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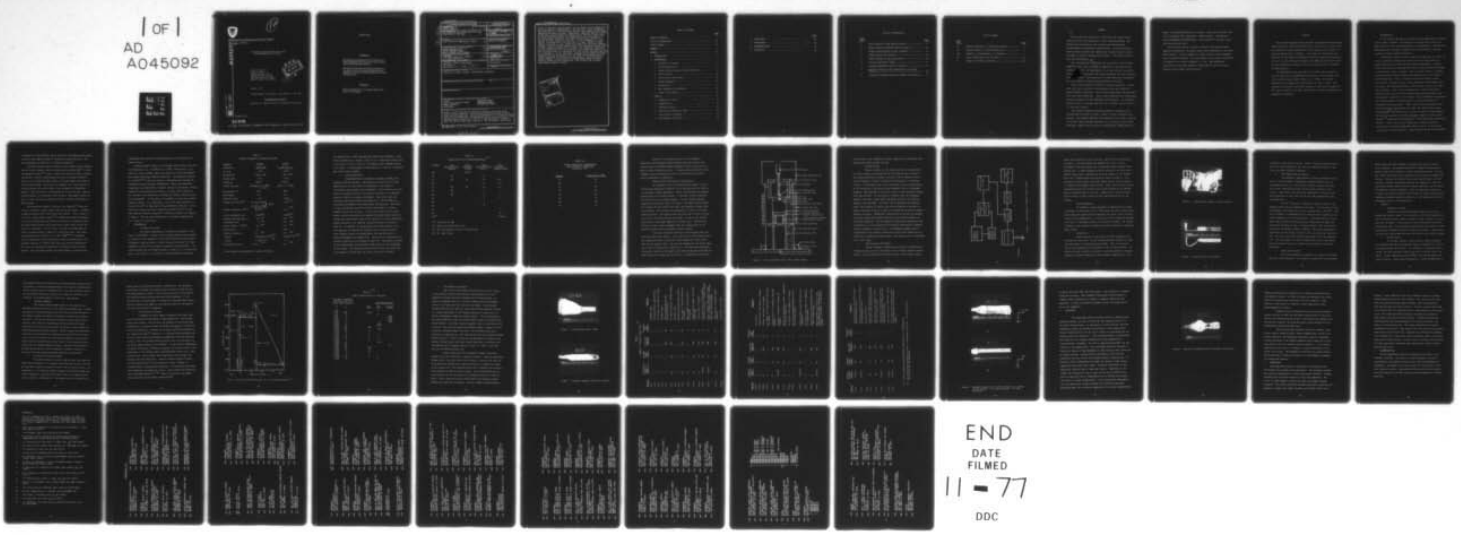

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THE SINGLE CRYSTAL GROWTH AND LASER ROD FABRICATION OF ND:YVO_4

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August, 1977

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Growth of [100] YVO_4:Nd was performed from melts contained in RF heated iridium crucibles. Initial growth experiments used phosphor grade YVO_4 and $NdVO_4$ until the growth parameters of structurally sound crystals were determined. Stoichiometric solid state reactions of the component high purity oxides, V_2O_5 (< 15 ppm impurities), 99.999 % Y_2O_3, and 99.99 % Nd_2O_3 were then used. During growth a significant

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amount of V_2O_5 was vaporized which led to changes in melt composition and crystallization temperatures. The YVO_4 melt slowly decomposed into YVO_3 and O_2. After prolonged heating, V_2O_5 depletion and sample decomposition limited growth. Experiments indicated YVO_4:Nd could be grown from a nonstoichiometric composition of 1Ø mole % excess Y_2O_3 at lower temperatures where V_2O_5 vaporization was noticeably less. The crystal-melt interface and thermal gradient were adjusted to produce the best growth in a 98 % N_2 - 2 % O_2 atmosphere at a pull rate of 1.25 mm/hr and a rotation rate of 4 rpm. Boules of [100] YVO_4:Nd 65 mm long x 6 mm x 2Ø mm were grown with excellent diameter control. Erratic growth occurred along [001] with large smooth facets on (001) planes the entire boule length. The thickness along [010] can be controlled by the seed, shoulder, and growth rate conditions. With slow pull rates of 1.25 mm/hr the [001] growth direction was much less pronounced. In the [100] axis orientation the growth interface contained the two directions [010] and [001] where differences for thermal expansion and conductivity are largest. Crystals showed a marked tendency to cleave along the {100} planes which seriously hindered growth and rod fabrication. The cleavage was strongly aggravated by impurity levels.

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SUMMARY

This project was initiated to investigate the single crystal growth and laser rod fabrication of [100] oriented Nd:YVO_4. The desired size and quality of the crystals were obtained most advantageously by Czochralski growth methods. We have utilized RF heated iridium crucibles and commercially developed crystal growth equipment to evaluate rapidly many variables. Two growth stations were used continuously.

Our investigations have shown that the purity of the starting components Y_2O_3, V_2O_5, and Nd_2O_3 is important for low defects and crack-free growth. The V_2O_5 appears to be very difficult to purify. Prepar[illegible]VO_4 was purchased from several suppliers but gave consistent crac[illegible]oblems. Our preparations of YVO_4 worked more efficiently but also exhibited cracking during mechanical processing.

Early in the program the effects of thermal gradients, rotation rate, pull rate, O_2 levels, and annealing cycles were studied to obtain reliable growth data. Most of these experiments were performed with lower purity materials. After growth conditions were established, the best available starting components were employed. Low gradients, rotation rates of 4-30 rpm, pull rates of 1.5 mm/hr, and O_2 levels of 2 % gave best results.

The crystal structure associated problems of morphology and cleavage were difficult to solve. Boules of [100] orientation were desired. Both thermal expansion and conductivity are widely different for the two other resulting directions in or adjacent to the growth interface. Smooth facets occurred on {010} planes, {001} planes are

absent, and $\{111\}+\{311\}$ planes are erratic. Boule cross sections tend to be rectangular with truncated or rounded corners. Cleavage was always along $\{100\}$ and $\{010\}$ planes. This resulted in fractures across and along the boule axis.

Boule fracture may be a result of severe strain during growth, impurity precipitation, Nd doping levels, melt stoichiometry, and other minor factors. We have attempted to study several of these systematically to prevent cracking. The boule growth at this time is restricted to lengths of 4-7 cm and "diameters" of 1 cm. Some mechanical fabrication methods were examined. Diamond wheels and core drills tended to give highly fractured pieces.

PREFACE

This Interim Technical Report describes experimental work performed under Contract No. DAAB 07-76-C-0908 from 1 July 1976 to 1 January 1977. The contract was titled objectively as "The Single Crystal Growth and Laser Rod Fabrication of Nd:YVO_4". The project was initiated by and performed for the Combat Surveillance and Target Acquisition Laboratory of the U. S. Army Electronics Command, Fort Monmouth, New Jersey 07703. Mr. John Strozyk was assigned as the contracting officer's designated technical monitor.

All experimental work described in the report was performed in the laboratories of the Lambda-Airtron Division, Litton Systems, Inc., 200 E. Hanover Avenue, Morris Plains, N. J. 07950. The general direction of the program was supervised by Dr. Roger F. Belt. The principal investigator and project engineer on all crystal growth was Dr. Larry E. Drafall. Mr. Karl Jensen served as senior technician and prepared all materials.

