DEFECT CHARACTERIZATION OF
YTTRIUM ORTHOVANADATE

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of JOEL BENJAMIN LEBRET find it satisfactory and recommend that it be accepted.

______________________________
Chair

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DEFECT CHARACTERIZATION OF
YTTRIUM ORTHOVANADATE

Abstract

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May 2004

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Single crystals of Nd:YVO₄ grown with the Czochralski technique frequently exhibit light scattering defects that are detrimental to the laser and optical properties. Defects in the form of low angle grain boundaries have been characterized in what are nominally “single crystals” with polarized light microscopy, orientation imaging microscopy, and transmission electron microscopy. The misorientation angle of a low angle grain boundary was determined to be <1°, which corresponds to a formation energy of 1000-2000mJ/m². It was found that dislocations generated during crystal growth and cooling have enough mobility in certain growth directions to form low angle grain boundaries through polygonization. Several suggestions are made to reduce or eliminate polygonization, including the addition of a small amount of an atom with a size much larger or smaller than Y⁺³. Light scattering centers were examined with computed tomography and determined to be voids approximately 10µm in diameter.
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Dedication

This thesis is dedicated to
my wife, Betsy, for her love and support
and to our Creator and Redeemer, Jesus Christ
who makes all things possible.
CHAPTER ONE
INTRODUCTION AND BACKGROUND

1.1 Yttrium Orthovanadate as a Laser Host Material

Laser Background

In the past 50 years or so, lasers have become a very important device which has seen use in many technical applications. An electron changing levels from an excited state to the ground state where the energy difference is \( \Delta E \) releases a photon of frequency \( \nu \) by the relationship \( \Delta E = h\nu \) [1]. If an electron in an excited state \( \Delta E \) above the ground state encounters a photon of frequency \( \nu = \Delta E / h \), the photon can stimulate the excited electron to fall back to the ground state, emitting a photon of the same energy, phase, and frequency. In a laser, a phase relationship exists between all of the emitted photons to form a coherent beam such that the emission intensity is proportional to the square of the sum of the amplitudes. This amplification of the light gives rise to the acronym laser (light amplification by the stimulated emission of radiation).

In order for this stimulation to produce a usable laser, the emitted radiation must be able to escape the material; this is accomplished if the probability of an atom emitting a photon is higher than the probability of absorbing one. Thus a population inversion is needed wherein greater than 50% of the ground state electrons are in an excited energy level. The easiest way to accomplish this is when the lifetime of a certain energy transition is longer than other transitions (such as \( E_3 \) to \( E_2 \) in Figure 1.1). This slower transition creates a bottleneck where a population inversion can be built up. The transition from higher energy levels to lower will result in different frequencies and thus wavelengths, depending on \( \Delta E \).
In solid state laser applications, the host crystal is doped with a substitutional ion which provides higher energy bands. The laser element is a single crystal material with parallel-polished optically flat faces. The faces are coated with a highly reflective coating on one end, and a slightly less reflective coating on the opposing face to allow a small fraction of the beam to be transmitted. A source of energy (commonly a laser diode) stimulates the electrons to be promoted into the higher energy levels and creates the population inversion. The stimulated photons of coherent light are totally reflected off the highly reflective face and partially transmitted at the other end. The reflected beam will excite the dopant ions to emit even more phonons, increasing the emitted radiation. The portion of the beam which escapes the laser element forms the desired laser output.

**Nd:YVO₄ as a Laser Material**

Neodymium doped yttrium orthovanadate (Nd:YVO₄) has been shown to have some very desirable properties as a solid state laser host material. Nd:YVO₄ is one of the most efficient solid state laser host materials for diode laser pumped applications. It has a large absorption coefficient, broad absorption bandwidth, large stimulated emission cross-section, and low lasing threshold. Nd:YVO₄ also has good chemical, mechanical and thermal properties that make it an ideal candidate for high power, stable and cost effective solid state lasers. Nd:YVO₄ can produce lasers in the IR, green and blue light spectra. The transitions observed in Nd:YVO₄ are shown in Figure 1.2 with peaks at 914nm, 1064nm and 1342nm.
Figure 1.1 Energy level schematic showing a population inversion at the $E_3$ to $E_2$ energy transition leading to laser output.

1.2 Other Properties and Applications of VYO₄

Nd:YVO₄ is a tetragonal crystal (a=0.71192nm, c=0.62898nm) of the zircon type symmetry (point group I4₁/amd); the YVO₄ unit cell is shown in Figure 3. The crystal melting point is around 2083K; the density is 4.22g/cm³; the hardness is ~700 Knoop. The thermal conductivity coefficient is 5.23 W/m/K; c and 5.10 W/m/K -c; the thermal expansion coefficients are \( \alpha_{a,b} = 2.2 \times 10^{-6}/K \), \( \alpha_c = 8.4 \times 10^{-6}/K \). The crystals are typically green to sky blue in color when viewed with incandescent lighting [2].

The maximum incident pump power of a diode pumped solid state laser is ultimately limited by the stress fracture caused by non-uniform temperature distributions through the crystal. The stress fracture is directly related to the elastic properties of the host crystal, i.e. the Young’s modulus, E, and Poisson’s ratio, \( \nu \). Inhomogeneous local heating and temperature distributions in the crystal produce distortion in the laser beam due to temperature and stress-related effects on the refractive index and end bulging of the pumped surface. These deformations result in the formation of a thermal lens which limits the quality of the laser. Peng et al. [3] used laser interferometry to measure stress and strain in the crystal through the thermally induced end bulging effect. Combined with finite-element analysis of the mechanical properties of Nd:YVO₄ were determined to be E = 133 GPa and \( \nu = 0.33 \). From these materials constants, a value of the shear modulus, \( G = 50 \) GPa can be calculated.

Pure YVO₄ is a positive uniaxial crystal with a wide transparency range and large birefringence which make it ideal for optical applications such as fiber optic isolators and beam displacers, circulators, and other polarizing optics (Figure 1.4a-c). YVO₄ has better temperature stability, physical, and mechanical properties than calcite (CaCO₃), easier handling and workability than rutile (TiO₂), and higher birefringence than LiNbO₃. YVO₄ has
Figure 1.3. YVO$_4$ unit cell, the dark atoms are Y, light atoms are V, and the small atoms are O.

Figure 1.4 YVO$_4$ as a) fiber optic isolator, b) beam displacer, c) circulator. Source: http://www.casix.com/product/B_Crystal_YVO4.htm.
also been found as an important material as a phosphor for television application. Since the crystal is birefringent, the optical properties parallel and perpendicular to the c axis are distinctly different. Kinsley et al. [4] measured values of the refractive indices, \( n \), for radiation polarized either parallel or perpendicular to the c axis with a Hg lamp at different energies. The refractive indices at various light wavelengths are given in Table 1.1.

Table 1.1 Refractive indices of YVO\(_4\) at different wavelengths.

<table>
<thead>
<tr>
<th></th>
<th>( n_o = n_a = n_b )</th>
<th>( n_e = n_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>@1064nm</td>
<td>1.9573</td>
<td>2.1652</td>
</tr>
<tr>
<td>@808nm</td>
<td>1.9721</td>
<td>2.1858</td>
</tr>
<tr>
<td>@532nm</td>
<td>2.021</td>
<td>2.2256</td>
</tr>
</tbody>
</table>

Any time there is a boundary between two dissimilar materials there will be a change in properties. For optical systems, this mechanism has been employed utilizing the change in refractive properties to steer light. Unfortunately, the necessary change in the index of refraction (\( n_A \neq n_B \)) will result in the loss of some of the light through reflection. Similar to this relationship is the interaction that takes place when ballistic electrons propagate through discontinuous media. Once again, refraction of the electrons will be associated with a small amount of reflection due to a difference in the effective masses (\( m_A \neq m_B \)). There is however, a category of materials with a unique type of interface which enables complete refraction for light as well as electron beams. In addition to total refraction, it has been discovered [5] that this same type of interface can result in either positive or negative refraction, depending on the incident angle. A YVO\(_4\) bicrystal was used to show the feasibility of this device. Two crystals were bonded together within 0.5° from the optical axis for each crystal. Using a 532nm laser beam and antireflection coating on the input and output planes the negative refraction could be seen at
Figure 1.5 Index of refraction in a bicrystal of YVO$_4$ a) positive and b) negative. *Source: Y. Zhang, B. Fluegal and A. Mascarenhas, Phys. Rev. Lett. 91 (2003) 157404.*

Figure 1.6 Experimental data compared to theoretical for amphoteric refraction in a YVO$_4$ bicrystal; refraction is negative when $\theta_B/\theta_A < 0$. *Source: Y. Zhang, B. Fluegal and A. Mascarenhas, Phys. Rev. Lett. 91 (2003) 157404.*
the interface of the bicrystal Figure 1.5. The sign of the index of refraction was dependant on the ratio of the refraction angle with the incidence angle of the incoming light (Figure 1.6). The power loss at the interface (i.e. reflection) was found to be minimal and only due to imperfection of the device. This ability to steer light without reflection could be very useful in high power optics.

1.3 Comparison of YVO₄ With Other Nd-Doped Materials

Much work has been done comparing the optical and laser properties of Nd:YVO₄ with other Nd doped laser crystals, especially yttrium aluminum garnet (YAG) [6-11].

Nd:YVO₄ and Nd:YAG were compared by Connor in one of the earliest studies of their relative spectral properties [6]. The absorption levels of Nd⁺³ doped crystals were measured between 0.6 and 1.0µm at 300K. For YAG, there was pronounced splitting of the \( ^4F_{3/2}, ^4F_{5/2}, \) and \(^2H_{9/2}\) levels. Whereas in YVO₄ very little Stark splitting was observed at these levels (Figure 1.7). The reduction in Stark splitting was attributed to a reduction in crystal symmetry around the site the Nd⁺³ ion occupies. It has been shown that when a rare earth ion is in a low symmetry position and lacks an inversion center a substantial admixture of \( 4f \) and \( 5d \) wave functions occurs; this leads to efficient, low threshold lasing. This work demonstrated that the stimulated emission cross section of YVO₄ was larger at 1.06µ than YAG. It was also observed that energy transfer from the lattice to the Nd⁺³ ion also contributes to the low threshold energies for YVO₄.

Tucker and co-workers [7] compared the performance of YVO₄ and YAG at 1.06 and 1.34µm by end pumping with an Ar⁺ laser. The slope efficiency of YVO₄ was found to be 20% at 1.06µ. Continuous wave operation at eye-safe wavelengths, 1.34µ, was readily achieved with a measured slope efficiency of 7%. It was noted that the large losses measured in the YVO₄
were due to light-scattering defects in the crystal. Tucker et al. later obtained the stimulated-emission cross sections (σ) of both crystals from measurements of laser thresholds as a function of the mirror reflectivities [8]. These were measured to be $12 \times 10^{-19}$ and $6.1 \times 10^{-19}\text{cm}^2$ for 1064 and 1342nm respectively. Typical values for YAG range from $2.7-8.8 \times 10^{-19}\text{cm}^2$. The stimulated emission cross section for YVO$_4$ was also found by Yaney et al. to be 4.6 times greater than YAG at 1.0634µ and 18 times larger at 1.34µ [9].

Using YVO$_4$ as a diode end pumped laser, lower threshold (30 mW) and higher output power (120mW) were observed compared to YAG [10]. Slope efficiency of 51% was obtained for YVO$_4$; these superior properties compared to YAG were attributed to lower laser threshold. Fields and co-workers also reported the bandwidth of YVO$_4$ at 1064nm is nearly double YAG and the laser emission cross section for YVO$_4$ at 1342nm is almost equal to YAG at 1064nm.

The optical properties and laser performance of eight different Nd doped laser crystals grown by the Czochralski method were compared by Bornel et al. (Table 1.2) [11]. Using a longitudinally pumped 1W SDL 2460 laser diode the laser performance of the materials was tested. The absolute polarized emission cross section for Nd:YVO$_4$ was calculated to be $10-20 \times 10^{-19}\text{cm}^2$, an order of magnitude higher than the other crystals. The slope efficiencies, maximum power, absorption coefficients and absorption cross sections were also determined. YVO$_4$ was found to show the best laser performance as a diode pumped material with its high slope efficiency of 65% (Figure 1.8). Other superior properties included absorption coefficient 11.5 cm$^{-1}$, absorption 9nm (FWHM) and maximum laser output of 396.8mW (Table 1.3).
Figure 1.7 Comparison of peaks for YAG and YVO₄. Source: J.R. O’Connor, Appl. Phys. Lett. 9 (1966) 407.


<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>Structure</th>
<th>Melting point (°C)</th>
<th>Nd³⁺ concentration in the melt (%)</th>
<th>Nd³⁺ concentration in the melt (10²⁰ at/cm³)</th>
<th>Growth direction and atmosphere</th>
<th>Distribution coefficient (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YAG</td>
<td>Garnet (Cubic)</td>
<td>−1950</td>
<td>1,1</td>
<td>1,52</td>
<td>sample from Crimatex</td>
<td>k=0,18</td>
</tr>
<tr>
<td>YVO₄</td>
<td>Tetragonal</td>
<td>−1850</td>
<td>2</td>
<td>2</td>
<td>sample from NEC</td>
<td></td>
</tr>
<tr>
<td>YSO</td>
<td>Monoclinic</td>
<td>1930</td>
<td>1</td>
<td>1,87</td>
<td>&lt;010&gt; = b N₂</td>
<td>k=0,7</td>
</tr>
<tr>
<td>GSO</td>
<td>Monoclinic</td>
<td>1900</td>
<td>2</td>
<td>3,86</td>
<td>&lt;01 0 4&gt; N₂</td>
<td>k=1</td>
</tr>
<tr>
<td>Gd₂SiO₅</td>
<td>Apatite (hexagonal)</td>
<td>−1900</td>
<td>1,5</td>
<td>2,22</td>
<td>&lt;0 0 1&gt; N₂</td>
<td>k=1</td>
</tr>
<tr>
<td>SGS</td>
<td>Gehlenite (tetragonal)</td>
<td>−1900</td>
<td>1</td>
<td>1,34</td>
<td>&lt;1 1 0&gt; N₂</td>
<td>k=1</td>
</tr>
<tr>
<td>CASIO</td>
<td>Gehlenite (tetragonal)</td>
<td>1580</td>
<td>1</td>
<td>4,42</td>
<td>&lt;1 1 0&gt; or &lt;1 0 0&gt; N₂</td>
<td>k=0.7-0.8</td>
</tr>
<tr>
<td>LMA</td>
<td>hexagonal</td>
<td>1910</td>
<td>13</td>
<td>1,3</td>
<td>&lt;1 0 0&gt; N₂</td>
<td>k=1</td>
</tr>
<tr>
<td>CYAO</td>
<td>tetragonal</td>
<td>1810</td>
<td>1</td>
<td>1,3</td>
<td>&lt;1 0 0&gt; N₂</td>
<td>k=1</td>
</tr>
</tbody>
</table>
Figure 1.8 Laser efficiency of eight Nd doped laser materials. Source: C. Bornel, N. Herlet, R. Templier, C. Calvat and C. Wyon, J. De Phys. IV 4 (1994) C4-549.


