Title
Synthesis, Consolidation, and Processing of Bulk Polycrystalline Transparent YAG, Ruby, and Over-Equilibrium Rare-Earth Doped Alumina for Photonic Applications

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Synthesis, Consolidation, and Processing of Bulk Polycrystalline Transparent YAG, Ruby, and Over-Equilibrium Rare-Earth Doped Alumina for Photonic Applications

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Mechanical Engineering

by

Elias Hank Penilla

August 2016

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Dedications

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To put it bluntly, not having it otherwise, as those of you that know me would agree, this dissertation and all of the work that has gone into it on my behalf would not have been possible without the efforts, sacrifices, and examples laid before me by my parents, my father Antonio Penilla and most especially my mother Lucia Penilla.

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ABSTRACT OF THE DISSERTATION

Synthesis, Consolidation, and Processing of Bulk Polycrystalline Transparent YAG, Ruby, and Over-Equilibrium Rare-Earth Doped Alumina for Photonic Applications

by

Elias Hank Penilla

Doctor of Philosophy, Graduate Program in Mechanical Engineering
University of California, Riverside, August 2016
Dr. Javier E. Garay, Chairperson

The past decade has seen significant advances in the development and improvements to high-energy laser technologies, with improvements coming from all directions, i.e. pumping technology, cavity design, cooling methods, and improved gain media quality, etc. Regardless, the continued development of high-energy lasers and the supporting technologies remains intense. From a materials development perspective, the need for gain media with superior optical, thermal, and mechanical properties is alluring because improvements in the materials properties often translate directly to increases in device performance. Advances in powder processing and sintering/consolidation techniques, in the past two decades have produced polycrystalline ceramics with the requisite densities, transparencies, and photoluminescence properties to be viable laser gain materials. In fact, the performance of some cubic (optically isotropic) ceramics now rival and even surpass their single-crystal counterparts.
In the first portion of this dissertation **Current Activated Pressure Assisted Densification (CAPAD)** is implemented to process and consolidate transparent bulk polycrystalline YAG and Ce:YAG ceramics via a simultaneous solid-state synthesis and densification route. The simultaneous reaction/densification during CAPAD processing results in improved densification rates and with reaction kinetics that are about 2 orders of magnitude higher when compared to traditional solid-state reaction pressureless sintering and that the higher reaction kinetics occurring during CAPAD result at much lower temperatures, (~600°C) compared to conventional reaction sintering.

In the second portion of this dissertation, the increased consolidation and reaction kinetics are leveraged to develop transparent bulk polycrystalline Cr:Al$_2$O$_3$ (ruby) and rare-earth (RE), RE:Al$_2$O$_3$ into viable laser gain materials. The advantages of Al$_2$O$_3$ as an optical gain media over state of the art gain materials such as YAG and laser glasses are significant; it has higher thermal conductivity, chemical inertness and higher mechanical toughness, all attributes that could lead to more stable, more powerful lasers. Despite these promising attributes, producing RE:Al$_2$O$_3$ ceramics with suitable functional properties for laser applications has steep processing challenges. RE:Al$_2$O$_3$ cannot be made using traditional equilibrium methods because the equilibrium solubility limits of REs in the Al$_2$O$_3$ is on the order of 10$^{-3}$ to 10$^{-4}$ %, not high enough to produce lasing (~10$^{-1}$ %, required). In addition, Al$_2$O$_3$ is birefringent which can cause severe scattering in ceramics. These obstacles are mitigated through careful powder and CAPAD processing in order to produce ceramics with fine grain sizes that mitigate
scattering and with rare-earth dopant concentrations as high as 0.5 at.% (RE:Al), orders of magnitude higher than previously reported. Results are presented that prove for the first time that bulk polycrystalline RE:Al₂O₃ is a viable laser gain media. A common theme of this work will be the interplay between material processing, the resultant material properties, and the development of optical devices using bulk polycrystalline transparent ceramics.
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Chapter 1: Simultaneous Synthesis and Densification of Transparent, Photoluminescent Bulk Polycrystalline Yttrium Aluminum Garnet (YAG) and Cerium Doped YAG (Ce:YAG) by Current Activated Pressure Assisted Densification (CAPAD)

Keywords: Spark Plasma Sintering (SPS); Optical Ceramics; YAG; Densification; Photoluminescent Ceramics; White Light Emission

1.1 Abstract

We report a method for the synthesis and processing of transparent bulk polycrystalline yttrium aluminum garnet (YAG) and photoluminescent Ce-doped YAG ceramics via solid-state reactive-Current Activated Pressure Assisted Densification (CAPAD). The process uses commercially available γ-Al₂O₃, Y₂O₃, and CeO₂ nanopowders. The nanopowders were reacted and densified simultaneously at temperatures between 850°C and 1550°C and at a maximum pressure of 105MPa. The solid-state reaction to phase pure YAG occurs in under 4 minutes at processing temperatures 1100°C which is significantly faster (on the order of tens of hours) and occurs at much lower temperatures (~600°C) compared to conventional reaction sintering. We found that the reaction significantly improves densification—the shrinkage rate of reaction-produced YAG was three times higher than that of YAG using pre-reacted powder. The Ce additions were found to retard the reaction driven shrinkage kinetics by a factor ~3, but are still faster (by a factor ~1.6) than those associated with direct densification (no synthesis). Densities >99% were achieved in both pure YAG and Ce doped YAG (Ce:YAG). Results of optical measurements show good
transparency in the visible and photoluminescence (PL) in the Ce:YAG. The PL peak is broad and appears white when excited using blue light confirming that the ceramics can be used in solid state lighting to produce white light.

1.2 Introduction

Polycrystalline ceramics are important materials for applications in demanding environments because they offer high hardness, high melting points and chemical stability. Moreover, their development as transparent materials has seen a recent resurgence in activity due to their viability as optical-structural materials\cite{1} as well as for light emitting applications such as laser host\cite{2}\cite{3} and efficient white light emission materials\cite{4}. Recently, polycrystalline ceramics have been developed to the point where they can compete with and in some cases exceed the performance of single crystals for light emitting applications\cite{2}\cite{5}–\cite{8}.

Arguably the most important oxide for luminescent applications is yttrium aluminum garnet, YAG. When doped with Nd it forms Nd:YAG, perhaps the most well known and used laser crystal. Ce:YAG is an important PL material used in scintillators\cite{9} and for white light production\cite{4} in a solid state lighting. Specifically, when Ce:YAG is excited by light in the blue range, it produces yellow light that when combined with the incident blue light appears bright white to the human eye. Most work on Ce:YAG has been on single crystal or thin films, but ceramic Ce:YAG has serious potential for large scale efficient white light production.
The seminal work of Akio Ikesue and coworkers can be credited with starting a movement towards the development and implementation of polycrystalline transparent YAG for laser applications\(^{10}\). Their work proposed the solid-state reaction of yttria and alumina powders via traditional high-temperature pressure-less sintering. To limit residual porosity, this process relies on extremely high temperatures, \(>1700^\circ\text{C}\) and hold times greater than 80-100 hours per batch. Recently, Guo et al., improved both the hold time requirements for processing to \(\sim 30\) hours per batch by the introduction of tetraethoxysilane (TEOS) as a sintering aide\(^{11}\). However, it has been shown that the presence of Si within the YAG lattice serves as an additional optical absorber, which leads to unwanted thermal generation.\(^{12}\) Regardless, of the use of sintering additives, these processing times and temperatures are quite extensive and can be improved upon.

A technique that has been extensively used to lower the processing temperatures and times is the Current Activated Pressure Assisted Densification (CAPAD), otherwise known as Spark Plasma Sintering (SPS)\(^{13}\). CAPAD has been previously used to densify YAG. In particular, direct densification of pre-reacted YAG nanopowders was conducted by Chaim et al.\(^{14}\) without sintering additives and by Dariel et al. with LiF as a sintering additive\(^{15}\) \([18]\). They were able to densify YAG to optical transparency at temperatures \(\sim 1500^\circ\text{C}\) in a matter of 10 minutes. However, because their approach relies on the use of pre-reacted YAG nanopowder, it remains unclear
whether the solid-state reaction is viable under CAPAD conditions. Moreover we are not aware of any successful attempts of solid state doping of YAG via CAPAD.

Here we introduce a method for the solid state reaction/densification of undoped and Ce-doped YAG using CAPAD. We explore the effects of processing parameters on the densification and optical properties of YAG. In addition we examine the densification and synthesis kinetics of YAG, for which there is surprisingly little information available in the literature.

1.3 Experimental Materials and Methods

1.3.1 Powder Processing for Producing YAG and Ce:YAG

Commercial (Inframat Advanced Materials LLC, Manchester, CT, USA) nanocrystalline β-Al₂O₃ (99.99%), α-Al₂O₃ (99.85%), Y₂O₃ (99.95%), and CeO₂ (99.97%) powders with a reported and confirmed via TEM, (Figure 1.1) crystallite size of 20-50nm, 30-50nm, 30-40nm, and 50-80nm, respectively, were solid-state reacted and densified via the CAPAD technique for the production of transparent YAG and fluorescent Ce:YAG bulk polycrystalline ceramics. Pre-reacted YAG (99.0%) nanopowder, (MTI International, Richmond, CA) with a crystallite size of 75nm was directly was also densified via the CAPAD technique.
Figure 2.1: TEM micrographs of commercial (Inframat Advanced Materials LLC, Manchester, CT, USA) (a) Yttria (Y$_2$O$_3$), (b) γ-alumina (γ-Al$_2$O$_3$), and (c) ceria (CeO$_2$) starting nanopowders.

The phase purity of the starting powders were confirmed with x-ray diffraction (XRD) on a Bruker AXS D8 Advance X-Ray Diffractometer implementing a Cu Kα$_1$ ($\lambda = 1.54058$ Å) radiation operated at 40kV and 40mA and these results are reported in Figure 1.2.
Figure 1.2: XRD patterns of starting nanopowders prior and post mixing by ball milling. Square(s) denotes $\gamma$-Al$_2$O$_3$ peak(s), and circles denote Y$_2$O$_3$ peak(s).

The powders were weighed appropriately to satisfy stoichiometric considerations as follows,

$$5(Al_2O_3) + 3(Y_2O_3) \rightarrow 2(Y_3Al_5O_{12}),$$  \hspace{1cm} (1.1)

for the synthesis of pure YAG phase. For doped samples, appropriate additional weights of CeO$_2$ such that the Ce content ranged from 1-3 at.% for the synthesis of Ce:YAG. These dopant concentrations were chosen in order to systematically study the effect of dopant concentration on the reaction and densification kinetics.

The weighed powders were mixed in a mortar to achieve satisfactory macroscopic mixing of the reagents, then to achieve the requisite microscopic mixing, these powders were low energy ball milled in a glass container with 8 mol% yttria stabilized zirconia (8YSZ) grinding media. The powders were milled dry with a 20:1 ball
weight to powder weight ratio. To prevent glass and zirconia contamination, ball milling was conducted with macroscopically mixed powder for 3 hours with corresponding media at a 60:1 ratio to coat the container walls and media with reagent powder. After the coating procedure, new reagents were introduced and milled for 12 hours. The mixed powders were removed from the jar, sieved and stored dry until processed.

For the purposes of this work, low energy ball milling was selected and implemented to achieve requisite mixing of the starting solid reactants, i.e. the breaking and redistribution of soft agglomerates without altering the crystal structure of the starting powder. Simply, the ball milling parameters were chosen such that no chemical reaction/alloying was detected with XRD. As can be seen from the XRD of the starting powders prior and after ball milling in Figure 1.2, the ball milling did not induce phase changes in the starting powders, nor were any chemical reactions evident.

1.3.2 CAPAD Processing of YAG and Ce:YAG

The mixed powders were processed via the CAPAD technique. For the production of all of the samples for this work, 1.2500g±0.0001g of powder was poured into a graphite die with an inner diameter of 19 mm and secured between two graphite punches of the same outer diameter. The die, plunger, and powder set were placed into the CAPAD, (Figure 1.3), and secured between two graphite spacers and copper electrodes, all contained within a vacuum chamber. A maximum vacuum of $1 \times 10^{-3}$ Torr was achieved in all cases.
A custom constructed CAPAD apparatus that has been described previously\textsuperscript{[13]} was used. Briefly, the vacuum chamber, electrode, spacer, is contained within a load cell controlled twin ball screw h-frame Instron mechanical testing system (Instron 5584) capable of producing loads of up to 150kN. In all cases the mixed powder was pre-pressed at 70 MPa for 1 minute in order to create a green body. The green pellet was subsequently subjected to an applied compressive load, which was linearly increased to its maximum value of 105MPa over a time interval of 3 minutes and held constant throughout until the maximum temperature set-point was achieved; upon reaching the
temperature set-point the load was linearly reduced to 70 MPa over 1 minute and held constant until the end of processing, whereby the load was released.

Simultaneously with the aforementioned load parameters, the green pellet was heated to high temperature(s) by passing a current through the die assembly, thus creating joule heating. Samples were produced at 1400°C, 1450°C, 1500°C, and 1550°C respectively, with a heating rate ~200°C/min, and held at these temperatures for 10 minutes.

It has been found that the reaction and densification are strongly coupled to the processing temperature. In order to determine the true sample contraction $\Delta L_{Tr}$, during processing, CAPAD experiments were conducted under identical heating and load profiles with and without nanopowder inserted within the graphite die/plunger assembly. For those experiments with nanopowder we refer to the extension data as the total system extension, $\Delta L_{Tot}$. The “blank die” experiments allow us to determine the true total system compliance, denoted as $\Delta L_{Com}$, by subtracting the true total system compliance from the true total system extension we are able to ascertain true sample contraction $\Delta L_{Tr}$:

$$\Delta L_{Tr} = \Delta L_{Tot} - \Delta L_{Com}$$ (1.2)

The normalized true sample contraction $N(\Delta L_{Tr})$ can then be calculated as:

$$N(\Delta L_{Tr}) = (\Delta L_{Tot}) / L_{\text{max}}$$ (1.3)

where $L_{\text{max}}$ is the maximum extension value. In order to elucidate the solid-state reaction and densification mechanisms, a series of truncated experiments were
performed under the same heating conditions. Experiments were truncated at 235s, 240s, 250s, 280s, 300s, and 320s to elucidate the kinetics occurring immediately prior to and during two extension contractions as discussed below.

### 1.3.3 Microstructural and Optical Characterization of YAG and Ce:YAG

The processed samples were then removed from the CAPAD and mechanically polished when possible. The chemical phase of the processed samples was characterized via the implementation of non-destructive XRD under the same conditions as conducted for the starting powders as denoted above. Additionally, phase purity and homogeneity was also investigated upon polished samples with Back-Scattered Electron (BSE) Microscopy within a Phillips XL-30 Field-Emission Scanning Electron Microscope (FE-SEM). The microstructure of fracture surfaces was characterized by FE-SEM, utilizing secondary electron detection.

The optical properties, namely the reflectance, absorption, and transmission, of the translucent and transparent processed samples were quantitatively ascertained for the UV-VIS portion of the spectrum via the implementation of a modified double integrating sphere technique. In particular, the classic double integrating sphere apparatus was modified by substituting an integrating cylinder for the second integrating sphere, and this set-up is depicted in **Figure 1.4**. All samples measured had a thickness of 0.9mm.
The light source consisted of a Q-Switched, Nd:YAG laser coupled to an Optical Parametric Oscillator (OPO), capable of emitting 9 ns laser pulses at wavelengths spanning from 355 to 2300 nm at a repetition rate of 10 Hz. The experiments were carried out at wavelengths of 420, 532, 709 and 1064 nm. The energy in each laser pulse was $1 \pm 0.3$ mJ; this energy value was selected because it was appropriate for the experiments as it did not cause ablation of the samples with the unfocused beam. In order to adequately resolve the light pulses from the nanosecond laser, photodiodes with a 1 ns time response (DET10A, Thorlabs) were used.

The specimen to be tested was placed in the posterior port of the integrating sphere and precisely aligned normal to the incident beam. The beam splitter
transmission and reflection were measured for each \( \lambda \); it transmits 98% and reflects 2% of the incident light. The laser energy incident on the sample was monitored an energy meter, EM1. The reflected light from the sample collected by the sphere was monitored by PD2, which was previously calibrated against EM1. The total sample transmission was collected by the integrating cylinder and measured via photodiode 1, PD1, which was previously calibrated against EM1.

Photoluminescent data were taken on a Horiba Spex Fluorolog 3 Spectrophotometer system using a tungsten deuterium lamp with monochromators as a light source. All measurements were taken in front face mode on polished bulk samples. Excitation scans were taken between \( \lambda = 280 \text{nm} \) and \( \lambda = 530 \text{nm} \) with the monitoring sample emission at \( \lambda = 550 \text{nm} \) and this allowed the determination of the pumping bands. Emission scans were taken between \( \lambda = 485 \text{nm} \) and \( \lambda = 680 \text{nm} \) with the pumping wavelength \( \lambda_p = 465 \text{nm} \) as it was determined to be the most efficient pumping wavelength from the excitation spectra. These results will be discussed in detail below. All measurements were taken with an integration time of 1s per nanometer.

1.4 Results and Discussion

1.4.1 Reaction and Densification of Pure YAG

Figure 1.5 plots the results of the contraction profiles for YAG densified via CAPAD; the YAG directly densified from commercial pre-reacted YAG nanopowder along with solid-state reacted (SSR) YAG produced using two different forms of alumina,
Figure 1.5: (a) Extension profile comparisons for solid-state reacted (SSR) YAG produced with $\gamma$- and $\alpha$-$\text{Al}_2\text{O}_3$, and directly densified YAG from pre-reacted nanopowder. The curves were calculated using measured extension data and Eq. (3). The temperature profiles are plotted on the same graph. (b) Typical extension profile for un-doped solid-state reacted YAG indicating times for truncated experiments.
γ-Al₂O₃ and α-Al₂O₃. Contraction in these experiments can be caused by pure densification (elimination of pores) or by reaction of the constituents to form reactants. Examination of Figure 1.5a reveals that both the SSR γ-Al₂O₃ and α-Al₂O₃ YAG cases have steeper slopes than the YAG directly densified using pre-reacted powders suggesting that the simultaneous reaction/densification cause has faster contraction kinetics. In addition the pre-reacted densification profile shows only one contraction event while the solid-state reacted cases each show two major contraction events.

As displayed in Figure 1.5a, the production of YAG in the CAPAD via the solid-state chemical reaction route has a unique 2-step extension profile. That is, there are 2 regions of steep extension contraction with varying slopes, indicators of densification activated by 2 distinct mechanisms. The positive slopes in the extension profiles displayed in Figure 1.5a-b and Figure 1.8a at 225s and 275s are areas where the samples are thermally expanding in response to the increasing temperatures. The slopes become negative, i.e. sample contraction occurs when densification is activated and is outpacing thermal expansion. There are also significant differences in the γ-Al₂O₃ and γ-α-Al₂O₃ experiments. The γ-Al₂O₃ is much steeper (faster) contraction than the α-Al₂O₃.

It is well known that γ-Al₂O₃ is metastable[16] and upon exposure to elevated temperatures transforms to α-Al₂O₃. It has been shown using traditional pressureless sintering that this phase change occurs in the alumina system at T=1100°C[17]. Our experiments show the first major contraction occurring at in a temperature range of 850°C-1150 °C, therefore we believe first extension contraction is accelerated the γ-α
alumina phase change. Since the kinetics are accelerated using $\gamma$-$\text{Al}_2\text{O}_3$, we conclude that is the $\gamma$-$\alpha$ transition is ultimately better for YAG formation.

In order to better understand these two steep extensions in the $\gamma$-$\text{Al}_2\text{O}_3$ case a series of experiments were truncated at 235s, 240s, 250s, 280s, 300s, and 320s to elucidate the kinetics occurring immediately prior to and during two extension contractions as shown in Figure 1.5b.