1 INTRODUCTION

At the present time the most widely used and commercially available crystal laser is Nd:YAG. This material is incorporated in nearly all modern military laser target designators and rangefinders. Research and development were performed on Nd:YAG during 1964-1968 while limited production followed shortly thereafter.

Considerable savings in cost, weight, and simplicity can result in a laser transmitter through the substitution of crystals which are birefringent and have lower threshold energy requirements. Theoretically such crystals are available but thus far none have been developed to the practical state of Nd:YAG. One such single crystal is Nd:YVO_4, a material which initially showed great promise but was abandoned as Nd:YAG progressed. YVO_4 is a highly birefringent uniaxial single crystal with a zircon structure. When doped with Nd and pumped along the a-axis, the stimulated emission cross section is about five times that of Nd:YAG. Such a laser rod should have a lower oscillation threshold and be useful for both CW and pulsed operation where total energy input is desired to be a minimum. Laser performance measurements on a limited number of Nd: YVO_4 pieces of "a-axis" material have confirmed these expectations. Small selected rods have demonstrated lasing thresholds approximately 50% lower than Nd:YAG under similar pulse pumping.[1a] Performance with dye laser or argon ion laser pumping has also been superior in Nd:YVO_4 specimens compared to high quality Nd:YAG.[1b] Some recent CW experiments[2] show that Nd:YVO_4 outperforms Nd:YAG. A laser rod of a-axis Nd:YVO_4 has a strongly polarized emission and an excellent TEMoo mode should result. It can also be used without a cavity polarizer. Light emitting diodes can be matched

efficiently to small Nd:YVO_4 rods in an end or face pumped configuration to give a very compact system for ranging or integrated optics. The self Q-switching of Nd:YVO_4 is a distinct possibility.

The main difficulty which slowed the early exploitation of Nd:YVO_4 was the crystal growth, since the properties were recognized[3] in 1966 and emphasized again[4] in 1969. Because the crystal of YVO_4 is highly anisotropic, contains vanadium which can exist in several oxidation states, and is refractory (M.P. 1825°), one might expect the growth to be more than routine. The history of attempts to get good crystals is long and extends over the Verneuil, flux, Bridgman and Czochralski methods. Only the latter is considered here to give the size, quality and performance in a relatively short period of development similar to YAG. In fact, one may use similar facilities already established for Nd:YAG growth.

The Czochralski growth of YVO_4 was first reported[5] using gas fired Ir crucibles. These crystals were all c-axis growth. A similar attempt was made later[6] with little more success. After a lapse of 5-6 years, several workers again[7,8] studied the growth and obtained fair c-axis crystals with RF heated Ir crucibles in standard systems. The major growth problems were inclusions, cracks, color centers and control of conditions. At this stage, crystals of Nd:YVO_4 were not large or perfect enough to obtain 3 x 30 mm laser rods. Two recent investigations were funded by U. S. Army, ECOM[9,10] to determine the most appropriate growth technique, to assess the magnitude of the problems involved, to evaluate pure YVO_4 for polarizer applications and study the spectroscopic properties of Nd:YVO_4 as well as other dopants. These programs yielded sufficient samples to provide laser

performance data and warrant continued interest in developing the growth process.

Yttrium vanadate (YVO_4) is a tetragonal single crystal with unit cell dimensions of $\underline{a}$ = 7.123Å and $\underline{c}$ = 6.191Å. Structurally, it is similar to zircon, $ZrSiO_4$, which also possesses a unique arrangement with highly anisotropic physical properties. The principle features of structure[11] in YVO_4 are chains of alternating edge sharing VO_4 tetrahedra and YO_8 triangular dodecahedra. These are undoubtedly responsible for growth habit, cleavage, extreme birefringence, thermal conductivity and expansion differences, and many growth anomalies. The favorable laser properties of Nd:YVO_4 are closely associated with the YO_8 polyhedra. In the latter, the symmetry is lower than similar groups in garnet. As a consequence, very little Stark splitting is observed for Nd^{3+} in YVO_4 and the $^4F_{3/2}$ metastable level has a large oscillator strength and lower radiative lifetime than Nd^{3+} in YAG. Some important physical properties of Nd:YVO_4 and Nd:YAG are compared in Table I. The few laser measurements are firmly established but are a result of limited work.

2 EXPERIMENTAL

a Crucibles for Growth

The growth temperatures of Nd:YVO_4 are typically in the range of 1825-1900°C. Iridium is the crucible material most suitable for growth at this temperature for RF heated Czochralski procedures. Iridium has a melting point of 2450°C but must be heated in an inert atmosphere or very low O_2 pressure to prevent rapid oxidation. For initial growth runs an iridium crucible 1.5 inch I.D. x 2.0 inch high with a 1.75 inch O.D. x 0.87 inch I.D. washer shaped lid was used.

TABLE I

Physical Properties of Nd:YVO_4 and Nd:YAG

Property	Nd:YVO_4	Nd:YAG
Formulation	$Y_{.99}Nd_{.01}VO_4$	$Y_{2.97}Nd_{.03}Al_5O_{12}$
Wt. % Nd	0.87	0.725
Nd atoms/cm^3	1.536×10^{20}	1.38×10^{20}
Density g/cm^3	4.22	4.55
Formula wt.	204.42	595.28
Crystal structure	tetragonal a= 7.12 (11), c= 6.29	cubic, a = 12.005
Melting point ^oC	1825	1950
Moh hardness	4 - 5	8.5
Refractive index	1.97	1.823
Thermal cond. $Wcm^{-1}K^{-1}$	∥c axis 0.0523; ⊥c axis 0.0510 (12) @ 300°K	0.13 (13)
Thermal expansion, $10^{-6}C^{-1}$	da-4.43, dc-11.37	6.9 (15)
*Laser wavelength, μcm	1.0644 (14)	1.0643 (14)
*Fluorescence lifetime, μs	96 (14)	230 (14)
*Linewidth, cm^{-1}	7 (14)	6.5 (14)
*Cross section, $10^{-19}cm^2$	30 (14)	6.5 (14)
*Polarization	π	none
*Pulsed threshold, J	0.5 (14)	1.1 (14)
dno/dt	$8.5 \pm 0.9 \times 10^{-6}$ $^oK^{-1}$ (16)	7.3×10^{-6} $^oC^{-1}$ (15)
dne/dt	$3. \times 10^{-6}$ $^oK^{-1}$ (16)	----
Nd segregation coef.	~ 0.3 (14)	0.2 (14)

* Laser property measurements for a-axis direction.

