IMPROVED CZOCHRALSKI GROWTH AND ACTIVATOR EFFICIENCY OF CERIUM DOPED YTTRIUM ALUMINUM GARNET BY DEFECT ENGINEERING

By

DREW THOMAS HAVEN

A dissertation submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

WASHINGTON STATE UNIVERSITY
Materials Science and Engineering Program

May 2013

© Copyright by DREW THOMAS HAVEN, 2013 All Rights Reserved
To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation/thesis of DREW THOMAS HAVEN find it satisfactory and recommend that it be accepted.

______________________________
Kelvin G. Lynn, Ph.D., Chair

______________________________
Matthew D. McCluskey, Ph.D.

______________________________
Gary S. Collins, Ph.D.
ACKNOWLEDGEMENT

First and foremost, I would like to express my deepest appreciation to my advisor, Dr. Kelvin G. Lynn, who continually conveyed a strong sense of passion in both research and learning. Without his ambition, guidance, and continual sharing of wisdom and knowledge, this dissertation would not have been possible.

My sincere thanks go out to my graduate committee members, Dr. Matt D. McCluskey and Dr. Gary S. Collins for their time in advising and evaluating my research.

I am equally grateful to all the members of the CMR team, both student and employee, whose hard work has been invaluable to the completion and publication of this research.

Last but not least, many thanks to Dr. Marc H. Weber, Dr. Denys Solodovnikov, Joshah Jennings, Peter Dickens, Jeremy Kingma, Ihar Viarenich, Romit Dhar, and Jalal Nawash for the help with equipment training, performing many of the measurements, and numerous discussions regarding the research.

Finally, in fear of forgetting to mention anyone that has been an important figure, I would like to thank everyone that has had a helping hand in the completion of this research.

This research was sponsored by: The II-VI Foundation and Domestic Nuclear Detection Office, Award No. 2009-DN-077-ARI029-02
IMPROVED CZOCHRALSKI GROWTH AND ACTIVATOR EFFICIENCY OF CERIUM DOPED YTTRIUM ALUMINUM GARNET BY DEFECT ENGINEERING

Abstract

by Drew Thomas Haven, Ph.D.
Washington State University
May 2013

Chair: Kelvin G. Lynn

The past several decades have seen a genuine surge in development of scintillator materials for use in a multitude of applications ranging from high energy physics to medical imaging. Despite the rapid materials discovery that has been undertaken in the search for better scintillators, a host of defects still limit scintillator performance in many promising materials. Thus the key to tapping into a scintillators full potential lies in understanding and modifying their defect structure through a process known as defect engineering.

One such promising visible light scintillator is cerium doped yttrium aluminum garnet (Ce:YAG). Despite characteristics that make Ce:YAG an excellent yellow phosphor that see it commonly used in fluorescent lights and while light LEDs, performance hindering defects severely limited its potential as a bulk scintillator, a critical defect being that of UV defect luminescence. By successfully building a new Czochralski (CZ) furnace, samples could be grown with careful control over growth conditions to study and reduce these defects. All
samples were grown in similar conditions by the CZ method with a (111) oriented undoped YAG seed.

Several original approaches were developed in this study to reduce defects or mitigate their influence. The first method of solving the problem relied on recognizing that what many in the past identified as visible scintillation light was in fact UV defect luminescence. By using multiple photodetectors it was demonstrated that when higher cerium doping levels are involved in Ce:YAG, luminescence is not decreased due to self-absorption as previously thought, but rather UV defect emission is quenched in favor of visible emission.

Once established, new avenues of research became available. Another study demonstrates Ce:YAG grown by the Czochralski method in alumina rich conditions is an effective method for reducing the number of UV producing yttrium antisite defects. This culminated in record energy resolution of Ce:YAG in a bulk sample.

A final study investigated Ce:YAG grown in a rhenium crucible, both to investigate the future of high temperature oxide crystal growth, and to investigate potential benefits of Ce:YAG growth outside of an iridium crucible. The study showed significant promise in both of these categories.
TABLE OF CONTENTS

ACKNOWLEDGEMENT ........................................................................................................ iii

ABSTRACT ........................................................................................................................ iv

LIST OF TABLES ................................................................................................................. x

LIST OF FIGURES ............................................................................................................... xi

CHAPTER 1 SCINTILLATION BACKGROUND ..................................................................... 1

1.1 Scintillator Principles and Processes ............................................................................ 2

1.1.1 Photoelectric Absorption ......................................................................................... 4

1.1.2 Compton Scattering ................................................................................................. 6

1.1.3 Pair Production ......................................................................................................... 8

1.2 Scintillation – Energy Resolution and Photodetectors ...................................................... 12

1.2.1 The Photo Multiplier Tube ...................................................................................... 17

1.2.2 The Photodiode ....................................................................................................... 21

1.2.3 The Avalanche Photodiode ...................................................................................... 23

1.3 The Ideal Scintillator - Introduction of Ce:YAG .............................................................. 24

1.4 Crystallographic Defects within Scintillators ................................................................. 26

1.4.1 Absorption ............................................................................................................... 29

1.4.2 Photoluminescence ................................................................................................. 30

1.4.3 Lifetime .................................................................................................................. 33
1.4.4 Thermoluminescence

1.4.5 X-Ray Diffraction

References

CHAPTER 2 CONSTRUCTION OF CMR’S CZOCHRALSKI FURNACE

2.1 A Brief History of Crystal Growth and the Czochralski Method

2.2 Build of CMR’s CZ Furnace

2.2.1 The Power Supply

2.2.2 The Cooling System

2.2.3 The Furnace Chamber and CZ Assembly

2.2.4 The Insulation

2.2.5 The Software and PID Controller

References

CHAPTER 3 HIGH CERIUM IN CE:YAG

3.1 Background and Motivation

3.2 Crystal Growth and Preparation

3.3 Scintillation and Energy Resolution

3.4 Photoluminescence

3.5 Lifetime Measurement

3.6 Summary

References
LIST OF TABLES

Table 1.1: Comparison between YAG and two commercially available materials. .................. 26
Table 2.1: Ziegler-Nichols method of PID tuning. ................................................................. 66
Table 3.1: Energy resolutions, photoluminescence, and lifetime measurements of Ce:YAG. ... 83
Table 4.1: Characteristics of the as grown samples. The largest improvements can be seen with
the 10.0 at% alumina rich melt grown sample........................................................................ 102
Table 4.2: Energy resolution comparison of the 2.0 at.% Ce, 10.0 at.% alumina rich sample... 104
LIST OF FIGURES

Figure 1.1: A primary electron and hole relax by creating secondary e-h pairs. These secondary e-h pairs thermalize near the conduction and valence bands and find their way to luminescence centers. Lastly, a scintillation photon is emitted. (From [23] with modification) ........................... 3

Figure 1.2: Plot displaying the relationship between the three dominant gamma interaction effects. .................................................................................................................................................................................. 4

Figure 1.3: The photoelectric absorption process. An incoming photon (left) is completely absorbed by the atom and a photoelectron is emitted. ........................................................................................................... 5

Figure 1.4: The compton scattering process. An incoming photon (left) is deflected by an atom's electron. The product is a recoil electron and a less energetic scattered photon ......................... 6

Figure 1.5: Plot of gamma scattering angle based on energy. (1) .......................................................................................... 7

Figure 1.6: Plot of interaction probabilities, and their total in sodium iodide. Of interest to note is the K edge, which is caused when incoming photons no longer have the energy needed to eject a K shell electron, and absorption can only occur in less tightly bound shells. M and L edges also exist at lower energies. ................................................................................................................................................... 9

Figure 1.7: Absorption pathways in sodium iodide. (1) .................................................................................................................. 10

Figure 1.8: Representation of a differential pulse height spectrum. ......................................................................................... 13

Figure 1.9: Origin of the Compton continuum. .......................................................................................................................... 14

Figure 1.10: Measure of energy resolution based on the full energy peak. ................................................................. 14

Figure 1.11: Displaying the importance of energy resolution. Better energy resolution means much more resolving power. (1) .......................................................................................................................... 15

Figure 1.12: Many common scintillators plotted along with theoretical maximums based on light yield. .................................................................................................................................................................. 17
Figure 1.13: Diagram of a general PMT. The top part contains the photocathode and electron optics, and the lower portion contains the electron multiplier. .......................................................... 18
Figure 1.14: Spec sheet of spectral characteristics of several Photonis PMT’s. ............................... 20
Figure 1.15: Spectral sensitivity of a common photodiode, a Hamamatsu 3590-18. ......................... 22
Figure 1.16: Three types of trapping defects as seen in a crystal with sodium chloride structure. ........................................................................................................................................ 27
Figure 1.17: Several traps and defects as seen in the band gap. ...................................................... 28
Figure 1.18: The absorption spectrum of doped and undoped Ce:YAG. An absorption peak at 255nm is clearly evident in the undoped YAG and can contribute to the broad absorption in the CZ grown Ce:YAG. ............................................................................................................. 30
Figure 1.19: Output emission from Ce:YAG when pumped with 266 nm laser light. The bulk of the emission is centered at 550 nm and the defect emission in the UV is relatively small. ........ 32
Figure 1.20: The emission and excitation spectrum of Ce:YAG. Figure (a) is emission under gamma excitation, where the UV is now a significant portion of the emission spectrum. Figure (b) is the emission (dotted) and excitation (solid) under 345nm excitation. ......................... 32
Figure 1.21: Small UV photopeak seen around channel 360 in an undoped YAG sample grown at CMR........................................................................................................................................ 33
Figure 1.22: Lifetime of Ce:YAG when excited with 450 nm and 178 nm light. 450nm excitation results in a single exponential fit of 67 ns. When pumping at 178 nm (near the band edge) there are two decays present. One short (85 ns Ce) and one long (320 nm UV). ............ 34
Figure 1.23: Lifetime of Ce:YAG when excited with a gamma source. The longer UV lifetime is much more evident........................................................................................................................................ 35
Figure 1.24: Diagram of TL electron trapping (a) and thermal release (b). (20) ............................ 36
Figure 1.25: Example of two glow curves from a TL measurement. Curve I is representative of first order decay kinetics, where re-trapping is negligible. Curve II is nearly a perfect Gaussian, and represents the case where re-trapping is not negligible. (19)

Figure 1.26: Approximation of a TL curve for analysis. Here, \( \omega \) is the FWHM of the peak. (19)

Figure 1.27: Table of values for calculating trap depth energies based off peak characteristics. The variable \( (a) \) is related to the frequency factor, typically with values of \(-2 \leq a \leq 2\). (19)

Figure 1.28: Figure of Bragg's Law derivation. (22)

Figure 1.29: XRD of YAP, another yttrium aluminum crystal structure.

Figure 2.1: CZ grown crystals controlled by visual observations and operator controlled temperature changes. (5)

Figure 2.2: Schematic of a common direct weight CZ pulling assembly.

Figure 2.3: Modern perovskite crystals grown by direct weighing with a PID controller. (5)

Figure 2.4: Modern Er YAG Laser Crystal. (6)

Figure 2.5: Front Panel of the Pillar MK-25CG power supply. The left gauges indicate cooling water input and output pressure. The power supply also has settings for manual and external control.

Figure 2.6: The 200 Gallon reservoir used in cooling the furnace. The large blue unit in the back is the industrial chiller. The two vertical copper pipes supply the power supply and furnace chamber respectively.

Figure 2.7: Radiators in the main reservoir. Return water from the furnace and power supply is on the left. Due to the elevated temperatures of the water during crystal growths, water needed
to be changed every several months with fresh DI water. The above picture was taken just prior to cleaning.

Figure 2.8: The furnace chamber as seen from the front. Black tubes provide the plumbing for cooling water.

Figure 2.9: Atmosphere port for the furnace chamber. To the right is the valve leading to the mechanical vacuum pump. The far 90 degree valve dumps chamber gasses to a vent. Two pressure gauges are situated above.

Figure 2.10: The scale used to weight the crystal in real time.

Figure 2.11: Diagram of the inner insulation cylinder. Diagram by Peter Dickens.

Figure 2.12: Diagram of complete insulation build. Diagram by Peter Dickens.

Figure 2.13: National instruments controller bank for reading and controlling the power supply.

Figure 2.14: Screenshot of the LabVIEW software showing power supply and chamber data. Gas flows, oxygen %, power supply and chamber water temperatures, and power readings are all recorded by region. Input control is on its own tab to the left, and pulling and rotation rates are always visible.

Figure 2.15: Screenshot of the growth data. Target weight plot and real weight plot are recorded, as well as optical pyrometer readings. PID settings are also contained in the growth section of the software, as well as the on/off switch to the PID furnace control.

Figure 2.16: The first crystal grown using the CZ furnace and proportional method of furnace control. It is an undoped YAG boule, where the large ridges are from the slow response of the proportional system.
Figure 2.17: The third crystal grown using the proportinal system with minor modifications. The ridges are smaller but still very much present. ................................................................. 65

Figure 2.18: First CZ growth using the PID controller................................................................. 67

Figure 2.19: CZ Growth after some minor tuning ........................................................................... 68

Figure 2.20: Slice from the a Ce:YAG boule showing optical quality. Dimensions are roughly 32 mm diameter by 30 mm high................................................................. 68

Figure 3.1: Cut and polished samples. From left to right, 0.25, 0.5, 2.0, and 4.0 at.% Ce concentrations. The rightmost sample displays some structural defects, suggesting poor crystal quality beyond 4.0 at.% Ce. Some tiny edge chips can be seen, which were caused by cutting. 75

Figure 3.2: Absorbance of the 460 nm peak vs. cerium concentration in the melt, indicating a rough linear relationship between the as grown samples. The inset displays the visible light absorption of cerium in the four samples.................................................................................... 76

Figure 3.3: Energy resolution as seen on a Photonis XP2018B® PMT and a S3590-18 PD. The PD improves dramatically with higher Ce concentrations as opposed to the PMT. Light output and resolution at 4.0 at.% Ce were comparable to 2.0 at.% Ce, despite macroscopic doping induced defects.................................................................................................................................. 77

Figure 3.4: $^{137}$Cs spectrums for 2.0% Ce:YAG on a PD and PMT, and CdWO$_4$ on a PD all with 2 μs shaping times. The peak on the right side is the pulser used in PD noise reduction. Highly doped Ce:YAG grown at CMR displays a narrower photopeak and thus better resolution on a PD compared to a PMT. Commercially prepared CdWO$_4$ displays a much smaller photopeak. ...... 79

Figure 3.5: Emission curve from 190 nm excitation, normalized to the visible emission peak. UV emission is significantly quenched as Ce concentrations increase. The PL setup is not calibrated below 285 nm, resulting in a sharp drop below this wavelength........................................... 80
Figure 3.6: Lifetime results from 0.25 at.% and 4.0 at.% doping with 137Cs excitation. The highly doped sample can nearly be described by a single, fast decay whereas the lightly doped sample has a significant slow decay component.

Figure 4.1: From left to right, samples from 10.0 at.% yttria rich, 5.0 at.% yttria rich, on stoichiometry, 5.0 at.% alumina rich, and 10.0 at.% alumina rich melts. Some cracks were caused by cutting and polishing.

Figure 4.2: Absorption of each sample. 1.0 at.% Ce displays good consistency among all of the samples, minimizing concerns of Ce concentration variability on further measurements.

Figure 4.3: XRD spectrum from the region immediately surrounding our samples, with peaks indicating a pure YAG phase. The excellent consistency between each sample indicates minimal, if any, contamination from secondary phases.

Figure 4.4: XRD of the crucible remains from the 10 at.% yttria and alumina rich runs. Different peaks correspond to differing amounts of remaining oxides.

Figure 4.5: Phase diagram of the alumina yttria system showing YAG, YAP and YAM. YAM is yttrium aluminum monoclinic. Source: (15).

Figure 4.6: PL from 190 nm excitation. Barring a small bump in the 10.0 at.% alumina rich sample, and the 380 nm peak due to a doubling reflection of the 190 nm excitation source, the peak centered around 300 nm decreases in a near linear fashion as alumina concentration is increased. Wavelengths below 285 nm are not calibrated, resulting in a sharp drop below this wavelength.

Figure 4.7: Drop in UV defect emission at 300 nm, when pumped with 190 nm excitation source.
Figure 4.8: Lifetime data displaying a significant and consistent decrease in the fast decay component of Ce:YAG as the melt shifts toward alumina rich. It should be noted that decay times were measured using a PMT due to electronic timing constraints. This produces accurate decay times, but we acknowledge a PMT’s spectral sensitivity will introduce a certain degree of error into intensity values due to its spectral sensitivity. ................................................................. 97

Figure 4.9: Glow curve of each sample from 500 – 650 nm. The spectrometer exhibited some drift, and although small, is evident at above 300°C. ................................................................. 98

Figure 4.10: TL sum from 200 - 400 nm. No signal can be seen above background noise. There is a small deviation from a zero average due to spectrometer drift in some samples. The small drift can be seen at higher temperatures in Figure 4.9 as well................................................................. 99

Figure 4.11: Scintillation results of all samples on a PMT and PD. Alumina rich samples show excellent consistency between the PMT and PD, however the trend breaks down with the yttria rich. Adding more Ce takes further advantage of an alumina rich melt. ................................................ 101

Figure 4.12: Lifetimes along with the 2.0 at.% Ce:YAG sample grown from a 10.0 at.% alumina rich melt. Increased Ce further improves the lifetimes seen earlier. ........................................ 103

Figure 4.13: PMT, PD, and PMT results from the 2.0 at.% Ce, 10% alumina rich melt grown sample. The PD photopake is visibly narrower than the PMT’s, even with the inherent noise of a Si-PIN PD. The APD photopake is even narrower as noise is reduced. Such results indicate a significant gain in visible emission from alumina rich growth conditions. ................................. 104

Figure 5.1: Diagram of the inner insulation cylinder................................................................. 114

Figure 5.2: From left to right: Ir grown sample in 100 ppm O₂ balanced N₂, Re grown sample in Ar, Re grown sample in CO/Ar. Each sample displays very consistent optical quality. The
foggy region in the rightmost thin sample is due to saw damage that could not be polished away.

Figure 5.3: Absorption of each sample compared to an Ir grown sample. The Re grown CO/Ar and Ir grown sample display remarkable similarity in their as grown characteristics.

Figure 5.4: PL from rhenium and iridium grown samples. Again, there is excellent consistency.
This dissertation is dedicated to my family and to my girlfriend Amber for all of their support through my education and this research.
Before getting into specifics about scintillation, its history, the use or development of scintillators, or heavy scientific defect studies, it seems necessary to have a proper definition of scintillation upon which the remainder of the paper is dependent. In short, scintillation is the conversion of ionizing radiation into visible (or near visible) emission. Various materials, be they gas, liquid, or solid of various sizes can make effective scintillators. The process is also, as we shall see later, closely tied to that of phosphors where incoming light is converted to light of a lesser energy upon interaction with the phosphor. The key difference is that phosphors are not designed for ionizing radiation, which can change material behavior significantly. With that said, a deeper discussion of scintillation can be carried out.

As described by Glenn Knoll, (1) “The detection of ionizing radiation by the scintillation light produced in certain materials is one of the oldest techniques on record.” In fact, the use of a scintillator to detect radiation goes back over a century, when CaWO₄ was used with an X-Ray screen as far back as 1895. (2; 3) Soon, ZnS was used by Crooks to detect alpha particles, and eventually by Rutherford which led to the discovery of the atomic nucleus in 1911. (2; 3) With the discovery of the photomultiplier tube in the 1940’s, and later the photodiode, a wave of new scintillation materials discovery was undertaken.

Eventually scintillators would serve in applications from simple detection to spectroscopy of various radiations, in fields including high energy physics, tomography, astrophysics, well logging, and many others. (2) To this day it remains one of the most useful and widely used methods available, with medical imaging alone requiring over 175 metric tons of scintillator
material annually as of 2002. (3) Detector setups at labs such as CERN can require 10 metric tons of scintillator material or more. (3) These materials may be organic or inorganic in nature, and may be in solid, liquid, or gas phase depending on the material, (4) though solid tends to be the more common material. The following research focuses on cerium doped yttrium aluminum garnet, so the remainder of this paper will focus on inorganic solids exclusively.