Figure 1.6 plots the XRD profiles of the truncated experiments. Samples made at varying temperature with hold time are also included. In Figure 1.6 we can see that the increasing temperature activated the solid-state reaction between the alumina and yttria nanopowders. The XRD analysis indicates that at stop 1 at 235s and 850°C that no remaining reactants are detectable and that only yttrium aluminum perovskite (YAP, $\text{YAlO}_3$) and yttrium aluminum garnet (YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$) are present. By the middle of the first extension contraction, i.e. at stop 2 (240s and 1100°C), the XRD analysis indicates a complete transition to the desired YAG phase. The XRD analysis indicates that at maximum the reaction to phase pure YAG takes 240s and that a temperature of 1100°C
Figure 1.6: XRD profiles showing the effect of processing temperature on solid-state reaction for un-doped YAG. The standards for YAG (ICSD #16825) and YAP (ICSD #69529) are plotted as well. Square(s) denotes YAG peak(s) and circles denote YAP peak(s).

is sufficient to achieve the desired phase purity. All other samples produced at higher temperatures show YAG phase purity. Therefore, it is believed that the second extension contraction is associated with pure densification of the already reacted pure YAG and this will be discussed in further detail below.

The reaction times and temperatures that we observe are substantially lower than in the previously reported free-sintering case\[^{18}\] where the onset of YAP phase formation was observed at 1100°C and 1200°C was required for significant YAP formation. Formation of YAG also required much higher temperatures; the onset of YAG formation was observed at 1300°C with reaction to completion occurring at 1700°C. It is
also worth mentioning that the free sintering experiment durations were as long as 100 hours, whereas those here were less than 10 min.

The rate of reaction of YAG according to Eq. 1 should be:

$$\frac{2}{5} \frac{d[Y_3Al_5O_{12}]}{dt} = - \frac{d[Al_2O_3]}{dt} = - \frac{3}{5} \frac{d[Y_2O_3]}{dt},$$

(1.4)

where the brackets denote concentration. The XRD analysis we performed is insufficient to determine the concentrations accurately, but we can use the data to provide a bounded estimate of reaction rates. Assuming 2\textsuperscript{nd} order reaction kinetics since the solid-state reaction for YAG is dependent on the concentration of 2 first-order initial reactants, alumina and yttria as shown in equation 1, the integrated 2\textsuperscript{nd} order reaction rate constant $k$, is given by

$$k = \frac{0.3}{t} \times \left[ \frac{1}{[Y_3Al_5O_{12}]_f} - \frac{1}{[Y_3Al_5O_{12}]_i} \right],$$

(1.5)

where $t$ is the experiment time in seconds and $[Y_3Al_5O_{12}]_f$ and $[Y_3Al_5O_{12}]_i$ are the final and initial concentration of YAG. Assuming the existence of a minimal initial amount of YAG i.e. $[Y_3Al_5O_{12}]_i = 0.01$ and if we use the XRD detection limits (usually taken as 5%) as an upper bound, i.e. $[Y_3Al_5O_{12}]_f = 0.95$ at $t = 240$ s, which is the time to complete reaction from our XRD analysis (see Figure 1.6), this gives a rate constant of $k = -1 \times 10^{-1}$ s\textsuperscript{-1}. The free sintering work\textsuperscript{[18]} does not provide sufficient XRD data for the an accurate calculation of their rate constant, but by doing a similar bounded approximation, given that the reaction time for YAG in their work takes at least 4800s (but in actuality might take as much as tens of hours) gives a $k = -6 \times 10^{-3}$ s\textsuperscript{-1}. If we assume that their reaction to
completion takes at most 10 hours (10% of their total experiment time) this results in a rate constant $k = -8 \times 10^{-4}$s$^{-1}$. Thus it is quite remarkable that our reaction constants are conservatively 2-3 orders of magnitude higher especially since our reaction is taking place at 1100°C while the range of reaction in this previous work for YAG was 1300-1700°C.

The decreases in reaction time and temperature for our experiments are attributed to the increased diffusion kinetics associated with the CAPAD process and the use of nanopowders. The exact mechanisms are not known at this time, but likely due primarily to the pressure and heating rate.

Relative sample density vs. temperature for the un-doped samples (truncated experiments as well as those with holding times) are displayed in Figure 1.7.

Figure 1.7: Effect of CAPAD processing temperature on sample density.
As expected, these results show that as the temperature increases, the resultant sample density also increases. At 235s and 850°C the sample relative density approaches 73% and increases to >87% by 250s and 1150°C. This pronounced increase in density during the first extension contraction is attributed to reaction. Since the reaction to phase pure YAG is completed by the middle of the first extension contraction we propose that the second extension contraction is due to pure densification. This corresponds to the section in Figure 1.7 where the density increases from 94% relative density to ~98% relative density. The effect of holding time on the density is most evident between Stop 6 and the experiment at 1400°C with 10 minute hold, where the relative density increases from ~98% to >99%. The temperature increments from 1400°C to 1550°C did not discernibly increase the relative density as measured by the Archimedes method, as all of these samples were measured to have relative densities >99% and the samples likely have density differences lower than the resolution limit of the Archimedes method. However increased temperature did have an effect on optical properties as will be discussed below. Chaim et al.\textsuperscript{[14]}, attribute short processing times to enhanced surface diffusion in YAG densification; it is likely that a similar process is operative in our experiments.
1.4.2 Effect of Ce dopant on Reaction Kinetics and Densification

The effect of Ce addition on the extension profile is presented in Figure 2.8, where

![Figure 1.8: Effect of ceria dopant concentration on (a) sample contraction (densification) with the temperature profiles plotted on the same graph and (b) relative density of processed samples.](image-url)
normalized extension is plotted for pure YAG along with varying content of Ce additions. By analyzing the extension profile during experimentation with a variance in ceria content (Figure 1.8a) we are able to see that as Ce addition slows the first contractions in all cases. In addition, the degree of retardation increases with Ce contents 1-3 at.%.

However, it can also be noted that as the experiments approach 315s the contraction of all samples approach the same asymptotic value. This indicates that the samples reach a similar final density regardless of Ce content. This is easier to see in Figure 1.8b, where relative densities are plotted vs. Ce content for samples made with hold 10 min hold times. The densities of these samples are all above 98%. Also shown in Figure 1.8b is the density of samples truncated at 250s (stop 3) for samples with 0 and 3 at% Ce. At stop 3 (the end of the first major contraction) adding 3 at.% Ce causes a more than 10% decrease in density.

The slopes of the curves in Figure 1.8a are a measure of the effective strain rate of the materials. Effective strain rates were determined using this data by determining the instantaneous rate of change of the curves. Figure 1.9 shows the maximum strain rate for YAG samples produced with varying amount of Ce additions. A maximum effective strain rate of 0.043 s\(^{-1}\) was measured for YAG produced via the solid-state reaction route with no Ce addition. Under identical CAPAD conditions the maximum effective strain rate of commercial pre-reacted YAG powder was about about 3 times smaller (0.014 s\(^{-1}\)). The Ce content monotonically decreased the maximum effective
strains rate up to a factor of ~2, (0.024 s\(^{-1}\)) for reactively densified 3 at.% Ce:YAG. These are higher strain rates than typically observed in ceramic systems (especially at relatively low temperatures). High strain rates have been reported before in the CAPAD processing of ‘superplastic’ nanocomposites at low temperatures. Zhan et al. measured 1.1 ×10\(^{-2}\)\(^{[19]}\), which is about 4 times lower than the highest rate we observed. Besides the benefits of CAPAD which include high heating rates and possible current effects, it is likely that the simultaneous synthesis and densification causes the higher strain rates.

Addition of Ce affects reaction as well. XRD results for the set of truncated experiments similar to those performed in the un-doped case using Ce addition (3 at.%) are shown in Figure 1.10. In addition to truncated experiments at the beginning, middle,
Figure 1.10: XRD profiles of ceria doped (3%) samples processed under various conditions (truncated experiments and experiments with holding time), showing phase transition to Ce:YAG. The square(s) denote YAG peak(s), the triangles denote γ-alumina peak(s), and circles denote yttria peak(s).

and end of the first extension contraction i.e. at stops 1, 2, and 3 at 235s, 240, and 250s, we have also truncated the experiment at 220s, immediately prior to the initial extension contraction and we denote this experiment as Stop A. The XRD analysis indicates that the added ceria decreases the reactivity of the original nanopowder mixture. At stop A, at durations and temperatures where YAP and YAG previously existed there are now only peaks corresponding to the starting phases i.e. no indication of reaction onset. However, the effect of Ce seems to retard not inhibit reaction—by stop 3 where the first extension contraction completes, the peaks indicate a complete transition to YAG.
The decreased densification and kinetics in Ce doped samples is likely related to ceria additions decreasing reaction rates at grain/particle interfaces. Calculating the grain boundary volume ($V_{GB}$) in a our solid-state reacted YAG sample produced at Stop 2 (235 s and at $T = 1100^\circ$C), we find that $V_{GB} \sim 0.2\%$, assuming a grain boundary size of 1 nm and a measured grain size of 500 nm. Based on our sample density this corresponds to a grain boundary volume of $6 \times 10^{-4}$ cm$^3$. Since the ceria content ranges between 1-3 at.%, this corresponds to a volumetric content ranging between $9.5 \times 10^{-4}$ cm$^3$ and $2.9 \times 10^{-3}$ cm$^3$. These amounts are 1.5-4.5 greater than the grain boundary volume as calculated above, suggesting that it is possible that at these dopant concentrations there is enough ceria present to ‘coat’ all grains thus inhibiting diffusion and retarding the densification kinetics. Moreover, the non-linearity of the volumetric dopant concentrations also qualitatively explains the non-linearity in the densification retardation with increasing ceria content.

1.4.3 Optical Properties and YAG and Ce:YAG

Figure 1.11 shows pictures of the samples produced at 1450°C a) without a hold time (i.e. stop 6) and b) with a 10 minute hold time, as densified and with a post heat treatment in air at 950°C for 12 hours on top a transparency on top of a light table.
Figure 1.11: Pictures showing the effect of hold time and annealing on transparency for un-doped solid-state reacted YAG produced at 1450 °C (a) as densified without a hold time (i.e. stop 6), (b) as densified sample with a 10 min hold time, and (c) as densified sample with a 10 min hold time and with a post-densification heat treatment in air at 900 °C for 12 h. The pictures are taken on top of a transparency on a light table.

Some light transmittance is evident at Stop 6 with the text below clearly legible, although faintly. The transparency substantially increases with a 10 minute hold. This increased transparency is attributed to an increased density from ~98% relative density to >99% relative density as measured by the Archimedes method and reported earlier in Figure 1.7. In this regard, the sample processing temperature also affects the transparency. That is, as the density is increased with processing temperature so is the transparency.
The increases in the density can also be correlated to changes in the microstructure. Scanning electron micrographs of each sample produced at 1450°C without and with a 10 min hold are presented in Figure 1.12. The micrograph of the no hold experiment, i.e. stop 6, reveals a microstructure with residual porosity, while the micrograph corresponding to the experiment performed at 1450°C with a 10 minute hold reveals a microstructure with minimal residual porosity. In both cases the back-
scattered electron micrographs of the polished surfaces indicate a singular phase presence, which correlates with the above discussion of our XRD results.

Figure 1.13: Optical measurements of solid-state reacted YAG samples processed at varying temperatures. The symbols represent different wavelengths. (a) Reflectance vs. processing temperature and (b) transmittance vs. processing temperature.
It is clear that although each sample produced with a holding time of 10 minutes measures >99% relative density (Figure 1.7), the optical transparency is significantly increased with the temperature increments. This improvement can be quantitatively seen in Figure 1.13 where we report the total reflectance and transmission at various wavelengths for the samples produced with hold times between 1400°C and 1550°C.

The reflectance of the samples measured ranged between 10-12% (Figure 2.13a) with no dependence on processing temperature or wavelength. This is expected since the refractive index is not expected to change significantly with microstructure. In addition, it suggests that all samples were polished equally well. The transmittance, however, was found to be dependent on the incident wavelength and processing temperature. The transmission measurements Figure 1.13b, show that the samples have low transmission (<3%) at 420nm and 532nm, i.e. the absorption in the blue and green is high (>80%), and the samples transmittance is significantly increased to 25% at 709nm and as high as 55% at 1064nm.

As can also be seen, the produced samples are red/brown in color, although undoped YAG is theoretically colorless. One cause might be oxygen reduction of the samples. CAPAD processing produces highly reducing conditions. Oxygen vacancies can trap electrons and act as color centers; this situation has been observed in CAPAD processing of another oxide previously, in particular yttria stabilized zirconia\(^{[20]}\). Figure 1.11b shows the sample produced at 1450°C with a 10 minute hold as densified after polishing and Figure 1.11c displays this same sample after a post-heat treatment in air.
at 900°C for 12 hours. The aim of the annealing is to diffuse oxygen back into the sample. As can be seen, the sample color changes from the red/brown color to colorless.

Figure 1.14 depicts the samples produced with a varying cerium content ranging between 1-3 at.% pictured on a black surface. All of these samples were subjected to a post-densification heat-treatment in air at 900°C for 12 hrs. The relative densities of each sample is >98% as displayed in Figure 1.8b. It is evident that as the cerium content increases the sample homogeneity is decreased. This is attributed to an increase in residual porosity associated with the initial retardation of the densification kinetics. These small differences in residual porosity can also be seen qualitatively in scanning electron micrographs shown in Figure 1.15. As the ceria content increases there is an
increase in residual porosity. The increase in residual porosity also reduces the optical transparency. For all doped samples, we find the transmittance to be below 20% at 709nm and below 30% at 1064nm. Additionally, we observe near zero transmittance at 532nm and 420nm regardless of ceria content. We attribute this in part to the increased residual porosity, but also to an increased absorption cross-section directly associated
with the presence of Ce$^{3+}$ in the YAG, i.e. the dopant is responsible for photoluminescence. The excitation and emission spectra data are presented in Figure 1.16b-c and will be discussed further below. The back-scattered electron micrographs of the polished surfaces reveal a uniform phase distribution in all cases which is in agreement with the XRD data shown above. Additionally, it is shown by Bonnell and Brown [24], that the solubility limit of Ce in YAG is greater than 6 at.%, and that the Ce$^{3+}$

![Figure 1.16: PL results for Ce:YAG (a) picture of SSR densified 1 at.% Ce:YAG with blue laser ($\lambda = 465$ nm) incident on surface, (b) excitation scan for SSR densified 1–3 at.% Ce:YAG. Excitation scan performed by monitoring $\lambda = 550$ nm and (c) emission scan for SSR densified 1–3 at.% Ce:YAG. Emission scans were performed using a pumping wavelength of 465 nm.](image)
ion substitutes for $Y^{3+}$ in the dodecahedral site, and since we are investigating samples below this limit, the phase purity of our samples as indicated in the back-scattered electron micrographs in Figure 1.15 is in good agreement with their studies and further suggest that this is likely the state of the $Ce^{3+}$ in YAG.

Figure 1.16a depicts the solid-state reacted 1 at.% Ce:YAG sample with a blue laser ($\lambda = 465$nm) shone on its surface at normal incidence. As can be seen, a portion of the incident blue light is converted to white light upon hitting the sample, while a portion is unconverted and reflected. Figure 1.16b-c show the excitation and emission scans of the 1-3 at.% Ce:YAG. Note that in both plots, the intensity values for the 1 at.% Ce:YAG have been multiplied by an order of magnitude in order for ease of graphical representation. The excitation scans reveal that the doped samples have broad absorption peaks centers at 330nm and 465nm, with the latter being dominant. These absorptions originate from the $5d \leftarrow 4f$ transition of $Ce^{3+}$. The data also reveals that as the ceria content increases so does the absorption intensity, indicating larger amounts of doping within the YAG lattice. The emission scan conducted with $\lambda_p = 465$nm reveals the classic Ce:YAG broad emission peak centered at 530nm, explained by the $5d \rightarrow 4f$ transition of $Ce^{3+}$[4]. The full width half maximum value for the emission spectra was 89nm for the 1at.% Ce:YAG sample and 118nm for the 2-3at.% Ce:YAG samples. The appearance of white light emission is accomplished because of the broad band emission of the Ce:YAG in the blue, green, and red portions of the spectra, i.e. the mixing of these output wavelengths produces an apparent white output emission. The increase in the
broadness of the emission spectra indicates a higher degree of doping of ceria within the YAG lattice as well as higher output efficiency as the ceria content is increased. As with the excitation scans, the emission scans reveal increased photoluminescence intensity under equal excitation intensity with increased ceria content, further indication of increased ceria dopant within the YAG lattice. Additionally, no red or blue shifting was observed in the excitation and emission spectra. This indicates a similar crystal field environment for the Ce\(^{3+}\) present with the YAG, i.e. if the Ce\(^{3+}\) occupied sites other that the Y\(^{3+}\) site in YAG, the excitation and emission spectra would be shifted.

### 1.5 Summary

In summary, we present a successful method for synthesis and processing of transparent, (T≤55% at λ=1064nm), bulk polycrystalline yttrium aluminum garnet (YAG) and photoluminescent ceria-doped YAG ceramics via solid-state reactive-CAPAD of commercially available amorphous-like γ-Al\(_2\)O\(_3\), Y\(_2\)O\(_3\), and CeO\(_2\) nanopowders. The YAG produced with CAPAD from reactant powders displayed a unique two-step contraction profile; we believe the first is associated with the reaction/densification and second is pure densification (elimination of porosity). Reaction to phase pure YAG takes 240s at a temperature of 1100°C, resulting in a second order reaction rate constant of \(k=1 \times 10^{-1}\) s\(^{-1}\), 2 to 3 orders of magnitude higher than those calculated from previous works despite the lower temperatures used in this work. A maximum effective strain rate of 0.043 s\(^{-1}\) was measured for YAG produced via the solid-state reaction route versus a maximum
effective strain rate of 0.014 s\(^{-1}\) for directly densified YAG nanopowder under identical CAPAD conditions. The Ce additions caused a slowing of the shrinkage rates for reactively produced samples, but were still at least 1.6 times faster than those achieved via direct densification of pure YAG. We attribute the slowing of the shrinkage kinetics to a diminished surface diffusion associated with the volumetrically equivalent amount of ceria present in the grain boundary volume of the YAG. Regardless of the retardation, the solid state reaction led to high density phase-pure photoluminescent Ce:YAG with higher ceria concentrations yielding higher output intensity at 530nm under identical excitation conditions at 465nm. The additional ceria also improves the absorption at 465nm, the optimal pumping wavelength. While still requiring improvement to the optical properties of the resultant cerium-doped YAG, it is believed that this is the first report of doping of polycrystalline YAG produced via the CAPAD process. The PL YAG produced in this manner has potential to be used in solid state lighting applications.

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1.7 References


Chapter 2: The Role of Scattering and Absorption on the Optical Properties of Birefringent Polycrystalline Ceramics: Modeling and Experiments on Ruby (Cr:Al₂O₃)

Keywords: Transparent Ceramics, Light Absorption Model, Light Transmission Model, Current Activated Pressure Assisted Densification (CAPAD), Spark Plasma Sintering (SPS), Laser Ceramics.

2.1 Abstract

Light scattering due to birefringence has prevented the use of polycrystalline ceramics with anisotropic optical properties in applications such as laser gain media. However, continued development of processing technology has allowed for very low porosity and fine grains, significantly improving transparency and is paving the way for polycrystalline ceramics to be used in demanding optical applications. We present a method for producing highly transparent Cr³⁺ doped Al₂O₃ (ruby) using current activated pressure assisted densification (CAPAD). The one-step doping/densification process produces fine grained ceramics with well integrated (doped) Cr, resulting in good absorption and emission. In order to explain the light transmission properties, we extend the analytical model based on the Rayleigh-Gans-Debye (RGD) approximation that has been previously used for undoped alumina to include absorption. The model presented captures reflection, scattering and absorption phenomena in the ceramics. Comparison with measured transmission confirms that the model adequately describes the properties of polycrystalline ruby. In addition the measured emission spectra and
emission lifetime are found to be similar to single crystals, confirming the high optical quality of the ceramics.

