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Preparation and Properties of Crystalline Laser Oxide Materials*

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Research on solid state laser material began with the discovery of laser action in ruby in 1960. Shortly thereafter, a number of other laser hosts were investigated and from this work YAG (yttrium aluminum garnet) developed as *the* solid state crystal laser material of the industry.

Then efforts to find new materials practically ceased. The growth and properties of the various crystalline oxide laser material are presented with emphasis on YAG. The desirable properties and needs for new host materials are discussed.

Introduction

The solid state laser era began with Maiman's (*1*) use of ruby as the laser material. Upon demonstration that laser action could be achieved in ruby the search for new crystalline hosts began. Very shortly thereafter a number of different host crystals and dopants were successfully lasered.

Research from the crystal grower's viewpoint centered primarily on the growth of high optical quality of ruby. Maiman had used Verneuil grown ruby, the only available, large, synthetic ruby. Because of its poor optical quality, less than optimum output power was achieved because of scattering losses. Fortunately, at this time the techniques for fabricating iridium metal were developed and crucibles of this metal became available to the crystal grower, so that high temperature Czochralski crystal growth could be practiced. For this technique the use of iridium is essential for ruby, yttrium aluminum garnet (YAG), and many other high melting oxides, since it is one of few metals with a higher melting point than most oxide melts and does not react substantially with these melts. The standard iridium crucible in the early 1960's was about 1.5 in. high × 1.5 in. in diam. Today, crucibles measuring 7 × 7 in. are readily available.

Table I presents the physical and crystal growth properties of some of the historically more important oxides which have been grown since 1960. As can be seen from the list perhaps the material with the best overall physical and growth properties is α-Al_2O_3. Unfortunately, it cannot be doped with the large rare earth ions due to the small size of the aluminum site. It can be doped with transition metal ions but these ions, other than chromium, do not have spectroscopic properties conducive to lasing. Of the remainder in the list YAG and $YAlO_3$ have the most interesting physical properties and crystal growth characteristics. YAG doped with neodymium is the crystalline laser today, but $YAlO_3$ may hold promise for the future.

From the laser scientist's viewpoint a good host should: 1. be hard, so that rods can be machined, end faces highly polished, and the finished rods handled without fear of fracture; 2. have a high thermal conductivity so that excess heat may be readily removed from the laser rod; 3. have a low thermal coefficient of expansion so that the rod may be rigidly mounted and undergo a minimum of optical distortions when pumped; 4. have no active ions which destructively interfere with the pumping, or lasing of the active ion; 5. be chemically inert toward O_2, N_2, CO_2 and H_2O. Several elemental and compound oxide materials can satisfy these requirements.

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* Invited paper.

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TABLE I

PHYSICAL AND CRYSTAL GROWTH PROPERTIES OF IMPORTANT OXIDE HOST LASERS

Host	Crystal system	Thermal conductivity (W/°C cm at 300°K)	Coefficient of expansion ($\times 10^6$/°C)	Hardness (Mohs)	Melting point (°C)	Active ion distribution coefficient	Rotation rate (rpm)	Pull rate (mm/hr)	Year lased
α-Al_2O_3	Rhombohedral	$\parallel c$–0.35 $\perp c$–0.33	$\parallel c$–5.31 $\perp c$–4.78	9	2040	Cr: ~ 1.1	10–60	6–12	1960
$CaWO_4$	Tetragonal	$\parallel c$–0.033	$\parallel a$–11.2 $\parallel c$–18.7	4.5	1570	Nd: 0.8 with 3.5% Na^+ added to melt	20	12	1962
$Y_3Al_5O_{12}$	Cubic	0.13	6.9	8.25	1970	Nd: 0.18	50–60	0.5–1	1964
YVO_4	Tetragonal	$\parallel c$–0.051 $\parallel a$–0.051	$\perp c$–7.3	5.5	1810 with decomposition	Nd:	20–30	6	1967
Soaps									
$CaLa_4(SiO_4)_3O$ $SrLa_4(SiO_4)_3O$ $CaY_4(SiO_4)_3O$	Hexagonal	0.017	6–7	7	2180	Nd: 0.8–1.0	70–90	1–5	1969
$YAlO_3$	Orthorhombic	0.11	$\parallel a$–9.5 $\parallel b$–4.3 $\parallel c$–10.8	8.5–9.0	1875	Nd: 0.8	40	6–8	1969

Now from the crystal grower's viewpoint, a good host is one which has the following characteristics.