<table>
<thead>
<tr>
<th>Material</th>
<th>$\text{Nd}^{3+}$ in the melt ($\text{cm}^3/\text{cm}^3$)</th>
<th>Absorption coeff. at absorption coeff. at $\lambda_{\text{abs max}}$ ($\text{cm}^{-1}$)</th>
<th>$\lambda_{\text{pump}}$ ($\text{nm}$)</th>
<th>FWHM in absorption ($\text{nm}$)</th>
<th>Fluorescence lifetime ($\mu$s)</th>
<th>Pth abs (mW)</th>
<th>Pout max (mW)</th>
<th>Slope efficiency (%)</th>
<th>Output mirror reflectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YAG</td>
<td>1.52</td>
<td>3.41 at 806 nm</td>
<td>11.3 at 808.5 nm</td>
<td>1.5</td>
<td>255</td>
<td>$\pi$ : 49</td>
<td>235.8</td>
<td>52</td>
<td>94.8</td>
</tr>
<tr>
<td>YVO$_4$</td>
<td>2</td>
<td>11.5 at 809.4 nm</td>
<td>9</td>
<td>a</td>
<td>(4 mm)</td>
<td>$\pi$ : 32</td>
<td>396.8</td>
<td>65</td>
<td>92.0</td>
</tr>
<tr>
<td>LNA</td>
<td>4.42</td>
<td>$\approx$ 4.54 at 798 nm</td>
<td>17.3</td>
<td>260</td>
<td>c</td>
<td>$\alpha$ : 168</td>
<td>251.1</td>
<td>40</td>
<td>97.25</td>
</tr>
<tr>
<td>SGS</td>
<td>2.22</td>
<td>$\sigma$ : 6.6 at 808.5 nm</td>
<td>9.6 at 809.5 nm</td>
<td>4.1</td>
<td>168</td>
<td>$\sigma$ : 138</td>
<td>169.3</td>
<td>34</td>
<td>97.25</td>
</tr>
<tr>
<td>GSO</td>
<td>3.86</td>
<td>E/X at 804.5 nm</td>
<td>17.4</td>
<td>185</td>
<td>b</td>
<td>E/Y : 134</td>
<td>191,5</td>
<td>36</td>
<td>97.25</td>
</tr>
<tr>
<td>P1=Y</td>
<td>E/Y : 7.4 at 799 nm</td>
<td>14.1 at 801 nm</td>
<td>2.3</td>
<td>E/Z : 17.4</td>
<td>1.6</td>
<td>E/Z : 198</td>
<td>122.8</td>
<td>22</td>
<td>96.9</td>
</tr>
<tr>
<td>P2=Z</td>
<td>E/Z : 7.8 at 800 nm</td>
<td>17.4 at 810 nm</td>
<td>1.6</td>
<td>E/Z : 198</td>
<td>2.2</td>
<td>E/Z : 200</td>
<td>149.9</td>
<td>36</td>
<td>95.9</td>
</tr>
<tr>
<td>YSO</td>
<td>1.87</td>
<td>E/X : 5.4 at 810 nm</td>
<td>10.2 at 810.8 nm</td>
<td>1.8</td>
<td>~200</td>
<td>D1</td>
<td>259.5</td>
<td>54</td>
<td>97.25</td>
</tr>
<tr>
<td>(k=0.6)</td>
<td>E/Z : 3.9 at 810 nm</td>
<td>6.7 at 810.8 nm</td>
<td>1.8</td>
<td>E/D : 80</td>
<td>48</td>
<td>E/D : 200</td>
<td>149.9</td>
<td>56</td>
<td>95.9</td>
</tr>
<tr>
<td>CASIO</td>
<td>1.3</td>
<td>$\approx$ 7.10 at 807 nm</td>
<td>4.9</td>
<td>276</td>
<td>c</td>
<td>$\alpha$ : 198</td>
<td>149.9</td>
<td>25</td>
<td>94.8</td>
</tr>
<tr>
<td>CYAO</td>
<td>1.3</td>
<td>$\approx$ 9 at 806 nm</td>
<td>9.52 at 806.5 nm</td>
<td>4.3</td>
<td>123</td>
<td>c</td>
<td>$\alpha$ : 317</td>
<td>98.8</td>
<td>25.0</td>
</tr>
</tbody>
</table>
1.4 Growth Techniques

Several techniques have been explored for the growth of single crystal YVO$_4$. Crystals of large diameter and good quality have been grown with the Czochralski technique [12,13]; other successful growth methods include float zone [14-16], laser heated pedestal growth (LHPG) [17-19], flux growth [18-20], and top-seeded solution growth [21]. One reason for the abundance of growth techniques for this crystal is the presence of defects, which adversely affect the optical properties. The main obstacle for proliferation of YVO$_4$ is the challenge of growing large, defect-free single crystals.

Czochralski Growth

Czochralski (CZ) growth has been selected as the best way to grow single crystals of YVO$_4$ of large size, although problems with the quality of the crystal still need to be addressed. With CZ, the material to be grown is placed in a crucible and melted. At the center of the melt, the temperature is adjusted so the liquid and solid phases are in equilibrium. A seed crystal with the desired orientation is inserted into the melt and slowly rotated. The material at the equilibrium temperature will become solid and begin to grow on the seed crystal (Figure 1.9). The rotation of the seed crystal and the rate of extraction are controlled and have an influence on the crystal dimensions. A slower rotation rate will produce a larger crystal diameter. This process is shown schematically in Figure 1.10.

The starting material commonly consists of the desired stoichiometric mixture in powder form. The crucible of choice must be able to withstand high temperatures and ideally will not react with the material to be grown; the crucible material selected for YVO$_4$ growth is Ir. The dimensions of the crucible will also have influence over the final crystal diameter. The
atmosphere in the growth chamber can be controlled and usually has significant influence on the quality of the crystal grown. The material is heated either inductively or resistively; precise control over the temperature in the melt is essential for effective crystal growth.

Dess et al. used pure YVO₄ powder obtained from a commercial vendor and mixed with Nd₂O₃ and V₂O₅ powders to achieve varying concentrations of Nd³⁺ dopant [12]. The samples were grown in an oxyhydrogen gas-fired furnace with the melt contained in an Ir crucible. The crucibles were preheated to 2173K and the powder was added incrementally. Frequent crusting of the surface and bubbling was noted at high temperatures, which has been attributed to oxygen loss. By adjusting the atmosphere and flowing in argon and oxygen, melt temperatures around 2053K were measured pyrometrically. The first crystals were grown with an iridium seed crystal due to lack of YVO₄ seed availability. This initial crystal cracked catastrophically during the cool down. X-ray examination revealed significant polycrystallinity. A sufficiently large piece from the broken crystal was used for the seed crystal for the next attempt. The cracking decreased in the second crystal and the angle of misorientation was no greater than 30° for the boundaries in the crystal. This crystal was then used as seed material and subsequent crystals exhibited fewer growth difficulties. Growth rates were typically in the range of 6.35 to 12.7 mm/hr with rotation rates of 10 to 20 rpm. The resulting crystals had typical diameters from 6.35-12.7 mm and lengths from 25.4-50.8 mm. The crystals tended to grow along preferential growth directions of (001), (100) and (101). Fluctuation from the desired growth axis was common and required early termination of the crystal growth unless it could be corrected. The as-grown crystals were dark, but annealing in an oxygen atmosphere removed the dark hue. The samples were qualitatively analyzed for scattering centers and segregation of Nd concentration from the top to the bottom of the crystal.
Figure 1.9 Crystal being grown with CZ technique from melt. Source: [http://www.mpi-stuttgart.mpg.de/crystal/facilities.html](http://www.mpi-stuttgart.mpg.de/crystal/facilities.html)

Figure 1.10 Schematic of CZ growth furnace. Source: [http://www.mpi-stuttgart.mpg.de/crystal/facilities.html](http://www.mpi-stuttgart.mpg.de/crystal/facilities.html)
Meng et al. [13] have recently reported successful CZ growth of YVO$_4$ with growth parameters similar to those used in the growth of the crystals characterized in this study. Chemical compounds V$_2$O$_5$, Y$_2$O$_3$ and Nd$_2$O$_3$ were combined according to weight by the formula Nd$_x$Y$_{1-x}$VO$_4$ (where x is from 0.0005 and 0.05). The compounds were sintered in a Pt crucible at 1473K for 8-10hr to produce polycrystalline material. The single crystal was grown in a 2 kHz RF generator heated in an Ir crucible. The growth atmosphere was N$_2$ + 2%O$_2$. A rectangular single crystal of Nd:YVO$_4$ was used as a seed crystal, on either the a or c axis. The temperature used was 50-100K higher than the melting temperature in an attempt to eliminate the formation of polycrystalline material. At this temperature, the microcrystal particles on the surface of the melt in the crucible would be entirely melted. After lowering the temperature back down to the melting point the crystal was pulled at a rate of 0.5-3mm/h after the desired crystal diameter was reached. The crystal was rotated at a rate of 10-30rpm and after growth was allowed to cool to room temperature at a rate of 150K/h. X-ray analysis confirmed the space group of I4$_1$/amd with a=b=0.71183nm, c=0.62932nm, $\alpha = \beta = \gamma = 90$. Macroscopic defects observed in the crystals include light scattering pellets, cleavage, and low angle grain boundaries. The scatter could be reduced by adjusting the thermal fields, or replacing the melt. Cleavage along \{100\} and \{101\} could be avoided by reducing the cooling rate. Superheating of the melt prior to growth was found to be effective in reducing low angle grain boundaries. The crystals grown with the CZ method exhibited 12 definitive faces on the crystals which were found to be of the type \{100\} and \{101\}. X-ray fluorescence analysis was used to determine the segregation coefficients of Nd, Y and V for varying concentrations of Nd. The effective segregation coefficient of Nd was found to be 0.63 and was independent of Nd doping concentration as well as pulling rate. The crystals grown in this method were of good laser quality with the pumping threshold being
20mW, output power 921mW at 1064nm when pumped at 1840mW, and slope efficiency of up to 55.5%.

**Float Zone**

Float Zone (FZ) growth utilizes a traveling liquid zone through a material to facilitate single crystal growth and to eliminate defects in the crystal. A polycrystalline material is first sintered into a rod shape and affixed to the float zone apparatus as shown in Figure 2.11. As with CZ growth, a single crystal material is used to start the crystal growth along the desired growth direction. The melt zone is induced by either an RF source or in the case of YVO₄ growth, with IR radiation. The heating sources are composed of two halogen lamps with double elliptical mirrors focusing the radiation onto the specimen. FZ has a number of advantages over other growth processes. Since a crucible does not have to be used, contamination can easily be avoided. The furnace atmosphere can be selected to facilitate optimal growth conditions. Volatilization of the material can be reduced because the melt time is reduced. FZ can also evenly distribute the doped impurities through the crystal [14].

Thin single crystals of YVO₄ were grown with the FZ method by Shonai *et al.* [15-16]. Float zone was selected because of the ability to grow crystals at the high temperatures required without the use of a crucible and in pure O₂ atmosphere. The crystals were grown with the double-pass technique to keep a stable melt zone through the growth process and to produce a uniform Nd concentration through the length of the crystal. Polycrystalline material of the desired composition was sintered under a pressure of 100MPa and temperature of 1473K for 3 hours in air. The resultant rod was about 7mm in diameter and 80mm long. The crystals were grown along the c-axis so a uniform diameter could be obtained. The growth rate was 10mm/h;
the feed rate selected depended on the diameter of the feed crystal and the growing crystal; the rotation rate was 30 rpm for both the feed rod and the seed, which were counter-rotated. It was necessary to keep the relationship between the diameter of the feed crystal and the growing crystal \( \frac{D_f}{D_g} = 3 \) (Figure 1.12a). The crystals grown with this method had diameters ranging from 0.8-5.1mm. At low growth rates, second phases rich in Y would form. Low angle grain boundaries and dislocation density was reported to increase with the crystal diameter. An optimal crystal diameter was found to be 3mm for decreasing the dislocation density and eliminating low angle grain boundaries (Figure 1.12b). It is proposed that low angle grain boundaries form through dislocation migration at temperatures near the melting point. Dislocation origination is attributed to thermal shock in the crystal growth process. It was found through polarized light microscopy and dislocation etching that crystals below the critical diameter could relieve the strains originating from the dislocations, whereas the strains in the crystals above the critical diameter remained throughout the length of the crystal.

It has been generally accepted that increasing the concentration of the doping ion can improve the lasing properties of doped solid state lasers. Nd:YVO\(_4\) has been shown to be capable of being grown with Nd concentrations approaching 10 at% [16]. With growth rates between 5 and 25mm/h crystals with Nd contents of 2-8.5% could be grown without macroscopic defects. Growth rates lower than 5mm/h resulted in a second phase \( 4Y_2O_3 \cdot V_2O_5 \). With high dopant concentrations and growth rates, cellular growth was observed. These studies have shown that the float zone method is capable of rapidly producing crystals of high quality and higher Nd concentrations than CZ, but the crystal diameters are limited compared to CZ grown crystals.
Figure 1.11 Schematic of a FZ growth setup. Source: http://www.mpi-stuttgart.mpg.de/crystal/facilities.html

Figure 1.12 a) Required ratio for successful FZ YVO$_4$ growth, b) critical diameter for decreasing dislocation density. Source: T. Shonai, M. Higuchi, K. Kodaira, Mater. Res. Bull. 35 (2000) 225.
Laser-Heated Pedestal Growth

Laser-heated pedestal growth (LHPG) has been shown to be another possible way to grow crystals of good quality [17-19]. In LHPG the starting material is first sintered in a process similar to the FZ technique. The sample rod is melted by focusing a CO$_2$ laser beam on the polycrystalline surface. A single crystal seed is lowered onto the liquid surface and drawn up at a rate from 5-10 mm/h. The single crystal will grow from the seed similar to the CZ process. The advantages of LHPG are again, the lack of crucible and ability to grow in a selected atmosphere. A schematic of the growth process can be seen in Figure 1.13.