2.2 Introduction

Interest in polycrystalline ceramic materials for optical applications has been increasing tremendously. Some of the drivers are that polycrystalline ceramics can be made more efficiently than single crystal counterparts, and they can be more homogeneously doped and often have better mechanical properties. Interest is far ranging and includes structural applications such as windows for harsh environments or transparent armor\cite{[1]}\cite{[2]} to functional applications such as light emission often for laser applications\cite{[3]}\cite{[4]}. The vast majority of successful demonstrations of ceramics with high transparency have been in materials with cubic symmetry and thus isotropic optical properties\cite{[1]}–\cite{[4]}. In isotropic ceramics, pores are the main detrimental defects since they efficiently scattering light due to the large refractive index mismatch between air, vacuum, etc., and that of the ceramic. On the other hand, in anisotropic ceramics transparency can be reduced even with no porosity present, since in a randomly oriented polycrystal, each grain can represent a discontinuity in refractive index due to the random orientation of the microstructure. Higher in-line transmission can be achieved in textureless polycrystals by producing birefringent ceramics with fine grain sizes\cite{[5]}.
Perhaps the most successful case of producing high transparency in anisotropic polycrystalline ceramics has been in $\text{Al}_2\text{O}_3$ with fine grain sizes\textsuperscript{[6]–\textsuperscript{[8]}. Two notable processing techniques are free sintering followed by hot isostatic pressing\textsuperscript{[7]}\textsuperscript{[8]} and current activated pressure assisted densification (CAPAD)\textsuperscript{[6]}. In order to understand the light transmission in alumina, Pecharromán\textsuperscript{[8]} \textit{et al.}, following a similar approach to the pioneering work of Apetz and Van Bruggen\textsuperscript{[7]}, applied the Rayleigh-Gans-Debye (RGD) approximation in order to analyze the optical transparency in alumina. Their model relates alumina microstructure (grain size and texture) to in-line transmission and is shown to approximate experimentally measured transmission in samples with fine grain sizes. The continued development of next generation anisotropic ceramics for light emitting applications\textsuperscript{[9]–\textsuperscript{[11]} could greatly benefit from an understanding of absorption by dopants. However, absorption effects on polycrystalline ceramics have not been well studied since it has proven difficult to fabricating highly transparent doped ceramics.

In this work we present experimental and simulation results on polycrystalline alumina doped with $\text{Cr}^{3+}$ (Ruby). We start by presenting a model that extends the scattering model approach of Apetz and Van Bruggen\textsuperscript{[7]} and Pecharromán \textit{et al.}\textsuperscript{[8]} to include absorption caused by electronic transition of dopant atoms. We then apply our model to ruby. Ruby is an excellent model system because the absorption properties have been well characterized in the literature a priori for single crystals because ruby single crystals were the basis of the first laser, and because chromium is known to dope easily onto the aluminum sublattice since chromia and alumina form a complete solid
solution\textsuperscript{[12]}. The processing procedure outlined here produces polycrystalline rubies with fine (sub-micron) grain sizes and high density resulting in good optical properties. We report the transparency and photoluminescent properties of polycrystalline ruby as a function of concentration. The transparency and absorption characteristics can be reasonably explained using our model. Moreover the photoluminescent (PL) lifetimes are very similar to single crystal counterparts.

2.3 Theoretical Background and Model Development

In general, the amount of light transmitted through a material depends on reflection, scattering and absorption such that the in-line transmission can be written:

\[
T(\lambda) = [1 - 2R]e^{-i(\kappa + \alpha)}
\]

where \(l\) is thickness of the ceramic, \(R\) is the reflectivity, \(\kappa\) is the scattering coefficient and \(\alpha\) is the absorption coefficient.

Pecharromán\textsuperscript{[8]} et al. applied the RGD approximation in order to analyze the effect of reflection and scattering on the optical transparency in alumina with fine grains. Their approach treats the birefringent grains (with refractive indices \(n_o, n_e\)) as spheres embedded in a matrix with an average refractive index, \(\bar{n}\). The RGD approximation is valid when the scattering sites are not very efficient scatterers because their refractive index is very similar to their surroundings. In alumina, the ordinary refractive index, perpendicular to the c-axis is \(n_o = 1.7628\) and the extraordinary index, parallel to the c-axis is \(n_e = 1.7556\) at 700 nm; therefore, \(\Delta n = 0.008\) is small relative to the average
refractive index $\bar{n} = 2/3n_o + 1/3n_e = 1.7604$. Their analysis provides the important result that the wavelength dependent in-line transmission, $T$ considering birefringence of the grains and accounting for reflection can be written as:

$$T(\lambda) = \left[1 - 2 \left(\frac{\bar{n} - 1}{\bar{n} + 1}\right)^2\right] e^{-i\kappa}$$  \hspace{1cm} (2.2)

where $\kappa$ for a uniaxial crystal structure (like alumina) can be written as:

$$\kappa = d \frac{6\pi^2}{\lambda^2} \Delta n^2 \chi$$  \hspace{1cm} (2.3)

where $d =$ maximum grain size and $\chi$ is a parameter that depends on the degree of texturing in the ceramic. If there is no texture, \textit{i.e.} the grains are randomly oriented, then $\chi = 0.28$. \textbf{Equations 2.2 and 2.3} can be used to link measured in-line transmission with the microstructure$^8$.

In materials with absorption centers such as Cr$^{3+}$ in ruby, the absorption must also be considered to understand the in-line transmission as suggested by \textbf{Equation 2.1}. We start by assuming that electron transitions centered around an absorption band energy, $E_o$, result in finite absorption lines that can be described using a line shape function, $g(E)$. This line-shape is related to the probability of a photon absorbed at a given energy. For our purposes it is convenient to write the line-shape as a function of $\lambda$ and $\lambda_o$ which can easily be done using the relation $\lambda = hc/E$ (where $c$ is the speed of light). In many crystals, including ruby, the absorption and emission lines are known to have a
Lorentzian shape due to thermal broadening at finite temperatures\textsuperscript{[13]}. Thus we can write the wavelength dependent line-shape function for a fixed temperature as:

\[ g(\lambda) = \left( \frac{(\Delta \lambda)^2}{4} \right) \left( \frac{\lambda - \lambda_o}{\Delta \lambda} \right) \left( 1 + \left( \frac{\lambda - \lambda_o}{\Delta \lambda} \right)^2 \right)^{-1} \] (2.4)

where \( \Delta \lambda \) is the full width of the line at half the maximum value. We can account for the magnitude of the absorption caused by a finite number of absorbing sites using the absorption coefficient \( \alpha \) with units [cm\(^{-1}\)] which depends on the absorption cross section \( \mu \) [cm\(^2\)] and the volumetric concentration of absorbing ions, \( c \) [cm\(^{-3}\)] such that \( \alpha = \mu c \). The

![Diagram](image)

**Figure 2.1:** Schematic depicting the relationship between, \( c, \lambda, \alpha \) and the lineshape function \( g(\lambda) \) centered around \( \lambda_o \).
absorption cross section provides a measure of the strength of the absorption due to a particular transition. Figure 2.1 shows the relationship between $c$ and $\mu$ and the line-shape function $g(\lambda)$ centered around $\lambda_o$. Since each dopant element can have multiple transitions that cause absorption, the total absorption through a material depends on the total number of transitions, $j$, that cause absorption lines, $L_{\text{abs}}$:

$$L_{\text{abs}} = \sum_{i=1}^{j} g_i(\lambda) \alpha_i = \sum_{i=1}^{j} g_i(\lambda) c_i \mu_i$$

(2.5)

Similarly to the refractive index, crystals with anisotropic symmetry have direction dependent absorption properties. In this case we can use an average cross section, $\overline{\mu}$ which for uniaxial symmetry is:

$$\overline{\mu} = \frac{2}{3} \mu_o + \frac{1}{3} \mu_e$$

(2.6)

Combining Equations 2.1-2.6 gives the in-line transmission considering losses by reflection, scattering and absorption as:

$$T(\lambda) = \left[1 - 2 \left(\frac{\overline{\mu} - 1}{\overline{\mu} + 1}\right)^2\right] \exp \left[ -l \left( \kappa + \sum_{i=1}^{j} g_i(\lambda) c_i \overline{\mu}_i \right) \right]$$

(2.7)

Equation 2.7 is a simple analytical expression that can be applied to a birefringent polycrystalline ceramic with multiple anisotropic absorption lines.

We can apply Equation 2.7 to ruby by considering the energy levels of ruby that fall within our range of interest which is the visible and near infrared (near-IR). The energy levels can be found using the Tanabe-Sugano energy level diagram shown in Figure 2.2, which shows the splitting if the $\text{Cr}^{3+}$ free ion levels (shown on the left) in an octahedral
crystal field as the ratio of crystal field strength to interelectronic interaction (measured in Dq/B units) increases. The solid vertical black line corresponds to Dq/B = 2.8 for ruby where B = 918 cm^{-1} and the intersection of the energy level with this line demarcates the expected energy levels for ruby\textsuperscript{[14]}. We see that there are five absorption lines in our range of interest, corresponding to \(4A_{2g} \rightarrow 4T_{1g}, 4A_{2g} \rightarrow 2T_{2g}, 4A_{2g} \rightarrow 4T_{2g}, 4A_{2g} \rightarrow 2T_{1g}, \) and \(4A_{2g} \rightarrow 2E_g.\) We will consider only the 3 dominant bands, the violet (V), green (G) and red (R) centered at \(\lambda_o = 400, 555\) and 692/694 nm (R-lines), respectively. The violet \((4A_{2g} \rightarrow 2T_{2g})\) and green \((4A_{2g} \rightarrow 4T_{2g})\) transitions result in broad absorption bands, and the energy level corresponding to the transitions in the red is actually split into 2 \((4A_{2g} \rightarrow 2E_g)\) which are separated by 29 cm\(^{-1}\). We will consider this doublet as a single band. We will neglect the weak absorption lines corresponding to the transitions \(4A_{2g} \rightarrow 2T_{1g}\) and \(4A_{2g} \rightarrow 2T_{2g}\) (not observed). Thus we can re-write \textbf{Equation 2.7} for ruby as:

\[
T(\lambda) = \left[1 - 2 \left(\frac{\bar{n} - 1}{\bar{n} + 1}\right)^2\right] \exp\left[-l \left(\kappa + c (g_V \mu_V + g_G \mu_G + g_R \mu_R)\right)\right]
\]  

(3.8)
Figure 2.2: Tanabe-Sugano energy level diagram showing the splitting of the Cr$^{3+}$ free ion levels (shown on the left) in an octahedral crystal field. The solid vertical black line corresponds to Dq/B of 2.8 for ruby where B=918 cm$^{-1}$. The colored bands highlight the 3 dominant absorption bands (violet, green, and red) centered around $\lambda_0=400$, 555, and 692/694 nm, respectively. The red line is actually composed of 2 very closely spaced lines (separation is 29 cm$^{-1}$) but is treated as one line here. The red band is also the primary emission (R-lines) for ruby.

2.4 Experimental Materials and Methods

2.4.1 Powder Processing of Ruby

For this work, ultra-high purity alpha aluminum oxide, $\alpha$-Al$_2$O$_3$ (99.99% purity, TM-DAR, Taimei Chemicals, Nagano, Japan) was used as the starting powder to produce transparent polycrystalline alumina ceramics. The as-received powder will be referred to
as undoped for the purposes of this work. TEM images of the as-received TM_DAR power are presented in Figure 2.3. Chromium-doped (ruby) samples were produced by

mixing the undoped α-Al₂O₃ powder with specific quantities of chromium (III) nitrate nonahydrate, Cr(NO₃)₃·9H₂O, (99.99 % purity, Alfa Aesar, Ward Hill, MA, USA), such that the ratio of the chromium to aluminum ions were 0.25% and 0.5 atomic (at)%. The powders were mixed dry in an aluminum oxide mortar for ~20 minutes. The mortared powders were collected and processed via planetary ball milling for 3 hours using silicon nitride milling media and containment jars at 450 rpm and a 1:10 powder:ball weight
ratio. After milling, the powders were sieved to separate them from the milling media and stored dry until densification.

**2.4.2 CAPAD Processing of $\text{Al}_2\text{O}_3$ and Cr:Al$_2$O$_3$**

Current Activated Pressure Assisted Densification (CAPAD) was implemented to produce high density, fine grained transparent undoped alumina and ruby polycrystals. 1.2500 g ± 0.0001 g of powder was poured into a graphite die. The inner diameter of the die was 19 mm. The powders were secured between two graphite punches of the same outer diameter. The die, plunger, and powder set were placed into a custom constructed CAPAD apparatus that has been described previously $^{[15]}$. All CAPAD experiments were done in vacuum (maximum $1 \times 10^{-3}$ Torr).

The powders were pre-pressed at 70 MPa for 1 minute in order to create a green body. The green pellets were then heated to a maximum temperature of 1200$^\circ$C using a heating rate of approximately 300$^\circ$C/min via dc-joule heating of the graphite die and plunger set. The sample temperatures are measured with an optical pyrometer (Model IR GAP, Chino, Torrance, CA, USA), focused on a hole drilled in the graphite die located at the center point of the die height. The hold time at temperature was 10 min and total sample processing time was 14 minutes.

Simultaneously with this heating schedule, the green pellets were uniaxially loaded using a two-step loading schedule similar to one previously reported $^{[16]}$. The samples were subjected to a 30 kN load at a rate of 10 kN/min, resulting in an applied
stress of 106 MPa which was held constant for 1 min. Then the load was increased further to a total load of 40 kN, using the same load rate of 10 kNmin\(^{-1}\), resulting in a maximum applied stress of 141 MPa. This applied stress was held constant for the duration of sample consolidation.

2.4.3 Microstructural Characterization \(\text{Al}_2\text{O}_3\) & \(\text{Cr: Al}_2\text{O}_3\)

The relative density of all samples was measured using the Archimedes method. All images were acquired using a Phillips XL30 Field Emission Scanning Electron Microscope (FE-SEM) with secondary electron (SE) and back scattered electron (BSE) detection. Prior to SEM the surfaces were coated with a layer of platinum palladium using a Cressington 208 sample preparation system. The sputtering lasted for 10 s at a target to sample distance of 3.75 cm. Average grain sizes were measured from SEM fracture surfaces counting at least 250 grains per sample. These averages along with the standard deviation results are tabulated in Table 3.1.

2.4.4 UV-VIS-NIR Transmission Measurements

The densified samples were mechanically polished using diamond suspensions with increasingly finer crystallite sizes down to a final grit size of 0.5 \(\mu\)m. Optical transmission spectra were taken on a Varian Cary 50 UV-VIS spectrometer from 300 nm to 1050 nm. The bulk polished samples were placed at normal incidence to the beam path. The scans were obtained at a rate of 0.2 nm s\(^{-1}\).
2.4.5 Photoluminescence (PL) and Photoluminescence Lifetime Measurements

PL measurements were performed with an Oriel Corner Stone 260 1/4 m monochromator equipped with an Oriel 77341 photomultiplier tube operated in photon counting mode. Emission scans were taken between 580 and 800 nm, and emission was excited with a 470 nm cw diode laser. All measurements were taken in the backscattering geometry using a long pass cutoff filter to block laser scatter. For comparison, PL data were also taken on an Edinburgh Instruments Xe900 Spectrophotometer system using a xenon lamp as a light source, which is spectrally filtered using a monochromator. Measurements were taken with an integration time of 1 s nm\(^{-1}\). The spectrophotometer was calibrated for wavelength by measuring the PL emission of a commercial single crystal ruby under the same pumping wavelength.

The PL lifetimes of the densified samples and the commercial single crystal were taken by irradiating the samples with a frequency doubled Nd:YAG laser, 532 nm, with a 15 ns pulse width and 10 Hz repetition rate. The emission intensity at 694 nm as a function of time (fluorescence transient) was acquired with a Stanford Research Systems SR430 Multichannel Scaler/Averager. A single exponential fit of the resulting curves was used to extract the PL lifetime, where the lifetime is defined as the time required for the output signal intensity to decrease by a factor of 1/e.
2.5 Results and Discussion

A clear advantage of the CAPAD technique over traditional sintering is increased densification kinetics. Similar to our previous work on another oxide system\textsuperscript{14}, CAPAD processing with a two-step loading procedure resulted in highly dense (99+) samples in short processing times (< 15 min.). The average grain size of the undoped powder was 250 nm and the resulting ceramics had similar grain sizes (~350 nm) were similar for all dopant concentrations. The actual values are listed in Table 2.1. The similarity in grain sizes indicate no second phase grain boundary “pinning” effect during densification. We believe this is due to the relatively easy incorporation of Cr atoms into the Al\textsubscript{2}O\textsubscript{3} matrix; Cr\textsuperscript{3+} and Al\textsuperscript{3+} have similar ionic radii and thus Cr\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} form a complete solid solution\textsuperscript{12}. One potential drawback for CAPAD processing of ruby could be the reducing environment in which the sample is consolidated, i.e. the high temperature graphite environment, which has been shown to affect the oxidation state of the chromium dopant from Cr\textsuperscript{3+} to Cr\textsuperscript{2+}. The reduction of the oxidation state has been shown to causes dopant segregation and optical inactivity in single crystals\textsuperscript{17}. However, as will be discussed below we find no evidence of phase segregation in our samples via BSE SEM, nor any evidence of spectroscopic anomalies are present in the optical transmission spectra, PL emission, or PL lifetimes.
Table 2.1: Processing and optical data for the consolidated ruby samples. Cr concentrations are expressed in various units, at.%, wt.%, and atoms/cm$^3$. Our ceramics were processed according to at.% and atoms/cm$^3$ were used in calculations. The peak absorption coefficients were measured (see Figure 3.5) and the absorption cross section was obtained from the measured absorption coefficients using the relation $\mu = \alpha / c$.

Figure 2.4 shows pictures of CAPAD consolidated and polished samples with varying Cr dopant concentration a) 0 (undoped), b) 0.25at.% and c) 0.50 at.% (thickness $\sim$1.0mm) atop a light table with printed text behind the samples. The pictures qualitatively reveal the good optical transparency of the samples. The color change from a light pink to a red color is indicative of Cr absorption.
Figure 2.4: Picture of consolidated bulk polycrystalline a) Un-Doped $\alpha$-Al$_2$O$_3$, b) 0.25at.% Cr:$\alpha$-Al$_2$O$_3$, and c) 0.50at.% Cr:$\alpha$-Al$_2$O$_3$, ceramics atop printed text and a light table. The sample thickness is $\sim$ 1.0mm.

Figure 2.5 displays scanning electron micrographs of fractured surfaces using SE detection and also of the polished sample surfaces using SE and BSE detection of the same locations. The average grain size of the bulk consolidated samples were measured from these representative micrographs as described above and reported in Table 2.1.

The BSE micrographs in conjunction with the corresponding SE micrographs (Figure 2.5) do not show sign of phase separation (the corresponding SE micrographs of these polished surfaces were omitted for space consideration), confirming incorporation of Cr atoms into the Al$_2$O$_3$ lattice. Colored polycrystalline ruby has been successfully demonstrated before using the CAPAD process, although in this previous work, quantitative optical data was not presented$^{[18]}$.

Figure 2.6 shows the XRD profiles of the undoped alumina and polycrystalline ruby samples. The profiles are nearly identical to each other and to the ICSD $\alpha$-alumina standard, showing that there is no apparent texturing in the samples.
Figure 2.5: SEM Micrographs of Consolidated Bulk Polycrystalline Un-Doped α-Al₂O₃, 0.25at.% Cr:α-Al₂O₃, and 0.50at.% Cr:α-Al₂O₃ Ceramics.

