Laser Photothermal Investigation of Non-Radiative Bulk and Surface Sources in Solid-State Laser Materials

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
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Abstract

Title: "Laser Photothermal Investigation of Non-radiative Bulk and Surface Sources in Solid-State Laser Materials."


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The understanding of the problem of non-radiative energy conversion in solid-state laser materials is the key factor in improving the overall efficiency of solid-state lasers. Furthermore, the reduction of the heat generated in an optically pumped laser crystal can lead to several new applications of solid state lasers, especially in the high-power region. To improve the quality of grown crystals, laser crystal growers require accurate techniques to perform the quality control that is so vital to improving the growth process.

In this work, we quantified the problem of non-radiative (heat) energy conversion by using three techniques to monitor laser crystal quality. We used a technique known as photopyroelectric spectroscopy (PPES) to measure the optical absorption and nonradiative energy conversion efficiency of Ti: Sapphire laser materials. We unexpectedly found that the non-radiative processes at the surface of the crystal form a greater fraction of the overall losses in a crystal than had previously been assumed.

Based on our finding using PPES, we used the photothermal radiometry technique, which is more sensitive to surface effects than PPES. Using a time-domain approach and a time-domain theoretical treatment of the IR radiative emission signal, we determined that we can probe non-radiative surface and bulk processes by monitoring different time ranges. Our results show that photothermal radiometry can be used as a single technique to evaluate both the bulk and surface non-radiative energy conversion rates in a solid state laser material. The final technique we used was the standard method of laser crystal evaluation: measuring the laser output from a material in a laser cavity. By testing the same materials using PPES, PTR and a laser cavity, we were able to correlate our results with the standard method and also show that the PTR technique can give us information as to why a particular crystal is better than another, which cannot be done by the standard method.
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English Symbols

\( A_{ij} \) : Einstein A coefficient (spontaneous emission) from level i to j

\( A_s \) : Surface absorptance

\( b_{ij} \) : Thermal coupling coefficient between region i and j

\( B \) : Coefficient of thermal expansion

\( B_{ij} \) : Einstein B coefficient

\( c \) : Speed of light in a vacuum

\( c_\infty \) : Pyroelectric signal for an infinite airgap thickness

\( e \) : Charge on an atom

\( e(\omega) \) : Emission coefficient spectra

\( \bar{E} \) : Electric field

\( E_{ij} \) : Energy transition from level i to j

\( E_\omega \) : Energy in a beam of photons of frequency \( \omega \)

\( f_{ij} \) : Dimensionless oscillator strength for oscillations from i to j

\( f(\omega) \) : Photon intensity function

\( g_i \) : Number of degenerate levels associated with level i

\( g(\omega) \) : Lineshape function

\( Gr \) : Grashof number

\( h \) : Planck's constant = 6.6 x 10^{-34} Js

\( h_c \) : Convective coefficient

\( h_r \) : Radiative coefficient

\( H_2 \) : Hamiltonian of an atom

\( \hbar \) : \( h/2\pi \)
\( I_\omega \): Intensity of monochromatic beam at frequency \( \omega \)

\( K_b \): Boltzmann Constant

\( l \): Sample thickness

\( L \): Air gap thickness

\(< m > \): Thermal occupation factor for phonons

\( n \): Refractive index

\( N_i \): Population (number of atoms per unit volume) of level \( i \)

\( p \): Number of phonons in a multiphonon process

\( P \): Volume polarization

\( P_o \): Pump power

\( P_\omega \): Power per unit volume in a beam of frequency \( \omega \)

\( Q_b \): Bulk nonradiative energy generation rate

\( Q E \): Quantum efficiency

\( Q_s \): Surface nonradiative energy generation rate

\( Q_\omega \): Energy of a quantum of light of frequency \( \omega \)

\( \vec{r} \): Displacement vector

\( R \): Spot size

\( R_s \): Surface reflectance

\( S_{em} \): IR radiation emission from a material

\( T \): Temperature

\( V \): Perturbation hamiltonian

\( W_{bb} \): Energy density of blackbody radiation

\( W_{ij} \): Transition probability (rate) for transition from level \( i \) to \( j \)

\( W_{ijr} \): Nonradiative emission rate from \( i \) to \( j \)

\( W_{ijp} \): Spontaneous emission rate from \( i \) to \( j \)
$W_{ij}^e$: Stimulated emission rate from $i$ to $j$

$W_p$: Optical pumping rate

$x_{ij}$: Oscillator strength for transitions from $i$ to $j$

**Greek Symbols**

$\beta$: Optical absorption coefficient

$\beta_b$: Bulk optical absorption coefficient

$\beta_{ij}$: Optical absorption coefficient on transition $ij$

$\beta_{ir}$: Infrared absorption coefficient

$\beta(\omega)$: Optical absorption coefficient as a function of frequency

$\gamma(\omega)$: Gain coefficient as a function of frequency

$\Gamma_s$: Surface absorptance

$\epsilon$: Emissivity

$\eta_A$: Mode cross section efficiency

$\eta_c$: Output coupling efficiency

$\eta_p$: Pumping efficiency

$\eta_{NR}^{(6)}$: Bulk optical to thermal energy conversion efficiency

$\eta_{NR}^{(0)}$: Surface energy conversion efficiency

$\eta_s$: Slope efficiency

$\theta$: Total (surface and bulk induced) temperature at crystal surface

$\kappa$: Wave vector

$\lambda$: Wavelength

$\nu$: Fluid viscosity

$\xi$: Nonradiative coupling constant

$\varpi$: Vibrational energy
\( \rho_{BB} \): Energy density of Blackbody radiation

\( \varrho \): Relaxation time ratio

\( \sigma_{abs} \): Absorption cross section

\( \sigma_{em} \): Emission cross section

\( \sigma_{BB} \): Mode density

\( \sigma_i \): thermal diffusion coefficient in material \( i \)

\( \tau_\beta \): Thermal transfer time in solid

\( \tau_h \): Thermal transfer time from solid to gas

\( \tau_i \): Lifetime of atoms in level \( i \), considering decay to all lower levels

\( \tau_{ij} \): Lifetime of atoms in level \( i \) that decay to level \( j \)

\( \tau_p \): Pulse duration

\( \tau_{sp} \): Spontaneous emission lifetime

\( \phi \): Fitting parameter

\( \omega \): Frequency of light

\( \omega_c \): Chopping frequency

Abbreviations

FOM: Figure of Merit

IP: In-Phase Signal

IR: Infrared

LIA: Lock-in Amplifier

PPES: Photopyroelectric Spectroscopy

PTC: Positive Temperature Coefficient

PTR: Photothermal Radiometry

PVDF: Polyvinylidene Fluoride
QE: Quantum Efficiency

SNR: Signal to Noise Ratio
Chapter 1

Introduction

Although a solid state-laser produces a highly directional, high intensity beam that most often has a pure frequency or wavelength, the energy of the laser output is low compared to the energy used to produce this beam. Since typical values of the overall efficiency of solid-state lasers are less than 20% [1], there is a need to understand why solid-state lasers operate at such low efficiencies. Although the overall efficiency of a laser depends on several factors, such as input pumping energy transfer and resonator alignment, the most fundamental factor affecting the total losses involves the losses incurred in the laser medium [2].