The crucible has a 0.060 inch wall and 0.090 bottom thickness. After several growth runs, a larger 2 inch I.D. by 2 inch high crucible with a 2.25 inch O.D. by 1.5 inch I.D. lid enabled larger diameter boules to be grown. A second growth station employed a 2 inch by 2 inch heavy wall (0.120 inch) crucible.

b Starting Materials

Reacted materials of phosphor grade YVO_4 and $NdVO_4$ were obtained from GTE Sylvania. The material had high levels of trace impurities but was used until the parameters of the growth of structurally sound crystals were determined. Better control over the purity was achieved through a solid-state reaction of the component oxides at 1250°C in an oxygen environment. High purity V_2O_5 was purchased from United Mineral and Chemical Co., the 99.9999% Y_2O_3 from Research Chemicals and 99.999% Nd_2O_3 from Molycorp. The purity of V_2O_5 was important and often contains 50-100 ppm of residual elements such as Ca, Na and K. In the case of Y_2O_3 and rare earth oxides, purity designations are somewhat misleading since characterization was usually done solely on the basis of rare earth impurities. Typical analyses of our chemical starting materials are given in Table II. In addition to raw materials for crystal growth, it was also important to consider the material used to contain the melt since intimate contact was maintained by the crucible with its contents throughout the growth cycle. The purity of iridium used for crucible fabrication is presented in Table III. The impurity content of the iridium metal was relatively fixed since this was determined by the vendor. The crucible reactivity with the melt was small and trace amounts of metals were not likely to get into solution.

TABLE II

TYPICAL ANALYSIS OF STARTING MATERIALS (1)

Element	Y_2O_3 (Research Chem.) 99.9999	Nd_2O_3 (Molycorp) 99.999	V_2O_5 (United Mineral) Grade I	YVO_4 (Sylvania) Phosphor Grade
Sm		200(2)		
Al	ND		<1	
Ca	<20	12	<1	1-10
Cu			<1	<1
Si	<20	60	10	65
Ti	ND		2	
Mg	ND		<1	6
Cr			1	5
Mn			1	
Ag			<1	
Fe	ND			9
Ni				10
RE(4)				<3 each

(1) All values in PPM

(2) Other rare earths total 1-10

(3) ND = Not detected at limit of method used

(4) RE = Rare earths

TABLE III

TYPICAL ANALYSIS OF IRIDIUM METAL
USED IN CRYSTAL FABRICATION
(Engelhard, Inc.)

Element	Concentration (PPM)
Pt	25
Rh	55
Ag	20
Pb	40
Fe	50
Si	50
Mg	20
Ni	20

Because of the expensive nature of the chemicals, moderately priced phosphor grade materials have been used in the initial work to establish growth parameters without sacrificing too much in terms of material purity. As work progressed the best grade chemicals were substituted in order to investigate any internal quality dependence on impurities.

c Growth Station Construction and Gradients

The equipment used to grow Nd:YVO_4 was capable of maintaining high temperatures (1860°C) for an extended period of time in a satisfactory growth atmosphere. Figure 1 illustrates the detailed construction of the growth station. A 450 kHz, 30 kw RF generator was used to heat the iridium crucible. All the ceramic internal supports and forms were made of zirconia. The annular space between the crucible and the fused silica glass tube employed zirconia grog as insulation. The crucible was supported by a series of zirconia tubes and plates. The support tubes and discs were slotted to allow free flow of the gases through the system. On top of the zirconia grog rested a tube which supported a zirconia disc. The disc was slotted to allow careful alignment with the sighting path of the infrared detector used for diameter control sensing.

The outer enclosure consisted of two sections made from type 208 fused silica tubing. A gas tight seal on the bottom section was accomplished with a gland and O-ring between the fused silica tube and the support table. The top seal between the two silica tubes was a slip fit sealed with zirconia felt. The gases were introduced through the table into the lower quartz tube and passed up through the grog around the crucible and out the top. By maintaining the proper

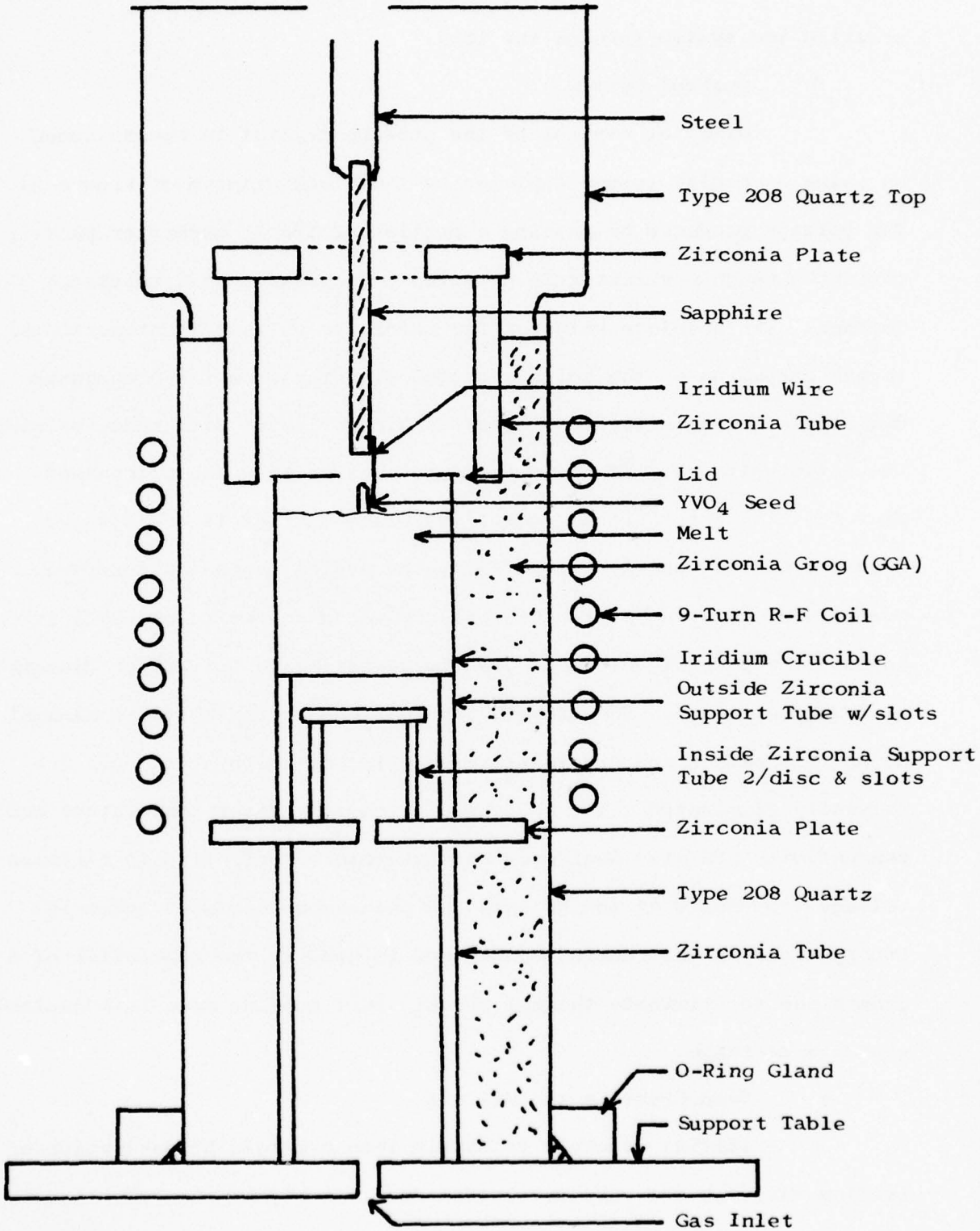


Figure 1 Cross sectional view of YVO_4 growth station.

flow of gases, most atmospheric gaseous impurities are prevented from entering the system through the top.

