single high quality crystals of cubic perovskites have been grown. Most of the difficulties are associated with phase behavior, melting points greater than 2000°C, and presence of inclusions or twins. During the course of our work, a few runs of polycrystalline $Gd_2SiO_5$ doped with $Ce^{3+}$ were produced for trial fluorescent experiments. This material showed some promise for ultraviolet excited emission and gave a broad band which peaked around 430-470nm. Since $Gd_2SiO_5$ and other rare earth silicates show some promise for shifting the emission with $Ce^{3+}$ doping and can be grown as single crystals, this appears to be a fortunate start for a blue-green laser. The thrust of our research effort was concerned with silicates of the type $R_2SiO_5$ where R= any rare earth.

The rare earth silicates are interesting laser hosts which exhibit nearly all of the features of doping, mechanical properties, low cost, congruently melting behavior, and apparently a completely isomorphous structure from La to Lu. A description of various compounds and structures in the $R_2O_3$-$SiO_2$ systems is given in a general reference.(2) The main compounds are 1:1 $R_2SiO_5$, 2:3 $R_4Si_3O_{12}$ and 1:2 $R_2Si_2O_7$. A typical phase diagram(3) is given in Figure 1; this figure is for $Gd_2O_3$-$SiO_2$ but all other rare earths are nearly identical. It is a general feature that only the 1:1 compounds of type $R_2SiO_5$ are all congruently melting with melting points in the range of 1900-2000°C. The remaining 1:2 or 2:3 type silicates are incongruently melting and special procedures must be used to obtain single crystals. Thus it appears that only the 1:1 composition may be grown large enough to yield traditional laser rods of 2-10cm length.

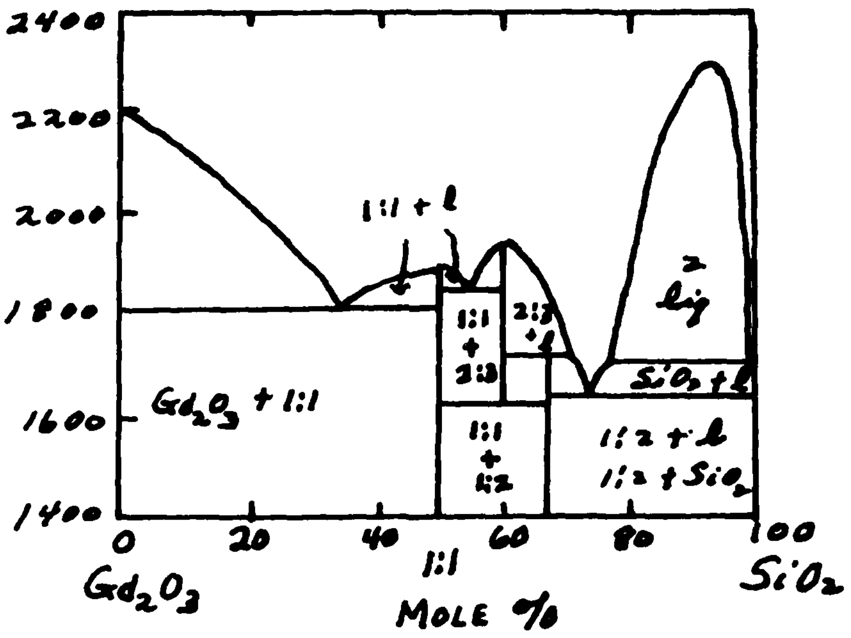


Figure 1   System $Gd_2O_3$-$SiO_2$. Oxide ratios of compounds are given as $Gd_2O_3$:$SiO_2$. (Ref. 3)

The few preliminary studies of rare earth silicate growth were all performed by the flux method.(4-8) This method utilizes fluxes such as $Bi_2O_3$, $Li_2O$-$MoO_3$, KF, PbO-$PbF_3$, or combinations of the preceding to grow a particular composition of silicate. The crystals grown from these fluxes were of mm size and useful for X-ray or other structural studies. In all cases the absorption or emission spectra were not recorded. Neither were there any laser studies performed because of the size of the crystals. No further efforts were described to obtain single crystals for any purpose.

The earliest growth of $Y_2SiO_5$ single crystals was done in conjunction with laser research in the Soviet Union. In 1973 it was reported (9,10) that $Nd^{3+}$:$Y_2SiO_5$ was lased successfully at 300°K. Rods of mm size were used and the material had a low threshold of a few joules in a pulsed mode of operation. The emission spectrum, threshold, and other laser parameters were highly dependent on the orientation of the crystal axes of the laser rods. It appears that the crystal structure is orthorhombic and the two site symmetries at the $Y^{3+}$ may be slightly different. What governs the site preference upon doping for laser action has not been explained. In $Gd_2SiO_5$ doped with $Ce^{3+}$, it may give rise to the small auxiliary peak near 545nm. In any case, a more detailed spectral study is required for the growth and doping of the single crystals.

In 1983, workers in Japan reported (11) the Czochralski growth of $Ce^{3+}:Gd_2SiO_5$ for a scintillator application. These crystals were 25mm diameter and 40mm long. The luminescence spectrum of the 1.0 atomic percent Ce crystal is shown in Figure 2. The excitation is by 254nm ultraviolet light. It can be seen that the broad band emission has a peak in the blue near 450nm. The substitution of Y for Gd shifts the peak further into the blue near 400nm. While no experiment was performed on La addition, the larger unit cell and reduced crystal field about $Ce^{3+}$ will probably shift the peak in the opposite direction, i.e. toward 470-480nm. The fluorescent lifetime of the $Ce^{3+}$ in $Gd_2SiO_5$ is about 60ns. This value is equal to or slightly larger than $Ce^{3+}$ in YAG or other oxide hosts.