The ratio of the amount of radiative energy emitted by a laser material to the amount of pump energy absorbed by the material is the most fundamental efficiency of a laser. If all the pump energy is not converted to useful radiative energy that forms the laser output, where does the rest of the energy go? The losses incurred can be separated into losses incurred in the gain medium and losses incurred in the resonator. The primary loss mechanisms in the laser gain medium are due to nonradiative energy conversion and spontaneous emission. The remaining nonradiative energy is dissipated as heat into the laser material. The nonradiative energy is detrimental to the operation of a laser in two ways. First, the more nonradiative energy that is generated, the less energy is available for useful, laser output. In addition,
this heat dissipation can cause other unwanted effects such as instabilities due to thermal birefringence [3]. The extent to which nonradiative energy is generated in laser materials is highly dependent on the manner in which the laser crystal is grown and the defects that are present in the crystal [4]. Because the laser material growth process is so essential to the overall efficiency of a solid-state laser, there is a need to develop methods of controlling and evaluating the quality of grown laser crystals.

A high efficiency solid-state laser requires both a high quality material and a resonator with minimal losses. In a recent review of the solid-state laser field, Chai [2] identifies the need for further improvements in laser crystal quality and in the crystal growth process. He claims that since laser resonator system design has already been pushed to the limit of material performance, improvements in material growth and processing are needed to further improve laser performance. In this work, we attempt to address these needs by dealing with the problem of non-radiative energy conversion in laser materials and by developing techniques to evaluate the extent of these nonradiative processes in solid-state laser materials in a non-contact, non-destructive manner.

1.1 Solid-State Laser Materials

In a solid-state laser, the atoms that absorb energy and emit laser light are contained in a crystal or glassy material. A solid-state laser is made up of two components: 1) a dopant metallic ion whose function is to absorb and emit light. 2) A crystalline or glassy host in which a small concentration of these dopant ions are embedded. Typically, the light emitting species accounts for a maximum of 1% of the material [5]. These atoms must have a set of energy levels that let it absorb pump light to populate the upper laser level. The best solid-state laser emitters are metallic elements such as chromium, neodymium and titanium.
The interaction between the light-emitting ion and the host material is vital to the operation of solid-state lasers. The host must be reasonably transparent to the pump light and absorb very little light at the laser wavelength. Too much absorption at either wavelength can greatly reduce efficiency or make laser action impossible.

In the past ten years, there has been a renewed surge of interest in the development of solid-state lasers due to the simultaneous development of several related technologies such as high-power laser diodes, new laser materials, laser designs, and nonlinear materials [6]. A special class of lasers known as tunable lasers extend the usefulness of single wavelength lasers by providing single-wavelength laser output at a wide range of wavelengths. Traditionally, dye lasers were used whenever tunability was required. Since dye lasers are difficult to operate and impractical for many applications, they are increasingly being replaced by tunable solid-state lasers, because of their reliability and ease of handling. With the recent development of diode-pumped solid-state lasers, improvements in cost and compactness render this type of laser one of the most important lasers of the future [7]. Such compact and low-cost solid-state lasers tuning throughout the visible and infrared spectral regions will be important for applications ranging from communications, data storage and display technology to environmental monitoring and medical diagnostics.

1.2 Reasons for Using Ti: Sapphire as the Material Under Study

The development of the Ti: Sapphire laser by Moulton [8] has heralded a revolution in tunable solid-state laser technology and application. Following the development of the Ti: Sapphire laser, a great deal of work done by the laser crystal growth community has resulted in the emergence of a number of new types of solid-state laser materials for various appli-
cations. The rapid advance in this field has resulted in the ability of broadband solid-state laser media to provide spectral output in a wide range of wavelengths from the ultraviolet to the near-infrared spectral regions [9].

Due to the importance of this material in the laser industry, we selected Ti: Sapphire as the material to evaluate in this study. However, the problem of non-radiative energy conversion that leads to lower overall efficiencies in optical systems is relevant to transparent optical materials that are used as solid-state lasers, frequency doublers, frequency triplers and frequency mixers [9]. The problem of non-radiative energy conversion in such materials limits the application of solid-state technology in high-power applications [10].

The work presented in this thesis is applicable to any optically active material that can emit fluorescent light when pumped with an optical source. The techniques presented in this work can determine the amount of non-radiative energy generated by such fluorescent materials. This information can be used to determine the amount of useful radiative (fluorescent) energy that such a material can yield.

1.3 Layout of Thesis

The next chapter contains a description of the laser crystal growth process and the types of defects present in these crystals. Based on this information and a survey of the existing methods of evaluating laser crystal quality, we define the problem that this thesis attempts to solve and the approach that we will take to reach this goal. In chapter 3, we describe some of the fundamental processes that occur when light interacts with a solid-state laser material. In doing so, we also define some of the key parameters which we determined experimentally in the following chapters. Chapters 4, 5 and 6 describe each of the three main sections of this thesis. In each of these chapters, we evaluate the quality of the crystal using a different
technique. In chapter 4, we use a technique known as photopyroelectric spectroscopy to probe the non-radiative processes occurring in the bulk of the crystal. Contrary to what we expected, our experiments showed that non-radiative processes occurring at the crystal surface can in some instances dominate the non-radiative energy generation in the crystal bulk. Having concluded that we require a single technique that can simultaneously monitor non-radiative processes at the bulk and surface, we use the photothermal radiometry technique in chapter 5 to perform this very function. In chapter 6, we evaluate the quality of the crystals tested in chapters 4 and 5 using a laser cavity, which is the the standard method for evaluating laser crystal quality. By doing so, we are able to correlate our results with this standard technique and also obtain first-hand knowledge of the pros and cons of our alternative techniques as compared to the standard technique.
Chapter 2

