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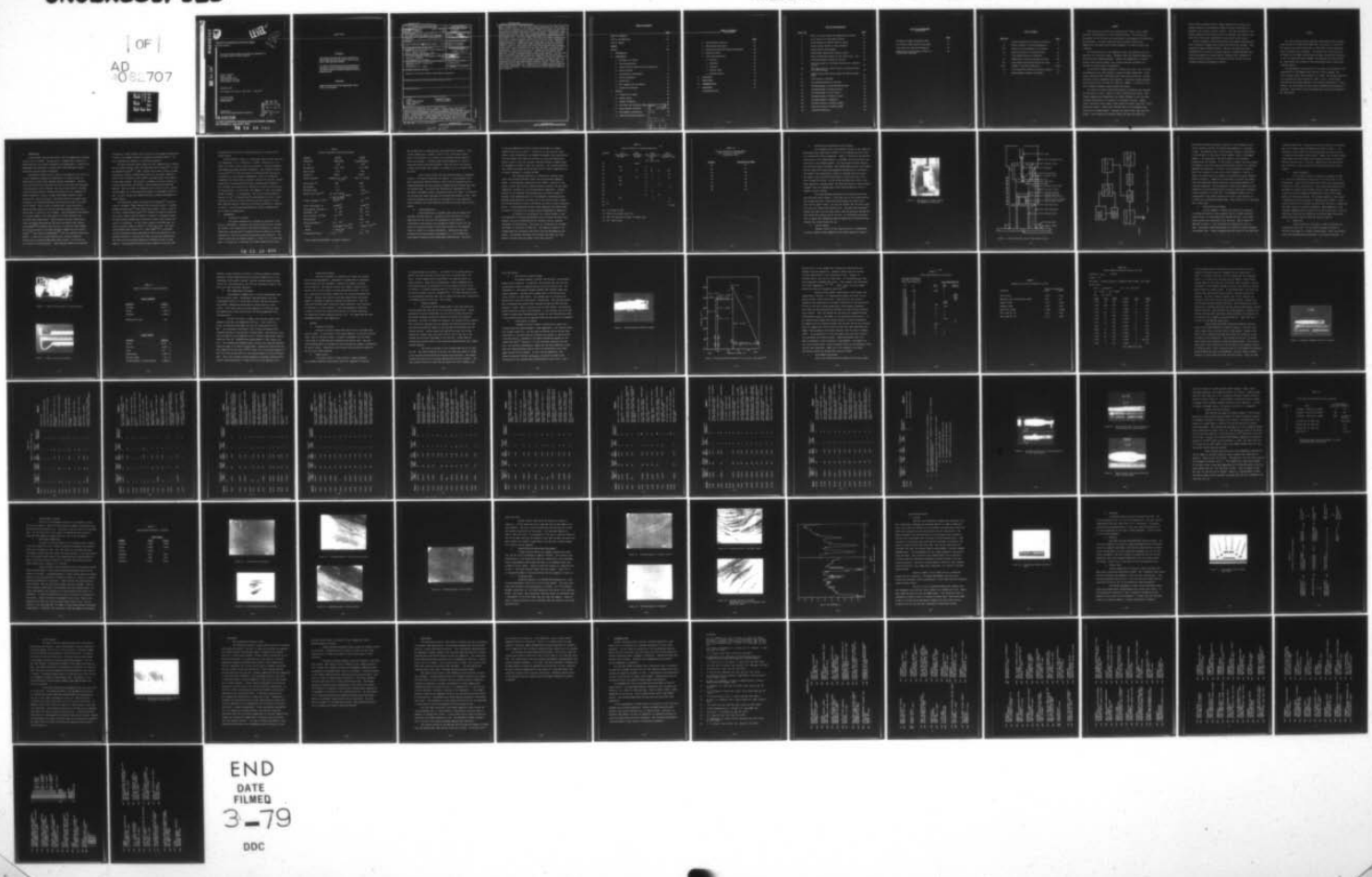

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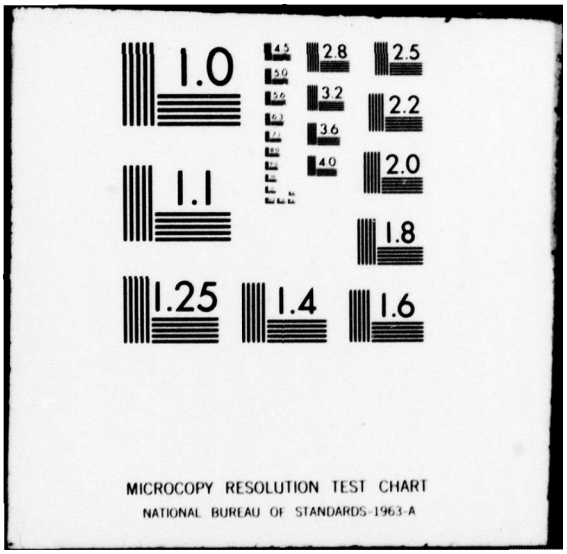
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Research and Development Technical Report

DELNV-TR-76-0908-F

THE SINGLE CRYSTAL GROWTH AND LASER ROD FABRICATION OF NEODYMIUM DOPED YTTRIUM VANADATE

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September 1978

Final Report for Period 1 July 1976 - 1 July 1978

Prepared for
Night Vision & Electro-Optics Laboratory

ERADCOM
US ARMY ELECTRONICS RESEARCH AND DEVELOPMENT COMMAND
FORT MONMOUTH, NEW JERSEY 07703

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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: DELNV-TR-76-0908-F	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER: rept.
4. TITLE (and Subtitle): THE SINGLE CRYSTAL GROWTH AND LASER ROD FABRICATION OF NEODYMIUM DOPED YTTRIUM VANADATE.	5. TYPE OF REPORT & PERIOD COVERED: Final 1 Jul [redacted]76 - 1 Jul [redacted]78.
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Larry E. Drafall [redacted] Roger F. Belt	8. CONTRACT OR GRANT NUMBER(s): DAAB 07-76-C-0908
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Lambda/Airtron Division, Litton Systems, Inc. 200 E. Hanover Avenue Morris Plains, New Jersey 07950	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 84p.
11. CONTROLLING OFFICE NAME AND ADDRESS: U.S. Army Research & Development Command DELNV-L-D (STROZYK) Fort Monmouth, N.J. 07703	12. REPORT DATE: Sep [redacted]78 / 13. NUMBER OF PAGES: viii + 64
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office): Commander, DCASD, Springfield 240 Route 22 Springfield, N.J. 07081	15. SECURITY CLASS. (of this report): Unclassified / 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release, distribution unlimited.

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

18. SUPPLEMENTARY NOTES

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

LASERS
SOLID STATE CRYSTAL
SINGLE CRYSTALS
LASER RODS
NEODYMIUM LASERS
YTTRIUM VANADATE

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

Good quality (100) YVO_4 with 1 atomic % Nd was grown from stoichiometric melts contained in RF heated 50 x 50mm iridium crucibles. Initial growth experiments used reacted phosphor grade YVO_4 and $Nd:VO_4$ 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 amount of V_2O_5 was vaporized which led to changes in melt composition and crystalliz-

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ation temperatures. The YVO_4 melt slowly decomposed into YVO_3 and O_2. High partial pressures of O_2 reduced decomposition rates, but the amount of crucible oxidation was very severe. 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 10 ~~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 99.5% N_2-0.5% O_2 atmosphere at a pull rate of 2.54mm/hr and a rotation rate of 4 rpm. Boules of (100) YVO_4:Nd up to 90mm long x 6mm x 20mm were grown with excellent diameter control. Preferred growth occurred along [001] with large smooth facets on (010) 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 1.25mm/hr the preferred growth direction was much less pronounced. Boules with the pulling axis parallel to [001] exhibited nearly square cross sections. 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) plane which seriously hindered growth and rod fabrication. The cleavage was strongly aggravated by impurity levels. Laser rods of [100] YVO_4:Nd 1%, 3mm O.D. x 30mm long, were fabricated by sectioning the boules followed by O.D. grinding with a diamond embedded wheel to the proper dimensions. The usual polishing and AR coating techniques were applied.

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SUMMARY

This project was initated 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.

The starting purity of the components Y_2O_3, V_2O_5 and Nd_2O_3 was very important for crack-free growth. Phosphor grade YVO_4 prepared commercially gave persistent cracking problems. However our preparations of Nd:YVO_4 worked successfully provided a very careful synthesis procedure was followed to insure proper stoichiometry.

The effects of thermal gradients, rotation rate, pull rate, O_2 levels and annealing cycles were studied to obtain reliable growth data. After growth conditions were established using lower purity materials, the best available starting components were employed. Successful growth parameters were rotation rates of 4 rpm, pull rates of 2.5mm/hr., O_2 levels of 0.5% and low thermal gradients during growth and cooling.

The crystal structure associated problems of morphology and cleavage were difficult to solve. Boules of [100] orientation were grown. 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.

Factors such as chemical purity, dopant concentration, cooling rate, thermal grandients and atmospheric composition were investigated to determine their effects on boule fracture. The large difference in the thermal expansion along the a and c crystallographic axes limited large crack-free crystals and contributed to some strain in the boules.

Several mechanical fabrication methods were examined including the usual technique of diamond core drilling and centerless grinding. Both resulted in highly fractured pieces. The best rod fabrication was accomplished by careful O.D. grinding against a diamond embedded wheel using large amounts of cooling fluid to dissipate heat accumulation. Polishing and AR coating of the finished rods were routine using the standard techniques developed for Nd:YAG.

PREFACE

This Final Technical Report describes experimental work performed under Contract No. DAAB 07-76-C-0908 from 1 July 1976 to 1 July 1978. 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. The passive tests on finished laser rods were performed by Mr. David Dentz.

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 haye 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. $Wcm^{-1}K^{-1}$	$\parallel$c axis 0.0523, $\perp$c axis 0.0510 @ 300°K	0.13 [13]
Thermal expansion, $10^{-6}C^{-1}$	da-4.43, dc-11.37 [12]	6.9 [15]
*Laser wavelength, μm	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	$8.5 \pm 0.9 \times 10^{-6}$ °K^{-1} [16]	7.3×10^{-6} °C^{-1} [15]
dne/dt	$3. \times 10^{-6}$ °K^{-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. Near the end of the program a heavy wall (0.100) inch crucible 1.5 inches I.D. by 1.5 inches high was used.

After several growth runs, the crucibles must be thoroughly cleaned. All traces of melt must be removed. A large diameter core drill removed the central section of solid from the crucible and the remaining material was then carefully chipped and grit blasted away from the crucible wall. The vessel was then placed in hydrochloric acid overnight, thoroughly rinsed, and pressure tested for leaks. If necessary, the crucible was welded and again grit blasted and cleaned in acid. This cleaning technique was important for the removal of trace impurities which accumulate and could otherwise interfere with good quality crystal growth.

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. Another source of V_2O_5 was obtained from GTE Sylvania as NH_4VO_3 which was decomposed at 200°C to NH_3, H_2O, and V_2O_5. The starting materials Y_2O_3, NH_4VO_3 and Nd_2O_3 were mixed and fired at various temperatures in an oxygen atmosphere to produce Nd:YVO4.

