Growth and Characterization of Large Nd, Cr: GSGG Crystals for High-Average-Power Slab Lasers

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(Invited Paper)

Abstract—Nd, Cr: GSGG crystal boules up to 13 cm in diameter and 20.5 cm long have been grown by the Czochralski method. We identified several problems with Nd, Cr: GSGG growth, which we have solved separately but not all at once: spiral boule growth, dislocations, and fine scattering ("smoke"). In our grown crystals we have measured the following parameters, which will be relevant to their eventual use as gain elements for large slab lasers: optical homogeneity, birefringence, absorption loss at 1 μm, scattering loss, and iridium inclusions. The optical homogeneity of the boules is good, except for a radial gradient in refractive index of about 10⁻⁴ cm⁻¹. The birefringence is low (< 3 nm/cm) in slabs cut from the boules. Scattering losses measured on small samples are < 0.002 cm⁻¹; absorption losses in the boules range from 0.01 to 0.08 cm⁻¹. This absorption has been reduced to < 0.0025 cm⁻¹ in small samples using reducing heat treatments, but appropriate treatment conditions for full scale slabs have yet to be determined. Low iridium inclusion densities, < 0.01 cm⁻¹, have been demonstrated in isolated boules; at this inclusion density large gain elements which are entirely inclusion-free should be possible. Additional development is required in order to grow large crystals with the desired quality for laser operation.

INTRODUCTION

Gadolinium scandium gallium garnet (GSGG) co-doped with Nd and Cr is a new laser material with high efficiency in flashlamp-pumped lasers [1]-[8]. This efficiency (the ratio of laser energy out to energy delivered to the flashlamps), which is about 5 percent in small rod systems, arises from the efficient absorption of pump photons by Nd, Cr: GSGG because of Cr³⁺ sensitization. Nd, Cr: GSGG is two to four times more efficient in lasers than the well-known Nd: YAG [1], so it is the better laser material when system size and weight are important. Furthermore, it is easier to grow Nd, Cr: GSGG in large sizes than Nd: YAG, and it can be grown without an optically inhomogeneous central core; Nd: YAG contains a core as usually grown. GSGG boules therefore yield larger rods and slabs than Nd: YAG boules. For example, we have obtained GSGG slabs with dimensions 8 × 19 × 0.6 cm³; the largest Nd: YAG slabs are about 2.5 × 20 × 0.5 cm³.

Because of these advantages, Lawrence Livermore National Laboratory (LLNL) has chosen Nd, Cr: GSGG as a baseline material for developing and demonstrating improved solid-state laser technology [9]-[11]. Our goal is to obtain large, high-quality Nd, Cr: GSGG slabs and to use them in constructing 100-1000 W slab lasers whose beam quality is near the diffraction limit. In particular, we are attempting to grow crystals from which we can fabricate slabs with a 10 × 20 cm² pumped area. This article describes our growth experiments and our solution of the problems associated with scale-up of crystal size, and gives the results of our measurements of the various parameters that affect the ability of these crystals to serve in the slab lasers we envision.

Short History of Nd, Cr: GSGG

Gadolinium scandium gallium garnet (Gd, Sc, Ga, O₁₂) is a member of the garnet family, whose molecular formula is Ca₃Al₂O₁₂ [12]. The C ion is in a relatively large, dodecahedrally coordinated site, called the c-site; the A ion is in the octahedrally coordinated a-site; and the D ion is in the tetrahedrally coordinated d-site. In those garnets in which C is a rare earth, Nd can be substituted for it. Chromium can be substituted for the A ion. The stoichiometric rare earth scandium garnets were first studied by Kotta [13] at Bell Laboratories as candidate substrate materials for magnetic bubble memory devices. Crystal growth of scandium garnets was first reported by Brandle et al. [14].

Neodymium-doped GSGG was first studied by Kamenskii et al. [15] in 1975. In 1982 Struve et al. [16] demonstrated laser action in Cr-doped GSGG. Shortly thereafter, Beimowski et al. [17] and Pruss et al. [18] reported efficient sensitization by Cr³⁺ of Nd³⁺ laser action in GSGG. Chromium, because of the breadth of its broad absorption bands, absorbs pump photons over a wider spectral range than Nd³⁺; the energy absorbed by the Cr³⁺ transfers, via a nonradiative process, to Nd³⁺. The measured efficiency of this transfer is 85-90 percent [19]. Stimulated by this observation, several researchers tested lasers using Nd, Cr: GSGG and found efficiencies of about 5 percent from laser rods 6 mm in diameter and 75 mm long [1]-[8].
In some possible space applications, the laser may be exposed to $\gamma$ radiation and to high energy particles. The radiation hardness of Nd,Cr:GSGG is therefore of interest. In 1984, Zharikov et al. [20] demonstrated that Nd,Cr:GSGG laser performance is unaffected by UV or $^{60}$Co $\gamma$ irradiation up to 10 Mrad, in contrast to Nd:YAG laser output, which drops by an order of magnitude after 1 Mrad $\gamma$-ray exposure. Subsequently, Smith and Shinn [21] determined that a 1-Grad $\gamma$-ray exposure decreases the output from a Nd,Cr:GSGG rod laser by no more than 5 percent. Ashurov et al. [22] showed that both Nd and Cr in GSGG are necessary to avoid solarization by $\gamma$-irradiation. Irradiation by 100 Mrad of 25 MeV protons or by 18 Mrad of 2 MeV electrons does not produce solarization in Nd,Cr:GSGG [23]. Thus Nd,Cr:GSGG is a radiation-hard laser material, which makes it more desirable than Nd:YAG for the space environment. Furthermore, Danileiko et al. [24] reported that GSGG has a high threshold for laser damage, which remains high even after $\gamma$-ray doses up to 100 Mrad.

In 1986 Krupke et al. [25] compiled measured values of Nd,Cr:GSGG properties. Using this compilation, Stokowski [26] showed that the spectroscopic and thermo-mechanical properties of Nd,Cr:GSGG make it a better laser material than Nd:YAG for use in large, efficient laser systems.

Progress in crystal growth techniques proceeded in parallel with Nd,Cr:GSGG laser development. In 1984, under contract to LLNL, four companies (Allied-Signal, Litton Airtron, Material Progress, and Union Carbide) grew Nd,Cr:GSGG crystals about 3.5 cm in diameter for laser tests and material characterization [27]-[29]. Based on the experience gained in this program and on the existing technology for growing large, undoped GGG crystals for magnetic bubble memory substrates, we decided that it should be possible to grow GSGG boules more than 10 cm in diameter. Such a boule could yield a $10 \times 20 \times 1 \text{ cm}^3$ gain element, which, used in a slab laser, could produce an average power of 1 kW. We therefore decided to develop the technology for growing large Nd,Cr:GSGG crystals.