Problem Definition and Approach

Having established the importance of laser materials evaluation in chapter 1, we now describe the sources of non-radiative energy generation in such materials. In this chapter, we describe the problem we are attempting to solve and the approach we will take to deal with this problem. Before we can define the problem clearly, we require some insight into the nature and origin of heat generation in laser crystals. We begin this chapter by describing the laser crystal growth process and the role that this process plays in the formation of heat-generating defects in these crystals. We next describe the industrial standard methods of laser crystal evaluation that are in current use. Based on the deficiencies we identified in the standard methods, we develop several criteria that our proposed technique must meet. We then review the scientific literature and develop an additional set of criteria that any accurate technique must address when applied to evaluate laser material quality. In view of the criteria mentioned, we justify the fact that photothermal techniques are ideally suited to characterizing the non-radiative processes in solid-state laser materials.
2.1 Heat Generation in Laser Materials: Background

The need to evaluate non-radiative energy conversion processes arises from the presence of defects which generate heat upon absorbing optical energy. These defects arise primarily due to the crystal growth process, which is described below. Solid-state laser crystals are most often grown from a molten liquid. There are a number of methods of growing crystals from a melt, such as the Bridgman method, the Czochralski method and the heat exchanger method [11, 12]. In this work, we evaluated crystals that were grown using the Czochralski method.

2.1.1 Laser Crystal Growth, Post-Growth Treatment and Surface Processing

In the Czochralski method shown in figure 2.1, crystal growth from a melt is accomplished by establishing an equilibrium between a solid seed crystal and a liquid melt and displacing the equilibrium very slightly in favour of the solid. The system will lower its overall energy by forming additional solid, thereby causing the crystal to grow. The crystal growth takes place in the presence of a temperature gradient normal to the solid-liquid interface (which coincides with an isotherm). Pulling the crystal upwards draws liquid across this isotherm where it forms new crystal [13].

Several factors pertaining to the crystal growth process contribute to the quality of laser crystals. The raw material, the growth conditions (such as the atmosphere and temperature gradients), and equipment can each contribute to the overall quality of the crystal. None of these factors can compensate for the other’s shortcomings. In other words, the use of the best possible equipment cannot compensate for inferior process control or impure raw materials [13]. If even one of these factors is not optimal, defects and impurities can result in
the grown crystals, leading to lower laser performance. In the specific case of Ti: Sapphire crystal growth, an important stage of the growth process is the control of the valence state of the dopant Ti ion. Ti can easily enter the crystal in the +4 state rather than the desired +3 state. The crystals used in this work were grown at Union Carbide, Inc. from raw materials \((Al_2O_3; Ti_2O_3)\) of 99.999% purity, using a pulling rate of 0.3 mm/h in an ambient environment of purified argon. The grown crystals were 2.5 inches in diameter and 10 inches long [14].

Post-Growth Annealing

An unavoidable problem associated with growing Ti: Sapphire crystals using the Czochralski technique is the presence of \(Ti^{4+}\) ion impurities [15. 16. 17]. The presence of these impurities leads to a parasitic absorption in the wavelength range overlapping the Ti: Sapphire emission range, thereby reducing the laser output in \(\text{Ti: Sapphire}\). These impurity \(Ti^{4+}\) ions occur
due to an oxidation reaction at the melt surface. Because attempts to modify the Czochralski technique to alleviate this problem have been unsuccessful, post-growth annealing treatments have been developed by the crystal growth community to remove these impurities [4]. For the crystals used in this work, the post-growth annealing process consisted of annealing at 1850 degrees C for 20 hours in an atmosphere of 50 % hydrogen and 50 % argon. The reducing atmosphere of the hydrogen gas converts the \( Ti^{4+} \) ions to \( Ti^{3+} \) [14]. A high degree of control over this process is required to prevent the formation of additional impurities or scattering centres.

**Surface Treatment**

Following the crystal growth and post-growth process, the grown boule is cut into smaller pieces which are then subjected to surface polishing. In any optical material, the polish processing is crucial to the overall performance of the material since the surface is more susceptible to damage or losses than the bulk [18, 19]. There are a number of polishing processes which are used to treat the surfaces of optical materials, including diamond turning, mechanical polishing with soft or hard materials, mechano-chemical polishing and etching [20, 21]. There are two schools of thought regarding mechanical polishing: that the polishing material should be considerably softer than the material to be polished and vice versa. The former technique is known as soft polishing and allows very smooth surfaces to be attained. The latter technique involves the use of a hard abrasive and polishing of the crystal using successively smaller grades. The method can be self-defeating if absorbent material is used, since the abrasive particles will become embedded in the surface of the optical material. In this technique, diamond paste is most often used as the abrasive.
2.1.2 Defects in Optical Materials

The nature of the entire crystal growth process (growth, post-growth annealing, cutting and surface polishing) will determine the concentration of defects in the laser crystal and thereby determine its overall laser output quality. To properly characterize such materials, we need to investigate the nature of the defects present in the crystal. The primary way in which these defects contribute to lower optical quality of a laser crystal is by absorbing or scattering a fraction of the pump light. Scattering leads to a lower amount of pump energy available for absorption by the $Ti^{3+}$ ion that will ultimately lead to radiative emission. Defect absorption will lead to a 100 % energy conversion from optical to thermal energy. As a result, the presence of defects can lower the optical performance of the laser crystal in these two ways. In this section, we discuss the nature of defects present at the surface and in the bulk of laser crystals.

Bulk Defects

As described in the previous section, the crystal growth process greatly affects the type and number of defects present in the crystal. The elevated temperature required for crystal growth results in the formation of lattice point defects [12, 11]. An increase in the temperature of the crystal is accompanied by an increase in the amplitude of oscillation of the atoms occupying the lattice sites. At elevated temperatures, an increasing fraction of these atoms are displaced from their sites, resulting in the production of lattice vacancies and interstitials. Lacovara et al. [15] discuss the presence of point defects in pure sapphire. In a Frenkel defect, a vacancy and an interstitial are produced. In a Schottky defect, the ejected atom migrates to a free surface, leaving behind a vacancy. When sapphire is doped with titanium, there are several additional ways in which the defect concentration is increased such as the formation of oxygen vacancies. Researchers have conducted electron paramagnetic resonance
measurements and have confirmed the presence of a high concentration of defects near Ti$^{3+}$ ions in Ti: Sapphire [17].