Further literature on the Czochralski type growth is not available. In November, 1984, a personal visit was made to Philips Laboratories in Eindhoven, The Netherlands. It was learned that this laboratory was growing single crystals of $Y_2SiO_5$ by pulling from the melt.(12) The crystals were about 2 x 8cm and desired for phosphor research. In some previous papers by Philips personnel, the silicates were found to be some of the most efficient phosphors available. The work at Philips also confirms that good single crystals can be grown.

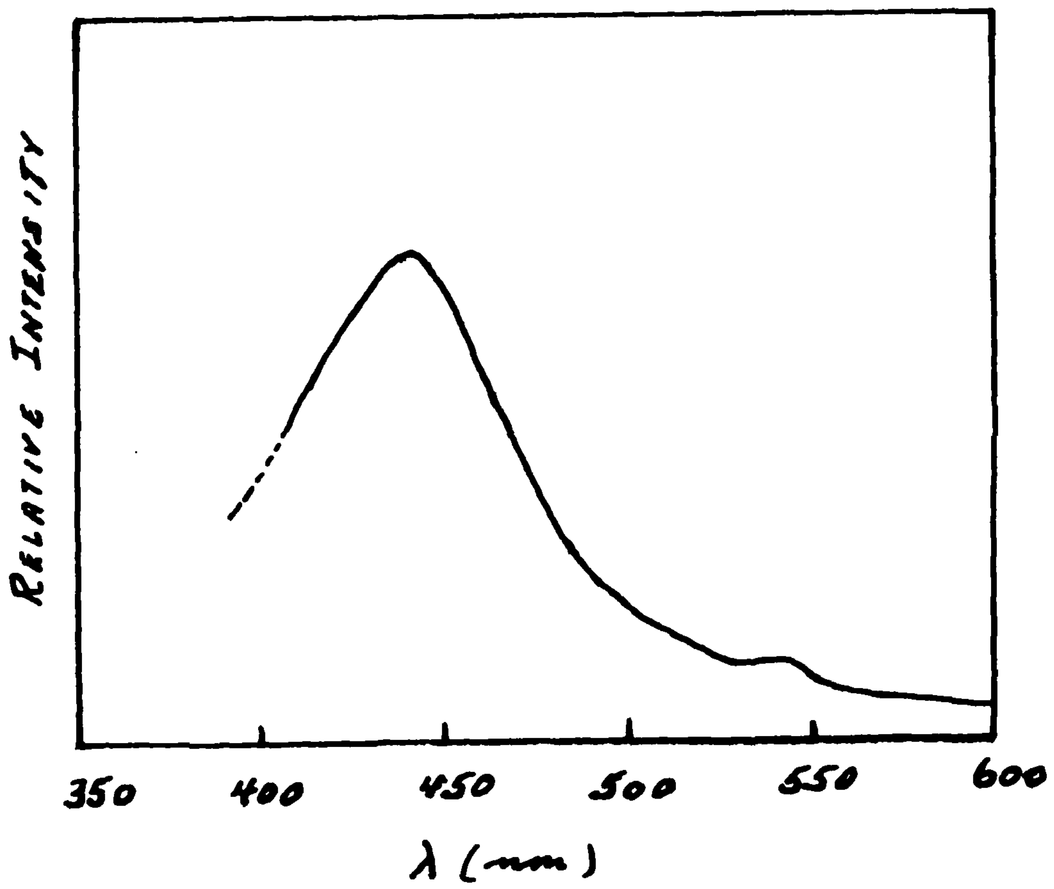


Figure 2 Luminescence spectrum of Ce:$Gd_2SiO_5$ single crystal excited by by ultraviolet (wavelength 254nm) at room temperature. (Ref. 11)