1.1 Scintillator Principles and Processes

The scintillation process can be thought of as occurring through a few stages. Piotr A. Rodnyi (2) labels these stages as such:

1. Absorption of the ionizing radiation and creation of primary electrons and holes.

2. Relaxation of the primary electrons and holes, i.e., production of numerous secondary electrons, holes, photons, plasmons, and other electronic excitations.

3. Thermalization of the low-energy secondary electrons (holes) resulting in a number of e-h pairs with energy roughly equal to the band gap energy $E_g$.

4. Energy transfer from the e-h pairs to the luminescent centers and their excitation.

5. Emission from the luminescence centers.

The first three steps can be considered part of the conversion process, the fourth step can be considered transport, and the last step is the emission of scintillation light which completes the process. Although a relatively simple process, each step can be quite involved and there are a multitude of defects that can hinder this progression. The three main steps can be visualized in Figure 1.1 below.
Figure 1.1: A primary electron and hole relax by creating secondary e-h pairs. These secondary e-h pairs thermalize near the conduction and valence bands and find their way to luminescence centers. Lastly, a scintillation photon is emitted. (From [23] with modification)

The first step of the conversion process starts with the interaction of radiation in matter, when energy is absorbed by the medium. This absorption, and the nature of the interaction, depends on the type of radiation incident on the material; be it charged particle (alpha, beta, etc), neutral particle (neutron), or photon (X-Ray, gamma). The remainder of the chapter will focus on photons and gamma and X-Ray radiation specifically, since this is the intended use for the research material.

As discussed in Glen Knoll’s book, *Radiation Detection and Measurement*, (1) though “a large number of possible interaction mechanisms are known for gamma rays [and X-Rays] in matter, only three major types play an important role in radiation measurements: photoelectric absorption, Compton scattering, and pair production. All of these processes lead to the partial or
complete transfer of the gamma ray photon energy to electron energy.” In addition, the energy of the photon and the effective atomic Z of the material will determine which interaction method dominates. Figure 1.2 below shows this graphically, where we can see that in general the photoelectric effect dominates under low energies, Compton scattering under medium energies, and pair production at higher energies.

Figure 1.2: Plot displaying the relationship between the three dominant gamma interaction effects. (1)

Despite the array of scintillator materials, where the behavior of various scintillators can behave quite differently, the basics of scintillation work similarly among all materials.

1.1.1 Photoelectric Absorption

Under the photoelectric process, an incoming photon completely disappears within the absorbing atom. (1; 2) The probability of photoelectric absorption within the atom depends on the atomic number (Z) and the energy of the incoming photon (Eγ) as follows:

\[ \tau \approx \text{constant} \times \frac{Z^n}{E_{\gamma}^{3.5}} \]
In the above equation, \( n \) varies from 4-5 depending on the energy of the incoming gamma ray.

(1) For compounds containing more than one kind of atom, the “effective Z” \((Z_{\text{eff}})\) must be calculated. The \( Z_{\text{eff}} \) calculation depends on the atomic number and weight percent \((W_i)\) of each atom in the compound, and as can be seen below is not a simple addition of the atomic numbers.

\[
Z_{\text{eff}} = \sqrt[4]{\sum W_i Z_i^4}
\]

Upon being absorbed, a photoelectron is ejected from a bound shell within the atom (Figure 1.3) with the following energy:

\[
E_{e^-} = h\nu - E_b
\]

Figure 1.3: The photoelectric absorption process. An incoming photon (left) is completely absorbed by the atom and a photoelectron is emitted. (1)

Where \( E_{e^-} \) is the energy of the ejected electron, \( h\nu \) is the energy of the incoming photon, and \( E_b \) is the binding energy of the photoelectron within its shell of the atom. (1; 2) It is important to note that this is an interaction process with the atom, and it cannot occur with a free electron. For a gamma ray or X-Ray of adequate energy the photoelectron typically originates from the K shell (most tightly bound) of the atom. However, absorption can also occur in less tightly bound shells such as L and M shells.

In the case of an ejected photoelectron, a hole and thus ionized atom is created in the solid.

\[ A + h\nu \rightarrow A^+ + e \]
The ionized atom then relaxes to a non-ionized state quite quickly, usually on the order of \(10^{-13}\) to \(10^{-15}\) seconds. (2) The relaxation can occur radiatively or nonradiatively, though the probability of nonradiative decay is usually much greater than radiative decay. (2) In radiative relaxation, the ionized atom can either fill the vacancy though capture of a free electron in the solid, or through shuffling of electrons in other shells of the atom. Either process will result in the emission of a secondary X-Ray photon, which can then undergo another photoelectric absorption. In the nonradiative process, the atom can relax through the emission of an Auger electron.

1.1.2 Compton Scattering

If the incoming gamma or X-Ray quanta are of a sufficiently high energy, then the Compton scattering effect begins to dominate. This effect is also the most common interaction mechanism for typical radioisotope sources. (1)

Under Compton scattering, an X-Ray or gamma ray is deflected by an electron within a particular material. Upon deflection, the photon transfers some of its energy to the electron which is known as the recoil electron. Figure 1.4 below illustrates this process.

![Compton Scattering Diagram](image)

Figure 1.4: The Compton scattering process. An incoming photon (left) is deflected by an atom's electron. The product is a recoil electron and a less energetic scattered photon. (1)
The deflection angle $\theta$ is measured with respect to the original direction, and can take any value from 0 to $\pi$. As a result, the energy transferred to the recoil electron can also vary from a large portion of the total energy to zero. (1) The equation below shows the scattered photon energy after Compton scattering at an angle $\theta$.

$$h\nu' = \frac{h\nu}{1 + \frac{h\nu}{m_0c^2(1 - \cos\theta)}}$$

Although all scattering angles are allowed, there is some energy dependence to the most probable angles. As can be seen in Figure 1.5 below, as the energy of the incident photon increases, forward scattering becomes predominant.

![Figure 1.5: Plot of gamma scattering angle based on energy. (1)](image)
1.1.3 Pair Production

Pair production can become possible once the photon energy exceeds twice the rest mass energy of an electron of 1.02 MeV. (1; 2) However, at gamma energies around this threshold, generally within a few hundred keV, the probability of pair production is small. As gamma energies and atomic mass increase, pair production becomes more prominent. (1; 2) Investigating the following equation, one can see that probability increases roughly with the square of the absorber atomic number for a given gamma energy (2):

$$\sigma_{\text{pair}} \propto Z^2 \ln(E_\gamma)$$

Under pair production, an incoming gamma ray interacts with the coulomb field of a nucleus. It subsequently disappears and is replaced by an electron-positron pair. If the energy of the photon is above 1.02 MeV, the excess energy is transferred into kinetic energy shared by the electron and positron. The ejected electron behaves in much the same way as a photoelectron in the photoelectric effect, or recoil electron in Compton scattering. The positron on the other hand will quickly annihilate with an electron in the absorbing medium, producing two 511 keV gamma rays which may then undergo Compton scattering or photoelectric absorption.

The absorption coefficient versus energy for each of these processes can be seen in Figure 1.6, as well as the total absorption.
Figure 1.6: Plot of interaction probabilities, and their total in sodium iodide. Of interest to note is the K edge, which is caused when incoming photons no longer have the energy needed to eject a K shell electron, and absorption can only occur in less tightly bound shells. M and L edges also exist at lower energies. (1)

Thus, the total probability of an X-Ray or gamma ray being absorbed is simply the sum of photoelectric, Compton, and pair production probabilities.

The initial photoelectric absorption, Compton scatter, or pair production event completes the primary conversion process. Each results in the production of an energetic electron and in
some cases secondary photons. (1; 2) At this point the relaxation process begins, where the still energetic particles lose energy through creating more secondary electron-hole pairs and photons.

Secondary photons can in turn be absorbed or scattered, in the same manner as the primary conversion processes. Fast electrons though, can lose their energy through several mechanisms. One is through inelastic scattering with phonons that produce no additional electron-hole pairs or photons. Another is through the fast electron moving through the crystal solid itself. This produces collective oscillations known as plasmons behind the path of the electron that can then decay into electron-hole pairs. The last method is through interaction with atoms in the solid by the following method:

\[ A + e \rightarrow A^+ + 2e \]

Both processes will continue to produce electron-hole pairs until the photons and electrons generated have insufficient energy to continue the process further. (2) As an example of how complex the process can become in just one compound, consider Figure 1.7, which shows gamma absorption and subsequent relaxation pathways in sodium iodide.

Figure 1.7: Absorption pathways in sodium iodide. (1)
Once the electrons and holes generated have insufficient energy to further ionize atoms, the thermalization stage begins. Here, electrons and holes move to the bottom of the conduction band and top of the valence band respectively, where the final energy of the electron-hole pairs becomes equal to the band gap energy $E_g$. (1; 2) See Figure 1.1 above. Although this process is still quite fast by everyday timescales, it is slower by a few orders of magnitude than the relaxation process, usually taking on the order of $10^{-11}$ to $10^{-12}$ seconds. (2) As a result, it can be safely said that thermalization occurs after relaxation and they do not occur concurrently. (2)

It is important to note that the total number of electron-hole pairs created in the whole conversion process ($N_{eh}$) is proportional to the incoming photon energy ($E_\gamma$). (2)

$$N_{eh} \propto \frac{E_\gamma}{\xi_{eh}}$$

Where $\xi_{eh}$ is the average energy needed to create a thermalized electron-hole pair. The fact that the number of electron-hole pairs created, and hence the amount of light generated per scintillation event, is proportional to the incoming energy is incredibly important. The significance of this will become apparent in the next section.

Upon the electron-hole pairs reaching the band gap energy, the transport process begins. During transport, thermalized electron-hole pairs find their way to luminescence centers. The order of capture can either be electronic recombination (hole capture then electron capture) or hole recombination (electron capture then hole capture), though electronic recombination is more common. So long as both electron and hole find their way to a luminescence center, the recombination process typically results in scintillation emission. For any scintillator to be effective though, its emission light must be picked up by a photodetector to be turned into and electrical signal.
1.2 Scintillation – Energy Resolution and Photodetectors

The function of any photodetector is to turn a light signal or pulse, into measureable electrical signal. Without the ability to turn the light pulses from a scintillator into a reliable electrical signal, the majority of applications that use scintillators would not be possible. The two most common devices that achieve this goal are the photomultiplier tube (PMT) and the photodiode (PD), although a third called an avalanche photodiode (APD) is beginning to see more use.

There are several modes of operation for these devices including current mode, mean square voltage mode, and pulse mode. Pulse mode is the most common operation, followed by current mode and finally mean square voltage. Both current mode and mean square voltage mode are used when the event rate of incoming radiation is too high to make pulse mode practical, which is why they are not as common. (1) However, the mode used for the research in this paper is pulse mode, and therefore will be the only operation mode discussed further.

The goal of pulse mode operation is to record every scintillation event encountered by the detector, including the amplitude and timing of individual events. Pulse mode is the only mode of operation capable of doing so. (1) The amplitude of the signal received at the end of the measurement is proportional to the total charge generated in the detector. Since the total charge generated in the detector is directly related to the energy of the incoming radiation, the pulse method can be used to obtain energy information about individual quantum of radiation, and allows for radiation spectroscopy. (1)

The output of a detector operated in pulse mode is typically a series of pulses over time, where each pulse carries energy information about the particular interaction that just occurred. A common method of analysis is to record the distributions of amplitude as they arrive from the
detector. This is known as a differential pulse height spectrum, and an example spectrum can be seen in Figure 1.8 below. (1; 2)

![Differential pulse height spectrum](image)

Figure 1.8: Representation of a differential pulse height spectrum. (1)

The x-axis is the amplitude of the received pulse, and the y-axis is the differential number of pulses observed (dN) within a certain pulse amplitude (dH), thus dN/dH. (1) If the pulse amplitude is within a certain value, it will register as a count at the corresponding amplitude. Over time, a series of pulses will give rise to a spectrum which can then be used in radiation spectroscopy.

The pulse on the right is called the full energy peak, “photopeak,” corresponding to full gamma or X-Ray energy deposition within the crystal. The counts on the left are known as the Compton continuum, and the drop in the Compton continuum that produces the valley is known as the Compton edge. The continuum is produced when gamma quanta Compton scatter but then escape the scintillation material before depositing the rest of their energy through photoelectric absorption. Since any scattering angle is allowed, the Compton continuum can take values from near zero, to a scatter of 180 degrees as seen in Figure 1.9 below. (1)
The full energy peak, also known as the photopeak, is what allows for radiation spectroscopy. A better scintillator will give rise to a narrower full energy peak. The measure of this property is known as energy resolution (typically expressed as a percentage) and is seen in Figure 1.10 below. (1; 2)

\[ R = \frac{FWHM}{H_0} \]

Figure 1.9: Origin of the Compton continuum. (1)

Figure 1.10: Measure of energy resolution based on the full energy peak. (1)
FWHM is the width of the pulse at half the pulse height (Full Width at Half Max), and $H_0$ is the centroid of the pulse. A better energy resolution results in a smaller percentage value and is desired due to better resolving power. This becomes important in radiation spectroscopy when multiple energies are incident on a scintillator detector. The best illustration of this is seen in Figure 1.11, where a good scintillator has two easily resolved photopeaks, and the poor scintillators have peaks that merge together. The good scintillator could easily resolve more energy, whereas the poor scintillator can hardly resolve two.

Figure 1.11: Displaying the importance of energy resolution. Better energy resolution means much more resolving power. (1)

Broadening in the photopeak occurs from fluctuation in the signal for a given energy deposition. If there were no fluctuation at all, the photopeak would be a line instead of a Gaussian. The source of this fluctuation has several origins, including drift in the instrumentation, noise in the photodetector, inhomogeneity within the scintillator that giving rise to changes in light output for the same energy deposition, and even statistical noise from the discrete nature of the measurement. (1) The first problem is of least consequence, and the
second has to do with the photo detectors used rather than the scintillator itself, though this can have a large impact depending on the scintillator used in the measurement. The last two are of the most importance and are a part of scintillator design.

In scintillator design, as used in radiation spectroscopy, design goals are twofold. One is to reduce the inconsistencies (relating to homogeneity) within the scintillator material so as to make the light yield per keV of deposited energy more consistent and thus narrowing the observed photopeak. YAlO$_3$:Ce is a good example of better energy resolution achieved through defects being eliminated from the system seen in Figure 1.12. (1)

The other and perhaps more important is to increase the light yield of the scintillator. This addresses the problem of the scintillation measurement being discrete in nature, where the number of charge carriers generated will fluctuate even under perfect conditions. The fluctuation induced broadening from this process is known as Poisson broadening, (1) as it follows a statistical Poisson process. It also presents a limiting energy resolution on any scintillator which is based solely on light output, such that:

$$\text{Resolution Limit} = \frac{2.35}{\sqrt{N}}$$

Here N is the number of charge carriers created, which is directly proportional to how many photons will be emitted by the scintillator. For a given scintillator material, increased light yield generally means better energy resolution. Between different materials though, one material having a better light yield than another does not mean that it necessarily has a better energy resolution, as seen in Figure 1.12. (5) For reference, the best performing 10x10x10 mm cerium doped yttrium aluminum garnet usually fall around 9-10% energy resolution.
Figure 1.12: Many common scintillators plotted along with theoretical maxima based on light yield. (1)

Here it can be seen that CaI$_2$:Eu, NaI:Tl, and CsI:Tl all have approximately the same energy resolution despite large differences in yield. Still, there is a general trend of better resolutions with increased light yield. Of course, the detectors used can also play a role in energy resolution.

1.2.1 The Photo Multiplier Tube

The most common of photodetectors in use is the PMT, which has been around since the 1940’s. Its longevity is due to its outstanding ability to amplify a small light pulse into a useable current signal without adding significant noise, were oftentimes, light pulses from scintillators can consist of a few hundred photons or less. (1) Additionally, PMT’s can generate this pulse on a timescale of 20-50 ns, and the conversion from photon to electron happens quickly enough that the time information about the scintillation pulse is retained in the generated electron pulse. (1) These properties serve to make PMT’s incredibly useful.
The basics of a PMT consist of two parts, though the geometry of competing PMT’s can vary greatly depending on the design metrics. Below is a basic PMT design displaying these two main components, which are enclosed in vacuum.

Figure 1.13: Diagram of a general PMT. The top part contains the photocathode and electron optics, and the lower portion contains the electron multiplier. (1)

The goal of the photocathode is to turn photons from the scintillation pulse into electrons through photoemission. For the PMT to properly function, the photocathode needs to be able to absorb scintillation photons, transport excited electrons to the materials surface, and allow their
escape from the surface. For the photocathode to be effective it needs to balance each parameter, as working to maximize one means sacrificing another. This is due to several conditions.

First, a photon can only be absorbed if its energy is greater than the band gap energy of the material. For blue light, each photon has energy of around 3 eV. For green light, this is closer to 2.25 eV, and it continues to drop as the light moves toward the infrared. Second, an electron moving to the surface will lose energy through electron-electron collisions. Finally, the electron needs to have enough energy at the surface to overcome the photocathode material work function and escape from the surface. For a metal this is around 3-4 eV or greater, but can decrease to 1.5 eV for certain semiconductors. (1) However, as the work function decreases, the chance for electrons to be thermally ejected from the photocathode increases, giving rise to noise concerns.

Aside from energy concerns are thickness concerns. The thicker the photocathode, the more probable a photon will be absorbed by the material rather than pass through. However, the electron needs to find its way to the surface with sufficient energy to be ejected. The rate of energy loss for an electron while transporting is quite high in most materials. Even in the best materials an electron generated with a typical scintillation photon usually cannot travel more than 25 nm before having insufficient energy to escape the materials surface. (1) This puts an upper limit on the thickness of the photocathode.

One can now see the constraints when designing a photocathode. These can be summarized as follows:

A) Photocathode thickness is limited by the requirement that electrons transport to the photocathode surface with greater than the work function energy of the photocathode. Generally, this is 25 nm or less.

B) A thin photocathode of 25 nm or less is semitransparent. Thus, photocathode material should be tailored to the target scintillation emission to maximize absorption.

C) Due to a minimum work function of around 1.5 eV, all photocathodes regardless of photocathode material stop functioning around the red to infrared. As the work
function of the photocathode decreases to include this part of the spectrum, noise from thermally generated electrons emitted from the photocathode tends to increase.

D) Taken together, photocathodes are most efficient in the near ultraviolet and blue regime. As emission moves toward the red, the photocathode will become less efficient.

As an example of how these constrains can limit real world PMT’s, see Figure 1.14 below which covers several PMT’s manufactured by Photonis.

![Figure 1.14: Photo from specification sheet of spectral characteristics of several Photonis PMT's.](image)

To convert the above into quantum efficiency (QE), one can use the following equation, where it can be seen that efficiency falls off rapidly as photon wavelength moves toward the red.

\[
QE = \frac{(Ske \ in \ \frac{A}{W}) \times 1240}{\lambda}
\]

Typical maximum values for a PMT are a quantum efficiency of 25-30% in the blue to near UV region. As the wavelength moves to green and yellow the value falls to 5-11%. Finally a QE of less than 1% is observed in the near infrared.
Once a photoelectron is ejected from the photocathode, it must find its way to the electron multiplier structure which is what gives the PMT its great properties. This is achieved through electron optics and a bias voltage that is often on the order of several hundred volts. The bias voltage also serves to accelerate the ejected electrons from their energies of 1 eV or less to higher energies around several hundred eV. When the accelerated electrons find their way to the first dynode, as seen in Figure 1.13, numerous secondary electrons are generated. This process repeats in an avalanching process from dynode to dynode generating more electrons (electrical signal), at each stage. Clearly, the overall gain can change based on the operating voltage of the PMT, but an average PMT can turn a typical scintillation pulse into $10^7 - 10^{10}$ electrons by the time the signal reaches the anode.

Despite the excellent gain and low noise characteristics of the PMT, they still have several significant drawbacks. First, the PMT itself needs to be large enough to house the electron optics and electron multiplier structure, limiting its minimum size. Second, PMT’s require significant voltages for proper operation. Typical voltages of 1000 – 2000 V limit their portability. Last is that the design constraints above limit quantum efficiencies to below 30%, which limits the measurement precision of the device through Poisson broadening.