**Nd,Cr:GSGG Program Outline**

To use Nd,Cr:GSGG effectively in a large slab laser system, we needed to grow large boules of high optical quality, develop a satisfactory finishing process, and develop claddings for the slab edges and evanescent-wave coatings for the large slab faces. The key optical quality requirements for a laser crystal are small wavefront distortion ($\lambda/10$), low birefringence ($<3 \text{ nm/cm}$), low absorption coefficient ($<10^{-3} \text{ cm}^{-1}$) around 1 $\mu$m, and no iridium inclusions. (In the boule, an inclusion density of $<0.01 \text{ cm}^{-3}$ can be tolerated.) Our initial goal was growth of 13 cm diam cylinders, which could yield several 10 cm wide slabs. We encountered several problems, which we describe in the next section. To reduce the cost and time for additional experiments, we decreased the target boule diameter to 9.5 cm. This phase of the program yielded crystals usable in a laser (Fig. 1) and gave us considerable information on the scaling of Nd,Cr:GSGG crystal growth.

A study of polishing compounds and laps showed that the anatase form of TiO$_2$, suspended in a colloidal solution of SiO$_2$, is best for producing smooth ($3 \text{ Å rms}$ roughness) surfaces on GSGG at reasonable removal rates (100 $\mu$m/h) [30]. Low subsurface damage can be realized by removing enough material at each grinding step to eliminate subsurface damage from the previous grinding step [31], [32]. Epitaxial coatings to provide resistance to abrasion and to water exposure for surfaces of materials with high fracture strength are also being studied [33].

Absorbing glass edge claddings on laser gain elements are required to reduce energy losses resulting from amplified spontaneous emission (ASE) or parasitic oscillations. The cladding must absorb 1.06 $\mu$m light, match the refractive index and thermal expansion of the laser material, and not fracture under high thermal loadings. As part of this program, glass edge claddings were developed for GSGG [34]; crystalline claddings are being studied. Silicon dioxide, deposited by electron beam evaporation on GSGG, is being studied as an evanescent wave coating. Such coatings are necessary on the large slab faces of high-average-power lasers to prevent phase perturbations due to refractive index fluctuations in the cooling fluid.

**Czochralski Growth of Garnets**

In growing Nd,Cr:GSGG, we based our work on a sizable body of information and experience in growing gadolinium gallium garnet, Gd$_3$Ga$_5$O$_{12}$ (GGG) [35]-[39], which is grown commercially in 10 cm diam $\times 25$ cm boules for magnetic bubble memory substrates. These boules must be nearly dislocation-free and must have an iridium inclusion density no greater than about 0.1 $\text{ cm}^{-3}$. They are grown by the Czochralski technique [35], in which the boule is pulled from its melt (Fig. 2). The melt is contained in a crucible, which is most commonly made of iridium if the crystal to be grown is a high-melting-point oxide. An induction coil heats the crucible, which is insulated by a zirconia ceramic furnace. During growth the crystal is rotated about its axis; this averages azimuthal variations in temperature and pumps the melt, thereby increasing mixing.

Two variations of the Czochralski technique are used in oxide-crystal growth; they are known as the "deep-interface" and "flat-interface" techniques, from the shapes of the solid/melt interface during growth. In deep-interface growth the interface is a cone, with a half-angle of about 30 to 45°, that projects into the melt. Because the interface covers a large range of crystallographic orientations, it may become faceted. (The facet planes in oxide garnets are generally [211] and [110]; the crystal growth axis is generally [111].) The crystal material grown on a facet has a slightly different composition and lattice constant from that grown off-facet [40]. Stresses
Fig. 1. Section of a Nd,Cr: GSGG crystal 9.5 cm diam \times 19.5 cm in length grown by the Czochralski method.

Fig. 2. Schematic diagram of a Czochralski system, showing the natural convection cell due to buoyancy-driven flow and the forced-flow cell due to centrifugal pumping by crystal rotation.

and refractive index gradients result from this difference, and substantial birefringence occurs around the facet boundaries [41]. The resulting optical distortion is readily visible to the naked eye and lies along the boule axis. Because of the presence of this so-called core, the largest width that can be cut from a deep-interface crystal is less than 40 percent of the boule diameter. All commercial Nd: YAG is grown with the deep-interface technique.

In the flat-interface method, generally used in growing Nd,Cr:GSGG and GGG, faceted growth does not occur, except perhaps on the boule periphery. When the boule grows along the \langle 111 \rangle crystal axis, the nearest \langle 211 \rangle facets are at an angle of 19.5° away from the \langle 111 \rangle direction. As long as the normal to the interface makes an angle less than 19.5° with the growth axis, no faceting will occur. Flat-interface boules are core-free, so almost the entire cylinder diameter is available for fabricating laser gain elements.

For a given garnet composition, the nature of the growth that takes place (that is, deep- or flat-interface) is primarily determined by the flow conditions in the melt [42], [43]. Melt flow is driven by both natural and forced convection. In the annular natural convection cell in a Czochralski system (Fig. 2), melt material flows up along the crucible wall and down in the center. Opposing this flow is the forced convection cell pumped by crystal rotation. The strength of this flow increases with crystal rotation rate and diameter.

At low crystal rotation rates, natural convection dominates and the isotherms have a dip in the center of the melt. The crystal/melt interface is then convex, and deep-interface growth occurs. The depth of the interface is increased to the extent that radiative heat transfer through the crystal can occur.

At high crystal rotation rates the forced convection cell dominates the flow at the interface. The hotter melt material flowing up at the center flattens out both the isotherms and the melt/crystal interface. Depending on the rotation rate, there may be a small region near the boule periphery where the natural and forced convection cells converge. Conical interface growth occurs outside this region. Fig. 3, showing an axially cut slab of Nd,Cr: GSGG in a polariscope, illustrates this condition. The growth striations made visible in this way indicate the interface shape at various times during crystal growth.

The general procedure for growing oxide crystals by the Czochralski method is as follows. Powdered raw materials are blended and compressed hydrostatically at about 100 MPa (15000 psi). In some cases they are then dehydrated by heating to 1000°C in a dry nitrogen atmosphere. The charge is melted in the crucible and the temperature at the center of the melt surface is raised to several degrees above the melting point, which is 1860°C for GSGG. A seed crystal is lowered to contact the melt center, and growth begins.

A good “start” is necessary for growing a high-quality crystal; the nature of the start depends sensitively on the melt temperature. If the temperature is too high, the seed rod end will melt and de-wet, or “burn off,” and lose contact with the liquid. If the temperature is too low, rapid crystallization, or “flash-out,” occurs around the seed, and the resulting crystal contains bubbles and second-phase inclusions.
Once a good start is obtained, the shape of the growing boule is generally determined by a computer controller. Control is provided by feedback loops that use furnace power and crystal weight as process variables. The control program gently brings the boule out to full diameter. In this phase the boule is grown with a deep interface so as to remove dislocations that may have formed during the start.