## 2.0 Experimental Procedures

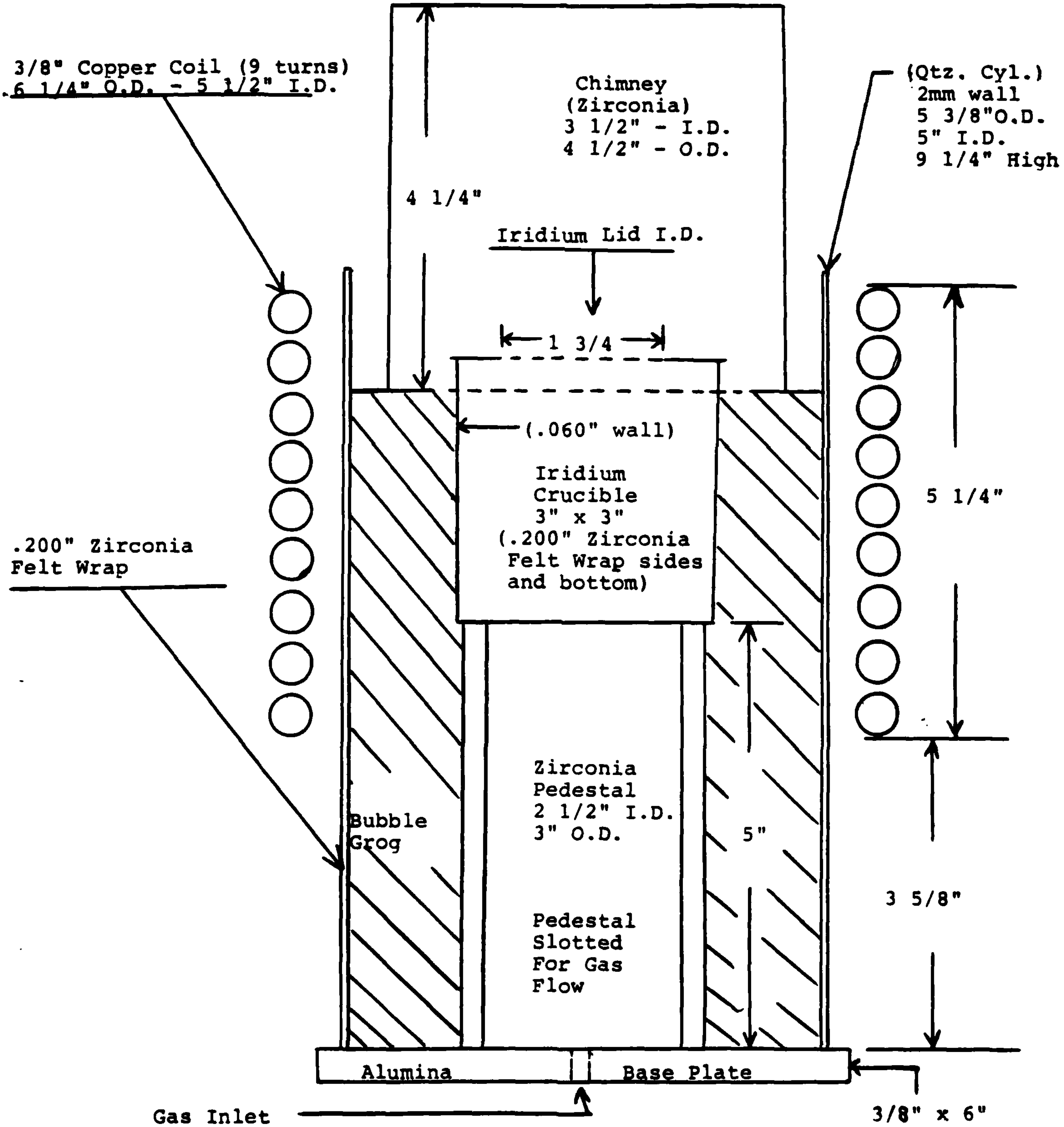
### 2.1 Feed Material

The precursor powders used in these experiments were of 4-9's purity or better. The $CeO_2$ was purchased from Spex Industries, Inc., the $Gd_2O_3$ and $SiO_2$ from the United Mineral Corporation, the $Y_2O_3$ from Rhone-Poulenc, and the $La_2O_3$ and $Lu_2O_3$ from Research Chemicals. These powders were weighed to the nearest tenth or hundreth of a gram and were then blended together in a polycarbonate plastic divider/mixer for three to four hours. This mixture was then charged via a quartz funnel into the crucible which was at a temperature to cause pre-reaction and sintering of the powdered components. Upon completion of the sintering of the full charge (usually accompanied by partial melting of the charge in the bottom of the crucible) the crucible temperature was raised to above the mixture's melting point where it was held for 24 to 48 hours to ensure complete mixing. Radial flow lines were clearly visible once the melting point of the charge was reached.

### 2.2 Czochralski Technique

The standard set-up for this series of growth runs is shown in Figure 3. A 3 inch by 3 inch iridium crucible, capped with a 2 inch I.D. iridium lid was used for most of the runs. The crucible is heated by RF coils powered by a 30 kw Lepel generator. The cover atmospheres for each run are detailed in the listing of experimental results (Table 1). The gases used ($N_2$/forming gas or $N_2$ alone) were fed through holes centered in the steel table and zirconia base plate. The gas then exited from vertical slots cut in the zirconia support cylinder to flow up through the grog. The flow rates were generally in the range of 25 liters/min. The pulling rates and

Figure 3 RF Growth Furnace Schematic



rotation rates are detailed in Table 1. Melt drop compensation was employed during runs where a boule was pulled.

## 2.3 Seed Generation

Bootstrapping seeds from previous growth runs has proven to be most successful in generating new single crystal growth from subsequent melts.

The first series of seeds were cut from spontaneously crystallized melts in 1.5 inch by 1.5 inch crucibles. These were used to grow small boules which yielded larger seeds. In the current run series all boules were grown from seeds mined from boules. The use of a 3 inch by 3 inch crucible and cooling the boule in contact with the melt has also produced sizeable sections of single crystal material from the frozen melt. Seeds have generally been suspended from an alumina rod on an iridium wire hook, although this has sometimes caused mechanical stability problems during growth. These larger single crystal pieces yield larger seeds, which will lead to improved growth. When suitably sized material is grown and large enough seeds can be manufactured, then a more rigid seed platform will be employed. This will reduce mechanical instabilities and facilitate better crystal growth. Some attempts at alternate orientations based on growth morphology and cleavage planes have been attempted, but the best growth direction appears to be parallel to the main cleavage plane. X-ray orientation of the seeds will also be used to more accurately determine the preferred growth orientation. Figure 4a shows a crystallized $Gd_2SiO_5$ melt while figure 4b shows a small seed crystal mined from a crystallized melt. Figure 4c shows some of the seeds mined from boules and used in later growth runs.