Surface Defects

The cutting of a laser crystal and the subsequent surface treatment procedure can result in the presence of surface defects. Sharma et al. [22] have shown that the cutting process causes a strained layer of about 5 $\mu m$ thickness. Another problem that arises during the fabrication procedure is that the polishing material is embedded into the surface layer. In a theoretical treatment, Bloembergen [23] has shown that these absorbing inclusions can greatly increase the generation of heat at the surface. The concentration of defects at the surface is dependent on the cutting and polishing procedures only and not on the quality of the bulk material.

2.1.3 Current State-of-the-Art Methods of Laser Material Evaluation

Once a crystal is grown and processed using the procedure described above, the success of the growth process in producing a high quality crystal has to be determined. There currently are two methods of characterizing newly-grown laser crystals in order to evaluate their optical quality. One method is to evaluate the figure-of-merit (FOM) of the crystal. The figure-of-merit parameter is defined as

$$FOM = \frac{\beta_{\text{absorption peak}}}{\beta_{\text{emission peak}}}$$  \hspace{1cm} (2.1)

where $\beta_{\text{absorption peak}}$ is the optical absorption of the crystal at the wavelength corresponding to the peak absorption of the crystal. $\beta_{\text{emission peak}}$ is the optical absorption of the crystal
at the wavelength corresponding to the peak emission of the crystal. Since a high optical absorption at the absorption peak is a desirable condition for laser emission, as is a low optical absorption at the emission peak, taking the ratio of these two parameters gives a number that indicates the "goodness" of the material. This method of characterization gives an accurate indication of the crystal quality if the measured absorption is due to "electronic" Ti\(^{3+}\) absorption only. As we have discussed in the previous section, the presence of bulk and surface defects in the crystal are also responsible for absorption. As a result, this method of characterization can provide misleading information about the quality of a crystal. For example, consider a crystal with excellent bulk quality and very poor surface quality. The high defect concentration at the low-quality surface will result in a high measured absorption at the emission wavelength, which in turn will result in a low FOM. By using this method of characterization in this instance, we are inaccurate in claiming that this high bulk-quality material has a low figure of merit. Such inaccuracy results because this method does not account for bulk and surface quality separately. Another drawback to the FOM technique is the fact that the denominator (the measured absorption at the emission wavelength) is usually a small number that is limited by a relatively high degree of uncertainty, which in turn limits the accuracy of the FOM measurement.

The other current method of evaluation of laser crystal quality involves testing the crystal in a laser cavity [24]. The crystal is first cut and polished to the specifications set by the geometry of the laser cavity, following which it is aligned in the cavity to produce laser output. As we will see in more detail in Chapter 6, this method requires a high degree of alignment to produce accurate results. From an industrial quality control point of view, this method is not practical since the crystal must be cut to the specification required by the cavity that is being used to test it. This restriction puts a limit on the size of the crystals that can be tested using a particular cavity. The other problem with this method is that
the laser output (which is supposed to characterize the "goodness" of the crystal) is highly sensitive to how well the cavity is aligned. When comparing the laser output from two different crystals, it is difficult to ensure if the cavity alignment is identical for both cases. Based on the shortcomings of the existing techniques for laser material evaluation, we define below the problem that we will attempt to solve in this work.

2.2 Thesis Problem Definition

Given the problems associated with the existing methods of laser crystal quality control, the primary goal of this thesis is to identify the nonradiative energy generating sources in an optically excited laser crystal and to develop a technique that can monitor these sources. Such a technique must:

1. account for all the non-radiative energy loss mechanisms that occur in the material, such as residual absorption and non-radiative energy conversion due to bulk and surface defects.

2. characterize the laser material quality in a non-destructive, non-contact manner.

3. be able to characterize and compare two crystals of different sizes.

4. be easily incorporated into an industrial crystal growth environment, with a view towards *in situ* evaluation of the crystal quality.

2.3 Approach

In this section, we consider the various approaches that we can take to address the problem of non-radiative energy conversion in laser materials, based on the requirements mentioned above. We conducted a review of existing methods in the scientific literature that address
this problem. Based on this literature review, we identified several important experimental criteria that must be considered in order to accurately evaluate the quality of laser crystals. Most of the techniques described below attempt to measure the radiative quantum efficiency (QE) of the laser material that is being evaluated, where QE is the probability of emission of a photon per photon absorbed by the material.

2.3.1 Prior Attempts at Laser Material Evaluation

Byvik et al. [25] performed luminescence measurements using an integrating sphere to obtain the quantum efficiency of Ti: Sapphire. An integrating sphere is a large globe covered on the inside with a highly reflective coating, such as gold. The primary purpose of the sphere is to average out (by multiple reflections) any spatial anisotropy of the emission. A radiant source (in this case, the laser material being evaluated) is placed at the center of the sphere and the emission intensity of this material is detected by a photomultiplier which views an arbitrary position of the sphere’s inner surface. The primary drawback of this technique is that it requires correction procedures involving calibration of the wavelength response of the detector. This technique also suffers from a need to exactly duplicate the sample position in the sphere from one reading to the next. This issue has not been addressed by these researchers and hence it is difficult to get a quantitative measure of the possible error that could occur. The integrating sphere technique is also not well suited to samples whose absorption and emission spectra overlap, since the sphere causes multiple passes through the sample and multiplies the loss due to reabsorption.