A transition from deep-interface to flat-interface growth, which is commonly called the "interface-flip," is made as the diameter approaches the desired value. Growth at full, constant cylinder diameter then begins. There are two methods for achieving this transition. One, called the "natural flip," depends on the increasing strength of the forced convection as the boule diameter increases. The boule rotation rate is set at a constant value chosen so that the interface change occurs spontaneously near full diameter. In the alternative technique, called the "artificial flip," the rotation rate is kept low until the boule diameter reaches about 80 percent of the desired value. The rate is then increased, over a few minutes, to a value that drives the interface flat.

When the boule has grown to the desired length, it is lifted clear of the melt and cooled over 10-40 h by a programmed decrease in the power applied to the inductively heated crucible.

**Nd, Cr: GSGG Growth Experiments**

Commercial producers grow 10 cm diameter by 25 cm long GGG boules with no dislocations and with iridium inclusion densities below 0.001 cm$^{-3}$ [44]. Growth of Nd, Cr: GSGG is complicated by the dopants and by the additional crystal constituent (Sc$_2$O$_3$). Nonunity segregation coefficients of the dopants can cause solidification instability of the growth interface due to dopant rejection [39]. (The segregation coefficient of a dopant is defined as the ratio of its concentrations in the crystal and the melt.) Radiative transport within the melt and the crystal boule is inhibited because of Cr and Nd absorption. The dopant and impurity concentrations in the final crystal depend on the crystal growth rate; fluctuations in this rate arising from melt flow and temperature fluctuations will result in striations in the boule. Radial segregation of the dopants may also occur. Finally, the melting point of GSGG is 100°C higher than that of GGG.

The initial work on Nd, Cr: GSGG in 1984 [27]-[29] identified the major problems we encountered in scaling up Nd, Cr: GSGG growth: spiral growth, absorption loss at 1 μm, iridium inclusions, and strong birefringence due to dislocations were observed. These problems are to some extent interrelated. At small scale, they are not a fundamental obstacle: we grew 3.5 cm diam flat-interface sections of Nd, Cr: GSGG that exhibit generally excellent optical quality. A few representative runs are noted in Table 1.

We began these and subsequent GSGG growth experiments using conditions typical for growing GGG. After slight modifications as our work proceeded, we generally used a furnace atmosphere of about 2 percent oxygen in dry nitrogen, a boule pull rate of 1.5 mm/h, and rotation rates of 10-20 rpm. The melt fractions crystallized were between 30 and 40 percent.

The raw materials were high-purity powders of the oxide constituents. The purities were: gadolinium oxide, 99.999 + percent; gallium oxide, 99.9999 percent; scan-
dium oxide, 99.995 percent. High-purity scandium oxide was initially difficult to obtain in the desired quantities. Before the GSGG application started, the entire United States consumption of scandium oxide was less than 5 kg/yr; we are currently using 20–25 kg/yr. Under contract to LLNL, Ames Laboratory (Ames, IA) is providing Sc2O3 for our work, using the ion exchange method [45]. They have purified some lots of Sc2O3 to better than 99.999 percent.

The desired crystal diameter and length determine the crucible size needed in the growth system. Our initial target was a cylindrical crystal 13 cm in diameter and 21 cm long, from which several laser plates 10 × 20 × 1 cm could be fabricated. Based on the estimated boule weight of 21 kg and a 42 percent melt fraction crystallized, the required crucible size was calculated to be 23 cm (9 in) diam × 23 cm high. The results of growth runs made using this crucible are summarized in Table II.

The target crystal size was later reduced to 9.5 cm diam × 20 cm long, using a crucible 19 cm (7.5 in) in diameter. We made this change to solve more cost effectively some of the problems encountered during growth runs in the 23 cm crucible. The results of runs with this smaller crucible are summarized in Table III.

A crystal of uniform composition throughout its length can only be grown from a melt that has the so-called congruent melting composition. When this composition is used in the melt, the composition at the melt/crystal interface remains stable even when the growth rate fluctuates because of fluctuations in melt flow or temperature. This minimizes growth striations and the tendency toward constitutional supercooling, and results in better crystal quality. Under contract to LLNL, Fratello, Brandle, and Valentino [46] at AT&T Bell Laboratories determined that the GSGG congruent melting composition is Gd2.95Sc1.903Ga3.13O12. We used this composition in growth runs starting with run 478. With Nd and Cr dopings of 2 × 10²⁰ and 1 × 10²⁰ cm⁻³, respectively, Nd replaces 0.05 formula units of Gd and Cr replaces 0.025 formula units of Sc. The lattice constant of the crystal grown in run 478 was 12.560 Å (at both ends of the boule), in good agreement with the measurements of Fratello et al.

We encountered several problems in scaling up Nd,Cr:GSGG growth. These included 1) spiral boule morphology, 2) absorption loss at 1 μm, 3) iridium on the melt surface, 4) iridium inclusions in the crystal, 5) boule cracking, 6) dislocations, and 7) fine scattering, or “smoke.” We have demonstrated separate solutions to each of these problems; now we must bring all these solutions together so that we can reliably produce large, high-quality Nd,Cr:GSGG boules. We consider each of these problems in turn.

**Spiral Morphology**

More than a decade ago growers of GGG noticed that boules occasionally grew in a spiral or corkscrew form rather than the desired cylindrical form [35]. Usually the spiral would be preceded by an azimuthal asymmetry, which has the appearance of a “foot.” (Such a foot is shown at the bottom right of the boule in Fig. 4.) A related phenomenon, the flash-out/burn-off instability, is observed in attempting to start growth in melts with a strong tendency to acentric growth. After the seed crystal is dipped it de-wets or grows rapidly, depending on the melt surface temperature. There appears to be no temperature that gives stable growth at the seed diameter. Further growth attempted after flash-out will lead rapidly to foot formation and partial de-wetting. This problem is more acute in larger Czochralski systems, presumably because of lower thermal gradients at the growth interface. More or less by accident, it was discovered that adding 20–40 ppmw Ca to the melt suppressed acentric growth [47]. Other divalent ions, such as Mg, Sr, Mn, and Ni, are also effective.

In contrast to the effect of divalent ions, Brandle et al. [48] and we (Run 178, Table I) found that the tetravalent ions Si and Zr in the melt markedly increase the tendency of GSGG boules to spiral. Other tetravalent impurity ions, such as Th (a common tetravalent impurity in Sc2O3), may also have this effect.