Figure 4a  Crystallized Melt of $Gd_2SiO_5$ cooled from 1900°C in a 2" x 2" iridium crucible

Figure 4b  Original seed crystal of $Gd_2SiO_5$ culled from frozen melt

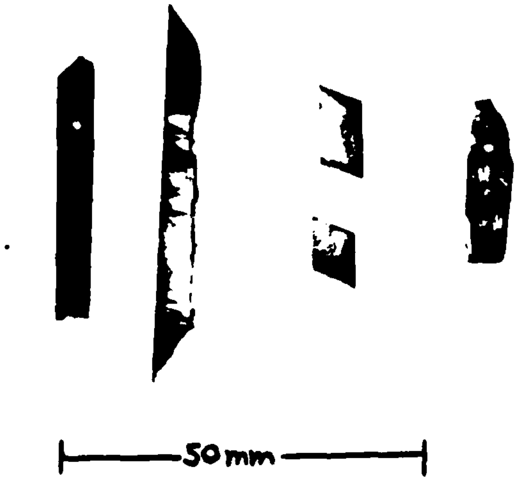


Figure 4c  Sample of larger $Gd_2SiO_5$ seeds used for later boule growth

## 2.4 Polycrystalline Preparation

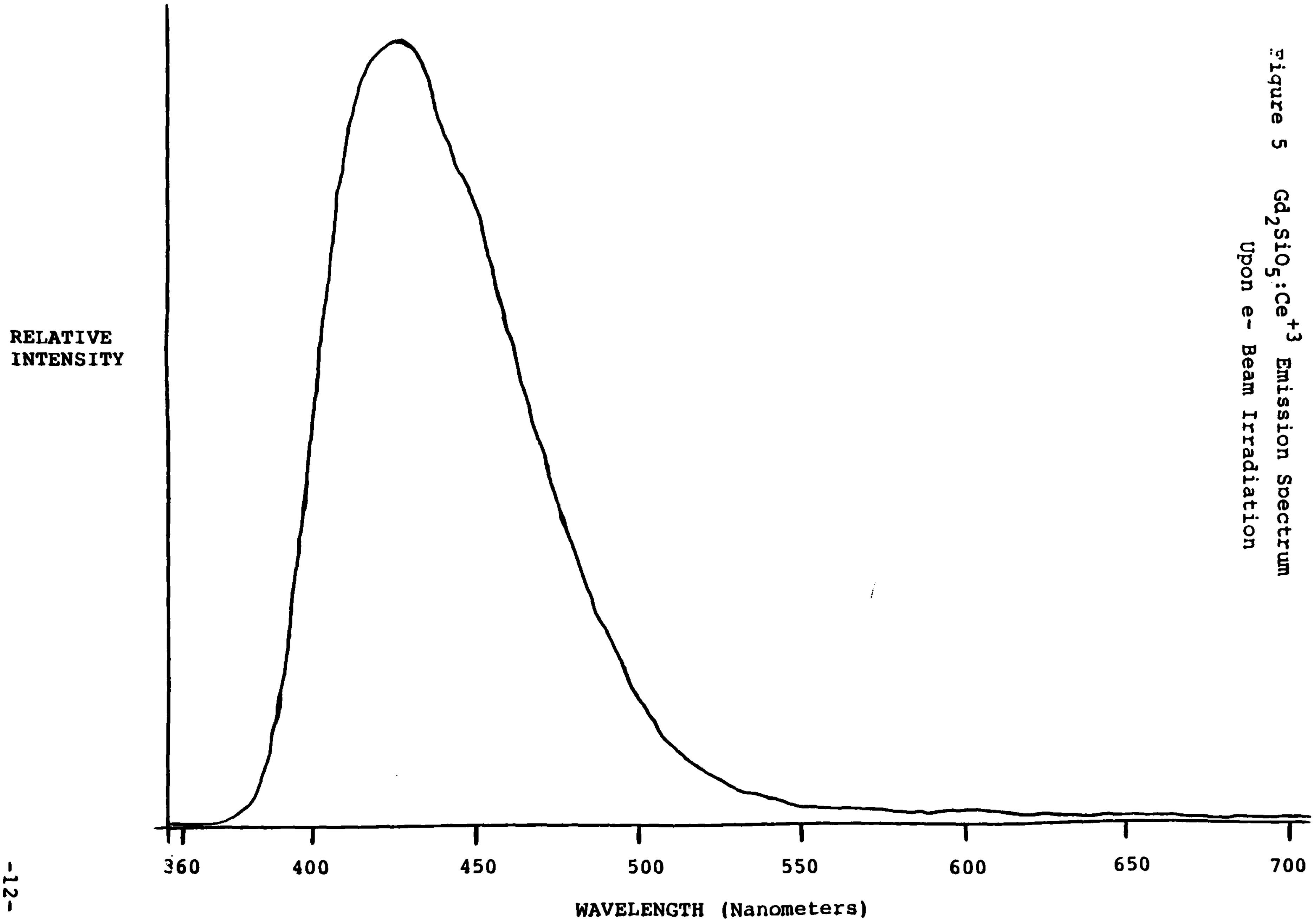
During this reporting period, it was determined that a quick survey of the potential for shifting the $Ce^{+3}$ emission spectrum using compositional variations was in order. This was to be accomplished by a partial substitution of similar rare earths for the Gd in the $Gd_2SiO_5$ structure. Ten percent substitution was chosen as sufficient to cause an observable effect and this was carried out by using the precursor materials listed in the feed materials section of this report.