Figure 2.7 shows measured transmission spectra in the visible and near-IR. The theoretical transmission of alumina considering reflection from two surfaces is 86% at 700 nm thus the transmission of these samples approach the theoretical transmission in the near-IR. The doped samples in display three absorption bands centered around λ = 400, 550, and 692 nm expected from the transitions of Cr³⁺ in the Al₂O₃ lattice (see Figure 2.2).
The appearance of the 3 absorption bands strongly corroborates the SEM results (Figure 2.5) that showed no phase separation. These absorption bands are indicative of a change in electronic environment caused by the incorporation of the Cr$^{3+}$ atoms in Al$_2$O$_3$. In order to check to see if the observed in-line transmission decreases with decreasing wavelength can be attributed to more efficient scattering of the anisotropic grains at lower wavelengths (see Equations 2.2 and 2.3), we plot the transmission data as a log($T$) vs. $1/\lambda^2$ in Figure 2.8. Indeed, the very good linear fit indicates that the transmission is dominated by birefringence scattering and not porosity. A linear relation of log($T$) vs. $1/\lambda^4$ would indicate pore scattering, which is not the case for this wavelength regime.
The measured transmission data from Figure 2.7 can be converted into absorption, $\alpha$ and scattering, $\kappa$ coefficients using Equations 2.1 and 2.3. Figure 2.9 plots $\alpha$ and $\kappa$ for the Cr doped and undoped Al$_2$O$_3$ ceramics. The grain sizes used in the calculations were the maximum (average plus standard deviation listed in Table 2.1) for the corresponding samples, they were $\sim$380 nm for the samples. A random orientation texture parameter, $\chi = 0.28$, and measured sample thickness $l = 1$ mm were used in the calculations for $\alpha$ and $\kappa$. The use of the random texture parameter $\chi = 0.28$ is justified by the XRD data (Figure 2.6) which showed no texturing. Using this methodology, the absorption
coefficients have been corrected for reflection and scattering. It should be noted that often in the literature only reflection is corrected for and potential loss from scattering is neglected. While this is a reasonable procedure for low porosity isotropic crystals, it is not a good approach for anisotropic ceramics. Not accounting for scattering leads to an overestimate of absorption in the samples. The absorption coefficients, $\alpha$, are listed for each of the samples in Table 2.1.

Figure 2.8: Log(T) vs. $1/\lambda^2$ for undoped and Cr doped alumina ceramics. The linear behavior suggests that the dominant scattering mechanism is scattering from birefringent grains.
The Cr concentrations of the samples can be used to calculate peak absorption cross sections which are also tabulated in Table 2.1 for the violet, green and red bands. The peak absorption cross sections for both concentrations agree within 2.3 % for the violet and green case which is a reasonable agreement. The peak absorption cross sections for the red band however, is 31% different. The reason for a large difference is likely to be the formation of Cr-Cr pairs. Similar results (a clear dependence on concentration for the broad green and violet bands but no clear dependence for the red lines) were observed by Dodd et al. 16.

Figure 2.9: Absorption coefficients, $\alpha$ for undoped and Cr doped alumina ceramics. The scattering coefficient, $\kappa$ is also shown.
They attribute this discrepancy to deviation from the Beer-Lambert law (Equation 2.1) at concentrations over 0.2 weight (wt) % of Cr$_2$O$_3$, which is the case for our ceramic samples. The measured PL spectra of the ceramics (discussed below) indicate formation of Cr-Cr pairs.

Absorption cross sections have been previously measured on single crystals; Dodd et al.[19] and Cronemeyer[20] measured $\mu_v$ and $\mu_c$ on single crystal rubies. Using Equation 2.6 we can convert the reported absorption cross section data into average absorption cross sections. The measurements by Dodd et al. find: $\bar{\mu}_v = 1.907 \times 10^{-19}$, $\bar{\mu}_c = 1.145 \times 10^{-19}$, and $\bar{\mu}_e = 1.098 \times 10^{-20}$ cm$^2$. These cross-sections are higher (~40%) than the measured values (Table 2.1). It should be noted that Cronemeyer[20] data differs from Dodd et al.[19] by as much as 80%. There could be several reasons for this discrepancy. It is possible that the concentration of Cr atoms contributing to absorption in our rubies is lower than expected. It is possible that the global concentration of Cr is correct, but some of the Cr atoms are in locations that do not contribute to absorption i.e. in interstitial sites or segregated at grain boundaries. The similarity of ionic radii between Al and Cr precludes the Cr from incorporating interstitially so we can neglect that possibility. The SEM results (Figure 2.5) show no sign of segregation so we can also exclude that possibility. It is more likely that some of the originally added Cr was lost during processing or it might still be a possibility that the oxidation state of the Cr ion has been affected from Cr$^{3+}$ to Cr$^{2+}$ by the processing[17], although this remains unlikely.
as the PL emission profiles and lifetimes match those of the single crystal variants with Cr$^{3+}$ oxidation state.

Figure 2.10: Comparison of calculated (Equation 3.8) and measured transmissions spectra for Cr doped alumina ceramics. Measured peak absorption cross sections (see Table 2.1) were used in calculations.

In Figure 2.10 we plot the results of the model (Equation 2.8) using our measured peak absorption cross sections (see Table 2.1) along with the measured transmission results. The grain sizes used in the calculations were the maximum (average plus high value listed in Table 2.1) for the corresponding samples. The other size and microstructural parameters were $l = 1$ mm and, $\chi = 0.28$. A comparison of the
model shows good agreement between model and experiment, for not only the undoped data (as was shown in Figure 2.8), but the two different dopant cases as well. It is possible that the agreement would be improved by using a Pekarian distribution rather than a Lorentzian distribution for the line shape function (**Equation 2.4**). However we have chosen to stay with the more commonly occurring Lorentzian distribution to keep the model more general.

![Emission spectra of Cr doped ceramics showing strong emission lines in the vicinity of 692 nm from the R-Lines. The inset shows a narrower wavelength range highlighting the N-lines indicative of Cr-Cr pair formation.](image)

**Figure 2.11:** Emission spectra of Cr doped ceramics showing strong emission lines in the vicinity of 692 nm from the R-Lines. The inset shows a narrower wavelength range highlighting the N-lines indicative of Cr-Cr pair formation.
Figure 2.11 shows emission spectra of our ceramic rubies. The intensities have been normalized and found to be very similar for both concentrations. The spectra clearly show the expected R-lines\textsuperscript{[13]} in the vicinity of 692 nm. The insert in the figure shows emission spectra for a narrower wavelength range in the vicinity of the N-lines of ruby. Both concentrations show peaks in this range which can be attributed to Cr-Cr.

![Lifetime measurement of R-line (\(k_{\text{o}}\%694\) nm) for polycrystalline ruby. The black line is measured data and the red line is an exponential fit (Equation 3.9) which yields \(\tau = 3.44\) ms.](image)

**Figure 2.12**: Lifetime measurement of R-line (\(k_{\text{o}}\%694\) nm) for polycrystalline ruby. The black line is measured data and the red line is an exponential fit (Equation 3.9) which yields \(\tau = 3.44\) ms.
pairs. The emission intensity of the 0.5 at% Cr:Al$_2$O$_3$ ceramic is higher as expected with for a higher global concentration of Cr. The PL spectra of ceramic ruby has been measured previously by Toyoda et al.$^{19}$ They concentrated on a wide range of dopant concentrations of Cr in non-transparent (fully opaque) ceramics. The results on our transparent ceramics results are similar to theirs at low dopant concentrations. **Figure 2.12** shows the fluorescence transient of the R1 line (694 nm) for our ceramic ruby. In order to get the characteristic lifetime ($\tau$), the experimental results have been fit to a familiar exponential decay expression as:

$$I = I_o + A \exp\left[\frac{-(t-t_o)}{\tau}\right]$$

(2.9)

where $I$, is intensity, $t$ is time and $I_o$, $t_o$ and $A$ are constants. The resulting lifetime is $\tau = 3.44$ ms, which is similar to that reported for single crystals$^{[13]}$. The long lifetimes of the important emission peak, similar to those of single crystals, are indicative of high quality of our ceramic rubies and indicate the dominant presence of Cr$^{3+}$ in our samples rather than the less desirable Cr$^{2+}$ incorporation.

**2.6: Summary**

In summary, we have presented a method for producing polycrystalline Cr doped and measured their optical properties in the visible and near-IR. This simultaneous reaction/densification procedure results in doping of Cr$^{3+}$ ions onto the Al sites in Al$_2$O$_3$. The ceramic rubies have good transparency and display well defined absorption peaks in
the visible as expected from the ruby energy diagram. They also display the characteristic emission in the R-lines (at 692 and 694 nm); the lifetime of these 694 nm emission is similar to single crystals. We have also presented an analytical model that takes into account the effects of reflection, scattering and absorption on transmission. The model explains our measured results well and can be used to extract absorption coefficients from polycrystalline ceramics accounting for scatter. This model is general and should be useful for analyzing scattering and emission in other anisotropic ceramics for demanding optical applications.

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2.8 References


Chapter 3: Blue-green Emission in Terbium-doped Alumina (Tb:Al₂O₃) Transparent Ceramics

Keywords: Transparent Alumina, Bulk Rare-Earth Doped Alumina, Non-Equilibrium Processing, Current Activated Pressure Assisted Densification (CAPAD), Spark Plasma Sintering (SPS), Laser Ceramics, High-Energy Lasers, Polycrystalline Gain Media

3.1 Abstract

Alumina (Al₂O₃) is one of the most versatile ceramics, utilized in an amazing range of structural and optical applications. In fact, chromium doped single crystal Al₂O₃ was the basis for the first laser. Today, most photoluminescent (PL) materials rely on rare earth (RE) rather than transition-metal dopants because RE doping produces greater efficiencies and lower lasing thresholds. RE-doped alumina could provide an extremely versatile PL ceramic, opening the door for a host of new applications and devices. However, producing transparent RE:Al₂O₃ suitable for PL applications is a major challenge due to the very low equilibrium solubility of RE (~10⁻³%) in Al₂O₃ in addition to alumina’s optical anisotropy. We present a method for successfully incorporating Tb³⁺ ions to a concentration of 0.5 at.% into a dense alumina matrix, achieving a transparent light emitting ceramic. Sub-micron alumina and nanometric RE-oxide powders were simultaneously densified and reacted using current-activated pressure-assisted densification (CAPAD) often called spark plasma sintering (SPS). These doped ceramics have a high transmission (~75% at 800 nm) and display PL peaks centered at 485 nm and 543 nm, characteristic of Tb³⁺ emission. Additionally, the luminescent lifetimes are long and compare favorably with lifetimes of other laser ceramics. The high transparencies
and PL properties of these ceramics have exciting prospects for high energy laser technology.

3.2 Introduction

Although functional transparent polycrystalline ceramics have been studied for decades\textsuperscript{[1][2]} their continued development as an alternate or replacement for single crystal optical materials remains intense\textsuperscript{[3]}. The allure is twofold, first polycrystalline ceramics are often more efficiently manufactured and second it is possible to fabricate bulk ceramics compositions that simply cannot be made as single crystals. The first impetus is exemplified by the development of polycrystalline neodymium doped yttrium aluminum garnet (Nd:YAG) to a point where they have lasing slope efficiencies on par with single crystal variants\textsuperscript{[4][5]}. The second incentive stems from the fact that single crystal manufacturing methods such as the Czochralski and Verneuil techniques are bound by thermodynamic equilibrium which limits possible crystal structures and dopant concentrations. On the other hand, certain polycrystalline ceramic preparation techniques offer the flexibility of producing compounds not dictated by equilibrium.

Of particular interest is current-activated pressure-assisted densification (CAPAD) that employs very high heating rates and thus can potentially operate far from equilibrium\textsuperscript{[6]}. One major driver for the search for single crystal replacement has been in finding laser host materials for tomorrow's high power lasers \textsuperscript{[7][8][9]}. Currently, the relatively low thermal conductivity of the state of the art host material, yttrium
aluminum garnet (YAG) is the bottleneck for the development of higher power and/or higher duty-cycle solid state lasers. This is because low thermal conductivity causes high thermal gradients in the material as it is pumped and consequentially degrades the beam quality. Thus the power deliverable by a laser directly scales with the thermal conductivity for a given pumping/cooling scheme. In response researchers have been working on developing gain materials with higher thermal conductivities than YAG, \([10][11]\) (YAG has thermal conductivities between 9 to 14 W m\(^{-1}\) K\(^{-1}\))\([12][13]\). Notable examples are Y\(_2\)O\(_3\)\([14]\) and Sc\(_2\)O\(_3\)\([14][15]\) which have been shown to have thermal conductivities \(\sim 17 \text{ W m}^{-1} \text{ K}^{-1}\) in polycrystalline form. An even greater improvement in thermal conductivity and therefore device power could be achieved by using alumina (Al\(_2\)O\(_3\)) as a rare earth host—alumina has a single crystal conductivity between 32 and 35 W m\(^{-1}\) K\(^{-1}\) at room temperature\([16]\), representing a possible doubling in the peak output power, duty cycle, or compactness of a laser system when comparing to state of the art lasing media.

There are several major hurdles to producing transparent polycrystalline alumina doped with rare earths (RE) for photonic functionalization. The first is that alumina has a hexagonal symmetry and is birefringent so that there is significant scatter at grain boundaries in polycrystalline materials. This problem can be solved by producing ceramics with relatively fine average grain size (AGS). Several researchers including the groups of Klimke\([17]\) and van Bruggen\([18]\) have demonstrated highly transparent polycrystalline Al\(_2\)O\(_3\) with sub-micrometer AGS. The second and more difficult problem
is the very low RE equilibrium solubility in alumina, which is $\sim 10^{-3}$ at.\%\cite{19}, a concentration too low for efficient light production—RE levels greater than 0.1 at.\% are typical in ruby\cite{20} and RE:YAG\cite{21} based devices. This requirement indicates that at least a 100 fold higher than equilibrium dopant concentration is needed to make a RE:Al$_2$O$_3$ ceramic a viable laser host material. The limitation imposed by processing under conditions dictated by thermodynamic equilibrium precludes the use of the single crystal growing, as well as traditional sintering techniques that are the standard for producing optical quality alumina ceramics\cite{22}.

In order to achieve the elusive goal of producing rare-earth doped alumina ceramics suitable for laser applications, a material processing technique is needed that can deliver the proper control of microstructure (fine grains and very low porosity), ensuring high transparency, and can operate out of thermodynamic equilibrium conditions, so that a higher functional level of RE-dopant concentration can be achieved. Here we present a method for the successful incorporation of Tb$^{3+}$ ions to a concentration as high as 0.5 at.\% relative to the Al$^{3+}$ ion, into a sub-micron highly dense alumina matrix, resulting in a transparent visible light emitting ceramic.

The transparencies of our Tb$^{3+}$ doped alumina (Tb:Al$_2$O$_3$) ceramics approach the single-crystal limit for alumina of $\sim 86\%$ and the dopant concentration of 0.5 at.\% represents a 500 fold improvement over the concentrations achievable by traditional techniques bound by thermodynamic equilibrium, surpassing the requisite metric for laser operation mentioned above by a factor of 5. Our method relies on the
simultaneous densification and reaction of sub-micron alumina powder along with rare earth oxides as a photoluminescent source using CAPAD. To the best of our knowledge, this is the first time a birefringent (non-cubic) polycrystalline oxide bulk ceramic has been shown to possess both high transparency and RE induced light emission properties. The high transparency and photoluminescent properties associated with the high RE-dopant concentration of our samples indicate that these materials are promising candidates for photonic applications such as laser host ceramics. In particular the higher thermal conductivity of these ceramics enables the doubling of peak power, duty cycle, or the compactness of the laser system can be doubled in comparison with state of the art laser host ceramics.

3.3 Experimental Materials and Methods

3.3.1 Powder Preparation

Commercially available aluminum oxide, α-Al₂O₃ (99.99% purity, TM-DAR, Taimei Chemicals, Japan) was processed as received (referred to as un-doped) as well as doped with Terbium Oxide, Tb₄O₇ (99.9% purity, Nanostructured & Amorphous Materials, Inc., USA). The powders were weighed to achieve a Tb doping level of 0.5 at.%. The powders were mixed for 12h by ball milling in a glass container. Ultra-High Purity (99.99% purity) water was used as a dispersant at a ratio of 10 grams total powder to 200 mL of UHP water. Alumina balls (99.9% density and purity, Performance Ceramics Co., Penninsula, OH, USA) with a 5mm diameter were selected for the milling media, at a 1:15
powder:ball weight ratio. After milling the powders were sieved to separate them from the milling media, then dried in air at 120°C for 12h in a furnace.

3.3.2 CAPAD Processing

The as received alumina powder and the as mixed Tb:Al₂O₃ powders were densified and processed using the CAPAD technique. In all cases, 1.2500 g ± 0.0001 g of powder was poured into a graphite die with an inner diameter of 19 mm and secured between two graphite punches of the same outer diameter. The die, plunger, and powder set were placed into the CAPAD and secured between two graphite spacers and copper electrodes. A maximum vacuum of 1x10⁻³ Torr was achieved in all cases. A custom constructed CAPAD apparatus that has been described previously[6] was used. Briefly, the CAPAD consists of a vacuum chamber, within which an electrode set has been inserted and are all contained within a load cell controlled twin ball screw H-frame Instron mechanical testing system.

The powder was pre-pressed at 70 MPa for 1 minute in order to create a green body. Simultaneously with the subsequently mentioned heating parameters, the green pellet was subjected to an applied compressive load, which was linearly increased to its maximum value of 105 MPa over a time interval of 3 minutes and held constant throughout until sample processing was completed, whereby the load was released. We use DC power supplies (Model XDC 10-1200, Xantrex, Burnaby, B.C., Canada), with which the samples are brought to and maintained at temperature via joule heating of
the graphite plunger and die assembly. The sample temperatures are measured with an optical pyrometer (Model IR GAP, Chino, Torrance, CA, USA), focused on a hole drilled in the graphite die located at the center point of the die height. This location was chosen as it has been found previously[23][24] to best represent the true sample temperature during CAPAD processing.

Samples were produced at temperatures ranging between 700°C – 1200°C with a 10 min holding time (HT) at temperature with a 300°C min⁻¹ heating rate (HR) in order to determine the effect of temperature on the resultant sample density and transparency.

Since it was found that the highest density and best optical quality was obtained at 1200°C, we also produced samples at this temperature with various HR's (150°Cmin⁻¹, 300 °Cmin⁻¹, and 600°Cmin⁻¹) in order to study the effects of HR on the resultant sample transparency and photoluminescence properties. Since samples produced at different HR’s reach the maximum sample temperature at different times, this means that the total experiment times (TET) are also varied when the HR is varied and the HT is maintained constant. Therefore, in order to de-couple the effects of HR and HT samples were produced at the three HR mentioned above, with the HT held constant at 10 min and then with the HR held constant at 300 °C min⁻¹ and the HT varied at 10 min, 20 min, and 30 min. In all cases the maximum achieved temperature was 1200°C.
3.3.3 Microstructural Characterization

The AGS of the undoped densified and reaction densified ceramics were obtained by measuring approximately 500 grains over multiple scanning electron micrographs of fracture surfaces using the ImageJ software. In addition to the AGS, a statistical standard deviation of the measured grains was calculated from the AGS measurements. All images were acquired using a Phillips XL30 Field Emission Scanning Electron Microscope (FE-SEM) with secondary electron detection. Prior to SEM the fracture surfaces were coated with a monolayer of platinum palladium using a Cressington 208 sample preparation system. The sputtering lasted for 10 sec at a target to sample distance of 3.75 cm.

3.3.4 UV-VIS-IR Transmission Measurements

Optical Transmission spectra were taken on a Varian Cary 50 UV-VIS spectrometer from 275 nm to 1050 nm. The bulk polished samples were placed at normal incidence to the beam path. The scans were obtained at a rate of 0.2 nm s\(^{-1}\).