1.2.2 The Photodiode

Photodiodes (PD’s) have since been created as an alternative to PMT’s which overcome several of their issues. They are small, often with a thickness of only a 1-2mm, and require very little power which allows for battery operation. Perhaps most importantly, generated electrons do not need to escape the surface as in a PMT, therefore they do not need to be as thin. This greatly improves quantum efficiency through the entire range of blue to the near
infrared. As Figure 1.15 shows, the spectral characteristics of a Hammamatsu 3590-18 photodiode are significantly above that of the PMT’s seen earlier.

![Spectral sensitivity of a common photodiode, from a Hammatsu 3590-18 specification sheet.](image)

Notice there that the photosensitivity is presented in A/W rather than mA/W as with the PMT in Figure 1.14. Converting this into quantum efficiency shows that the entire region from 400-950 nm is greater than 85% efficient, with a maximum QE of over 90% in some regions. Such high quantum efficiency means a PD detects significantly more light than PMT’s, and therefore have a chance at higher energy resolutions since it will significantly increase the Poisson limit. (1)

The reason for only having a chance at better operation, despite detecting at least 3-4 times more light, is that photodiodes have some considerable drawbacks. The most significant of these is that standard photodiodes do not have gain and therefore cannot amplify the signal. The
current generated in the PD by the photoelectric effect is what is seen later on by the amplifier, meaning noise sources become a serious concern.

One source of noise is inherent to the material used, where semiconductors with a band gap around 1-2 eV or less will begin producing electrons thermally around room temperature. The signal created is known as dark current. Other sources of noise stem from PD properties themselves which change based on thickness and active area, limiting the useful size of PDs to the realm of 1-2 cm$^3$. (1) In all cases, the noise mixes with the scintillation signal produced. Therefore PDs are most effective when large amounts of light are generated in a short time by the scintillator, thus maximizing the signal-to-noise ratio. (1)

1.2.3 The Avalanche Photodiode

The last photodetector that will be discussed is the avalanche photodiode (APD). The goal of the APD is to take the QE of a standard PD, but produce signal gain as in PMT’s. Generally QE’s are not quite as good as standard PD’s, gains are not as high as with PMT’s, and they are much more prone to breakdown. Even so, under the right conditions the resulting output can be quite effective.

There are many different configurations for APD’s, but in short they work on the principle of operating a PD at an elevated voltage to create an avalanche effect. Operating in this manner, the initial charge carriers created are accelerated through the APD to the point where electronic collisions have sufficient energy to generate additional electron-hole pairs. These can then be accelerated to generate additional charge carriers and so on, with gains of several hundred observed in many APD’s by the time the signal is collected. Such gain can pull the signal from the scintillator above the randomly generated noise of the photodiode, therefore
significantly cleaning up the output signal while at the same time taking advantage of increased quantum efficiency.

Unfortunately, the method of achieving gain is achieved by operating the APD near its breakdown voltage. The gain is also very sensitive to temperature, with roughly a 2% change per degree Celsius. (1) Thus small changes in temperature can induce variability in the measurement, as well as drive the APD into the breakdown region from a temperature change of only a few degrees Celsius. This can be partially controlled through good stabilization schemes, but APD’s should be used in areas of small temperature fluctuations to maximize their advantages and limit factors of noise.

Despite several sources of photodetection available, no one detector can compensate for a poor scintillator. Therefore significant time, resources, and engineering go into crafting better and better scintillators for various applications.

1.3 The Ideal Scintillator - Introduction of Ce:YAG

The effectiveness of a scintillator material is quite often application specific and dependent on the end users’ needs. P. Lecoq et al. (6) defines the major distinguishing parameters of inorganic scintillators as density and/or effective Z, response time, light yield (light yield per unit time as opposed to absolute), particles identification, production volume, parameters stability under ionizing radiation, and durability of operational parameters. E. Zych et al (7) defines the three most important properties as density and/or effective Z, light yield, and response time.

Other real world application requirements can include scintillation light wavelengths matched to a particular photodetector, inertness to moisture, mechanical ruggedness, and use of
non-toxic materials. Crystal growth and implementation should be simple, cost effective, and have high yield.

The ideal scintillator would have high density, high effective Z, high light yield, and fast decay times. Additionally, it would be capable of cost effective production. Unfortunately, no material has been discovered that is a leader in multiple parameters, let alone all of them. Because of this, the drive to find a scintillator that combines as many characteristics as possible remains strong. One such material known as Yttrium Aluminum Garnet (Y₃Al₅O₁₂ or YAG) has promise to be a good contender in many of these categories.

YAG single crystals have been grown since the 1960’s for various purposes including applications in phosphors, lasers, and scintillators. This is in part due to YAG’s good mechanical, chemical, and thermal stability. Additionally, to create a fast scintillator, lanthanide ions have become increasingly used as a dopant in scintillator materials. They utilize a 5d to 4f transition, have respected decay times in the realm of 10-100ns, and have an expected light yield of more than 20,000 photons per MeV.

In YAG, the lanthanide ion Ce³⁺ produces yellow light with a decay time on the order of 70 ns and produces roughly 17,000 photons per MeV. The typical dopant is CeO₂ (Ce⁴⁺), which becomes Ce³⁺ in YAG. Other advantages of Ce:YAG include very low background counts, a reasonable density, it is non-hygroscopic and incredibly rugged, and can be cost effectively mass produced by the CZ method. Table 1.1 demonstrates some of the properties of YAG compared to other commercially available and commonly used materials.
As can be seen in the table, YAG has a reasonable density, high hardness and melting point, and is much faster than commonly used materials. It is thus shows tremendous potential as a scintillator compared to the most common materials in use today.

However, the above information begs the question, “If Ce:YAG has so many great properties, why is it not a commonly used scintillator today?” The answer to that question is defects. Defects are the largest drawback to Ce:YAG thus far, and tremendously limit the reproducibility of manufacturing, light output, and resolution of Ce:YAG. The remainder of the paper, and the direction of this research, will be to focus on the defects within Ce:YAG and their eventual removal from an industrially grown sample. Before diving into that though, a quick background on many problematic defects within scintillators, including Ce:YAG should be covered.

1.4 Crystallographic Defects within Scintillators

Crystallographic defects play the largest role in hindering the scintillation process, by trapping electrons and holes by slowing or stopping their transfer to luminescence centers. Since average carrier migration can be as much as 100 to 1000 nm, and atomic spacing is on the order of angstroms, lattice defects and impurities can have a large effect on the scintillation process. (2) Figure 1.16 shows some common defects in ionic crystals with the sodium iodide structure.
Figure 1.16: Three types of trapping defects as seen in a crystal with sodium chloride structure. (2)

Vacancies are a very common trap in many crystal systems. In the above figure, an anion (negative ion) vacancy is known as an F center which is a very effective electron trap. Another defect, an anion interstitial known as an H center, can result in a trapped hole. The duration of trapping depends on the depth of the trap within the band gap, as trapped carriers can be thermally released. A carrier in a shallow trap for example may have enough thermal energy at room temperature to be released in a few microseconds and then take part in the scintillation process. Deeper traps, on the other hand, may trap a carrier nearly indefinitely and completely remove charge carriers from the scintillation process. Analysis techniques investigating this problem will be covered later.

Electrons and holes can also create a localization effect within the lattice, bringing about a process known as self-trapping, or a $V_k$ center. In self-trapping, a hole at one anion creates a polarizing effect with a neighboring anion based on the charge difference, effectively trapping the hole between the two anions. Impurities and antisites create potential traps and defect
scintillation as well. Figure 1.17 shows many of the traps within the band gap of a scintillator that can detrimentally effect scintillation, where $h\nu_A$ represents the desired emission.

Figure 1.17: Several traps and defects as seen in the band gap. (2)

The goal of a good scintillator is to minimize these defects, so that charge carriers effectively make their way to desired luminescence centers as quickly as possible. Many of these problems, though not all, are present in Ce:YAG and have limited its use as a scintillator for decades.

For cerium doping in YAG, which is most commonly used as a phosphor in white light LEDs and far less for scintillators, the 5d to 4f transition results in a broad band yellow light centered at 550 nm. (9; 10) This process works very well in powders used as phosphors, but quantum efficiencies have been shown to drop with increasing crystal size as well as increasing energy of the exciting photons. In particular, it has been demonstrated that luminescence efficiency drops significantly in melt grown single crystals of Ce:YAG when the sample size is
greater than 1mm thick. (8; 14) The suggested reasons for the drop in luminescence have been intrinsic defects in the form of oxygen vacancies, aluminum vacancies, impurities, and $\text{Y}^{3+}$ antisites. (15; 16)

Without proper analysis techniques though, none of the aforementioned defects could be discovered, nor what role they play in the scintillation process. This includes optical techniques such as absorption, photoluminescence (PL), Thermoluminescence (TL), or Lifetime as well as non-optical techniques such as X-Ray Diffraction (XRD). The following will cover many of these defects within YAG, and the most common analysis techniques for their identification.

1.4.1 Absorption

Absorption measurements, as used in optical physics, measure the degree to which particular photon energies are absorbed by a sample. The process occurs from either the excitation of an electron from one atomic orbital to a higher orbital, or from the excitation of an electron from the valence band to the conduction band. In the case of a valence to conduction transition, the absorbance will be a line corresponding to the band edge. The measured quantity is known as absorbance, and is based on a log scale as in the following equation.

$$A_\lambda = -\log_{10} \left( \frac{I_{\text{out}}}{I_{\text{in}}} \right)$$

In the above equation, $A$ is the absorbance, and $I$ is the intensity of light measured. It is used not only to measure the amount of dopant in a material, but also any parasitic absorption from either defects or impurities within the sample. As seen in Figure 1.18 below, the YAG sample not only shows the characteristic 3 peaks related to Ce doping, at 227, 340, and 458 nm, but also defect absorption at 255 nm.
Figure 1.18: The absorption spectrum of doped and undoped Ce:YAG. An absorption peak at 255nm is clearly evident in the undoped YAG and can contribute to the broad absorption in the CZ grown Ce:YAG. (16)

Many papers suggest this is due to an oxygen-iron transfer within YAG due to small iron impurities within the crystal. (16) Though defect absorption is not necessarily bad in its own right, it is a parasitic form of absorption that can reabsorb scintillation light. This can either remove it from the total output or delay the overall emission as photons are absorbed and reemitted.

Ultimately, absorption measurements are a quick and very effective way to compare dopant concentration between samples, investigate dopant segregation in the boule (which is typically below 1 in Ce:YAG due to the large Ce atom), as well as check for certain defects.

1.4.2 Photoluminescence

$Y^{3+}$ antisites (Y on Al site) have been shown to be one of the most detrimental defects in Ce:YAG and contribute to peaks in YAG emission in the UV. One of the analysis techniques
that are capable of displaying the optical properties of this defect is PL. In short, PL is the process of recording the output emission of a sample when excited by light of sufficient energy to create electronic excitations. When exciting at a specific wavelength, and recording emission, this is known as excitation mode. Many PL setups are also capable of recording what wavelengths excites a particular emission as well, and is known as emission mode.

The advantages of the technique are that it is non-destructive, it is a very sensitive measure of electronic states, and it is fast enough that time resolved studies can be carried out on the right equipment. However, the material tested needs to have good optical properties to see beyond the surface, and PL only sees optically active phenomena.

Figure 1.19 and Figure 1.20 display PL and emission under gamma excitation of Ce:YAG respectively. Notice the 300 nm UV defect emission present in both, where PL is capable of displaying properties to come under gamma excitation with a deep enough excitation wavelength. Most notable of the below figures, is that as the excitation source becomes more energetic, the amount of UV emission increases significantly. This is consistent with research conducted previously by our group, which found under excitation with a gamma source significant emission in Ce:YAG is in the UV.
Figure 1.19: Output emission from Ce:YAG when pumped with 266 nm laser light. The bulk of the emission is centered at 550 nm and the defect emission in the UV is relatively small. (24)

Figure 1.20: The emission and excitation spectrum of Ce:YAG. Figure (a) is emission under gamma excitation, where the UV is now a significant portion of the emission spectrum. Figure (b) is the emission (dotted) and excitation (solid) under 345nm excitation. (14)
This defect luminescence does not just present itself in photoluminescence measurements though. As seen in Figure 1.21 below, an undoped sample grown in our furnace displays a clear photopeak on a PMT (UV sensitive), but not on a PD (visible sensitive). This can have a significant impact on scintillation performance, as any light being output in the UV is lost to the desired Ce luminescence centers.

![Graph showing UV photopeak around channel 360 in an undoped YAG sample grown at CMR.](image)

Figure 1.21: Small UV photopeak seen around channel 360 in an undoped YAG sample grown at CMR.

### 1.4.3 Lifetime

As a consequence of these defects within YAG, the emission lifetimes are affected. This is primarily from changes in decay kinetics, where lifetime investigates the decay time of the sample from a single gamma event. An ideal scintillator would have only one decay time representing one optical carrier recombination pathway, with quicker decay times being preferable. Certain defects though, can introduce 2 or more lifetimes within a sample.
Take a look at the following figures for Ce:YAG. Under excitation with 450 nm light, which pumps only the 460 nm Ce absorption peak, just one lifetime is observed with a decay time of 67 ns. (7) However, the decay can no longer be described by one exponential when exciting at the band edge. As Figure 1.22 shows, the decay is best described by a short and long lifetime with the short lifetime describing the Ce emission and the longer lifetime describing UV or UV related emission. (7)

Figure 1.22: Lifetime of Ce:YAG when excited with 450 nm and 178 nm light. 450nm excitation results in a single exponential fit of 67 ns. When pumping at 178 nm (near the band edge) there are two decays present. One short (85 ns Ce) and one long (320 nm UV). (7)

Figure 1.23 demonstrates a longer UV lifetime becomes much more prevalent when the crystal is excited with a gamma source. (7)
Longer lifetimes also become more dominant with less Ce doping. (17; 18) Longer lifetimes under gamma excitation as seen in Figure 1.23 are consistent with increased UV emission under gamma excitation as seen in Figure 1.20.

1.4.4 Thermoluminescence

Thermoluminescence (TL) is a way of identifying crystallographic defects known as carrier traps, which were discussed briefly at the beginning of section 1.4. As stated by Chen et al, (19) “In a given crystal, the study of TL is actually the study of imperfections in the lattice. In principle, a perfect crystal with no impurities or defects is not expected to exhibit any TL.” Such trapping is problematic as it keeps charge carriers from effectively reaching luminescence centers and potentially hurting scintillation performance.

Information about the defects can be obtained from the measurement, such as a rough quantification of defect concentrations through integration of the counts, as well as trapping
energies of the particular trapping sites. For all TL, the rate of release of trapped carriers is proportional to the Boltzmann factor.

\[
\exp\left(\frac{-E_t}{k_B T}\right)
\]

Where \(k_B\) is the Boltzmann constant, \(E_t\) is the activation energy (in eV) of the carrier trap, and \(T\) is the temperature in Kelvin.

TL measurement operates as follows. A cooled sample (room temperature or below) is excited with UV light to fill available traps with charge carriers. After a set amount of time, the excitation is stopped. The sample is then heated, typically at a constant rate (\(dT/dt = \beta\)), and the trapped charge carriers are released upon reaching a sufficient temperature as seen in Figure 1.24 below.

Figure 1.24: Diagram of TL electron trapping (a) and thermal release (b). (20)
The resulting emission is integrated over a desired wavelength range, the data (presented as intensity as a function of temperature) is known as a glow curve, which can be used to extract information such as the activation energy of the trap. An example of two such curves can be seen below in Figure 1.25.

Figure 1.25: Example of two glow curves from a TL measurement. Curve I is representative of first order decay kinetics, where re-trapping is negligible. Curve II is nearly a perfect Gaussian, and represents the case where re-trapping is not negligible. (19)

Curve I represent first order kinetics, where re-trapping upon heating is negligible and thus the curve falls off rapidly after reaching its maximum. Curve II represents second order kinetics, where re-trapping upon heating is not negligible and the resulting curve is a near Gaussian. Identification of decay kinetics is essential for proper analysis of TL data, where our samples display a near perfect Gaussian, indicating second order kinetics.
To obtain the activation energies of the various traps, one can approximate a curve as a triangle, with the maximum at the peak max, and the sides running through the FWHM points. This can be seen in Figure 1.26.

Figure 1.26: Approximation of a TL curve for analysis. Here, ω is the FWHM of the peak. (19)

Under this approximation, one can make the assumption that

\[ \delta I_m = \beta n_m \]

Where \( \delta \) is defined in Figure 1.26, \( I_m \) is the peak intensity, \( \beta \) is the heating rate, and \( n_m \) is the number of charge carriers at the maximum. The above equation can also be expressed as a ratio equal to one. In practice, the number is approximately one, and has been found experimentally to be \( 0.92 \pm 0.8\% \) under a wide range of conditions. This is an astonishingly small variation, and lends confidence to the approximation model proposed. Ultimately, activation energies of carrier traps can be found as follows in Figure 1.27, some of which was obtained experimentally.
Figure 1.27: Table of values for calculating trap depth energies based off peak characteristics. The variable (a) is related to the frequency factor, typically with values of $-2 \leq a \leq 2$. (19)

The values are then used in the following general equation which can be tailored to the peak shape method of choice, where $E_a$ is the trapping depth energy and depends on the parameters of Figure 1.27:

$$E_a = c_a \left( \frac{k_B T_m^2}{a} \right) - b_a (k_B T_m)$$

The above value (a) in Figure 1.27 is determined by the relation of the frequency factor to temperature ($s \propto T^a$). For a frequency factor with minimal fluctuation with temperature, (a) can be taken to be zero, and we arrive at the following equation for the activation energy of a second order trap, which was also used in (21).

$$E_t = 3.54 \left( \frac{k_B T_m^2}{FWHM} \right) - 2k_B T_m$$

1.4.5 **X-Ray Diffraction**

X-Ray Diffraction (XRD) is a method of testing for phase purity in a material. A common form used is powder XRD analysis, where the sample to be tested is ground into a fine powder (thus randomly orienting the material for all possible reflection planes) and placed on a flat surface for measurement. An X-Ray beam is then made incident upon the material, as the sample is slowly rotated by an angle $\Theta$. The method at work is Bragg’s Law, where incoming X-Rays are reflected off a crystal lattice planes as seen below in Figure 1.28.
From this, it can be seen that when the reflection angle equals an integer multiple of the incoming X-Ray wavelength, then there is strong constructive interference in the reflection and a large signal is seen at the detector. For angles where these values are not equal, a much smaller signal makes its way to the detector. The final data signal thus depends on the crystallographic nature of the material, which changes significantly based on the lattice constant and crystal structure. Therefore, XRD can be an incredibly useful tool for analysis of phase purity. Figure 1.29 shows XRD data of yttrium aluminum perovskite (YAP), a potential source of secondary phase contamination when growing YAG. Notice the strong peaks that arise when Bragg’s Law is satisfied.
Figure 1.29: XRD of YAP, another yttrium aluminum crystal structure. (25)
References


[22] Georgia State University, http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html


CHAPTER 2
CONSTRUCTION OF CMR’S CZOCHRALSKI FURNACE

The Czochralski (CZ) furnace used to grow Ce:YAG in the following experiments is unique for a crystal growth laboratory in the United States. It has been used in the successful growth of high temperature oxides including both ruby and Ce:YAG. Although it has always been a radio frequency furnace, it was not until recently capable of growing crystals by the CZ method. Several changes to the cooling system had to be undertaken, new insulation was designed, a pulling arm and load cell based scale were installed, crucible rotation was added, and a new program written with LabVIEW had to be created. The learning process was in some ways similar to the learning experience of those with the first CZ systems.