d Control System

Diameter control of the growing crystal is accomplished by using a special system depicted by the block diagram of Figure 2. The voltage produced by passing a portion of the RF generator plate current through a resistor is detected and compared to a reference voltage. The absolute value of the reference voltage is proportional to the deviation of the actual crystal diameter from its programmed diameter. The magnitude of the error signal is the difference between these two voltages. If the crystal is smaller than the programmed diameter, the error signal causes the plate current to be adjusted downward and conversely. In effect, the system keeps the generator power level constant as long as the crystal diameter is correct; it adjusts the power level up or down to re-establish the proper diameter whenever necessary. Temperature fluctuations in the melt are minimal using this method and crystal flaws due to non-uniform diameter are virtually eliminated. The RF generator cooling water temperature and conductivity are also monitored and accurately controlled to minimize voltage transients at the RF coil. A programmed cooldown cycle is incorporated in the control system and is used at the conclusion of a growth run to eliminate thermal shock. This cooling rate is adjustable over a wide range.

e Seed Crystals and Holders

Initial attempts to obtain seed crystals by nucleation on iridium wire was not very successful due to a highly insulated growth system. By slow cooling the crucible and melt, solid single crystal

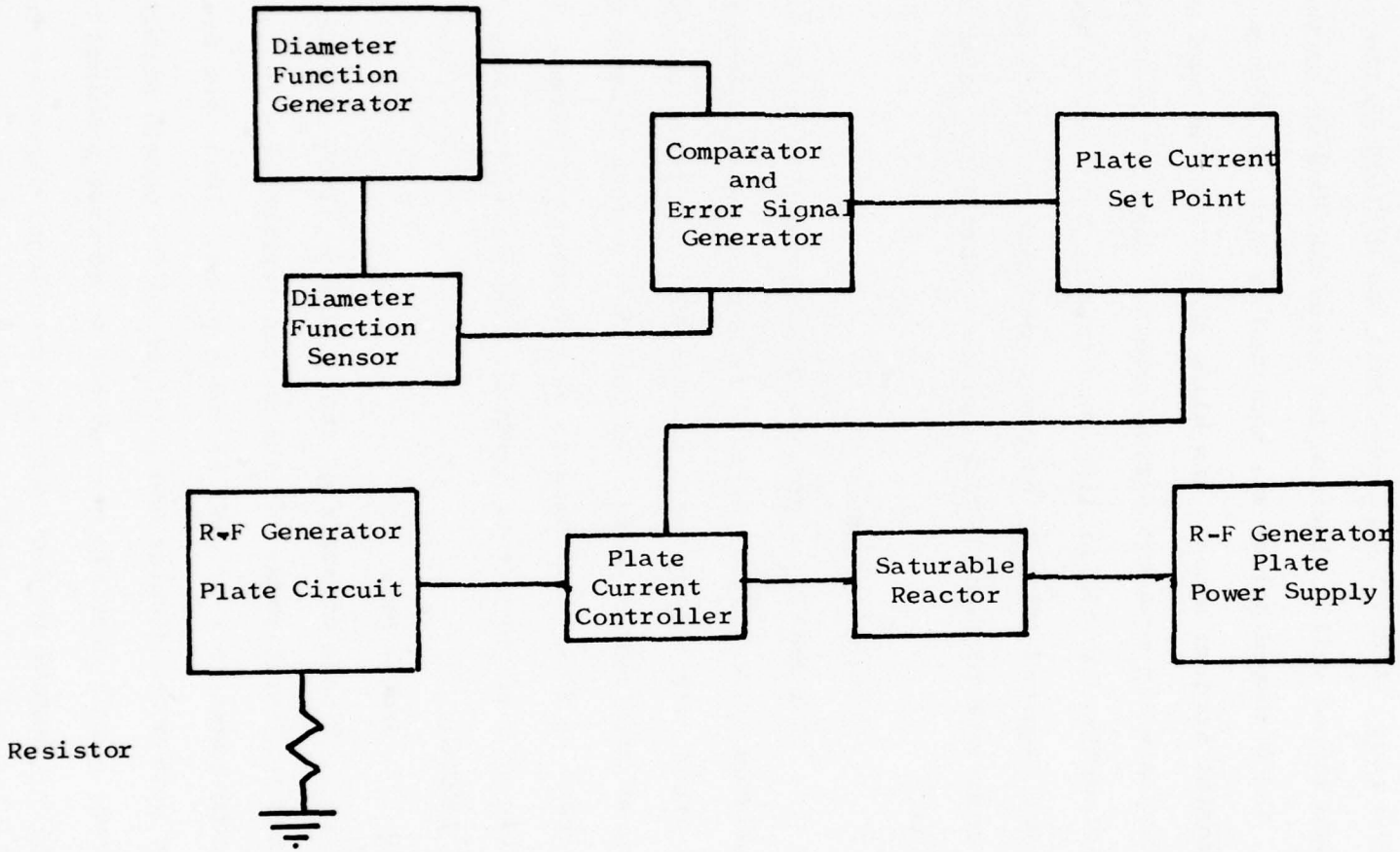


Figure 2 Block Diagram of Diameter Control System

pieces were extracted by core drilling. Some of these are depicted in Figure 3. One large piece was selected for use as a seed. Rectangular seeds were mounted on S shaped wire hooks suspended from alumina rods. A small elongated hole was drilled in the seeds with a diamond tipped drill. Because the seeds can "swing" on the iridium wire, the S shaped holder was modified as shown in Figure 4. The horizontal iridium support was blade shaped and the seed was pinned to eliminate any movement during growth. Vapors from the melt reacted significantly with the alumina rods causing brittleness and replacement was required after a few runs. Sapphire pull rods proved much more resistant to vapor attack and were substituted later for the alumina.

f Growth Atmosphere

For Nd:YVO_4 a growth atmosphere of 98% N_2-2% O_2 has been established at flow rates of 11.2 ft^3/hr and 0.244 ft^3/hr respectively. Inert argon with oxygen would be desirable but tends to give crucible arcing at high temperatures. In pure N_2 gas both iridium and vanadium will react to form small amounts of refractory nitrides. The iridium crucible is also subject to oxidation and the O_2 pressure is important above 1300°C.

g Growth Axis

Single crystals of the a-axis or [100] orientation are required for laser rods. In the zircon tetragonal structure of YVO_4 the (100) plane is a natural cleavage plane. Thus, the crystals cleave both perpendicular and parallel to the growth direction. In addition, a-axis crystals are subject to adverse problems of thermal expansion, thermal conductivity and rotational asymmetry due to the

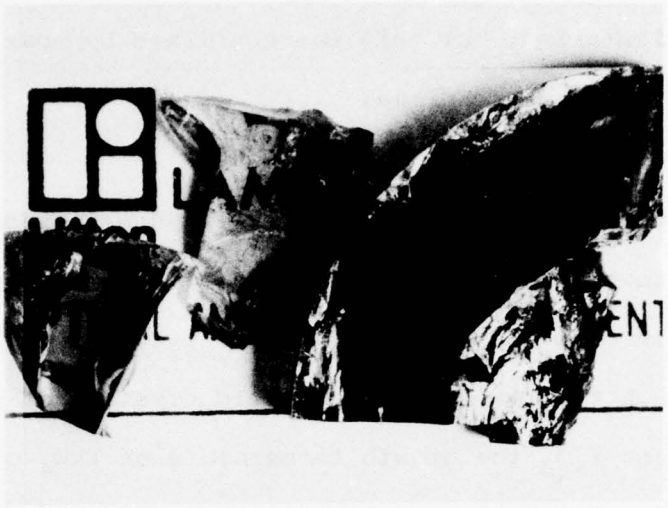


Figure 3 Single crystal pieces of YVO_4 from melt.