The samples weighed approximately 0.22g each and were pressed into aspirin sized tablets in a stainless steel die. The pellets were then sintered on the bottom of an iridium crucible to produce the orthosilicate structure. Then they were individually crushed and spectrally analyzed for their $Ce^{+3}$ emission peak as outlined in the next section.

## 2.5 Cathodoluminescent Evaluation

Preliminary evaluations for luminescence were done under UV light. If a sample exhibited a visible response then a small single or polycrystalline sample was prepared for e- beam excitation. Upon exposure to the e- beam, the sample luminesces due to its $Ce^{+3}$ content and this emitted radiation is scanned by a very accurate monochrometer and its itensity versus wavelength profile (from 300 nm to 700 nm) is recorded on a strip chart. This allows evaluation of the relative strength and peak wavelength position of the $Ce^{+3}$ emission spectrum. A typical spectrum for $Gd_2SiO_5:Ce^{+3}$ is shown in Figure 5.

Figure 5 $Gd_2SiO_5:Ce^{+3}$ Emission Spectrum Upon e- Beam Irradiation



## 2.6 Optical and Laser Evaluation

Optical and laser evaluation of samples from successful runs were to be performed at NRL. Samples for this purpose were to be prepared at Airtron by cutting single crystal sections from each boule and polishing them to optical clarity.

## 3.0 Results and Discussion

Since it appears that all the rare earths (R) form an isomorphous series in the compounds $R_2SiO_5$, the crystal grower is presented with tremendous latitude in the preparation of both hosts and dopants for laser application. Let us consider the host crystal first. The elements La, Gd, Y and Lu span the full range of rare earth radii. Furthermore, each of these elements or their mixtures have trivalent ions with half or full shell electron complements; thus they are fully transparent in the absence of defect chemistry. The choice of $Gd_2SiO_5$, which was grown first, is in the middle of the rare earth series. Doping with $Ce^{3+}$ gives emission near 450nm. If Gd is mixed with Y, the emission should shift more towards the blue. If one mixes La and Gd, the peak emission may shift towards the red. By tailoring the <u>type</u> of mixed crystal, it should be possible to shift $Ce^{3+}$ emission to the range of interest. Combinations of La-Gd, La-Y, La-Lu may be necessary.

The large size of the $Ce^{3+}$ generally leads to a low distribution coefficient (k) in Y, or Lu analogs. The values are sometimes as low as 0.1-0.2. For $Gd_2SiO_5$,k increases to about 0.4-0.5. If the $La_2SiO_5$ analog can be made, the k values are very close to 1. However, with the low dopant levels of $Ce^{3+}$ ($\sim$0.1%) which are needed, there is not much difficulty in the phase behavior or crystal growth. We fully expected that $Ce^{3+}$ could be introduced in low amounts (0.1%) in all crystals such as La, Gd, Y, or Lu compounds and so far this has been borne out.

Seed orientation plays a large part in both the crystal growth and the resulting laser properties. For noncubic materials, there may be serious reasons for investigating the optimum direction for growth. Similarly the polarization properties of emitted light are a topic for their efficient use in any laser. It has also been reported that the $R_2SiO_5$ type silicates have a possible plane of separation, and this has been observed in our growth runs. However, this does not seem to pose a problem since large single crystal sections have been grown.

Our preliminary effort concentrated on the growth of large single crystals, doping, orientation, crystal structure effects, and finally the mechanical processing of any grown crystals. The primary objective was the growth, but closely tied to this were physical studies on the absorption, fluorescent emission, lifetime, polarization, and other laser parameters. Most of the latter is to be done at the Naval Research Laboratory.

### 3.1 Phase Diagrams

A thorough examination of the available relevant phase diagrams (from the A.C.S.'s "Phase Diagrams for Ceramists" series) for the $R_2O_3$-$SiO_2$ systems (where R is a rare earth) was performed during this report period. All the phase diagrams exhibited similar structure especially around the one to one molar percent ratio line. The existence regions for the $R_2SiO_5$ compositions are bounded by solidus and liquidus curves and two eutectics around the 1:1 line. This can be seen in Figure 1 of the introductory section to this report. The temperature ranges of these existence regions are also very closely centered around 1900°C. This would indicate that $R_2SiO_5$ single crystal material should be isostructural as R is varied allowing mixed composition single crystal boules to be pulled stoichiometrically from the melt.

### 3.2 Doping and Atmosphere Control

The crystals grown in this series of experiments were doped by adding $CeO_2$ at about the 0.1% level of the precursor powder mixture. Conversion from $Ce^{+4}$ to $Ce^{+3}$ is thought to have been incomplete in the early growth runs. This was revealed by a yellowish colouration in portions of the melt and crystals. There was, however, always sufficient conversion to cause a very bright luminescence under UV illumination. More complete conversion appeared to be achieved in later runs by going from a flowing atmosphere of $N_2$ and forming gas to only a flowing $N_2$ gas cover. This was evidenced by the growth of transparent water white boules.