The starting materials for charging the crucibles were always the prereacted Nd:YVO_4 rather than the unreacted component oxides. At the melting temperatures near 1900°C, a portion of the highly volatile V_2O_5 could be vaporized before reaction with the other components, resulting in a non-stoichiometric composition. Typical analysis of our chemical starting materials are given in Table II. 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.

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 Lot 1	V_2O_5 Lot 2	V_2O_5 Lot 3	YVO_4 (Sylvania) Phosphor Grade
Sm		200(2)				
Al	ND		<1	1		
Ca	<20	12	<1	10	<1	1-10
Cu			<1	3		<1
Si	<20	60	10	2	5	65
Ti	ND		2			
Mg	ND		<1		<1	6
Cr			1			5
Mn			1	2		
Ag			<1		<1	
Fe	ND			1		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

c. Growth Station Construction and Gradients

The equipment used to grow Nd:YVO_4 (Figure 1) was capable of maintaining high temperatures (1860°C) for an extended period of time in a satisfactory growth atmosphere. Figure 2 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 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 3.

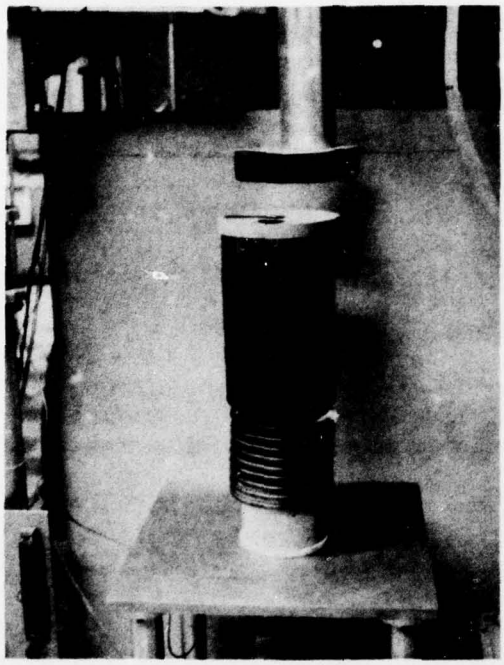


Figure 1. Photograph of Growth Station and Temperature Controls.

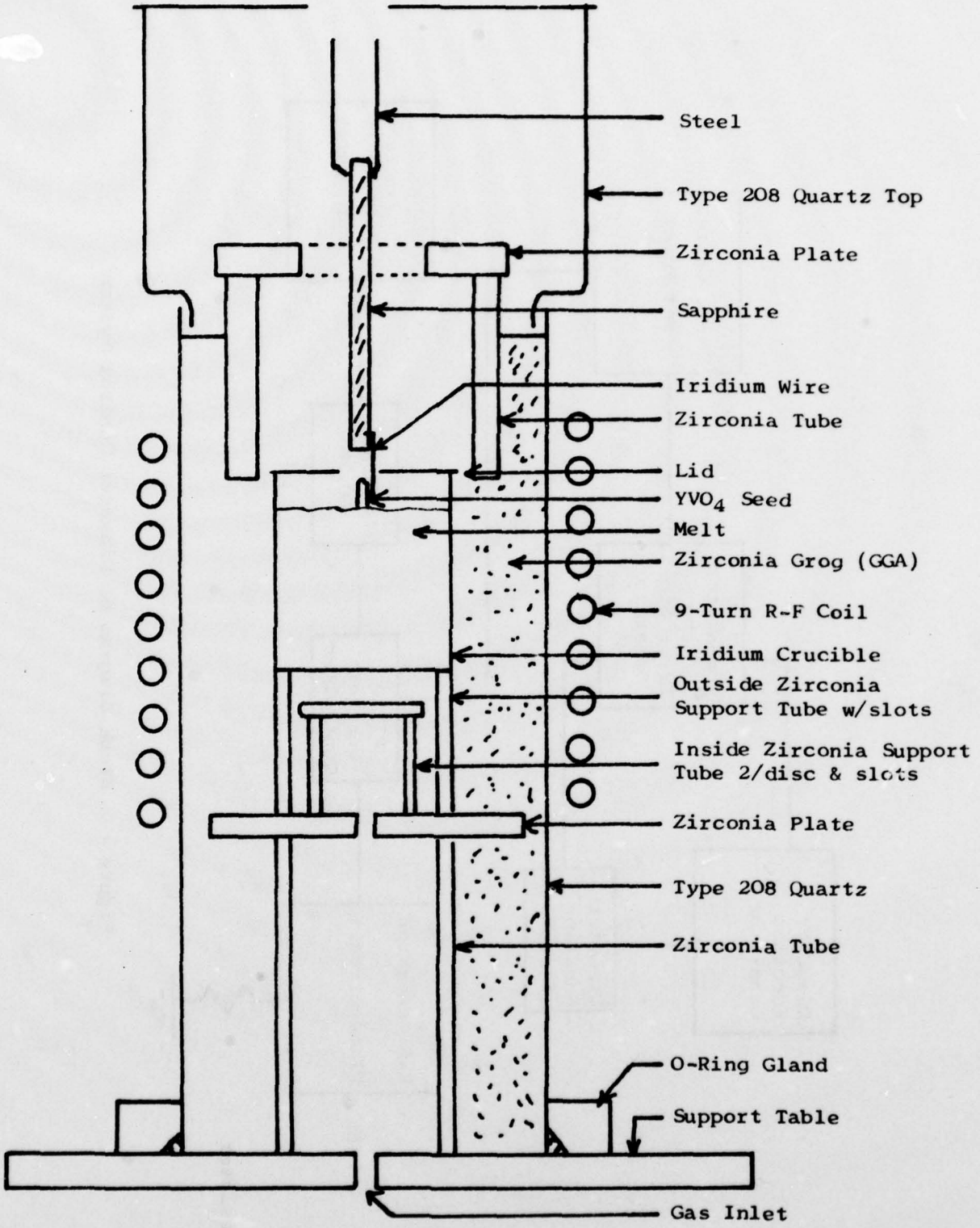


Figure 2. Cross sectional view of YVO_4 growth station.

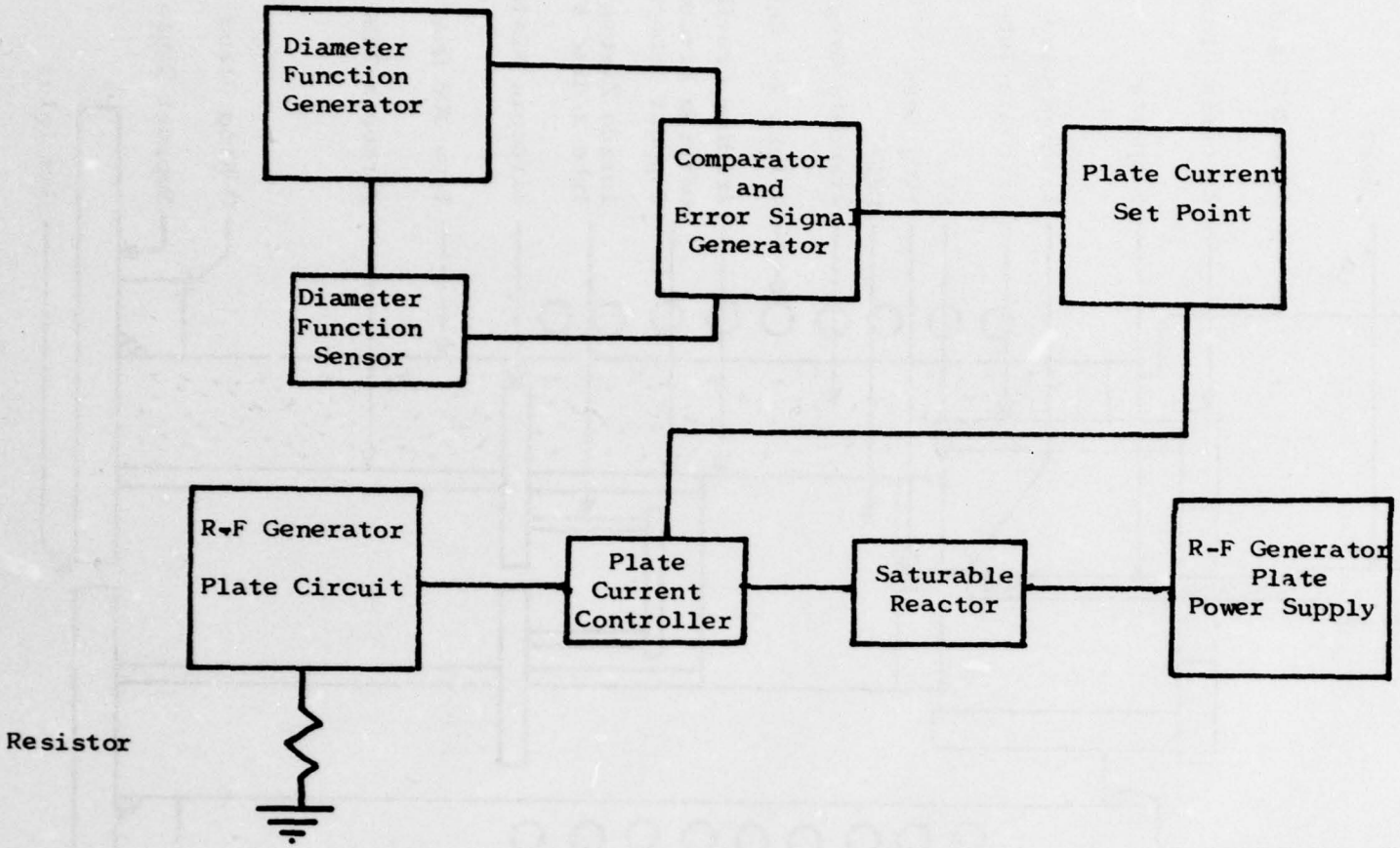


Figure 3. Block Diagram of Diameter Control System

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 were not very successful due to a highly insulated growth system. By slow cooling the crucible and melt, solid single crystal pieces were extracted by core drilling. Some of these are depicted in Figure 4. 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 5. 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 the initial growth of Nd:YVO_4 an atmosphere of 98% N_2 - 2% O_2 was established at flow rates of 11.2 and 0.244 ft ^{3}/hr., respectively. Later in the program better results were obtained with O_2 levels of 0.5% O_2 instead of 2%. 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. Liquid storage facilities for nitrogen and oxygen were used where by impurities like water vapor are virtually eliminated. Solid impurities in the cryogenic atmosphere tend to settle out in the storage tank. Since the tanks have liquid and gas coexisting, the solids remain there inert. Typical purities of the two gases are given in Table IV.