Ramponi and Caird [26] used a photocaloric method to measure the quantum efficiency in Nd$^{3+}$ doped laser glasses. Their method consists of measuring temperature changes in the sample with a pair of thermistors. One thermistor is embedded inside a small hole drilled in the sample and the other is well removed from the sample. Using optical excitation from
an ion laser. These researchers measured temperature changes in the laser material over the period of an hour. The problem with this technique is that the thermistor is in contact with the sample. Such contact does not permit the determination of an accurate bulk temperature, since the measured temperature can be lower or higher than the actual sample temperature due to the presence of surface absorption. In addition, drilling a hole in the sample is undesirable for two reasons. First, the sample cannot be used after the experiment and second, the presence of the hole will affect the thermal properties of the sample (especially thermal conductivity), which in turn will affect the analysis and calculations of the quantum efficiency. Li et al. [27] used a photocalorimetric compensation technique (similar to the one used by Ramponi and Caird) to determine the quantum efficiency of ruby and Ti: Sapphire. This version involves coating a small area of the sample with black paint and comparing the rise in temperature in the blackened and unblackened areas. This method, along with that of Ramponi and Caird may be of limited use to study weakly absorbing laser materials primarily because they are dc temperature techniques. The dc temperature fields cannot discriminate between surface and bulk heat transport, since the heat distribution does not depend on a spatial average [28, 14]. Therefore, a dc technique can only account for bulk transport. Any presence of surface heating will lead to a misleadingly high quantum efficiency measurement.

Quimby and Yen [29] used a gas-microphone photoacoustic spectroscopic technique to measure the radiative quantum efficiency of Nd$^{3+}$ ions doped in a solid matrix. They then related the photoacoustic signal to a theoretical expression that is a function of the quantum efficiency of the material and the ion concentration. Because it is difficult to determine a numerical value of the absolute ion concentration, this particular version of photoacoustic spectroscopy cannot be used to compare materials of different doping concentrations. To overcome this problem, Quimby and Yen [30] and Shand [31] suggested a modification using two lasers at different wavelengths to obtain ratios of the photoacoustic signal. However, a
two laser method is inconvenient from an industrial standpoint. Other researchers [32, 33, 34] have also used similar photoacoustic methods to evaluate various laser materials, with a common drawback being the fact that these techniques require the prior knowledge of the absorption characteristics of the laser material.

Based on our evaluation of the existing experimental techniques available, we defined a set of criteria that are relevant to the problem of laser crystal evaluation. In devising an approach that addresses this problem, we must ask the following questions of the technique we propose:

1. Is the absorption measured simultaneously along with the heat generated in the crystal, or is the absorption value taken from another experiment? A self-consistent measurement of these two parameters is important, especially for materials with asymmetric absorption bands such as that of Nd: YAG [5]. In such cases, even a slight shift in wavelength will yield a large variation in absorption and can cause an erroneous determination of the quantum efficiency.

2. Are the measured parameters evaluated as a function of pump wavelength or is only one pump wavelength being used?

3. Was the effect of surface absorptions accounted for? Were bulk and surface effects separated out? Such correction procedures are especially necessary if the sample is very thin, since the surface absorption component may dominate in this case.

4. Does the technique require the knowledge of absolute ion concentration? It is very difficult to determine the accurate value of this parameter. Thus, any technique requiring this knowledge is undesirable, since the ion concentration can vary greatly over the cross-section of a sample.
5. What assumptions were made in relating the energy level diagram of the particular material to the measured heat signal?

6. Were any corrections made for self-absorption in materials where the absorption and emission spectra overlap?

These criteria along with the criteria mentioned in section 2.2 lead us to consider a class of methods known as photothermal methods to investigate the problem of non-radiative energy conversion in laser materials.

2.3.2 Suitability of Photothermal Methods for Laser Crystal Evaluation

Photothermal techniques can be broadly classified as materials evaluation methods where the following three processes take place [35]:

1. A modulated source (optical, x-ray, electron beam, ion beam) provides energy to the sample being tested.

2. Some or all of the energy deposited in the sample is converted to heat. The energy converted to heat often involves a time delay, especially in semiconductors and laser materials. Such delays are usually caused by the production of intermediate states during excitation. The energy converted to heat then diffuses through the sample, altering its temperature field.

3. Changes in sample temperature are measured by a detector.

These temperature changes are then related to some material property. Photothermal characterization methods are ideally suited to studying non-radiative processes in laser materials for two reasons. First, we can use as a modulation source the same source that is used to
pump the laser material in a laser resonator. By doing so, we replicate in the photothermal experiment the exact conditions under which the laser crystal operates. Second, since photothermal experiments detect thermal energy changes, we obtain experimentally a direct measure of the quantity we want to determine. In Chapters 4 and 5, we use two photothermal techniques to determine quantitatively the non-radiative energy conversion processes occurring in optically pumped laser materials.
Chapter 3

Interaction of Light with Laser Materials

Because solid-state lasers require optical pumping, we must understand clearly the interactions between the photons of the pump light and the laser material. We begin by discussing the need to establish a non-equilibrium situation known as population inversion in the laser material. Next, we describe the interaction of a two level atom with a radiation field, providing the basis for understanding multilevel processes such as laser transitions. We then describe the three basic radiative processes that occur in a material when it operates as a laser: optical absorption, spontaneous emission and stimulated emission. We then discuss various nonradiative processes that may occur in solid state laser materials.

The radiative and nonradiative transitions involved in three and four level laser systems are then presented, following which we narrow the focus to the physics of solid state lasers. A particular type of solid state laser (namely, Ti: Sapphire) involving vibronic transitions is discussed next. A discussion of parameters that are experimentally measurable are discussed next, followed by a discussion of the use of these parameters.
A necessary condition for producing laser action is the establishment of a population inversion, a situation in which the population of atoms occupying a high energy level is greater than the population at a lower energy level. Such a situation does not exist under conditions of thermal equilibrium, where the population distribution is given by the Boltzmann distribution [36]:

$$\frac{N_2}{N_1} = e^{-\frac{\Delta E_{21}}{k_B T}}$$  \hspace{1cm} (3.1)

where the left hand side of the equation gives the ratio of the population densities $N_2$ and $N_1$ (number of particles per unit volume) of atoms with electrons occupying energy levels 2 and 1 (with corresponding energies $E_2$ and $E_1$) for a body at absolute temperature $T$ ($k_B$ is the Boltzmann constant). The comparison of an inverted population with a population in thermal equilibrium at some temperature $T$ is shown in figure 3.1 [36]. To produce this population inversion, energy from another source must be transferred to the atoms of the laser material. In the case of solid-state laser materials, this energy is provided by an external
optical source such as a lamp or a pump laser.