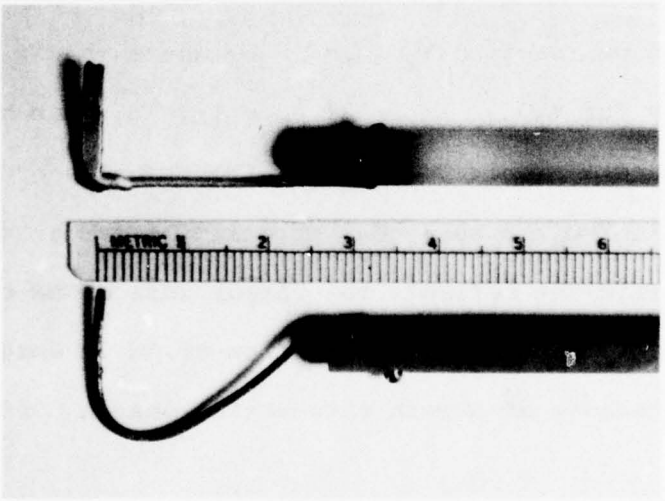


Figure 4 Single crystal seed holders.

anisotropy in the plane of growth. Natural cleavage planes provided a basis for rough orientation, but this was confirmed by means of the Laue x-ray back reflection technique.

h Melt Composition and Doping

Stoichiometric compositions of yttrium orthovanadate were used for crystal growth. Experiments indicated however that non-stoichiometric melts of 5 and 10 mole % excess Y_2O_3 were sucessful with growth, although the latter did not yield crystals of good quality. With excess Y_2O_3 the growth temperature of YVO_4 was lower and vaporization of V_2O_5 from the melt and YVO_4 decomposition were noticeably less.

The Nd^{3+} activator, as Nd_2O_3 was initially added to the phosphor grade YVO_4 and compensated with V_2O_5. After growth run YV-10, the phosphor grade $NdVO_4$ was used for incorporation of the Nd^{3+}. Both YVO_4 and $NdVO_4$ are isomorphous with no reported phase transitions for either compound up to the melting point. Starting materials of high purity were prepared by reacting Y_2O_3 and V_2O_5 where the Nd_2O_3 was substituted directly for Y_2O_3. In small amounts, Nd^{3+} can be substituted for Y to produce 1 atomic % Nd:YVO_4. The actual segregation coefficient for Nd in YVO_4 is about 0.3 or a little larger than Nd in YAG. The small coefficient reflects the larger size of Nd compared to Y. The occurrence of a radial distribution of Nd in some boules must be considered because of growth rate variations in different directions.

i Growth Run Procedure

The usual procedure for growth was to charge the crucible with the starting material. Each amount of powder must be thoroughly

molten before the next increment of material was added to prevent crust formation. The charged crucible was "soaked" overnight with a partial crust on the surface to reduce vaporization losses. The next day a seed crystal was slowly lowered into the furnace and dipped into the melt. The pull and rotation rates were adjusted and the crystal tapered to diameter by manually lowering the temperature. Once the boule grew straight under relatively stable conditions, the IR detector was employed to control diameter. After the appropriate length was attained, the boule was removed from the melt by slowly increasing the temperature without changing the pull rate. The temperature was then programmed cooled to room temperature.

3 RESULTS

a Production of Seeds

Sections of crystal boules which usually did not have cracks were used for seeds. As the quality of the boules improved, so did the resulting seeds. When a seed had a crack, it tended to propagate into the boule. A long seed of 15-20 mm proved more successful than shorter ones. The long seeds extended above the crucible lid and increased the gradient resulting in much easier growth. Vaporization from the melt often etched the seeds but did not cause growth problems.

b Oxygen Levels

In the melt growth of oxide crystals, oxygen equilibria are extremely important, particularly where one component is volatile or valence changes are possible. For Nd:YVO_4 at its melting point of 1825°C, the vapor pressure of pure V_2O_5 rises to greater than a few mm Hg. At melt temperatures around 1900°C, the vapor pressures are nearly 10 mm Hg. Under these circumstances a slight decomposition of

YVO_4 occurred which was governed by the total pressure related to the O_2 pressure. A partial oxygen pressure of 2% was used to maintain the correct valence state for vanadium (V^{5+}). The lower oxidation states are increasingly refractory with loss of oxygen and form haze, precipitates, or secondary phases in the Y_2O_3 - V_2O_5 system.

c Thermal Gradients

The initial boules showed growth on the seeds but was directed toward one side and off the rotational symmetry axis. Growth continued for several millimeters but the crystal usually burned-off. The thermal gradient was much too shallow for growth to be properly initiated. In order to steepen the gradient, the crucible lid was removed. This resulted in nucleation on the crucible wall where projections from the wall grew toward the center of the crucible and interfered with the growing crystals. Better success was achieved by using the lid and raising the crucible about one inch in the RF coil so the top of the crucible was even with the middle of the top coil. Growth from the crucible wall and the "feet" on the seed were eliminated with this steeper thermal gradient. Several crystals about 15 mm long were grown but burn-offs remained a problem. Removal of a portion of the ZrO_2 insulation helped eliminate the burn-offs.

d Pull Rate and Interface Shape

By quickly removing a crystal from the melt, the interface shape could be observed. As expected, the interface was very flat and was made more convex by changing the pull rate and rotation rate. The adjustment of a satisfactory thermal gradient and interface shape were largely empirical. Rotation rates ranged from 4 to 30 rpm with pull rates of 0.050 to 0.200 inch/hr. The optimum rates for rotation and

pulling were 4 rpm and 0.100 inch/hr, respectively. The resulting boules had a flattened cross-section with faceting on (010) and the long edge parallel to [100]. With a slow pull rate of 0.050 inch/hr the preferred growth direction was much less pronounced. A fast rotation rate of 30 rpm tended to produce more equidimensional boules but also flattened the shape of the interface which was the opposite effect we were trying to accomplish.

e X-ray Results on Phases

A diamond core drill sample of material was taken from a crucible which was cooled slowly to room temperature. Two distinct layers were evident. The top layer was Nd:YVO_4 and the bottom layer consisted of a two phase mixture of Nd:YVO_4 and $Y_8V_2O_{17}$ as identified by x-ray diffraction. According to the phase equilibrium diagram for the system Y_2O_5-V_2O_5[17] (Figure 5), if V_2O_5 was being vaporized from the melt, the starting stoichiometric composition was being depleted in V_2O_5. With slow cooling Nd:YVO_4 would be first to crystallize in the cooler upper portion of the crucible. At the eutectic temperature, two phases crystallize, Nd:YVO_4 and $Y_8V_2O_{17}$, and would be found in the bottom part of the crucible where crystallization occurs last. From previous runs, it was evident that vaporization from the melt was changing the bulk composition. Deposits removed from the crucible lid were identified by x-ray diffraction as YVO_4. However, as described above, V_2O_5 also was vaporizing. At the melting point YVO_4 also decomposed to produce YVO_3 and O_2. Other workers have identfied these same compositions.[17, 18] Table IV gives the x-ray powder diffraction data for the phases identified[18].