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

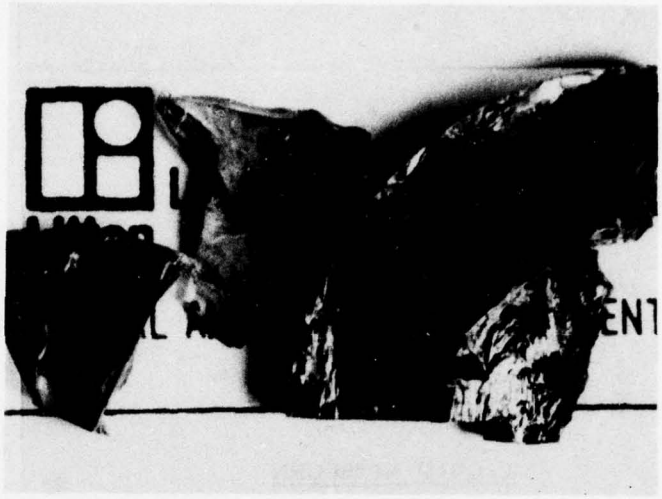


Figure 4 Single crystal pieces of YVO_4 from melt.

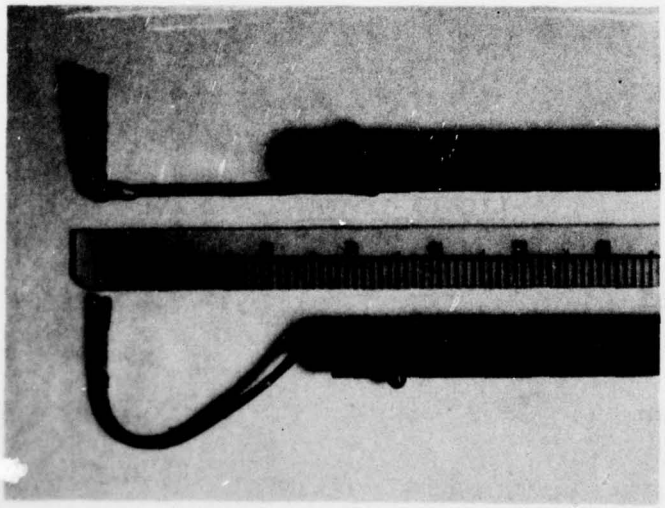


Figure 5 Single crystal seed holders.

TABLE IV

Impurity Analysis of Liquified Gases

LIQUID NITROGEN

Analysis	Typical
Nitrogen	99.997 %
Oxygen	0.0015 %
Hydrogen	0.0005 %
Carbonaceous Gases	Nil

LIQUID OXYGEN

Analysis	Typical
Oxygen	99.70 %
Nitrogen	0.005 %
Argon	0.3 %
Hydrocarbons	0.0015 %
Nitrogen Oxide	Nil %
Carbon Monoxide & Carbon Dioxide	0.00015 %

addition, a-axis crystals are subject to adverse problems of thermal expansion, thermal conductivity and rotational asymmetry due to the 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 successful 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+} The segregation coefficient of Nd in YVO_4 was measured from elemental analyses of top portions of grown boules. The analyses of Nd were performed by first preparing a set of standard compositions from 0-2 atomic per cent Nd. Standards were mixed powders of Y_2O_3, Nd_2O_3, and V_2O_5. The standards and powdered single crystals were analyzed simultaneously by means of an optical spectrograph. Segregation coefficients (k) were computed from the ratio, $K=^{Cs}/Cl$, where Cs is the analyzed amount of Nd in the solid crystal and Cl is the initial amount of Nd in the liquid melt. From a set of three crystals prepared at different intervals with various starting materials, a range of 0.31-0.33 was obtained for k.

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 slowing 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 were free of all 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 15-20mm was more successful than shorter ones. The long seeds extended above the crucible lid and increased the gradient sufficiently for 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 0.5-2.0% 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 which 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.

The level of the melt in the crucible must not be too near the top. The surface tension of the melt was large and tended to "creep" up the crucible walls wetting the zirconia grog insulation. The thermal gradient was then very low causing repeated burn-offs and flashing. The only recourse would be to shut down the growth run after cleaning, and

reset the station.

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 slowing to room temperature. Two distinct layers were evident (Figure 6). 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 $Y2O_5$-V_2O_5[17] (Figure 7), 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

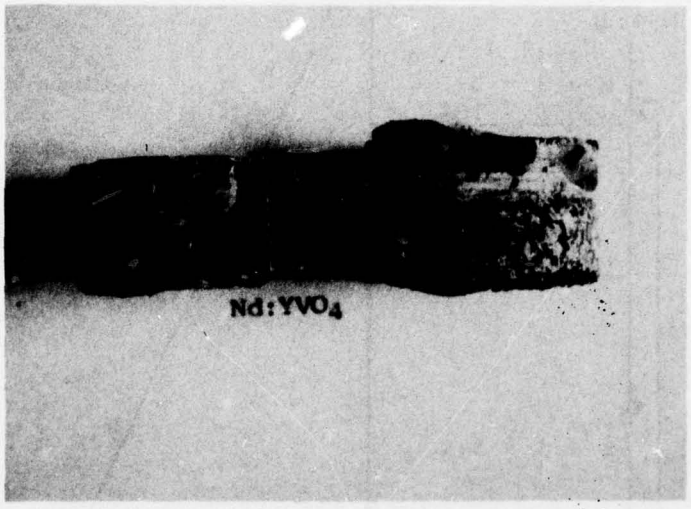


Figure 6. YVO_4:Nd Showing Two Distinct Layers.

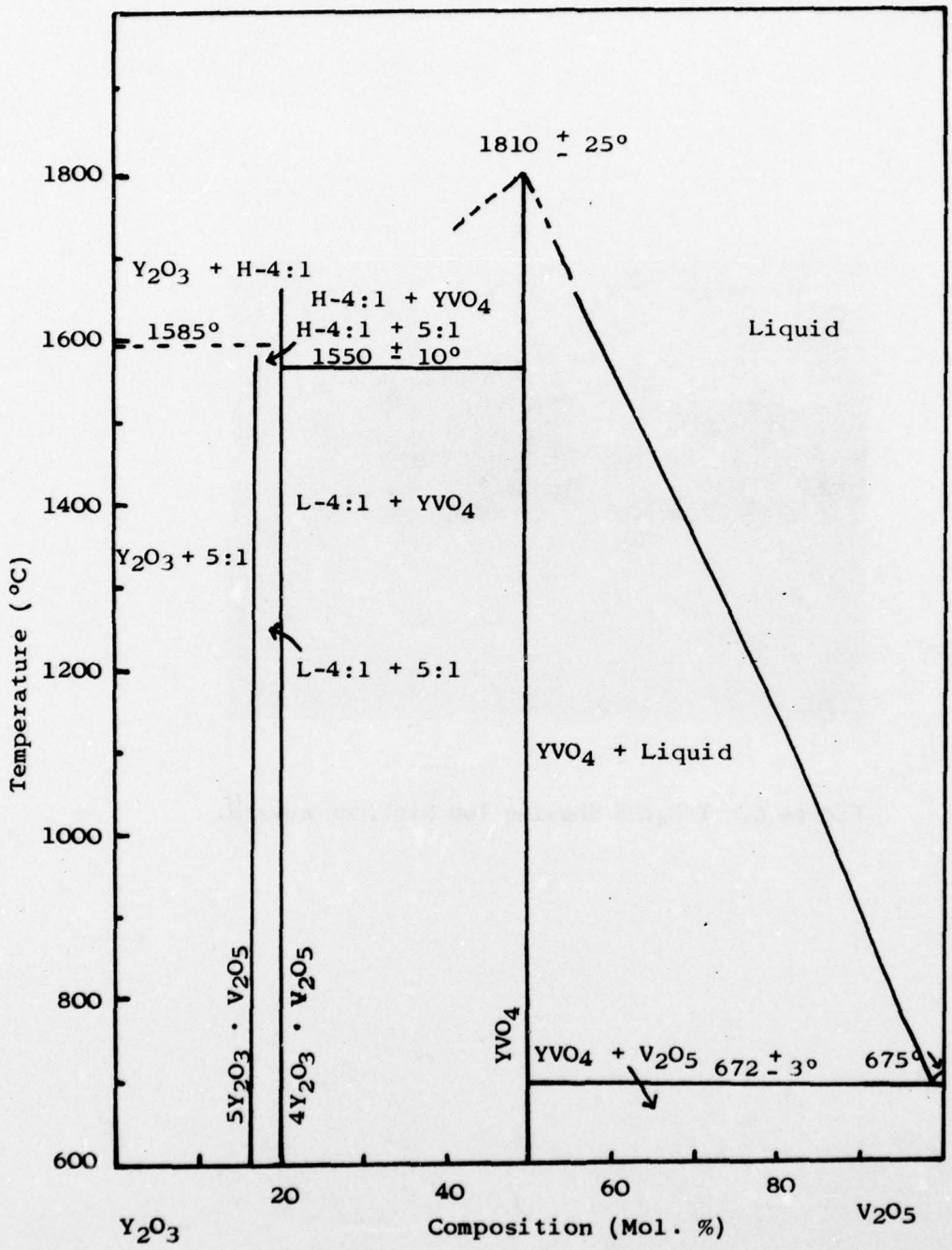


Figure 7. Phase equilibrium diagram for the system Y_2O_3-V_2O_5.[17]

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 identified these same compositions [17, 18] Table V gives the x-ray powder diffraction data for the phases identified [18]

During crystal growth, vaporization of V_2O_5 changes the composition of the melt. If compositional changes also occur in the pulled crystal, cracks could occur. Precision unit cell lattice parameters were measured by x-ray powder diffraction on the top portion (YV-44) of the first crystal grown from a fresh charge of phosphor grade YVO_4 and the bottom portion (YV-50)of the third crystal from the same crucible. After each growth run the charge was compensated with fresh material equal to the weight of the previously grown crystal. If any compcsitional changes occur during growth, it would be magnified by sampling the first material pulled from the melt and the last portion. Table VI compares the results from the study with other published data. Sample YV-44 parameters were almost identical with the work of Schwarz (1963). The a parameter of YV-50 also agreed well with other work but the c parameter was slightly larger. More measurements need to be made to determine if this variation is reproducible. The samples for this study contain about 1 mole % Nd dopant which did not measurably alter the unit cell parameters. Table VII is the complete x-ray powder diffraction pattern for undoped YVO_4 measured by NBS.

f. Run Examples and Results

Most of the difficulties with growth in the early stages

(18)

TABLE V

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	

TABLE VI

Comparison of Lattice Constants for YVO_4

Reference	Unit Cell Parameters $\underline{a}$ (Å)	$\underline{c}$ (Å)
Broch (1933)	7.140	6.191
Milligan, Watt and Rachford (1949)	7.10	6.27
Nautov (1962)	7.114	6.258
Schwarz (1963)	7.123	6.291
NBS (25°C) (1965)	7.1192	6.2898
This study No. 44	7.122	6.291
This study No. 50	7.123	6.306

TABLE VII

X-Ray Powder Diffraction Pattern for YVO_4

Radiation: $Cu_{K\alpha_1}$ 1.5405 Å

Filter: Ni

Reference: National Bureau of Standards Report 8944, July (1965)

Crystal Data:

Syst.: Tetragonal S.G. I 4_1/ amd (141)

a_o: 7.1192 c_o: 6.2898

Z=4 Dx 4.247

d (Å)	I/I_1	(hkl)	d (Å)	I/I_1	(hkl)
4.711	8	101	1.5915	8	420
3.559	100	200	1.5722	4	004
2.831	2	211	1.5485	2	402
2.668	45	112	1.4805	12	332
2.518	12	220	1.4381	8	204
2.357	6	202	1.3884	4	501
2.220	12	301	1.3334	8	224
2.012	6	103	1.2894	<1	314
1.884	6	321	1.2761	8	512
1.830	45	312	1.2586	2	440
1.780	14	400	1.1865	6	600
1.751	2	213	1.1783	4	503,404
1.666	2	411	1.1699	2	215

Plus additional lines

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 30mm, but the taper was large which caused cracking. 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 85 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 8). Table VIII 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 9. 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 to cleave along the (100) and (010) planes. Figure 10 shows

Figure 8. Excellent diameter control of crystal.