2.1 A Brief History of Crystal Growth and the Czochralski Method

The fundamentals of crystal growth have been studied to some degree for several centuries, dating back to experiments by Gibbs, Arrhenius, Fahrenheit, and Lowitz from the 18th and 19th centuries. (1) However, it was Auguste Verneuil in 1902 that pioneered the first industrial method for crystal growth by being the first to reliably control crystal nucleation for the fabrication of “large” single crystals of 1 cm in diameter by 2 cm long. (1) The method became known as flame fusion (or Verneuil process) which Verneuil used for the fabrication of ruby and other corundum crystals. By 1907 his lab was producing 5 million carats of ruby, and by 1913, was producing 10 million carats of ruby and 6 million carats of sapphire annually. (1)

Since then, the flame fusion method was used for several decades in the growth of gemstones as well as optical crystals for physics and mechanical components. In fact, a flame
fusion grown ruby was used as the first laser material demonstrated in 1960. (2) However, advances in optical physics and the development of lasers required larger and better optical quality single crystals. Despite improvements to the flame fusion method, the high strain, small size, and other problems were too much to overcome. (2) A new method for growing large, low strain, single crystals had to be developed. Despite the development of many other growth methods such as flux, Bridgman-Stockbarger, Kyropoulos, and vertical gradient freeze, the most successful method became the Czochralski method. (1)

First developed by Jan Czochralski in 1916, (1; 3) the CZ method has become by far the growth method of choice as well as the most advanced method for a variety of materials. (4) Considering this, it may come as a surprise the method was initially developed by accident.

“As the story goes, the young Czochralski, then chief of AEG’s metals laboratory in Berlin was studying crystallization of metals. A crucible containing molten tin was left on his table for slow cooling and crystallization. Czochralski was preparing his notes on the experiments carried out during the day when at some point, lost in thought, he dipped his pen into this crucible instead of inkwell placed nearby the crucible. He withdrew it quickly and saw a thin thread of solidified metal hanging on the tip of the nib. The discovery was made! He had generated a phenomenon never occurring in nature – crystallization by pulling from the surface of a melt.” (3)

Since then, the method has undergone a gamut of changes to transform it into today’s modern process. Starting as soon as 1918, only two years after Czochralski’s discovery,
Wartenberg modified the method by introducing a seed crystal to begin the growth process instead of a capillary as Czochralski had done. (3) Next in 1922, Gomperz used a floating die to control the diameter of the crystal, (1; 3) with subsequent publications for shaping crystals followed by Mark et. Al., Linder, and Hoyem and Tyndall in 1923, 1925, and 1929 respectively. (3) During this time, and for subsequent decades, the method was used for growing single crystals of metals only.

The advent of the transistor necessitated the growth of single crystals outside of metals. It was Teal and Little of Bell Laboratories in 1948 that first applied the method to semiconductors, (1; 2; 3) where heavy modifications to the method allowed for the growth of single crystal germanium. This included the first use of seed crystal rotation as well as changes in melt temperature to control the crystal shape. These changes brought Czochralski crystal growth into the modern era, where the growth of semiconductor crystals of germanium and silicon became well established by the mid 1950’s.

Later in 1960, calcium tungstate (CaWO₄) became the first oxide material to be grown by the CZ method, (5) and was soon applied to many other oxide materials. The application of radio frequency heating and an iridium crucible by East Chicago and Speedway Laboratories allowed for the growth of high temperature oxides by the CZ method. (2) By 1964, the quality of single crystal CZ grown rubies far surpassed the quality that could be supplied by flame fusion, and soon became the dominant method for laser crystal manufacturing in addition to its dominance in semiconductor growth.

Improvements to the CZ system did not stop in the 1960’s though. Despite high temperature capabilities, and the advent of power control to influence diameter, the crystals grown were still of relatively small (1-2 cm) diameter. This was in large part due to limitations
in good methods for diameter control. The first such methods relied on nothing more than an operator to change the temperature control based on visual observations of the growing crystal. (5) Despite the obvious drawback that the system had to be monitored 24 hours a day, manual control left much to be desired in terms of shape and strain. This limited size and several examples can be seen in Figure 2.1.

![Figure 2.1: CZ grown crystals controlled by visual observations and operator controlled temperature changes. (5)](image)

By the late 1960’s and early 1970’s a new method of diameter control relied on “an optical sensor to detect the position of the crystal/liquid interface. This system was mechanically linked to the puller so that it would gradually change the viewing angle during growth to compensate for the liquid level drop.” (5) Although somewhat successful, it “still required a clear, unobstructed view of the crystal/liquid interface during the entire growth process,” and put large constraints on the build of insulation materials. (5)
The next evolution came in the form of weighing control, where power was modified based on changes in weight. The major advantages were increased precision in power control, and the ability to more finely tune the furnace and insulation builds since a direct line of site was no longer necessary. The first systems that monitored weight relied on measuring changes in the melt weight. Unfortunately, this also required measuring the crucible and surrounding insulation. As crystal size scaled up, so did insulation and crucibles to the point that weighing the melt was no longer sensible. (5)

Considering the advantages of the method though, this was quickly replaced in the mid 1970’s by a means of measuring the crystal weight directly as the mechanical hurdles were overcome. A diagram of a basic system employing this method can be seen in Figure 2.2. (5)

Figure 2.2: Schematic of a common direct weight CZ pulling assembly. (5)
Such a system, utilizing a good feedback method such as a PID (Proportional - Integral - Derivative) controller, became capable of growing good quality single crystal with an excellent shape. Examples of modern oxide crystals can be seen in Figure 2.3 and Figure 2.4.

Figure 2.3: Modern perovskite crystals grown by direct weighing with a PID controller. (5)

Figure 2.4: Modern Er YAG Laser Crystal. (6)
With the direct weighing method the modern CZ system was born, with the drive changing from better control to crystal size and materials discovery. To this day, the freedom of control, reproducibility capability, and rapid growth of the CZ method continue to drive its dominance in the crystal growth community. As of 2000, the amount of bulk single crystals grown annually surpasses 20,000 tons. (1) At the time, roughly 60% was dominated by the semiconductor industry, where 95% was grown by the CZ method. (1)

2.2 Build of CMR’s CZ Furnace

The CMR CZ furnace employs the direct weighing method that became popular in the mid 1970’s which was discussed earlier. Although there are many similarities between our CZ furnace and others used for the growth of high temperature oxides, there are some aspects of the build which are unique to our CZ furnace specifically. Additionally, it is unique for a crystal growth laboratory, capable of growing larger single crystals than any other university in the United States. Each major aspect of the furnace will be discussed, from the power supply and cooling system to the PID controller that monitors weight, detailing the system that is used to grow the crystals in the following chapters.

2.2.1 The Power Supply

At the heart of any furnace system is the power supply. Without appropriate levels of power or control, the functions required in many modern furnaces could not be achieved. The power supply used in the CMR’s CZ furnace is a custom built 75 kW, 25 kHz, RF induction furnace manufactured by Pillar Induction. It is important to note the operating frequency is higher than the typical operating frequency of around 10 kHz of many high temperature oxide furnaces, though it can be reduced to 20 kHz. Such a power supply is unique for a research
university in the United States, and the power supply front panel can be seen below in Figure 2.5 below.

![Figure 2.5: Front Panel of the Pillar MK-25CG power supply. The left gauges indicate cooling water input and output pressure. The power supply also has settings for manual and external control.](image)

The advantage of such a power supply can be described by the penetrating depth of an AC current in a material, which is given by the following equation:

$$\delta = \sqrt{\frac{2\rho}{\omega \mu}}$$

Where $\delta$ is the skin depth, $\rho$ is the resistivity, $\mu$ is the magnetic permeability, and $\omega$ is the frequency of the AC signal. With other factors remaining unchanged, it can be determined that 25 kHz compared to 10 kHz will decrease the skin depth by a factor of $1/\sqrt{2.5}$, or 1.58. This
corresponds to improved RF coupling in standard materials, and simultaneously allows for the use of other materials with higher resistivity for crucible construction.

As can be seen in Figure 2.5, the power supply can also be set for external control, allowing for computer automation. External control was implemented through a National Instruments controller bank and LabVIEW software, discussed later. Cooling water runs throughout the power supply and must be kept under 35°C in order to keep the power supply operational. Temperatures above this set point will result in power supply shutting down.

2.2.2 The Cooling System

To provide the cooling, the CZ furnace utilizes a closed loop cooling arrangement. A 200 gallon reservoir supplies the plumbing (Figure 2.6), which feeds the power supply and furnace chamber on separate lines, and then feeds back to the main reservoir.
Reservoir cooling was overhauled extensively in the build of the CZ system, and ultimately was accomplished through the implementation of two systems. The first uses chilled building water run through two heat exchangers. They are fed by an industrial pump, which pulls directly from the reservoir and returns chilled water directly to the reservoir, and act as a secondary cooling solution. The primary cooler is an industrial 26 kW chiller that has radiators placed directly into the reservoir as seen in Figure 2.7. The chiller utilizes its own 40 gallon reservoir, set to 12°C, which is pumped through the radiators seen below. Incoming hot water is directed from the copper pipe across the surface of the radiators to maximize water flow and cooling.

Figure 2.7: Radiators in the main reservoir. Return water from the furnace and power supply is on the left. Due to the elevated temperatures of the water during crystal growths, water needed to be changed every several months with fresh DI water. The above picture was taken just prior to cleaning.

The purpose of the two systems is to provide redundancy in cooling, since the power supply must be kept at less than 35°C. If the water temperature becomes greater than 35°C, the
power supply will shut down and result in a quench of the insulation and crucible, significantly reducing their lifetime. With two cooling systems, average water temperatures can be held to $22^\circ C \pm 1.0^\circ C$, which is safely below the setpoint threshold. Additionally, in the event that one system fails, the other will be able to provide several hours of cooling before the cooling water reaches $35^\circ C$. This allows the furnace and power supply to be shut down in a controlled manner.

Finally, pressure sensors measure the water pressure in the lines directed to the furnace chamber and power supply. In the event of a pump failure and water pressure drops to zero, the pressure sensors will trigger several switches on the cooling lines to transition cooling water from the closed loop system to city water. The power supply will be shut down, but it will continue to receive cooling and thus be protected against damage.

2.2.3 The Furnace Chamber and CZ Assembly

The furnace chamber is composed of a double walled stainless steel chamber, allowing cooling water to flow between the two walls. There are a total of six ports for connecting external equipment, as well as one double walled window in the front door. Two of the six ports are angled at $39^\circ$, which are aimed at the middle of the heating coil. One port is designed for additional visibility into the melt, and the other houses an optical pyrometer for precise temperature readings.

Internal dimensions of the chamber are as follows:

- Diameter: 24.8”
- Height: 33.66”
- Coil ID: 8.25”
- Coil Height: 13.25”

The furnace chamber allows for a large coil and a crucible as large as 150 mm in diameter to be used. Such a large crucible allows for near industrial sized crystals to be grown, which is unique for a research university in the United States. The furnace chamber is pictured in Figure 2.8.
To make the system CZ capable, a number of changes had to be made to the existing chamber. To facilitate forced mixing in the CZ system, a stepper motor was added to the bottom of the furnace chamber in line with the pulling arm (the center) of the furnace. A stepper motor allows for excellent torque at slower rotational velocities, and is responsible for rotating the crucible and surrounding insulation. To the right is the multi-port for pulling vacuum within the
chamber, monitoring pressure, and evacuating gasses. It is pictured in Figure 2.9. Up to three gas tanks can be used with the multiport at one time.

![Atmosphere port for the furnace chamber](image)

Figure 2.9: Atmosphere port for the furnace chamber. To the right is the valve leading to the mechanical vacuum pump. The far 90 degree valve dumps chamber gasses to a vent. Two pressure gauges are situated above.

Above the furnace chamber, and pictured in Figure 2.5, is a translation stage used for centering the pulling arm and scale with the crucible and insulation materials. This houses the pulling arm assembly, where a stepper motor was added. As with the stepper motor added for rotation, slow but precise (down to 0.5 mm/hr) pulling velocities can be achieved. Without a reliable and steady pulling assembly, reproducible CZ growth would not be possible.

Above the pulling assembly, a high precision scale from Cyberstar that was also added to the system (Figure 2.10). The scale can weigh up to 10 kg with 10 mg sensitivity. The scale is arguably the most important piece of equipment in the system, as it is the single setpoint variable...
for the PID controller, which will be discussed in more detail later in the chapter. The entire system (furnace chamber, pulling arm assembly, and scale) can be pulled to a vacuum of ~17 mTorr, unique for many CZ systems, for the ability to tightly control the chamber atmosphere.

Figure 2.10: The scale used to weight the crystal in real time.

2.2.4 The Insulation

Heating a crucible and YAG powder to 1970°C requires significant insulation to keep the chamber and RF coil from getting dangerously hot, despite an industrial cooling system. The Stefan-Boltzmann equation shows that the total irradiated power (RP) from an object is equal to

$$RP = A \varepsilon \sigma (\Delta T)^4$$
Where $A$ is the surface area of the heated object, $\varepsilon$ is the material emissivity, $\sigma$ is the Stephan Boltzmann constant, and $\Delta T$ is the temperature difference in Kelvin between the object and its surroundings. Clearly, irradiated power increases significantly as temperature rises.

To protect the furnace chamber and RF coil, significant insulation needed to be constructed to protect the surrounding environment. Additionally, the insulation needed to allow a seed rod through the top so a crystal could be pulled, allow line of site visibility for an optical pyrometer, and be stable for days at operating temperature.

The two primary insulators that ended up being used in the system were a calcium stabilized zirconia, and a yttria stabilized zirconia. The calcium stabilized zirconia made up the majority of the outer insulation and core insulation due to its strength and ability to withstand several hot cold cycles with minimal degradation. The yttria stabilized zirconia made up the interior insulation next to the crucible, as well as wrapping on the outer pieces of insulation due to its porosity and superior insulating characteristics. It was used in two different forms. One was a zirconia FBD board (rigid) which was used as the crucible base, and the other was a felt (flexible) for wrapping around materials. Specification sheets of all materials can be found in the appendix. Figure 2.11 details the cross section of inner cylindrical insulation used in the build.

Lifetimes of all components varied greatly depending on proximity to the crucible. The zirconia felts placed around the crucible and the zirconia FBD board upon which the crucible sat had to be replaced every run. The inner calcium stabilized zirconia cylinder would need to be changed (or flipped over to be reused) approximately every 4-6 runs depending on the nature of cracking. The secondary cylinder and components could last as long as 15 runs before replacement became necessary. Finally, the crucible itself needed to be reshaped every 4-6 runs due to significant deformation.
Due to the mechanical constraints of the system (the furnace uses crucible rotation instead of seed rotation), the insulation was composed of a double walled setup with two cylinders. The inner cylinder was composed of the calcium stabilized zirconia, and housed the crucible at the proper height for the coil. This entire assembly was rotated during the crystal
growth. The outer cylinder was a stationary calcium stabilized zirconia. It effectively allowed the insulation system to be closed on all sides by allowing a cap to be installed above, but still allow for a seed rod and line of site into the crucible. A picture of the outer insulation in the furnace can be seen in Figure 2.12.
2.2.5 The Software and PID Controller

The software used in the CZ system was created using LabVIEW and National Instruments controllers. Both are a powerful means of reading and controlling various aspects of the system for CZ control. The power supply has every aspect of operation recorded and controlled, up to 8 thermocouples per thermocouple bank can be populated, oxygen sensors, optical pyrometers, and chamber pressure data among other are read into the system. A picture of one section of the National Instruments controller bank can be seen in Figure 2.13, which is responsible for power supply monitoring and control.

![National Instruments controller bank](image)

Figure 2.13: National instruments controller bank for reading and controlling the power supply.

To make use of all the monitoring equipment in a useful way, as well as to control the power supply, an organized and easy to use program needed to be created. This was accomplished with the visual programming software LabVIEW, which allowed for each aspect of furnace control and measurement to be presented visually in an organized manner.
Screenshots of the final implementation of the software can be seen in Figure 2.14, and Figure 2.15.

Figure 2.14: Screenshot of the LabVIEW software showing power supply and chamber data. Gas flows, oxygen %, power supply and chamber water temperatures, and power readings are all recorded by region. Input control is on its own tab to the left, and pulling and rotation rates are always visible.
Figure 2.15: Screenshot of the growth data. Target weight plot and real weight plot are recorded, as well as optical pyrometer readings. PID settings are also contained in the growth section of the software, as well as the on/off switch to the PID furnace control.

The initial build of the LabVIEW software though, did not utilize a PID controller. Instead a simple proportional method was used to control the power supply, where the speed of power change was based on how far off target the boule weight was. Three regions of error (process variable minus target weight) determined the rate of change in power as follows:

0 – 2.5% off target weight: Slow power correction

2.5 – 7.5% off target weight: Medium power correction

Greater than 7.5% off target: Fast Power Correction
Despite the relatively slow changes in weight observed during crystal growth, and several attempts at tuning, the system proved inadequate for the production of high quality single crystals, as can be seen in the samples pictured in Figure 2.16 and Figure 2.17.

Figure 2.16: The first crystal grown using the CZ furnace and proportional method of furnace control. It is an undoped YAG boule, where the large ridges are from the slow response of the proportional system.

Figure 2.17: The third crystal grown using the proportional system with minor modifications. The ridges are smaller but still very much present.
Although the differential method of control ended up being inadequate for proper power supply control, it did serve one very important purpose when the system was replaced by a PID controller. This has to do with tuning the PID controller to the characteristics of a particular system. One can either tune through a trial and error method, or through a method known as Ziegler-Nichols.

First though, the fundamentals of a PID controller should be explained. As explained in national instruments documentation, PID controller operates by taking three factors into account, and is where its name is derived. P stands for proportional, which looks simply at how far off track the process variable (in our case weight), is from the set point (target weight). The farther off the process variable, the faster the proportional portion of a PID tries to react proportional to the gain factor P. I stands for integral, which adds all of the error over a specified amount of time, T_i. D is for derivative, which looks at how quickly the process variable is changing over a specified amount of time, T_d. A well tuned PID controller takes each factor into account to make many minute adjustments to a system to maintain the process variable as close to the set point as possible. A poorly tuned PID system can oscillate out of control, and is where the Ziegler-Nichols method is derived.

The Ziegler-Nichols method operates by setting the integral and derivative method of the PID controller to zero, and increasing the gain factor until the system begins to oscillate. This gain is known as the critical gain, K_c, and the period of oscillation as the critical period P_c. The PID variables can then be set according to Table 2.1.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.6K_c</td>
</tr>
<tr>
<td>I</td>
<td>0.5 P_c</td>
</tr>
<tr>
<td>D</td>
<td>P_c/8</td>
</tr>
</tbody>
</table>

Table 2.1: Ziegler-Nichols method of PID tuning.
The differential method developed previously was essentially a tuned proportional system, where the time between ridges on the best runs was the critical period. Thus, the new PID controller implemented in LabVIEW could be tuned with minimal guesswork or additional trials to determine the critical tuning values. Once the PID system was implemented, boule quality and optical quality improved significantly, as seen in the figures below.

Figure 2.18: First CZ growth using the PID controller.
Figure 2.19: CZ Growth after some minor tuning.

Figure 2.20: Slice from the a Ce:YAG boule showing optical quality. Dimensions are roughly 32 mm diameter by 30 mm high.
With a reliable CZ system for growing high optical quality Ce:YAG boules, research on eliminating and understanding defects could begin, with crystals that could be methodically changed as the conditions required.
References

CHAPTER 3
HIGH CERIUM IN CE:YAG

Single crystal cerium doped yttrium aluminum garnet boules (Ce:YAG, 0.25-4.0 at.% Ce) were grown under similar conditions by the Czochralski method. Scintillation, photoluminescence, and lifetime measurements demonstrate reduced UV defect emission and increased visible emission as cerium doping increases, resulting from greater competitiveness of cerium luminescence centers among defect centers. Photodiode (PD) energy resolutions improved significantly, where 2.0 at.% Ce:YAG displayed 8.9% (6.14% with noise reduction) at 662 keV without post-processing. Therefore large, highly doped, as grown Ce:YAG, can achieve resolutions on cost effective photodiodes that are generally observed only with photo multiplier tubes and avalanche photodiodes at low doping levels.

Such a finding has not been demonstrated in the previous literature, in no small part due to tests traditionally being conducted on photo multiplier tubes (PMT’s). In such papers, maximum light yield is reported for cerium concentrations under 0.21%,[7,13] therefore deterring higher doping levels. In fact, cerium doping levels tend to stay well under 1.0 at.% in most papers.[7-14]

Previous research and specification sheets will show PMT’s are much more sensitive in the UV than they are in the visible spectrum due to the nature of the photocathode. This is problematic because Ce:YAG has a large UV defect emission peak centered around 300 nm, even though scintillation is supposed to be centered around 550 nm. The problem is if a method were developed to increase visible light emission by quenching UV defect emission, a PMT’s spectral sensitivity could easily mislead one to suspect they are witnessing decreasing light yield,
even though such an explanation may not convey reality. Reports of maximum light yield at such low cerium doping suggest this may be the case.