A study of LHPG grown YVO$_4$ crystals was conducted by Ardila et al. in an attempt to reduce inhomogeneities introduced in the growth process [17]. Inhomogeneities commonly observed in YVO$_4$ crystal growth such as opaque inclusions and non-stoichiometry degrade the optical properties of the crystal. Part of these problems might be due to insufficient attention being paid to the starting reagents and the difficulties involved in growing in an oxygen atmosphere. Laser heated pedestal growth technique was used to grow single crystals of YVO$_4$ and Nd:YVO$_4$. The crystals were grown in isostatic O$_2$ atmosphere at 1.0, 5.0, and 10.0 atm. The crystals were characterized with absorption, photoluminescence, X-ray powder diffraction, and Raman shift spectra. The occurrence of opaque inclusions was not observed on any of the crystals grown in O$_2$ atmosphere. XRD indicated that only YVO$_4$ was present in the crystal, but in one sample Raman spectra picked up extra peaks that were due to precipitation of another phase.
Flux Growth

Flux growth of YVO$_4$ involves the dissolution of Y$_2$O$_3$ in molten Pb$_2$V$_2$O$_7$ at high temperatures to nucleate and grow YVO$_4$ as the solution is slowly cooled. Several fluxes have been successful in YVO$_4$ growth but the Pb$_2$V$_2$O$_7$ flux is chosen because of its ease of preparation and low vapor pressure. The charge is placed in a crucible and heated to 1573K and allowed to soak in the furnace for about 20h. The charge is then slowly cooled to 1173K at a rate of about 2K/h. The crystal is then quickly removed from the furnace and inverted to separate the growing crystals from the flux and to prevent the crystals from breaking due to the solidification of the flux [18-20]. One advantage to the flux growth method is that the lower growth temperature allows growth without loss of material due to vaporization at higher temperatures, which will be discussed later.

Top-seeded solution growth (TSSG) has been shown to be another feasible way to grow single crystal YVO$_4$. In TSSG YVO$_4$ is grown with a LiVO$_3$ flux material which was chosen as it regulates the formation of non-stoichiometric material. The crystal is grown at 1645K at a very slow rate of 0.04mm/h. This process is shown in Figure 1.14. Obvious drawbacks to this process are the extremely long times required for crystal growth and the precise growth conditions needed for exact YVO$_4$ stoichiometry [21].

Figure 1.14 Schematic of the TSSG technique. Source: http://www.mpi-stuttgart.mpg.de/crystal/facilities.html
1.5 Defects

Defects introduced in the growth of YVO₄ are problematic for maintaining high laser efficiency. Light scattering defects such as voids or inclusions, color centers, residual stress from processing, stoichiometric fluctuations, and low angle grain boundaries have all been observed in YVO₄ crystals [21-26]. Through appropriate selection of constituent materials and improving the growth parameters such as atmosphere, pull rates and temperatures, some of these problems can be reduced or avoided. Low angle grain boundaries remain an elusive defect, as there has yet to be a means of eliminating them in the growth process of large crystals. Low angle grain boundaries have been included in the colloquial label of “veils” as a light scattering defect. Other crystal defects under the veil description include microcracks and other as-yet uncharacterized defects. Previous work [26] has identified low angle grain boundaries with polarized light microscopy. The focus of this current study is to characterize the low angle grain boundaries in YVO₄ with the hope that a better understanding of them will lead to improved crystal growth techniques and improve overall crystal quality.

Melting Behavior of YVO₄

The formation of second phases in CZ growth of YVO₄ has been studied by Ropp et al. to better define the solid state chemistry of YVO₄ at elevated temperatures. At high temperatures, above 1723K, a very slow weight loss of less than 1%/h is observed; this is accompanied with a change in color as the crystal turns yellow. X-ray diffraction indicated the presence of YV₂O₁₇ which is formed by the following solid state reaction:

\[ 8\text{YVO}_4 \overset{\Delta}{\rightarrow} \text{Y}_8\text{V}_2\text{O}_{17} + 3\text{V}_2\text{O}_5 \]
Near the melting point (here 2083K) the formation of a black phase was observed and the melt was noted to bubble and fume considerably. Again, X-ray diffraction indicated the black phase was YVO$_3$, which is a semiconducting phase formed by the reaction:

$$2\text{YVO}_4 \xrightarrow{\Delta} 2\text{YVO}_3 + \text{O}_2$$

It is thought that both reactions occur simultaneously. The formation of either phase is problematic for growth of high quality YVO$_4$. The change in valence from V$^{5+}$ in YVO$_4$ to V$^{3+}$ in YVO$_3$ and the accompanying change in structure from tetragonal to orthorhombic could cause other defects in the crystal such as particles, dendrites, and helices. Reoxidation was possible by annealing the crystal in oxygen; this also demonstrates the importance of growing the crystals in an oxygen atmosphere [22].

**Segregation in YVO$_4$**

Erdei *et al.* performed SEM and EDS on cleavage surfaces of CZ grown crystals to determine the composition of precipitates formed during crystal growth [23]. The study indicated that either yttrium or vanadium excess precipitates can grow close to a quasi congruent (50.7 ± 0.2 mol% Y$_2$O$_3$) composition. Segregation curves were thus proposed to the phase diagram (Figure 1.15) to determine the amount of precipitation and the limited solid solution homogeneity region in the Y$_2$O$_3$ – V$_2$O$_5$ system.

Katsumata and co workers examined non-stoichiometry in YVO$_4$ crystals by evaluating the compositional variations and lattice parameters as well as photo-luminescence of specimens containing various vanadium mole fractions $x = \frac{\text{V}_2\text{O}_5}{(\text{Y}_2\text{O}_3+\text{V}_2\text{O}_5)}$ from 47 to 51 mol%. It was found that lattice parameters, $a$-axis, $c$-axis, and $c/a$ ratio varied with the composition. This implies a solid-solution region in
YVO$_4$. The c lattice parameter was found to decrease with vanadium content, x, from 47 to 51 mol%; the a lattice parameter increased from 47 to 51 mol%. The c/a ratio decreased from 47 to 51 mol%, but the unit cell volume remained constant. The compositional variations were also observed through photoluminescence; this supports the existence of a solid-solution region in YVO$_4$. The vanadium deficient non-stoichiometric solid-solution region is estimated to range from x = 48 to 50 mol% at 1473K (Figure 1.15 inset). A vanadium vacancy model is proposed to explain the vanadium deficient solid-solution.

A structural investigation by Sangaletti et al. of the Y$_2$O$_3$ – V$_2$O$_5$ system was conducted on possible segregated phases appearing during flux growth of YVO$_4$. An opaque inclusion was identified to be either 4Y$_2$O$_3$ – V$_2$O$_5$ or 5Y$_2$O$_3$ – V$_2$O$_5$ and was found to be nearly trigonal.

Erdei et al. concluded that inherent to CZ growth of YVO$_4$ is shifting stoichiometry with yttrium and vanadium. The valency state of vanadium changes from +5 to a lower state, which produces oxygen vacancies to maintain charge balance. Thus the CZ technique can only produce near congruent YVO$_{4-x}$ crystals. These crystals have inhomogeneities in the Y and V stoichiometry and will undergo metastable phase transitions producing scattering centers in the crystal. Other growth methods were suggested and described for stoichiometric YVO$_4$ growth including TSSG, liquid phase epitaxial (LPE) growth, and FZ. It was shown that crystals of stoichiometric composition could be grown using LiVO$_3$ flux but long growth times (0-0.04 mm/h) and highly optimized growth regimes were necessary [21].
Figure 1.15 Phase diagram of the Y$_2$O$_3$ – V$_2$O$_5$ system near 50.7% Y$_2$O$_3$. Source: S. Erdei, B.M. Jin, F.W. Ainger, B. Keszei, J. Vandlik, A. Suveges, J. Crystal Growth 172 (1997) 466.

Other Defects

Hu et al. described several defects have been commonly associated with the growth of single crystal YVO$_4$; all of which are harmful to the optical properties of the material [26]. Color centers have been observed and have been attributed to oxygen deficiency. Caution must be exercised when characterizing color centers that the changes in observed color are not due simply to the optical source used. The relative changes in the blue color when viewed with a fluorescent lamp are due to the Nd$^{3+}$ ion concentration. Yellow coloration is due to oxygen deficiency; this can often be returned to the blue color by annealing the crystal in an O$_2$ rich atmosphere.

Inclusions in the form of micro-pieces of iridium from the crucible material or other contamination have been noted as well as micro-bubbles. Other frequent inclusions are micro pieces of the segregation phases which can form during crystal growth. All inclusions or bubbles will act as scattering centers and be very problematic to the homogeneity of the laser. Often these scattering centers can be observed with use of intense light such as a fiber optic light or He-Ne laser. It is suggested that control of the raw material homogeneity and mixing, and the O$_2$ levels in the sintering and growth process will reduce the number of inclusions.

The appearance of substructure has been noted in a-grown crystals. This substructure is composed of low angle grain boundaries that are nearly parallel to the a-faces displayed during a-axis growth. Many dislocations will be introduced during the growth process at high temperatures just below the melting point. These dislocations which are free to move will migrate to produce low angle grain boundaries. The large difference in thermal expansion coefficient between the a and c directions produces stress in the crystal due to inhomogeneous cooling. These stresses will force the dislocations and boundaries to migrate to form large
boundary domains in the crystal. No suggestion was given to reduce or eliminate boundary growth.

The concentration of Nd was discovered to vary with the crystal length. This is because the segregation constant of Nd$^{+3}$ ions is about 0.58 to 0.63 in YVO$_4$ and not 1. The variation in Nd$^{+3}$ concentration was measured to be 0.002/mm. This change in concentration produces a small change in the crystals refraction which is problematic when the laser beam is traveling parallel through the concentration change. It is suggested that the concentration change could be reduced by decreasing the ratio of the volumes of the grown crystal vs. the grown melt.

Processing stresses have also been demonstrated in machined laser elements. These stresses can cause the beam to change its direction or become diffuse. These stresses can be reduced by very careful controlling each step in the laser element machining process.

**Low Angle Grain Boundaries**

Grain boundaries separate regions of different crystallographic orientation in a material. The simplest form of a grain boundary is a tilt boundary which is composed of a parallel array of edge dislocations [27,28]. The array of dislocations is formed by two crystal regions which have a small angular difference and thus a degree of misfit as seen in Figure 1.16. The spacing between the dislocations which make up the boundary is determined by the angle of misorientation as is the energy of the resulting low angle grain boundary. As the angle increases to about 15° the dislocations are too close together to accurately describe the grain boundary.

Low angle grain boundaries in YVO$_4$, as discussed previously, are disruptive to the optical properties. The goal of this work is to characterize low angle grain boundaries in YVO$_4$ with the hopes that a better understanding will result in a way to eliminate them in CZ growth.
References


CHAPTER TWO
EXPERIMENTAL METHODS AND TECHNIQUES

2.1 Materials Studied

Boules of Nd:YVO$_4$ grown with the CZ method in the a- and c-directions were secured from commercial vendors for defect characterization. The crystals had Nd concentrations varying from 0.27-2.0% where the percentage of Nd is given as a substitutional amount for Y. The Nd is introduced by the addition of Nd$_2$O$_3$ along with the appropriate excess of V$_2$O$_5$ to maintain crystal stoichiometry. The crystals were grown above 2053K with pull rates ranging from 0.5-3mm/hr and rotation rates from 10-30rpm. The crystals had been previously inspected and qualitatively rated for defects by the commercial vendors.

The crystals analyzed came from different manufacturers in the form of boules and boule caps, finished laser elements, and crushed powders (Figure 2.1). Occasionally crystals that had failed in an unusual or catastrophic manner were sent for characterization as well. The crystals were typically green to sky blue or violet in color, depending on the doping concentration. Crystal diameters and lengths were in the order of one to two inches. Crystals with varying degrees of defects were sent; known defects included color centers, scatter centers, and defects colloquially known as veils.

2.2 Optical Methods

The crystals sent for characterization were commonly inspected by the vendor prior to receipt. Many of the crystal defects can be seen through visual inspection, occasionally with the use of intense light. Color centers are easily identified as the crystal will exhibit a region of
discoloration, typically yellow or brown, in a region of the crystal (Figure 2.2a). A fiber optic light or laser pointer can be directed through the polished sides of the crystal to illuminate the scattering centers and veils. The scattering centers are quite straightforward to identify in this method (Figure 2.2b), but the veils can be challenging to find, especially if the defects are not extensive. Since the veils only produce a slight change in the refractive index, the crystal must be rotated and the light source moved around the crystal until an appropriate configuration renders them visible (Figure 2.2c). In some instances, it was easier to locate veil defects by looking through the crystal at a light source several feet away. Veils were also located with a ring of fiber optic light when the crystal was tilted (Figure 2.2d). Even though these optical techniques make it possible to locate some of the defects, it can nevertheless be challenging to understand the full extent of the defects as well as isolate their exact location for further analysis. This is why several other techniques have been employed in the characterization of Nd:YVO₄.

2.3 Polarized Light Microscopy

Polarized light microscopy is commonly overlooked as an analytical tool due to its simplicity and the availability of more technologically advanced instruments such as electron microscopes. The information which can be obtained from polarized light microscopy is highly valuable however, and can be obtained quickly and without the high cost of many other microscopes. Polarized light microscopy is ideal for materials that are optically anisotropic, which includes about 90% of solid substances [1]. The principles of polarized light with an anisotropic material are straightforward. The description of light as a wave states that light traveling along any direction will be composed of light waves vibrating perpendicular to the
Figure 2.1 a,b) boules of Nd:YVO₄; c) 4x4x12mm laser brick elements.

Figure 2.2 a) color center observed optically and b) scatter observed with fiber optic lighting.  c) a veil seen through fiber optic lighting and rotation; d) the same veil as seen through ring lighting and tilting.
direction of travel, with all vibration directions being equally possible (Figure 2.3a). In a polarized light microscope, a polarizer is used to directionize the incoming light so only one vibration is allowed normal to the traveling direction (Figure 2.3b). The polarizers used in the microscope are either a birefringent crystal called a Nicol or a film of polymer chains with light absorbing dyes which allow light traveling perpendicular to the planes to be transmitted, and light parallel to the chains to be absorbed. In the microscope, a polarizer is placed before the specimen and another, called the analyzer, is placed between the objective and the viewing port. Commonly, the polarizer and analyzer are perpendicular to one another, although in many microscopes this can be adjusted. In this position, the polarizers are crossed and no light is transmitted through the system; this is called a position of extinction. When a birefringent material is placed in the optical path, the different refractive indices will produce mutually orthogonal light waves at different velocities; these are called the ordinary and extraordinary rays. These rays will be out of phase with each other when they leave the crystal but will be recombined when they reach the analyzer. When they are recombined, constructive and destructive interference in the rays will produce image contrast [2]. This is shown schematically along with the corresponding parts on the microscope in Figure 2.4 [1].

The velocity of the rays and thus the contribution to the resultant brightness will depend on the orientation of the crystal with the polarizer and analyzer. As the crystal is rotated 360° on the stage it will alternately appear light and dark. The crystal appears darkest when it is in a position of extinction parallel or perpendicular to the polarizer. This is shown in Figure 2.5a where P is the plane of the polarizer, A is the analyzer, and R is the resultant light contribution of the crystal in the orientation shown. In this orientation no light should be transmitted through the crystal; the crystal is visible in this figure to illustrate its orientation. As the crystal is rotated to
Figure 2.3 a) light waves with all possible vibrations; b) the effect of a polarizer to directionalize light to one orthogonal vibration.