3.3.5 Photoluminescence Measurements

Photoluminescence data were taken on a Horiba Spex Fluorolog 3 Spectrophotometer system using a tungsten deuterium lamp with monochromators as a light source. All measurements were taken in front face mode on polished bulk samples. Excitation scans were taken between \(\lambda = 275\) nm and \(\lambda = 430\) nm while monitoring the
sample emission at $\lambda_{Em} = 485$ nm, allowing the determination of the pumping bands. Emission scans were taken between $\lambda = 465$ nm and $\lambda = 560$ nm with the pumping wavelength $\lambda_p = 285$ nm as it was determined to be an effective pumping wavelength from the excitation spectra. All measurements were taken with an integration time of 1s per nanometer.

### 3.3.6 Photoluminescence Lifetime Measurements

The PL Lifetimes ($\tau$) were taken by irradiating the samples with a frequency tripled Nd:YAG laser, $\lambda = 355$ nm operating at 6 ns pulse width. The emission intensity was measured with a photodiode and captured with an oscilloscope. A double exponential fit\cite{19} of the resulting curves was used to extract the PL lifetime, whereas the lifetime is defined as the time required for the output signal intensity to decrease by a factor of $1/e$.

### 3.4 Results and Discussion

Commercial Al$_2$O$_3$ and Tb$_4$O$_7$ powders were mixed and prepared for CAPAD processing (see experimental section for details). The CAPAD processing parameters we used are tabulated in Table 3.1. In order to produce non-cubic (i.e. materials that can be birefringent) transparent polycrystalline ceramics, such as polycrystalline alumina, it is imperative to minimize the sample porosity and maintain a fine grain size. Since pores
TABLE 3.1: Processing parameters and properties of the CAPAD produced ceramics

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dopant (Atomic % Tb.)</th>
<th>Temp. (°C)</th>
<th>Heating Rate (°C/min)</th>
<th>Hold Time (min)</th>
<th>Relative Density (%)</th>
<th>Avg. Grain Size ± Std. Dev. (nm)</th>
<th>Transmittance @ λ &gt; 950 nm (%)</th>
<th>FWHM of 489 nm PL peak (nm)</th>
<th>FWHM of 543 nm PL peak (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1200</td>
<td>300</td>
<td>10</td>
<td>&gt;99</td>
<td>340 ± 10</td>
<td>83</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>1200</td>
<td>150</td>
<td>10</td>
<td>&gt;99</td>
<td>242 ± 69</td>
<td>81</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>1200</td>
<td>300</td>
<td>10</td>
<td>&gt;99</td>
<td>232 ± 63</td>
<td>83</td>
<td>14</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>1200</td>
<td>600</td>
<td>10</td>
<td>&gt;99</td>
<td>256 ± 56</td>
<td>82</td>
<td>16</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>1200</td>
<td>300</td>
<td>20</td>
<td>&gt;99</td>
<td>348 ± 10</td>
<td>81</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>1200</td>
<td>300</td>
<td>30</td>
<td>&gt;99</td>
<td>375 ± 10</td>
<td>80</td>
<td>15</td>
<td>13</td>
</tr>
</tbody>
</table>

are very efficient scattering sites\cite{25}, low porosity decreases light scattering and maintaining the AGS below 1-2 µm in diameter minimizes the effects of birefringence related scattering in alumina \cite{18}. The effect of CAPAD processing temperature on the density of alumina and 0.5 at.% Tb\(^{3+}\) doped alumina (Tb:Al\(_2\)O\(_3\)) samples is shown in Figure 3.1. As expected, density increases with temperature in both Tb\(^{3+}\) doped and un-
Figure 3.1: The effect of processing temperature on the relative density of un-doped alumina (Al₂O₃) and 0.5 at.% Tb doped alumina (Tb:Al₂O₃). The samples were all processed using a pressure of 105MPa, 300°C/min heating rate, and held at the temperature indicated for 10 min.

doped cases. At low and intermediate temperatures, the doped samples have a lower relative density than the un-doped case. We have observed this phenomena in another rare earth doped ceramic[26]. We attribute the observed lower densities to dopant atoms decreasing the densification rate, likely by inhibiting particle sliding and/or grain boundary diffusion. Both un-doped and doped samples reach near-full density, >99% relative density at temperatures of 1200°C.

Figure 3.2 shows pictures of un-doped (Figure 3.2a) and doped (Figure 3.2b) samples produced at 1200°C. The printed lettering is visible through the ceramic disks
The samples are processed using 1200°C, 105MPa, 300°C/min heating rate and 10 min hold time. The samples are 19 mm in diameter and 1 mm thick. The printed text below the sample is legible demonstrating the transparency of the ceramics. (a) Un-doped alumina (Al₂O₃) ceramic (b) 0.5 at.% Tb³⁺ doped alumina (Tb:Al₂O₃).

demonstrating good transparency. The high transparency of our ceramics is attributed to the high relative density and fine average grain size of our ceramics which are listed in Table 3.1. The AGS was determined by measuring approximately 500 grains from multiple fracture surface scanning electron microscope (SEM) micrographs of each sample (for further details please refer to the experimental techniques section). Representative SEM fracture surfaces are presented in Figure 3.3 for the Al₂O₃ and
Figure 3.3: Representative Fracture Surface Scanning Electron Micrographs for the undoped Al₂O₃ and Tb:Al₂O₃ samples produced at 1200°C, 105MPa, and with a 10min hold time, with various heating rates (HR), where (a) Un-doped Al₂O₃, (b) Tb:Al₂O₃, HR=150°Cmin⁻¹, (c) Tb:Al₂O₃, HR = 300°Cmin⁻¹, and (d) Tb:Al₂O₃, HR = 600°Cmin⁻¹.

Tb:Al₂O₃ samples produced at various heating rate (HR) with constant hold time (HT). The SEM micrographs do not show evidence of residual porosity, which corroborates the high density measurements reported in Figure 3.1. It is possible that low concentrations of very fine diameter pores are present but are difficult to detect with SEM.

The un-doped Al₂O₃ sample produced at 1200°C, with a heating rate (HR) of 300°Cmin⁻¹, and a 10 min hold time (HT) has an AGS of ~340 nm with a standard
deviation of ~10 nm, indicating a very homogenous fine grained microstructure with minimal grain growth (the starting powder crystallite size is ~150-250 nm). The AGS of the Tb:Al₂O₃ samples produced at the same temperature and HT with varying HR are smaller than in the un-doped case; the AGS is approximately 250 nm ± 50-60 nm. We observe no strong trend with respect to the HR. The smaller AGS can be indicative of a grain boundary pinning effect associated with dopant segregation at the grain boundary, an effect similar to that seen when MgO is used as a sintering additive for alumina ceramics[1]. Such grain boundary pinning likely occurs at the early stages of reaction-densification when the Al₂O₃ and Tb₄O₇ phases are still separate phases. This coupled with the short processing times associated with CAPAD explain the minimal grain growth in these Tb:Al₂O₃ samples. The effect of HT on the resultant microstructure followed the usual trend, i.e. increasing the HT to 20 and 30 min with all other parameters held constant results in an increased AGS of ~348 ± 110 nm and of ~375 ± 100 nm, respectively.

The high transparency of the samples over the entire visible (VIS) range (400-800 nm) as well as the ultra-violet (UV) and near infrared (NIR) can be quantitatively appreciated in Figure 3.4 which shows the percent total transmission as a function of
Figure 3.4: (a) Total transmission vs. wavelength for doped (Tb:Al$_2$O$_3$) and un-doped alumina (Al$_2$O$_3$) ceramics. The processing parameters were held constant (1200°C, 105MPa, 300°C/min heating rate and 10 min hold time). (b) The same data as in Figure 3a, plotted as the logarithm of the total transmission vs., $1/\lambda^2$. The dashed lines are straight lines, demonstrating the good linear fit of the data.

wavelength for un-doped and doped alumina produced using identical processing conditions. The values were corrected to account for reflectance losses at the front and back polished sample surfaces, assuming a reflectance of 14%, based on the refractive index of polycrystalline alumina.$^{[18]}$ In both cases the transparency increases with wavelength from the UV through the VIS and into the NIR. The un-doped alumina has slightly higher transmission below ~775 nm than the Tb:Al$_2$O$_3$ samples; at higher wavelengths the transparencies are quite similar. These results reveal that both Al$_2$O$_3$ and Tb:Al$_2$O$_3$ ceramics have a transparency of ~75% at the edge of the visible (800 nm) and actually reach ~83% total transmission at $\lambda > 950$ nm, approaching the maximum theoretical transparency for single crystal sapphire (~86%).$^{[18]}$ These are impressive transparencies for polycrystalline ceramics especially in a birefringent material.
Pecharromán\cite{27} et al., following a similar approach to Apetz and Van Bruggen\cite{18}, applied the Rayleigh-Gans-Debye (RGD) approximation in order to analyze the optical transparency in alumina with small grain sizes. They derive the following expression that relates the real in line transmission, $T$ with microstructural parameters and wavelength, $\lambda$ as:

$$\log(T) = \log(T_0) - \frac{6\pi^2\langle a_g \rangle}{\lambda^2} \Delta n^2 \alpha d$$  

(3.1)

where $\langle a_g \rangle$ is the maximum grain size, $\Delta n$ is the change in refractive index (birefringence), $\alpha$ is texture parameter and $d$ is the sample thickness. In Figure 3.4b, we plot the transmission results shown in Figure 3.4a as $\log(T)$ vs. $1/\lambda^2$. The dashed lines are straight lines showing the good linear fit of the transmission curves. The good fit to Equation 3.1 indicates that the consolidated ceramics possess a relatively fine grain size, i.e. the grain size of the ceramics is comparable to the incident wavelength. They also indicate that there is not significant scattering from residual porosity; a $1/\lambda^4$ relationship would be expected if significant porosity were present. The results in Figure 3.4b are consistent with our measured AGS of less than 400 nm as discussed above and they also corroborate our lack of observable residual porosity in the fracture surface SEM.

In addition to being highly transparent, the doped ceramics display photoluminescence (PL). The strong (a quantitative analysis of the PL will be presented...
below) visible fluorescence of the Tb:Al$_2$O$_3$ sample when exposed to UV light can be appreciated in Figure 3.5. Figure 3.5 shows pictures of un-doped Al$_2$O$_3$ and Tb:Al$_2$O$_3$.

\[
\text{Al}_2\text{O}_3 \quad \text{Tb:Al}_2\text{O}_3
\]

Figure 3.5: Photographs of CAPAD processed ceramics being exited with 355 nm UV pulsed laser light. The laser light is incident on the back of the samples. The samples were processed using 1200°C, 105MPa, 300°Cmin$^{-1}$ heating rate and 10 min hold time. (a) Un-doped alumina. The sample does not photoluminescence causing the picture to be dark. The incident UV light is barely visible near the center of the sample. (b) Tb:Al$_2$O$_3$ alumina. The picture clearly shows blue and green photoluminescence of the ceramic caused by UV (355 nm) excitation.

samples subjected to a 355 nm pulsed laser with a 0.5 cm diameter spot size. The pictures are top-views of the ceramics where the laser light is incident on the back of the ceramic. The pictures were taken in a darkened room so that ambient light would not overwhelm the possible luminescence from the samples. The un-doped sample shows a very faint color near the center where the 355 nm is transmitted through the
sample. The rest of the sample is dark as expected since it does not display luminescence. The difference when the Tb:Al$_2$O$_3$ is exposed to UV light is dramatic. The picture (Figure 3.5b) clearly shows a bright green spot where the 355 nm pulsed laser is incident on the sample. In addition there is also a blue halo visible around the sample. It is worth emphasizing that since the incident UV light is not visible, all of the blue-green light visible in Figure 3.5b is coming from the sample. As will be discussed in further detail below, the PL spectra Figure 3.6 reveals that the Tb:Al$_2$O$_3$ ceramics produce two distinct PL peaks, one at 485 nm which should appear blue while the second at 543 nm should appear green. The mixing of these two peaks explains the blue-green appearance of the PL in Figure 3.5.

Figure 3.6 shows excitation and emission scans of Tb:Al$_2$O$_3$ ceramics produced using different processing conditions. The measurements shown in Figure 3.6a and Figure 3.6b were for samples produced using 3 different HR, 150, 300 and 600°C min$^{-1}$ with the same HT of 10 min and temperature, 1200°C. The spectra shown in Figure 3.6c and Figure 3.6d were taken from samples produced with varying HT keeping the HR constant at 300 °C min$^{-1}$ and maximum process temperature of 1200°C. The excitation scans (Figure 3.6a, 3.6c) were taken by monitoring the 485 nm peak and show that UV excitation below ~375 nm can be used to produce significant luminescence at 485 nm. The emission scans of the Tb:Al$_2$O$_3$ (Figure 3.6b, 3.6d) show two distinct sharp luminescence peaks. These peaks correspond to the $^5$D$_4 \rightarrow ^7$F$_6$ transition centered on
Figure 3.6: Excitation and emission scans of Tb:Al₂O₃ produced using varying processing conditions (heating rate or hold time). The processing temperature and pressure were held constant, 1200°C and 105MPa. The Excitation Scans were taken monitoring at 485 nm (λₑm=485nm) and the emission scans were taken using 285nm illumination (λᵢ=285nm). The emission scans reveal two sharp PL peaks corresponding to the ⁵D₄ → ⁷F₆ and ⁵D₄ → ⁷F₅ transitions of Tb³⁺ ion (a) Excitation scan of Tb:Al₂O₃ produced using varying heating rates and constant hold time, 10 min. (b) Emission scan of Tb:Al₂O₃ produced using varying heating rates and constant hold time, 10 min. (c) Excitation scan of Tb:Al₂O₃ produced using varying hold time and constant heating rate 300°Cmin⁻¹. (d) Emission scan of Tb:Al₂O₃ produced using varying hold time and constant heating rate 300°Cmin⁻¹.

485 nm and the ⁵D₄ → ⁷F₅ transition centered at 543 nm. These transitions corresponding to Tb³⁺ were labeled according to the Dieke diagram[28]. These spectra confirm that Tb³⁺ dopants were successfully incorporated into the alumina matrix. We
attribute the successful incorporation of Tb$^{3+}$ to the increased processing kinetics offered by the CAPAD process. We have previously shown that high HR in CAPAD processing can promote rapid diffusion and drastically increase processing kinetics when compared to free sintering[26] in another oxide system. The increased diffusion and processing kinetics of CAPAD processing allow for higher than equilibrium rare-earth dopant concentration. The heating rates of 150-600°C min$^{-1}$ for this work is significantly higher than the HR associated with free sintering and hot pressing, which are typically on the order of 10°C min$^{-1}$ to 50°C min$^{-1}$.

Similarly the cooling rate (CR) of our process is about 300°C min$^{-1}$ which is again substantially higher than CR$^{15}$ for free sintering and hot pressing (typically <5°C min$^{-1}$), because most furnaces and hot presses are heavily insulated and tend to rely only on convection for cooling. These high CR allow the ‘freezing-in’ of the higher than equilibrium concentration of Tb$^{3+}$. It should be noted that although these ceramics have higher RE-dopant concentrations than the equilibrium solubility limit there is little chance that dopant segregation will occur in applications. The typical operation temperatures of devices such as solid state lasers are never more than ~200°C, a temperature at which the diffusivity of Tb$^{3+}$ ions would be prohibitively low.

Interestingly, the heating rate used during CAPAD processing plays a significant role on the PL intensity of the samples; higher heating rates produce higher intensity from both peaks as can be seen in Figure 3.6b. For example, in the $^5D_4 \rightarrow ^7F_6$ transition centered around 485 nm, increasing the HR from 150°C min$^{-1}$ to 300°C min$^{-1}$ and
600°Cmin\(^{-1}\) results in a ~1.5 and ~5.5 increase in the PL output intensity, respectively (at the same pumping intensity). Similarly for the \(^5\text{D}_4 \rightarrow ^7\text{F}_5\) transition centered at 543 nm, the same increases in HR results in increased PL intensities by factors of ~1.3 and ~4.9, respectively. These measurements indicate that varying HR during CAPAD processing affects the relative efficiencies of the Tb:Al\(_2\)O\(_3\) transparent ceramics. Since the pumping intensity is the same in all instances, this indicates that using a higher HR can cause as much as a five-fold increase in the relative efficiency of these materials.

An increase in PL intensity can be caused by decreased scattering, absorption or a change in electron environment around the luminescent ion. One possibility for the observed dependence of PL intensity on HR is that varying HR causes varying levels of residual stress or distortion of the lattice around the active Tb\(^{3+}\) ions. However, comparison of the full width at half the maximum value (FWHM) (Table 3.1) of the PL peaks shows that they are all very similar suggesting similar electronic environment near the Tb\(^{3+}\) ions. Measurements of residual stress in sintered alumina by Krell\(^{(29)}\) et al. show that although residual stress levels in alumina are grain size dependent due to an anisotropic (hexagonal) crystal structure, they reach a plateau in small grained samples and thus remain similar in alumina with sub-micron grains. Since our ceramics have an AGS < 400 nm, at all HR’s, the residual stress levels are also likely to be independent of HR, which is consistent with our observation that the FWHM values of the PL peaks are similar irrespective of HR. Thus we do not feel the HR affected the residual stress levels,
coordination number, etc. around the Tb$^{3+}$ ions. A change in scattering is also not responsible since the HR does not affect grain sizes.

Instead, we feel that the changes in PL intensity can be attributed to changes in oxygen stoichiometry and/or change in the oxidation state of the Tb ions incorporated within the samples caused by low oxygen partial pressure during processing. In another oxide system, Shen and Clarke found exposure to a very low oxygen partial pressure environment causes a decrease in luminescent intensity$^{[30]}$. In our case, a low oxygen partial associated with CAPAD processing can cause changes in oxidation state of the Tb ions or oxygen reduction of the alumina itself, leading to oxygen vacancies. Tb ions are multivalent and can be Tb$^{4+}$ or Tb$^{3+}$ yet only Tb$^{3+}$ ions cause PL at the wavelengths observed in Figure 3.6 (485 nm and 543 nm). These PL transitions prove the existence of Tb$^{3+}$ ions in the Tb:Al$_2$O$_3$ ceramics, however a varying Tb$^{3+}$ to Tb$^{4+}$ ratio would cause a difference in PL intensity from the samples. As we vary the HR the amount of time the ceramics are exposed to reducing atmospheres also varies. The experiments we conducted with varying holding times (Figure 3.6c and 3.d) show a similar trend— the longer the exposure time, the lower the PL intensity.

We used X-ray photoelectron spectroscopy (XPS) analysis to examine the local structure around the Tb ion. XPS is a powerful and appropriate technique to determine the local structure of the incorporated Tb ions, such as spin-orbit splitting, binding energies of core levels of the Tb and valence number$^{[31][32]}$. Although the XPS results (not shown here), clearly revealed the existence of Tb in the samples, unfortunately the
analyses was inconclusive with regard to a varying Tb$^{3+}$ to Tb$^{4+}$ ratio. The XPS analysis was complicated because of overlapping of the Tb peaks with the O and/or Al peaks. Further investigations into the cause of the varying PL intensity are underway.

