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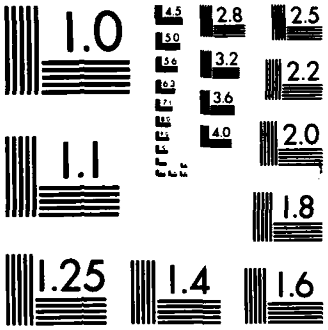

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INVESTIGATION OF SINGLE CRYSTAL SILICATES FOR BLUE TUNABLE LASERS

by

R.F. Belt and J.A. Catalano

Final Report
September 1, 1985 - September 1 , 1986
Contract No. N00014-85-C-0823

Airtron Division
Litton Industries, Inc
200 East Hanover Avenue
Morris Plains, New Jersey 07950

September 1986

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The single crystal growth of rare earth silicates was investigated for the purpose of tunable laser host. Silicates of the type R_2SiO_5, where R = La, Gd, Y were prepared from stoichiometric melts and doped with Ce^{+3} activator. Seed crystals were obtained from crystallized melt sections or by growth on an iridium wire. 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 370-525 nm. The peak emission can be centered near 450-460 um by other compositions. Large single crystals of $Gd_2SiO_5:Ce^{+3}$ were grown. One growth run of $Mg_2SiO_4:Ti^{+3}$ yielded a small boule which showed cathodoluminescence under e-beam illumination.

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FOREWORD

This final 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 September 1, 1986. 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 September 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 fluoresecent 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 or yttrium.

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_5 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.

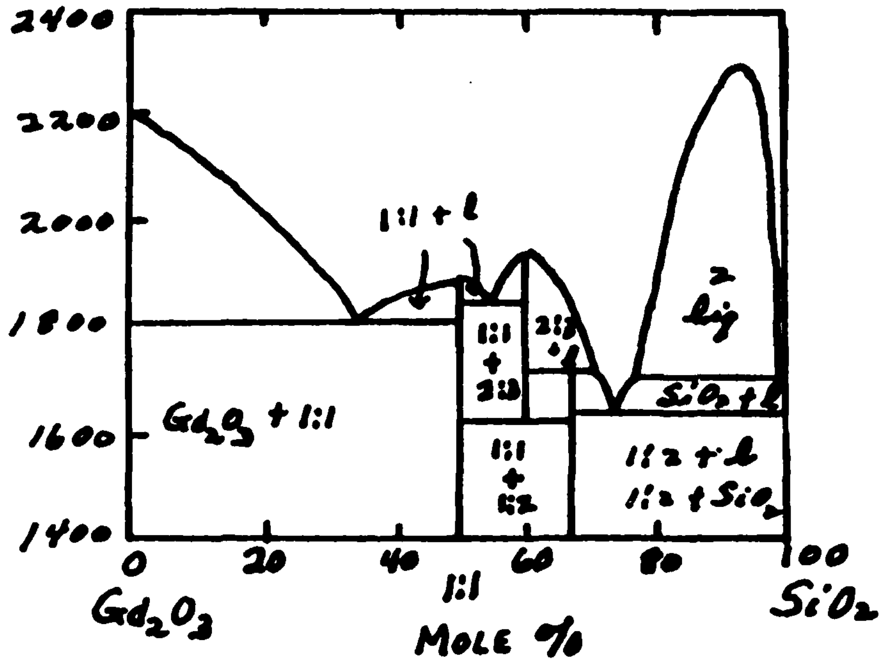


Figure 1 System Gd_2O_3-SiO_2. Oxide ratios of compounds are given as Gd_2O_3:SiO_2. (Ref. 3)

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 40 mm 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 450 nm. The substitution of Y for Gd shifts the peak further into the blue near 400 nm. 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 470-480 nm. The fluorescent lifetime of the Ce^{+3} in Gd_2SiO_5 is about 60 ns. 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 8 cm and desired for phosphor research. In some previous papers by Philips personnel, the silicates were found to be some of the most efficient phospors available. The work at Philips also confirms that good single crystals can be grown.