TABLE VIII

Summary of Nd:YVO_4 growth runs*

Run No.	Crystal (1) Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Starting (2) Material	Comments
YV-1	--	--	--	--		Crucible leak
YV-2	--	--	--	--	A	Crucible melted, sprayed YVO_4.
YV-3	--	--	--	--	A	No crystal, fast cool for seeds.
YV-4	--	--	--	--	A	Crucible leak.
YV-5	--	--	1.25	50	A	Small pulled crystal, melt cut up for seeds.
YV-6	11	60	1.25	24	A	No haze in crystal, botton cracked.
YV-7	--	--	--	--	A	Crucible leak.
YV-8	--	--	--	--	A	Material extruded from crucible.
YV-9	15	30	1.25	24	A	Clear part of crystal looks good, no cracks.
YV-10	--	--	--	--	A	Seed & holder fell into melt. No crystal.
YV-11	10	13	2.50	30	A	Crystal has no cracks, very short, looks clear.
YV-12	12	20	2.50	4	A	Crystal short & cracked.
YV-13	(12)(6)	61	5.0	4	A	Fast pull rate, crystal cracked, transverse cracks at diameter changes.

Run No.	Crystal (1) Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Starting (2) Material	Comments
YV-14	(11)(6)	43	2.50	4	A	Top of crystal looks good, cracks start at diameter changes.
YV-15	14	10	2.50	20	A	Short crystal, irregular shape, cracked.
YV-16	--	--	--	--	A	No crystal - melt used for seeds.
YV-17	--	--	--	--	A	No crystal. Seed broke and fell into melt.
YV-18	--	--	--	--	A	Surface froze, shut down, no crystal.
YV-19	15	5	2.50	10	A	Crystal very short, no cracks.
YV-20	--	--	--	--	A	For seeds, try to dip seed & cool melt for seeds.
YV-21	17	50	2.54	4	A	Crystal about 2", cracked at diameter changes.
YV-22	(12)(6)	16	2.54	4	A	Crystal is irregular in shape and cracked.
YV-23	15	40	2.54	4		Boule very irregular in shape, composition 10 mole % excess Y_2O_3.
YV-24	--	--	--	--	D	No crystal, melt wet grog.
YV-25	--	--	--	--		No crystal, nonstoichiometric melt, 5 mole % excess Y_2O_3. Seed too short after burnoff.
YV-26	(16)(10)	30	2.54	4	A	Crystal cracked, boule shifted and is asymmetric.
YV-27	--	--	--	--	A	No crystal, V_2O_5 added to compensate for vaporization. Impossible to start.

Run No.	Crystal (1) Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Starting (2) Material	Comments
YV- 28	11	5	2.54	4		Small crystal, nonstoichiometric melt, 5 mole % excess Y_2O_3.
YV-29	(14)(7)	40	2.54	4	A	Small crucible (1 1/2" ID x 2" hi.) longitudinal cracks, crystal has an hourglass type shape, no transverse cracks.
YV-30	(17)(7)	30	2.54	4	A	Longitudinal and transverse cracks, diameter control fair.
YV-31	(13)(7)	30	2.54	4	A	Transverse cracks at diameter changes. No longitudinal cracks.
YV-32	--	--	--	--	A	Crucible failure.
YV-33	20	30	1.25	4	A	Boule more equidimensional, quality looks good, some longitudinal cracks.
YV-34	10	10	2.54	4	A	Poor quality, many cracks, may be from poor quality seed.
YV-35	(16)(6)	57	2.54	4	A	Good length, good diameter control, quality looks good, transverse and longtitudinal cracks.
YV-36	(14)(7)	10	2.54	4	A	Very short boule, transverse cracks.
YV-37	(14)(6)	65	2.54	4	A	Good length, good diameter control. Transverse and longitudinal cracks.
YV-38	(15)(6)	15	2.54	4	A	Very short crystal, longitudinal crack.
YV-39	(13)(8)	53	2.54	4	A	Good length, longitudinal and transverse cracks.
YV-40	(12)(10)	15	1.25	4	A	Very short.

Run No.	Crystal (1) Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Starting(2) Material	Comments
YV-41	(10)(4)	38	2.54	4	A	Crystal looked good, cracked after removal from station.
YV-42	(13)(7)	47	1.25	4	A	Good length, good diameter control, longitudinal & transverse cracks.
YV-43	(15)(4)	50	1.90	4	A	Good length, crystal cracked during cutting.
YV-44	(11)(8)	65	2.54	4	A	Good length, crystal looks good, one crack and diameter change.
YV-45	(14)(6)	60	2.54	4	A	Good length, longitudinal and transverse cracks.
YV-46	7	60	2.54	4	A	Crystal cooled in melt, very thin, longitudinal crack.
YV-47	(15)(6)	50	2.54	4	B	Medium length, paddle shape, longitudinal and transverse cracks.
YV-48	(10)(6)	39	1.25	4	B	Medium length, control good, longitudinal crack after removal from station.
YV-49	(14)(6)	48	1.25	4	B	Good length, excellent shape, no cracks.
YV-50	(14)(7)	35	1.25	4	A	Short crystal, paddle shape, longitudinal and transverse cracks.
YV-51	(10)(6)	38	1.25	4	B	Short crystal, good diameter control, longitudinal and transverse cracks.
YV-52	(15)(8)	20	1.25	4	A	Short crystal, poor quality, crystal cracked, 50% normal Nd. content.

Run No.	Crystal (1) Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Starting (2) Material	Comments
YV 53	(13)(7)	37	1.25	4	B	Short crystal, excellent control, transverse and longitudinal cracks.
YV-54	(10)(3)	20	1.90	4	A	Short crystal, irregular shape, longitudinal cracks.
YV-55	(10)(6)	20	1.90	4	A	Short crystal, irregular shape, longitudinal cracks, iridium seedholder.
YV-56	(12)(6)	40	1.25	4	A	Short crystal, etched by vapor, longitudinal cracks.
YV-57			2.54	4	A	Very small crystal, used for a seed.
YV-58	(12)(8)	50	2.54	4	A	Medium length, transverse and longitudinal cracks, iridium seedholder.
YV-59	(10)	48	1.25	4	A	Poor control, irregular shape, very cracked, iridium seedholder.
YV-60	(12)(8)	55	1.25	4	A	Medium length, fair control, longitudinal and transverse cracks.
YV-61	(10)(6)	55	1.25	10	A	Medium length, good control, transverse and longitudinal cracks.
YV-62	(14)(6)	41	1.25	4	A	Short crystal, longitudinal and transverse cracks (after heater).
YV-63	(7)(5)	48	2.54	4	A	Medium length, good control, O_2 from 2.0% to 0.5%, crack free.
YV-64					A	No crystal, melt wet the grog.
YV-65	(9)(7)	61	2.54	4	D	Good length, good control, no cracks, 0.5% O_2.

Run No.	Crystal (1) Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Starting (2) Material	Comments
YV-66	(10)(6)	65	2.54	4	A	Good length, poor control, irregular shape, longitudinal and transverse cracks.
YV-67	(8)(5)	45	2.54	4	D	Good length, good control, no cracks, 0.1% O_2 .
YV-68					A	No crystal melt wet grog.
YV-69	(10)(6)	38	2.54	4	A	Short crystal, tapered, longitudinal crack, no O_2 for this run.
YV-70	(10)(6)	60	2.54	4	A	Good length, poor control, irregular shape, longitudinal and transverse cracks 2.0% O_2.
YV-71	(10)(5)	55	2.54	4	A	Good length, poor control, irregular shape, longitudinal and transverse cracks .1% O_2.
YV-72	(6)	60	2.54	4	B	Good length, excellent control, no cracks .5% O_2.
YV-73	(7)	60	2.54	4	B	Good length, excellent control, 1.0 % O_2 , cracking caused by power failure.
YV-74	(11)(6)	60	2.54	4	B	Good length, excellent control,1% O_2. transverse longitudinal cracks due to power failure.
YV-75	(12)(6)	55	2.54	4	B	Good length, good diameter control, longitudinal crack, 1.0% O_2.
YV-76	(10)(8)	60	2.54	4	B	Good length, fair control, cracked aftergrowth, heavy wall crucible.
YV-77	(10)(7)	45	2.54	4	B	Short crystal, fair control, longitudinal crack, extra reflector in after heater.

Run No.	Crystal (1) Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Starting (2) Material	Comments
YV-78	(8)(7)	25	2.54	4	B	Short crystal, used for seed.
YV-79	(6)(4)	64	2.54	4	B	Good length, excellent control, no cracks.
YV-80	(11)(4)	50	2.54	4	C	Poor crystal, poor control, longitudinal and transverse cracks, blue color.
YV-81	(8)	35	2.54	4	C	Poor crystal, good control, longitudinal and transverse cracks, power failure, blue color.
YV-82					B	No crystal decomposed melt.
YV-83	(12)(6)	60	2.54	4	CB	Good length, fair control, longitudinal cracks, blue color NH_4VO_3.
YV-84	(11)(6)	55	2.54	4	B	Good length, excellent control, no cracks .5% O_2.
YV-85	(9)(6)	85	2.54	4	B	Excellent length, excellent control, no cracks .5% O_2.
YV-86	(11)(6)	70	2.54	4	CB	Good length, fair control, longitudinal cracks, blue color, NH_4VO_3.
YV-87	(12)(7)		2.54	16	A	Good length, fair control, longitudinal and transverse cracks.
YV-88					B	No crystal (crucible leaked).
YV-89					CB	No crystal (coil arced and leaked).
YV-90	(10)(6)	50	2.54	4	A	Medium length, poor control, longitudinal cracks.

Run No.	Crystal (1) Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Starting (2) Material	Comments
YV-91	(7)(5)	40	2.54	4	B	Short crystal, fair control, no cracks.
YV-92	(10)(6)	50	2.54	4	B	Medium length, poor control, longitudinal and transverse cracks.
YV-93			2.54	4	B	No crystal, decomposed melt.
YV-94	(10)(6)	70	2.54	4	B	Good length, poor control, longitudinal and transverse cracks.
YV-95				4	B	No crystal, decomposed melt.
YV-96				4	B	No crystal, decomposed melt.
YV-97	(10)(5)	80	2.54	4	B	Good length, good control, longitudinal and transverse cracks.
YV-98	(10)(5)	70	2.54	4	B	Good length, poor control, no cracks.
YV-99	(12)(7)	90	2.54	4	C	Good length, fair control, longitudinal and transverse cracks, blue color.
YV-100	(10)(5)	45	2.54	4	B	Short crystal, poor control, longitudinal and transverse cracks
YV-101	(12)(6)	60	2.54	4	C	Medium length, poor control, longitudinal and transverse cracks, blue color.
YV-102	(11)(5)	80	2.54	4	C	Good length, poor control, longitudinal and transverse cracks, blue color.
YV-103	(12)(7)	70	2.54	4	B	Good length, fair control, longitudinal and transverse cracks.
YV-104	(11)(6)	50	2.54	4	B	Medium length, fair control, no cracks, very good quality.
YV-105	(11)(6)	55	2.54	4	B	Medium length, fair control, no cracks.