3.1 Interaction of a Two-Level Atom with a Radiation Field

The emission characteristics of a body in thermal equilibrium with its surroundings at an absolute temperature $T$ were described by Planck in 1900 [37, 38]. In the ideal case where the emission of the body is independent of emission frequency and having a value of unity, this radiation is known as blackbody radiation. Planck noted that radiation at a particular frequency $\omega$ is emitted and absorbed in quanta of energy. The energy of a quantum, $Q_\omega$, is proportional to the frequency of light:

$$Q_\omega = h\omega$$  \hspace{1cm} (3.2)

where $h = h/2\pi$ (Planck's constant $h = 6.6 \times 10^{-34} J.s$). The total energy in a monochromatic beam of frequency $\omega$ containing $K$ photons is then given by

$$E_\omega = KQ_\omega \text{ for } K = 0, 1, 2,...$$  \hspace{1cm} (3.3)

Planck deduced an expression for the blackbody energy density (specifically, the [energy] / [unit frequency interval] / [unit volume]) at a particular frequency $\omega$ using two key ideas. First, he noted that this energy density is the product of the mode density (the [total number of modes] / [unit frequency] / [unit volume]) multiplied by the average energy in a cavity mode at a frequency $\omega$ in thermal equilibrium. Second, Planck applied thermal equilibrium arguments and invoked the Boltzmann distribution to obtain the thermal average of the
energy in a mode. For a cavity at temperature $T$, this average energy is

$$E_{\omega} = \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_b T}\right) - 1} \quad (3.4)$$

where $k_b (= 1.34 \times 10^{-23} J/K)$ is Boltzmann’s constant. The mode density can be calculated [37] to be

$$\sigma_{BB}(\omega) = \frac{n^3 \omega^2}{\pi^2 c^3} \quad (3.5)$$

where $c$ is the speed of light and $n$ is the refractive index of the medium. The energy density of the blackbody radiation is

$$\rho_{BB}(\omega) = \sigma_{BB}(\omega) E_{\omega} = \frac{n^3 \omega^2}{\pi^2 c^3} \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_b T}\right) - 1} \quad (3.6)$$

Einstein used Planck’s blackbody radiation formula given by equation 3.6 to construct a microscopic model for processes involving the absorption and emission of radiation by individual atomic oscillators. Consider a material that is placed in a blackbody cavity whose walls are kept at a constant temperature $T$. Once thermodynamic equilibrium is reached, the material will exchange energy with the blackbody radiation field which has an energy density with a spectral distribution $\rho_{BB}(\omega)$ given by equation 3.6. On the basis of equilibrium thermodynamics and the principle of detailed balance, Einstein argued that each pair of energy levels associated with a radiative transition is in thermal equilibrium with the blackbody radiation field. This situation is shown in figure 3.2.

Consider that the material has two energy levels given by $|i>$ and $|j>$. Let $g_i$ and $g_j$ be the degeneracy parameters which represent the number of states which correspond to each of these levels, and $N_i$ and $N_j$ their equilibrium populations per unit volume. If these particular levels are associated with the exchange of energy (via the absorption and emission
Figure 3.2: Detailed balance between a blackbody radiation field of energy density $\rho_{BB}$ and the atomic energy levels given by $|i>$ and $|j>$ with degeneracies $g_i$ and $g_j$ and populations $N_i$ and $N_j$, exchanging quanta of energy $\hbar \omega$.

of radiation of frequency $\omega$) between the blackbody radiation field and the two levels of the material, the principle of detailed balance states that the net flow of energy between the atoms and the radiation field at this particular frequency $\omega$ is zero. This statement implies that over a sufficiently long period of time, the total number of emission events must exactly equal the total number of absorption events. According to Einstein, there are three ways in which the atoms and the blackbody radiation field can exchange energy at a frequency $\omega$: absorption, spontaneous emission and stimulated emission, as shown in figure 3.3.

Figure 3.3: The processes of absorption, spontaneous emission and stimulated emission of photons of energy $\hbar \omega$ by a two level atom. In spontaneous emission, atoms decay to lower energy levels of their own accord, whereas in stimulated emission they are induced to do so by an incoming photon.
3.1.1 Absorption

The process of absorption involves the transfer of a photon of energy $h\omega$ from the radiation field to an atom residing in the lower level $|i\rangle$. The absorption of this photon energy induces the atom to be excited to the higher energy level $|j\rangle$. The rate at which absorption events occur is defined as the number of $i \rightarrow j$ transitions per unit time per unit volume. This rate is given by the product of the population of atoms per unit volume in the lower level ($N_i$) multiplied by the probability of a transition per unit time to level $|j\rangle$ (defined as $W_{i\rightarrow j}$). According to Einstein, the transition probability $W_{i\rightarrow j}$ is directly proportional to two quantities: the density of radiation at frequency $\omega$ that is absorbed by the atom, $\rho(\omega)$ and an intrinsic atomic parameter $B_{i\rightarrow j}$. $B_{i\rightarrow j}$ is the probability per unit time and per unit energy density at $\omega$ that an absorption transition will occur from the $|i\rangle$ to $|j\rangle$ and is referred to as the Einstein B coefficient. The number of absorption ($|i\rangle$ to $|j\rangle$) events per unit time and per unit volume can then be given by the equation

$$N_i W_{i\rightarrow j} = N_i \rho(\omega) B_{i\rightarrow j}$$ (3.7)

3.1.2 Spontaneous Emission

The process of spontaneous emission involves atoms in the upper, excited state $|j\rangle$ dropping to a lower level $|i\rangle$ naturally without any external stimulus. This process does not involve any interaction with the blackbody radiation field. According to Einstein, the probability of a spontaneous emission transition $W_{j\rightarrow i}$ depends only on a single atomic parameter $A_{j\rightarrow i}$ which is referred to as the Einstein A coefficient. The number of spontaneous emission events per unit time and per unit volume can then be given by the equation

$$N_j W_{j\rightarrow i} = N_j A_{j\rightarrow i}$$ (3.8)
3.1.3 Stimulated Emission

The process of stimulated emission involves atoms in the excited energy state $|j>$ being stimulated to the lower state $|i>$ by the external radiation field. Einstein stated that in the presence of a radiation field $\rho(\omega)$ at frequency $\omega$, atoms in level $|j>$ can be stimulated to give up a quantum of energy at a rate proportional to the product of the intrinsic atomic parameter $B_{j\rightarrow i}$ multiplied by the blackbody energy density $\rho(\omega)$. The number of stimulated emission events per unit time per unit volume is given by the equation

$$N_j W_{j\rightarrow i} = N_j B_{j\rightarrow i} \rho(\omega)$$  \hspace{1cm} (3.9)