Figure 2.4 Interactions of light through the polarized light microscope and components of the microscope. Source: http://www.microscopyu.com/articles/polarized/polarizedintro.html.
an angle $\alpha$, the contributions of the ordinary ray (o) and extraordinary ray (e) will increase as a portion of the light is able to make its way through the analyzer (Figure 2.5b). The contributions and thus brightness will increase as $\alpha$ increases. The crystal will be brightest when it is oriented 45º to the analyzer and polarizer as can be seen in Figure 2.5c [3].

Polarized light microscopy was used to better understand the extent to which the crystals were non-uniform. The samples analyzed included CZ grown boules, boule caps, and finished laser bricks. The samples which required sample preparation were cut with a diamond embedded saw operated at low cutting speed. The samples were subsequently ground from 320 to 1200 grit SiC and polished through 0.05µm diamond paste with gold-label cloth and oil suspension. The samples were analyzed on a Nikon Optiphot-Pol transmitted light polarized microscope near a position of extinction. Images were captured with a SPOT CCD camera and software.

Figure 2.5 Effects of angle of crystal with polarizer and resulting illumination. Source: http://www.microscopyu.com/tutorials/java/polarized/crystal/index.html accessed 4/4/04
2.4 Scanning Electron Microscopy

Usefulness of Electrons

The ability to resolve two discrete points of distance \( r_1 \) from each other depends on Equation 2.1:

\[
\frac{r_1}{\lambda} = \frac{0.61\lambda}{n \sin \alpha}
\]  \hspace{1cm} [2.1]

where \( \lambda \) is the wavelength of the light, \( n \) is the refractive index, and \( \alpha \) is the semi angle; the value \( n \sin \alpha \) is known as the numerical aperture, NA [4]. Intuitively, the resolution can be improved (smaller distance between points) by either decreasing \( \lambda \) or increasing the NA. In light microscopy by using green light, \( \lambda \) can be decreased to 400nm and with oil immersion, the NA can be increased to about 1.6. Thus the resulting absolute resolution for using green light is about 150nm. For resolution of features smaller than this a radiation of smaller wavelength is necessary.

Another important consideration is the depth of field, \( h \), which is related to the resolution by the semi angle according to Equation 2.2.

\[
h = \frac{0.61\lambda}{n \sin \alpha \tan \alpha}
\]  \hspace{1cm} [2.2]

The depth of field is the range of positions for which our eye can not detect a change in the focus [4]. The areas above and below the depth of field will be out of focus equivalently. For light microscopy, one way of increasing \( h \) is by decreasing \( \alpha \), but this will lead to a loss in resolution. Therefore, the best way to increase \( h \) and subsequently increase resolution is by decreasing \( \lambda \). Electron wavelengths are several orders of magnitude smaller than visible light (from 0.001 to 0.01nm); this is a major advantage in using electrons for microscopy. The wavelength of an
electron is proportional to the accelerating voltage, $E$, of the electron by Equation 2.3 (neglecting relativistic effects):

$$\lambda = \frac{1.22}{E^{1/2}}$$  \[2.3\]

For typical accelerating voltages from about 20-200 eV (depending on the microscope), $\lambda$ will be from 0.27 to 0.09nm.

Electrons offer some very desirable features in microscopy such as higher resolution, higher magnification, greater depth of field and other useful information obtained from electron interactions with the sample. Several considerations must first be made for effective use of an electron beam. Electrons are much more sensitive to scattering by gasses than light; in order to use electrons the microscope must be under a strong vacuum. Electrons, as charged particles, have the advantage that they can be directed with the use of electromagnetic lenses. Despite the uniform index of refraction that electromagnetic lenses provide aberrations in the lenses limit the theoretical resolution from a fraction of the size of a single atom to about 0.2nm.

A number of interactions take place when a sample is hit by an electron beam. These interactions are used to obtain surface topography, chemical information, crystallographic information and other very useful data. Each signal will require a different way to get useful information from the beam sample interactions. Some electron microscopes have the capability to collect numerous signals.

**Electron Microscopy Components**

Several components are necessary for effective electron microscopy such as electron sources, lenses and apertures, signal detection/viewing screens, pumps, sample holders, and any other peripheral detection devices.
Electron Sources

Electrons used for electron microscopy are generated by either thermionic emission or field emission sources. A thermionic source works by heating the source to a high enough temperature so that electrons have enough energy to escape the material. This is done by resistive heating as a current is passed through a cathode with a high melting temperature or low work function such as tungsten or lanthanum hexaboride (LaB$_6$), respectively. Tungsten filaments similar to incandescent light bulbs are drawn into a fine thread which is bent to form a V-shape. LaB$_6$ sources are ceramic sources which are grown with a <110> orientation to enhance emission [5]. With thermionic sources it is important that they are operated at or just below the saturation condition where additional heating current produces little additional beam current. Field emission sources, (commonly called FEG sources) take advantage of the high electric fields from sources at very sharp points. The work function required to remove an electron from the material at a sharp point is low enough to let electrons tunnel at relatively low potentials. With FEG sources it is important to have either a very high vacuum or heat the tip as contamination and oxide formation will inhibit the field effect.

In order to use the electrons from the source the electrons must be controlled. The electron source is combined with a Wehnelt cylinder which is negatively biased and a highly positively biased anode plate; this assembly is called the electron gun (Figure 2.6). The anode attracts the negatively charged electrons down the column and the Wehnelt cylinder focuses the electrons into a crossover point.
Pumps

As discussed previously, the chamber in the electron microscope must be at low pressure (about $10^{-7}$ to $10^{-9}$ Pa) so that electron mean free path is large enough to insure minimal scattering by atoms. A variety of pumps are used in electron microscopes including and often a combination of mechanical, diffusion, turbomolecular, and cryogenic pumps.

Lenses and Apertures

Once the electron beam has been accelerated past the anode a series of electromagnetic lenses will focus the beam to its desired convergence point on the sample. Lenses are constructed of soft iron pole pieces with a hole drilled down the center. The hole is called the bore and it is where the electron will travel through the lens. Within the pole piece is a coil of copper wire which surrounds each polepiece as seen in Figure 2.7. A current passed through the copper coil will produce a magnetic field in the bore. This magnetic field will focus the electron beam to a crossover point. The strength of the magnetic field will determine how close to the lens the crossover point is; the higher the field, the closer the crossover is to the lens. Controlling the crossover point will determine the spot size of the electron beam and the beam spreading. The first lenses the beam will encounter after the anode are the condenser lenses which control the spot size and beam current. As the strength of the condenser lens increases, the current decreases which will increase the resolution [6].

The objective lens is a very strong lens which is used as a final focus of the beam to the sample. It is desirable to have the objective lens as close to the sample as possible since the highest resolution will be possible for very short focal lengths due to minimization of lens aberrations.

In transmission electron microscopy the objective lens plays a very important role in forming the first intermediate image and the diffraction patterns, which will be discussed later.

Apertures are another important component in the electron column. An aperture is often inserted into a lens, which selects the angular range of electrons which can travel down the column (Figure 2.8). Several aperture sizes are usually available to be selected with varying hole diameters from about 10\(\mu\)m to 300\(\mu\)m [6]. In the TEM column, the objective aperture controls the resolution of the image, the depth of field and focus, the image contrast, the angular resolution of the diffraction pattern, and other functions [6].

Scan coils, although not actually lenses, use electromagnetic fields to deflect the electron beam. In SEM this is used to raster the beam back and forth across the sample. This field is applied perpendicular to the beam direction but with smaller fields than the lenses. The scan coils will be positioned in a perpendicular arrangement to allow beam control in X and Y directions. Most microscopes have a dozen or more scan coils which enable finer control of the beam position [7].

**Signal Detection**

When the electron beam impinges on the sample a number of interactions occur including generation of low energy secondary electrons, high energy backscattered electrons, X-rays, cathodoluminescence, and forward scattering electrons as well as transmitted electrons depending on the thickness and potential of the incoming beam (Figure 2.9). There are numerous techniques to capture different signals and much valuable information can come from the interactions.
Figure 2.8 Beam diagrams of the TEM column a) without and b) with the condenser aperture inserted. *Source: D.B. Williams, C.B. Carter, Transmission Electron Microscopy: Basics, 1996, pp 133-153.*

Figure 2.9 Interactions that take place when an electron strikes a material *Source: P.J. Goodhew, J. Humphreys, R. Beanland, Electron Microscopy and Analysis, 2001, p 126.*
**Secondary Electrons**

In SEM, secondary electrons are used to provide information about the surface topography. These electrons, which escape from the specimen, are quite abundant and have energies below about 50eV \[7\]. Secondary electrons are collected by a scintillator which has a Faraday cage biased at +300V to attract electrons from all scattering angles and positions on the sample. The secondary electrons are attracted to the positive charge and thus strike the scintillator, which, combined with a photomultiplier tube converts the electrons from the sample to an image on the monitor. Since the beam is rastered across the sample signal is captured from the entire radiated surface; regions where the signal is not as strong will result in darker contrast on the monitor.

Since electrons are charged particles, it is important that the sample be electrically conductive or a conductive path to ground must be provided. If the sample is nonconductive, a negative electric charge can build on the surface of the material and repel the incoming electrons in an effect known as charging. For nonconductive samples, a thin layer of a conductive material such as Au or C is deposited on the surface.

**Backscattered Electrons**

Backscattered electrons can also be used for imaging, but they must be captured with a different technique. A detector for backscattered electrons must be in a line of sight since they retain much of the energy and are scattered at an angle close to the incident beam. Thus, backscattered electron detectors are often on the pole piece, near the bore. Backscattered electrons will experience little effect from the positively biased faraday cage, although some will still impinge onto the secondary electron scintillator due to their projection angle. Images
formed with backscattered electrons will vary slightly from secondary electron images because the illumination is direct instead of diffuse. Compositional contrast can be seen with backscattered electrons because of the dependency of the signal with the atomic number, Z [8].

Backscattered electrons can be used to obtain crystallographic information about the material surface through obtaining electron backscatter diffraction (EBSD) patterns. When an incoming radiation impinges on a sample it can be diffracted off the lattice plains at the same angle of incidence or it can pass through the crystal. Diffracting electrons that satisfy the Bragg criterion, Equation 2.4:

\[ n\lambda = 2d \sin \theta \]  

where \( n \) is an integer, \( \lambda \) is the wavelength of the electron, \( d \) is the \( hkl \) lattice spacing, and \( \theta \) is the diffraction angle as shown in Figure 2.10. A second electron beam diffracting off another plane \( hkl \) and traveling the extra distance \( ABC \) will interfere with the other diffracting beams. If the value of \( ABC \) is an integer value of \( \lambda \), the diffracted beams will be coherent and constructively interfere. In EBSD, the sample is tilted to an angle of bout 70° as shown in Figure 2.11. The tilt allows the EBSD pattern to be captured by the phosphor screen. The backscattered electrons which satisfy the Bragg condition will create a band which corresponds to the \( hkl \) plane that corresponds to that diffraction. The formation of these bands is similar to the formation of Kikuchi bands in TEM which will be discussed later. A CCD camera on the other side of the phosphor collects the EBSD pattern that the bands form which is then fed to a PC. The data analysis program on the PC measures the position of the lines and the angles between them to index the pattern and yield crystallographic information. The angular precision of the measurement is from 0.5-2.0° [8]. When the beam is rastered across the sample, EBSD of an area can be performed to yield a crystallographic map showing orientation information. Since
Figure 2.10 Bragg diffraction of an electron off the crystal planes. Source: D.B. Williams, C.B. Carter, Transmission Electron Microscopy: Basics. 1996, p 46.

Figure 2.11 Schematic of the EBSD technique. Source: P.J. Goodhew, J. Humphreys, R. Beanland, Electron Microscopy and Analysis. 2001, p. 153.
the information in EBSD patterns is from the surface of the material, it is important that the material surface be flat, highly polished, and free of coating which would interfere with the signal.

**Chemical Analysis**

One common peripheral device used in many electron microscopes is energy dispersive spectroscopy (EDS). As electrons impinge on the sample and collide with atoms, electrons in the inner shells of the atom will be ejected. Electrons from higher energy levels will quickly move into the vacancy produced and in doing so will release an X-ray characteristic to the element and electron interaction that takes place. The X-ray detector must be in line of sight of the sample and is best to be close to the specimen. The detector is made from a semiconductor, usually silicon which is p-i-n doped and reverse biased. A thin layer of gold coats the p and n faces to provide the bias potential. A thin polymer film or Be window is used to prevent contamination from forming on the surface and blocking the incoming X-rays. These materials are selected because of their minimal interaction with the X-rays. The detection takes place in the semiconductor when an incoming X-ray produces electron-hole pairs proportional to the X-ray energy. The reverse bias attracts the corresponding charges and a current will flow with energy exactly proportional to the X-ray [9]. This interaction is assisted by cooling the semiconductor with liquid nitrogen to 77K to increase the resistivity. This detection can be useful for probing small areas of the sample. The computer is able to detect elements of higher Z than Na and yield the number of counts of each element present to give their relative abundance in the material.
Samples

Samples were analyzed with SEM for topographical and crystallographic information. Samples prepared for EBSD analysis using OIM were prepared using the traditional metallographic techniques described for the polarized light microscopy samples. Some of the samples were coated with an amorphous C layer in an attempt to reduce charging in the SEM chamber. The samples were secured to the mounting stub with hot glue and were kept as flat as possible on the stub. Silver paint was applied to the edges and corners of the samples to provide a conductive path to ground. OIM was used to verify and determine the degree of misorientation of low angle grain boundaries. The areas analyzed were known to contain low angle grain boundaries and were scribed to indicate their location. A scan area of 780 by 2104µm was used with a step size of 15µm. The average confidence for the scan was 0.52. The samples were analyzed with a W filament CamScan Series 4 SEM operated at 20keV and equipped with a DigiView II slow scan CCD camera and OIM data collection and analysis software from EDAX.

Samples prepared for topographical analysis of etch pits underwent the same metallographic techniques described for EBSD analysis. The samples were subsequently etched in HNO$_3$ at about 373K for times ranging from 40 minutes to 2 hours. The etch pits were imaged with secondary electrons in a JEOL JSM-6400 operated at 20keV.

2.5 X-ray Computed Tomography

Computed tomography (CT) is a valuable non-destructive technique for determining the internal homogeneity of materials. The sample is placed on an automated stage that rotates as the machine captures a series of X-rays with an amorphous silicon detector, which feeds the data directly to the computer. The computer then processes the X-ray images and creates a 3D
reconstruction of the sample; an example of this can be seen in Figure 2.12. Sectional views can be produced of the specimen in the XY, XZ and YZ planes. Any areas of lower density such as cracks, voids, and some precipitates will appear as darker contrast in the reconstruction of the sample. Areas of higher density will produce lighter contrast. The high voltage X-ray capabilities allow analysis to be done on materials of large size or density. The high resolution micro-focus beam is particularly useful in precisely locating defects to within several microns in three dimensions. For defects beyond the resolution capabilities of CT, other techniques are necessary.