The mechanism of acentric growth is not known with certainty. There are two main theories. In one theory, suggested by Fratello et al. [49], the spiraling tendency is dependent on the number density of uncompensated tetravalent species in the melt. These ions form com-

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Dopants (ppmw)</th>
<th>Fraction Crystallized (percent)</th>
<th>Cylinder Length (cm)</th>
<th>Spiral or Foot?</th>
<th>Absorption at 1061 nm (cm⁻¹)</th>
<th>Cracked?</th>
</tr>
</thead>
<tbody>
<tr>
<td>172</td>
<td>0</td>
<td>39</td>
<td>10</td>
<td>No</td>
<td>0.001</td>
<td>No</td>
</tr>
<tr>
<td>174</td>
<td>0</td>
<td>34</td>
<td>8</td>
<td>Yes</td>
<td>0.002</td>
<td>No</td>
</tr>
<tr>
<td>175</td>
<td>80 Sr</td>
<td>34</td>
<td>8</td>
<td>No</td>
<td>0.0035</td>
<td>No</td>
</tr>
<tr>
<td>176</td>
<td>120 Sr</td>
<td>35</td>
<td>8</td>
<td>No</td>
<td>0.005</td>
<td>During slicing</td>
</tr>
<tr>
<td>177</td>
<td>120 Sr, 80 Ce</td>
<td>36</td>
<td>8</td>
<td>No</td>
<td>0.0025</td>
<td>During slicing</td>
</tr>
<tr>
<td>178</td>
<td>160 Zr</td>
<td>19</td>
<td>4</td>
<td>Yes</td>
<td>—</td>
<td>No</td>
</tr>
<tr>
<td>179</td>
<td>160 Zr, 88 Ca</td>
<td>39</td>
<td>10</td>
<td>No</td>
<td>high</td>
<td>No</td>
</tr>
<tr>
<td>182</td>
<td>75 Ca, 300 Ce</td>
<td>44</td>
<td>11</td>
<td>No</td>
<td>0.001</td>
<td>No</td>
</tr>
</tbody>
</table>

*Nd: 2 × 10²⁰ cm⁻³, Cr: 2 × 10²⁰ cm⁻³. Boule diameter: 3.5 cm. Pull rate: 1.5 mm/h. Rotation rate: 40–50 rpm.
TABLE II
GSGG GROWTH RUNS FROM 23 cm DIAMETER CRUCIBLE*

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Dopants (ppmw)</th>
<th>Rotation Rate (rpm)</th>
<th>Fraction Crystallized (percent)</th>
<th>Cylinder Length (cm)</th>
<th>Spiral or Foot?</th>
<th>Top*</th>
<th>Bottom*</th>
<th>Cracked?</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>468</td>
<td>80 Sr</td>
<td>—</td>
<td>0</td>
<td>0</td>
<td>Yes</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Flashed out at start</td>
</tr>
<tr>
<td>469</td>
<td>66 Ca</td>
<td>18</td>
<td>32</td>
<td>18</td>
<td>No</td>
<td>1.4</td>
<td>2</td>
<td>No</td>
<td>Undoped, 4.5 mm/h pull</td>
</tr>
<tr>
<td>470</td>
<td>75 Ca</td>
<td>12.5</td>
<td>32</td>
<td>18</td>
<td>Yes</td>
<td>0.16</td>
<td>0.19</td>
<td>Yes</td>
<td>Nd,Cr doped</td>
</tr>
<tr>
<td>471</td>
<td>87 Ca, 300 Ce</td>
<td>18</td>
<td>30</td>
<td>16</td>
<td>Yes</td>
<td>11</td>
<td>—</td>
<td>Yes</td>
<td>Ce added</td>
</tr>
<tr>
<td>472A</td>
<td>87 Ca, 300 Ce</td>
<td>20</td>
<td>12</td>
<td>8</td>
<td>Yes</td>
<td>11</td>
<td>—</td>
<td>Yes</td>
<td>11 cm diameter</td>
</tr>
<tr>
<td>472B</td>
<td>87 Ca, 300 Ce</td>
<td>20</td>
<td>26</td>
<td>14</td>
<td>No</td>
<td>0.008</td>
<td>0.05</td>
<td>Yes</td>
<td>Run stopped due to swinging about rotation axis</td>
</tr>
<tr>
<td>473</td>
<td>97 Ca, 440 Ce</td>
<td>20</td>
<td>22</td>
<td>11</td>
<td>No</td>
<td>0.008</td>
<td>0.05</td>
<td>—</td>
<td>Ended at 1 cm due to swinging</td>
</tr>
<tr>
<td>474</td>
<td>97 Ca, 440 Ce</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Crucible leaked</td>
</tr>
<tr>
<td>475</td>
<td>125 Ca, 500 Ce</td>
<td>9 to 20</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Many starts unsuccessful due to iridium on melt surface</td>
</tr>
<tr>
<td>476</td>
<td>200 Ca, 500 Ce</td>
<td>10</td>
<td>14</td>
<td>11</td>
<td>No</td>
<td>0.002</td>
<td>—</td>
<td>Yes</td>
<td>Run stopped due to excessive iridium</td>
</tr>
<tr>
<td>477</td>
<td>200 Ca, 500 Ce</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Crucible leaked, Water in system reduced to &lt;5 ppmw</td>
</tr>
</tbody>
</table>

*Nd:2 × 10^19 cm⁻³, Cr: 1 × 10^20 cm⁻³. Boule diameter: 13 cm. Pull rate: 1.5 mm/h.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Dopants (ppmw)</th>
<th>Rotation Rate (rpm)</th>
<th>Iridium</th>
<th>Fraction Crystallized (percent)</th>
<th>Cylinder Length (cm)</th>
<th>Spiral or Foot?</th>
<th>Top*</th>
<th>Bottom*</th>
<th>Treated*</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>478</td>
<td>75 Ca, 300 Ce</td>
<td>12</td>
<td>Heavy</td>
<td>31</td>
<td>16</td>
<td>No</td>
<td>0.019</td>
<td>0.061</td>
<td>0.0025</td>
<td>Ir inclusions in first 5 cm which was deep interface</td>
</tr>
<tr>
<td>479</td>
<td>62 Ca, 270 Ce</td>
<td>16 → 9.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.01</td>
<td>0.08</td>
<td>0.0025</td>
<td>Rotation rate decreased</td>
</tr>
<tr>
<td>480</td>
<td>62 Ca, 240 Ce</td>
<td>16 → 9.7</td>
<td>0.1 cm⁻³</td>
<td>36</td>
<td>19.5</td>
<td>Yes</td>
<td>0.021</td>
<td>0.049</td>
<td>—</td>
<td>Spiral starting at end Smoke, heavy on bottom 5 cm 20 percent CO₂, in N₂ atmosphere</td>
</tr>
<tr>
<td>481</td>
<td>62 Ca, 220 Ce</td>
<td>18 → 12</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Crucible lift implemented. Generator shutdown terminated the run</td>
</tr>
<tr>
<td>482</td>
<td>65 Ca, 325 Ce</td>
<td>18 → 10</td>
<td>High</td>
<td>38</td>
<td>16</td>
<td>Yes</td>
<td>0.02-0.03</td>
<td>0.02-0.025</td>
<td>0.025</td>
<td>Crucible lift induced higher temperature gradients. Ir coated foot formed after particulate material fell into melt</td>
</tr>
</tbody>
</table>

*Nd:2 × 10^20 cm⁻³, Cr: 1 × 10^20 cm⁻³. Boule diameter: 9.5 cm. Pull rate: 1.5 mm/h.