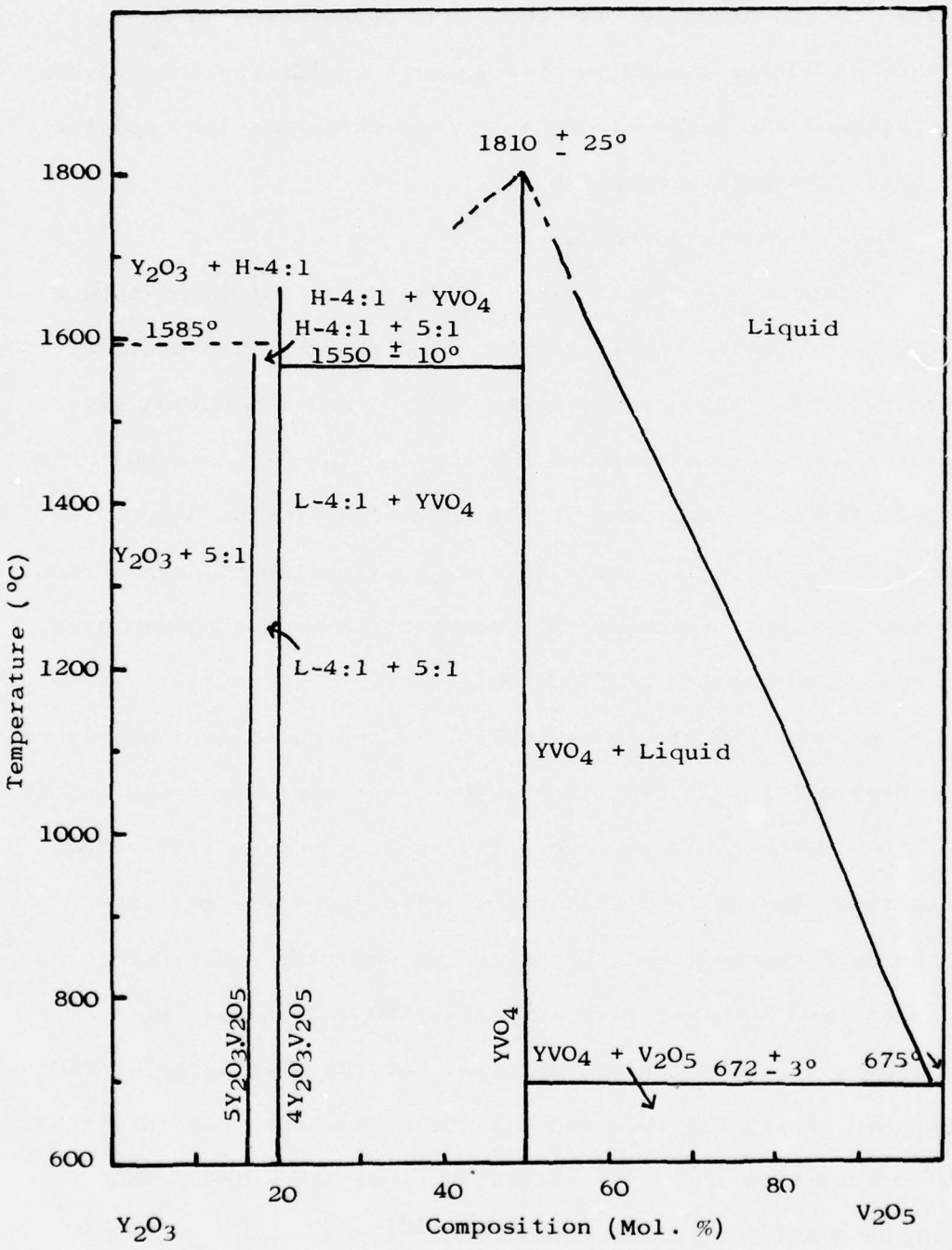


Figure 5 Phase equilibrium diagram for the system Y_2O_3-V_2O_5.(17)

(18)

TABLE IV

X-Ray identification of YVO_4 melt.

YVO_4 Melt (200<mesh)				
X-Ray Lines Observed		Line Identified As		
d	I	YVO_4	YVO_3	$Y_8V_2O_{17}$
3.79	5		X	
3.56	100	(100)		
3.42	3		X	
3.09	6			(80)
3.01	7			(100)
2.944	3			(90)
2.903	4			(80)
2.796	2		(20)	
2.694	11		(100)	
2.663	89	(90)		
2.637	17		(30)	
2.519	21	X		
2.357	9	X		
2.246	5		X	
2.222	16	X		
2.166	4		X	
2.010	7	X		
1.920	14		(20)	
1.888	14			X
1.861	11			X
1.832	70	(74)		
1.781	13	X		
1.751	2	X		
1.711	6	X		
1.592	1		X	
1.570	28	X		
1.530	8		X	

f Run Examples and Results

Most of the difficulties with growth in the early stages of the program resulted from burn-offs during growth due to melt composition changes caused by decomposition and vaporization. In order to counteract burn-offs, the melt temperature was programmed cooled at a certain rate once the seed was dipped. Boule lengths reached 30 mm, but the taper was large which caused cracking. (Figure 6) Further adjustments in the thermal gradient by various heat reflector arrangements helped the growth process. In the Nd:YVO_4 melt, very dark convection lines were present which tended to interfere with the IR detector. By using a smaller diameter "eye" in the detector and setting it only after the boule was growing straight, lengths of up to 65 mm were obtained without burn-offs. The IR detector was never successful in tapering the boule from the seed and then growing straight without burn-offs. Once the boule was grown manually to diameter and growing straight under relatively stable conditions, the detector did an excellent job of diameter control (Figure 7). Table V lists the data for the Nd:YVO_4 growth runs.

Boules grown with [100] orientation showed a preferred growth in the [001] direction as shown in Figure 8. This was especially evident with a fast pull rate of 0.20 inch/hr. Growth on the seeds in the c direction occurred very easily with little or usually no growth in the a direction. The resulting boules had a flattened cross-section with faceting on (010) the entire length. This crystal habit made it very difficult for the IR sensor on the diameter control to track the boule. With a slow pull rate of 0.050 inch/hr the preferred growth diameter was much less pronounced. Crystals showed a marked tendency

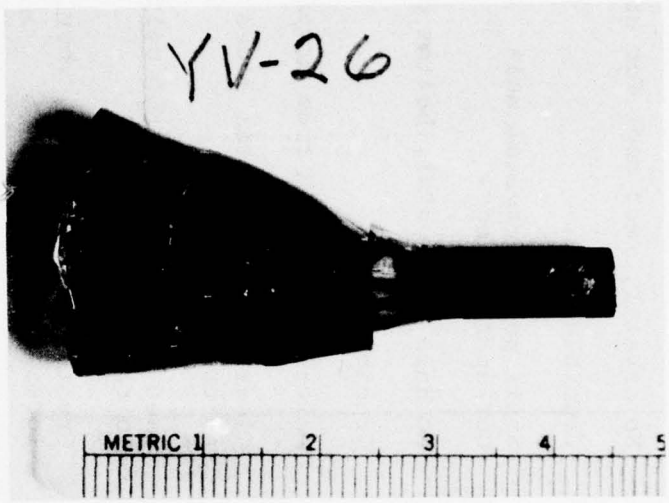


Figure 6 Crystal grown with a taper.