**Figure 3.7** shows the time dependent luminescence of the Tb:Al$_2$O$_3$ ceramics produced using a 300$^\circ$C min$^{-1}$ and 600$^\circ$C min$^{-1}$ HR. **Figure 3.7a and 3.7c** shows the normalized emission vs. time while the insets, respectively, show the luminescent

![Figure 3.7: Photoluminescence Lifetime (τ) Curves for the Tb:Al$_2$O$_3$ samples produced at 1200 $^\circ$C, 105 MPa, and with a 10 min hold time for heating rates of 300 $^\circ$C min$^{-1}$ and 600 $^\circ$C min$^{-1}$ for the Tb$^{3+}$ ion transitions. The excitation source was a frequency tripled Nd:YAG laser, $\lambda = 355$ nm, operating at 6 ns pulse width. (a) Normalized intensity vs. time for 485 nm ($^5D_4 \rightarrow ^7F_6$) (b) Natural log intensity vs. time for 485 nm ($^5D_4 \rightarrow ^7F_6$). The insets are same data plotted as Natural Log Intensity vs. Time intensities decay on a natural log scale vs. time. For the emission at 485 nm the lifetimes are 750 $\mu$s and 680 $\mu$s for the Tb:Al$_2$O$_3$ ceramics produced using a 300$^\circ$C min$^{-1}$ and 600$^\circ$C
min$^{-1}$ HR, respectively. And for the emission at 543 nm the lifetimes are 720 µs for 300°C min$^{-1}$ and 670 µs for the 600°C min$^{-1}$ sample. These lifetimes are long and well within the range of lifetimes seen in other luminescent ceramics that are used for laser applications. For example, fluorescence lifetimes of polycrystalline Nd:YAG ceramics used as gain media are typically about 250 µs$^{[33]}$. The lifetimes of various Tb doped oxides and nitrides have been presented by Chambers and Clarke$^{[19]}$ to be on the order of ~1000 µs, which compares well with the lifetime values presented here for these ceramics. It should be noted that while the HR does effect the PL lifetime, its dependence is not strong. At most there is a ~10% change in the lifetime values as a function of HR. This is markedly different than the effect of HR in PL intensity which causes as much as a fivefold increase in the PL intensity, as discussed above. These results further corroborates that HR does not significantly change the local electronic environment around the luminescent Tb$^{3+}$ ions.

Preliminary thermal characterization of the ceramics via the 3ω-method shows a thermal conductivity of ~30 W m$^{-1}$ K$^{-1}$ at room temperature which is significantly higher than the state of the art gain media. Full thermal characterization studies are underway and will be presented in a subsequent communication. Ceramics that emit in the green and blue wavelengths with high thermal conductivity have the potential to be used in producing substantially higher powered green lasers. This opens the door for producing more compact and stable, higher power green lasers at 543 nm.
3.5 Summary

In summary, we have demonstrated the successful incorporation of above equilibrium concentrations of Tb$^{3+}$ dopant in polycrystalline bulk alumina for the first time. The Tb:Al$_2$O$_3$ ceramics show two sharp visible photoluminescent peaks, a blue one centered at 485 nm and a green one at 543 nm. The CAPAD processing conditions namely the sample hold time and heating rate have significant effects on the PL intensity, but do not strongly affect PL lifetimes. Increasing the HR from 150°C min$^{-1}$ to 600°C min$^{-1}$ causes an approximate fivefold increase in the PL intensity, yet has a minimal effect on the PL lifetime (a ~10% decrease). The changes in the PL intensity are likely due to changes in the oxygen stoichiometry of the samples as a function of the HR. These results show that it is possible to produce highly transparent light emitting ceramics that are not based on optically isotropic crystal structures. These findings have great promise for the design of alumina-based light producing devices and should be especially interesting for the continued development of high-powered lasers.

3.6 Acknowledgments

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3.7 References


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Chapter 4: Photoluminescence, Population Inversion, and Optical Gain of Stimulated Emission at 1064nm in Over-Equilibrium Neodymium Doped Bulk Polycrystalline Aluminum Oxide Transparent Ceramics for High-Energy Laser Applications

Keywords: Non-Equilibrium Processing, CAPAD, SPS, Rare-Earth Alumina, Transparent Anisotropic Bulk Polycrystalline Ceramics, High-Energy Lasers, Single-Pass Optical Gain

4.1 Abstract

Recent advancements in powder processing and consolidation techniques, (presented in Chapters 1-3) have indicated the feasibility of producing bulk polycrystalline rare-earth doped α-aluminum oxide (RE: α-Al₂O₃) ceramics with sufficient purity, density, optically active dopant, and optimized microstructure to obtain the requisite transparency for photoluminescence applications. The goal of fabricating a laser grade RE:α-Al₂O₃ has remained elusive. Here we report on the successful reaction/densification of over-equilibrium neodymium doped (0.25 at.% and 0.35 at.% Nd³⁺:Al³⁺) α-aluminum oxide (Nd³⁺:Al₂O₃) bulk polycrystals using Current Activated Pressure Assisted Densification. The measured transparency of the ceramics is high (real-in-line (RIT) of ~75% at 1064nm). A comprehensive spectroscopic investigation of the transparent ceramics proves their viability as laser-gain media at 1064nm with adequate optical absorption cross-section at 806nm, suitable for direct diode pumping. Single pass gain experiments were used to demonstrate optical gain of stimulated emission at 1064 nm of 0.25at.% and 0.35at.% Nd³⁺:Al₂O₃ transparent bulk polycrystals for the first time in RE:Al₂O₃. Single pass gain coefficients as high as 2.27 and 2.42 cm⁻¹
are measured and reported for the 0.25 at.% and 0.35 at.% Nd\(^{3+}\) concentrations, respectively. In addition, the measured positive gain coefficients are the first reported proof of a population inversion in RE:Al\(_2\)O\(_3\) ceramics. This work is believed to also be the first comprehensive proof for gain and population in any non-textured polycrystalline anisotropic media. The PL bandwidth (approximate G\(_{bw}\)) of the Nd\(^{3+}:Al_2O_3\) polycrystals is broad (~13THz) This bandwidth is approximately 2.5 and 80 times larger than for Nd\(^{3+}:\)Glass and Nd\(^{3+}:\)YAG of similar dopant concentration, respectively, indicating the possibility of producing ultra-short pulses using this gain media (~8fs), while retaining the superior thermo-mechanical properties (R\(_s\)=19,500 Wm\(^{-1}\)) of polycrystalline alumina. This work indicates the possibility of producing HEL with improved performance over state-of-the-art technology.

### 4.2 Introduction

The past decade has seen significant advances in the development and improvements to high-energy laser technologies, with improvements coming from all directions, i.e. pumping technology, cavity design, cooling methods, and improved gain media quality, etc. Regardless, the continued development of high-energy lasers and the supporting technologies remains intense. From a materials development perspective, the need for gain media with superior optical, thermal, and mechanical properties is alluring because improvements in the materials properties often translate directly to increases in device performance.\(^{[1]}\)
Advances in powder processing and sintering/consolidation techniques, in the past two decades have produced bulk polycrystalline ceramics with the requisite densities, transparencies, and photoluminescence properties to be viable laser gain materials. In fact, the performance of some cubic (optically isotropic) bulk polycrystalline ceramics now rival and even surpass their single-crystal counterparts.

Despite all of these advances, the low thermal conductivities of the state-of-the art laser gain media (~1-2 Wm\(^{-1}\)K\(^{-1}\) RE:Glass\(^[4]\), and 7-14Wm\(^{-1}\)K\(^{-1}\) for RE:YAG\(^[5]\)) continues to represent a limit to the further power scaling of high-energy lasers.

In response to this need, other gain media based on the garnet and sesquioxide cubic symmetry materials, such as LuAG\(^[6]\), Sc\(_2\)O\(_3\)\(^[7]\), Y\(_2\)O\(_3\)\(^[8]\), and most recently, Lu\(_2\)O\(_3\)\(^[9]\) with improved thermal conductivities over YAG have been developed via multiple traditional ceramics processing approaches. Cubic-symmetry materials are the mainstay of transparent polycrystalline ceramics because 1) their isotropic optical properties (i.e. lack of birefringence scattering) allow these materials to be processed at high-temperatures because grain growth need not be avoided 2) the ability to process at high-temperatures allows these materials to be easily consolidated to theoretical densities, which leads to optical transparency, with traditional free-sintering and hot-pressing approaches, and 3) the garnet and sesquioxides readily accommodate rare-earth dopants within their respective lattices because the ionic radii of the dopants are similar to the cation which they substitute\(^[10]\).
Impressive advances in processing science that have led to very good optical quality have lead to successful lasing demonstrations. However the improvements in thermal conductivity and luminescence characteristics have not been a large enough impetus to supplant YAG as the state-of-the art laser gain media. From a materials technology perspective, it is obvious that to supplant RE:YAG, a material with superior *thermal and mechanical properties* is needed. The challenge then becomes improving these properties while retaining the material optical properties, i.e. transparency and photoluminescence characteristics must be suitable for laser applications.

For decades the desire to develop sapphire or polycrystalline alumina as a rare-earth laser gain media has pervaded the scientific community because Al₂O₃ offers a superior thermal conductivity (k~30-35 Wm⁻¹K⁻¹)[11] to the garnets and sesquioxides, a high-fracture toughness (3.5 MPam⁻¹/²)[12], which leads to a far superior thermal shock resistance (Rₛ~19,500 Wm⁻¹) over Glass (Rₛ~1 Wm⁻¹)[13] and YAG (Rₛ~800 Wm⁻¹)[1][14]. Further advantages include good chemical stability and large optical band-gap (~9.9 eV), i.e. offering optical transparency throughout the visible and infrared regions. This combination of thermal, mechanical, and optical properties makes Al₂O₃ a highly-alluring candidate for a rare-earth doped laser gain media with attributes that could lead to more stable, more powerful lasers in the laboratory and in mobile applications.

Despite these promising attributes, producing RE-Al₂O₃ ceramics for lasers has steep processing challenges. The two main obstacles to overcome are 1) the disparity in ionic radii between the rare-earth dopant and the Al³⁺ ion, which leads to low-
equilibrium solubility limit (~$10^{-3}$%)$^{15}$ of rare-earths in Al$_2$O$_3$, hindering efficient PL, and 2) the optical anisotropy rising from the hexagonal crystal structure of Al$_2$O$_3$ leads to birefringence scattering that must be mitigated in order to achieve adequate optical transmission for lasing applications. In order to overcome these obstacles multiple approaches all reliant on materials processing approaches that offer access to kinetic windows outside of equilibrium have been implemented in order to produce a functional RE:Al$_2$O$_3$ material.

The most successful approaches have been for the production RE:Al$_2$O$_3$ powders and thin films. Tanner et al.$^{16}$ used a combustion synthesis approach to obtain Eu$^{3+}$:Al$_2$O$_3$ with Eu$^{3+}$ concentrations as high as 1 at.%, but in all of the cases reported herein, no-phase pure doping was achieved and/or the resultant product was amorphous. Similar results were obtained by various other groups$^{17}$ with perhaps the most promising results coming from the groups of Rand and Laine, where random lasing was observed in strongly scattering rare-earth doped δ−Al$_2$O$_3$ powders obtained from flame-spray pyrolysis techniques under electron-beam pumping.$^{18}$[19] Er$^{3+}$ and Er$^{3+}$/Yb$^{3+}$ doping of alumina has also been reported in amorphous thin films fabricated by microwave enhanced RF-magnetron sputtering$^{20}$ and conventional PLD$^{21}$[22] to concentrations as high as 1 at.%, that resulted in amorphous and/or a mixture of amorphous and crystalline films with measurable PL in all cases. These reports represented the first indicators for the possibility of producing HEL from RE:Al$_2$O$_3$ media, but because they were powder and amorphous thin film based they were not suitable
candidates for power scaling because their thermo-mechanical properties were poor. Molecular beam epitaxy has been used to produce monolithic Nd\textsuperscript{3+}:\textalpha-Al\textsubscript{2}O\textsubscript{3}\textsuperscript{[23]} and Nd\textsuperscript{3+}:\textalpha-(Al\textsubscript{1-x}Ga\textsubscript{x})\textsubscript{2}O\textsubscript{3}\textsuperscript{[24]} crystalline thin films, but only PL was reported. No other evidence (PL-lifetime, emission cross-section, gain coefficients, etc.) for their feasible use as a lasing media were reported.

With regards to bulk RE:Al\textsubscript{2}O\textsubscript{3} only very few works can be found. Krebs and Happek\textsuperscript{[25]} used a laser-heated pedestal growth (LHPG) approach starting from sol-gels of RE-doped precursors to produce single-crystal Yb\textsuperscript{3+}:Al\textsubscript{2}O\textsubscript{3} fibers and were able to systematically determine that single-site doping of Yb\textsuperscript{3+} onto the Al\textsuperscript{3+} lattice was possible with this approach at concentrations below the rare-earth solubility limit, but that at higher concentrations secondary phases that hindered PL formed. Apart from a detailed spectroscopic study of the Yb\textsuperscript{3+} in Al\textsubscript{2}O\textsubscript{3}, no evidence for lasing or the possibility of lasing was reported. Sanamyan\textsuperscript{[26]} et al. used a combination of powder synthesis processing, followed by SPS to form dense Er\textsuperscript{3+}:Al\textsubscript{2}O\textsubscript{3} polycrystals that had rare-earth cation concentrations as high as 0.065%. There work indicated that the as-synthesized starting powders and SPS densified polycrystals produced PL indicative of single-site doping of the rare-earth within the matrix host. Although these authors claimed that their polycrystals were dense and transparent, they offered no evidence to support these claims. It also remains unclear whether this dopant concentration was sufficient to produce an adequate amount of PL for lasing applications.
In our previous work\cite{27} we reported efficient PL in the visible ($\lambda$=485nm and 543nm) in conjunction with high-density phase pure, optically transparent ($T\sim75\%$ at $\lambda>$800nm) bulk polycrystalline $\text{Tb}^{3+}:\text{Al}_2\text{O}_3$ ceramics with dopant concentrations as high as 0.5at.% $\text{Tb}^{3+}$ relative to $\text{Al}^{3+}$, 500 times above the equilibrium solubility limit. The measured luminescence lifetimes were long (~700$\mu$s) and comparable to those measured in $\text{Tb}^{3+}:\text{YAG}$ ceramics\cite{28} of similar dopant concentration. This combination of high optical transparency, intense PL, with long lifetimes was the first report of any RE:Al$_2$O$_3$ bulk polycrystalline ceramic with a combination of properties that indicated the feasibility for using RE:Al$_2$O$_3$ as laser gain media. However, even in our previous report, there was no clear evidence for the presence of stimulated emission, much less optical gain of stimulated emission, which is required for lasing.

In this work, we extend our previous work on the $\text{Tb}^{3+}:\text{Al}_2\text{O}_3$ system to the $\text{Nd}^{3+}:\text{Al}_2\text{O}_3$ system. This dopant was chosen because 1) as has been discussed above, for HEL applications lasing associated with $\text{Nd}^{3+}$ PL is required in order to supplant the existing state-of-the-art technology and 2) our previous works suggested that the best optical transparency in our matrix material occurred at wavelengths above 800nm, which will be essential for adequate diode pumping at 806nm and lasing at 1064nm, arising from the presence of optically active $\text{Nd}^{3+}$ dopant. Using a solid-state powder processing route along with a one-step simultaneous reaction/densification approach with \textbf{Current Activated Pressure Assisted Densification} (CAPAD) processing, we are able to produce bulk polycrystalline optically transparent ceramics with $\text{Nd}^{3+}$ dopant.
concentrations as high as 0.35 at.% (Nd³⁺:Al³⁺ ratio), approximately 350 times greater than the equilibrium solubility limit. We report for the first time the presence of absorption bands centered at \( \lambda = 585\text{nm}, 748\text{nm} \) and \( 806\text{nm} \), corresponding to the \( ^4G_{5/2}, ^2H_{3/2} \), and \( ^4F_{9/2} \) Stark transitions from the \( ^4I_{9/2} \) manifold, associated with the presence of optically active Nd³⁺ present within the doped transparent ceramic matrix. The gain bandwidth, \( G_{bw} \), for these materials is \( \sim 13\text{THz} \) centered at 1064nm and to the best of our knowledge represents a new record for any Nd³⁺ gain media, suggesting the possibility of producing ultra-short time pulses (\( \Delta \tau \sim 8\text{fs} \)) which represents a factor \( \sim 2.5 \) and \( \sim 80 \) improvement in the single-shot peak power output over Nd³⁺:Glass and Nd³⁺:YAG media, respectively. Moreover, because the thermo-mechanical properties of Nd³⁺:\( \alpha \)-\( \text{Al}_2\text{O}_3 \) (\( R_s \sim 19,500 \text{ Wm}^{-1} \)) are far superior to Nd:Glass (\( R_s \sim 1 \text{ Wm}^{-1} \)) and Nd:YAG (\( R_s \sim 800 \text{ Wm}^{-1} \)), this improvement is conservative with regards to single-shot peak power output, and also represents the possibility of producing a laser with higher duty cycles than are obtainable with Nd³⁺:Glass and Nd³⁺:YAG.

Most importantly, we present for the first time unambiguous proof for lasing in RE:Al₂O₃. Optical gain of stimulated emission is observed, measured, and reported at \( \lambda = 1064\text{nm} \) under direct-diode pumping at \( \lambda = 806\text{nm} \), with single pass gain coefficients, \( G \), as high as 2.27 and 2.42 cm\(^{-1}\) for 0.25 at.% and 0.35 at.% Nd³⁺ dopant concentrations, respectively. The measured positive gain coefficients are the first reported proof of a population inversion in any RE:\( \alpha \)-\( \text{Al}_2\text{O}_3 \) ceramics and ultimately represent the first comprehensive proof for lasing in any non-textured polycrystalline anisotropic media.
4.3 Experimental Materials and Methods

4.3.1 Preparation of Nd\textsuperscript{3+}:α-Al\textsubscript{2}O\textsubscript{3} Powders

Commercially available aluminum oxide, \( \alpha-\text{Al}_2\text{O}_3 \) (99.99% purity, TM-UF, Taimei Chemicals, Japan) was processed as received (referred to as un-doped) as well as doped with Neodymium Oxide, \( \text{Nd}_2\text{O}_3 \) (99.99% purity, Alfa Aesar, USA). The powders were weighed to achieve an Nd doping level such that the \( \text{Nd}^{3+} \) to \( \text{Al}^{3+} \) ratio was 0.25 and 0.35 at.%. The powders were mixed dry in an aluminum oxide mortar by hand for 20min, followed by low-energy ball milling for 12h with Ultra-High Purity (UHP, 99.99% purity) water as a dispersant. The low-energy ball milled slurries were sieved to separate them from the milling media and centrifuged for 15min at 3400RPM to separate the powder from the UHP water. The semi-wet powders were dried in a vacuum oven at 70\(^\circ\)C and under a vacuum of 30mm Hg for 12hrs. These dried powders were subsequently planetary ball milled with UHP water at 150 RPM for 6 hours. Finally, the powders were sieved to separate them from the milling media and dried in air at 120\(^\circ\)C for 12h in a furnace and kept stored dry until consolidation.

4.3.2 CAPAD Processing

The as received alumina powder and the as mixed Nd\textsuperscript{3+}:α-Al\textsubscript{2}O\textsubscript{3} powders were densified and processed using the CAPAD technique. In all cases, 0.3300 g ± 0.0001 g of
powder was poured into a graphite die with an outer diameter of 19mm and an inner
diameter of 10mm and secured between graphite punches with a 10mm outer
diameter. This small die and plunger set was secured between two 19mm punches and
placed within a larger graphite die with a 19mm inner diameter. The complete die,
plunger, and powder set were placed into the CAPAD and secured between two
graphite spacers and copper electrodes. A maximum vacuum of 1x10^{-3} Torr was
achieved in all cases. A custom constructed CAPAD apparatus that has been described
previously\textsuperscript{[29]} was used. Briefly, the CAPAD consists of a vacuum chamber, within which
an electrode set has been inserted and are all contained within a load cell controlled
twin ball screw H-frame Instron mechanical testing system.

Once inserted within the CAPAD the powder was pre-pressed at 106 MPa for 20
minutes in order to create a green body. The pre-press load was released. During
consolidation, the green pellet was subjected to an ultimate compressive stress of 106
MPa with a linear pressure ramp of 35.33 MPamin^{-1} and this pressure was held constant
throughout consolidation.