Top refers to a crystal section just below the interface flip.

Bottom refers to a section near the boule end.

plexes that are rejected by the growing crystal and then interfere with further crystal growth, causing instability. If this mechanism were at work, one would expect a correlation between the occurrence of acentric growth and other phenomena characteristic of growth from incongruent melts, such as constitutional supercooling and/or multiple solid phases. No such correlation is observed.

One of the present authors (Morris) suggests the following explanation for acentric growth, based on Marangoni flow (fluid flow driven by gradients of surface ten-
dissolved quietly. These results are consistent with the picture of an unstable surface resulting from Ga depletion, as described above. The induced flow is vigorous and undoubtedly contributes substantially to convective thermal transport in the near-surface region. The depth affected is probably about the same as the lateral extent of the flow cells, which is roughly 0.5-1 cm.

Anticipating the additional possibility of surface-driven or Maragoni flow in the meniscus region where the melt contacts the periphery of the boule, we have made preliminary measurements of the effects of tetravalent (Zr\(^{4+}\)) and divalent (Ca\(^{2+}\)) impurities on the surface tension of GSGG melts. In these measurements, the details of which will be published separately, the addition of 160 ppmw Zr to a GSGG melt caused an approximate 33 percent increase in the surface tension force on a 6 mm diam iridium rod suspended in a GSGG melt. Subsequent addition of 88 ppmw of Ca to the same melt reduced the force to a value approximately 15 percent above its original value.

On the basis of these results, and assuming less-than-unity distribution coefficients for surface-active impurities, one would expect surface tension gradients and resulting surface-driven flow at the intersection of the meniscus with the diffusion boundary layer immediately adjacent to a growing crystal. In the case of an impurity such as Zr\(^{4+}\), which increases surface tension and whose distribution coefficient is less than unity [51], [52], the resulting surface flow would be toward a growing crystal and away from a melting crystal.

One would further expect significant interactions between the surface flow in the meniscus and the turbulent flow in the main melt nearby. To the extent that the crystal-pumped flow cell rotates nearly as a solid body with the crystal, localized self-sustaining regions of either rapid radial growth or melt-back may result from this interaction. While certainly not proven, this mechanism for acentric growth and for related phenomena such as the flash-out/burn-off instability is consistent with experimental observations. The matter should be investigated further.

One experimental observation relevant to this discussion is illustrated in Fig. 4, which shows a polariscope view of an axially cut section through a Nd,Cr:GSGG crystal in which the growth interface striations are visible. When this crystal began to experience mild acentric growth in its lower portion, it was abruptly removed from the melt, so that its lower boundary is the growth interface as it existed during the acentric growth. This interface is clearly not parallel to the interfaces that existed earlier in the growth: the side of the crystal that was growing radially outward (bottom right in Fig. 4) was closer to the melt surface than the edge on the undercutting (inward-growing) side (bottom left in Fig. 4). This indicates that the acentric growth resulted directly from a distortion of the melting point isotherm in the system.

Spiraling is generally less common in small-crucible systems, although the addition of Si to the melt causes spiraling even in small crucibles [48]. In larger crucibles,
acentric growth commonly occurs unless Ca or another divalent ion is added. It is significant, we believe that thermal gradients in the vicinity of the growing crystal are lower in large systems than in small systems. For example, in the 23 cm crucible, with no crystal present, the radial temperature gradient at the melt surface was 3°C/cm; the corresponding gradient in the 7.5 cm crucible was 15°C/cm. We believe that these low gradients tend to destabilize growth in the larger systems. Thermal gradients also decrease as the melt level in the crucible drops, because the melt surface sees more and more of the hot crucible wall, which reduces surface cooling. Thus growth may be stable at the start of a run but may degenerate into spiral growth later. This occurred in runs 479 and 480, for example: they developed acentric growth at boule lengths of 20.5 and 19.5 cm, respectively.

One way to maintain thermal gradients as the melt level drops is to lift the crucible relative to the induction coil [53]. If this is done there is less heating of the crucible wall above the melt surface, so that the cooling rate at the melt surface is increased. We lifted the crucible in runs 481 and 482 (Table III). In run 481 we raised the crucible so as to keep the melt surface at a constant height with respect to the induction coils. The induction power generator shut down at a boule length of about 15 cm because of circuit detuning. In run 482 we raised the crucible at half the rate of the melt surface drop. The boule reached a length of 16.5 cm before surface iridium initiated acentric growth.

Two observations indicate that lifting the crucible maintains the thermal gradient, so that the technique should allow us to grow long garnet crystals. First, the generator power remained almost constant during run 482; without crucible lift generator power usually drops by about 10 percent. Second, the crystal produced in run 482 does not have faceting on its side, which usually occurs toward the end of growth runs without crucible lift.

If the tendency to spiral growth increases as the thermal gradient at the crystal periphery decreases, it should be possible to suppress this instability with a redesigned Czochralski system in which the thermal gradient were higher than in the standard system. This would eliminate the need to add a divalent ion to the melt. This approach is beyond the state of the art in large-crystal growth, however, and we continue to resolve the spiraling problem by using Ca additions in the GSGG melts, combined with crucible lift.

1 μm Absorption Loss

Soon after Nd,Cr:GSGG was identified as an efficient laser material, it was noted that it sometimes exhibited absorption loss near 1 μm [54], with an absorption coefficient as high as 2 cm⁻¹ at the 1061 nm laser wavelength. We have determined that this absorptive defect, or center, has three absorption bands, as shown in Fig. 5. Caird et al. [1] reported that the absorption coefficient (and the concentration of the center) is proportional to the calcium concentration in GSGG. Brandle et al. [48] found that Mg also causes 1 μm absorption loss: the absorption spectrum of this center in Mg-doped Cr:GSGG is identical to that in Ca-doped Cr:GSGG. We have found a similar absorption spectrum in YAG doped with Ca and Cr.