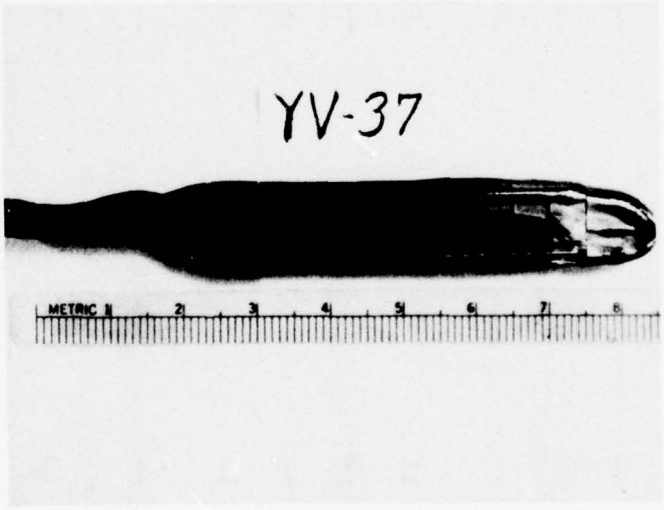


Figure 7 Excellent diameter control of crystal.

TABLE V

Summary of Nd:YVO_4 growth runs (1)

Run No.	Crystal (2) Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Comments
YV-1	--	--	--	--	Crucible leak.
YV-2	--	--	--	--	Crucible melted, sprayed YVO_4.
YV-3	--	--	--	--	No crystal, fast cool for seeds.
YV-4	--	--	--	--	Crucible leak.
YV-5	--	--	.050	50	Small pulled crystal, melt cut up for seeds.
YV-6	11	60	.050	24	No haze in crystal, bottom cracked.
YV-7	--	--	--	--	Crucible leak.
YV-8	--	--	--	--	Material extruded from crucible.
YV-9	15	30	.050	24	Clear part of crystal looks good, no cracks.
YV-10	--	--	--	--	Seed & holder fell into melt. No crystal.
YV-11	10	13	.100	30	Crystal has no cracks, very short, looks clear.
YV-12	12	20	.100	4	Crystal short & cracked.
YV-13	(12)(6)	61	.200	4	Fast pull rate, crystal cracked, transverse cracks at diameter changes.
YV-14	(11)(6)	43	.100	4	Top of crystal looks good, cracks start at diameter changes. Crystal only grew in 2 directions.
YV-15	14	10	.100	20	Short crystal, irregular shape, cracked.
YV-16	--	--	--	--	No crystal - for seeds.

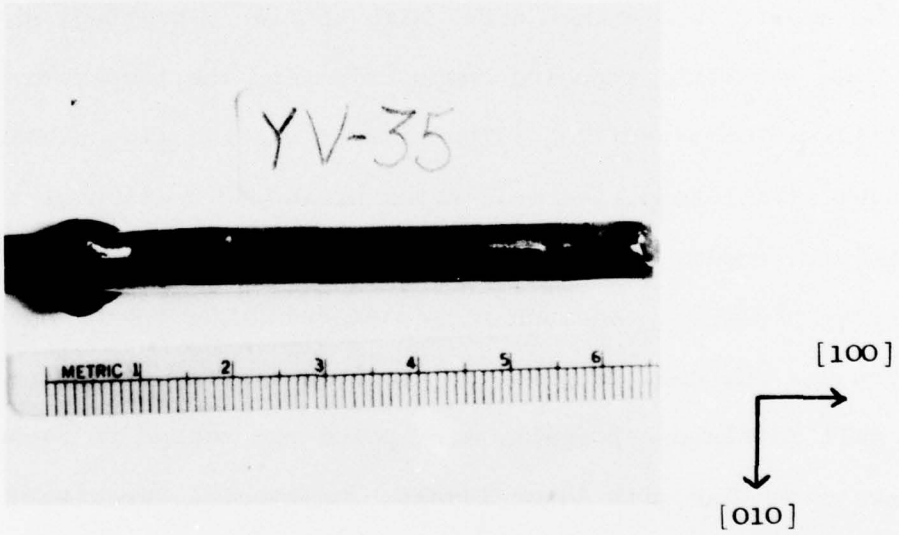
Run No.	Crystal Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Comments
YV-17	--	--	--	--	No crystal.
YV-18	--	--	--	--	Surface froze, shut down, no crystal.
YV-19	15	5	.100	10	Crystal very short, no cracks.
YV-20	--	--	--	--	For seeds, try to dip seed & cool melt for seeds.
YV-21	17	50	.100	4	Crystal about 2", cracked at diameter changes.
YV-22	(12)(6)	16	.100	4	Crystal is irregular in shape and cracked.
YV-23	15	40	.100	4	Boule very irregular in shape, composition 10 mole % excess Y_2O_3.
YV-24	--	--	--	--	No crystal, used crackle for charge.
YV-25	--	--	--	--	No crystal, nonstoichiometric melt, 5 mole % excess Y_2O_3.
YV-26	(16)(10)	30	.100	4	Crystal cracked, boule shifted and is asymmetric.
YV-27	--	--	--	--	No crystal, V_2O_5 added to compensate for vaporization.
YV-28	11	5	.100	4	Small crystal, nonstoichiometric melt, 5 mole % excess Y_2O_3.
YV-29	(14)(7)	40	.100	4	Small crucible (1 1/2"ID x 2" hi) longitudinal cracks, crystal has an hourglass type shape, no transverse cracks.

Run No.	Crystal Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Comments
YV-30	(17)(7)	30	.100	4	Longitudinal and transverse cracks, diameter control fair.
YV-31	(13)(7)	30	.100	4	Transverse cracks at diameter changes. No longitudinal cracks.
YV-32	-	-	-	-	Crucible failure.
YV-33	20	30	.050	4	Boule more equidimensional, quality looks good, some longitudinal cracks.
YV-34	10	10	.100	4	Poor quality, many cracks, may be from poor quality seed.
YV-35	(16)(6)	57	.100	4	Good length, good diameter control, quality looks good, transverse and longitudinal cracks.
YV-36	(14)(7)	10	.100	4	Very short boule, transverse cracks.
YV-37	(14)(6)	65	.100	4	Good length, good diameter control. Again transverse and longitudinal cracks.

(1) Unless otherwise stated material composition is stoichiometric

(2) For pronounced preferential growth, 2 dimensions are given. The (c) direction first, then the (a) direction.

(a)



(b)

Figure 8 Preferred growth in the [001] direction of a typical Nd:YVO_4 crystal. (a) View along [010] (b) View along [001].

to cleave along the (100) and (010) planes. Less frequently, irregular cracks were present. Since diameter fluctuations usually produce a tendency toward cracking as in Figure 9, diameter control was very important. In order to produce reasonable control, the boules could not be too asymmetric.