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_3MgO, Ti_2O_3, and some SiO_2 from the United Mineral Corporation, the Y_2O_3 from Rhone-Poulenc, and the La_2O_3, Lu_2O_3 and the remaining SiO_2 from Johnson Matthey. These powders were weighed to the nearest tenth or hundreth of a gram and were then

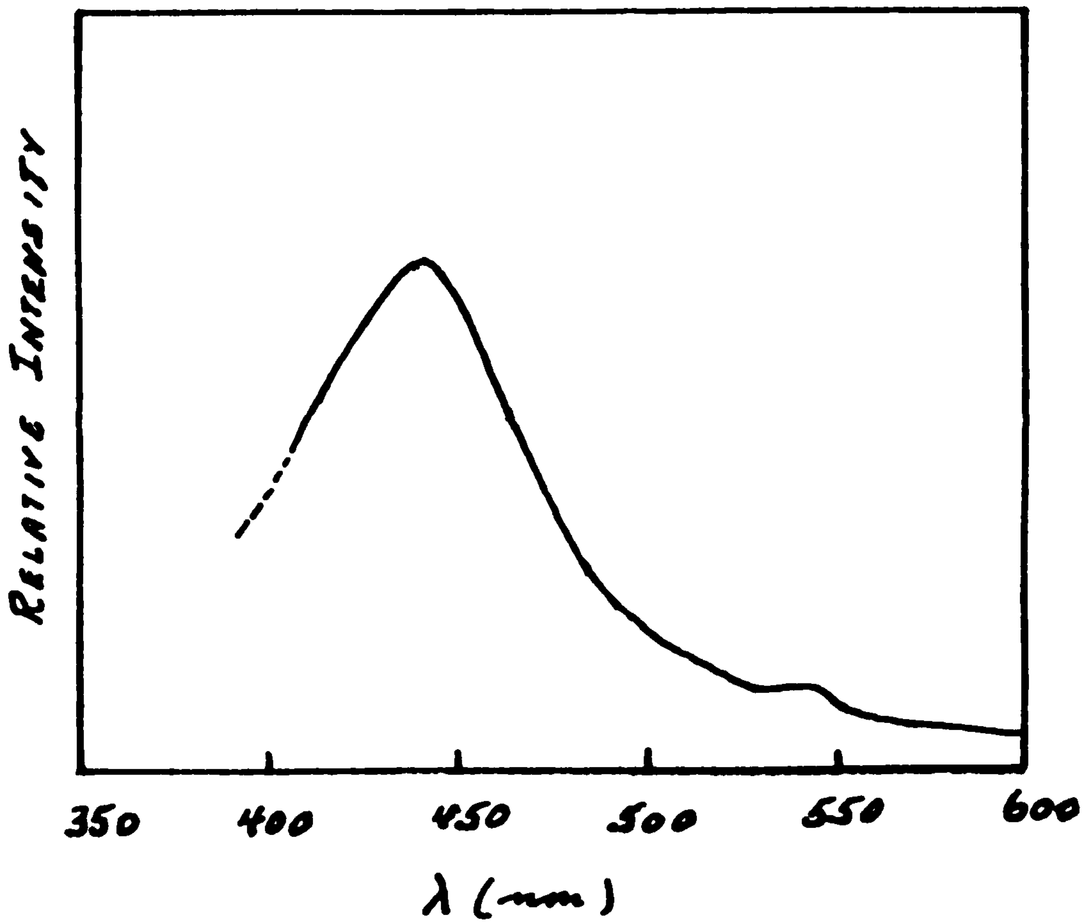


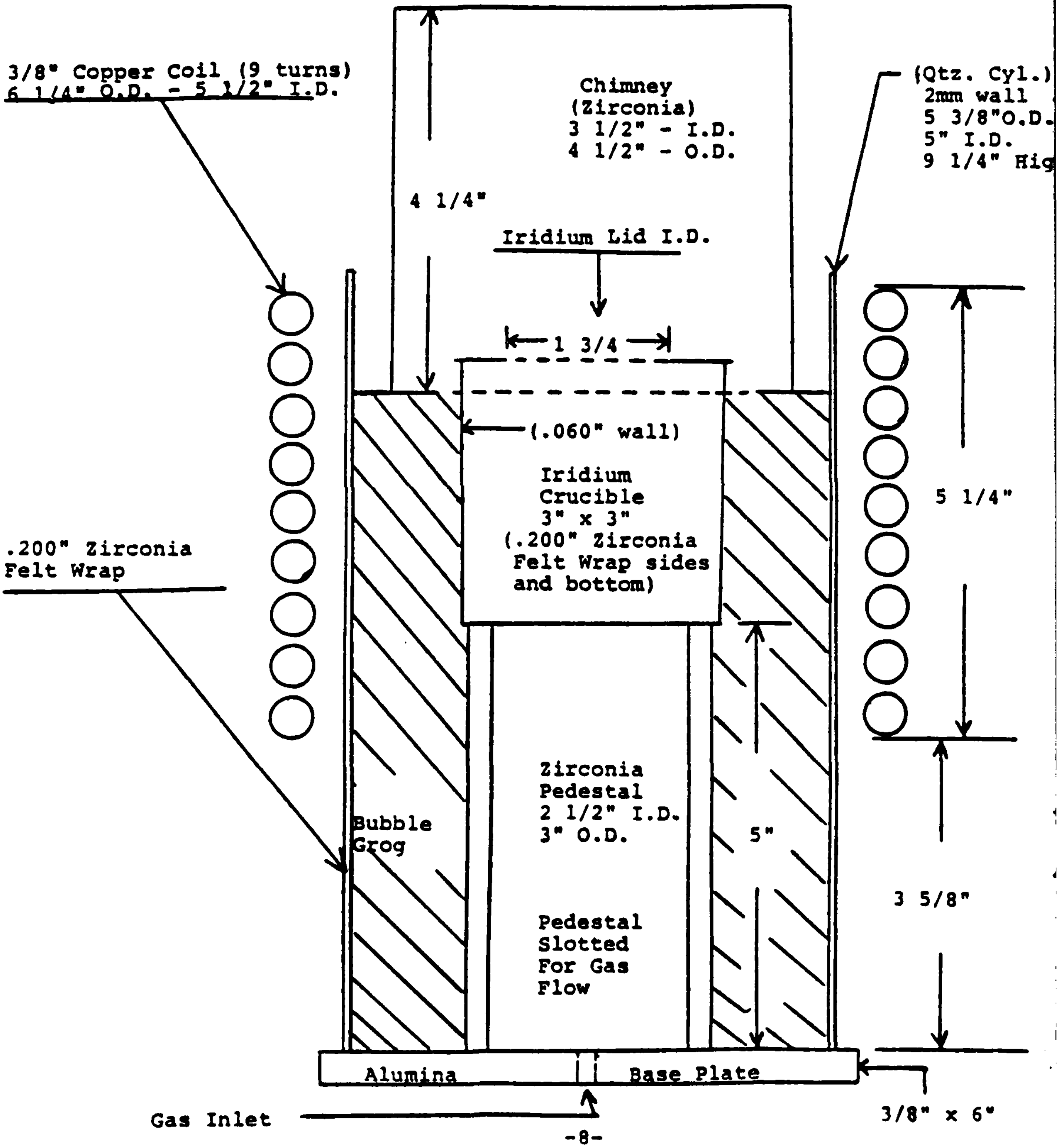
Figure 2 Luminescence spectrum of $Ce:Gd_2SiO_5$ single crystal excited by by ultraviolet (wavelength 254nm) at room temperature. (Ref. 11)

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 prereaction 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 gemetrical arrangement 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 atmosphere for each run was high purity nitrogen from a cryogenic source mixed with forming gas for some of the earlier runs. The gas was 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 rotation rates are detailed in Table I. Melt drop compensation was employed during runs where a boule was pulled.

Figure 3 RF Growth Furnace Schematic



2.3 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 intensity versus wavelength profile (from 300nm to 700nm) 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 4.