## 3.3 $Gd_2SiO_5$ Experimental Runs

The basic experimental conditions of each of the growth runs performed during this period are outlined in Table 1. $Gd_2SiO_5$ growth runs were attempted in experiments 10 through 16 and 18. Run 10 was an attempt to grow large enough single crystal sections to cut up for seeds. The result was a mostly single crystal boule with a strong yellowish cast which yielded four 30 mm long seeds. A seed from run 10 was used to initiate growth in run 11 which yielded a boule about 120 mm long but of widely varying diameter (from 8 to 28 mm). This boule had high surface stresses indicated by crazing of the surface and also exhibited a yellowish colour. Run 12 was seeded with material from run 10. Boule growth was eccentric and in trying to keep the boule from wobbling the growth axis was slowly shifted until there was an internal 130° angle between the longitudinal axis of the seed and the boule's longitudinal axis. The boule itself was mostly single crystal with some yellow colour being 22 mm in diameter by 57 mm long. Run 13 was an attempt to grow along the same axis as the boule tended to in the previous run using seeds cut from run 12's boule. This proved unsuccessful as the seeds kept burning off so the run was terminated. Run 14 was aborted after three days due to leakage in the crucible bottom. Another seed from run 10 was used to initiate growth in run 15. The seed was longitudinally bicrystalline and this propagated into the boule. Other than this, the boule was of water white transparency and highly single crystal. The lack of yellowish colour in the boule may be due to the absence of forming gas during the run. The same seed as was used in run 15 (split to eliminate its bicrystallinity) initiated growth in run 16. The resulting boule showed an oblate cross-section (21/25mm) but was only grown to about 56mm in length due to arcing of the RF coils to the quartz cylinder. Run 18 was a test of the feasibility of growth of $Gd_2SiO_5$ along a different axis from those tried previously. Seeds were cut from the boule grown in run 16 at an orientation approximately 45° from both longitudinal and radial axes of the boule. This was parallel to regular fracture lines observed in the boule and thought to be crystallographic fracture planes. The boule grown at this orientation was mostly single crystal of water white transparency, but there was brittle fracture and extensive surface crazing which may have been due to the new growth direction. A photograph of sections of boules (oriented head up) are shown in Figure 6. From left to right they are from runs 11, 15, 16, and 18.

### 3.4 Polycrystalline Experimental Run

The luminescence results from run 17 are given in Table 1. Four samples were made up: one with all $Gd_2SiO_5$ as a reference, and three others, each with 10% substitution of Gd by Lu, Y, and La respectively. The average luminescence was about the same in all four samples as was the shape of the main $Ce^{+3}$ emission peak. The secondary peak in the spectrum (observed at about 540 to 545nm) is suspected to be due to alternate site placement of the $Ce^{+3}$, but did not appear to shift in concert with the main peak. In fact, it almost disappeared into the slope of the primary peak when the primary peak shifted up in wavelength with the 10% Lu substitution. These results indicate that the pellet's crystal structures are basically identical and orthosilicate in form since the sintered $Gd_2SiO_5:Ce^{+3}$ spectrum matched the single crystal $Gd_2SiO_5:Ce^{+3}$

Figure 6   Boule Sections from (left to right) Runs 11, 15, 16, and 18

luminescence pattern with peak emission at the same wavelength. These shifts were small however and went against the expected shift direction which would have the substitution of Y or Lu shift the luminescence peak to the blue and La substitution shift it to the red. No explanation of this reversal was known at the time of this writing although it appears to be a function of the polycrystalline preparation as is shown in Section 3.5.

### 3.5 $Y_2SiO_5$ and $La_2SiO_5$ Experimental Runs

Run 19 was an attempt to crystallize from the melt $Y_2SiO_5:Ce^{+3}$ using a $Gd_2SiO_5$ seed. This would allow verification of the crystal structure of $Y_2SiO_5:Ce^{+3}$ with X-ray analysis and comparison of its luminescence to that of $Gd_2SiO_5:Ce^{+3}$. The melt was allowed to mix by convection for about 48 hours, the $Gd_2SiO_5$ seed was dipped in, allowed to equilibrate and the melt was set for a programmed cool-down. The frozen melt's surface showed a crystallization pattern emanating from the seed contact site, but core drilling revealed incompletely mixed material in the lower portions of the crucible mass. This may explain why the X-ray results indicate the possible presence of more than one phase and don't correlate with the X-ray patterns observed for $Gd_2SiO_5$ to date. An island dipped from the melt prior to seeding was analyzed using the e- beam luminescence system and showed a peak emission at 414nm. Although this is more in line with the published data, the result is suspect due to the incomplete mixing of the melt. Run 20 was performed using $La_2SiO_5:Ce^{+3}$ in a manner similar to run 19, but even worse segregation was obvious upon core drilling. Both these experiments will be repeated in future runs with better mixing.

### 3.6 Cathodoluminescence Results

Samples from all the runs which yielded boules and runs 17, 19, and 20 exhibited bright luminescence from their $Ce^{+3}$ content when exposed to UV radiation. Measurements using the e- beam cathodoluminescence apparatus gave luminescence spectrums showing the typical broad band $Ce^{+3}$ profile. Shifts were observed which have been tentatively assigned to compositional variations, but these have to be confirmed with further single crystal growth runs.

### 3.7 Optical and Laser Evaluations

Samples from runs 10, 11, 12, 15 16, and 18 were sent to the NRL in or shortly after the period covered by this report. Results from NRL tests will indicate whether these materials are suitable candidates for laser substrates.