In parallel with this single step linear pressure ramp, the samples were subjected
to a maximum temperature of ranging between 700-1300ºC with a hold time of 5 min in
all cases. The heating rate was \textasciitilde 300ºCmin^{-1} and this was achieved via dc-joule heating of
the graphite die and plunger set. The surface temperature of the graphite die was
monitored with a dual wavelength optical pyrometer focused at the midpoint of the die
as has been described in detail previously herein\textsuperscript{[27]}. 

4.3.3 Microstructural Characterization

The AGS of the densified ceramics were obtained from fracture surfaces of the densified polycrystals. The polycrystals were notched to a depth of ~0.1mm with a 300µm diamond saw blade and cracked in flexure along the notch. The fractured surface was mounted perpendicular atop an aluminum stub with carbon adhesive and coated with a thin film of approximately 1-2nm of platinum/palladium using a Cressington 108 sample preparation system. The microstructure of the mounted and coated fracture surfaces were obtained from secondary electron detection with a Phillips XL30 Field Emission Scanning Electron Microscope (FE-SEM). The average grain size with standard deviation was obtained by measuring approximately 300 grains over multiple scanning electron micrographs of the fracture surfaces at various random locations in the fractured zone, using the ImageJ software.

The distribution of the Nd dopant within the polycrystalline matrix was obtained from high-resolution EDS mapping of a 10µm x 20 µm x 50 nm specimen from each sample and imaged in a Titan Transmission Electron Microscope (TEM). The TEM specimen was prepared using a Focused Ion Beam (FIB) with a gallium beam. The FIB’ed specimen was attached to a copper TEM grid using a Pt focused ion beam.

4.3.4 UV-VIS-IR Transmission Measurements

Prior to optical analysis, the densified polycrystals were polished with diamond suspensions of decreasing grit size in the following order: 9µm, 6µm, 3µm, 1µm, and 0.5
µm, by spraying the diamond suspensions atop acrylic platens. Parallelism of the polished Fresnel surfaces was controlled by mounting the polycrystals to a ground steel tooling plate with epoxy. The final thickness of the polished specimens was 0.8mm ± 0.05 mm, in all cases. Optical Transmission spectra were taken on a Varian Cary 500 UV-VIS-IR spectrometer from 300 nm to 2500 nm, operating in single-beam mode with a rectangular spot size of 2mm by 9mm. The bulk polished samples were placed at normal incidence to the beam path. The scans were obtained at a rate of 0.2 nm s\(^{-1}\).

4.3.5 Photoluminescence Measurements

Photoluminescence data were taken on a Horiba Spex Fluorolog 3 Spectrophotometer system using an 806nm laser diode as the excitation source with a 100mW incident power and a spot size of 2mm. All measurements were taken in front face mode at an angle of incidence of 45°, on polished bulk samples. Emission scans were taken between \(\lambda = 1000\) nm and \(\lambda = 1100\) nm. All measurements were taken with an integration time of 1s per nanometer.

4.3.6 Single-Pass Gain of Optical Stimulated Emission

Optical Gain of Stimulated Emission was measured using a single-pass arrangement. For a detailed diagram please refer to Figure 5.x.x. For these experiments the samples are mounted with a Thorlabs SM05 aluminum lens mount and this unit (sample and holder) are mounted to a 6-axis kinematic mount, allowing for complete
manipulation of the optical alignment of the sample within the pump and probe beam axes. The sample kinematic mount was modified to accept water cooling. The coolant temperature was 15°C in all cases and the flow rate was always sufficient to maintain the sample temperature constant throughout the optical testing.

A continuous mode Nd:YAG laser, operating at the fundamental wavelength (λ=1064nm) was used as the probe laser for stimulated emission. The collimated probe beam (~1mm Diameter) was focused onto the sample with a 100mm focal length lens, resulting in a spot size of ~400µm. A Coherent FAP 40W laser diode coupled to an optical fiber and collimator was the pumping source, and the wavelength of the diode was tuned to 806nm. The 806nm pump laser was focused onto the sample in collinear with the probe beam in counter-propagation with a 35mm focal length lens resulting in a spot size of ~400 µm. The pump beam waist was injected into the arrangement via a dichroic mirror (Thorlabs DMSP1000) with a reflective cut-on wavelength of 1000 nm at a 45° AOI. The focusing optics for both the probe and pump beams were also mounted atop 6-axis kinematic fixtures, allowing precise spatial alignment of the two interaction volumes within the sample. The incident power of the pump and probe beams were constantly monitored with germanium photodetectors (Thorlabs PDA50B), labeled PD1 and PD2, respectively. A third germanium photodetector, labeled PD3, was used to monitor the intensity of the transmitted probe beam as a function of pump intensity. All of the photodetectors were calibrated against an optical power meter (Ophir Nova 2).
4.4 Results and Discussion

A one-step solid-state reaction densification approach was used for the production of transparent bulk polycrystalline undoped $\alpha$-Al$_2$O$_3$ and Nd:$\alpha$-Al$_2$O$_3$ ceramics by Current Activated Pressure Assisted Densification (CAPAD), using a custom built apparatus described previously. In our previous work, we presented a detailed processing study on the effects of CAPAD processing for producing undoped $\alpha$-Al$_2$O$_3$ and Tb$^{3+}$-doped $\alpha$-Al$_2$O$_3$ with optically active, over-equilibrium rare-earth dopant concentrations.$^{[27]}$ In Figure 4.1 we plot the resultant relative density of the consolidated bulk ceramics as a function of CAPAD processing temperature set-point. In all cases the heating rate was 300°C/min$^{-1}$ and the CAPAD temperature set-point was held for 5 min.

Figure 4.1 clearly displays a dependence of the densification onset temperature with the concentration of rare-earth dopant present. For the 0.25at.% and 0.35at.% Nd:Al$_2$O$_3$ samples, the major densification onset temperature is shifted from the undoped case from $\sim$900°C to $\sim$1100°C. In all cases, however, the reduced densification kinetics are overcome in CAPAD processing by operating at slightly higher dwell temperatures. Relative densities greater than 99% are achieved in the undoped $\alpha$-Al$_2$O$_3$ case at 1200°C and at $T>1260^\circ$C for the Nd:$\alpha$-Al$_2$O$_3$ samples. In all cases the highest relative densities are achieved at 1300°C, however, all samples obtained at these temperatures are white and diffusively opaque. This is due to an increased average
grain size of ~2.1 µm ± 0.25µm for the undoped α-Al₂O₃, and 1.91 µm ± 0.22µm and 1.87 µm ± 0.23µm, for the 0.25 at.% and 0.35 at.% Nd³⁺:α-Al₂O₃. This behavior has been observed, reported, and explained previously by Pechorraman et al. and this work and those referenced therein should be consulted for further detail.\[^{30}\]

Figure 4.1: Plot of the Relative Density for the Undoped α-Al₂O₃, 0.25at.% Nd³⁺:α-Al₂O₃, and 0.35 at.% Nd³⁺:α-Al₂O₃ bulk polycrystals as a function of the CAPAD Processing Temperature. The heating rate was ~300°Cmin⁻¹ and the hold time was 5 min at the temperature set-point.

As is reported in detail, within Chapter 1 and Chapter 3, the reduced diffusion kinetics and increased densification onset temperature is observed in other oxide systems during reaction/densification in CAPAD\[^{27}\][\(^{31}\)] and it is due to the homogenous
presence of the rare-earth oxide dopant powder within the matrix, primary along the grain boundaries when the two phases are just mixed and still separate reactants. The presence of the secondary phase inhibits direct diffusion of the matrix specie from grain to grain, therefore inhibiting the densification rate as well as the densification onset temperature. In our previous work with Tb$^{3+}$:Al$_2$O$_3$, we also observed and reported that the densification was inhibited by the presence of the Tb$^{3+}$ within the α-Al$_2$O$_3$ matrix, however, the degree of densification suppression observed was less in comparison to this case with Nd$^{3+}$ as a dopant, even at similar global concentrations.

The difference in behavior between the Nd$^{3+}$ and Tb$^{3+}$ cases can be possibly attributed to a disparity between the dopant ionic radii. The ionic radius of Nd$^{3+}$ is 0.983Å and it is 0.923Å for Tb$^{3+}$, representing a difference of ~1.065%. This greater increase in disparity between the Nd$^{3+}$ and the Al$^{3+}$ cation, for which the Nd$^{3+}$ will substitute, may explain the increased difficulty in doping Nd$^{3+}$ into the α-Al$_2$O$_3$ matrix, although at this point this work does not provide any definitive proof for this justification, except that the onset of densification is increased from the undoped α-Al$_2$O$_3$ and the Tb$^{3+}$:Al$_2$O$_3$ cases. A similar trend of a shift in the densification onset temperature with respect to lanthanide ionic radius was observed and reported for the Nd$^{3+}$, Er$^{3+}$, and Eu$^{3+}$ doped (0.2 at.% RE:Al$_2$O$_3$ ratio) α-Al$_2$O$_3$ system via free-sintering and hot-pressing by Maca et al.\textsuperscript{[32]} However, under their experimental conditions the densification onset temperatures were >1400°C and >98% relative density was only achieved at processing temperatures greater than 1500°C. It should be noted that in
**Figure 4.1** that the degree of densification suppression increases with the Nd$^{3+}$ concentration from 0.25 at.% to 0.35 at.% as well, but that by 1260°C the relative densities for both concentrations approach unity, strongly indicating that it is likely that the separate phases are becoming miscible at elevated temperatures, i.e. the solubility of Nd$^{3+}$ is higher within the $\alpha$-$\text{Al}_2\text{O}_3$ matrix at elevated temperatures, allowing over-equilibrium levels of rare-earth to become soluble within the polycrystalline matrix.

One possibility that may explain the ability of the $\alpha$-$\text{Al}_2\text{O}_3$ lattice to accommodate greater amounts of RE-dopants, is that the grain boundary volume of the ceramics may have a different solubility limit than the bulk crystal lattice. Since these ceramics have a sub-micron average grain size (250nm), the grain boundary volume (~10%) is significant and cannot be ignored. We do not discard this possibility and would propose further microstructure studies, such as atomic probe microscopy that would enable a more detailed characterization of the local stoichiometry and coordination. However, since CAPAD processing differs significantly than free-sintering and hot-pressing in systems with similar grain size, this indicates a unique and/or augmented mechanism being activated during CAPAD processing. Another possibility that we and others have observed that may affect the degree of RE solubility may be the presence of a reducing atmosphere$^{[27][33]}$ during CAPAD processing that may change the reaction kinetics either in totality or synergistically with the other processing parameters.

**Figure 4.2** reports the X-Ray diffraction (XRD) analysis of the starting powders (**Figure 4.2a**) and of the polished bulk polycrystals (**Figure 4.2b**) with variance in Nd$^{3+}$
Figure 4.2: X-ray diffraction spectra (XRD) for a) starting powders and b) CAPAD reaction/densfied bulk polycrystals. In both cases the undoped $\alpha$-Al$_2$O$_3$, 0.25 at.% and 0.35 at.% Nd$^{3+}$:\(\alpha\)-Al$_2$O$_3$ stoichiometries were analyzed.
dopant concentrations without any changes in powder and CAPAD processing from sample to sample. From the starting powders XRD spectra it can be clearly determined that the neodymium dopant is present within the α-Al₂O₃ starting powders as Nd₂O₃, as there is a minor peak present in the doped powders at 2Θ= 30.72⁰, corresponding to the 100% peak for Nd₂O₃ (ICSD#: 26867). Comparison of the mixed starting powders diffraction spectra to the reference for α-Al₂O₃ (ICSD#: 63647) shows no discernible shift in the location of the Bragg reflections from the undoped α-Al₂O₃ reference spectra. This analysis reveals that Nd³⁺ doping into the α-Al₂O₃ matrix did not occur through powder processing.

The X-Ray Diffraction spectra of the fully dense CAPAD processed polycrystals (T=1260⁰C, 5 min dwell, 105MPa) presented in Figure 4.2b, reveal that all of the samples are single phase α-Al₂O₃ and that there is not any measurable diffraction from the starting Nd₂O₃ dopant nor from the ternary NdAlO₃ phase, which would in the XRD analysis and has been observed and reported previously by multiple groups when α-Al₂O₃ has been over-equilibrium solubility doped with rare-earths using other processing approaches.[32][34] The absence of the starting Nd₂O₃ reactant and NaAlO₃ ternary in our samples strongly indicates a fundamental difference in the reaction kinetics associated with CAPAD processing in comparison to traditional processing approaches.

Moreover, careful inspection of the 100% peak for the α-Al₂O₃ phase, centered at 2Θ= 35.18⁰ shifts to lower 2Θ angles, 2Θ_{0.25} = 34.93⁰ and 2Θ_{0.35} = 34.89⁰ as a function of Nd³⁺ dopant concentration. The shift to the lower angles indicates a
stretching of the $\alpha$-$\mathrm{Al}_2\mathrm{O}_3$ lattice, indicating the presence of $\mathrm{Nd}^{3+}$ moving into solution within the matrix, corroborating the results observed and reported in Figure 4.1 that the two reactants indeed start as two separate phases and then become miscible at elevated temperatures.

As in the previous work in 0.5 at.% $\mathrm{Tb}^{3+}$:$\alpha$-$\mathrm{Al}_2\mathrm{O}_3$ system, the increased solubility of rare-earth in the $\alpha$-$\mathrm{Al}_2\mathrm{O}_3$ matrix is attributed to an increase in the reaction kinetics associated with high heating rates in CAPAD processing. This behavior was first reported in another oxide system. In cerium doped yttrium aluminum garnet, (Ce:YAG), for example, there is an approximate 20-fold increase in the second-order reaction coefficients for reaction/densified CAPAD processed samples in comparison to reaction/densification during free-sintering. Moreover, these second-order reaction coefficients were obtained at processing temperatures that were conservatively $\sim$600$^\circ$C lower during CAPAD processing to achieve full reaction of the Ce:YAG specie in comparison to the free-sintering case.$^{[31]}$ Consequently, a heating rate $\sim$300$^\circ$Cmin$^{-1}$ was implemented in order to achieve over-equilibrium doping of $\mathrm{Nd}^{3+}$ in $\alpha$-$\mathrm{Al}_2\mathrm{O}_3$.

The distribution of Nd throughout the matrix was analyzed by Energy –dispersive X-ray Spectroscopy (EDS) of sectioned portion of a 0.35 at.% $\mathrm{Nd}^{3+}$:$\alpha$-$\mathrm{Al}_2\mathrm{O}_3$ bulk
Figure 4.3: High-Angle Annular Dark-Field Transmission Electron Micrograph of a FIB’ed portion of the 0.35 at.% Nd$^{3+}$:α-Al$_2$O$_3$ ceramic with corresponding EDS elemental maps for Al, O, and Nd (L-Lines). The EDS mapping reveals the presence of Nd primarily along the grain boundaries and triple-points, but also within the grain interiors. The black portion of the maps along the bottom right hand corner pertains to a portion where no sample is present.

polycrystal (T=1260°C, 5 min dwell, 105MPa), that was prepared in an ultra-high vacuum environment using a focused-ion-beam (FIB). Figure 4.3 depicts a High-Angle Annular
Dark-Field transmission electron micrograph of the FIB’ed section with the corresponding EDS elemental maps for Al, O, and Nd (L-lines). The quantitative analysis from the L-line spectra from this EDS elemental mapping reveals that the Nd$^{3+}$ dopant is found in higher concentrations along the grain boundaries and triple points than within the grain interiors. Nonetheless, a significant portion of the Nd$^{3+}$ dopant is found within the matrix. This analysis does not allow us to determine the oxidation state of Nd$^{3+}$ within the matrix, but the PL spectra which is presented below is indicative of the presence of Nd$^{3+}$. The quantitative EDS analysis from a grain interior indicates that the local concentration of Nd$^{3+}$ is as high as 0.2 at.%, slightly lower than expected from the starting powder stoichiometry (0.35 at.%), but still ~200 times more than the equilibrium solubility limit. Quantitative analysis of the local stoichiometry of the grain boundaries and triple points indicate that under the same spectroscopic conditions the Nd concentration is approximately 2 and 3 times higher, respectively, in comparison to the grain interiors. This spectroscopic analysis corroborates what is observed and discussed in Figure 4.1 and 4.2 above that over-equilibrium Nd$^{3+}$ doping occurs during CAPAD processing.

It is likely that further refinement of CAPAD processing, namely adjustments in ultimate temperature, heating rates, cooling rates, and dwell at temperature can affect the degree of miscibility. Recent work by Rohrer and Harmer et al. on lanthanide doping of polycrystalline $\alpha$-Al$_2$O$_3$ suggests that differences in grain boundary structure in
undoped vs. doped cases may play a role in the diffusion kinetics, and hence the resultant microstructure and solubility of lanthanides within $\alpha$-$\text{Al}_2\text{O}_3$.\textsuperscript{[35],[36]}

From these CAPAD processing parameters the densification sigmoids and XRD analysis indicates that the ultimate processing temperature has the strongest effect on the miscibility, however, this also results in an unfavorable microstructure (large AGS) with regards to optical transparency, as discussed above. Therefore, for multi-functionality purposes, of particular interest is the effect of temperature dwell and cooling/quench rate. These results indicate that a longer dwell at ultimate temperature could result in reaction to completion. And an increased cooling/quench rate could serve as a mechanism for “freezing” in the dopant within the grain interior. Because the overwhelming majority of traditional ceramics processing approaches rely on very slow cooling/quench rates, even when SPS processing is implemented, this processing parameter has largely been neglected within the literature and should be further explored. The ability of our custom constructed CAPAD apparatus that utilizes copper electrodes and forced-convection water cooling of these electrodes allows our samples to be cooled/quenched at significantly higher rates (CR~$300^\circ\text{Cmin}^{-1}$) than those employed in free-sintering (CR<$10^\circ\text{Cmin}^{-1}$), hot-pressing (CR<$50^\circ\text{Cmin}^{-1}$), and even commercial SPS equipment (CR<$10^\circ\text{Cmin}^{-1}$). Further investigations are underway to fully ascertain the detailed effects of such CAPAD processing parameters on the resultant microstructure and stoichiometry and will be presented in a later communication.
The high optical transparency of the consolidated bulk Nd\textsuperscript{3+}:\textalpha-Al\textsubscript{2}O\textsubscript{3} polycrystals can be qualitatively appreciated in Figure 4.4 where a picture of Bourns College of Engineering at UCR is taken looking through the sample. The camera was ~25mm from the sample surface and BCOE was <20m from the back surface, showing that the transmission is high in the far-field. The image is crisp, indicating a minimal effect of birefringence scattering. Further quantitative data and discussion will be presented below.
Figure 4.5 plots the total transmission of the bulk polished $\alpha$-$\text{Al}_2\text{O}_3$ polycrystals as a function of Nd$^{3+}$ dopant concentration from $\lambda=300\text{nm}$ to $2200\text{nm}$. All of the samples were polished to a final thickness of $\sim1\text{mm}$ and characterized without anti-reflective coatings present. Inset within the data plot, are pictures of the polished polycrystals atop a printed text, displaying their high-optical transmission. The data presented is not
corrected for Fresnel reflections (~14%)\textsuperscript{[37]}. In all cases, the total transmission increases with wavelength and approaches the single crystal limit (losses due to Fresnel reflections only) at wavelengths greater than 1500nm. In the area of particular interest for lasing at 1064nm (\( ^4F_{3/2} \rightarrow ^4I_{3/2} \) transition), the total transmission is \( \sim 75\% \) for the Nd\(^{3+}\) doped ceramics. The transmission values of our undoped and doped samples rival those presented previously in the literature without the need of sophisticated powder processing in conjunction with sinter-HIP'ing approaches\textsuperscript{[37]} or without the need of a high-pressure SPS approach.\textsuperscript{[38]} This transmission behavior has been reported and discussed in our previous communication and the references therein\textsuperscript{[27]} and is attributed to a combination the samples’ near unity theoretical density and fine AGS. Here the relative densities are conservatively >99% and the AGS are approximately 250nm for each concentration and therefore this transmission behavior is expected for materials with these microstructures.