Run No.	Crystal (1) Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Starting (2) Material	Comments
YV-106	(11)(6)	90	2.54	4	D	Good length, fair control, longitudinal and transverse cracks.
YV-107					B	No crystal, decomposed melt.
YV-108	(10)(6)	65	2.54	4	D	Good length, poor control, longitudinal and transverse cracks.
YV-109	(10)(5)	55	2.54	4	B	Medium length, fair control, new lot V_2O_5, no cracks, very good quality.
YV-110	(11)(	75	2.54	4	B	Good length, good control, longitudinal and transverse cracks.
YV-111	(11)(5)	50	2.54	4	B	Medium crystal, fair control, no cracks, very good quality.
YV-112	(10)(6)	68	2.54	4	B	Good length, poor control, longitudinal and transverse cracks.
YV-113	(10)(7)	80	2.54	4	B	Very good length, good control, no cracks, excellent quality crystal.
YV-114	(10)(7)	94	2.54	4	B	Excellent length, good control, longitudinal cracks.
YV-115	(10)(7)	94	2.54	4	B	Excellent length, good control, longitudinal cracks.
YV-116	(10)(7)	80	2.54	4	B	Very good length, good control, longitudinal and transverse cracks.
YV-117	(11)(7)	60	2.54	4	B	Good length, very good control, no cracks.

Run No.	Crystal (1) Diameter (mm)	Crystal Length (mm)	Pull Rate (mm/hr)	Rotation Rate (rpm)	Starting (2) Material	Comments
YV-118					B	No crystal melt wet to grog.
YV-119					B	No crystal melt wet to grog.

* Unless otherwise stated, material composition is stoichiometric

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

2- The starting materials for growth are designated as follows:

A) Sylvania phosphor grade YVO_4.

B) Our preparation using UMC Grade I V_2O_5.

C) Our preparation using Sylvania NH_4VO_3.

D) "Crackle" from previously grown boules.

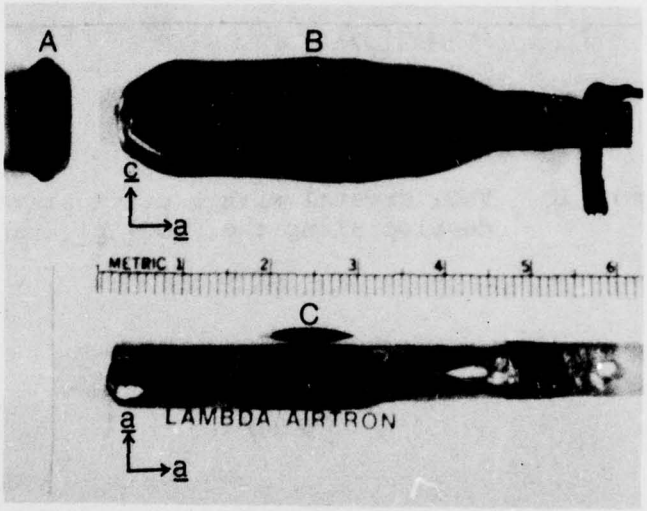


Figure 9 Preferred growth in the [001] direction of a Nd: YVO_4 crystal

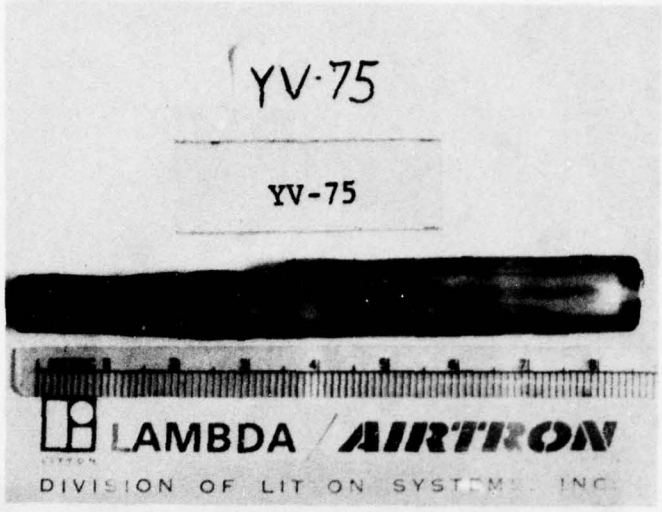


Figure 10 YVO_4 crystal with a crack starting to develop along the (100) cleavage.

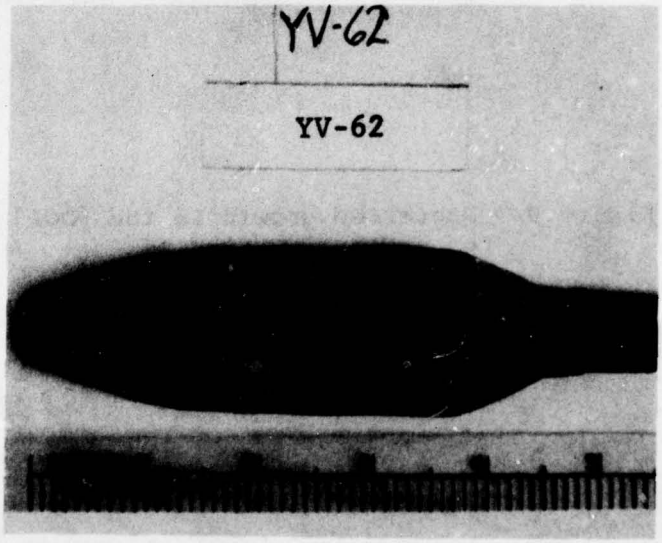


Figure 11 Single crystal with cracks along the (010) cleavage plane.

the color fringes of a crack along the (100) cleavage. Such a crack invariably propagates the length and width of the crystal. Typical cracks along the (010) plane and a less frequently occurring irregular vertical crack are shown in Figure 11. Since diameter fluctuations usually produce a tendency toward cracking, diameter control was very important. In order to produce reasonable control, the boules could not be too asymmetric.

g. Neutron Activation Analysis

Since Nd:YVO_4 was grown in iridium crucibles, several boules were sent to Union Carbide Research Center for neutron activation analysis to determine the amount of iridium in the crystals. The detection of low levels of Ir (under 1ppm) is difficult but can be done best by neutron activation method. The procedure was performed on 1-5 g of powdered crystal with a sensitivity of about .01-0.1 μg. The analysis is based on the detection of 0.316 and 0.468 meV γ-rays from decay of Ir^{192} which has a half life of 74.2 days. The Nd in the yttrium orthovanadate complicates the analysis because of the Nd^{147} decay via the 0.319 meV γ-rays. The short half life of 11 days and the small amount of Nd in the samples however does not cause long delays before counting can begin.

Three crystals grown in various O_2-N_2 atmospheric compositions and one sample of the melt along with three standards were submitted for analysis. Table IX lists the results. The amount of Ir in the three crystals was extremely low except for No. 4. This sample had a small dark stringer in the boule along a crack which apparently was iridium according to the very high iridium values for this particular crystal. Even the sample of YVO_4 melt (No. 70) had very low Ir content. Based on a limited amount of data, the crystal grown in 1% O_2 had more Ir present than the 2% O_2 atmosphere, but still was very low.

TABLE IX

1% Nd doped YVO_4 Neutron Activation Analysis

Sample No.	Source	Ir Content(ppm) Calculated	Ir Content(ppm) Measured
1	Standard - High purity powder	0	.01
2	Standard - High purity powder	200	155
3	Standard - High purity powder	1000	too high to measure
4	Crystal No. 50, 2%O_2 atm.	--	very high*
5	Crystal No. 76, 1%O_2 atm.	--	.92
6	Crystal No. 70, 2%O_2 atm.	--	<.04
7	Melt No. 70	--	<2.1-1.6

*Crystal had dark colored "stringer" in crack which apparently was iridium.

h. Spectrographic Analysis

Results of spectrographic analyses of two Nd:YVO_4 crystals are given in Table X. Boule YV-99 was grown with NH_4VO_3 starting materials and YV-110 with high purity V_2O_5. Both boules used the same lot of 99.9999% Y_2O_3. The two boules were quite similar in composition with potassium being the major impurity ranging from 0.01-.02% in the two samples.

i. Microscopic Examination

In order to study the quality of the Nd:YVO_4 boules, cleavage pieces were etched in a 50-50 volume % solution of phosphoric and sulfuric acids for 30 seconds at 130°C. The etch figures on the (100) plane has rectangular outlines with the longer dimensions parallel to the [010] direction. The crystals grown early in the program had etch figure densities of about $2 \times 10^5/cm^2$ as seen in Figure 12. The more recent boules were of better quality with a density of $2 \times 10^4/cm^2$.

Figure 13 shows a feature observed early in the growth program. Boule sections appear to have slight grain misorientations which run the length of the boule. A photomicrograph of a boule section which was cleaved parallel to the misorientations is shown in Figure 14. There is a definite preferred orientation of the grains. Figure 15 shows the same direction after etching. Note the etch figures which form long stringers. Many of these stringers extend across the boundaries into the adjacent grain. By careful measurement the stringers do not form straight lines across the boundaries. A slight misorientation of about 1-2° exists for the ones in this figure. Figure 16 shows an enlargement of this area. Some of the boundaries have many etch figures present while others do not. As the quality of the seeds improved, the number of grain misorientation decreased significantly. Eventually only seeds with a very low number of misorienta-

TABLE X

Spectrographic Analyses of Nd:YVO_4

	Boule Number	
ELEMENT	YV-99	YV-110
Aluminum	0.002%	0.002%
Sodium	0.002%	0.003%
Silicon	0.002%	-
Vanadium	High	High
Yttrium	High	High
Potassium	0.01%	0.02%