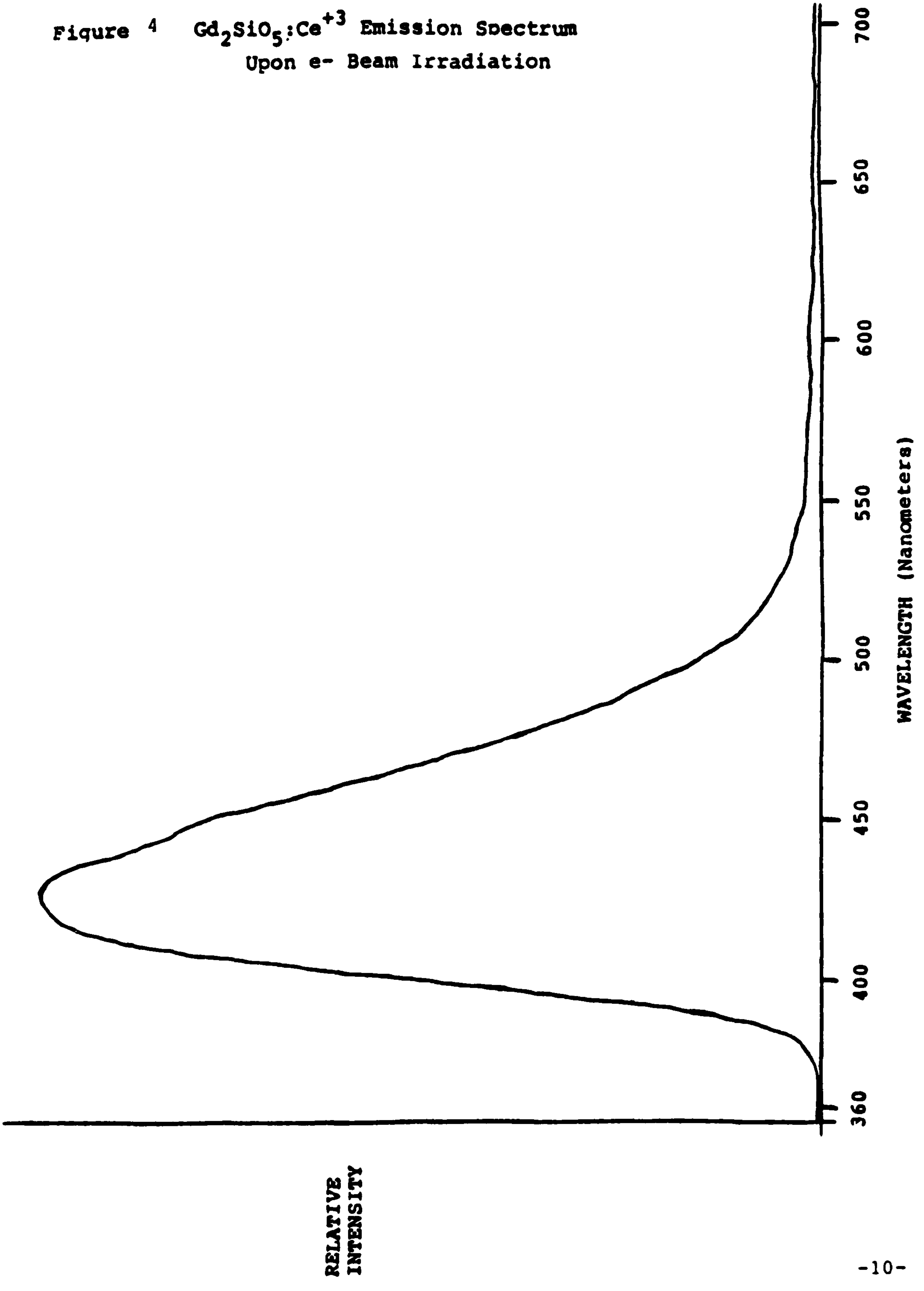
2.4 Optical and Laser Evaluation

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. Gd_2SiO_5, which was grown first, was chosen as it is in the middle of the rare earth series. Doping with Ce^{3+} gives emission near 450nm. If Gd is mixed with

Figure 4 $Gd_2SiO_5:Ce^{+3}$ Emission Spectrum Upon e- Beam Irradiation



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 type 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+} (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 for the Gd_2SiO_5 composition. However, this does not seem to be true for the Y_2SiO_5 crystalline material and only mildly so for the mixed composition $(Gd/Y)_2SiO_5$.

One experiment was performed on a non rare earth silicate ($Mg_2SiO_4:Ti^{+3}$) and this showed favorable growth parameters but the dopant did not activate to the degree desired. These other systems could be a rewarding area for future exploration for laser host materials.