Under the condition of thermal equilibrium between the external radiation field and the energy levels, the number of absorption events equals the total number of (spontaneous and stimulated) emission events. This balance of events can be represented by

$$N_j (A_{j\rightarrow i} + B_{j\rightarrow i} \rho(\omega)) = N_i \rho(\omega) B_{i\rightarrow j}$$  \hspace{1cm} (3.10)

Rearranging this equation to obtain the ratio of the populations in levels $|i>$ and $|j>$, we obtain

$$\frac{N_j}{N_i} = \frac{\rho(\omega) B_{i\rightarrow j}}{(A_{j\rightarrow i} + B_{j\rightarrow i} \rho(\omega))}$$  \hspace{1cm} (3.11)

We compare the above expression for the equilibrium population ratio with the Boltzmann ratio for the ratio of populations

$$\frac{N_j}{N_i} = \frac{g_j}{g_i} \exp\left(-\frac{h\omega}{k_b T}\right)$$  \hspace{1cm} (3.12)

The above two conditions yield an expression for the energy density of the blackbody radi-
ation field that is in thermal equilibrium with the atoms:

\[
\rho(\omega) = \frac{A_{j\rightarrow i}}{B_{j\rightarrow i}} \frac{1}{\frac{B_{i\rightarrow j}}{B_{j\rightarrow i}} g_i \exp\left(\frac{\hbar\omega}{k_b T}\right) - 1}
\]  \hspace{1cm} (3.13)

We may now compare the Einstein expression for the blackbody radiation field \( \rho(\omega) \) given by equation 3.13 with Planck's expression for \( \rho_{BB} \) given by equation 3.6. By equating these two expressions, we obtain the relation

\[
\frac{g_i B_{i\rightarrow j}}{g_j B_{j\rightarrow i}} = 1 \quad \text{or} \quad g_i B_{i\rightarrow j} = g_j B_{j\rightarrow i}
\]  \hspace{1cm} (3.14)

and the relation

\[
A_{j\rightarrow i} = \frac{n^3 \hbar \omega^3}{\pi^2 c^2} B_{j\rightarrow i}
\]  \hspace{1cm} (3.15)

Equations 3.14 and 3.15 give insight into the processes of absorption, stimulated emission and spontaneous emission via the Einstein A and B coefficients. Equation 3.14 implies that in the absence of degenerate levels, the probability of stimulated emission is equal to the probability of stimulated absorption. To interpret equation 3.15 we rewrite it as

\[
A_{j\rightarrow i} = \hbar \omega \sigma_{BB}(\omega) B_{j\rightarrow i}
\]  \hspace{1cm} (3.16)

This relation implies that spontaneous emission (represented by \( A_{j\rightarrow i} \)) is equivalent to stimulated emission for one quantum of energy in one of the modes of frequency \( \omega \). The spontaneous rate is also proportional to the total density of final states \( \sigma_{BB} \) into which the atom can release its excess energy. In other words, spontaneous emission can be considered (like nonradiative transitions) to be a mechanism that limits the laser output, since it robs the laser of power in the laser mode. Although spontaneous emission will occur before the onset of and during lasing, only a small fraction of the spontaneously emitted photons are emitted.
into the laser mode. The rest of the spontaneous emission is lost in other propagation directions. We must also note that although spontaneous emission represents a loss in a laser, this process serves the purpose of allowing the laser oscillations to build up from spontaneously emitted quanta emitted into the laser mode.

### 3.1.4 Ratio of Stimulated to Spontaneous Emission

Having defined expressions for the stimulated and spontaneous emission rates, we can examine the ratio of stimulated to spontaneous emission transition rates from level $|j>$ to $|i>$. By using equations 3.6 and 3.15, we obtain

$$\frac{W_{\text{stimulated}}}{W_{\text{spontaneous}}} = \frac{B_{j \rightarrow i} \rho(\omega)}{A_{j \rightarrow i}} = \frac{1}{\exp\left(\frac{\hbar \omega}{kT}\right) - 1} \quad (3.17)$$

It is important to note that this expression for the ratio of transition rates holds for a thermal equilibrium situation where a two level system of atoms interact with a radiation field. The stimulated emission rate dominates the spontaneous emission rate only for temperatures where $k_B T$ is much greater than the photon energy $\hbar \omega$ of the radiation field. For radiative transitions in the visible range, the spontaneous and stimulated emission rates become equal only at temperatures higher than 30000K. For transitions occurring in the visible range at room temperature, equation 3.17 predicts that the spontaneous emission rate is at least $10^{13}$ times greater than the stimulated emission rate [36].

We next consider how the ratio of stimulated to spontaneous emission rates is affected when the two level system of atoms is confined in a laser cavity. In such a situation, the radiation field $\rho(\omega)$ can build up to a high value such that the stimulated emission rate is much greater than the spontaneous emission rate. In other words, the radiation field in a laser cavity builds up to a value equivalent to that of a very high temperature radiation field.
For example, consider a Ruby laser operating at 694.3 nm that has an 1 mm diameter output beam with a power of 1 mW. We can compute the energy density of the beam by dividing the laser beam power in the cavity by the beam cross sectional area and the frequency width of the beam. For such a situation, we obtain a ratio of stimulated to spontaneous emission rates of about 40. Therefore, in a laser cavity, the stimulated emission rate will dominate the spontaneous emission rate. Alternatively, for such a ratio to be established in a two level system of atoms in the presence of a blackbody radiation field, the temperature of that blackbody must be on the order of 10^6 K [36].

### 3.2 Two Level Atoms

The energy level spectrum of an atom is determined from the time-independent Schrödinger equation with a Hamiltonian \( H_0 \). As a result of the atom's interaction with an electric field, the atom acquires an additional energy \( V \). In the presence of the electric field one can determine the new energy level spectrum by solving the Schrödinger equation with the new Hamiltonian

\[
H = H_0 + V
\]

where the perturbation Hamiltonian of the electric field is

\[
V = +e\vec{E}(\vec{r}, t) \cdot \vec{r}
\]

where \( e \) is the charge on the electron. We assume this energy is due to the interaction of the electric dipole moment of the atom with the electric field \( \vec{E} \) of the electromagnetic wave, where we assume that the wave is a plane, monochromatic wave of the form \( E = E_0 \cos(\omega t - \vec{k} \cdot \vec{r}) \), where \( \vec{k} \) is the wavevector. We further assume the electric field to be
linearly polarized along the $x$-direction.