This paper will demonstrate that when higher cerium doping levels are involved in YAG, UV defect emission is quenched in favor of visible emission.

3.1 Background and Motivation

Yttrium aluminum garnet (Y₃Al₅O₁₂ or YAG) single crystals have been grown for several decades for various purposes including applications in phosphors, lasers, and scintillators. In the case of cerium doping in YAG, the cerium ion (Ce⁺³) undergoes a 5d to 4f transition resulting in broad band yellow light centered at 550 nm.[1-14] Although it would be natural to assume this is where the scintillation wavelength always occurs, a number of studies have shown this is not the case under all conditions. A broad UV peak at around 300 nm has been well documented[3-11], and several papers have shown significant UV output under cathodoluminescence and ionizing radiation.[3-6] Suggested reasons for the UV emission have been intrinsic defects in the host lattice which include impurities[12], oxygen vacancies[4,15,16], aluminum vacancies[15], and Y₃⁺antisites[3,6,7,15]. More recent research has suggested color centers[11,12] and Y₃⁺antisites[3,6,7,15] as dominant contributors to 300 nm emission in bulk melt grown YAG.

Apart from defects in Ce:YAG, cerium concentrations have traditionally been kept under 1.0 at.%[7-14] in scintillation crystals for a variety of reasons. Reports of maximum light yield for cerium concentrations under 0.21%[7,13] can be found, as well as reports of cerium self-absorption in thick samples.[5,7] Additionally, despite 550 nm light being better suited to photodiodes (PD’s) compared to photo multiplier tubes (PMT’s)[7,11,12,17], energy resolution and light yield are rarely reported on PD’s. When PD’s are used, results are generally poor[3]
with better resolution coming in at 11.7% at 662 keV.[14] As a result of the above discussed issues, development of Ce:YAG scintillators have been hindered by defects preventing efficient energy transfer to Ce luminescence centers and have been limited to lower doping concentrations.

This research demonstrates bulk single crystal Ce:YAG grown at the Center for Materials Research with increased visible light output and decreased UV emission. This has been achieved with highly doped samples, where emission at 550 nm has been increased, allowing better coupling to visible light sensitive devices. The resulting emission is evident with record performance of Ce:YAG on a PD that is mainly sensitive to visible emission. This allows for applications where Ce:YAG can be more effectively coupled to cheap, low power, and portable PD’s rather than traditionally used expensive, high voltage PMT’s and avalanche photodiodes (APD’s).

3.2 Crystal Growth and Preparation

Four YAG boules were grown in similar conditions by the CZ method with cerium concentrations with respect to yttrium of 0.25 at.%, 0.5 at.%, 2.0 at.%, and 4.0 at.. Growth at 4.0 at.% cerium experienced voids, stress, and cracking, suggesting limited performance for doping beyond this amount. Each boule was ~32 mm in diameter, and between 113 – 125 mm in length. The starting materials used were high purity yttria (Y$_2$O$_3$, 99.999%), alumina (Al$_2$O$_3$, 99.997%), and either Ce$^{3+}$ carbonate (Ce$_2$(CO$_3$)$_3$*10H$_2$O, 99.999%) or Ce$^{4+}$ oxide (CeO$_2$, 99.99%). Work at CMR showed no measureable difference between Ce sources in the grown boules. The powders were mixed in a stoichiometric ratio (10 mg precision, adjusting for inherent moisture content in the powders) to a target weight of 400 g, and then ball milled using
high purity (99.8%) alumina milling balls for 18 hours. After mixing, the powders were compressed in an isostatic press to ~20 kpsi, and then calcined at 1400 °C for 15 hours to make the final charge. Upon calcining, the charges lost an average of ~0.78% of their weight from moisture losses.

The crystals were grown with an iridium crucible (86 mm outside diameter by 60 mm high) using an RF induction furnace operating at 20 kHz and an atmosphere of 200 ppm oxygen balanced with nitrogen. First, one charge was melted down over the course of ~5 hours and then cooled. After this, a second like charge was added to the crucible to increase the melt volume to ~800 g to improve heat flow and maintain stable flow patterns during growth. The crystal was pulled using a 6 mm diameter [(111) orientation] undoped YAG rod at 4 mm/hr to grow the cone of the crystal, then 1 mm/hr to grow the full diameter section. The crucible and melt were rotated at 6 RPM, while the pulling arm was not rotated. Weight was monitored through the pulling arm, and adjusted via a PID controller.

Right cylinders were cored from the untreated boules of Ø10 mm by 10 mm thick, with a bordering Ø10 mm by 1 mm sample cut for optical absorption and transmission measurements. A thin sample assured cerium lines would not become saturated in absorption measurements. Each of the samples were taken in the bottom half of the boule (last to grow) and cored from the most stress free region as observed using crossed polarizers. Sample surfaces were mechanically polished to a final grit of 0.3 µm with an alumina polishing compound (Figure 3.1).
Figure 3.1: Cut and polished samples. From left to right, 0.25, 0.5, 2.0, and 4.0 at.% Ce concentrations. The rightmost sample displays some structural defects, suggesting poor crystal quality beyond 4.0 at.% Ce. Some tiny edge chips can be seen, which were caused by cutting.

Once cut and polished, an Ocean Optics PC2000® Spectrometer using a deuterium light source measured Ce absorbance in the 1 mm thick samples. As can be seen in Figure 3.2 below, there is good consistency between all of the samples, with cerium concentrations displaying an approximate linear relationship as Ce concentrations are increased. This measurement confirms the Ce concentrations in the boule are at or near the target concentrations, and more importantly confirms that they are consistent with respect to one another.
3.3 Scintillation and Energy Resolution

The rough sides of the Ø10 mm by 10 mm right cylinders were wrapped in Teflon tape and coupled to a Photonis XP2018B® PMT with optical grease so a $^{137}$Cs spectrum could be taken. The reflectivity of Teflon tape is greater than 96% in the entire working range of Ce:YAG (Source: Newport Optics), which provides an excellent reflective surface for scintillation measurements. Figure 3.3 shows the PMT scintillation results, where two μs shaping time provided the best resolution with each crystal.
Figure 3.3: Energy resolution as seen on a Photonis XP2018B® PMT and a S3590-18 PD. The PD improves dramatically with higher Ce concentrations as opposed to the PMT. Light output and resolution at 4.0 at.% Ce were comparable to 2.0 at.% Ce, despite macroscopic doping induced defects.

To test scintillation emission in the visible wavelengths, a 10x10 mm square Hamamatsu S3590-18 photodiode was also used to obtain a $^{137}$Cs spectrum as previously employed by our group.[3] The difference in light sensitivity between the PMT and diode detector lies in the quantum efficiency versus wavelength of emission light; the PD being much more sensitive in the visible than the PMT. As per manufacturer’s specifications, the Photonis XP2018B PMT is sensitive to wavelengths of 160 – 650nm. It has a quantum efficiency (QE) of 23.1% at a
wavelength of 300 nm, but a QE of <4.9% at 550 nm and above, where the scintillation emission is supposed to occur. The S3590-18 PD on the other hand, has a QE of >85% between 400-800 nm (90% at 550 nm) and a QE << 10% (undefined) at wavelengths of <300 nm.

Results obtained with the S3590-18 PD can be seen compared to the PMT in Figure 3.3, with 2 μs shaping providing the best resolution of 8.9 ± 0.04%. An observed resolution of 8.9 ± 0.04% on a PD is the best reported in the literature. The PD results had on average 2.05% better resolution for doping levels of 2.0 at.% and above, while the PMT was only better at <0.5 at.% Ce. This suggests a change in emission spectrum, where more light is coming out at 550 nm as UV emission is quenched by higher Ce concentrations. Future work will investigate light yield changes in more detail. Figure 4 compares a 2 μs shaping $^{137}$Cs spectrum for 2.0 at.% Ce:YAG on a PD and PMT, as well as commercially prepared CdWO$_4$ (10x10x8 mm) on a PD.

A pulser was also used with the PD to decouple scintillation resolution from electronic noise, and observe true statistical energy resolution.
Figure 3.4: $^{137}$Cs spectrums (662 keV photopeak) for 2.0% Ce:YAG on a PD and PMT, and CdWO$_4$ on a PD all with 2 μs shaping times. The peak on the right side is the pulser used in PD noise reduction. Highly doped Ce:YAG grown at CMR displays a narrower photopeak and thus better resolution on a PD compared to a PMT. Commercially prepared CdWO$_4$ displays a much smaller photopeak.

This is unnecessary with PMT’s and APD’s as their inherent gain will boost scintillation signals beyond a significant electronic noise contribution. [1] Knoll [1] states observed energy resolution can be described as a quadrature sum of each source of fluctuation.

$$(\text{FWHM})^2_{\text{overall}} = (\text{FWHM})^2_{\text{statistical}} + (\text{FWHM})^2_{\text{noise}} + (\text{FWHM})^2_{\text{drift}} + \ldots$$

Negligible drift and other sources of error were observed; therefore this can be approximated as,

$$(\text{FWHM})^2_{\text{overall}} = (\text{FWHM})^2_{\text{statistical}} + (\text{FWHM})^2_{\text{noise}}$$

Here $(\text{FWHM})^2_{\text{overall}}$ describes the FWHM of the observed photopeak, $(\text{FWHM})^2_{\text{statistical}}$ is the FWHM of the true statistical limit of our detector, and $(\text{FWHM})^2_{\text{noise}}$ is the pulser FWHM.
arises from electronic broadening in a single channel pulse. Using this method with the 2.0 at.% Ce:YAG, an observed 8.9 ± 0.04% corresponds to a statistical limit of 6.14% ± 0.1% which rivals the best results of Ce:YAG on APD’s[7,17].

3.4 Photoluminescence

Photoluminescence (PL) was measured using a Horiba Jobin Yvon Fluorolog-3® Spectrofluorometer with a deuterium arc lamp for pumping down to 180 nm. Results can be seen in Figure 3.5 below.

![Emission curve from 190 nm excitation, normalized to the visible emission peak. UV emission is significantly quenched as Ce concentrations increase. The PL setup is not calibrated below 285 nm, resulting in a sharp drop below this wavelength.](image)

Figure 3.5: Emission curve from 190 nm excitation, normalized to the visible emission peak. UV emission is significantly quenched as Ce concentrations increase. The PL setup is not calibrated below 285 nm, resulting in a sharp drop below this wavelength.
Analysis was performed with samples pumped at 190 nm at room temperature, where visible light was integrated from 500-650 nm and UV integrated from 400 nm and below. Ce:YAG with 2.0 at.% Ce and above displayed >99% of emission in the visible range. 0.5 at.% Ce:YAG had <95% emission in the visible and 0.25 at.% Ce:YAG had <85% emission in the visible. This is due to both increased visible emission and decreased UV emission. As can be seen in Figure 3.5, UV defect emission is significant in samples with low cerium concentrations.

It should be noted that 190 nm excitation is non-ionizing for YAG. However, E Zych et al.[8] describes that “there is a non-negligible probability for the electron excited with 230 nm light to escape the Ce ion before relaxation…such excitation begins to take on some of the delocalized characteristics typical of ionizing radiation.” Thus, while 190 nm photoluminescence is non-ionizing, it can provide a glimpse of behavior to come under gamma excitation. With that said, greater visible and less UV emission suggests electron-hole pair recombination becomes more probable at Ce luminescence centers over defect centers as Ce concentration increases. As less energy is lost to UV defect centers, scintillation performance improves significantly on a PD compared to a PMT.

3.5 Lifetime Measurement

Lifetime measurements were performed using a Photonis XP2020 PMT coupled to a Tektronix MSO 4104 oscilloscope, with the samples excited by a $^{137}$Cs gamma source. A three lifetime fit was taken using the following equation:

$$y = A1 \exp\left(-\frac{x}{t1}\right) + A2 \exp\left(-\frac{x}{t2}\right) + A3 \exp\left(-\frac{x}{t3}\right) + y0$$

Figure 3.6 demonstrates that as Ce concentrations increase, the short lifetime comes to
dominate the decay profile, as well as exhibit a shorter overall scintillation pulse. As such, 2.0 and 4.0 at.% Ce:YAG can nearly be described by a single, short exponential of under 110ns. These findings are in agreement with Ludziejewski et al.[13] who measured lifetimes with Ce concentrations up to 1.0 mol.%, and observed faster scintillation pulses with more Ce.

Figure 3.6: Lifetime results from 0.25 at.% and 4.0 at.% doping with 137Cs excitation. The highly doped sample can nearly be described by a single, fast decay whereas the lightly doped sample has a significant slow decay component.

Slow lifetime components have been attributed to defect emission[5,8-10], where our results demonstrate higher cerium concentrations hinder UV defect centers as desirable carrier recombination pathways for Ce:YAG grown under similar conditions.
3.6 Summary

In summary, the performance of these highly doped Ce:YAG samples surpass previously reported results on a PD. Results from each of these measurements can also be seen compared in Table 3.1.

Table 3.1: Energy resolutions, photoluminescence, and lifetime measurements of Ce:YAG. Energy resolutions were performed with a $^{137}$Cs source at different doping levels with a shaping time of 2 μs.

*Decay times were measured using a PMT due to electronic timing constraints. This produces accurate decay times, but we acknowledge a PMT will introduce a certain degree of error into intensity values due to its spectral sensitivity. The provided ratio serves only to illustrate the trend.

<table>
<thead>
<tr>
<th></th>
<th>0.25 at.% Ce</th>
<th>0.5 at.% Ce</th>
<th>2.0 at.% Ce</th>
<th>4.0 at.% Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMT Resolution</td>
<td>12.0 ± 0.1%</td>
<td>11.65 ± 0.05%</td>
<td>10.8 ± 0.1%</td>
<td>11.0 ± 0.1%</td>
</tr>
<tr>
<td>PD Resolution</td>
<td>13.8 ± 0.2%</td>
<td>10.4 ± 0.03%</td>
<td>8.9 ± 0.04%</td>
<td>8.9 ± 0.05%</td>
</tr>
<tr>
<td>PL Emission</td>
<td>&lt;85% visible</td>
<td>&lt;95% Visible</td>
<td>&gt;99% visible</td>
<td>&gt;99% visible</td>
</tr>
<tr>
<td>Fast Decay Time</td>
<td>215.7 ± 0.1 ns</td>
<td>152.9 ± 0.7 ns</td>
<td>106.7 ± 0.2 ns</td>
<td>90.5 ± 0.2 ns</td>
</tr>
<tr>
<td>% Fast Decay*</td>
<td>78%</td>
<td>74%</td>
<td>94%</td>
<td>96%</td>
</tr>
</tbody>
</table>

Contrasts in energy resolution between PMT and PD demonstrate the PD’s as a more suitable detector for Ce:YAG when high Ce doping levels are involved. This is due to decreased UV output, where PMT’s are most efficient, and increased visible emission, where PD’s are most efficient. These results are corroborated by photoluminescence and lifetime measurements, where less UV and faster emission are attributed to greater competitiveness of cerium luminescence centers with defect centers. The observed trends continue to 4.0 at.% Ce, despite macroscopic doping related defects at this Ce concentration. Compared to commercially available and commonly used scintillators such as CdWO₄, which has a longer lifetime and worse resolution, highly doped as grown Ce:YAG on a PD presents a viable alternative in many commercial systems.
References


CHAPTER 4
OFF STOICHIOMETRIC CE:YAG GROWTHS

Single crystal cerium doped yttrium aluminum garnet (Ce:YAG) boules were grown by the Czochralski method. Cerium concentrations were held at 1.0 at.% in the melt, but melt stoichiometry ranged from 10.0 at.% yttria rich to 10.0 at.% alumina rich in 5.0% increments. Scintillation and photo-luminescence demonstrate a measurable decrease in UV defect emission as the melt becomes alumina rich, suggesting a shift in equilibrium $Y_2 Al^3+$ antisite defect concentrations in the boule as melt stoichiometry is altered. A large increase in visible emission results in an excellent resolution of $5.04\pm 0.07\%$ (662 keV; 10 mm thick) with noise reduction on a photodiode.

Such a finding has not been demonstrated in the previous literature, particularly because YAG is shown as a line compound on the phase diagram. This would suggest that deviations from stoichiometry are forbidden, resulting in little research involving YAG melt stoichiometry. Such an assumption though, ignores the role of constituent concentrations in the development of antisite defects.

The study was formed when a well known detail about YAG was considered with two lesser known aspects. These are that antisite defects (and yttrium antisites in particular) have the lowest defect formation energy in YAG, such that thermal energy is sufficient for their formation in melt grown YAG; excess oxides preferentially form antisites over other intrinsic defects; and aluminum antisites do not readily form, leading to off stoichiometric YAG when the crystal is free to “pull” from the melt. These facts together, though they definitively demonstrate that yttrium antisites will exist in melt grown YAG, also strongly suggest that changes to melt stoichiometry can effect antisite concentrations in pulled crystal growths.
Our research has shown that when YAG is grown in alumina rich conditions, UV defect emission is reduced in favor of visible emission, which we attribute to a reduction in yttrium antisites.

4.1 Background and Motivation

Yttrium aluminum garnet (Y₃Al₅O₁₂ or YAG) has long been used in many industrial applications. When doped with cerium it often sees use in phosphor applications where the cerium ion (Ce³⁺) undergoes a 5d to 4f transition resulting in broad band yellow light centered at 550 nm.¹⁻²⁻³⁻⁴⁻⁵⁻⁶ Such emission gives Ce:YAG tremendous potential as a visible light scintillator when grown in bulk. Unfortunately several studies have demonstrated significant UV defect luminescence centered around 300 nm under cathodoluminescence and ionizing radiation.³⁻⁴⁻⁵⁻⁶ Such a defect limits total cerium luminescence by competing with the 550 nm emission, and hinders overall scintillation performance.

UV defect emission has been attributed in the past to one or more of several intrinsic defects; however, the prevailing thought now suggests yttrium on aluminum antisites (Y₃⁺) as the primary defect responsible.⁵⁻⁶⁻⁷⁻⁸ This is unfortunate, as antisites have been shown in numerous studies to be the most energetically favorable intrinsic defect in YAG.⁹⁻¹⁰⁻¹¹⁻¹²⁻¹³ Additionally, Y₃⁺ on the aluminum octahedral site is the most likely to be thermally produced in melt grown YAG¹³⁻¹⁴ as it is much more energetically preferable to the opposite antisite, Al₃⁺.⁹⁻¹⁰⁻¹¹ This is in agreement with several papers that either could not identify Al₃⁺ defects within their samples,¹²⁻¹³ or demonstrated they did not readily form.¹¹

Despite such studies, YAG is represented as a line compound in the Al₂O₃-Y₂O₃ phase diagram,¹¹⁻¹²⁻¹⁵ suggesting deviations from stoichiometry should yield some mix of phases rather than a pure YAG phase. Nevertheless in cases where YAG melt stoichiometry has been
seen to drift over time,\textsuperscript{(16)} the resulting crystal is that of a pure garnet phase facilitated by antisite formation.\textsuperscript{(9; 13; 17)} It would appear then that the YAG “line” is actually wider, where deviations from stoichiometry are accommodated by the formation of antisite defects rather than the formation of other crystalline phases along with the garnet phase, such as aluminum oxide on the Al rich side and yttrium aluminum perovskite (YAP) on the Y rich side.

Here it is examined how the above information relates to formation of equilibrium antisite defect concentrations in YAG. It can be summarized as follows; excess oxides preferentially form $Y_{Al}^{3+}$ antisites over other intrinsic defects which allow the formation of off stoichiometric YAG since $Al_{Y}^{3+}$ antisites do not readily form.\textsuperscript{(11; 12; 13)} This makes the case that control of excess oxides in the melt is a way to reduce equilibrium antisite concentrations without creating additional intrinsic defects. Successful reduction of $Y_{Al}^{3+}$ would result in less UV emission and increased 550 nm emission.