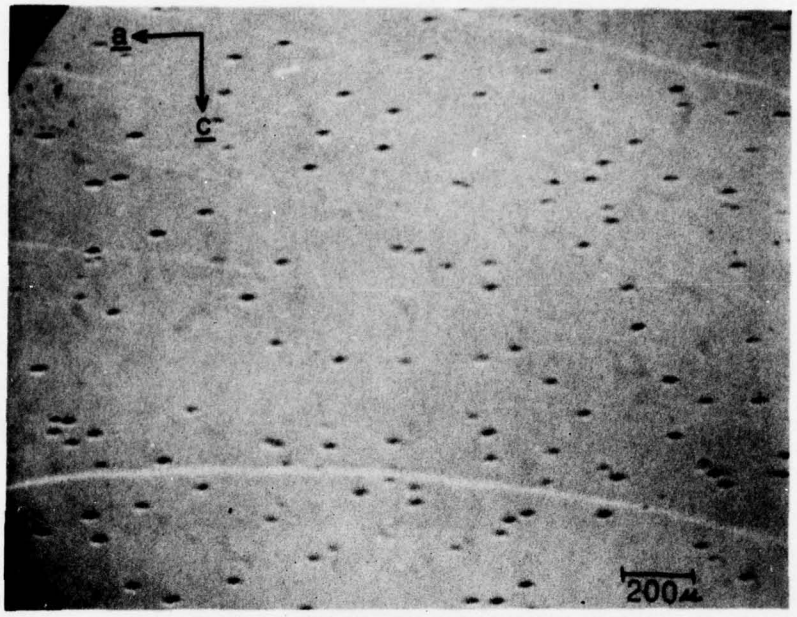


Figure 12 Etch figures in Nd:YVO_4

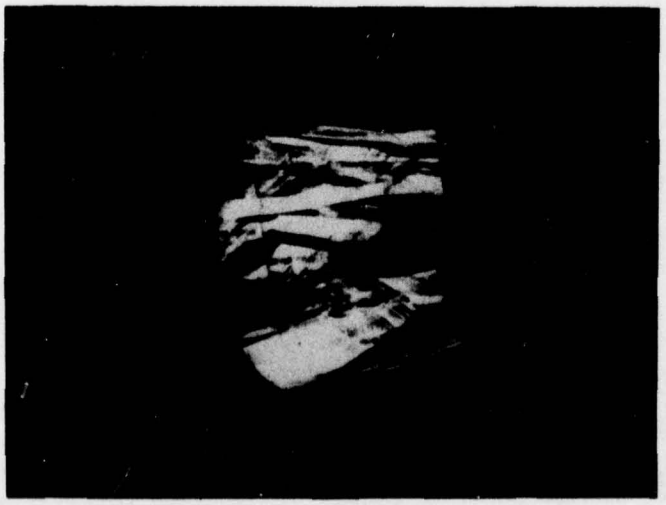


Figure 13 Grain misorientations in Nd:YVO_4

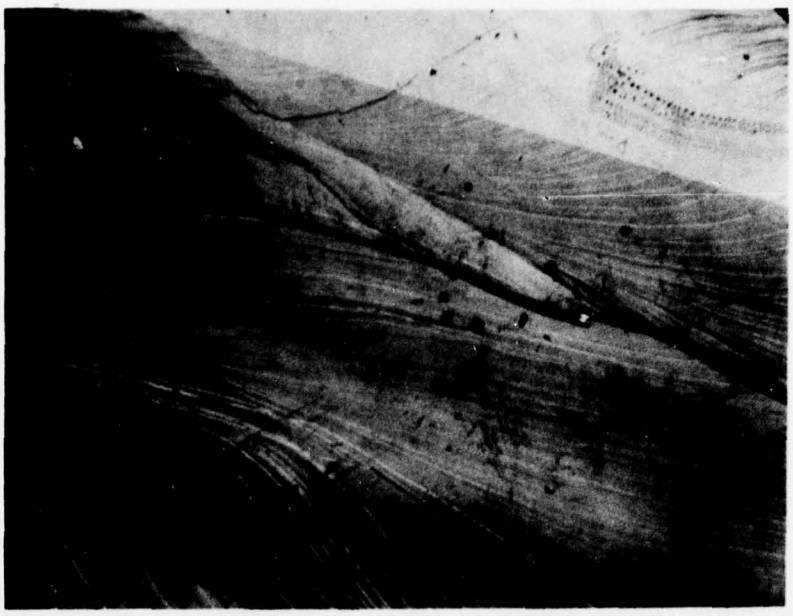


Figure 14 Photomicrograph of grain misorientations.

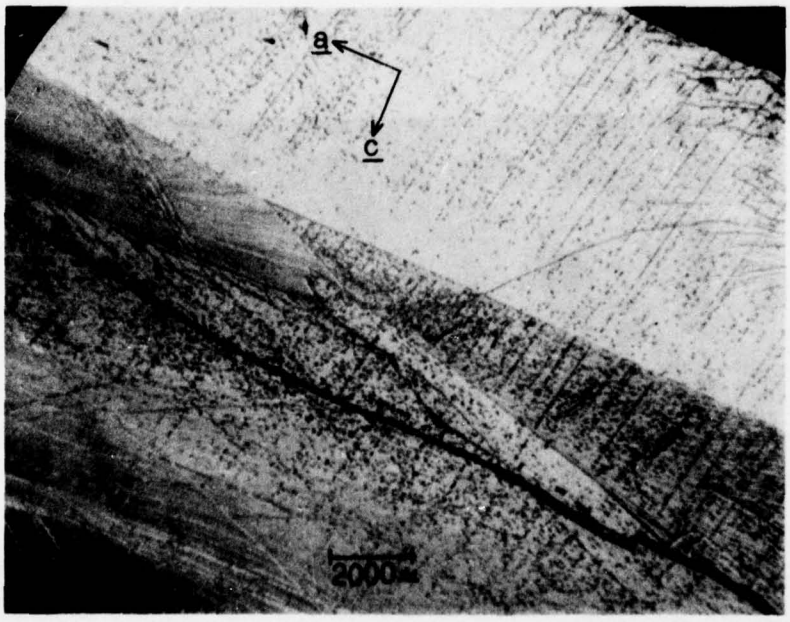


Figure 15 Photomicrograph of etched surface.

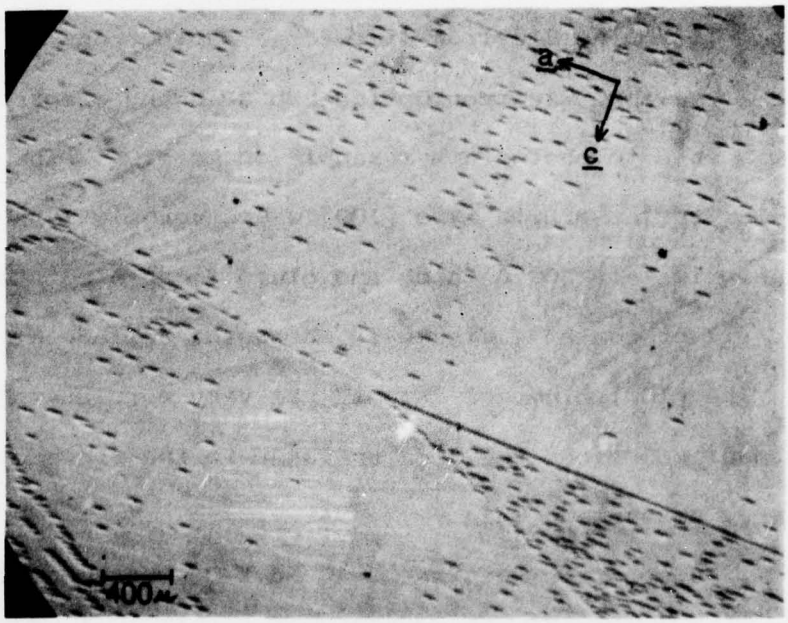


Figure 16 Photomicrograph of etch figures.

tions were used.

Another feature observed in the crystals is shown in Figure 17. In this boule there was a 1mm wide band of what appear to be small bubbles. The size is quite variable and the band does not follow any definite orientation in the crystal. The individual bubbles do tend to form long lines. An enlargement of the area is shown in Figure 18. One can see many rows with the bubbles in the same row about the same size. These bubbles are probably formed because the YVO_4 melt contains oxygen as a volatile solute component.

j. Scanning Electron Microscope Photographs

A Japan Electron Optics Lab scanning electron microscope Type JSM was used to photograph a sample of Nd:YVO_4. The cleavage piece perpendicular to the growth axis [100] was covered with a gold palladium coating approximately 200 Å thick and glued to an aluminum holder with conductive silver cement. Figure 19 shows the surface at a magnification of 200 x. The (100) cleavage "steps" are very evident. Figure 20 is an enlargement (600x) of the area enclosed in the rectangle of Figure 19.

k. Absorption Data

Absorption spectra of 1% Nd:YVO_4 were measured with a Cary 14 spectrophotometer from 0.35-1.0 μm for three samples. The boules were grown with different starting materials as follows: No. YV-71 Sylvania phosphor grade YVO_4, No. YV-73 UMC high purity V_2O_5 and No. YV-83 Sylvania NH_4VO_3. The spectra were essentially identical except the absorption near 1 micrometer for YV-73 was lower than the other two samples. Figure 21 shows a typical spectrum for our 1% Nd:YVO_4 which was identical with other published data.

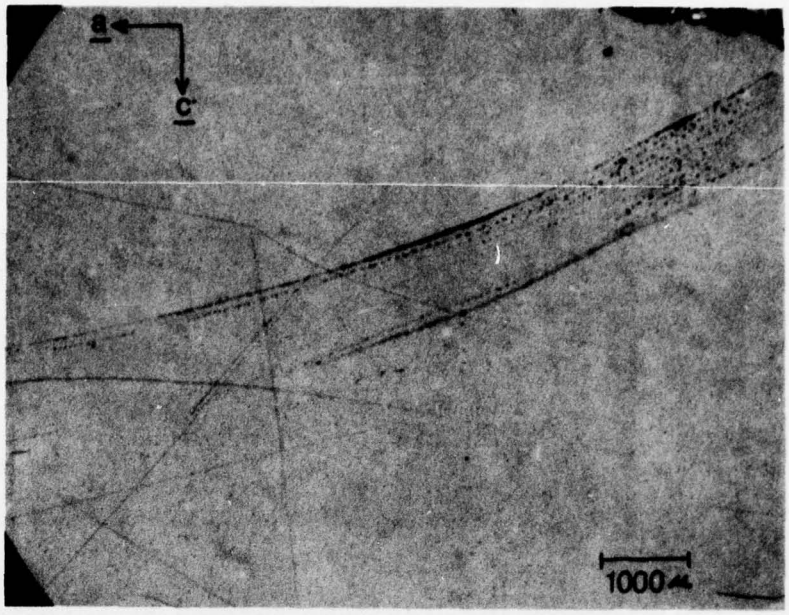


Figure 17 Photomicrograph of "bubble trails".

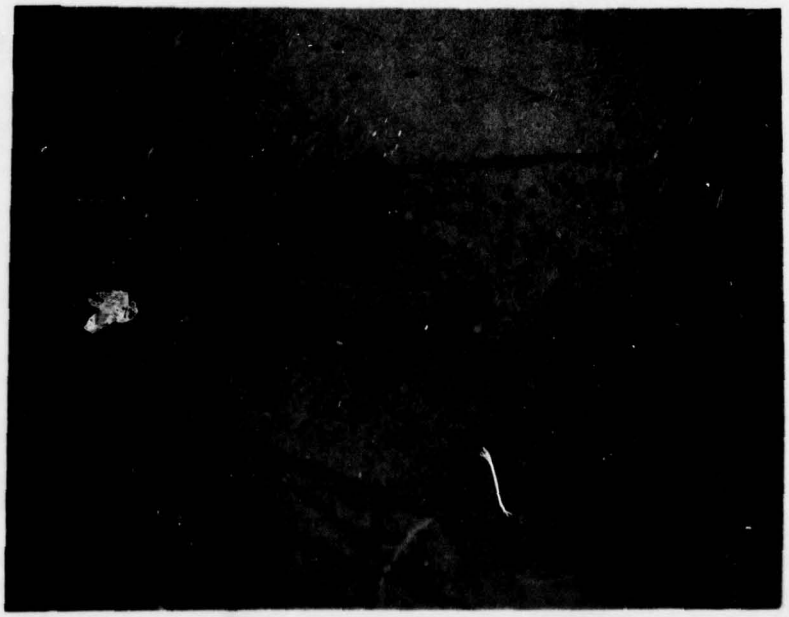


Figure 18 Photomicrograph of "bubbles".