Samples were analyzed with a HYTEC FCT-4200 high resolution X-ray computed tomography machine. The CT machine used has two high voltage sources; a 420kV source and a 225kV microfocus X-ray tube. The resolution for the 420kV tube is 800µm, whereas the 225kV source is capable of 5µm resolution. The specimen stage has a 68kg capacity and is automated to rotate and move in the z-direction. The beam projection size of the sample on the detector will be a function of the distance from the sample to the source and the detector to the sample. Samples can vary in size from only a few mm to over 25cm. The samples were placed on the stage 8cm from the 225kV source and 49cm from the detector with the polished face perpendicular to the tube. The sample was rotated 360° as the X-rays images were collected with a PaxScan 2520 high energy amorphous silicon detector. The X-ray collection took approximately 20 minutes. With eight processors performing the reconstruction, the data processing took approximately 1 hour.
2.6 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is similar in many ways to the electron microscopes discussed previously, but TEM provides important information that other methods can not. TEM operates at voltages from 100-1000keV which is why it provides high magnification and the highest resolving power of electron microscopes, around 0.12nm. Important crystallographic information can be obtained quite straightforwardly in TEM. TEM, like SEM uses a monochromatic beam of electrons to image with, but where SEM collects data from the surface of a material from electron-sample interactions, TEM uses a transmitted electron beam. In TEM multiple contrast mechanisms are used to obtain information about the orientation, chemistry, phase, and structure of the material. The nature of TEM requires that the samples be very thin to allow electron transparency, typically <200nm thickness.

TEM Sample Preparation

Samples to be analyzed with TEM must be pre-thinned if they are not already thin enough to be electron transparent. Very few samples are actually thin enough to begin with so most materials must go through a TEM sample preparation process; this is the major drawback to using TEM. TEM samples will fall into the bulk, surface, or small piece category of sample preparation. For most bulk materials, (such as the materials examined in this study) the sample preparation technique is shown schematically in Figure 2.13. The bulk material is first cut, punched, or cored into a 3mm disk (Figure 2.13a), which is the size most sample holders can accept. The sample must be mechanically thinned and polished on both sides (unless it is a surface sample) to a thickness of about 100µm (Figure 2.13b). The sample is then mechanically dimpled in abrasive slurry to a final thickness from 5-20µm at the center of the dimple (Figure
2.13c). The final thinning will slowly remove material and create a small hole in the sample as in Figure 2.13d; the material approaching the hole should be electron transparent. This is typically accomplished through ion milling using \text{Ar}^+ ions or through a chemical removal process until perforation.

**TEM Components**

The components in a TEM are similar to SEM with a slightly different configuration and a few additional components. After the electron gun system there are a series of condenser lenses and aperture. Next in the column is the sample which is immediately before the objective lens, objective aperture and diffraction aperture. After the objective lens there is another lens called the intermediate lens which is followed by the projector lens. Finally the viewing screen and camera are at the bottom of the column. Other analytical tools such as EDS and electron energy loss spectroscopy (EELS) might also be in the column.

The condenser lenses in the TEM serve to control the amount of the sample irradiated by the electron beam. The first condenser lens demagnifies the beam diameter from the electron gun crossover point. The second condenser lens controls how much of the sample is irradiated by the beam. A condenser aperture can be inserted at the second condenser lens to block high angle electrons as in Figure 2.9. The beam will be most coherent when it is parallel; this will allow the best image contrast and sharpest diffraction patterns [10]. Certain techniques require the second condenser lens to focus the beam to a small convergent point on the sample. This is useful in forming convergent beam electron diffraction patterns and when probing small areas of the sample.
Figure 2.12 3D computed tomography map.

Figure 2.13 Schematic of TEM sample preparation a) sample is cored to 3mm diameter, b) sample is mechanically thinned to 100µm, c) sample is mechanically dimpled to 5µm, d) sample is chemically etched until perforation.
The sample is the next component in the TEM column. The 3mm samples are placed in the TEM sample holder, which is a long rod with an o-ring seal. Some sample holder also have specialized control apparatus for different functions such as double tilting, heating, or straining in situ. The sample is secured in the sample holder which is inserted into the microscope. Care must be taken so the vacuum seal is not broken in inserting and removing the sample holder.

The objective lens is in a fixed position with respect to where the sample will rest when the holder is in the TEM. This is so the images and diffraction patterns can be captured in with precision. In addition to the close proximity of the objective with the stage, the sample must be adjusted slightly so that it lies in the eucentric plane. When the sample is in the eucentric plane the image will not translate when the sample is tilted and the objective lens is at its optimum current value [10]. The objective lens is responsible for forming the first intermediate image as well as diffraction patterns.

When the electron beam travels through the sample, it is diffracted according to Equation 2.4. The objective lens focuses the diffracted electrons onto what is known as the back focal plane. The diffracted electrons produce reflections from the crystallographic planes which satisfy the Bragg condition. If the area of the sample is single crystalline this will result in a spot pattern; if it is polycrystalline, the diffracting planes will produce rings which correspond to every possible orientation of the $hkl$ reflecting planes. All the diffracting electrons will contribute to the image formed; in this condition, the image will be at minimal contrast. If an objective aperture is inserted, it will eliminate the higher angle diffracted electrons and only those within the aperture will contribute to the image contrast. This is known as diffraction contrast and is an important contrast mechanism in the TEM. Under bright field conditions, the objective aperture will be centered around the center spot, which is the incident beam. If another
spot is selected only the diffracted electrons which contribute to that spot will form the light contrast in the image; this condition is known as dark field imaging.

The distance between the specimen and the intermediate lens is fixed. The strength of the intermediate lens controls whether an image or diffraction pattern is formed. When a diffraction pattern is formed the intermediate lens is focused on the back focal plane where the objective formed the diffraction pattern (Figure 2.14a). When the intermediate lens is focused on the image plane of the objective, the image is projected onto the viewing screen (Figure 2.14b) [10].

The last lens in the TEM column is the projector lens which magnifies the image formed by the objective lens and projects it to the viewing screen. Several projector lenses might be used in conjunction with one another to provide a total magnification of up to about one million times. The viewing screen for TEM is a phosphorescent material which emits green light when electrons strike the surface.

**Diffraction Patterns**

Diffraction patterns formed by the objective lens on the back focal plane contain important crystallographic information. The diffracted electrons will form an array of spots with a single crystal or a series of concentric rings if the material is polycrystalline. Since the spot reflections are related to the diffraction from the crystallographic planes, their intensity will change if the sample is tilted. When the spots are in a uniform and symmetric brightness around the incident beam the sample is on a zone axis orientation (Figure 2.15a). In this position, the number of diffracted electrons contributing to the image is large and the resulting image features will be at maximum contrast. The sample can also be tilted to another important orientation known as a two beam condition where the direct beam and one other spot will be highly
reflecting and others will not be as much (Figure 2.15b). This condition is useful in many TEM techniques. The vector \( g \) between the direct beam and a reflection is related to the crystallographic spacing \( d_{hkl} \) by Equation 2.5:

\[
|g| = \frac{1}{d_{hkl}} \tag{2.5}
\]

This relationship relates the real space of the crystal with the reciprocal space. Using the fact that spacing of the reflections corresponds to the real crystal, we can index diffraction patterns to find the interplaner spacing of the diffracting planes giving rise to the reflections. The distance between the direct beam and a reflection can be measured on a recorded diffraction pattern. This distance, \( r \), can be used to determine the interplaner spacing, \( d_{hkl} \), if the camera constant, \( L\lambda \) is known by Equation 2.6.

\[
d_{hkl} = \frac{L\lambda}{r} \tag{2.6}
\]

The camera constant combines the camera length, \( L \) and the wavelength, \( \lambda \) of the electron beam, which can be calculated from Equation 3 if the accelerating voltage is known. If the reflecting plane, \( hkl \) is unknown, it can be determined from \( d_{hkl} \) with Equation 2.7 for a tetragonal crystal with lattice parameters \( a \) and \( c \).

\[
\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \tag{2.7}
\]

Figure 2.15 Electron diffraction patterns a) on axis, b) in a two beam condition.
Occasionally, in a thick sample on a zone axis orientation, a reflection from a spot which should be forbidden by the crystal’s selection rules will appear on the diffraction pattern. This is known as double diffraction and is caused by dynamical scattering in the crystal. In YVO₄, the 002 reflections are forbidden but are formed from the dynamical scattering event:

\[(101) + (01) = (002)\]

**Contrast Mechanisms**

As mentioned previously, there are three main contrast mechanisms used in TEM. Often times a combination of contrast mechanisms will be visible so it is important for the microscopist to know which contrast mechanisms are contributing to the image.

Mass-thickness contrast is formed in a bright filed image by comparatively more scattering events in one area of the specimen relative to another. As the beam travels through the material it will be scattered to a certain degree by the sample. The number of scattering events and scattering angle of electrons will increase with increased sample thickness or in areas with higher atomic number. The high angle scattered electrons will be blocked by the objective aperture and will therefore not be used in forming the image; darker contrast will result.

Diffraction contrast is a very important contrast mechanism that is encountered with crystalline materials. Diffraction contrast is dependant on the Bragg condition of diffraction of the electron beam with the crystallographic planes. Diffraction contrast enables imaging of anything that changes the way that electrons are diffracted including different orientations of crystals, dislocations, stacking faults, stress in the sample, sample shape and others. The diffraction contrast produced by a dislocation in the sample is shown schematically in Figure 2.16. As the electrons travel through the sample they are diffracted differently when they
encounter the distorted crystal planes near the dislocation core. These diffracted electrons will not contribute to the image along their original path. What results is a dark band corresponding to where the electrons would have formed the image (Figure 2.16a). In this orientation, the diffraction vector, \( \mathbf{g} \), is parallel to the Burgers vector, \( \mathbf{b} \), and the dot product of the two (Equation 2.8) is an integer value, \( n \), and the dislocation is visible. Methods for determining Burgers vectors are described in Appendix A.

\[
\mathbf{g} \cdot \mathbf{b} = n \]  \hspace{1cm} [2.8]

If the sample is tilted to an orientation where the diffraction vector is perpendicular to the Burgers vector, (as in Figure 2.16b) the dot product is zero and the invisibility criterion is fulfilled. The dislocation will be at minimal contrast with the rest of the specimen. In practice, there might be a small amount of contrast remaining but for the most part this technique works well (Figure 2.17). The ability to directly image defects in the crystal structure with diffraction contrast makes TEM a valuable and unique tool.

Mass-thickness and diffraction contrast are both examples of amplitude contrast; the other contrast mechanism commonly used in TEM is phase contrast. Phase contrast is seen whenever electrons of different phase are allowed to pass through the objective aperture [10]. This effect is sometimes noticeable as a speckled background on the image. When operating in a two beam condition and using a large objective aperture at high magnification, phase contrast will give rise to lattice fringes which can give valuable information about lattice spacing. Phase contrast is also used in high resolution TEM to obtain images with capability of resolving atomic columns. When tilted to a zone axis orientation, several diffracted beams will contribute to the image; the intersection of lattice fringes will produce a pattern of light or dark spots which
Figure 2.16 Schematic of diffraction contrast of a dislocation when a) $\mathbf{g} \cdot \mathbf{b} = n$ and b) $\mathbf{g} \cdot \mathbf{b} = 0$.

Figure 2.17 Bright field image of a dislocation contrast when a) $\mathbf{g} \cdot \mathbf{b} = n$ and b) $\mathbf{g} \cdot \mathbf{b} = 0$. 
correspond to atomic columns. Caution must be exercised as the spots can correspond to a column of atoms, spaces between atoms, or a pair of atoms. This technique can be used to image individual dislocations and confirm the description of an extra half plane at an edge dislocation. Phase contrast imaging relies heavily on specimen thickness and the resolution of the microscope, so the thinner the sample, the better.

**Image Simulation**

High resolution TEM images can be simulated using specially designed TEM programs. The program performs a fast Fourier transform of an image to form the reciprocal of it, which will be a diffraction pattern. If an inverse Fourier transform is performed on the pattern, a simulation of the original image will be formed. This simulation can be used to show individual lattice plans and can be helpful in finding the exact location of a defect such as a dislocation.

**Kikuchi Patterns**

Kikuchi patterns are formed in a relatively thick specimen from diffusely scattered electrons which satisfy the Bragg criterion. The formation of Kikuchi lines is shown schematically in Figure 2.18. As these forwardly scattered electrons are diffracted they will form what are known as Kossel cones which constitute all the diffracted electrons oriented at angle $\theta_B$ to the $hkl$ plane. When these cones intersect with the Ewald sphere, they form parabolas which resemble straight lines on the pattern since $\theta_B$ is small. Kikuchi lines will be composed of two lines – one called the excess line which corresponds to $\theta_B$ and a complementary parallel line called the deficient line which comes from $-\theta_B$. In an ideal situation, the sample will be thick...
enough so that Kikuchi bands can be seen as well as diffraction spots (Figure 2.19). Kossel cones and the resulting pattern behave as if they were rigidly attached to the sample. Because of this relationship, a small tilt will produce an obvious movement in the Kikuchi lines whereas the movement and change in intensity of the diffracted spots will not change noticeably. It is this effect which allows Kikuchi patterns to be used to determine the orientation of a crystal with an accuracy of about 0.1°. The fixed position to the $hkl$ planes also means that Kikuchi maps can be used to find specific crystallographic orientations. If a map is available, it can be used to guide the tilting of the sample to find the desired zone axis; a Kikuchi map of YVO$_4$ can be seen in Figure 2.20. The most accurate information about crystallographic orientation can be determined using Kikuchi patterns. A technique of determining orientation information on a zone axis orientation is described in Appendix B.

**Samples Analyzed**

TEM specimens were prepared from crystals which contained low angle grain boundaries. The samples were cored with a 3mm diamond coated bit from regions identified by polarized light to contain boundaries (Figure 2.21). The disks were mechanically ground and polished to a thickness of 100µm with the same techniques described for bulk samples. The disks were dimpled with diamond solution from 6µm to 0.05µm to a final thickness of 5µm. The samples were etched in a 3:1 solution of H$_3$PO$_4$ and H$_2$SO$_4$ at 393K. The samples were agitated in the solution to avoid contamination growth on the surface and to keep the acid solution in contact with the samples fresh. The samples were kept in the solution until perforation, which typically occurred within 10-15 minutes. The samples were rinsed with copious amounts of DI water, dried with methanol, and subsequently cleaned in an ion mill for 1 hour.
Figure 2.19 An ideal Kikuchi pattern showing Kikuchi bands as well as diffraction spots.