Research performed at WSU investigated far off stoichiometric melts as a method for modifying equilibrium $Y_{Al}^{3+}$ concentrations in Czochralski (CZ) grown Ce:YAG. Photoluminescence and lifetime data clearly show a reduced UV emission (attributed to $Y_{Al}^{3+}$) as the melt is shifted toward alumina rich, and thermoluminescence data demonstrates that the change in defect structure is not related to above room temperature trapping defects within YAG. This work resulted in Ce:YAG scintillators mounted on simple photodiodes (PDs) with the best energy resolution to date of $5.04 \pm 0.07\%$ at 662 keV.

4.2 Crystal Growth and Preparation

Five Ce:YAG boules were grown under similar conditions by the CZ method. The cerium concentration was fixed at 1.0 at.% with respect to yttrium in an on stoichiometric charge. Melt stoichiometry was varied in 5.0 at.% increments from 10.0 at.% yttria rich to 10.0 at.% alumina...
The raw materials used were high purity powders of yttria (Y$_2$O$_3$, 99.999%), alumina (Al$_2$O$_3$, 99.997%), and Ce$^{4+}$ oxide (CeO$_2$, 99.99%) from Alfa Aesar. The powders were weighed with 10 mg precision (adjusting for inherent moisture content in the powders) to a target weight of 400 g, then ball milled using high purity (99.8%) alumina milling balls for 18 hours. After mixing, the powder mixture was compressed in an isostatic press to ~20 kpsi and then calcined at 1400ºC for 15 hours to make the final charge. Upon calcining, the charges lost an average of ~0.77% of their weight from moisture losses.

The crystals were grown using an iridium crucible (86 mm outside diameter by 60 mm high) using a RF induction furnace operating at 20 kHz and an atmosphere of ~100 ppm oxygen balanced with nitrogen. First, one charge was melted over the course of ~5 hours and then cooled. After this, a second like charge was added to the crucible to increase the melt volume to 800 g to improve heat flow and maintain stable flow patterns during growth. The crystal was pulled from melt using a 6 mm diameter, (111) orientation, undoped YAG rod at 2 mm/hr to grow the cone of the crystal, then 1 mm/hr to grow the full diameter section. The crucible and melt were rotated at 6 RPM while the pulling arm was not rotated. The crystal weight was monitored through the pulling arm and adjusted via a PID controller. Each boule was ~32 mm in diameter and between 116 - 126 mm in length.

Right cylinders of Ø10 mm by 10 mm thick were cut from the bottom half (last to grow) of the as grown boules with a Ø10 mm by 1 mm sample cut from an adjacent location for absorption/transmission measurements. A thin sample assured cerium lines would not become saturated in optical absorption measurements. All samples were cored from a stress free region as observed using crossed polarizers and were mechanically polished to a final grit of 0.3 µm (Figure 4.1). Relative Ce concentrations displayed good consistency with a Gaussian fit of the
460 nm peak varying by no more than 8% from the mean area of 71.5. (Table I) The small fluctuations observed were consistent with Ce segregation related variation caused by small differences in the coring location between samples.

Figure 4.1: From left to right, samples from 10.0 at.% yttria rich, 5.0 at.% yttria rich, on stoichiometry, 5.0 at.% alumina rich, and 10.0 at.% alumina rich melts. Some cracks were caused by cutting and polishing.

Absorption/transmission measurements were carried out with an Ocean Optics PC2000® Spectrometer using a deuterium light source to measure Ce intensity in the 1 mm thick samples. The measurement can be seen in Figure 4.2.
Figure 4.2: Absorption of each sample. 1.0 at.% Ce displays good consistency among all of the samples, minimizing concerns of Ce concentration variability on further measurements.

Relative Ce concentrations displayed good consistency with a Gaussian fit of the 460 nm peak varying by no more than 8% from the mean area of 71.5. (Table 4.1) The small fluctuations observed were consistent with Ce segregation related variation caused by small differences in the coring location between samples.

4.3 X-Ray Diffraction Measurements

X-Ray Diffraction (XRD) was performed with a Siemens Kristalloflex powder XRD analyzer to investigate secondary phases. All sections used for XRD were cut from the low stress region surrounding the cored samples to ensure relevance to the tested pieces and were
powdered using a porcelain mortar and pestle. Each sample, seen in Figure 4.3, exhibited identical peaks corresponding to YAG phase planes, \(^{(18,19)}\) and no peaks from other secondary phases (excess oxides) were observed above the detection limit of 1%.

![XRD Spectrum](image)

**Figure 4.3**: XRD spectrum from the region immediately surrounding our samples, with peaks indicating a pure YAG phase. The excellent consistency between each sample indicates minimal, if any, contamination from secondary phases.

To confirm where the excess oxides reside, left over melt from the crucible was also tested. Figure 4.4 displays significant differences between the yttria rich and alumina rich melts, where differing amounts of remaining oxides are observed.
XRD of the remaining yttria rich melt shows YAP, which is not present in the alumina rich melt remnants. XRD from the remainder of the alumina rich melt shows excess alumina. This is consistent with the alumina-yttria phase diagram (Figure 4.5). The YAP and alumina XRD peaks were identified from (20) and (21) respectively. Thus the CZ method is able to “pull” a YAG phase with no secondary phase contamination from a highly off stoichiometric melt while leaving behind the excess oxides.
Figure 4.5: Phase diagram of the alumina yttria system showing YAG, YAP and YAM. YAM is yttrium aluminum monoclinic. Source: (15)

4.4 Photoluminescence

Photoluminescence (PL) was measured using a Horiba Jobin Yvon Fluorolog-3® Spectrofluorometer with a deuterium arc lamp for excitation down to 180 nm, which allows for a rough quantification of optically active point defects. Analysis was performed with the 1 mm samples at 190 nm excitation at room temperature where 190 nm light provided the brightest hard UV illumination. It is important to note that 190 nm excitation is non-ionizing for YAG. However, as described elsewhere, (22) electrons excited by 230 nm light and below have non-
negligible probabilities of escaping the Ce ion and producing characteristics of ionizing radiation. This provides an indication of behavior to come under gamma excitation.

The results in Figure 4.6 show a clear trend of decreasing UV emission with increasing alumina content in the melt.

Figure 4.6: PL from 190 nm excitation. Barring a small bump in the 10.0 at.% alumina rich sample, and the 380 nm peak due to a doubling reflection of the 190 nm excitation source, the peak centered around 300 nm decreases in a near linear fashion as alumina concentration is increased. Wavelengths below 285 nm are not calibrated, resulting in a sharp drop below this wavelength.

Looking at the 300 nm line (Figure 4.7), UV emission decreases nearly linearly by ~50% from 10.0 at.% yttria rich to 10.0 at.% alumina rich.
This strongly suggests a reduction in Y\textsubscript{Al}\textsuperscript{3+} antisites, which are considered to be the source of UV defect emission.

4.5 **Lifetime**

Scintillation pulse lifetime measurements were performed with the Ø10 mm by 10 mm samples to investigate the change in decay kinetics. The long decay components in Ce:YAG have been shown to result from UV emission within Ce:YAG.\(^{4, 22, 23, 24}\) Thus a change in the Y\textsubscript{Al}\textsuperscript{3+} antisite concentration should manifest as a change in intensity of the long decay time. In particular, a reduction in Y\textsubscript{Al}\textsuperscript{3+} antisites and corresponding UV emission should result in a shorter average decay time resulting from less long decay contribution.
Data was taken using a Photonis XP2020 photo multiplier tube (PMT) coupled to a Tektronix MSO 4104 oscilloscope with the samples excited by a $^{137}$Cs gamma source (Figure 4.8), and a three lifetime fit was taken using the following equation:

$$y = A_1 \exp \left(-\frac{x}{t_1}\right) + A_2 \exp \left(-\frac{x}{t_2}\right) + A_3 \exp \left(-\frac{x}{t_3}\right) + y_0$$

![Lifetime data](image)

Figure 4.8: Lifetime data displaying a significant and consistent decrease in the fast decay component of Ce:YAG as the melt shifts toward alumina rich. It should be noted that decay times were measured using a PMT due to electronic timing constraints. This produces accurate decay times, but we acknowledge a PMT’s spectral sensitivity will introduce a certain degree of error into intensity values due to its spectral sensitivity.

It can be seen that as the melt moves toward alumina rich the scintillation pulse becomes shorter. The sample from an on stoichiometric melt has a short decay component from the three lifetime fit of $121.3 \pm 0.4$ ns, whereas the 10.0 at.% yttria rich and 10.0 at.% alumina rich melt samples are $155.6 \pm 0.4$ ns, and $98.4 \pm 0.5$ ns respectively. This is evidence of reduced $\text{Y}_{\text{Al}}^{3+}$ antisite concentrations as UV emission is reduced.
4.6 Thermoluminescence

Thermoluminescence (TL) was measured with the Ø10 mm by 10 mm samples to investigate \( \text{Y}_{\text{Al}}^{3+} \) antisites potential role with above room temperature traps. Each sample was de-glowed to a temperature of 425°C, cooled, and then solarized (excited) with a xenon lamp for 20 minutes at room temperature. After excitation, TL from the samples was measured from room temperature to 400°C at a heating rate of 12°C/min. TL emission was integrated over the \( \text{Ce}^{3+} \) emission band of 500 – 650 nm and the UV emission band from 200 – 400 nm. The resulting glow curves from each sample can be seen in Figure 4.9 (\( \text{Ce}^{3+} \) emission) and Figure 4.10 (UV emission).

![Glow curve of each sample from 500 – 650 nm.](image)

Figure 4.9: Glow curve of each sample from 500 – 650 nm. The spectrometer exhibited some drift, and although small, is evident at above 300°C.
Figure 4.10: TL sum from 200 - 400 nm. No signal can be seen above background noise. There is a small deviation from a zero average due to spectrometer drift in some samples. The small drift can be seen at higher temperatures in Figure 4.9 as well.

The Ce\textsuperscript{3+} emission glow curve revealed 3 distinct glow peaks with peak maxima occurring at temperatures (T \textsubscript{m}) of 122ºC, 178ºC, and 285ºC which represented different trapping depth energies. Each peak was nearly Gaussian in shape which is indicative of second order trapping kinetics.\textsuperscript{(25)} Although there appears to be a slight increase in counts at all trapping levels as the melt became more alumina rich, much of this can be attributed to the drift observed near the right side of Figure 4.9. There is also error (~10%) in the measurement itself. As such, it is hard to ascribe any significance to the change in total counts observed.

In the UV glow curve no signal was evident above background noise and spectrometer drift, indicating thermally released charge carriers cannot excite the 300 nm emitting defect site
(presumed to be $Y_{Al}^{3+}$ antisites) regardless of concentration. Therefore, thermally activated electrons or holes are not transferring to the conduction or valence band respectively, but are undergoing thermally assisted tunneling to nearby recombination centers as described in (26), indicating trapping sites must be located in close proximity to $Ce^{3+}$ luminescence centers.

With these TL results, the following conclusion is most probable: Although pulling Ce:YAG crystals from an alumina rich melt works to reduce the number of $Y_{Al}^{3+}$ antisites (as PL and lifetime indicate), it does not alter the concentration of carrier traps in the material. Therefore carrier traps and $Y_{Al}^{3+}$ antisite formation are two independent YAG defects.

4.7 Energy Resolution

The Ø10 mm by 10 mm right cylinders were wrapped in Teflon tape and coupled to a Photonis XP2018B® UV sensitive photo multiplier tube (PMT) with optical grease so a $^{137}$Cs spectrum to measure scintillation performance and energy resolution could be recorded. Two $\mu$s shaping time provided the best resolution with each crystal. As shown in Figure 4.11, any deviation from stoichiometry was detrimental to energy resolution measured by the PMT. The change was more significant in the alumina rich melt.
To investigate change in scintillation emission, a 10x10 mm square Hamamatsu S3590-18 photodiode (PD) was also used to obtain a $^{137}$Cs spectrum as previously employed by our group. As per manufacturer’s specifications, the PMT had a quantum efficiency (QE) of 23.1% at a wavelength of 300 nm, but a QE of $<$4.9% at 550 nm and above where the scintillation emission is supposed to occur. The S3590-18 PD on the other hand, had a QE of $>$85% between 420-800 nm (90% at 550 nm) and a QE $<$ 10% (undefined) at wavelengths of $<$300 nm.

Results obtained with the S3590-18 PD are compared to the PMT in Figure 4.11 and Table 4.1. Two μs shaping provided the best resolution, where the PD displayed a remarkable trend toward better energy resolutions with an alumina rich melt and was consistent with the PL data.
Such a dramatic improvement on the PD (visible sensitive) and degradation on the PMT (UV sensitive) indicates $\text{Y}_{\text{Al}}^{3+}$ antisite concentrations are reduced. This provides significantly increased 550 nm emission due the alumina rich melts. The greatest change occurred in the 10.0% alumina rich melt, where the 10 mm thick as grown sample displayed an impressive resolution of $8.2 \pm 0.04\%$ FWHM on a PD.

Table 4.1: Characteristics of the as grown samples. The largest improvements can be seen with the 10.0 at.% alumina rich melt grown sample.

<table>
<thead>
<tr>
<th></th>
<th>10.0 at.% Y Rich Melt</th>
<th>5.0 at.% Y Rich Melt</th>
<th>On Stoichiometry</th>
<th>5.0 at.% Al Rich Melt</th>
<th>10.0 at.% Al Rich Melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMT Resolution at 662 keV (%)</td>
<td>10.4 ± 0.08</td>
<td>10.35 ± 0.07</td>
<td>9.92 ± 0.07</td>
<td>10.56 ± 0.08</td>
<td>10.67 ± 0.08</td>
</tr>
<tr>
<td>PD Resolution at 662 keV (%)</td>
<td>9.52 ± 0.08</td>
<td>9.8 ± 0.05</td>
<td>9.49 ± 0.05</td>
<td>9.31 ± 0.05</td>
<td>8.19 ± 0.04</td>
</tr>
<tr>
<td>PL Counts at 300 nm Peak 460 nm Absorption Area</td>
<td>2.99x10^4</td>
<td>2.57x10^4</td>
<td>2.04x10^4</td>
<td>1.82x10^4</td>
<td>1.47x10^4</td>
</tr>
<tr>
<td></td>
<td>68.8</td>
<td>69.2</td>
<td>77.2</td>
<td>73.9</td>
<td>68.0</td>
</tr>
</tbody>
</table>

A crystal was then grown with 2.0 at.% Ce in a 10.0% alumina rich melt (the highest Ce and alumina rich melt that can be grown well) under otherwise identical growth conditions. As determined in our previous work,\(^{(27)}\) higher Ce concentrations also led to reduced UV luminescence and increased visible emission through improved competition between Ce and $\text{Y}_{\text{Al}}^{3+}$ luminescence centers. If $\text{Y}_{\text{Al}}^{3+}$ defects are in fact reduced in an alumina rich melt, then there is no reason the effects cannot be cumulative and result in further reduced UV emission and further increased visible emission.

When tested on a PMT and PD, this is exactly what was observed. The 2.0 at.% Ce sample is included in Figure 4.11, and showed further improvement in resolution on a PD ($7.6 \pm 0.05\%$) and degradation on a PMT ($11.1 \pm 0.08\%$). A pulser was used to decouple true energy
resolution from the electronic noise inherent in Si-PIN PD’s and is described elsewhere.\(^{(27)}\) The true energy resolution with noise subtracted was calculated to 5.04 ± 0.07%.

The scintillation lifetime data was also measured and shown in Figure 4.12 where the short decay component was reduced to 84.7 ± 0.5 ns.

![Figure 4.12: Lifetimes along with the 2.0 at.% Ce:YAG sample grown from a 10.0 at.% alumina rich melt. Increased Ce further improves the lifetimes seen earlier.](image)

As seen here and confirmed in \((27)\), growth of Ce:YAG with higher cerium mitigates the effect of luminescence centers. As the alumina concentration in the melt are increased, fewer yttrium antisite defects are formed as well. The result is an even shorter average decay time.

The lifetime and energy resolution measurements were verified by measuring the 2.0 at.% Ce, 10.0 at.% alumina rich sample on a Hamamatsu S8664-1010 avalanche photodiode (APD). Although the quantum efficiency of 75-85% from 450-800 nm is slightly less than the Hamamatsu S3590-18 PD, it does provide signal gain and thus has significantly less noise. The
results can be seen with the PD and PMT spectra in Figure 4.13 and Table 4.2, where the best spectrum utilizes a 0.75 µs shaping time, which is a result of the faster lifetime seen in Figure 4.12.

Table 4.2: Energy resolution comparison of the 2.0 at.% Ce, 10.0 at.% alumina rich sample.

<table>
<thead>
<tr>
<th>Energy Res. (%)</th>
<th>PMT</th>
<th>PD</th>
<th>APD</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Noise Reduction</td>
<td>11.1 ± 0.08</td>
<td>7.6 ± 0.05</td>
<td>5.9 ± 0.02</td>
</tr>
<tr>
<td>With Noise Reduction</td>
<td>11.1 ± 0.08</td>
<td>5.04 ± 0.07</td>
<td>5.5 ± 0.03</td>
</tr>
</tbody>
</table>

Figure 4.13: PMT, PD, and PMT results from the 2.0 at.% Ce, 10% alumina rich melt grown sample. The PD photopeak is visibly narrower than the PMT’s, even with the inherent noise of a Si-PIN PD. The APD photopeak is even narrower as noise is reduced. Such results indicate a significant gain in visible emission from alumina rich growth conditions.
A value of $5.9 \pm 0.02\% \ (5.5 \pm 0.03\% \text{ with noise subtraction})$ confirmed the PD results. These results are unmatched by any previous results on a PMT, PD, or even APD, for as grown Ce:YAG of this size.

4.8 Other Considerations

A final study was carried out to investigate the nature of change in $Y_{Al}^{3+}$ antisites. The 5.0 at.% yttria rich melt, 5.0 at.% alumina rich melt, and on stoichiometry melt grown samples underwent an oxygen anneal and aluminum in-diffusion process as described in (6). These samples were chosen because they had the most similar growth conditions experienced by the boule in (6), where small deviations in melt stoichiometry (toward yttria rich) were likely. Each of the samples demonstrated negligible differences in scintillation performance compared with the as grown results. This is in stark contrast to Solodovnikov et al (6) which demonstrated a remarkable increase in UV emission and decrease in visible emission due to a modification of antisite-vacancy complexes. Such differences in result demonstrate that the samples from this study were not altering antisite-vacancy complexes or their concentrations, but were in fact altering $Y_{Al}^{3+}$ antisite concentrations alone through adjustment of the growth conditions.

4.9 Conclusions

Without a doubt, Ce:YAG grown from a highly alumina rich melt works to reduce the concentration of $Y_{Al}^{3+}$ antisites along with their corresponding defect emission, and increase visible emission. A highly doped sample further mitigates their negative influence. Together, the two methods provide excellent results even with larger sample sizes.

In conclusion, Ce:YAG grown from an alumina rich melt appears to be an effective method of reducing $Y_{Al}^{3+}$ antisite concentrations and hence UV defect emission as seen by PL and lifetime data. This in turn increases visible light output and results in record performing
Ce:YAG scintillators on cost effective PD’s. Future work will investigate light yield in both the UV and visible spectrums in these and other sample. At present, an off stoichiometric alumina rich melt provides a new method for further improving visible light emission in Ce:YAG, and demonstrates potential as a cost effective scintillator in commercial systems.
References


CHAPTER 5

RHENIUM AS A CRUCIBLE MATERIAL:
GROWTH OF CE:YAG AND THE FUTURE OF HIGH TEMPERATURE

The Czochralski (CZ) method is by far the most popular method for the bulk growth of crystalline materials, including oxide single crystals used as lasers and scintillators. Unfortunately, iridium presents a limiting factor in traditional high temperature CZ growth (softens at ~2150°C), hindering practical research and development in the laser and scintillator field among higher temperature host materials. The Center for Materials Research has thus investigated rhenium, with a melt temperature of 3186°C, as a potential crucible material for high temperature CZ growths where a single crystal of cerium doped yttrium aluminum garnet (Ce:YAG, 1.0 at.% Ce) was successfully grown. The goal of the growth was not to push high temperature, but rather to highlight limitations or problem areas when growing a well-known material in rhenium, and to ultimately provide direction for the future of high temperature CZ growths.