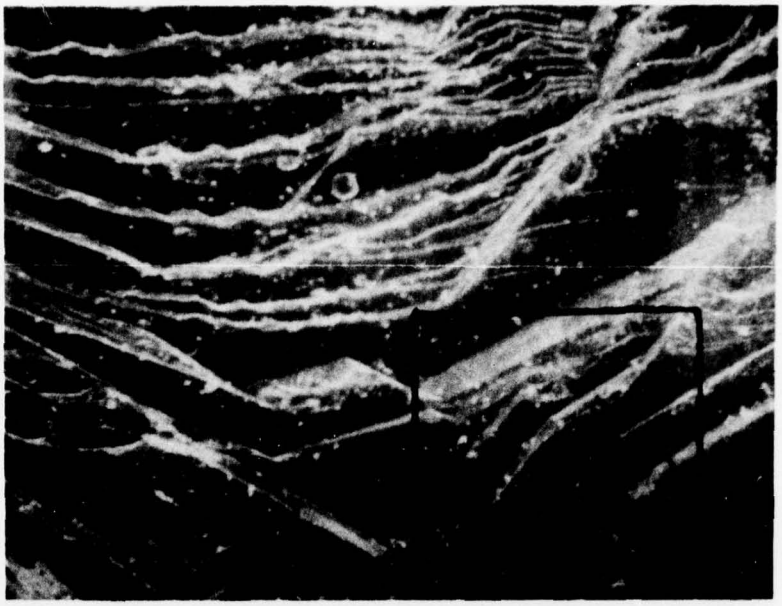


Figure 19. Cleavage surface of Nd:YVO_4 (200x).

Figure 20. Cleavage surface of Nd:YVO_4 (Enlargement of area in rectangle from Figure 19, 600x).

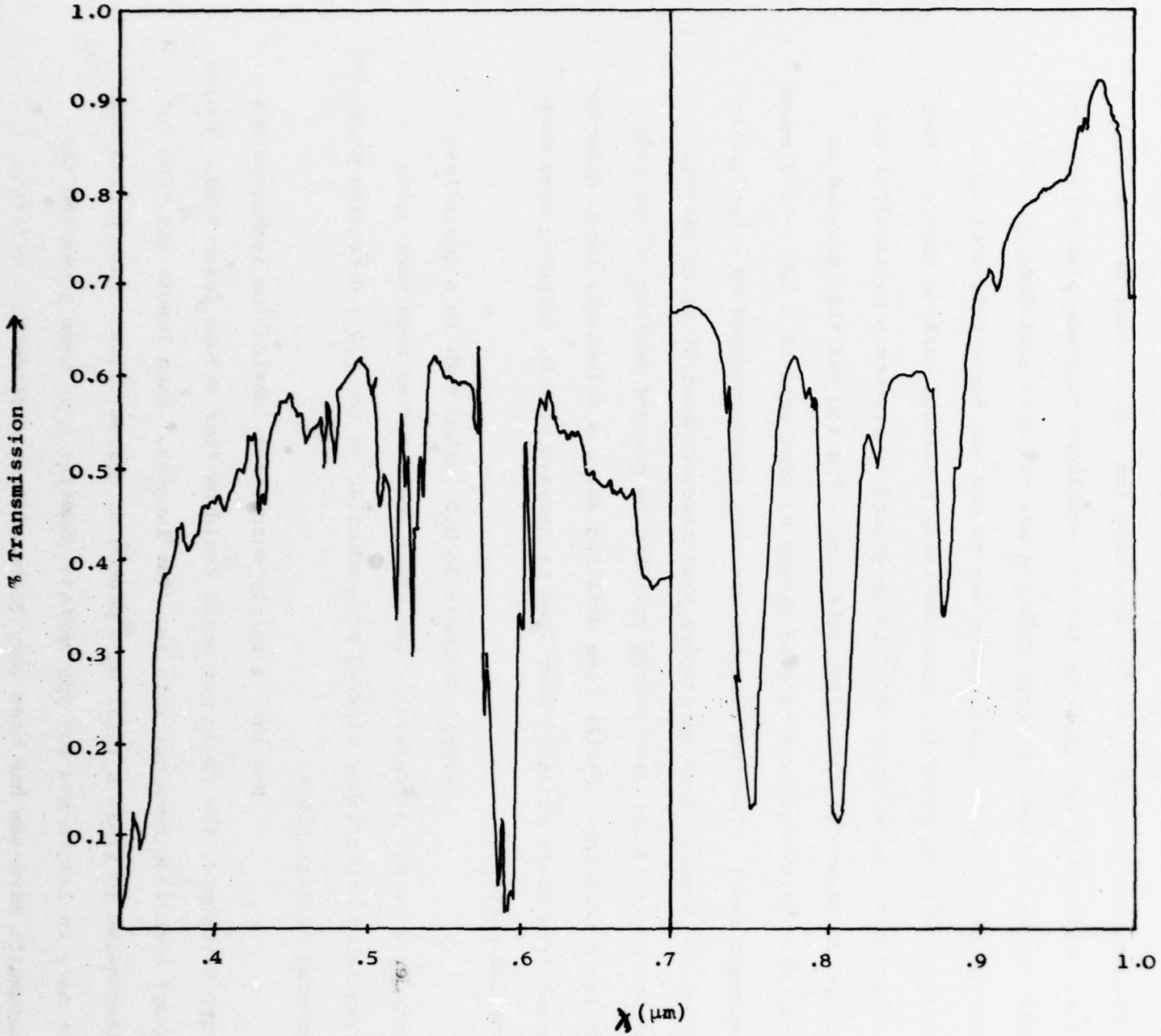


Figure 21. Absorption Spectra

1. Laser Rod Fabrication

1. Cutting

With most laser materials, diamond core drilling is the most satisfactory technique for obtaining 3mm O.D. by 30mm or 50mm long rods. With [100] axis Nd:YVO_4 the two excellent cleavage planes (100) and (010) cause problems and core drilling was not very satisfactory. The general procedure for fabrication was to cut the boule into rectangular sections with an automatic wire saw using a silicon carbide slurry. Next the edges of the section were slowly ground to produce a cylindrical rod. Figure 22 shows the rods after this step. The rod was then mounted on a Rotadex "All-tool" and rotated slowly by hand against a 320 grit diamond embedded wheel. The rod diameter was very slowly reduced by transversing along the wheel. Each successive pass removed about 10 μm of material. A cooling fluid was used during grinding to prevent heating of the rods during processing. Unlike core drilling where a relatively large diameter crack-free boule at least 30mm long is necessary, O.D. grinding used much smaller pieces.

Several attempts to O.D. grind rods in a centerless grinder were not successful. The small 3mm diameter rods were quite fragile and invariably cleaved perpendicular to the [100] direction producing several smaller pieces.

Now that a fairly successful fabrication technique has been developed, the yield per boule could be four 3x30mm laser rods. Boules about 60mm long were cut into two 30mm lengths. Each length was then cut lengthwise to yield a total of 4 pieces of correct size. Many boules 60mm or more in length and the appropriate diameter have been grown and the automatic wire saw has been very successful in sectioning crystals.

Figure 22. Preliminary shaped cylindrical rods.

2. Polishing

A polishing block was used for mounting the rods. The initial polishing used a tin lap with diamond paste. The grit size was reduced where the final stage used a 0.1 - 0.2μm paste. To maintain parallelism and perpendicularity of the rods, small polishing feet of the same orientation as the laser rod were necessary. Figure 23 shows six rods after polishing.

3. Coatings

The laser rods were antireflection coated with MgF_2. The rods were subjected to an optical cleaning procedure before coating and stored on a laminar flow bench. The rods were then coated in a vacuum coating system where an optical monitoring technique was used for the coating thickness. The first surface of coating was given an initial examination and a more complete examination after the second surface was coated. Figure 24 is a flow chart of the rod processing steps.

4. Passive Tests

Visible examination for distinct visible scattering was made using a He-Ne laser operating at 6328Å. The 3 milliwatt laser source was well collimated and expanded to cover the full rod aperature. The beam was propagated down the axis of the rod and visual observation for scattering was made at 90° to the direction of beam propagation.

The optical homogeneity of each rod was evaluated using a double pass Twyman-Green Interferometer with a He-Ne laser source. An interferogram was taken with a "zero" background (background fringe spacing at least twice the rod diameter). A fringe count was then made based on the greatest number of fringes intersecting a diameter.