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) show that the phase diagrams exhibit 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. The phase diagram for MgO-SiO_2 shows a structure and temperature range very similar to the above mentioned compositions.

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. The Mg_2SiO_4 run had Ti_2O_3 added to give a dopant level of about .2% molar. Conversion from Ce^{+4} to Ce^{+3} is thought to have been incomplete in the early growth runs. This was revealed by yellowish coloration in portions of the melt and and crystals. There was, however, always sufficient conversion to 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 just a flowing N_2 gas cover. Ti^{+3} may have converted to Ti^{+4} due to the use of the inert N_2 gas cover during growth. A reducing atmosphere may be necessary to stabilize the titanium +3 state.

3.3 Experimental Runs

The basic experimental conditions of each of the growth runs performed during this report period are outlined in Table I. Three experimental runs not reported previously are discussed in more detail below as well as being included in the Table I descriptions. The first run was an experiment with Ti^{+3} doping into a non rare earth silicate. The last two runs were attempts to grow large good quality single crystal sections of $Gd_2SiO_5:Ce^{+3}$.

Run 24 was an attempt to grow forsterite (Mg_2SiO_4) doped with Ti^{+3}. The forsterite grew with no real problems but the Ti^{+3} did not go into the boule in an amount sufficient to visibly color it. Some purplish coloration was segregated towards the crucible walls and bottom. A cathodoluminescence spectrum of a sample from near the tail end of the boule had peaks in the blue around 415 nm and in the orange red around 630 nm. The full spectrum is shown in Figure 5. Unfortunately an absorbtion spectrum of the same sample showed no structure with an absorbtion edge starting at about 250 nm. This indicates the emission seen under e-beam excitation will probably not be excitable by optical means. Although the melt was prepared using a Ti^{+3} oxide, an inert atmosphere was used during growth and this may have allowed the Ti^{+3} to convert to Ti^{+4}. It is possible the purplish coloration in the melt was due to Ti^{+4}. The use of a reducing atmosphere should prevent this.

Run 25 was an attempt to grow the $Gd_2SiO_5:Ce^{+3}$ in a fashion similar to Nd:YAG. This meant using the pull rate, rotation rate etc. used in Airtron's standard Nd:YAG system. The main exception was that the cover atmosphere used was still pure nitrogen. A boule 30 mm in diameter by 85 mm long was grown (see figure 6) with large single crystal sections (see Figure 7). Much of the cracking observed in the crystal was due to the process of detaching the boule from the crucible mass. Upon cool-down the boule was found to be totally embedded in the crucible mass although the run had been terminated because it was thought that the boule was undercutting. This made it necessary to use a hammer and chisel and even bending of the boule to detach it from the frozen melt. The boule fluoresced blue white under UV illumination. Cleavage planes are still very evident.