5.1 History of Rhenium as a Crucible Material

The development of new laser and scintillator host material remains very active area of research in the energy field to this day. Though there is no shortage of yet to be tested compounds for laser and scintillator use as identified by Klintenberg et al (1) and Setyawan et al (2), there still remains significant hurdles to the discovery and adoption of new materials. One such hurdle is the fabrication of crystal systems at temperatures higher than iridium crucibles can tolerate, where iridium beings to soften and become unusable at temperatures higher than 2150°C. (3)
One particularly promising group of materials already discovered where melt temperature is a leading concern, are the rare earth doped sesquioxides of yttrium, scandium, and lutetium. All have higher thermal conductivities than yttrium aluminum garnet (YAG) (3; 4; 5; 6; 7; 8; 9) one of the most widespread solid state laser host materials. In addition, they have been shown to have maximum phonon energies much less than YAG, providing potential for much higher quantum efficiencies. (3; 5; 7) Taken together, they exhibit considerable promise as a new high power laser host material. However, with melt temperatures over 2400°C, (3; 4; 5; 6; 7; 8; 9) their fabrication has been met with only moderate success.

Various crystal growth methods have been experimented with for fabrication at these temperatures including micro-pulling-down, Verneuil, flux, floating zone, laser heated pedestal growth, and others. (3; 6; 7) Though such methods are adequate for materials discovery and characterization, they leave much to be desired in both crystal size and optical quality. (3; 6; 7) To facilitate the move to larger single crystals of the sesquioxides of scandium, yttrium, and lutetium both the Bridgeman (4) and Heat Exchanger Methods (HEM) (5) have also been used.

Bridgeman, though successful at creating boules of ~25 cm³, suffered from parasitic crystallization from the crucible walls creating polycrystalline boules. (4) Single crystal sections were therefore limited to less than 1 cm³ and contained significant stress. The heat exchanger method (HEM) has been used moderately more successfully, creating single crystals of Sc₂O₃ of several cm³ with less stress than Bridgeman. However, the grown boule was still polycrystalline, and the gas flow cooling was unable to draw enough heat from the system to crystallize the top region of the melt. (5) This indicates potentially significant problems to overcome when using HEM for crystal growth at sizes needed for commercialization.
Thus if promising high temperature materials are going to transition to widespread adoption, substantial advancement has to be undertaken in a growth method capable of high quality bulk production. By far the most popular crystal growth method with the best track record for cost effective, high optical quality, bulk production, is the CZ method. Though to facilitate growths at these temperatures, a new crucible material needs to be used. It should be capable of withstanding the elevated temperatures, and not react with an oxide melt.

Rhenium, with a melt temperature of 3180°C, (3; 4; 5; 6) becomes a logical choice for replacing iridium as a crucible material in CZ growths. Out of tests with molybdenum, tungsten, and carbon, it has been found to fulfill the above requirements in the best way. (5; 6; 7) Rhenium’s melt temperature of 3180°C is over 700°C higher than iridium, and it is significantly cheaper than iridium as of this writing. Furthermore, rhenium has been shown to not react with Al2O3 and the rare earth oxides, (3; 4; 5; 6; 7) making it an excellent candidate for high temperature oxide growth.

Unfortunately, rhenium will react with zirconium oxide and hafnium oxide above 2000°C, both of which compose the most common insulation materials for high temperature crystal growths. (6; 7) Therefore the first CZ growth attempts utilizing rhenium crucibles relied upon isolating the crucible from its surrounding insulation by hanging the crucible from above, which resulted in a poor thermal profile. (6; 7) In the case of growing the sesquioxides, less than ideal convection flows formed a w-shaped isotherm within the melt, causing the grown crystals to separate from the melt after only a few mm of growth. (6; 7) The resulting crystals were therefore less than a cubic cm.

The following research uses rhenium as a crucible material in the CZ method to further research in ultra-high temperature crystal growth. However, rather than begin with a high
temperature material, such as the sesquioxides, the following research focuses on the growth of a more common crystal; Ce:YAG. The goal is not to immediately push higher temperature growths, but to better understand rhenium’s behavior as a crucible material. The main points of interest were to see if it can grow Ce:YAG as effectively as iridium (without Re inclusions), and if thermal problem relating to insulation can be overcome, thus directing future work with rhenium crucibles by highlighting problem areas. Ultimately, these areas of interest proved successful.

5.2 Ce:YAG Growth in a Rhenium Crucible

Two YAG boules were grown during this study by the CZ method in a rhenium crucible. For both boules cerium concentrations were held to 1.0 at.% with respect to yttrium. The starting materials used were high purity yttria (Y$_2$O$_3$, 99.999%), alumina (Al$_2$O$_3$, 99.997%), and Ce$^{+4}$ oxide (CeO$_2$, 99.99%), where two charges were created for each growth. The powders were weighed out with 10 mg precision, (adjusting for inherent moisture content in the powders) to a target weight of 400 g, then ball milled using high purity (99.8%) alumina milling balls for 18 hours. After mixing, the powders were compressed in an isostatic press to ~20 kpsi, and then calcined at 1400ºC for 15 hours to make the final charge. Upon calcining, the charges lost an average of ~0.79% of their weight from moisture losses.

The dimensions of the rhenium crucible are 86 mm outside diameter, 60 mm high, with 2 mm wall and base thickness. Roughly 8 mm of space were in between the crucible wall and the zirconium oxide cylinder surrounding the crucible since no insulation could come into direct contact with the crucible itself. To create the base, the crucible sat on an iridium plate with a 6
mm hole in the center, which sat on a zirconium oxide disk with a 6 mm x 6 mm hole drilled in the center. It was insulated as seen in the Figure 5.1.

Figure 5.1: Diagram of the inner insulation cylinder.
The purpose of the hole was to improve upon the previous rhenium insulation designs, where a lack of proper insulation resulted in a poor thermal profile. A hole acting as a heat sink in the middle of the crucible facilitated a more ideal convection flow within the melt. The authors would like to acknowledge that a setup utilizing an Ir disk is unfeasible for higher temperature growths, as iridium will begin to melt. The design was for proof of concept only. Future rhenium growths can make use of more ideal insulation, and design decisions will be discussed in more detail later in the chapter.

First, one charge was melted down over the course of ~5 hours and then cooled. After this, a second like charge was added to the crucible to increase the melt volume to 800 g to improve heat flow and maintain stable flow patterns during growth. The crystal was pulled using a 6 mm diameter, (111) orientation, undoped YAG rod at 2 mm/hr to grow the cone of the crystal, then 1 mm/hr to grow the full diameter section. The crucible and melt were rotated at 6 RPM, while the pulling arm was not rotated. Weight was monitored through the pulling arm, and adjusted via a PID controller.

To account for rhenium’s propensity to oxidize at elevated temperatures, the growth atmosphere had to be closely controlled. Two different atmospheres were used in the following growths. During the first growth, an ultra-high purity (UHP) argon atmosphere was used. Unfortunately, an atmosphere of Argon alone was insufficient to control oxidation of the crucible, and the run was terminated early under quenching cooling conditions. Likely sources of oxygen during the growth were from off-gassing of the surrounding insulation at elevated temperatures, or from small leaks with the outside atmosphere, though the first instance is more likely.
The second growth used a mixture of 20% CO and 80% Ar. A strong reducing atmosphere of CO ensured that any small leak in the system, as well as oxides coming off the insulation, would be unable to significantly affect the rhenium crucible. The atmosphere facilitated a much longer growth time than the Ar only growth, and the resulting boule was over twice as long. Despite this, there was still some degree of rhenium deposition with the furnace chamber, and the run had to be terminated early again. Future work will focus on finding a more ideal atmosphere. It is possible that a CO/N\(_2\) based atmosphere would be more ideal, as N\(_2\) has been shown to limit glow discharge from rhenium. (5)

5.3 Sample Processing

A right cylinder was cut from the lower region of the boule of Ø10 mm by 10 mm thick, with a bordering Ø10 mm by 1 mm sample cut for absorption and transmission measurements. A thin sample assured cerium lines would not become saturated in optical absorption measurements. The region for coring was chosen from the most stress free as observed using crossed polarizers.

It was particularly interesting to see the difference in stress patterns between the boules during observation under crossed polarizers, or more specifically, the lack of stress pattern seen in the CO/Ar rhenium grown sample. The Ir grown sample displays the typical stress pattern (clover shape) in the core of the boule that is characteristic of many YAG growths. The rhenium grown sample on the other hand, had a much smaller region of stress and did not display the characteristic shape. If this pattern holds for future growths, rhenium presents itself as a potentially excellent crucible material for Ce:YAG growth to either reduce stress an increase boule yield, or to push the limits of Ce:YAG dopant incorporation and melt stoichiometry.
The cored region was then cut and mechanically polished to a final grit of 0.3 µm. Pictures of each sample in their as grown state can be seen in Figure 5.2 next to an Ir grown sample in 100 ppm O₂ balanced with N₂.

![Figure 5.2: From left to right: Ir grown sample in 100 ppm O₂ balanced N₂, Re grown sample in Ar, Re grown sample in CO/Ar. Each sample displays very consistent optical quality. The foggy region in the rightmost thin sample is due to saw damage that could not be polished away.](image)

It is interesting to note that both of the as grown samples pictured in Figure 1 display no discoloration from that of the iridium grown sample with 100 ppm O₂. In (4), the grown sesquioxide crystal came out black due to oxygen deficiency and color center formation, which disappeared after anneal. This is investigated further with additional optical measurements.

5.4 Optical Measurements

Once cut and polished an Ocean Optics PC2000® Spectrometer using a deuterium light source measured Ce intensity in the 1 mm thick samples. The measurement can be seen in Figure 5.3 below, compared to a Ce:YAG sample grown in iridium with 100 ppm oxygen balanced with nitrogen.
Figure 5.3: Absorption of each sample compared to an Ir grown sample. The Re grown CO/Ar and Ir grown sample display remarkable similarity in their as grown characteristics.

Each of the samples displays similar absorption characteristics. The sample grown in pure Ar seems to have slightly lower absorption than the following two samples; however, this is in line with where the sample was cut from the boule. Since the run had to be ended early due to rhenium oxidation, the cored section was taken from higher in the boule growth, and hence segregation can become a factor in Ce concentration measurements.

What is most interesting from the growth is that the CO/Ar growth has nearly identical absorption characteristics to the iridium grown sample, even in the as grown sample. Past work on YAG and other crystals show that when using a reducing atmosphere of H₂, significant oxygen depletion in the melt created enough color centers to visibly alter the color of the boule.
As in the case of the sesquioxide growth, the boule was able to return to standard optical properties after oxygen anneals.

A similar outcome was anticipated with CO/Ar, but the grown boule appeared of standard color, and absorption measurements confirm standard Ce behavior for the given Ce concentration. Therefore, growth in a CO/Ar atmosphere may prove to be a more economical method for crystal growth when a reducing atmosphere is needed, though better control of rhenium deposition needs to be found in future growths.

To confirm the measurement, Photoluminescence (PL) was measured using a Horiba Jobin Yvon Fluorolog-3® Spectrofluorometer with a deuterium arc lamp for excitation down to 180 nm. Analysis was performed with the 1 mm samples at 190 nm excitation at room temperature, where 190 nm light provided the brightest hard UV illumination. Each sample can be seen in

![Graph showing PL from rhenium and iridium grown samples.](image)

Figure 5.4: PL from rhenium and iridium grown samples. Again, there is excellent consistency.
PL confirms the absorption measurements, where both samples grown in the rhenium crucible display comparable luminescence characteristics to that of the iridium grown sample. Again, the sample that displays the greatest discrepancy is from the quenched Ar atmosphere run, were we would expect to see some difference based on the different growth parameters. Therefore, rhenium presents itself as a capable material for the bulk growth of high temperature oxides, as it is able to match the optical properties of iridium grown samples.

5.5 The Future of High Temperature (>2400°C) Oxide Growth

The crystal growths conducted in this research set out mainly to answer two specific questions. The first is whether or not rhenium could serve as a capable crucible material. In other words, could it be used to grow well studied crystal systems with the same optical properties and performance characteristics as crystal systems grown by traditionally used iridium? In this regard, rhenium has shown itself to be a capable material. The grown samples displayed produced Ce:YAG with nearly identical optical properties to that of iridium grown Ce:YAG. What was most surprising was the as grown optical properties of Ce:YAG in the CO/Ar reducing atmosphere, which displayed no signs of significant color center formation.

The second question was whether or not several of the high temperature issues discovered by other groups were capable of being overcome. The w-shaped isotherm was perhaps the largest issue experienced, and prevented the growth of the sesquioxides after less than 10 mm of growth. By utilizing a solid base disk upon which to set the crucible, and an appropriately sized heat sink in the middle of this disk, convection can be forced into a more ideal flow pattern, as evidenced by the successful growth of Ce:YAG. This is still without insulation in direct contact with the walls of the crucible.
As mentioned previously, the authors acknowledge that an Ir base disk is clearly not feasible for higher temperature crystal growths as it will begin to melt. The insulation design was chosen as a proof of concept only and was fabricated with one major constraint in mind: cost.

Ultimately, new insulation materials are going to be needed to facilitate true CZ production of high temperature crystal systems. However, such insulation is almost certainly not going to be cheap, and undoubtedly fabrication of specific parts to surround a crucible is going to be much more costly than a simple board or a disk. Therefore, insulation design was undertaken with available materials, but in what should be the most cost effective arrangement after the development of better high temperature insulation. Thus we were able to show that rhenium, with no nearby insulation on the crucible walls, could still facilitate bulk CZ growth by forcing strong convection currents within the melt.

The answer to higher temperature crystal growths then, is in new insulation materials which can replicate the current setup without posing an issue to the rhenium crucible. Some contenders that have shown promise recently are carbon based synfoams, which are capable of standing much higher temperature than standard oxide insulations. Depending on the specific makeup, they are capable of withstanding temperatures as high as 2600ºC.(10) A base disk made of a carbon based synfoam could be capable of replacing the iridium and zirconia base that was used in the previous growths. Such a setup should further the goal of higher temperature oxide crystal growth.
References


CHAPTER 6

CONCLUSION

With all of the research that has occurred with Ce:YAG, and in particular with the work that has gone into our CZ furnace and research that has been covered over the course of this thesis, it seems necessary to ask the following question: What are the most critical issues with Ce:YAG as a scintillator? The answer to this question lies in three parts, as it can really only be appropriately answered by considering the problems of the past, present, and future.

One of the most critical issues, and in my opinion the most significant issue, that faced Ce:YAG in its infancy was not necessarily a problem with Ce:YAG at all. This was a problem of photodetector selection for Ce:YAG’s emission wavelength, which persisted for well over a decade. Despite availability of PD’s, earlier units had worse quantum efficiency and higher noise than the products on the market today that were used in the thesis. This made PMT’s the much more attractive option for use with scintillators, including use with Ce:YAG. Though as mentioned in Chapter 1, most PMT’s have a spectral sensitivity that is heavily biased toward the UV/blue, yet it was the photodetector of choice for years when testing Ce:YAG which is supposed to emit in the yellow.

Since Ce:YAG has defect luminescence, much research going into improving Ce:YAG as a scintillator was held back by the use of PMT’s. If improvements were made that increased yellow emission at the expense of UV emission then a PMT may easily lead to conclusions that do not convey reality. Reports of maximum light yield at such low cerium doping suggest this may be the case. This was demonstrated in Chapter 3, where visible emission was increased at the expense of UV emission with greater Ce concentrations. Under such conditions there was
dramatic improvement on a modern PD with minimal improvements seen on a PMT.

With the problem of proper photodetector selection solved to a great extent, the present greatest problem with Ce:YAG is that of UV defect emission which is attributed to yttrium on aluminum antisites. Such parasitic emission is a killer for scintillators, as it prevents absorbed ionizing energy from reaching desired luminescence centers, thus reducing light yield at the desired wavelength. Also, depending on the distribution of these defects, it can lead to broadening of a full energy pulse as the emitted light experiences more fluctuation. Both can greatly hinder energy resolution.

Research was undertaken to alter yttrium antisites in Ce:YAG through the use of highly off stoichiometric melts. This may cause concern about creation of other defects within the material, but YAG has been found to preferentially form antisites over other intrinsic defects when grown in off stoichiometric conditions due to their lower formation energies. Additionally, aluminum antisites do not readily form as they have the highest formation energy of the antisite defects. By taking advantage of these characteristics, significant progress was made in removing yttrium antisites as seen in Chapter 4.

The accomplishment was achieved through the use of alumina rich melts of Ce:YAG (10.0 at.% Al rich), where decreased UV emission is attributed to a reduction of yttrium antisites. A reduction in yttrium antisites resulted in increased charge carrier recombination at Ce centers and correspondingly increased visible light emission while reducing UV defect emission. Despite the research resulting in record energy resolution for a Ce:YAG sample of the size demonstrated in Chapter 4 (5.04±0.07%), there is still room for further improvement as yttrium antisites were not removed from the system, only reduced. Though further improvements may
rely more on further improved growth methods, as a 10.0 at.% alumina rich melt presented the extent what could be grown well with acceptable levels of stress.

Thus the future of Ce:YAG growth may depend on further improved growth methods to either grow in higher alumina rich conditions, or to simply reduce stress and increase yield of presently grown alumina rich samples. Work was conducted on the growth of Ce:YAG in a rhenium crucible (as opposed to iridium crucible) as seen in Chapter 5. Though this work was aimed at investigating higher temperature growths, it did demonstrate rhenium’s ability to grow Ce:YAG effectively. This approach to using materials outside of those traditionally used may be the key to further improve Ce:YAG.
Standard very fast, 12-stage, 51 mm (2") round tube

<table>
<thead>
<tr>
<th>Applications</th>
<th>High and medium energy physics where the number of photons to be detected is very low and where utmost time characteristics are required. This tube features a good linearity, a very low background noise and extremely good time characteristics and good single electron spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>Window : Material : boasilicate glass</td>
</tr>
<tr>
<td></td>
<td>Photocathode : bi-alkali</td>
</tr>
<tr>
<td></td>
<td>Refr. index at 420 nm : 1.48</td>
</tr>
<tr>
<td></td>
<td>Multiplier : Structure : linear focused</td>
</tr>
<tr>
<td></td>
<td>Nb of stages : 12</td>
</tr>
<tr>
<td></td>
<td>Mass : 240 g</td>
</tr>
</tbody>
</table>

Photocathode characteristics

<table>
<thead>
<tr>
<th>Spectral range : 270-550 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum sensitivity at 420 nm : 70 μA/lm</td>
</tr>
<tr>
<td>Sensitivity : Luminous : 70 μA/lm</td>
</tr>
<tr>
<td>Blue : min. : 10 μA/lmF</td>
</tr>
<tr>
<td>Radiant, at 420 nm : typ. : 80 mA/W</td>
</tr>
</tbody>
</table>

Characteristics with voltage divider A

<table>
<thead>
<tr>
<th>Gain slope (vs supp. volt., log/log) : 3x10^7</th>
</tr>
</thead>
<tbody>
<tr>
<td>For a gain of : 9</td>
</tr>
<tr>
<td>Supply voltage : max. : 2800 V</td>
</tr>
<tr>
<td>min. : 1750 V</td>
</tr>
<tr>
<td>Anode dark current @ : max. : 100 nA</td>
</tr>
<tr>
<td>Background noise @ : max. : 2500 c/s</td>
</tr>
<tr>
<td>Single electron spectrum @ : resolution : typ. : 70 %</td>
</tr>
<tr>
<td>peak to valley ratio : typ. : 2.5 %</td>
</tr>
<tr>
<td>Pulse amplitude resolution for 137Cs @ : 7.2 %</td>
</tr>
<tr>
<td>Gain halved for a magnetic field of : perpendicular to axis &quot;n&quot; : 0.15 mT</td>
</tr>
<tr>
<td>parallel with axis &quot;n&quot; : 0.12 mT</td>
</tr>
</tbody>
</table>

Characteristics with voltage divider C @ :