In a careful study of the effects of divalent and tetravalent ionic additions to Cr:GSGG melts, we, in collaboration with Brandle et al., have determined the following facts regarding the 1 μm absorptive center.

1) The center appears in GSGG and GGG only when they contain Cr.
2) The divalent ions Ca and Mg cause this center to appear. Its concentration is approximately linearly dependent on the divalent ion concentration; Fratello et al. [49] describe a more accurate functional dependence, derived from a chemical model.
3) Tetravalent ions, in particular Si or Zr, decrease the 1 μm absorption loss.
4) Lower partial pressures of oxygen in the Czochralski system during GSGG growth result in lower 1 μm absorption loss.
5) The absorption is very strong, implying a high oscillator strength for the optical transitions of the center. For example, the absorption coefficient at 1044 nm is greater than 30 cm⁻¹ when 600 ppmw equivalent of Ca is added to a Cr:GSGG melt.

We note that divalent and tetravalent ions in the gallium garnet melts have opposite effects on 1 μm absorption loss and boule spiraling. A better understanding of the absorbing center and its chemistry in GSGG has led us to a solution of this problem. A model of the absorbing center that appears to explain the experimental observations is Cr⁴⁺ substituting for Ga in a tetrahedral site. (As pointed out earlier in this article, Cr is normally trivalent and substitutes in the octahedral Sc site.) In our model Cr⁴⁺ forms to compensate divalent impurities such as Ca and Mg. In the absence of Cr, these divalent ions are presumably compensated by oxygen vacancies. The spectrum of the 1 μm absorbing center (Fig. 5) is consistent with that expected for Cr⁴⁺, which has two 3d electrons. In cubic symmetry three major absorption bands are expected [55], but these bands will be split in the S₄ symmetry of the garnet tetrahedral site. We can
explain the high oscillator strength of the Cr$^{4+}$ transitions only if the ion is in the tetrahedral site, which is noncentrosymmetric. The spectroscopy of Cr$^{4+}$ will be analyzed in a separate publication.

This model suggests a way to overcome the spiral/1 μm absorption problem. We can suppress the tendency for Cr$^{4+}$ formation by adding another ion to compensate divalent impurities. This ion should have a lower ionization energy in its trivalent state than that of Cr$^{4+}$. Ions that meet this condition include Ce$^{3+}$, Ti$^{3+}$, and Fe$^{3+}$. We discarded Fe as a candidate because the only absorption band of Fe$^{3+}$ in an octahedral site is near 1 μm. To test the effects of CeO$_2$ and TiO$_2$ we added them separately to small GSGG melts containing 2 × 10$^{20}$ cm$^{-3}$ Cr and 50 ppmw Ca. In both instances the 1 μm absorption band was absent when Ce or Ti concentrations were above threshold values of about 200 and 50 ppmw, respectively. Because of this favorable result, and because it was known that Ce does not promote boule spiraling [56], we chose to add CeO$_2$ to the large GSGG melts.

Subsequently, Brandle et al. [48] have found that TiO$_2$ does not cause spiraling. For future Nd:Cr:GSGG growth, we may add TiO$_2$ rather than CeO$_2$ to the melts because Ti$^{3+}$ has low absorption loss in the visible, whereas Ce$^{3+}$ has major bands at 440 and 350 nm.

To check on the effectiveness of Ce in preventing 1 μm loss without affecting laser performance, we grew the 3.5 cm diameter boule 182 (Table I) with 75 ppmw Ca and 300 ppmw Ce concentrations in the melt. The crystal grew to 11 cm long or 44 percent of the melt without a spiral, and the 1 μm loss was 0.001 cm$^{-1}$. Our measurements of 1 μm loss in Ca, Cr-doped GSGG indicate that the 1 μm loss would have been 2 cm$^{-1}$ without the added Ce. This crystal was fabricated into laser rods 6 mm diam × 75 mm long, whose efficiency was as high as that of rods without the Ca and Ce additions. This high efficiency was somewhat surprising, because we found that Ce$^{3+}$ does not transfer its absorbed energy to Nd$^{3+}$.

In the 9.5 and 13 cm GSGG crystals we find that there is some residual 1 μm absorption loss due to Cr$^{4+}$ even with Ce added to the melt. This residual absorption loss can be removed by heating the crystals in a reducing atmosphere. We reason that the remaining Cr$^{4+}$ is removed by the addition of oxygen vacancies, which compensate Ca$^{2+}$ instead of Cr$^{4+}$.

Fig. 6 shows the elimination of the 1 μm band resulting from heating a sample to 1300°C, in a platinum container, in a 1:1 atmosphere of CO and CO$_2$. We find that changes in the absorption loss occur for temperatures above 1000°C and for oxygen partial pressures below 10$^{-10}$ atm. We now use atmospheres of 0.1 to 1 percent H$_2$ in argon and temperatures above 1200°C to reduce 1 μm absorption loss.

Two related complications can result from heat treatment. We have produced, in some cases, either smoke or “decorated” dislocations. Smoke could be a result of voids or second-phase particles with diameters less than 100 Å. We are attempting to identify the scatterers. We have also seen dislocations decorated by large (0.1 mm) voids, which arise from vacancies heterogeneously condensing on the dislocations.

An interesting sidelight is the use of the Cr$^{4+}$ center as a passive Q-switch, Zharikov et al. [57] found that the Cr$^{4+}$ absorption loss in GSGG is saturable; this property has been used for Q-switching [58] and mode-locking [59].

Iridium on the Melt Surface

At the high temperature at which GSGG growth takes place, volatile iridium oxide (IrO$_3$) forms by reaction of the iridium crucible with oxygen. With a 2 percent oxygen atmosphere the IrO$_3$ partial pressure is about 10$^{-3}$ atm. Substantial vapor-phase iridium transport therefore takes place; the iridium moves from the high-temperature crucible wall to the relatively lower-temperature melt and crystal surfaces, where iridium crystals can form and grow. If iridium transport is high, this surface iridium can interfere with the symmetric growth of the boule by distorting the liquid surface in the meniscus region.

We encountered severe problems with surface iridium in run 476: we terminated the run when iridium completely covered the melt surface near the crystal. We attribute the high iridium transport in this run to high water vapor concentration (about 50 ppmw) in the growth chamber. We decreased the water concentration to 5 ppmw, and surface iridium was not a problem in subsequent runs (478–481).