One remarkable difference measured within the transmission spectra are the presence of the absorption bands centered at \( \lambda = 585\text{nm}, 748\text{nm} \) and \( 806\text{nm} \), corresponding to the \(^4G_{5/2}, ^2H_{3/2}, \) and \(^4F_{9/2} \) Stark transitions from the \(^4I_{9/2} \) manifold, associated with the presence of optically active Nd\(^{3+}\) present within the doped ceramic matrix. To the best of our knowledge this is the first time the presence of any absorption bands associated with rare-earth doping have been measured and reported for \( \alpha\text{-}\text{Al}_2\text{O}_3 \). Moreover, the depth of the absorption bands increases with an increase in dopant concentration, indicating a higher-degree of optical activity from the Nd\(^{3+}\) ion. It is well
known that at high concentrations, optical activity diminishes due to concentration quenching, i.e. the distance between successive dopant ions is short enough that relaxation occurs through phonon scattering rather than optical decay. These results unambiguously prove the feasibility of optically pumping Nd$^{3+}$:α-Al$_2$O$_3$ via direct diode pumping, a pre-requisite for producing a compact, economical, and stable high-energy laser (HEL) from a solid-state media. The need for supporting electronics and the instability associated with flashlamp pumping precludes their use for portable HEL-technologies, although for a laboratory/manufacturing application this option remains.

Further confirmation of the presence of optically active Nd$^{3+}$ within the α-Al$_2$O$_3$ matrix is observed as a result of spontaneous photoluminescence (PL) signature resulting from optical pumping at λ=806nm ($^4I_{9/2} \rightarrow ^4F_{9/2}$). In Figure 4.6 the spontaneous PL in the near infrared portion of the spectrum can be qualitatively appreciated by taking a picture of a 0.35 at.% Nd$^{3+}$:α-Al$_2$O$_3$ polycrystal while being irradiated with an 806nm laser diode, focused down to an approximate spot size of ~400µm. Because the optical response of the infrared viewer is limited to a band between λ=1000-2000nm, all of the light collected (represented as purple within the image) is due to PL from the presence of Nd$^{3+}$ in the transparent media and not from the pumping source.
Figure 4.6: Picture of a consolidated and polished 0.35 at.% Nd$^{3+}$:α-Al$_2$O$_3$ bulk polycrystalline ceramic, viewed with a bandpass infrared camera (Transmission Band 1000nm-1200nm). The spot of light on the right portion of the ceramic is the induced spontaneous photoluminescence in the near infrared from direct diode pumping at $\lambda=806$nm. This picture qualitatively demonstrates the PL signature from the transparent gain media, resulting from the optically active Nd$^{3+}$ dopant present at over-equilibrium concentrations within the matrix.

Figure 4.7 presents the PL emission spectra for the 0.25 at.%, 0.35 at.% Nd$^{3+}$:α-Al$_2$O$_3$ samples as well as for 0.5 at.% Nd$^{3+}$:Glass (Schott), and 1.1 at.% Nd$^{3+}$:YAG (single crystal, Litton Technologies, Inc.), all being pumped with the same laser diode used in to obtain the infrared image in Figure 4.6. These compositions of the commercially available laser media were chosen for comparison to our samples because the
volumetric concentrations of Nd$^{3+}$ ions are similar and because these two gain media are arguably the most important materials for HEL-technology. Nd$^{3+}$:Glass is still the mainstay material for producing ultra-short, high peak power laser pulses from a Nd$^{3+}$ active ion$^{[13][39]}$ and Nd$^{3+}$:YAG is undoubtedly the king of all laser media, including CW- and quasi CW-HEL-technology$^{[2]}$.

Figure 4.7: Photoluminescence Emission Spectra for single crystal Nd$^{3+}$:YAG (Litton Technologies, Inc.), Nd$^{3+}$:Glass (Schott), and the 0.25 at.% and 0.35 at.% Nd$^{3+}$:$\alpha$-Al$_2$O$_3$ bulk polycrystals. The excitation wavelength was 806nm in all cases and the spectra are normalized.
The relative intensities for all of the emission spectra presented are normalized, so no quantitative data can be extracted with respect to the relative intensities in this case. However, the gain bandwidth ($G_{bw}$) can be determined for each of the PL media by measuring the full-width at half-maximum of the normalized intensity of the PL spectra. This is a valid approximation because, as will be discussed below, gain has been measured at 1064nm for the Nd$^{3+}$:α-Al$_2$O$_3$ materials and for the commercial materials the PL spectra is equivalent to the gain spectra. However, since gain has not been directly observed or measured throughout the entire PL bandwidth for the Nd$^{3+}$:α-Al$_2$O$_3$ ceramics at this time, we proceed with caution. From a simple inspection of the PL curves it is clear that the $G_{bw}$ for Nd$^{3+}$:α-Al$_2$O$_3$ is significantly larger than for the other commercial Nd$^{3+}$ gain media. From our measurements, for Nd$^{3+}$:YAG $G_{bw}$=0.6nm (0.16 THz), for Nd$^{3+}$:Glass $G_{bw}$=20nm (5.4 THz), and these measurements agree with previous reports from the literature$^{[40]}$.$^{[39]}$. Measuring the FWHM of the PL emission spectra for the Nd$^{3+}$:α-Al$_2$O$_3$ results in a 49nm (13 THz) and 48nm (12.7 THz) for each dopant concentration. These gain bandwidths are the largest ever reported for any Nd$^{3+}$ media.

This is important because the gain bandwidth determines the temporal pulse limit possible from the gain media PL. This temporal pulse limit is called the bandwidth-limited pulse width, $\Delta \tau_p$. The larger bandwidth of Nd$^{3+}$:Glass is what allows its use for the generation of high peak-power lasers over Nd$^{3+}$:YAG, in lieu of its poor thermo-mechanical properties, because the larger $G_{bw}$ allows the generation of ultra-short time pulses. Taking the inverse of the $G_{bw}$ gives the bandwidth-limited pulse width $\Delta \tau_p$, which
results in $\Delta \tau_p = 6.3$ ps for Nd$^{3+}$:YAG, $\Delta \tau_p = 18.5$ fs for Nd$^{3+}$:Glass, $\Delta \tau_p = 7.7$ fs for 0.25 at.% Nd$^{3+}$:α-Al$_2$O$_3$, and $\Delta \tau_p = 7.9$ fs for 0.35 at.% Nd$^{3+}$:α-Al$_2$O$_3$. These bandwidth-limited pulse widths represent a 2.5 fold increase in the single-shot peak power over Nd$^{3+}$:Glass and >80 fold increase over Nd$^{3+}$:YAG. Moreover, because the thermo-mechanical properties of the Nd$^{3+}$:α-Al$_2$O$_3$ polycrystals are superior, these increases are conservative. Further discussion will be presented below.

The increased gain bandwidth of the Nd$^{3+}$:α-Al$_2$O$_3$ media indicate 1) that a strong coupling between the crystal field of the matrix and the Nd$^{3+}$ dopant$^{[41]}$ and 2) could be indicative of multisite rare-earth dopin within the matrix. The former behavior is common in transition-metal doped media, such as Ti$^{3+}$:Al$_2$O$_3$ and is due to vibronic interaction between the dopant and crystal field, which results in a high degree of homogenous spectral broadening. When rare-earths such as Nd$^{3+}$ are doped within large crystal fields, such as in YAG, the vibronic interactions are weak and a narrow gain bandwidth results. Doping in amorphous media, i.e. glasses results in homogenous broadening and explains the PL behavior observed in Nd$^{3+}$:Glass.$^{[42]}$ A large PL/G$_{bw}$ has not been reported for has not been reported for Nd$^{3+}$ ceramics (only moderately in glasses), but has been seen in amorphous thin films of Al$_2$O$_3$ prepared by PLD, when doped with Er$^{3+}$ or co-doped with Yb$^{3+}$/Er$^{3+}$.$^{[22][21]}$ This may be explained by vibronic interaction, but is most likely attributed to multi-site rare-earth doping. In order to fully explain and de-couple the effects of phonon interactions and lattice coordination on the PL, the PL spectra at cryogenic temperatures needs to be investigated. Should PL
narrowing occur at cryogenic temperatures, this would indicate a vibronic interaction, the degree of which can be ascertained from FT-IR measurements at cryogenic temperatures as well.

Regardless of the originating nature for the PL/Gbw broadening in Nd³⁺:α-Al₂O₃ it is likely that the ligand field around the Nd³⁺ is glassy in nature, while the global crystal field of the media is highly crystalline (Figure 4.2). This is a unique combination of properties because it produces a material with the optical properties of a glass, while retaining all of the thermo-mechanical properties of a crystalline matrix, i.e. a large gain bandwidth in a material with a high thermal conductivity (k~28 Wm⁻¹K⁻¹) and high fracture toughness (3.37 MPam⁻²), resulting in an astronomical thermal shock resistance (Rₛ~19,500 Wm⁻¹). Ultimately, these combinations of properties indicate a possible quantum leap in the ultimate power output attainable from laser gain media.

In order to unambiguously ascertain the viability for lasing in our Nd³⁺:α-Al₂O₃ ceramics, the net optical gain under direct diode pumping at λ=806nm was measured at an emission wavelength of λ=1064nm using a single pass arrangement that is depicted in Figure 4.8 and has been used a priori by Lai et al. for other material systems.[43]
Figure 4.8: Schematic of the single-pass gain experimental set-up implemented to measure the single-pass gain coefficients of the 0.25 at.% and 0.35 at.% Nd\textsuperscript{3+}:\textalpha-Al\textsubscript{2}O\textsubscript{3} bulk polycrystalline ceramics.

Briefly, the 1064nm probe beam was passed through a specimen at a constant incident power and the transmitted intensity of the probe beam was monitored with a photodiode only sensitive to that wavelength. Simultaneously, in perfect spatial counter-propagation, the specimen was pumped with an 806nm laser diode by means of a dichroic optic. The increase/decrease in the probe beam intensity as a function of absorbed 806nm pump power was monitored by the same photodiode. Using a modified version of the Beer-Lambert law for homogenous/Doppler broadened gain media, it is possible to determine the single-pass gain coefficients should the physical interaction of the pump and probe beam result in stimulated emission with the condition that the incident intensity and final intensity be known. This relationship is presented below
Where $I_0$ is the initial intensity of the probe beam, $z$ is the sample thickness, and $G$ is the gain coefficient, often displayed as $\alpha$ ($\alpha$ is often used to denote the absorption coefficient in a material and it is by definition equal to the negative of $G$, $\alpha = -G$). A negative gain in the presence of stimulated emission means that the losses of the media (combination of absorption, scattering, reflection, etc.) are not overcome by the amplification of the incident stimulated emission resulting from external pumping, which means that positive amplification cannot occur under those experimental conditions, i.e. lasing will never occur. If the amplification of the stimulated emission probe beam surpasses the losses of the system, $G$ will be positive, indicating a net positive gain, i.e. amplification.

Figure 4.9 plots the results obtained from the single-pass pump/probe experiment for the 0.25 at.% and 0.35 at.% Nd$_3^+$:Al$_2$O$_3$ ceramics as a function of absorbed pump power. As can be seen a net positive gain is achieved at $P > 2.25W$ for
Figure 4.9: Single-pass gain coefficients for the Nd$^{3+}$:α-Al$_2$O$_3$ ceramics as function of Absorbed Pump Power ($\lambda=806nm$). The single pass probe wavelength was 1064nm and its incident power was held constant at 150mW for of the measurements. These results are unprecedented for RE:Al$_2$O$_3$. The positive gain coefficients are proof of a population inversion under these conditions and represent the first quantitative proof for Nd$^{3+}$:α-Al$_2$O$_3$ as a viable laser gain media.

both materials and the magnitude of G increases linearly as a function of the absorbed pump power. This is the first time that a net positive gain has been observed and reported for bulk RE:Al$_2$O$_3$ polycrystal and they explicitly prove that lasing is possible in these materials. As the 806nm pump power is increased the net positive gain increases to values as high as 2.27 and 2.42 cm$^{-1}$ for the 0.25at.% and 0.35at.% Nd$^{3+}$
concentrations, respectively. Because the gain coefficient, $G$, is directly related to the product of the emission cross-section, $\sigma$, and the population difference of optically active photoelectrons in the excited state ($N_E$) and the ground state ($N_G$) such that\textsuperscript{[41]},

$$G = \sigma \cdot (N_E - N_G) \quad (4.2)$$

this suggests that if the gain coefficient is positive ($G > 0$), that $N_E > N_G$, since a negative $\sigma$ is not possible in the presence of stimulated emission. \textit{Therefore, the positive gain coefficients also represent the first observation and report of a population inversion in any RE:Al$_2$O$_3$ material and is a further unambiguous proof of the viability of Nd$^{3+}$-$\alpha$-Al$_2$O$_3$ as a new laser gain media.} These results in combination with the superior thermo-mechanical properties, and the increased PL/gain bandwidth observed, produce a large driving force for pursuing the further development of this new gain media because their synergy represents an overwhelming improvement in device performance. Nd$^{3+}$:Al$_2$O$_3$ has significant potential to be an important laser gain media in cw- and ultra-short pulse- regimes at room temperature and possibly down to cryogenic temperatures.

Further improvements in material performance are needed to truly understand and determine the limits of Nd$^{3+}$-$\alpha$-Al$_2$O$_3$ as a laser gain media. However, the prospects of further material refinement are bountiful even within our currently presented approach, i.e. solid-state powder processing in conjunction with simultaneous reaction/densification with CAPAD as has been discussed above. It is likely that other
materials processing approaches either in conjunction with this approach or entirely independent exist that could achieve similar or improved performance; however, to date none have been successful. What is clear from these results is that regardless of the approach, access to kinetic windows outside of equilibrium conditions are needed to obtain materials with the demanding combination of optical, thermal, and mechanical properties required for high-performance laser gain applications.

For lasing to occur, the lasing threshold must be overcome by pumping sufficiently. For Homogenous/Doppler broadened systems, the lasing threshold is typically defined when the gain surpasses a value of $G=16 \text{ cm}^{-1}$. From a linear extrapolation of the gain coefficients presented in Figure 4.9 an absorbed pump power of ~86W will be needed to overcome the lasing threshold condition in a single-pass arrangement as is used in the above experiments. This behavior is expected as our material is largely un-optimized and because the large $G_{bw}$ directly indicates a higher threshold condition as pumping at 806nm results in significant PL at wavelengths other than 1064nm. Further improvements in dopant distribution, dopant concentration, and overall transparency will result in improved device performance.

Regardless, this bounded calculation for the lasing threshold in Nd$_{3+}^\alpha\text{-Al}_2\text{O}_3$ is high in comparison to Nd:YAG as can be seen in Figure 4.10, where lasing slope efficiencies are presented as a function of pump power for different Fabry-Perot laser cavity configurations in a single-pass pump arrangement utilizing the same/similar
pumping activation volume as in the above single-pass probe experiments. While it is difficult to directly compare the lasing thresholds presented in Figure 4.10 to the bounded estimate for the lasing threshold in Nd$^{3+}$:α-Al$_2$O$_3$ from the data in Figure 4.9, a useful semi-quantitative comparison is possible. By calculating the losses in a laser cavity with an input/output coupler efficiency of 0.99 and taking into account the losses due to imperfect optical transmission at 1064nm in our sample (T~75% at 1064nm), an

![Figure 4.10: Lasing slope efficiencies for 1.4 at.% Nd:YAG single crystal (Litton Technologies, Inc.) as a function of direct diode(λ=806nm) pump power for various cavity configurations. In all cases a Fabry-Perot arrangement was used and the pump interaction volume was the same/similar to that used in the single-pass probe gain experiments used above to characterize the Nd$^{3+}$:α-Al$_2$O$_3$ ceramics.](image-url)
overall cavity efficiency of $\sim 74\%$ is obtained. This scenario is approximated in the Nd$^{3+}$:YAG lasing scenario where an output coupler of $T \sim 21.35\%$ is operated. In that case an absorbed pump power of $\sim 4.25W$ was required to overcome the threshold condition. The disparity in the lasing threshold condition between this Nd$^{3+}$:YAG scenario and the Nd$^{3+}\alpha$-Al$_2$O$_3$ system suggest that the increased $G_{bw}$ and un-optimized material properties are each responsible for this behavior and should be investigated further.

Due to a practical lack of sufficient pump power, lasing has not been directly observed yet in this material system. Our results also indicate that more efficient use of our current pump lasers can be obtained with further optimization of the pump/probe arrangement and this avenue will be pursued. One improvement that could drastically affect the optical gain is the cooling configuration. While much care has been given to maintain a steady-state temperature during experimentation, further improvements will yield superior device performance. Since this avenue is a subject unto itself, it has been largely un-addressed in this dissertation and could serve as the basis for further studies. Another approach to obtain lasing would be to adequately engineer a cavity into a multiple-pass arrangement. This latter approach is the current subject of further investigations and will be reported in further communications to the scientific community through journals or other dissertations by continuing doctoral/masters students.
4.5 Summary

An all solid-state powder processing route in conjunction with a single-step reaction/densification CAPAD approach was implemented to produce transparent bulk polycrystalline Nd<sup>3+</sup>:α-Al<sub>2</sub>O<sub>3</sub> with over-equilibrium neodymium doped (0.25 at.% and 0.35 at.% Nd<sup>3+</sup>:Al<sup>3+</sup>) concentrations. The transparent ceramics have a real-in-line (RIT) of ~75% at 1064nm and display optical absorption bands at centered at λ = 585nm, 748nm and 806nm, corresponding to the $^4G_{5/2}$, $^2H_{3/2}$, and $^4F_{9/2}$ Stark transitions from the $^4I_{9/2}$ manifold, associated with the presence of optically active Nd<sup>3+</sup> present within the doped transparent ceramic matrix. The gain bandwidth, $G_{bw}$, for these materials is ~13THz centered at 1064nm and represents a new record for any Nd<sup>3+</sup> gain media. The resultant bandwidth-limited pulse, $\Delta \tau_p$, for these ceramics is ~8fs and represents a factor ~2.5 and ~80 improvement in the single-shot peak power output over Nd<sup>3+</sup>:Glass and Nd<sup>3+</sup>:YAG media, respectively. Moreover, because the thermo-mechanical properties of Nd<sup>3+</sup>:α-Al<sub>2</sub>O<sub>3</sub> ($R_\sigma$ ~19,500 Wm<sup>-1</sup>) are far superior to Nd<sup>3+</sup>:Glass ($R_\sigma$ ~1 Wm<sup>-1</sup>) and Nd<sup>3+</sup>:YAG ($R_\sigma$ ~800 Wm<sup>-1</sup>), this improvement is conservative with regards to single-shot peak power output, and also represents the possibility of producing a laser with higher duty cycles than are obtainable with Nd<sup>3+</sup>:Glass and Nd<sup>3+</sup>:YAG.

Optical gain of stimulated emission is observed, measured, and reported at λ=1064nm under direct-diode pumping at λ=806nm, for the first time in any RE:Al<sub>2</sub>O<sub>3</sub> materials, with single pass gain coefficients, G, as high as 2.27 and 2.42 cm<sup>-1</sup> for 0.25 at.% and 0.35 at.% Nd<sup>3+</sup> dopant concentrations, respectively. The measured positive
gain coefficients are the first reported proof of a population inversion in any RE:α-Al₂O₃ ceramics and ultimately represent the first comprehensive proof for lasing in any non-textured polycrystalline anisotropic media. It is the unique combination of the near unity relative density, fine average grain size (AGS), and 3 orders of magnitude over-equilibrium Nd³⁺ dopant concentration that makes bulk polycrystalline Nd³⁺:α-Al₂O₃ a uniquely optical/structural material for applications such as high-energy lasers with superior performance.

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4.7 References