1. Crystal can be readily grown; preferably by a fast growth technique which will not require many years of R & D. In many ways this limits the technique to one of melt growth which imposes further restrictions on the solidification and thermodynamic properties of the melt.
2. If the material is to be grown from the melt, it must be fusible within the working constraints of the apparatus, i.e., temperature, pressure, and chemically nonreacting with the crucible or ambient atmosphere.
3. It is also desirable that the host contain sites of a size and electronic charge which are compatible with the dopant or active ions.
4. Finally, cubic or materials with nearly isotropic coefficients of expansion and thermal conductivities can usually be grown more readily than those with extraordinary anisotropies.

Of the materials listed in Table I, YAG satisfies all conditions from both viewpoints and accounts for it being the solid state oxide laser material today.

Growth of YAG: Nd

Apparatus and Conditions

Figure 1 outlines the apparatus and furnace typically employed in the growth of YAG using 450 kHz induction heating. The seed holder is attached to a mechanism capable of rotation and slow elevation. A mixture of argon and nitrogen at rates of 4–10 liter/hr is used to prevent serious oxidation of the iridium crucible and prevent rf arcing. Rotation of the seed is usually 40–60 rpm and withdrawal rates may vary from 0.1 to 1.5 mm/hr depending on the dopant level and crystal diameter. Typically, a pulling rate of 0.75–1.0 mm/hr can be employed for crystals of 1–1.2% neodymium and diameter of 19–25 mm.

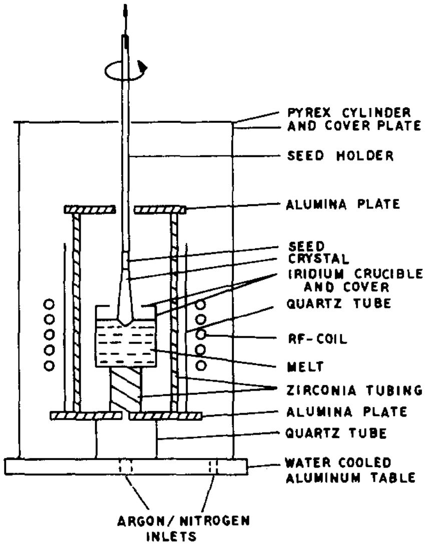

FIG. 1. Cutaway section of a YAG crystal growth station.

High quality crystals can be grown easily in the low index directions of $\langle 111\rangle$, $\langle 100\rangle$ and $\langle 110\rangle$. The $\langle 111\rangle$ direction is that normally employed for YAG:Nd because of the smaller central facet core produced by growth in this direction.

The starting materials for high quality, high purity YAG:Nd should be dry 99.999% Y_2O_3, α-Al_2O_3, and Nd_2O_3. Lesser purity reagents can contribute impurity ions capable of absorbing the 1.06 μm radiation or in other ways may be deleterious to the performance of the laser crystals.

Facet Effect Core

If one desires to grow a boule sufficiently large for fabrication of say, 6.5 mm rods, it is necessary that he grow a boule slightly two times larger than diameter or about 15 mm. This is due to the fact that a core of optically inhomogeneous material runs through the center of the boule. This core can be eliminated by cutting through the center of the boule. The core or tube effect is due to facetting on the $\{211\}$ or $\{110\}$ faces which appear on the convex surface of the crystal interface during growth. This phenomena is well known and is most probably caused by differences in impurity segregation on the nonfacetted and planar facetted interface (*2*).