Iridium Inclusions

Iridium particle inclusions nucleate bulk damage within GSGG or GGG when exposed to 1064 nm laser fluences above 2–3 J/cm$^2$ with pulse durations of 9 or 50 ns [60]. Damage occurs because the small iridium particles absorb enough energy vaporize them; the resulting pressure is above the fracture limit of GSGG or GGG. The fractures created by the first damaging laser pulse, which are smaller than about 25 μm, grow with subsequent pulses. (Thresholds for laser damage can be obtained from Pitts’s calculations for a similar system, platinum particle in laser glass [61].) Fractures in the laser crystal cannot be toler-
ated because, in combination with the high thermal stresses present in laser operation, they lead to catastrophic failure by brittle fracture.

Commercial growers of GGG for magnetic bubble memory substrates have minimized iridium inclusions to increase their yield of good substrates. In production they achieve iridium particle densities below 0.001 cm\(^{-3}\). In our GSGG growth runs we have found iridium particle densities varying from 0.01 to 100 cm\(^{-3}\).

We suggest the following mechanism for iridium incorporation into the growing crystal. As described in the previous section, iridium particles form and grow on the melt surface because of vapor-phase transport. They are then entrained into the forced-convection cell and eventually attach to the growing interface. We believe that little iridium dissolves directly from the crucible into the melt, because the crucible wall grows thinner above the melt surface, but not below it. The results of run 482 support this picture. Boule 482 has a very high iridium particle density, except in the last 1.7 cm of growth. At the time that the iridium incorporation stopped, the boule had developed an iridium-caused foot. This foot appears to have swept out iridium particles from the melt surface, because it is solidly coated with iridium.

Uhrin [62] has suggested that a CO\(_2\) atmosphere might reduce iridium transport. The oxygen partial pressure in CO\(_2\) depends on the dissociation reaction of CO\(_2\), which depends on the temperature. For a 20 percent CO\(_2\) atmosphere, the oxygen partial pressure is 0.02 atm at 1850°C. In run 480 (Table III), in which we achieved our lowest number density (0.01 cm\(^{-3}\)) or iridium particles, we used an atmosphere of 20 percent CO\(_2\) in nitrogen.

**Boule Cracking**

The first two 13 cm diam GSGG crystals we grew were uncracked (Table II), but the next four 13 cm diam boules, and an 11 cm diam boule, fractured during cool-down. We believe that these fractures were caused by a combination of thermal stresses and grown-in stresses [63], [64]. Thermal stresses are high in a Czochralski system, even during cool-down, because the heat source (the crucible) is below the crystal, so that there is a substantial axial thermal gradient in the boule. The highest gradient occurs between 700 and 1000°C, where the thermal conductivity of the boule is at a minimum because radiative and conductive heat transport are both low.

The initial boule fractures occur in the cone section, the section where the grown-in stresses are high because of the transition from deep-interface to flat-interface growth, and where stress-raising mechanical defects such as voids are common. The maximum grown-in stress varies substantially from run to run, because each boule has a unique growth pattern in the cone section.

The only obvious common feature of the cracked boules is that they all contain Ce, whereas the first two 13 cm boules (uncracked) do not. This observation may be significant in light of later measurements, described below, that show both axial gradients in the Ce concentration.

To decrease thermal stresses we increased the cool-down time from 20 to 30 h, but were unable to obtain uncracked 13 cm boules. To further decrease the thermal stresses we decreased the boule diameter from 13 to 9.5 cm; thereafter, we were able to produce crystals that were uncracked or that contained only small cracks.

We believe that additional investigations will make it possible to eliminate cracking in 13 cm diam Nd,Cr:GSGG crystals.

**Dislocations**

Dislocations arise from defects in the crystal, such as voids, iridium inclusions, and second-phase inclusions [65], [66]. These defects result from interface breakdown that results from rapid growth. They commonly originate when growth initiates on the seed and during the "flip" from a convex to a flat interface.

Dislocations can be made visible by etching the crystal section in a mixture of phosphoric and sulphuric acids. For example, Fig. 7 shows the dislocation patterns observed in boules 478-480. At the top of the crystal we typically observe 20-200 dislocations over the full crystal diameter. Boules grown with an artificial flip typically have one-tenth as many dislocations as those grown with a natural flip. The dislocation density is higher at the bottom of the crystal than at the top, particularly when the density of iridium inclusions is high. We therefore believe that iridium inclusions cause dislocations in some cases.

Many dislocations propagate approximately normal to the growth interface [67]. With a convex interface, therefore, they will eventually reach the boule periphery, while in flat-interface growth they will remain within the crystal cylinder. It is thus imperative that dislocation formation at the interface flip be minimized, and that iridium inclusions be avoided. The interface flip must be well controlled to avoid interface breakdown. We have demonstrated our ability to do this with the artificial flip technique.

Dislocations have an associated stress field, which causes optical birefringence. Single dislocations generally do not cause detectable birefringence. When several dislocations form a bundle, however, the sum of the individual dislocation stress fields results in observable birefringence.

**Fine Scattering ("Smoke")**

We found high scattering loss in the one crystal grown in a CO\(_2\) atmosphere (run 480, Table III). The scattering, which makes the affected region look like smoke, presumably results from a great number of small voids (presumably 50-100 Å diameter) that are produced by condensation of cation and anion vacancies. The vacancy concentration can be very high at the GSGG melting temperature of 1860°C. In fact, in a recent X-ray analysis, Voloshina et al. [68] found that GSGG contains about 1 percent vacancies, a surprisingly high value. This value implies that the activation energy for vacancy formation is about 0.8 eV.
There is a critical range of temperature in which the rates of void nucleation and growth are both high enough to permit the formation of stable voids. Void nucleation occurs when a critical number of vacancies coalesce; this process depends on the vacancy diffusion rate, which decreases exponentially as temperature decreases. Void growth depends on the vacancy supersaturation, however, which increases as the temperature decreases. Thus at high temperatures void nucleation is probable, but the vacancy supersaturation is low, so voids do not grow; at low temperatures the nucleation rate is low, so few voids form even in the presence of high vacancy supersaturation. Our results with postgrowth heat treatment indicate that the critical range is 1200-1400°C for GSGG.

**Bole Quality**

We have characterized our Nd,Cr:GSGG crystal sections with respect to the following parameters, which are important in slab lasers: optical homogeneity, birefringence, absorption loss, scattering loss, and iridium inclusions.

**Optical Homogeneity**

Crystals 479 and 480 show a surprisingly high radial refractive index gradient, as evidenced by the "bull's-eye" interference fringes in Fig. 8. The index at the boule center is approximately $4 \times 10^{-5}$ higher than at the edge of the flat interface region. Suspecting that the index gradient is caused by gradients in the concentrations of the dopant ions, we measured the concentrations of Cr, Nd, and Ce$^{3+}$ in boule 479 at various radii. Our results, given in Fig. 9, show that all three concentrations decrease with distance from the center. The concentration gradients of the three dopants are in the same order as their segregation coefficients (0.96 ± 0.02 for Cr, 0.65 for Nd, and 0.2-0.3 for Ce). Crystals 478 and 480 show similar concentration gradients.