Figure 2.20 A Kikuchi map centered on the [010] zone axis of YVO$_4$. 
Some of the samples were carbon coated to reduce charging in the TEM. The samples were analyzed with a Phillips CM 200 TEM and a JEOL 2010 HRTEM, both operated at 200keV.

**Anneal**

Some laser brick samples were annealed in an attempt to get the low angle grain boundaries to migrate and to determine the feasibility of annealing them out. The laser brick samples were documented with polarized light microscopy to compare the locations of the low angle grain boundaries before and after annealing. The samples were packed around scrap pieces of YVO₄ and placed in an alumina boat. The furnace used is a Lindberg box furnace capable of temperatures up to 2073K. The samples were annealed with the following process: 5°/min up to 1623K, 3°/min up to 1973K, hold at 1973K 15 minutes, 1°/min up to 2023K, hold at 2023K for 5 hours, furnace cool to room temperature at ~1-3°/min. After annealing, the positions of the low angle grain boundaries were compared with the images taken prior to annealing.

**Etch**

Samples were etched in an attempt to reveal the dislocation pits which would accompany the low angle grain boundaries. Samples were placed in HNO₃ and heated on a hot plate up to 373K for times ranging from 40 minutes to 2 hours. The samples were heated and allowed to cool in the solution to avoid thermal shock. The samples were suspended in a Pt wire basket in the acid to prevent violent bouncing and chattering from the boiling acid. The etch pits were analyzed with reflected light microscopy, transmitted light polarized microscopy and SEM.
Figure 2.21 TEM sample containing a low angle grain boundary in the thin electron transparent region, as indicated by arrows.
References


3.1 Optical Characterization

Samples were characterized optically for identification of scatter and veil defects. Scatter could be identified easily with the use of fiber optic lighting. Scatter was commonly found in the center of the crystals in a dense group of scattering centers. Concentric rings of scatter centers were also observed (Figure 3.1). Veils in the form of low angle grain boundaries and microcracks could also be seen with fiber optic lighting, but it was difficult to determine their exact location in the crystal and further characterize them (Figure 3.2).

3.2 Polarized Light Characterization

Polarized light microscopy was found to be the best method for locating low angle grain boundaries in YVO$_4$ crystals. The slight change in orientation causes contrast in the image when viewed near an extinction point (Figure 3.3). The severity and number of low angle grain boundaries could be readily seen for the crystals which contained them.

Distinct low angle grain boundaries were found on the growth face of crystals which were grown in the $a$ direction. From inspection of the top and bottom faces of the crystals it was apparent that these features increase in number and severity as the crystal grows. It was possible to track the location and shape of low angle grain boundaries through the length of the crystal (Figure 3.4). It was determined that the boundary in Figure 3.4 propagated through the crystal at an angle of about 16° respective to the growth direction. Linear features of contrast were noted on the faces perpendicular to the growth direction in crystals with six polished faces (Figure 3.5).
Figure 3.1 Concentric rings of scatter illuminated with fiber optic lighting. (a-grown; 1.0%Nd)

Figure 3.2 Low angle grain boundary illuminated with fiber optic lighting. (a-grown; 1.7%Nd)
Figure 3.3 Laser element with low angle grain boundaries images with polarized light. (a-grown; 0.27%Nd)
Figure 3.4 a) Comparison of a low angle grain boundary shape and size at the top of the crystal (dark) with the bottom (light); b) translation of the grain boundary from top to bottom, recorded from four locations. (a-grown; 1.7% Nd)

Figure 3.5 a) Lines of contrast viewed on the c face of an a-grown crystal with veils; b) lines of contrast noted on the a face perpendicular to the growth direction. (a-grown; 0.11% Nd)
Crystals grown in the c direction, (001) did not exhibit the normal low angle grain boundary contrast since the crystals viewed are optically isotropic. Veil features were noted on c-grown crystals, but these were not due to low angle grain boundaries (Figure 3.6). It was noted that on all the c-grown samples which contained light-scattering linear defects there were also large cracks which appeared to be in close proximity. Along the orthogonal (100) and (010) faces, features could be seen which exhibited contrast with polarized lighting (Figure 3.7). Of note in Figure 3.7a are fringes which are due to small spacing between surfaces; this implies that the feature is a microcrack.

Crystals which were rated low for the number of veils from the vendor’s initial visual inspection were found to contain numerous veils when inspected with polarized light. The number of low angle grain boundaries for the low veil rating crystals was found to be very near the number found in high veil rated crystals (Figure 3.8). This observation indicates that the visual-optical inspection technique is not adequate for accurate description of the extent of low angle grain boundaries. It was noted that the contrast was greater with polarized light for the crystals in which boundaries could be seen visually. This indicates that there is a difference in low angle grain boundaries in the crystals which causes them to be more or less visible. It is reasonable to conclude that the misorientation for the highly visible boundaries is greater than the less visible boundaries. This implies that the laser elements made from regions containing higher misorientation will be more adversely affected than those where the misorientation is smaller.

Caps of the CZ grown boules were inspected with polarized light microscopy to determine where in the crystals the low angle grain boundaries form. The boundaries were identified at the topmost and center part of the boule cap (Figure 3.9a). The boundaries formed
Figure 3.6 a-d) Light scattering features observed on c-grown crystals with polarized light. (c-grown; a-c: 0.27%Nd, d: 2.0%Nd)

Figure 3.7 a) Features on an a face perpendicular to the images in Figure 3.6, note the fringes; b) lines of contrast observed on the other a face. (c-grown; 2.0%Nd)
Figure 3.8 Low angle grain boundaries identified in a-grown crystals with veil ratings of a) 1, b) 2, c) 4, and d) 5. (a,b,d: 1.0%Nd, c: 1.7%Nd)
early in the crystal growth leads to many subsequent low angle grain boundaries throughout the crystal, as can be seen in Figure 3.9b, which is from the bottom of this crystal.

Single crystal seeds of undoped YVO$_4$ were analyzed with polarized light to verify that low angle grain boundaries were not present in the seed which would undoubtedly form low angle grain boundaries in the growing crystal. No low angle grain boundaries were found on any of the seed crystals analyzed, but this does not necessarily preclude the seed material from being a source of low angle grain boundaries in all instances.

Polarized light was used to identify the location of low angle grain boundaries in a YVO$_4$ laser element prior to annealing (Figure 3.10). The laser element was annealed at 1973K for 5 hours with the process described in Chapter 2 and subsequently analyzed with polarized light to determine any change in the low angle grain boundaries. Of note were small boundaries surrounded by larger boundaries which would likely be recrystallized and incorporated into the larger grains if the thermal energy were enough to allow dislocation migration. It was apparent that the location and size of the grain boundaries did not change due to annealing at 1973K (Figure 3.11). It was noted that Al$_2$O$_3$ crystals from the crucible grew on the surface of the YVO$_4$ during annealing. The sample was annealed again for 5 hours at the maximum limit of the furnace at 2023K. Once again, the position of the grain boundaries and size did not change (Figure 3.12). These observations imply that the low angle grain boundaries are very energetically stable and that it is not feasible to remove them through annealing.
Figure 3.9 a) Low angle grain boundaries on the topmost center of the boule cap; b) the resulting low angle grain boundaries at the bottom of the crystal. (a-grown; 1.0%Nd)
Figure 3.10 Location of low angle grain boundaries on this laser element prior to annealing. (a-grown; 0.27%Nd)
Figure 3.11 Location of low angle grain boundaries after annealing at 1973K; additional features are alumina crystallites grown during the anneal. (α-grown; 0.27%Nd)
Figure 3.12 Location of low angle grain boundaries after annealing at 1973K and 2023K, the position and shape of the boundaries have not changed. (a-grown; 0.27%Nd)
3.3 Etch Pits

Samples were etched with the technique described in Chapter 2 in an attempt to determine a correlation with defects and etch pits. Since a low angle grain boundary is composed of many edge dislocations which are at higher energy than the bulk crystal we expect these to etch preferentially.

It was discovered that YVO$_4$ etches preferentially along the a-directions, as can be seen in Figure 3.13. A diamond shape can be seen at the center of the etch pit that is deeper than the rest of the etch pit. The etch pits on the a faces exhibit an elongated morphology in the a direction and tend to conglomerate along the c direction (Figure 3.14). This type of etch pit morphology is consistent with etching experiments performed on similar crystals [1-5]. In Nd:GdVO$_4$, rectangular dislocations were noted on the (100) and (010) planes. These dislocations were found to be either single dislocation pits, arrays of pits, or clusters of pits [1]. Dislocation etch pit arrays which form low angle grain boundaries in these systems were consistent with those observed in YVO$_4$. Etch pits on the a faces were found to accompany defects and artifacts on the surface such as scratches or low angle grain boundaries. The bulk of the crystal was not as affected by the chemical etch. It was also observed that regions of the low angle grain boundary closely parallel to [100] will tend to etch preferentially (Figure 3.15).

In the c-grown crystals, the distribution of etch pits was much more uniform (Figure 3.16). Etch pits on the c-faces were noted to be square shaped, unlike those on the a-faces. This etch pit morphology is consistent with dislocation etch pits observed on (001) planes for Nd:GdVO$_4$, Yb:YAG, and YAlO$_3$ [1-4]. Since the crystal is isotropic on the (001) plane it is intuitive that the etching would be uniform. The density of dislocations was found to increase with the concentration of Nd. The addition of Nd causes a difference in lattice constant; for
NdVO$_4$ $a=0.73290$nm and $c=0.64356$nm. This distortion of the lattice produces stress in the crystal which produces a higher dislocation density as the concentration of Nd increases [6]. Other factors which increased dislocation density included crystal diameter and growth rates. Numerous microcracks were noted on samples which had light scattering veils (Figure 3.17). These microcracks corresponded with the observed light scattering featured from Figure 3.6.

The information about the etch pit density and distribution is very important in understanding the mechanisms of low angle grain boundary formation. The presence of dislocations has been verified in both a- and c-grown crystals. The dislocations in a-grown material tend to be localized at the low angle grain boundaries whereas the dislocations in the c-grown material are evenly distributed. The shapes of dislocation etch pits in a-grown verses c-grown are also different, which is to be expected given the anisotropy of the crystal and the different packing of the atoms in the two directions.

For future work, it is suggested that samples be made from smaller pieces of the crystal instead of an entire boule. It is also suggested that the (100) and (010) faces be cleaved since polishing scratches on these faces are problematic and interfere with the observation of dislocation etch pits. The (001) planes do not seem to be effected as much by polishing artifacts and can be readily observed with the preparation methods previously described. Future work in characterizing the microcracks observed on c-grown crystals will be necessary if c-grown crystals are to be used commercially in the near future.
Figure 3.13 Dislocation etch pits on a-grown YVO$_4$ (100) face. (a-grown; 1.7%Nd)

Figure 3.14 Conglomeration of etch pits along [001]; (100) face. (a-grown; 1.7%Nd)
Figure 3.15 Etch pitting of a low angle grain boundary at an area parallel to [100]; (100) face. (a-grown; 1.7%Nd)

Figure 3.16 Dislocation etch pits in c-grown material; (001) face. (c-grown; 2.0%Nd)
Figure 3.17 Microcracks in the c-grown crystals, denoted by arrows; (001) face. (c-grown; 2.0%Nd)

References


CHAPTER FOUR
ORIENTATION IMAGING MICROSCOPY

OIM Characterization of Low Angle Grain Boundaries

OIM was performed on several samples known to contain low angle grain boundaries to determine the approximate angle of misorientation. Important crystallographic information can be obtained from indexing EBSD patterns. The symmetry of the crystal can easily be seen in the pattern, the band width and intensity are related to the crystal atomic spacing, and the angle between bands corresponds to the angle between crystallographic planes.

Even though YVO$_4$ is an insulating material and charging can be problematic, good quality EBSD patterns were obtained (Figure 4.1a). This pattern had a confidence index of 0.53 and could be readily indexed (Figure 4.1b). An orientation map of the area surveyed indicated that the crystal orientation was on (100) as can be seen in Figure 4.2. The dark areas are spots of low confidence which were thrown out of the calculation by the computer. A quality index map of the area scanned revealed the low angle grain boundary in Figure 4.3a. The quality index map shows lighter contrast in the regions of the crystal which have higher quality and darker contrast where the indexed pattern quality is not as good. For the quality index map in Figure 4.3b the low angle grain boundary was of higher quality than the rest of the crystal. A comparison of the EBSD patterns from the high and lower quality patterns showed a definite shift when compared (Figure 4.4). This shift indicates a change in the direction of the crystal between the two regions. A directional map of the crystal along the radial direction revealed a misorientation of about 1-2° (Figure 4.3c). Since the sensitivity of OIM is only from about 0.5-1.5°, we are unable to determine the exact angle of this low angle grain boundary with this method.
Figure 4.1 a) EBSD pattern of YVO$_4$ b) indexed with high confidence near [110] pole.
Figure 4.2 OIM map of a region containing a low angle grain boundary, the area is (100) type.

Figure 4.3 a) Polarized light image of the low angle grain boundary imaged with OIM; b) quality index map, c) radial direction map showing directional misorientation. (a-grown 1.7%Nd)
Figure 4.4 Approximate misorientation in the EBSD pattern between the two regions.
CHAPTER FIVE
TRANSMISSION ELECTRON MICROSCOPY CHARACTERIZATION OF LOW ANGLE GRAIN BOUNDARIES

Low Angle Grain Boundaries

Low angle grain boundaries have been identified in YVO$_4$ crystals by several previous works and have been observed in this present study through a number of techniques. Despite mentions to the effect that they exist and are problematic, little work has been done in characterizing them in order to try to reduce their occurrence in crystal growth. Currently, the only way to avoid low angle grain boundaries is by growing crystals in the c-direction which has problems of its own including a higher propensity to fracture. The focus of this study is to characterize the low angle grain boundaries in YVO$_4$ using TEM with the hopes that a better understanding of them will lead to improved crystal growth techniques and improve overall crystal quality.

TEM is a valuable instrument for obtaining crystallographic information. The data collected from polarized light microscopy and OIM about the nature of low angle grain boundaries can be quantified to a much higher accuracy with TEM through measurement of dislocation spacing and analysis of Kikuchi bands. The ability to image dislocations in YVO$_4$ allows calculation of Burgers vectors and gives a better understanding of dislocation interactions in the crystal. Once the Burgers vector of the dislocation and the angle of misorientation are known, the energy required to form the low angle grain boundary can be calculated. The sample analyzed with TEM was an a-grown specimen doped with 1.7%Nd.
Low angle grain boundaries are formed by a tilt boundary between two crystals which is made up of a periodic array of edge dislocations. This is precisely what is observed with TEM (Figure 5.1). The sample was of excellent quality and the low angle grain boundary could be followed for almost 100µm. The low angle grain boundaries within this electron transparent area of the sample were composed of edge dislocations with an average spacing of about 250nm between dislocations. Using the dislocation spacing, \( D \), and the Burgers vector, \( b \), the misorientation angle can be determined by Equation 5.1.

\[
\tan \theta = \frac{b}{D} \tag{5.1}
\]

The Burgers vector and dislocation reactions in \( \text{YVO}_4 \) are discussed further in Appendix A. For unit translation dislocations of the type \( \frac{1}{2}[111] \) the magnitude of the Burgers vector is 0.594nm. With an average dislocation spacing of 250nm, the misorientation angle, \( \theta \), was calculated to be about 0.14°.