FIGURE 5

Cathodoluminescent Spectrum

of $Mg_2SiO_4:Ti^{+3}$

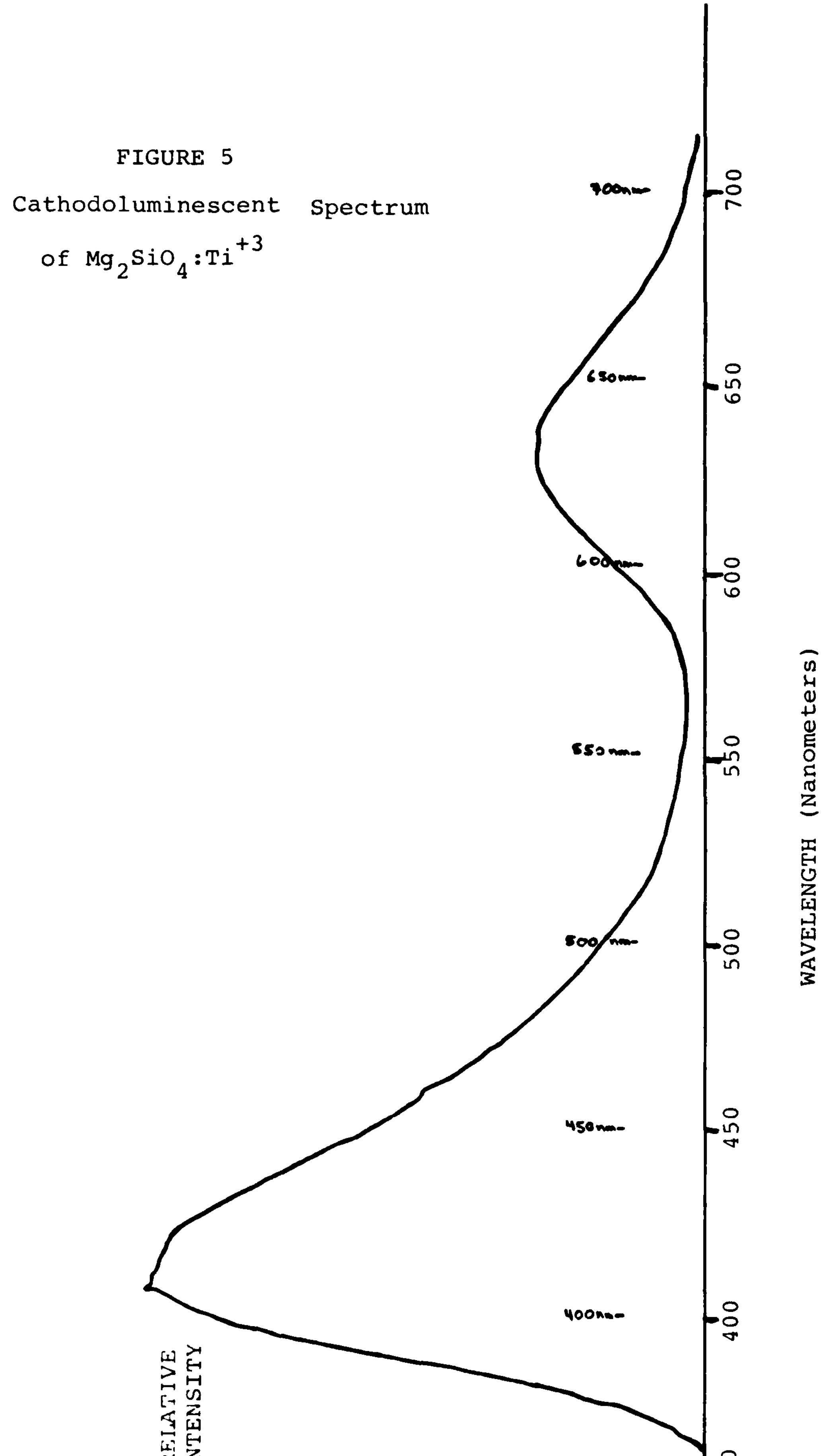


FIGURE 6

$Gd_2SiO_5:Ce^{+3}$

Boule Grown In

Run 25

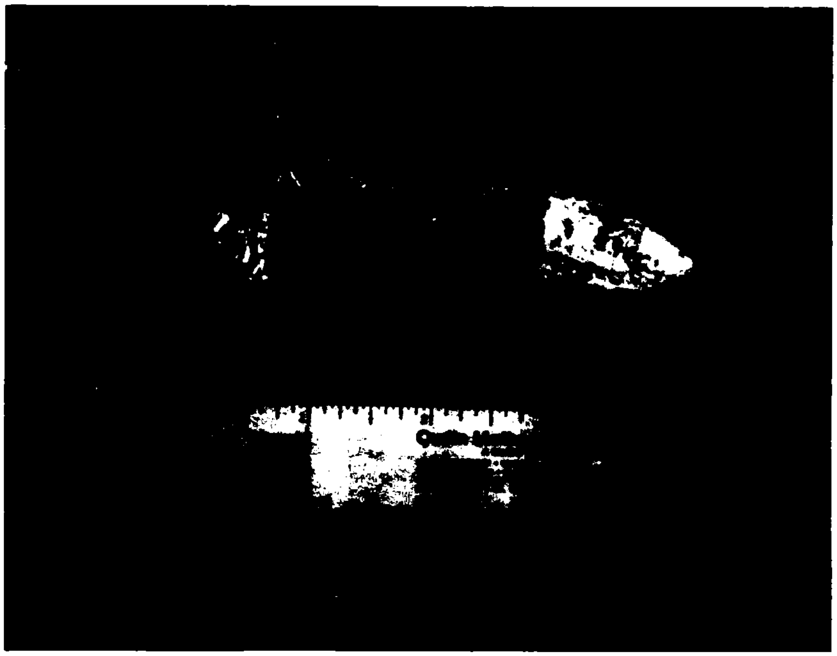


FIGURE 7

Cleaved Boule

Section from

Run 25

Run 26 was very similar to run 25 except it was decided to try and grow a smaller diameter boule of longer length. The boule grown was 157 mm in length by 25 mm in diameter. The boule was pulled up 5mm prior to cooling but this failed to free it from the melt to any significant degree. The stresses encountered during removal from the crucible mass caused much longitudinal cracking. Otherwise the material was very typical. The boule is shown in Fig. 8.

3.4 Cathodoluminescence Results