Comparing measured refractive indices of gallium garnets containing Nd or Ce with those of garnets not containing them [69], [70], we find that a 1 percent substitution of Nd or Ce increases the refractive index by approximately $2 \times 10^{-4}$. Using the nominal doping of these ions in these crystals, we calculate an index change of $2.8 \times 10^{-5}$, which is in reasonable agreement with the measured value of $4 \times 10^{-5}$.

An unexpected feature of the radial segregation of impurities is that the concentrations are highest in the boule center. We would expect no radial gradient at all in flat-interface growth if the melt flow near the interface were dominated by the forced pumping action of the rotating crystal, because the diffusion boundary layer would then be independent of radius. In deep interface growth (as in Nd:YAG) the dopant concentration is greatest in the boule center, because the natural convective flow from the boule periphery to the center enriches the boundary layer in the dopants.

Weakness in the crystal-pumped flow may account for
the observed sign of the gradients of radial dopant concentration. Model calculations by Derby [71] and others [72]-[74] suggest that this is the case. We then have two options for eliminating radial refractive index gradients: 1) increase the crystal rotation rate to strengthen the forced convection flow, or 2) use another dopant whose segregation coefficient is less than unity and that can compensate for the Nd and Cr effect on the refractive index. Either approach would represent a significant change in growth procedure or in materials, so that a substantial development effort would be required to reduce the radial index gradient. Meanwhile we will have to compensate for the gradient by external optical means or by figuring in optical fabrication, which should be straightforward because it is highly symmetric.

**Birefringence**

We measured the birefringence of our crystals in a polariscope using circularly polarized light. Fig. 10 shows photographs of boules 479 and 480 as seen in the polariscope. The threefold symmetry associated with the (111) crystallographic axis is obvious. The substantial birefringence near the boule periphery is due to the convex interface and the faceted growth in that region. Birefringence due to dislocation bundles is also evident. In cut slabs the birefringence values range from <3 to 8 nm/cm.

**Absorption Loss**

All the large Nd, Cr: GSGG crystals, as grown, have absorption loss around 1 μm. Fig. 11 shows the IR absorption spectrum of crystal run 479. It shows a 1 μm absorption band of a defect we call CR4’. We believe that this defect is Cr4+ in the tetrahedral site of the garnet crystal, but perturbed by a neighboring defect. For comparison Fig. 11 also shows a portion of the spectrum of the unperturbed Cr4+, which we call CR4. (Fig. 5 shows the full CR4 spectrum.) The CR4 center can be converted to CR4’ by exposing the sample to UV or blue light; CR4’ can be converted to CR4 by heating the sample above 200°C. Near 1 μm the CR4’ center absorbs less than CR4, so the minimum 1 μm absorption loss is obtained when CR4 is converted to CR4’. This could be accomplished by exposure to UV or to sunlight.

The tables give the absorption coefficients at 1061 nm for top and bottom slices of the as-grown crystals. Heat treatment in a reducing atmosphere reduced the 1061 nm absorption loss in small plates cut from boules 473, 478, and 479 to 0.0025 cm⁻¹ as measured spectrophotometrically. Using calorimetric methods [75], we found the absorption loss at 1064 nm of small heat-treated samples from boules 473 and 182 to be 0.0032 ± 0.0002 and 0.0029 ± 0.0003 cm⁻¹, respectively. However, scattering induced by the annealing process has presently precluded successful treatment of large slabs.

**Scattering Loss**

We have determined bulk scattering loss by the somewhat imprecise technique of subtracting measured absorption loss from measured total loss. Milanovich and Robel [76] determined the total loss coefficient of crystal samples from boules 473 and 182 with a cavity loss meter. This instrument measures the total loss of a sample by observing the change in decay time of a laser pulse injected into a cavity with and without the sample present. The total loss coefficients for samples from boules 473 and 182 are 0.0045 ± 0.0005 and 0.0060 ± 0.0003 cm⁻¹, respectively.

Subtracting the absorption loss contribution as measured by calorimetry (see the previous section), we obtain differences of 0.0013 ± 0.0007 and 0.0031 ± 0.0006 cm⁻¹ for runs 473 and 182, respectively. Some of this loss may due to surface scattering. We find high scattering loss (smoke) in boule 480. Smoke appears on a few planes in boules 478 and 479, but only in the convex growth region near the boule periphery and not in the central 8 cm of the cylinder.

**Iridium Inclusions**

There are iridium inclusions in all our grown crystals. While inclusion densities are generally low, they are high in the top 5 cm of boule 478 and almost all of boule 482.
Fig. 11. Infrared absorption spectra of CR4 and CR4' centers in a Nd:Cr::GSGG crystal that also contains Ce and Ca.

The best boule is 480, which (as already described) was grown in an atmosphere of 20 percent CO₂ in nitrogen: in most of this boule, the iridium concentration is 0.01 inclusions/cm³. Further tests must be conducted to confirm that CO₂ lowers iridium inclusion content. Iridium inclusions appear whenever the thermal system is strongly perturbed, as would result if particulate matter fell into the melt or if there were a power fluctuation. Clean, stable growth stations are therefore essential, and improvements to the present system along these lines are under consideration. In addition, we are investigating the chemistry of iridium in crystal growth systems to see if it might be possible to dissolve the iridium particles in the melt. Platinum particles have been eliminated in laser glass melts using this approach [77], [78].

**SUMMARY AND CONCLUSIONS**

We have made substantial progress toward obtaining large, high-quality Nd:Cr::GSGG crystals for use in slab lasers. We have demonstrated that large GSGG boules can be grown by the Czochralski method. We have identified several problems in large-crystal Nd:Cr::GSGG growth, which we have solved individually. Spiral and 1 μm absorption loss are both controlled by adding Ca and Ce to the melt. Boule spiral is delayed during growth, and boule uniformity is improved, by lifting the crucible during the melt. Boule spiraling is delayed during growth, and cations and their associated birefringence are minimized at an atmosphere of 0.1 to 0.5 percent H₂. Surface and bulk absorption loss are both controlled by adding Ca and Ce to the melt. Cracking has been eliminated at 9.5 cm diameter, but not at 13 cm. Dislocation and their associated birefringence are minimized by using the "artificial flip" procedure.

Additional work is required to make it possible to grow large crystals of the desired quality for laser operation. In particular, iridium inclusions and the spiral/1 μm absorption loss problems are not yet sufficiently controlled for us to define a high-yield growth process. We must continue to seek a fundamental understanding of the chemical and physical mechanisms underlying these problems.

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M. H. Randies, photograph and biography not available at the time of publication.

R. C. Morris, photograph and biography not available at the time of publication.