### Table 1
### List of Experimental Runs

| RUN # | IRIDIUM CRUCIBLE SIZE | COVER GAS | PULL & ROTATION RATES | RUN DURATION | OTHER RUN PERAMETERS | RUN RESULTS |
|---|---|---|---|---|---|---|
| 10 | 1.5"X 1.5 | Forming & $N_2$ | .05"/Hr. | 22 days | seed suspended on Ir wire | Seed kept burning off, boule growth terminated by burn off, yellow translucent single crystal boule 17mm diameter by 45mm long. |
| 11 | 3" X 3" | " | " | 8 Days | " | Irregularly shaped yellowish boule, highly stressed mostly single crystal, leading section of boule 14mm diameter by 55mm long, trailing, section flared from 8mm diameter to 28mm over a length of 67mm. |
| 12 | " | " | .05/Hr.<br>45 RPM | 22 Days | " | Boule growth was eccentric and in trying to keep the boule from wobbling the growth axis shifted by about 50° from the vertical, the boule was mostly single crystal with some yellow color and 22 mm diameter by 57mm long. |

Table 1 (continued)

| RUN# | IRIDIUM CRUCIBLE SIZE | COVER GAS | PULL & ROTATION RATES | RUN DURATION | OTHER RUN PERAMETERS | RUN RESULTS |
|---|---|---|---|---|---|---|
| 13 | 3" X 3" | Forming & $N_2$ | 45 RPM | 27 Days | seed suspended on Ir wire seed at same orientation as boule grew at in run #12 | Seed burn off prevented boule growth - run aborted when all of seed gone. |
| 14 | " | $N_2$ |  | 3 Days | Power off twice to switch control boards | Crucible bottom leaked possibly due to power shut-downs. |
| 15 | " | " | 48 RPM<br>.0075"/Hr. | 16 Days | Seed suspended on Ir wire | Boule come out bicrystalline due to seed, highly single crystal otherwise, water white transparency, some cracking, boule diameter went from 10mm at the seed to 30mm at a length of 34mm and maintained this diameter to the 55mm mark. |
| 16 | " | " | " | 15 Days | Some seed as for run #15 but split in half to eliminate bicrystallinity | Oblate boule with cracking, mostly single crystal, water white transparent, straight portion of boule about 44mm long with an oblate cross section of 21-25mm. |

## Table 1 (continued)

| RUN # | IRIDIUM CRUCIBLE SIZE | COVER GAS | PULL & ROTATION RATES | RUN DURATION | OTHER RUN PERAMETERS | RUN RESULTS |
|---|---|---|---|---|---|---|
| 17 | 2" X 2" | $N_2$ | | 1 Day | Four pressed powder pellets of varying composition sintered on the bottom of crucible | Pellets crushed and analyzed for e-beam fluorescence, excitation, the results:<br>$Gd_2SiO_5$: $Ce^{+3}$ = 429nm pk.<br>$(Gd_{.9}La_{.1})_2SiO_5$: $Ce^{+3}$ = 427nm "<br>$(Gd_{.9}Y_{.1})_2SiO_5$: $Ce^{+3}$ = 432nm "<br>$(Gd_{.9}Lu_{.1})_2SiO_5$:$Ce^{+3}$ = 435nm " |
| 18 | 3" X 3" | " | 48 RPM<br>.025"/Hr. | 39 Days | Seed cut from and oriented 45° from radial and longitudinal axes of boule from run #16 | Crystal started to spiral crack on lifting from melt, therefore cooled in contact with melt, badly frosted surface due to surface crazing, bulk cracked also but water white transparent mostly single crystal, large pieces of single crystal in melt due to contact with boule during freeze out. |
| 19 | " | " | | 7 Days | $Y_2SiO_5$:$Ce^{+3}$ melt<br>$Gd_2SiO_5$Seed | Melt allowed to cool in contact with seed, produced radial crystallization pattern, core drilling of crucible mass shows segregation in lower portions, X-ray diffraction results indicate multiple phases none of which correlate with $Gd_2SiO_5$ patterns. |

Table 1 (continued)

| RUN# | IRIDIUM CRUCIBLE SIZE | COVER GAS | PULL & ROTATION RATES | RUN DURATION | OTHER RUN PERAMETERS | RUN RESULTS |
|---|---|---|---|---|---|---|
| 20 | 3" X 3" | $N_2$ | | | $La_2SiO_5:Ce^{+3}$ melt<br>$Gd_2SiO_5$ seed | Melt allowed to cool in contact with seed, some large single crystal areas but core drilling revealed large segregation in lower reaches of crucible mass, left out overnight solid crucible mass turned to less dense powder (probably $La_2O_3$), X-ray results of crystalline portion do not correlate with $Gd_2SiO_5$ patterns. |

## 4.0 Conclusions

The work performed so far under this contract has served to point out the most productive direction for further research. We now know that $Ce^{+3}$ exhibits a very high luminescent activity in a wide range of $R_2SiO_5$ compounds when present at about the 0.1% level. We have also observed shifts in the $Ce^{+3}$ cathodoluminescent spectrum due to compositional substitution of the rare earth component of the orthosilicate structure. The wavelength shift from R = 100% La to R = 100% Lu may be as much as 50 to 70nm. One objective now is to optimize compositions so as to produce the desired emission spectrum together with exploration of other orthosilicate systems which may broaden the available wavelength range.

Growth of small boules of $Gd_2SiO_5$ has been successfully undertaken during this report period. The goal now is to extend these growth techniques to produce larger, more perfect boules of $Gd_2SiO_5$ for laser rod fabrication. This can then be easily adapted to other orthosilicate systems for production of large boules from these materials as well.