**Kikuchi Angle Measurement**

On-axis Kikuchi patterns taken from either side of the low angle grain boundary were compared and the misorientation angle of the direction cosines was determined using the technique described in Appendix B (Figure 5.2). Using this technique, the misorientation angle of the low angle grain boundary in Figure 5.1 was determined to be 0.14°. This is in excellent agreement with the calculations made from the average dislocation spacing. This calculation was made using the camera length of 103cm, which was calculated using Equation 2.6 with known \( r \) and \( d \).
With the misorientation angle known it is possible to calculate the energy required to form the low angle grain boundary. Using the Read and Shockley equation derived for a boundary composed of an array of dislocations, the energy, $E$, can be found (Equation 5.2) [1].

$$E = E_0 \left[ A - \ln \theta \right]$$  \hspace{1cm} [5.2]

$A$ is an integration constant ranging from about 0.345 to 0.5, and $E_0$ for an edge dislocation is found by Equation 5.3.

$$E_0 = \frac{Gb}{4\pi(1-v)}$$  \hspace{1cm} [5.3]

For YVO$_4$, the shear modulus, $G$, is 50GPa and Poisson’s ratio is 0.33. For a unit translation dislocation, this will give a value of 3528mJ/m$^2$ for the elastic strain energy, $E_0$. With a misorientation of 0.14º and a value of 0.4 for $A$, an energy of 1169mJ/m$^2$ is obtained. This energy is comparable to strain energies in metallic systems which are typically from 1000-2000mJ/m$^2$. To put these energies into perspective, typical values for an fcc metal might be 600-2000mJ/m$^2$ for surface energies and about 10-200mJ/m$^2$ for stacking fault energies. A high angle grain boundary and the bulk cleavage energy might be 2000-5000mJ/m$^2$ [2].
Figure 5.1 Edge dislocations forming a low angle tilt boundary.
Figure 5.2 Kikuchi Patterns taken from both sides of the boundary used to determine the misorientation angle.
High Resolution TEM

High resolution TEM of the dislocations from Figure 5.1 revealed an interesting dislocation structure. It was expected that the dark regions in Figure 5.1 were due to the strained lattice around a single dislocation, but upon closer examination, it was found that each dark area was composed of many dislocations (Figure 5.3). The dislocations can be seen in the region where the lattice is disrupted in Figure 5.3b. At some sites where the lattice strain does not interfere too badly, the extra half-plane of atoms can be seen. Since the sample was prepared from an α-grown crystal oriented along (010) the nearest zone axis was [010]. A fast Fourier transform (FFT) of the high resolution image can be seen in Figure 5.4a. The inverse FFT selecting the 200 and 002 reflections produced the lattice image in Figure 5.4. The extra half plane of atoms can be easily seen in the expanded inset in Figure 5.4. Examination of the dislocations revealed six of one sign and five of the opposite. The resulting Burgers vector for the whole area has a magnitude of only one lattice displacement. This was proven by performing Burgers circuits as described in Appendix A around each individual dislocation and the whole dislocation area. Individual dislocation circuits were performed on the high resolution image in order to verify its correlation with the IFFT image (Figure 5.5). The Burgers circuit around the whole region agreed with the summation of each individual Burgers circuit (Figure 5.6).

It was important to understand how the high resolution image of the atomic columns agreed with the YVO₄ lattice. The unit cell of YVO₄ can be seen in Figure 5.7. The large spheres on the corners are Y and the smaller spheres represent VO₄ tetrahedra. Since we know the specimen orientation from the sample preparation and the diffraction information we know that the atomic plane in the high resolution image should be (010). Using Desktop Microscopist, the projection of the YVO₄ unit cell along [010] was obtained (Figure 5.8). With initial
Figure 5.3 a) TEM bright field image of dislocations, b) similar dislocation region recorded with high resolution TEM.
Figure 5.4 a) FFT of the high resolution image and the resulting IFFT selecting the \( \{200\} \) reflections.
Figure 5.5 Burgers circuits performed around each dislocation.
Figure 5.6 Burgers circuit around the dislocation area showing a net Burgers vector of one translation.
Figure 5.7 YVO$_4$ unit cell; light spheres are Y, dark spheres are VO$_4$ tetrahedra. Source: D.E. Eakins, J.B. LeBret, M.G. Norton, and D.F. Bahr, J. Crystal Growth (in press).
Figure 5.8 [010] projection of YVO$_4$ unit cell.
examination of a single unit cell, it is not obvious how the image corresponds. When several are combined the arrangement seen in the high resolution images starts to take shape (Figure 5.9). The Y atom at \([\frac{a}{2} 0 \frac{3c}{4}]\) (M1) and the Y atom at \([00c]\) (F1) as well as \([\frac{a}{2} \frac{a}{2} \frac{c}{2}]\) (M2) and \([0 \frac{a}{2} \frac{c}{2}]\) (F2) combine to form what appears in the high resolution image to be a singular atomic column. A direct comparison of the proposed cell and the atomic positions can be seen in Figure 5.10.

Since the atomic positions and the Burgers vectors are known, it is possible to see exactly which dislocations are contributing to the low angle grain boundaries. From Figures 5.5 and 5.6 it is apparent that the Burgers vectors join the close atomic positions. This vector corresponds to \(b_3\) from Figure 5.7 which is the unit translation \(\frac{1}{2}[111]\) which can be seen in the [010] projection in Figure 5.11. This translation is the combination of partials \(b_1\) and \(b_2\) [2].
Figure 5.9 Multiple [010] YVO$_4$ cells showing the proposed atomic columns observed with HRTEM.
Figure 5.10 Correlation of the proposed [010] projection with the HRTEM image.
Figure 5.11 Burgers vector determined from Burgers circuits around dislocations corresponding to $\frac{1}{2}[111]$. 
Low Angle Grain Boundary Formation in YVO₄

Low angle grain boundaries are not unique to YVO₄; other single crystals such as rutile (TiO₂), LiNbO₃, LiTaO₃, YAlO₃, Al₂O₃, and GdVO₄ also exhibit this defect from growth [3-17]. Of particular interest are Nd:GdVO₄, rutile, and yttrium orthoaluminate perovskite (YAP) as they have properties very comparable to Nd:YVO₄ (Table 5.1) and are used in similar applications.

Table 5.1 Comparison of four similar CZ grown single crystal materials which exhibit low angle grain boundaries.

<table>
<thead>
<tr>
<th></th>
<th>Nd:YVO₄</th>
<th>Nd:GdVO₄</th>
<th>Nd:YAP (YALO₃)</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Structure</td>
<td>Tetragonal, I₄/mmm</td>
<td>Tetragonal, I₄/mmm</td>
<td>Orthorhombic, D₂h</td>
<td>Tetragonal, 4/mmm</td>
</tr>
<tr>
<td>Lattice Constants (nm)</td>
<td>a=0.71192, c=0.62898</td>
<td>a=0.72126, c=0.63483</td>
<td>a=0.5176, b=0.5307, c=0.7355</td>
<td>a=0.4593, c=0.2958</td>
</tr>
<tr>
<td>Melting Point (K)</td>
<td>2083</td>
<td>2053</td>
<td>2143</td>
<td>2113 +/- 10</td>
</tr>
<tr>
<td>Density g/cm³</td>
<td>4.22</td>
<td>5.47</td>
<td>5.35</td>
<td>4.24 - 4.28</td>
</tr>
<tr>
<td>Knoop Hardness</td>
<td>560-700</td>
<td>560</td>
<td>980</td>
<td>840-930</td>
</tr>
<tr>
<td>Thermal Expansion Coefficients 10⁻⁶/K</td>
<td>αₐ=2.2, α₇=8.4</td>
<td>αₐ=1.5, α₇=7.3</td>
<td>αₐ=9.5, α₈=4.3, α₇=10.8</td>
<td>αₐ = 9.19, α₇=7.14</td>
</tr>
<tr>
<td>Nd Concentration</td>
<td>0.2 - 10 at%</td>
<td>0.2 - 3 at%</td>
<td>1 at%</td>
<td>-</td>
</tr>
</tbody>
</table>

Dislocations are introduced in the crystal growth from thermal stresses and defects in the crystal or seed material. As discussed in Chapter 3, dislocation density increases with higher Nd concentrations due to increased distortion of the lattice [3,4]. Other factors that increase dislocation density were inclusions, crystal diameter, and growth rate [3,4]. Defects in the starting crystal are another source of dislocations and low angle grain boundary formation. Any
remaining crystallites floating on the surface of the melt may act as nucleation sites. Since this may lead to the formation of low angle grain boundaries, it is important to superheat the material 50-100°C above the melting temperature for at least one hour [3]. Thermal stresses due to anisotropy in thermal expansion coefficients have been shown to be a major source of stress during cooling [5,6]. Differential cooling between the crystal center and surface coupled with anisotropic contraction produces a radial hoop stress in the material which can activate slip systems at high temperatures which allows dislocation glide. The stress depends on the Burgers vector of the dislocation, the growth plane, and thermal expansion coefficients [7].

Certain positions are energetically favorable for dislocations to be in relative to other dislocations. For dislocations of the same sign, one such energetically favorable position is when the dislocations are stacked in a straight line. As discussed previously, this formation produces a tilt boundary. The process of low angle grain boundary formation through dislocation motion under stress at high temperatures in known as polygonization. Polygonization is known to be responsible for low angle grain boundary formation in YAP [6] and rutile [8-14]. It is likely that polygonization is the cause of low angle grain boundary formation in YVO₄ and GdVO₄.

The shear stress required to move a dislocation in a crystal at room temperature can be found with Equation 5.4:

$$\tau_p \approx \frac{2G}{1-\nu} e^{-\frac{2a}{b(1-\nu)|a|}}$$

[5.4]

where $a$ is the distance between slip planes and $b$ is the distance between atoms in the slip direction, typically $a/b \sim 1$ [18]. Using the values of $G$ and $\nu$ from equation 5.3, $\tau_p$ was found to be ~12.6MPa.

The critical resolved shear stress for dislocation movement on the $(\bar{11}2)\frac{1}{2}[\bar{1}11]$ system was calculated for stresses on [100] and [001]. The angles between the slip plane normal with the
stress directions and slip direction with the stress directions were calculated for tetragonal crystals using Equation 5.5 [19].

\[
\cos \Phi, \lambda = \frac{u_1u_2 + v_1v_2}{a^2} + \frac{w_1w_2}{c^2} \left( \frac{u_1^2 + v_1^2}{a^2} + \frac{w_1^2}{c^2} \right)^{1/2} \left( \frac{u_2^2 + v_2^2}{a^2} + \frac{w_2^2}{c^2} \right)^{1/2} \]  

[5.5]

Once the angles are calculated using Equation 5.5, the critical resolved shear stress, \( \tau_{crss} \), could be determined by Equation 5.6

\[
\tau_{crss} = \sigma \cos \lambda \cos \phi \]  

[5.6]

where \( \phi \) is the angle between the slip plane normal and the stress directions and \( \lambda \) is the angle between the slip direction and the stress directions. It was calculated that \( \tau_{(100)} = 0.207\sigma \) and \( \tau_{(001)} = 0.530\sigma \). With the value for \( \tau_p \) used as the critical shear stress, the applied stress, \( \sigma \), can be calculated to be 61.0MPa for \( \sigma_{(100)} \) and 23.8MPa for \( \sigma_{(001)} \). Since the thermal expansion coefficients are known it is possible to calculate the change in temperature for which the required stresses will be produced using Equation 5.7.

\[
\sigma = E\alpha\Delta T \]  

[5.7]

For YVO\(_4\), \( E=133\)GPa, and \( \alpha_{a,b}=2.2 \times 10^{-6}/K, \alpha_c=8.4 \times 10^{-6}/K \) [20], so \( \Delta T \) required to produce enough stress for dislocation movement is 21.3°C for [001] and 208.5°C along [100] and [010]. This stress, combined with the stress from lattice mismatch (due to Nd concentration and segregation) and increased ductility at high temperatures (due to thermal activation), is enough to overcome the energy barrier and cause slip along [001] for relatively small changes in temperature. Based on these calculations, it is apparent how the orientation of the crystal growth impacts the resulting dislocation mobility and thus the propensity to form low angle grain boundaries. This could explain why low angle grain boundaries are not observed in crystals.
grown on (001). Isotropic contraction along [100] and [010], combined with smaller stress, is not enough to overcome the energy required to move the dislocations into lower energy configurations, namely low angle grain boundaries [6]. Since dislocations perpendicular to (001) are locked, they are not able to relieve stress through low angle grain boundary formation; consequently c-grown crystals tend to crack.

If the movement of dislocations were hindered, it might be possible to stop the polygonization process in a-grown crystals. One such way to pin dislocations would be the addition of another material as with classic solid solution strengthening. If a material with a different ionic radius is added to the crystal, the lattice will experience a tensile stress for a larger ion and compressive stress for a smaller ion. The stresses effectively prohibit dislocation motion when they encounter the lattice near the solute ion. The ionic radii of $\text{Nd}^{+3}$ and $\text{Y}^{+3}$ are 0.108nm and 0.093nm, respectively. It has been observed that crystals with lower Nd concentrations exhibit a higher number of low angle grain boundaries, thus it is probable that the $\text{Nd}^{+3}$ ions contribute somewhat to dislocation pinning; a greater difference in radius would contribute to a further extent.

Solid solution strengthening has been shown to be an effective method to reduce low angle grain boundaries in rutile [8-11]. Rutile is grown with CZ, FZ, and Verneuil growth techniques. Like YVO$_4$, it exhibits low angle grain boundaries and black oxygen-deficient defects that cause scattering of light. For rutile, it has been shown that control of the O$_2$ atmosphere reduces low angle grain boundaries, but the instance of oxygen deficiencies becomes an issue. Alternately, it has been shown that addition of approximately 0.4at% ZrO$_2$, Sc$_2$O$_3$, and Al$_2$O$_3$ were effective in eliminating low angle grain boundaries due to dislocation pinning [8-11]. The ionic radius of $\text{Al}^{+3}$ is 0.051nm, Zr$^{+4}$ is 0.079nm and Sc$^{+3}$ is 0.081nm, compared to Ti$^{+4}$,
which is 0.068nm. Of the various additions, $\text{Al}_2\text{O}_3$ appeared to be the most effective in suppressing the formation of low angle grain boundaries. It is suggested that the addition of a small amount of a largely different ionic radius than $\text{Y}^{+3}$, such as $\text{Al}_2\text{O}_3$, might be an effective way to eliminate low angle grain boundaries in $\text{YVO}_4$. However, since dislocation movement producing low angle grain boundaries reduces stress in the crystal, problems might be encountered with crystal fracture as seen with c-grown $\text{YVO}_4$.