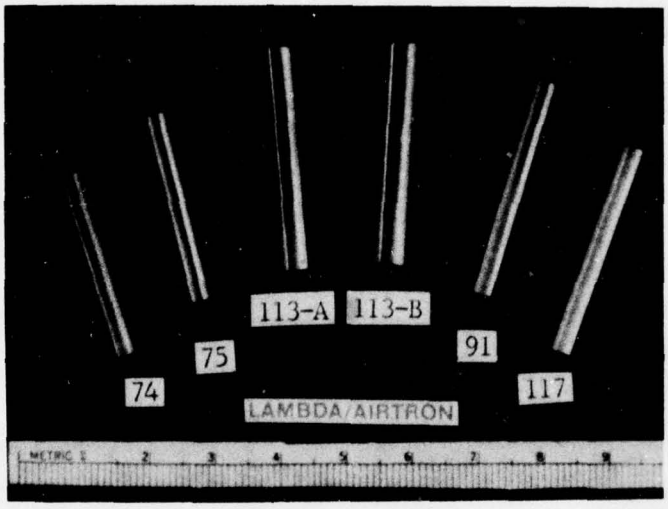
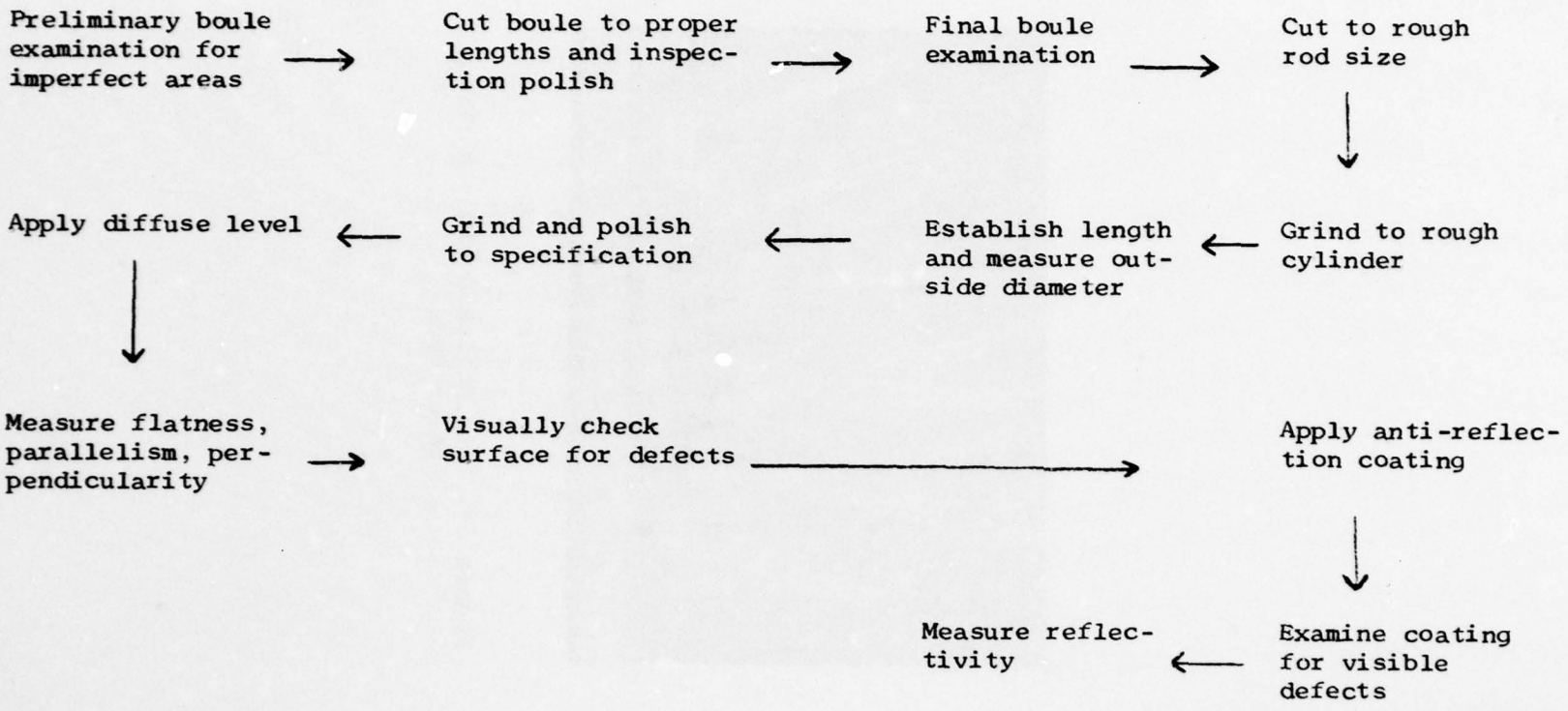


Figure 23. Six Polished [100] Nd:YVO_4 Laser Rods.

Figure 24

Flow Chart for Laser Rod Processing



5. Optical Quality

Six laser rods were fabricated from five of the boules grown during the contract. Several 3mm diameter rods were fabricated from boule numbers YV-74, YV-75, YV-91 and YV-117. From boule number YV-113 one 4mm and one 5mm diameter rod were fabricated. In general the wavefront distortion observed in the laser rods was sufficiently large enough to prevent an accurate quantitative analysis. For the 3mm rods, however, a qualitative estimate of the fringe distortion was made. The lowest distortion of 2 fringes is in rod YV-117 of Figure 25. Rods YV-91 and YV-74 are estimated to have distortions of the order of 3 fringes. A horseshoe shaped pattern is observed in rod YV-75 and the total number of fringes is approximately four. No analysis of the fringe patterns of the two larger diameter rods (4mm and 5mm) from YV-113 is possible.

No visible scattering was observed in the rods from YV-74, YV-75 and YV-91. No scatter was detected in the 4mm rod from YV-113 but the 5mm rod from the same boule appeared hazy over approximately one half of the length and diameter or the rod. Several distinct scattering sites were located near one end of the rod from YV-117. In summary visible scatter does not seem to be a major defect in the YVO_4 rods fabricated. The wavefront distortion of the YVO_4 rods is considerably higher than that or similar sized YAG rods. A typical wavefront distortion for a 3mm diameter YAG would be less than 0.5 fringe. However, some improvement in quality over the course of the contract is observed. The 3mm rod with the lowest distortion was fabricated from the most recent growth run.

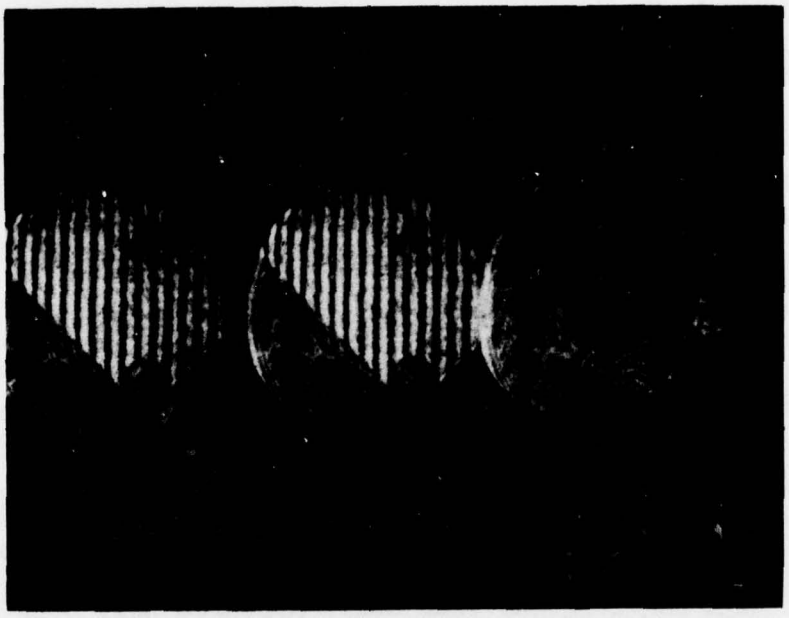


Figure 25. Twyman-Green interferometer pattern of YVO_4:Nd rod from YV-117.

4 DISCUSSION

a. Main Problems with Crystal Growth

The Czochralski growth of a-axis single crystal of 1% Nd:YVO_4 posed numerous problems. Ths first of which was attaining the appropriate thermal gradient and interface shape to eliminate the repeated burn-offs of boules during growth. Several factors contributed to the burn-off difficulties. 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 thermal equilibrium with the growing crystal causing burn-off. With continued heating, progressively more V_2O_5 was lost, changing composition and the temperature of crystallization of Nd:YVO_4. 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. A minor factor contributing to the burn-off problem was the melt crop 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 changes and adjusted the temperature to routinely grow long 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.

Another problem encountered during growth was diameter control of the boules. Pronounced crystal faceting on (010) and the longer edge parallel to [100] was produced by the preferred c-axis growth direction.

The most persistent problem to date was cracking of the boule after growth. Many factors such as chemical purity, dopant concentration, cooling rate, thermal gradients and atmospheric composition were investigated to determine their effects on cracking. A large difference in the thermal expansion exists along the a and c crystallographic axes which of course is inherent with the material. This large variation severely limits the size of large crack-free crystals. The thermal expansion variations surely contributed to some strain in the boule. The tendency for cracking to develop along cleavage planes appeared to be dependent on the purity of the starting materials. Our own preparation of YVO_4 using high purity chemicals produced crack-free boules whereas the phosphor grade material was not successful. Even very minor differences in the high purity Grade I V_2O_5 presented difficulties in growing good quality crack-free material.

5 CONCLUSIONS

The Czochralski growth of [100] boules of Nd:YVO_4 has been investigated for possible laser applications. The principal problems were solved systematically to obtain good quality material. After considerable experimentation the appropriate thermal gradients and interface shape were derived. Iridium crucibles were used with RF heating to melt the components. The growth parameters which proved most successful were an atmosphere of 99.5% N_2 - 0.5% O_2, a pull rate of 2.5 mm/hr., and a rotation rate of 4 RPM. Fair crystals were grown with low purity pre-reacted YVO_4 and $NdVO_4$. Our own preparations from high purity Y_2O_3, V_2O_5, and Nd_2O_3 produced excellent boules.

The growth of good quality [100] Nd:YVO_4 has been difficult and very time consuming. Certain precautions must be followed to insure good results. Very high purity V_2O_5 was necessary and very careful materials preparation technique was employed to produce stoichiometric starting compositions. Vanadium pentoxide was quite volatile at low temperatures so a slow heating rate was necessary to promote a reaction of the components. A very common practice of melting the component oxides in the crucible before growth would be unsatisfactory. Considerable V_2O_5 would vaporize producing a nonstoichiometric melt. The selection of a good quality seed crystal was very important to reduce defects that could propagate into the growing crystal.

With the large variation in the thermal expansion valves between the crystallographic axes, it was necessary to grow boules relatively small in diameter to minimize this effect. A slow cooling time of about 48 hours was used where the thermal gradient was low. Two concentric ceramic cylinders with a lid above the crucible provided adaquate heat reflection.

The surface tension of the YVO_4 melt was very high and tended to "creep" over the crucible wall when the melt level was too high. If the melt "wets"

the zirconia grog insulation, it was impossible to pull a boule without repeated flash-outs or burn-offs. After 2 or 3 growth runs in the same crucible, sufficient sample decomposition occurred along with the concentration of impurities that the boules cracked and the crucible had to be cleaned.

By following the precautions mentioned above, good quality crack-free crystals were grown of sufficient size to yield 3 mm O.D. by 30 mm long laser rods. The fabrication of the rods required considerable experimentation with various grinding techniques. As to date, the usual technique of diamond core drilling boules to obtain the appropriate size rods has not been successful. The most successful method was to very slowly O.D. grind the boules with sufficient cooling fluid to prevent rod heating. Polishing and AR coating of the finished rods was routine using the standard techniques developed for Nd:YAG.

6 RECOMMENDATIONS

In most solid state laser crystals, sufficient material of good quality has to be prepared for a thorough evaluation of active laser parameters. In this sense the objectives of this program have been met. However the most frequently used laser hosts are those crystals which are grown and fabricated with a minimum of difficulty. YVO_4:Nd certainly does not meet these criteria. Therefore our recommendations are based on current knowledge of production.

For the best growth we suggest that a high purity V_2O_5 is essential. In addition to thermal stresses, we feel that impurity induced stress and cleavage are important problems to solve. A satisfactory starting material can give a good crystal at nearly every attempt. Furnace design must be controlled to give low gradients during growth and annealing.

We recommend that laser rod processing be considered in terms of likely success. For long small-diameter cylindrical rods, processes are difficult, e.g. (3X30) or (3X50) mm rods. Rods of (5X30), (5X50), (4X30), (4X40) mm are not too bad. Rods of (6X75) mm may suffer from reduced quality. The polishing method must be done with care and little heat production.

If rod requirements of Nd:YVO_4 prove to be modest, we feel that most problems can be solved eventually. However extended production would probably face serious obstacles for 3 or 5mm rod sizes. Therefore, if military requirements for YVO_4 are generated, an engineering program for growth and fabrication should be considered. This program would address rod requirements to meet specific rod operating parameters.

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513 COMMANDER
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WHITE SANDS MISSILE RANGE
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002 WHITE SANDS MISSILE RANGE, NM 88002

527 COMMANDER
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563 COMMANDER, DARCOM
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606 CHIEF
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680 COMMANDER
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