4 DISCUSSION

The Czochralski growth of a-axis crystals of Nd:YVO_4 posed numerous problems, the first of which was the repeated burn-offs of the boules during growth. As vaporization of V_2O_5 occurred, the bulk composition changed and Nd:YVO_4 crystallized at lower temperatures. The melt temperature was too hot and no longer in equilibrium with the growing crystal and burned off. With continued heating, progressively more V_2O_5 was lost, changing composition and the temperature of crystallization of Nd:YVO_4. The rate of vaporization probably was not constant at all temperatures. After prolonged heating of the melt, a significant amount of YVO_4 decomposed to YVO_3 and O_2 so that growth was no longer possible. Another factor contributing to the burn-off problem was the melt drop in the crucible caused by vaporization. At high melt levels considerably more power was needed to reach growth temperatures than with lower levels. As material vaporized, the melt temperature increased due to lower melt levels. Experiments to determine the vaporization rate of V_2O_5 from the melt by weight loss would be impossible due to simultaneous loss of Nd:YVO_4 and iridium, and because of sample decomposition. After considerable experimentation, the appropriate thermal gradients and interface shape were determined where the IR detector compensated for the melt compositional

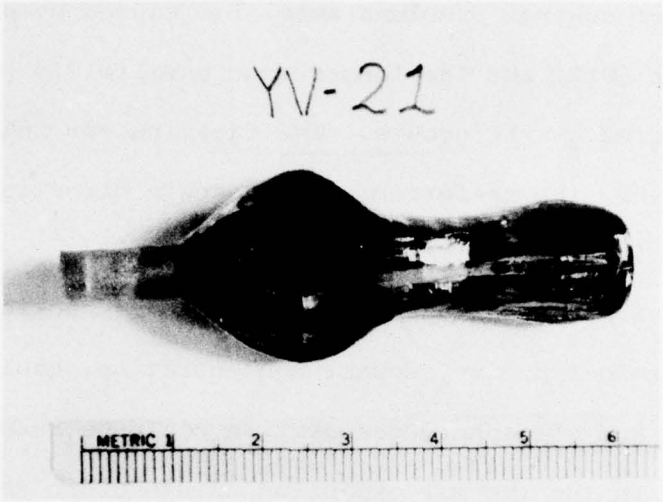


Figure 9 Transverse cracking caused by diameter fluctuations.

changes and adjusted the temperature to routinely grow boules with good diameter control. In order to reduce the problem of V_2O_5 vaporization, an external gas overpressure would be needed in a high pressure crystal puller or growing at lower temperatures from a nonstoichiometric solution.

Diameter control problems were also caused by pronounced crystal faceting on (010) and the longer edge parallel to [100] produced by the preferred c-axis growth. The faceting was inherent with the material, however, the preferred c-axis growth direction can be diminished by reducing the pull rate.

The most persistent problem to date was cracking. Many factors such as chemical purity, dopant concentration, cooling rate, thermal gradients, and atmosphere composition could be responsible. A large difference in the thermal expansion exists along the a and c axes which of course is inherent with the material. If the thermal expansion did not cause the cracking, it surely contributed to the strain in the boule. The parameters listed above are being investigated vigorously to obtain an insight into the fundamental problems of cracking and cleavage.

5 CONCLUSIONS

The Czochralski growth of [100] boules of $Nd:YVO_4$ has been investigated for possible laser application. The principal problems were solved systematically to obtain high quality material. Iridium crucibles were used with RF heating to melt the components. The 1.5 to 2.0 inch diameter crucible was chosen to minimize thermal gradients. The growth station was designed with heavy insulation and chambers to control the growth interface and thermal stress after

pulling. A most important factor was "diameter" control to prevent thermal excursions and "off axis" growth. Fair crystals were grown with low purity pre-reacted YVO_4 and $NdVO_4$. Our own preparations from Y_2O_3 and V_2O_5 gave better results. The best crystals were grown at a rotation rate of 4 rpm, pull rate of .100 inches/hr, and O_2 level of 2%. The single persistent problem of cracking and cleavage on (100) planes has limited size and quality. Cracking was partially associated with the growth parameters, the crystal structure, and purity of starting materials. The growth conditions were studied extensively this period. High quality [100] seed material was prepared from single crystal pieces and a technique was developed for mounting on an iridium wire. Under ideal growth conditions, smooth facets were found on the crystal boules. Initial trials of cutting, core drilling, and other fabrication procedures were deferred until better quality crystals were grown.

6 RECOMMENDATIONS

Further experiments should be conducted on the origin of the cleavage of Nd:YVO_4. The effects of growth gradients, O_2 levels, stoichiometry, and chemical reagent purity should be examined more thoroughly. Experiments on the best manner for fabrication of laser rods should be started. Some spectral data and optical tests should also be collected to correlate with the growth parameters of selected materials.

7 REFERENCES

1 (a) L.G. DeShazer, M. Bass, U. Ranon, J.K. Guha, E.D. Reed, J. Strozyk and L. Rothrock, Paper C1, VIIIth International Quantum Electronics Conference, San Francisco, California, June 10, 1974. (b) Private Communication, J. Strozyk, U.S. Army ECOM, Jan.-Feb, 1975.

2 A.W. Tucker, M. Birnbaum, C.L. Fincher and L.G. DeShazer, J. Appl. Phys. 47, 232 (1976).

3 J.R. O'Connor, Appl. Phys. Letters 9, 407 (1966).

4 W. Phillips and R.J. Pressley, RCA Laboratories Report and Communication on Growth and Properties of Nd:YVO_4 (1969).

5 J.J. Rubin and L.G. Van Uitert, J. Appl. Phys. 37, 2920 (1966).

6 H.M. Dess and S.R. Bolin, Trans. Metall. Soc. AIME 239, 359 (1967).

7 A.D. Morrison, J. Mat. Sci. 8, 1666 (1973).

8 K. Chow and H.G. McKnight, Mat. Res. Bull. 8, 1343 (1973).

9 H.G. McKnight and L.R. Rothrock, ECOM-TR0022F, Contract DAAB-77-C-0022, April, (1973).

10 M. Bass, L.G. DeShazer, U. Ranon, TR-ECOM-74-0104-1, Contract DAAB 07-74-C-010, October 1974.

11 K. Robinson, G.V. Gibbs and P.H. Ribbe, Amer. Mineral 56, 782 (1971).

12 H. C. Schopper, W. Urban and H. Ebel, Solid State Comm. 11, 955 (1972).

13 P.H. Klein and W.J. Croft, J. Appl. Phys 38, 1603 (1967).

14 M. Bass, L.G. DeShazer, and U. Ranon, Report No. ECOM 74-0104-1, 1974.

15 J.D. Foster and L.M. Osterink, Appl. Optics 7, 2428 (1968).

16 Private Communication, J. Strozyk, U.S. Army ECOM, 1977.

17 E.M. Levin, J. Am Ceram. Soc. 50, 381 (1967).

18 R.C. Ropp, Mat. Res. Bull. 10, 271 (1975).

19 G.J. McCarthy, C.A. Sipe, and K.E. McIlvried, Mat. Res. Bull. 9, 1279 (1974).

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