<table>
<thead>
<tr>
<th>For a supply voltage of : 2500 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gain : max. : 4x10^7</td>
</tr>
<tr>
<td>3x10^6</td>
</tr>
<tr>
<td>Linearity (2%) of anode current up to : 70 mA</td>
</tr>
<tr>
<td>Anode pulse @ : Rise time : 1.5 ns</td>
</tr>
<tr>
<td>Duration at half height : 2.4 ns</td>
</tr>
<tr>
<td>Transit Time : 30 ns</td>
</tr>
<tr>
<td>Transit Time Spread : Standard deviation : 0.25 ns</td>
</tr>
<tr>
<td>Capacitance : anode to all : 7 pF</td>
</tr>
<tr>
<td>grid to K + D1 + D5 : 20 pF</td>
</tr>
</tbody>
</table>
Photomultiplier tubes

Product Specification

Typical gain curve

Typical spectral characteristics

Accessories

Socket: FE1120
Mu-metal shield: MS172
Voltage divider: VD124K/T
APPENDIX B

**photomultiplier tubes**

**XP2018B**

**product specification**

UV sensitive, 10-stage, 38 mm (1.5”) round tube

<table>
<thead>
<tr>
<th>Applications</th>
<th>Applications where a high sensitivity in the ultraviolet region of the spectrum is required, such as spectrophotometry.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>Window :</td>
</tr>
<tr>
<td></td>
<td>Photocathode : bi-alkali</td>
</tr>
<tr>
<td></td>
<td>Refr. index at 400 nm : 1.47 (1.5 at 250 nm)</td>
</tr>
<tr>
<td></td>
<td>Multiplier : Structure : linear focused</td>
</tr>
<tr>
<td></td>
<td>Nb of stages : 10</td>
</tr>
<tr>
<td></td>
<td>Mass : 78 g</td>
</tr>
</tbody>
</table>

Photocathode characteristics

<table>
<thead>
<tr>
<th>Spectral range :</th>
<th>160-650 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum sensitivity at : 420 nm</td>
<td></td>
</tr>
</tbody>
</table>

Sensitivity Ω:

- Luminous : typ. : 85 μA/Im
- Blue : min. : 9 typ. : 11 μA/ImF
- Radiant, at 420 nm : typ. : 85 mA/W

Characteristics with voltage divider A

- Gain slope (vs supp. volt., log/log) : 7.5
- For an anode blue sensitivity of : 7.5 A/ImF
- Supply voltage : max. : 1600 typ. : 1350 V
- min. : 1150
- Gain : 8x10^5
- Anode dark current Ω : max. : 20 typ. : 5 nA
- Pulse height resolution for 137Cs φ : 7.5 %
- Mean anode sensitivity deviation φ :
  - long term (16 h) : 1 %
  - after change of count rate : 1 %
  - vs temperature between 0 and +40 °C at 420 nm : ± 0.1 %/K
- Gain halved for a magnetic field :
  - perpendicular to axis “n” of : 0.35 mT
  - parallel to axis “n” of : 0.15 mT

Characteristics with voltage divider Ω : B

For a supply voltage of : 1700 1200 V
Gain : 6.7x10^5 5.0x10^5 mA
Linearity (2%) of anode current up to : 200 65 mA
Anode pulse Ω:
- Rise time : 2.5 3 ns
- Duration at half height : 6 7 ns
- Transit Time : 26 28 ns
- Capacitance : anode to all : 5 pF

128
Si PIN photodiode  
S3590-18/-19  
Large area Si PIN photodiode for scintillation counting

**Features**
- Suitable for coupling with blue scintillator (LSO, GSO, etc.)
- Internal quantum efficiency: 100% (λ=420 nm)
- S350C-10: bare chip type (without window)

**Applications**
- Radiation detection (PET, etc.)
- X-ray detection

---

### Absolute maximum ratings

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverse voltage</td>
<td>VR</td>
<td>100</td>
</tr>
<tr>
<td>Power dissipation</td>
<td>P</td>
<td>100 mW</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>Topr</td>
<td>-20 to +80 °C</td>
</tr>
<tr>
<td>Storage temperature</td>
<td>Tstg</td>
<td>-20 to +80 °C</td>
</tr>
</tbody>
</table>

### Electrical and optical characteristics (Ta=25 °C)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Condition</th>
<th>S3590-18</th>
<th>S3590-19</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral response range</td>
<td>λ</td>
<td></td>
<td>Min.</td>
<td>Typ.</td>
<td>Max.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>320 to</td>
<td>1100</td>
<td>320 to</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1100</td>
<td></td>
<td>1100</td>
</tr>
<tr>
<td>Peak sensitivity wavelength</td>
<td>λp</td>
<td></td>
<td>Min.</td>
<td>Typ.</td>
<td>Max.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.55</td>
<td>0.58</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.33</td>
<td>0.37</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Photo sensitivity</td>
<td>S</td>
<td>λ=420 nm (LSO)</td>
<td>Min.</td>
<td>Typ.</td>
<td>Max.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.55</td>
<td>0.58</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>λ=480 nm (BGO)</td>
<td>0.34</td>
<td>0.37</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>λ=546 nm (Csl)</td>
<td>0.38</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Short circuit current</td>
<td>Isc</td>
<td>100 kΩ</td>
<td>Min.</td>
<td>Typ.</td>
<td>Max.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>86</td>
<td>86</td>
</tr>
<tr>
<td>Dark current</td>
<td>Id</td>
<td>VR=70 V</td>
<td>Min.</td>
<td>Typ.</td>
<td>Max.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>Temperature coefficient of</td>
<td>Tc(Ω)</td>
<td>VR=70 V</td>
<td>Min.</td>
<td>Typ.</td>
<td>Max.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-3 dB</td>
<td>1.12</td>
<td>1.12</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RL=50 Ω</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cut-off frequency</td>
<td>fc</td>
<td>VR=70 V, -3 dB</td>
<td>Min.</td>
<td>Typ.</td>
<td>Max.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RL=50 Ω</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Terminal capacitance</td>
<td>Ct</td>
<td>Vn=70 V, f=1 MHz</td>
<td>Min.</td>
<td>Typ.</td>
<td>Max.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Noise equivalent power</td>
<td>NEP</td>
<td></td>
<td>Min.</td>
<td>Typ.</td>
<td>Max.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.8×10^-4</td>
<td>7.8×10^-4</td>
<td>W/Hz^1/2</td>
</tr>
</tbody>
</table>

---

130
## APPENDIX D

### PHOTODIODE

## Si APD

### S8664 series

Short wavelength type APD

### Features

- High sensitivity at visible range
- Low noise
- High gain
- Low capacitance

### Applications

- Low-light-level measurement
- Analytical equipment

---

### General ratings / Absolute maximum ratings

<table>
<thead>
<tr>
<th>Type No.</th>
<th>Dimensional outline /Window material *1</th>
<th>Package</th>
<th>Effective area size *2 active area size</th>
<th>Effective active area</th>
<th>Absolute maximum ratings</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(mm)</td>
<td>(mm²)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S8664-02K</td>
<td>(K)</td>
<td>TO-5</td>
<td>40.2</td>
<td>0.03</td>
<td>-20 to +60</td>
</tr>
<tr>
<td>S8664-05K</td>
<td>(K)</td>
<td>TO-5</td>
<td>40.5</td>
<td>0.10</td>
<td>-55 to +100</td>
</tr>
<tr>
<td>S8664-10K</td>
<td>(K)</td>
<td>TO-5</td>
<td>41.0</td>
<td>0.78</td>
<td>-55 to +100</td>
</tr>
<tr>
<td>S8664-20K</td>
<td>(K)</td>
<td>TO-5</td>
<td>42.0</td>
<td>3.14</td>
<td>-55 to +100</td>
</tr>
<tr>
<td>S8664-30K</td>
<td>(K)</td>
<td>TO-8</td>
<td>43.0</td>
<td>7.0</td>
<td>-20 to +80</td>
</tr>
<tr>
<td>S8664-50K</td>
<td>(K)</td>
<td>Ceramic</td>
<td>45.0</td>
<td>19.6</td>
<td>-20 to +80</td>
</tr>
<tr>
<td>S8664-55</td>
<td>(E)</td>
<td>Ceramic</td>
<td>6 x 5</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>S8664-1010</td>
<td>(E)</td>
<td>Ceramic</td>
<td>10 x 10</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

### Electrical and optical characteristics (Typ. Ta=25 °C, unless otherwise noted)

<table>
<thead>
<tr>
<th>Type No.</th>
<th>Spectral response range λ</th>
<th>Peak sensitivity λp</th>
<th>Photocurrent efficiency QE</th>
<th>Temperature coefficient of VBR</th>
<th>Dark current (Id)</th>
<th>Cut-off frequency (fc)</th>
<th>Terminal capacitance (Ct)</th>
<th>Excess Noise Index λ=420 nm</th>
<th>Gain M λ=420 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(nm)</td>
<td>(A/W)</td>
<td>(%)</td>
<td>(°C)</td>
<td>(V)</td>
<td>(MHz)</td>
<td>(pF)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S8664-02K</td>
<td>320 to 1000</td>
<td>600</td>
<td>0.24</td>
<td>70</td>
<td>0.1</td>
<td>700</td>
<td>0.3</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>S8664-05K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td>680</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S8664-10K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
<td>530</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S8664-20K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.6</td>
<td>280</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S8664-30K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>140</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S8664-50K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>60</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S8664-55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>40</td>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S8664-1010</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>11</td>
<td>270</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1: K: Borosilicate glass  E: Epoxy resin
*2: Area in which a typical gain can be obtained.
*3: Values measured at a gain listed in the characteristics table.
- S8664-02K/05K-10K/20K
- S8664-30K/50K
- S8664-55
- S8664-1010

HAMAMATSU PHOTONICS K.K., Solid State Division
1125-1 Ikojih-cho, Hamamatsu City, 435-6558 Japan, Telephone: (81) 053-434-3311, Fax: (81) 053-434-5184, www.hamamatsu.com
# APPENDIX E

## ZIRCONIA BOARDS, DISCS & CYLINDERS
### TYPE FBD

## PROPERTIES & CHARACTERISTICS

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density, g/cc (pcf)</td>
<td>1.4 (90)</td>
</tr>
<tr>
<td>Porosity, %</td>
<td>76</td>
</tr>
<tr>
<td>Melting Point, °C (°F)</td>
<td>2500 (4694)</td>
</tr>
<tr>
<td>Flexural Strength, (Parallel to Thickness) MPa (psi)</td>
<td>8.27 (1200)</td>
</tr>
<tr>
<td>Compressive Strength, (Parallel to Thickness), MPa (psi) @ 10% Compression</td>
<td>5.52 (800)</td>
</tr>
<tr>
<td>Outgassing in Vacuum</td>
<td>Nil</td>
</tr>
<tr>
<td>Dilatometric Softening Temperature, °C (°F) at 10psi</td>
<td>1400 (2552)</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient RT - 1400°C (2552°F) (Perpendicular to Thickness)</td>
<td>$10.7 \times 10^{-6}$°C ($6 \times 10^{-6}$°F)</td>
</tr>
<tr>
<td>Linear Shrinkage (Perpendicular to Thickness), %</td>
<td></td>
</tr>
<tr>
<td>1 hour at 1650°C (3002°F)</td>
<td>0.0</td>
</tr>
<tr>
<td>24 hours at 1650°C (3002°F)</td>
<td>0.9</td>
</tr>
<tr>
<td>1/2 hour at 2000°C (3632°F)</td>
<td>2</td>
</tr>
<tr>
<td>Thermal Conductivity, (Parallel to Thickness)</td>
<td></td>
</tr>
<tr>
<td>W/mK (BTU/hr ft² °F/inch) at 400°C (752°F)</td>
<td>0.24 (1.7)</td>
</tr>
<tr>
<td>W/mK (BTU/hr ft² °F/inch) at 800°C (1472°F)</td>
<td>0.26 (1.9)</td>
</tr>
<tr>
<td>W/mK (BTU/hr ft² °F/inch) at 1100°C (2012°F)</td>
<td>0.31 (2.1)</td>
</tr>
<tr>
<td>W/mK (BTU/hr ft² °F/inch) at 1400°C (2552°F)</td>
<td>0.33 (2.3)</td>
</tr>
<tr>
<td>W/mK (BTU/hr ft² °F/inch) at 1650°C (3002°F)</td>
<td>0.35 (2.5)</td>
</tr>
</tbody>
</table>
# ZIRCONIA FELT
## TYPE ZYF

### PROPERTIES & CHARACTERISTICS

<table>
<thead>
<tr>
<th></th>
<th>ZYF-50</th>
<th>ZYF-100</th>
<th>ZYF-150</th>
<th>ZYF-A2.13</th>
<th>ZYF-S.75G</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thickness, inch</strong></td>
<td>0.05 +/- 0.015</td>
<td>0.10 +/- 0.03</td>
<td>0.15 +/- 0.03</td>
<td>0.128 +/- 0.01</td>
<td>0.10 +/- 0.03</td>
</tr>
<tr>
<td><strong>Bulk Porosity</strong></td>
<td>96%</td>
<td>95%</td>
<td>94%</td>
<td>94%</td>
<td>88%</td>
</tr>
<tr>
<td><strong>Bulk Density Lb/Cubic Foot</strong></td>
<td>15</td>
<td>15</td>
<td>20</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td><strong>Tensile Strength Lb/inch width</strong></td>
<td>0.6</td>
<td>1.6</td>
<td>2.0</td>
<td>7.0</td>
<td>1.7</td>
</tr>
<tr>
<td><strong>Weight/Area Lb/SQFT</strong></td>
<td>0.07</td>
<td>0.13</td>
<td>0.23</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td><strong>Melting Point °F</strong></td>
<td>4700</td>
<td>4700</td>
<td>4700</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Compressive Strength PSI @ 10% Compression</strong></td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td><strong>Composition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wt% ZrO₂ + Y₂O₃</td>
<td>99+</td>
<td>99+</td>
<td>99+</td>
<td>97+</td>
<td>56+</td>
</tr>
<tr>
<td>Wt% Al₂O₃</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>2 +/- 1</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Wt% SiO₂</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>43</td>
</tr>
<tr>
<td><strong>Minimum wrapping diameter before breaking</strong></td>
<td>0.25 Inch</td>
<td>0.75 Inch</td>
<td>3 Inches</td>
<td>3 Feet</td>
<td>2 Inches</td>
</tr>
<tr>
<td><strong>Specific Heat BTU/LB-°F</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>@ 200 °F</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>@ 4300 °F</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Vapor Pressure @ 2500 °F</strong></td>
<td>8 x 10⁻¹² Torr</td>
<td>8 x 10⁻¹² Torr</td>
<td>8 x 10⁻¹² Torr</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>%Shrinkage after 1 hr. @ 3000°F isothermal soak</strong></td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>1.5</td>
<td>5</td>
</tr>
</tbody>
</table>

*1-2 wt% hafnia occurs naturally with zirconia and does not affect performance

---

**Zircar Zirconia, Inc.**  
PO Box 287  
Florida, NY 10921-0287  
USA  
Tel: 845-651-3040  
Fax: 845-651-0074  
email: sales@zircarzirconia.com  
web: www.zircarzirconia.com  
Product Data Bulletin C-AB  
March 2006  
Page 3 of 4
Coarse Grain Tubes

Zircoa coarse grain tubes are used primarily in induction heating applications. They are either pressed or cast, and composed of calcia, yttria or magnesia stabilized zirconia. By varying the composition, manufacturing method, grain size, mass and shape, we manufacture tubes to satisfy the unique requirements of your application. Please contact us to discuss your specific needs.

Composition 1651

Tubes made of composition 1651 are typically used for high temperature induction heated crystal growing furnaces. 1651 is composed of zirconia, stabilized with 3.5% calcia by weight. These tubes will survive repeated cycling from room temperature to 2000°C (3632°F), when used with Zircoa backup material.

Cast Materials

Furnaces lined with Zircoa's cast materials not only stand-up to extremely high temperatures, you can expect a service life measured in years! Zircoa has the shape capability to line and insulate your furnace, regardless of its shape or size.

Fired Cast Shapes

Zircoa's standard fired cast shapes, including brick and tongue and groove arch brick, are ideal for many furnace liner installations. Standard shapes are available in various sizes. Available in calcia and yttria stabilized zirconia compositions. Non-standard shapes can be made to customer specification. Please contact Zircoa for more information.

Zirconia Burner Blocks

Oxy-fuel firing for glass is becoming more common because it reduces NOx emissions, reduces capital expenditures and improves glass quality. When fuel oil is used, the life of typical AZS oxy-fuel burner blocks are less than six months. This is due to the high temperatures generated by the burner and the contaminants present in the oil. Zirconia burner blocks provide the added resistance to corrosion and withstand high temperatures found in this environment. Using zirconia, burner block life is extended to more than one year.
Physical Properties of Various Zirconia Compositions

<table>
<thead>
<tr>
<th>Composition</th>
<th>1968</th>
<th>1651</th>
<th>0872</th>
<th>0871</th>
<th>0890</th>
<th>2290</th>
<th>3004</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stabilizer</td>
<td>CaO</td>
<td>CaO</td>
<td>CaO</td>
<td>CaO</td>
<td>Y₂O₃</td>
<td>Y₂O₃</td>
<td>MgO</td>
</tr>
<tr>
<td>(calcia)</td>
<td>(calcia)</td>
<td>(calcia)</td>
<td>(calcia)</td>
<td>(yttria)</td>
<td>(yttria)</td>
<td>(magnesia)</td>
<td></td>
</tr>
<tr>
<td>Bulk Density (g/cm³)</td>
<td>3.3</td>
<td>4.2</td>
<td>4.1</td>
<td>3.0</td>
<td>4.0</td>
<td>4.5</td>
<td>4.6</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>35</td>
<td>25</td>
<td>30</td>
<td>40</td>
<td>29</td>
<td>23</td>
<td>16</td>
</tr>
<tr>
<td>Modulus of Rupture (psi)</td>
<td>450</td>
<td>2,400</td>
<td>1,100</td>
<td>800</td>
<td>1300</td>
<td>2400</td>
<td>3500</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion RT-1300°C (in/in/°C)</td>
<td>8.2</td>
<td>7.3</td>
<td>8.0</td>
<td>7.9</td>
<td>9.4</td>
<td>5.9</td>
<td>2.3</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m-°K) 800°C</td>
<td>0.68</td>
<td>1.2</td>
<td>1.2</td>
<td>0.52</td>
<td>1.0</td>
<td>1.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Refractory Backup (Thermal Insulation)

Extend the life of your furnace, and maintain tighter control over your furnace temperatures with Zircoa’s pre-sintered grog refractory backup.

**Zircoa Backup 1859** — Partially stabilized with magnesium and calcia. Available in -8+100, -8+14, -14+28, -28+48 and -48+100 Tyler mesh sizes.

**Zircoa Backup 3001** — Partially stabilized with magnesium. Available in -8+14 Tyler mesh size.

**Zircoa Backup 0125** — Monoclinic zirconia, not stabilized. Available in -8+14 Tyler mesh size.

**Zircoa Backup 10B** — Calcia stabilized bubble zirconia. Available in -10+30 Tyler mesh size.

**Zircoa Grog 1593** — Magnesia stabilized. Available in -14+28, -28+48, -48+100, -100+325 and -325 Tyler mesh sizes.

Zircoa-Cast™ Castable Refractory

Engineered for cast-in-place/fire-in-use shapes made of zirconia, intended for extremely high temperature environments. Composition 0871 has the lowest conductivity and density. All compositions are self-setting, two component (solid-liquid) systems, that harden hydraulically in a mold. Please contact Zircoa for specific recommendations.

Available Particle Size Distributions (Cast Materials)

<table>
<thead>
<tr>
<th>Zircoa-Cast</th>
<th>Coarsest Particle Size (Tyler Mesh)</th>
<th>Application/Cross Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>0871-LD</td>
<td>-8</td>
<td>&gt; 2.5cm (1&quot;)</td>
</tr>
<tr>
<td>0872-8D</td>
<td>-8</td>
<td>&gt; 2.5cm (1&quot;)</td>
</tr>
<tr>
<td>0873-28D</td>
<td>-28</td>
<td>0.6 to 2.5cm (1/4&quot; to 1&quot;)</td>
</tr>
<tr>
<td>0874-60D</td>
<td>-60</td>
<td>&lt; 0.6cm (1/4&quot;)</td>
</tr>
</tbody>
</table>

Ready to Assist You

Need more help, or have a specialized need? We are ready to put our 50+ years of experience to work for you. Please contact our application engineers to discuss your requirements.