Samples from runs 25 and 26 exhibited bright bluish 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 profile of Ce^{+3} in Gd_2SiO_5. Samples from run 24 of the $Mg_2SiO_4:Ti^{+3}$ showed no real luminescence under ultraviolet illumination, perhaps a slight orangish tinge. The cathodoluminescent spectrum did show two peaks as previously mentioned. (see Figure 5).

3.5 Optical and Laser Evaluation

A sample from the boule grown in run 24 was sent to the NRL shortly after the period covered by this report. Results from the NRL tests will indicate whether it is possible to optically activate the Ti in the Mg_2SiO_4 and hopefully elucidate which oxidation state is present.

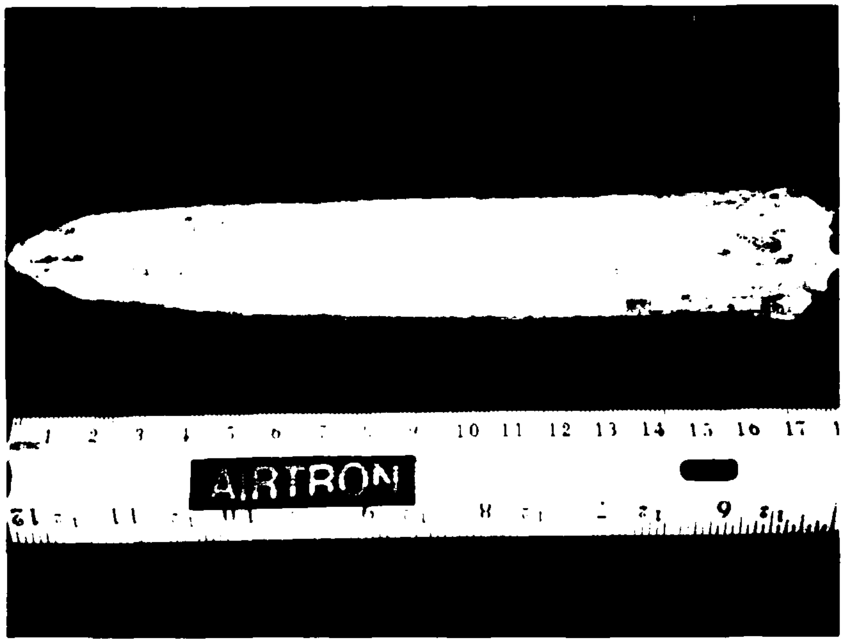


FIGURE 8 $Gd_2SiO_5:Ce^{+3}$ boule grown in Run 26.