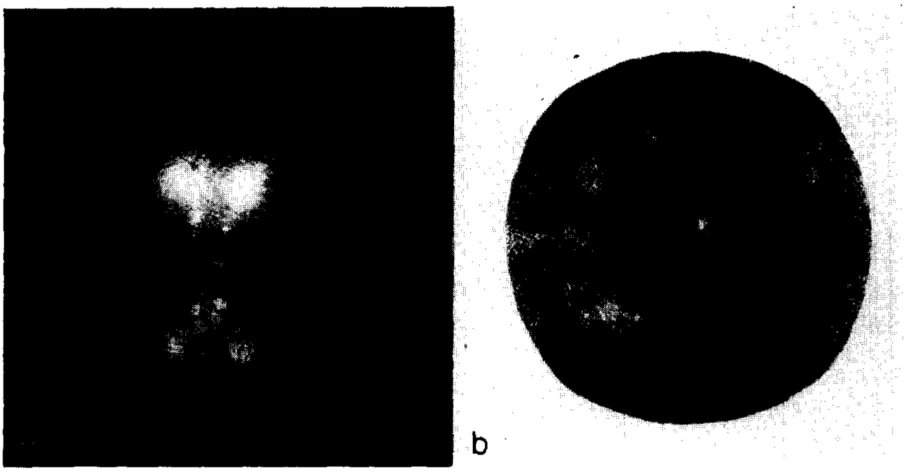

FIG. 2. (a) Photograph of ⟨111⟩ grown YAG boule showing 3 {211} faces; (b) photograph of ⟨100⟩ grown YAG boule showing large, widely separated {211} faces due to less convex nature of interface.

In crystals grown in the ⟨111⟩ direction three such {211} facets occur near the center tip of the crystal. Figure 2a shows a ⟨111⟩ orientated crystal in which these facets are rather large and accentuated for this direction.

In ⟨110⟩ and ⟨100⟩ grown crystals four such facets usually occur on the interface. These facets normally appear to be somewhat larger than those occurring on a ⟨111⟩ crystal. Thus, YAG:Nd for laser use is usually produced by growing in a ⟨111⟩ direction. Figure 2b shows an interface for a ⟨100⟩ grown crystal with even larger and more widely spaced facets. The reason for the large spacing on this crystal is due to the less convex nature of this interface. Figure 3 is a photograph of two boules in crossed polarizers showing the strained regions in the boules caused by the facet effect. Efforts have been made to eliminate these regions by increasing the rotation rate and thereby flattening the interface (*3*). Crystals grown by this technique often times are more grossly strained, and the high rotation rates (150 rpm) often lead to

FIG. 3. Two YAG boules between cross polarizers one in cross section, the other longitudinally showing nature of optically inhomogeneous core caused by the facet effect.

mechanical problems especially with large crystals.

Doping

Most neodymium doped YAG produced for lasers contains about 0.01–0.012 atomic fraction Nd^{3+} as defined by the Eq. (1) or 1–1.2 % as used by the laser scientist.

$$\text{Atom fraction } (RE^{3+}) = \frac{\text{No. g atoms } (RE^{3+})}{\sum \text{No. g atoms } (RE^{3+})(Y^{3+})}. \qquad (1)$$

This is a meaningful and easy to employ method of expressing concentration for rare earths in YAG since they substitute only in the yttrium sites. The neodymium dopant level is limited to 1–1.2 %, primarily because above these levels the lifetime of the Nd^{3+} excited state begins to decrease due to Nd^{3+} ion pair interactions (*4*). Second and fortunately, the ability to produce high optical quality Nd^{3+} doped YAG becomes very difficult at 1.5 % and almost impossible at 2.0 % even if rates as low as 0.1 mm/hr are employed in the latter case.

The reason for the very slow growth rate is that the distribution or partition coefficient for Nd^{3+} doping is only 0.18 (*5*). Figure 4 shows the concentration of Nd^{3+} in a crystal as a function of the amount of melt crystallized as calculated by the equation for normal freezing (*6*).

$$C_s = C_0 k(1 - g)^{(k-1)}. \qquad (2)$$

Thus, a YAG : Nd rod fabricated in the normal manner along the axis of the boule will have a composition gradient along its length. The degree of this gradient will depend upon the length of the rod and the size of the crucible which was used to grow the boule. As can be seen from Fig. 4, at 20 % of the melt crystallized, the Nd^{3+} concentration has already increased by 20 %, and at about 40 % of the melt crystallized the point is reached where growth cannot be easily accomplished.

One technique suggested for improving the quality of Nd^{3+} doped YAG was to add another ion for "size compensation" (*7*). The scheme intended here was that the Nd^{3+} ion (1.323 Å) is much larger than the Y^{3+} ion (1.281 Å) and therefore strain is introduced into the lattice. If an ion smaller than Y^{3+} were introduced and substituted for Y^{3+}, then less strain and perhaps better lasing characteristics could be achieved. The one such ion which seems to accomplish this goal is Lu^{3+} (1.262 Å).