References


Scatter

Several defects are frequently observed in Nd: YVO$_4$ single crystals, all of which adversely affect the laser performance. Light scattering defects, low angle grain boundaries, color centers, and stoichiometric fluctuations have been problematic for homogeneous YVO$_4$ growth [1-6]. One defect of interest in this present study is colloquially known as ‘scatter’. Scatter is identified by a dense cloud or rings of defects, which cause crystal inhomogeneity. Hu et al [6] identified scatter as possibly due to segregation phases of the vanadate constituents Y$_2$O$_3$ and V$_2$O$_5$. Other possibilities include micro-voids and iridium particles from the growth crucible. Scatter can be easily observed through a polished face by illuminating the crystal with an intense light such as a fiber optic light or laser. The inhomogeneous scattering centers scatter the light and become highly visible.

Computed Tomography

Computed tomography (CT) is a valuable non-destructive technique for determining the internal homogeneity of materials. The sample is placed on an automated stage that rotates as the machine captures a series of x-rays with an amorphous silicon detector, which feeds the data directly to the computer. The computer then processes the x-ray images and creates a 3D reconstruction of the sample. Sectional views can be produced of the specimen in the XY, XZ and YZ planes. Any areas of lower density such as cracks, voids, and some precipitates will appear as darker contrast in the reconstruction of the sample. Areas of higher density will
produce lighter contrast. The high voltage x-ray capabilities allow analysis to be done on materials of large size or density. The high resolution micro-focus beam is particularly useful in precisely locating defects to within several microns in three dimensions.

For defects beyond the resolution capabilities of CT, other techniques are necessary. TEM was used to augment the CT study and, although it is necessarily a destructive technique, it provides valuable information that the CT technique can not, such as crystallographic, chemical, and orientation information.

The crystal analyzed in this study contained scatter in the center region which formed concentric circles of the scattering defects. Utilizing the CT information, density scans from a cut section of this crystal indicated regions of lower density in the central area of the crystal and higher density at the edges (Figure 1a). In CT, low density will appear as dark contrast and higher density will appear as light contrast. The dark regions of lower density (Figures 1b and 1c) directly corresponded to the scatter regions identified with the fiber optic light (Figure 1d). Due to the low resolution of the images from the reconstructed sections, an exact size could not be obtained for the scattering defects with CT, but transmitted light microscopy images showed that the micro-voids were approximately 10µm in diameter (Figure 2).

The densities of the constituent materials V$_2$O$_5$ and Y$_2$O$_3$ are 3.36 and 5.01g/cm$^3$ respectively; the density of Ir is 22.6g/cm$^3$. Based on the density of YVO$_4$ being 4.22g/cm$^3$, this indicates that the scatter centers are not micro-pieces of any of these materials. Thus, the most likely source of inhomogeneous scatter is micro-voids.

The TEM results of the scatter containing area occasionally indicated the presence of particles of foreign materials identified with EDS as Sn, Pb, Ta, Cu, and Fe (Figure 3a). These particles were all sub-micron (50-500nm) and therefore could not be detected with CT. Other
Figure 6.1 a) Density scan from a scatter containing crystal with regions of low density in the center of the crystal, abrupt change in the density scan is from a crack or pinhole in the sample. b,c) Computed tomography reconstructed slices of a scatter containing crystal; darker contrast indicates areas of lower density. The columnar feature in the center is an artifact from the reconstruction. d) Optical image of the section scanned in Figure 1c.
inclusions were observed which did not contain any additional elements (Figure 3b); it is possible that these were particles of segregation phases. Once again, these particles were below the resolution limit of the CT machine. Due to the large size of the voids and the chemical etch sample preparation, no features resembling micro-voids were observed in any of the TEM samples.

Figure 6.2 Transmitted light optical image of scattering sites. The voids denoted by arrows are in the focal plane of the image.
Figure 6.3 a) TEM image of metal containing contaminants (likely oxides) in a scatter sample, b,c) TEM images of a scatter sample with inclusions (denoted by arrows).
References

CHAPTER SEVEN

CONCLUSIONS

Defects introduced in the growth of YVO$_4$ are problematic for maintaining the high laser efficiency. Light scattering defects and low angle grain boundaries have been characterized with the hopes that a better understanding of them will lead to improved crystal growth techniques and improve overall crystal quality. Some adjustments to the Czochralski method and alternate growth techniques have been discussed for reducing the occurrence of scattering defects. Low angle grain boundaries remain an elusive defect, as there has yet to be a good way to eliminate them in the growth process of large crystals.

Dislocations are introduced in the growing crystal due to thermal hoop stress, lattice mismatch from inclusions and dopant material, and imperfections in the seed crystal. The anisotropic thermal expansion coefficient in YVO$_4$ produces a larger stress along [001] in crystals grown in the a-axis. At high temperatures, thermal stresses from anisotropic compression during cooling provide adequate stress for dislocation motion. It is energetically favorable for dislocations to be in certain positions relative to other dislocations. For dislocations of the same sign, one such energetically favorable position is when the dislocations are stacked in a line; this formation produces a low angle tilt boundary. Low angle grain boundaries are not as likely to form in c-grown crystals due to the isotropic compression during cooling.

Transmission electron microscopy, as well as polarized light microscopy, and orientation imaging microscopy have been utilized to characterize low angle tilt boundaries in YVO$_4$. Etching of a-grown crystals has revealed that the dislocations are primarily located at low angle
grain boundaries. Dislocation etch pits on (001) were evenly distributed on the face of the crystal; microcracking was also observed in c-grown crystals. Dislocation etch pits were observed to be rectangular on (100) and (010), and square on (001); this is consistent with etch pits observed in studies of similar materials. A correlation of Nd concentration with dislocation density has been observed and is also consistent with studies of similar materials. Polarized light microscopy has shown that low angle grain boundaries with a higher degree of misorientation refract light to a greater extent and can thus be seen with visual inspection of the crystal. OIM and TEM were used to determine the misorientation of a low angle grain boundary to be 0.14°. High resolution TEM showed that the dislocation Burgers vector is \( \frac{1}{2} [111] \), which is consistent with our previous study.

Selection of defect free single crystal seed material is crucial for eliminating low angle grain boundaries. It is also important that the polycrystalline material be completely melted so that no unmelted crystallites remain which could nucleate low angle grain boundaries. This can be accomplished by superheating the melt by 50-100º above the melting temperature. The crystal diameter has been shown to influence the number of dislocations and low angle grain boundaries. The rate of change in the crystal diameter from the seed area to the final crystal diameter has been shown to influence low angle grain boundary formation with slower rates reducing the number of low angle grain boundaries. It has been shown that the formation energy of the low angle grain boundary analyzed is 1169 mJ/m².

If the movement of dislocations were hindered, it might be possible to stop the polygonization process. One such way to pin dislocations would be the addition of another material through solid solution strengthening. It is suggested that the addition of a small amount of a largely different ionic radius than \( \text{Y}^{+3} \), such as \( \text{Al}^{+3} \), might be an effective way to eliminate
low angle grain boundaries in YVO$_4$. It is likely that the Nd$^{+3}$ ions contribute somewhat to dislocation pinning, but a greater difference in radius would contribute to a larger extent. This method has been shown to be successful in other crystal systems with properties similar to YVO$_4$.

The appearance of low angle grain boundaries in a-grown crystals and microcracking in c-grown crystals is related. Crystals grown in the a-direction also tend not to crack as easily as those grown in the c-direction since dislocation slip and low angle grain boundary formation allows stress relief. Dislocations generated in c-growth have lower mobility and less stress due to isotropic contraction and cannot easily form energetically preferable low angle grain boundaries. Crystals grown in the c-direction have a higher degree of internal stresses and no accessible stress relief mechanism. Thus stresses locked in crystals grown in the c direction cause microcracking.

High resolution computed tomography has been shown to be a valuable instrument in characterizing the defect known as scatter in Nd: YVO$_4$ single crystals. CT is useful in that it is a non-destructive technique which can give a relatively rapid diagnosis of the nature of inhomogeneities in a material. The results of the computed tomography study indicate that the scatter region is an area of significantly lower density than YVO$_4$. This result rules out micro-pieces of iridium and the segregation phases of V$_2$O$_5$ and Y$_2$O$_3$ as the main scattering centers. The optically observable scatter in the crystal was thus determined to be micro-voids which were approximately 10µm in diameter. Metal contaminants and other features were also found in scatter regions using TEM. Although these particles were not the major scattering features, they likely contribute to the overall scattering effect.
APPENDIX
Determining the Burgers vector of a dislocation is necessary for obtaining important information about the crystal. The Burgers vector of a dislocation can be calculated from diffraction information or by examination of the atomic columns in a high resolution TEM image of an edge dislocation.

As discussed in Chapter 2, when tilted to a zone axis position, dislocations in the crystal will be at maximum contrast when the Burgers vector is parallel to the diffraction vector. When the sample is tilted to an orientation where the dislocations appear at minimum contrast with the rest of the material is will be in a two beam condition and the Burgers vector will be perpendicular to the diffraction vector. By taking a series of diffraction patterns corresponding to both image conditions the Burgers vector of the dislocations which change contrast can be calculated. When the two beam diffraction pattern is indexed the diffraction vector from the central spot to the highly reflecting spot can be measured. The Burgers vector will be orthogonal to the so that \( g \cdot b = 0 \). For the dislocations observed in YVO\(_4\), \( g \) was found to be \([11\bar{2}]\). The possible Burgers vectors which satisfy the invisibility criterion are: \([021]\), \([0\bar{2}1]\), \([201]\), \([\bar{2}01]\), \([\bar{1}10]\), \([\bar{1}10]\), \([111]\), \([\bar{1}11]\). Examination of the YVO\(_4\) unit cell indicated that \( \frac{1}{4}[021] \) and \( \frac{1}{2}[111] \) were the likely partial and full dislocations [1].

Another method to determine Burgers vectors of dislocations is by performing Burgers circuits around a dislocation core in a high resolution image. Edge dislocations in a high resolution image will appear as an extra half-plane of atoms in the lattice as seen in Figure A1.1. The two dislocations in this IFFT image are opposite in sign since one is facing right and the
other left. A Burgers circuit can be performed around the dislocation with the following steps.

An atomic column is chosen as the starting point and a circuit is drawn around the dislocation in a clockwise manner. Each step of the Burgers circuit should be a lattice translation and the same number of steps should be taken all the way around the crystal. In a perfect crystal, the end point will be the same as the staring point, but around a dislocation, the circuit will end at a different point (Figure A1.2). The vector between the end point and the starting point is the dislocation Burgers vector [2]. If the crystal planes and directions are known in the high resolution image, the Burgers vector can be easily identified. If a Burgers circuit is performed around two dislocations of opposite sign, the Burgers vectors will cancel each other out and the resulting circuit will be as if the crystal were perfect as with the green circuit in Figure A1.2. In ideal conditions, both techniques can be used to verify the correct Burger’s vector.
Figure A1.1 IFFT lattice image showing an extra half-planes of atoms causing edge dislocations opposite in sign.
Figure A1.2 Burgers circuits performed around two edge dislocations opposite in sign (yellow and blue) and the circuit around both (green). The Burgers vectors are the red arrows which connect the ending and starting points.

References


A method for determining misorientation between bicrystals was described briefly in Chapter 5. Calculating the misorientation from Kikuchi patterns yields much more accurate results than orientation information obtained from electron diffraction patterns. Traditionally this is accomplished by taking a pattern in an off axis position so the intersections of Kikuchi bands can be indexed and compared with the beam direction. The distances between the center of the pattern and the poles where the bands intersect are measured and used to yield angles which correspond to the angles between the $hkl$ planes which form the bands. When a sample is in an on-axis orientation, there might not be any intersecting planes to give poles from which to make this type of measurement as was in the case with our measurement. In this instance, a modified technique was necessary to calculate the angle between the two regions in the crystal. If the two crystals were only translated with respect to each other with no rotation difference it would be possible to measure this translation and convert it to an angular distance. For mixed rotation and translation in the crystal boundary more information is needed to determine the angle. This can be calculated from the normal vectors of the reflected bands with the beam direction at the pattern center. If the camera length is known the normal of this plane can be calculated with the following method:

The pattern center must be found for both Kikuchi patterns, this was found to be at the center of the images. Identical points must be found on each pattern from the same reflection. For this calculation, the $\left( \begin{array}{c} 3 \\ 0 \\ 1 \end{array} \right)$ and $\left( \begin{array}{c} 3 \\ 0 \\ 1 \end{array} \right)$ band was selected along the $hkl$ projection where it
intersected with a higher order multiple of \( \begin{pmatrix} 1 & 0 & 3 \end{pmatrix} \) and \( \begin{pmatrix} 1 & 0 & 3 \end{pmatrix} \) lines. The distance X and Y from the pattern center, O, was measured for each Kikuchi pattern at points P and R. The camera length was determined to be 103cm by diffraction information. The distance in cm for each pattern is given in Table B1.1. The direction normal to the plane is calculated from Equation B1.1:

\[
\hat{n}_1 = \frac{\overrightarrow{OP} \times \overrightarrow{OR}}{||\overrightarrow{OP} \times \overrightarrow{OR}||}
\]  
[B1.1]

The angle between the plane normals can then be calculated from Equation B1.2:

\[
\cos \theta = \hat{n}_1 \cdot \hat{n}_2
\]  
[B1.2]

Table A1.1. Distance in mm of the points P, and R with the pattern center, O.

<table>
<thead>
<tr>
<th>Pattern 3850</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
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<tr>
<td>OP</td>
<td>2.49</td>
<td>-1.36</td>
<td>103</td>
</tr>
<tr>
<td>OR</td>
<td>-2.67</td>
<td>1.6</td>
<td>103</td>
</tr>
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</table>

Pattern 3847

<table>
<thead>
<tr>
<th>OP</th>
<th>2.57</th>
<th>-1.29</th>
<th>103</th>
</tr>
</thead>
<tbody>
<tr>
<td>OR</td>
<td>-2.58</td>
<td>1.68</td>
<td>103</td>
</tr>
</tbody>
</table>
Figure B1.1. Kikuchi patterns taken from both sides of a low angle grain boundary.
Figure B1.2 Determination of the misorientation if the pattern difference is only translated and not rotated.
Figure B1.3 Determination of the orthogonal vectors to the planes