## References

1. See previous reports and data of Contract N00014-81-C-0656 and N00014-83-C-0072 by Airtron Division of Litton; other contractors such as EIC Laboratories, Crystal Systems, Inc., and MIT have obtained similar results in parallel programs under ONR.

2. J. Felsche is "Structure and Bonding", Vol. 13, p. 99 (Springer-Verlag, New York, 1973).

3. Phase Diagrams for Ceramists, 1969 Supplement, American Ceramic Society, Figure 2367.

4. G. Buisson and C. Michel, Mat. Res. Bull. 3, 193 (1968).

5. L. A. Harris and C. B. Fuich, Amer. Mineral. 50, 1493 (1965).

6. I. A. Bondar, L. N. Koroleva, and N. A. Toropov, Rost, Kristallov. Akad Nauk SSSR Ins. Krist 6, 111 (1965).

7. I. A. Bondar, L. N. Koroleva, and D. P. Sipovskii, Russ. J. Inorg. Chem. 13, 1635 (1968).

8. B. M. Wanklyn F. R. Wondre, G. B. Ansell, W. Davison, J. Mat. Sci. 9, 2007 (1974).

9. Kh. S. Bagdasarov, A. A. Kaminskii, A. M. Kevorkov, A. M. Prohkorov, S. E. Sarkison, T. A. Tevosyon, Soviet Physics-Doklady 18, 664 (1973).

10. A. A. Kaminskii, et al., Inorganic Materials (USSR) 12, 1238 (1976).

11. K. Takagi and T. Fukazawa, Appl. Phys. Letters 42, 43 (1983).

12. J. Pistorius, Philips Laboratory, Eindhoven, The Netherlands, 1984.

APRIL 1984

# REPORTS DISTRIBUTION LIST FOR ONR PHYSICS DIVISION OFFICE UNCLASSIFIED CONTRACTS

Director 1 copy
Defense Advanced Research Projects Agency
Attn: Technical Library
1400 Wilson Blvd.
Arlington, Virginia 22209

Office of Naval Research 2 copies
Physics Division Office (Code 412)
800 North Quincy Street
Arlington, Virginia 22217

Office of Naval Research 1 copy
Director, Technology (Code 200)
800 North Quincy Street
Arlington, Virginia 22217

Naval Research Laboratory 1 copy
Department of the Navy
Attn: Technical Library
Washington, DC 20375

Office of the Director of Defense 1 copy
  Research and Engineering
Information Office Library Branch
The Pentagon
Washington, DC 20301

U.S. Army Research Office 2 copies
Box 1211
Research Triangle Park
North Carolina 27709

Defense Technical Information Center 12 copies
Cameron Station
Alexandria, Virginia 22314

Director, National Bureau of Standards 1 copy
Attn: Technical Library
Washington, DC 20234

Director 1 copy
U.S. Army Engineering Research
  and Development Laboratories
Attn: Technical Documents Center
Fort Belvoir, Virginia 22060

ODDR&E Advisory Group on Electron Devices 1 copy
201 Varick Street
New York, New York 10014

| | |
|---|---|
| Air Force Office of Scientific Research<br>Department of the Air Force<br>Bolling AFB, DC 22209 | 1 copy |
| Air Force Weapons Laboratory<br>Technical Library<br>Kirtland Air Force Base<br>Albuquerque, New Mexico 87117 | 1 copy |
| Air Force Avionics Laboratory<br>Air Force Systems Command<br>Technical Library<br>Wright-Patterson Air Force Base<br>Dayton, Ohio 45433 | 1 copy |
| Lawrence Livermore Laboratory<br>Attn: Dr. W. F. Krupke<br>University of California<br>P.O. Box 808<br>Livermore, California 94550 | 1 copy |
| Harry Diamond Laboratories<br>Technical Library<br>2800 Powder Mill Road<br>Adelphi, Maryland 20783 | 1 copy |
| Naval Air Development Center<br>Attn: Technical Library<br>Johnsville<br>Warminster, Pennsylvania 18974 | 1 copy |
| Naval Weapons Center<br>Technical Library (Code 753)<br>China Lake, California 93555 | 1 copy |
| Naval Underwater Systems Center<br>Technical Center<br>New London, Connecticut 06320 | 1 copy |
| Commandant of the Marine Corps<br>Scientific Advisor (Code RD-1)<br>Washington, DC 20380 | 1 copy |
| Naval Ordnance Station<br>Technical Library<br>Indian Head, Maryland 20640 | 1 copy |
| Naval Postgraduate School<br>Technical Library (Code 0212)<br>Monterey, California 93940 | 1 copy |
| Naval Missile Center<br>Technical Library (Code 5632.2)<br>Point Mugu, California 93010 | 1 copy |

Naval Ordnance Station 1 copy
Technical Library
Louisville, Kentucky 40214

Commanding Officer 1 copy
Naval Ocean Research & Development Activity
Technical Library
NSTL Station, Mississippi 39529

Naval Explosive Ordnance Disposal Facility 1 copy
Technical Library
Indian Head, Maryland 20640

Naval Ocean Systems Center 1 copy
Technical Library
San Diego, California 92152

Naval Surface Weapons Center 1 copy
Technical Library
Silver Spring, Maryland 20910

Naval Ship Research and Development Center 1 copy
Central Library (Code L42 and L43)
Bethesda, Maryland 20084

Naval Avionics Facility 1 copy
Technical Library
Indianapolis, Indiana 46218

END

DTIC

6-86