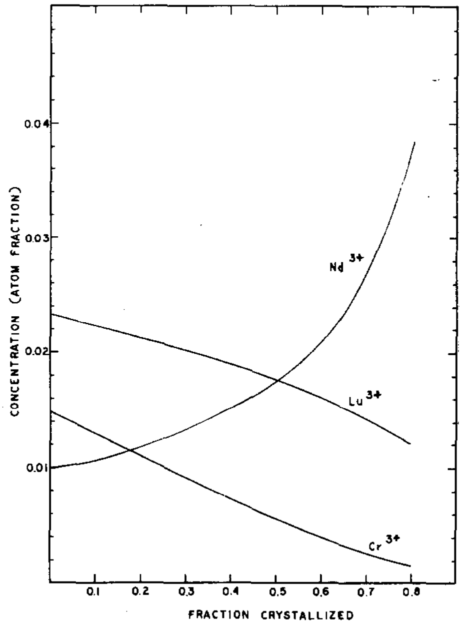

FIG. 4. Concentration of various dopants in crystalline YAG as a function of the fraction of the melt crystallized as calculated using the formula for normal freezing. The initial concentrations for Lu^{3+} and Cr^{3+} are those calculated to be ideal for the 1.0% Nd^{3+}.

One can calculate that a combination of approximately 7 Lu^{3+} and 3 Nd^{3+} will have a volume equal to about 10 Y^{3+} ions. Thus a factor 2.3 times as much Lu^{3+} must be added to the melt to accomplish ideal size compensation. However, the distribution coefficient for Lu^{3+} has been shown to be 1.38 (*5*) and at only one place in the crystal can this ideal be attained. This result is also shown in Fig. 4 where the initial concentrations are the ideal. One other unfortunate effect which develops is that the total dopant or impurity ion concentration increases.

This increase in total impurities only leads to enhancement of conditions in which constitutional supercooling becomes an even more serious factor in decreasing the boule quality, making the growth of such crystals very difficult. As a result of the increased crystal growth problems most of the size compensated crystals are grown with much lower concentrations of Lu^{3+}.

Riseberg and Holton (*8*) have recently shown that the Lu^{3+} may not be acting as a normal dopant, i.e., substituting on random Y^{3+} sites but appears to form microscopic regions of $Lu_3Al_5O_{12}$ crystals within the YAG host crystal. The laser community is still divided as to the value of Lu^{3+} additions as far as laser performance is concerned.

Finally, with regard to doping, another approach taken to improving the performance of YAG:Nd^{3+} is that of adding a sensitizing ion to the crystal which can absorb some of the pump lamp's spectrum and transfer such energy to the active laser ion. Perhaps the most successful such ion added to YAG: Nd^{3+} has been Cr^{3+}. Unfortunately again, the distribution coefficient is very high (2.4) and the ideal match of Cr^{3+} and Nd^{3+} concentration can only be made at one point in the crystal (Fig. 4). Furthermore, such crystals are also very difficult to grow because of constitutional supercooling effects. Other sensitizers investigated have included Mn^{2+}, Mn^{4+}, V^{2+}, V^{3+}, V^{4+}, and Ce^{3+} (*4*). In those cases in which the added ion is not tripositive an additional charge compensating ion must also be added to the melt. Thus it can be readily seen that 3, 4, and more dopant ions can be added to the melt simultaneously and crystal growth without constitutional supercooling or second phase formation becomes impossible.

Future Considerations

In the mid 1960s YAG had developed as *the* laser host and research for new materials had almost ceased. Yttrium orthoaluminate was discovered (*9*) as a potential replacement for YAG. It has a more favorable Nd^{3+} distribution coefficient of 0.8 and high quality doped crystals can be grown at 5 to 6 mm/hr. Unfortunately, because of the anisotropy of the thermal conductivity and thermal expansion the crystals tend to twin and crack. Perhaps the development work (*10*) which is continuing will resolve these problems and give the laser scientist a better, less expensive laser oxide material.

A second look is being taken at YVO_4 which holds great potential as a host material since the $(VO_4)^{3-}$ ions can absorb and transfer energy to Nd^{3+}, thus producing a host sensitized material. Problems of stoichiometry, decomposition, and stabilization of the oxidation state of the V^{5+} must be achieved.

From a laser scientist's viewpoint there is a need for optically pumped solid state lasers operable at room temperature and at frequencies other than 1.06 μm. Such frequencies include eye safe regions, e.g., 2.0 μm, and also the visible and near uv. It remains for the spectroscopist and laser scientist to suggest the active ions or ion combinations he would desire in a crystal and the crystal grower using the criteria given herein to search for a host wherein a new laser can be produced.

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