Table I
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. 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 I (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 .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 I (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: Gd_2SiO_5: Ce^{+3} = 429nm pk. $(Gd._9La.1)_2SiO_5$: Ce^{+3} = 427nm " $(Gd._9Y.1)_2SiO_5$: Ce^{+3} = 432nm " $(Gd._9Lu.1)_2SiO_5$:Ce^{+3} = 435nm "
18	3" X 3"	"	48 RPM .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 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 I (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 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.
21	3" X 3"	N_2	24 RPM .025"/hr	15 days	$Y_2SiO_5:Ce^{+3}$ melt Gd_2SiO_5 Seeds	Seed kept burning off, first boule all fine polycrystallites, redipped and pulled very small diameter boule, crystallized out melt by cooling it in contact with boule, most of crucible mass water white transparent crystal.
22	3" X 3"	N_2	24 RPM .025"/hr	19 days	La_2SiO_5"Ce^{+3} melt Gd_2SiO_5& Y_2SiO_5 seeds	Gd and Y silicate seeds kept burning off so iridium wire used to seed melt, a small boule was pulled and cooled in contact with melt to initiate crystallization of melt. Both boule and crucible mass have greenish coloration, crucible mass hydrated after a few days, boule was stable.

TABLE I (continued)

RUN #	IRIDIUM CRUCIBLE SIZE	COVER GAS	PULL & ROTATION RATES	RUN DURATION	OTHER RUN PERAMETERS	RUN RESULTS
23	3" X 3"	N_2	24 RPM .040"/hr.	8 days	$GdYSiO_5:Ce^{+3}$ melt Gd_2SiO_5 seed	Grew boule 82mm long by 31mm diameter, water white transparent mostly single crystal for first 62mm, remaining portion was fine polycrystalline, top portion of melt crystalline, boule showed some cleavage plane behavior.
24	3" X 3"	N_2	20 RPM .040"/hr.	9 days	$Mg_2SiO_4:Ti^{+3}$melt used Ir wire to seed	Seeded melt with iridium wire, good flow lines, no burn off or flashing of boule, 50mm long by 15mm diameter boule grown, boule cooled in contact with melt, central portion of melt crystallized in single crystal pieces, boule essentially colorless, central part of crucible mass also colorless but larger portion towards walls and bottom of crucible shot through with purplish coloration and mostly polycrystalline.

TABLE I (continued)

RUN#	IRIDIUM CRUCIBLE SIZE	COVER GAS	PULL & ROTATION RATES	RUN DURATION	OTHER RUN PERAMETERS	RUN RESULTS
25	3" X 3"	N_2	15 RPM	17 days	$Gd_2SiO_5:Ce^{+3}$ melt Gd_2SiO_5 seed-setup & pulled like YAG growth run	Seed broke off at seed holder after 1 day pulling, installed new seed and started pull again, started cooldown after only 6 days of growth because boule looked like it was undercutting, boule had to be cracked loose from frozen crucible mass, boule 105mm long by 30 mm diameter with strong cleavage planes.
26	3" X 3"	N_2	15 RPM .020"/hr	20 days	$Gd_2SiO_5:Ce^{+3}$ melt Gd_2SiO_5 seed-set up and pulled like YAG growth run.	Seed flashed overnight, redipped, boule pulled up 5 mm prior to cooldown, still embedded in crucible mass, cracked during extraction process, boule 157 mm long by 22 to 27 mm diameter, large pieces of water white transparent single crystal, strong cleavage.

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. It would be desireable to investigate other rare earth silicates to verify these wavelength shifts as well as to determine whether they exhibit the fracture plane behaviour of Gd_2SiO_5 or the tougher structure of Y_2SiO_5.

Another area which was only touched upon briefly in the research performed under this contract was that of other orthosilicate systems. Ti^{+3} or other dopants in Mg_2SiO_4 (Forsterite) and Cr^{+3} or other dopants in Al_2SiO_5 (Mullite) are potentially useful materials for future research. These systems may allow access to regions of the spectrum through their emmission which are not currently available.

Growth of single crystal boules of $Gd_2SiO_5:Ce^{+3}$, $GdySiO_5:Ce^{+3}$ and $Mg_2SiO_4:Ti^{+3}$ have been successfully undertaken during this contract. As well, growth of single crystal pieces of $Y_2SiO_5:Ce^{+3}$, and polycrystalline samples of $(Gd_{.9}La_{.1})_2SiO_5:Ce^{+3}$ and $(Gd_{.9}Lu_{.1})_2SiO_5:Ce^{+3}$ were successfully completed.

Large boules of Gd_2SiO_5 have been grown and there is no reason this cannot be done with the other rare earth silicates under the proper conditions. The goal now should be to to extend research into the other rare earth silicate systems as well as some non-rare earth silicate systems.

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