Consider a particular pair of energy levels of an atom labelled $|i>$ and $|j>$ such that the energy separation between them is

$$E_j - E_i = \hbar \omega$$  \hspace{1cm} (3.20)

For a particular pair of energy levels, we can deduce the perturbation induced transition rate using Fermi's Golden Rule [39, 40]. To arrive at the final result for the transition rate, we also assume the following: (1) The wavelength of the incident radiation is much greater than the dimensions of the atom (allowing us to use the electric dipole approximation for the hamiltonian $V$ by neglecting the higher order multipoles of the atomic charge distribution). (2) The wave interacts with the atom for a very long time. (3) The transition probability is weak, so that a perturbation analysis can be used. Under these conditions, the final result for the transition rate is

$$W_{i \rightarrow j} = \frac{\pi}{cn\epsilon_0} \frac{\hbar^2 e^2 |x_{ij}|^2 g_j g(\omega) I^\omega}{g_i} = \frac{g_j}{g_i} W_{j \rightarrow i}$$  \hspace{1cm} (3.21)

This expression is valid for a monochromatic beam and a linearly polarized applied electric field, in addition to the three assumptions mentioned above. In the above expression for the transition rate, $x_{ij}$ is the quantum mechanical analog of the classical oscillator strength, $g_j$ is the number of degenerate levels associated with the $|j>$ state, $g(\omega)$ is the lineshape function and $e, c, n, \epsilon_0$ are constants defined earlier. Equation 3.21 implies that (apart from degeneracy factors) the only two parameters affecting the transition rate are the quantum-mechanical analog of the oscillator strength $x_{ij}$ and the lineshape function $g(\omega)$. We will discuss these two parameters below.

The parameter $x_{ij}$ is proportional to the oscillator strength [37]. During a transition, we
may consider the atom to be an electric dipole oscillating at frequency \( \omega_0 \) and whose amplitude is proportional to the electric dipole moment of the atom. A transition is induced when this dipole moment interacts with the electric field of an electromagnetic wave. The degree of interaction between the dipole moment and the electric field determines the probability of a transition occurring. If there is no interaction, the parameter \( x_{ij} \) is zero and the levels \( |i> \) and \( |j> \) will never be associated with a radiative transition.

We can use this concept of the oscillator strength to estimate how strong a particular transition is compared to other transitions originating from the same energy level. Consider for example a one-electron atom that has level \( |i> \) as its lowest energy level and several upper levels. If \( f_{ij} \) is defined as a dimensionless parameter representing the strength of a transition from level \( |i> \) to \( |j> \), then the values of the absorption oscillator strength to all \( k \) higher levels obey the sum rule [36]

\[
\sum_k f_{ik} = 1
\]  
(3.22)

The above equation implies that an electron that undergoes absorption from state \( |i> \) to many excited states divides its absorption in proportion to the values of the individual oscillator strengths to each of these excited states. In other words, transitions to each of these excited states are governed by branching ratios to each of these levels.

The expression for the transition rate given by equation 3.21 can be rewritten in terms of the spontaneous emission lifetime \( \tau_{sp} \) once it is recognized that the Einstein \( A \) coefficient is the inverse of this parameter and also by noting that \( A_{j\rightarrow i} \) is a function of the oscillator strength \( x_{ij} \). Thus, we rewrite the expression for the transition rate in terms of the spontaneous emission lifetime:

\[
W_{i\rightarrow j} = \frac{3\pi^2 c^2 g_i}{g_i n^2_\omega^3 \tau_{sp}} \hbar^{-1} f^\omega g(\omega)
\]  
(3.23)
3.2.1 Lineshape Function

Apart from the oscillator strength, the only other factor that affects the rate of electric dipole transitions is the lineshape function $g(\omega)$. The lineshape function determines the frequency dependent response of the atom-field interaction near a particular resonance. This parameter represents the energy uncertainty or spread of a transition. Two types of processes can contribute to the width of the lineshape function: inhomogeneous and homogeneous broadening mechanisms [41]. During growth of a laser crystal, impurities, strains and dislocations can occur. Due to the presence of these defects, the sites occupied by the optically active lasing ion are not all identical. The ions in the host laser crystal lattice are distributed among sites whose environments are perturbed to a greater or lesser extent [1]. Since the frequency of a transition on the ion is influenced by the environment of the ion, we obtain a range of frequencies over which the transitions occur. In such a situation, the observed radiative line is said to be inhomogeneously broadened. The lineshape function is then due to the sum of the transitions from ions occupying sites whose environments are perturbed to different degrees. If the transitions we observe are due only to ions in identical sites, we would expect a much sharper lineshape function, which is said to be homogeneously broadened [42].

3.2.2 Interaction of a Monochromatic Wave with Two-Level Atoms

Having treated the microscopic picture of the interaction of light with a two-level atom, we now look at the macroscopic picture. We then use the macroscopic picture to derive an expression for the absorption / gain coefficient, which is an important measurable parameter. In this situation, we consider a uniform density of such two level atoms that do not interact with each other. Such a situation is depicted in figure 3.4.

For an incident monochromatic plane wave of intensity $I^w$ propagating along the $z$ direction, the net power $P^w$ per unit volume that is generated in the beam is given by the
difference between the number of stimulated emission events and the number of absorption events multiplied by the amount of energy involved in a transition:

$$\frac{dP^\omega}{dV} = [N_j W_{j\rightarrow i} - N_i W_{i\rightarrow j}] \hbar \omega$$  \hspace{1cm} (3.24)

By using equation 3.23, the expression for the net power per unit volume becomes

$$\frac{dP^\omega}{dV} = \frac{(N_j - g_j N_i)3\pi^2 c^2}{n^2 \omega^2 \tau_{sp}} g(\omega) I^\omega$$  \hspace{1cm} (3.25)

In the above expression, we have neglected any spontaneous emission that might be occurring, since spontaneous emission will make a negligible contribution to the intensity in a single mode.

Since the power generated per unit volume is equivalent to the change in intensity per
unit length, we may write

\[ \frac{dP^\omega}{dV} = \frac{dI^\omega}{dz} = \frac{(N_j - \frac{g_i}{g_j} N_i)3\pi^2 c^2}{n^2 \omega^2 \tau_{sp}} g(\omega) I^\omega \]  

(3.26)

Upon solving the above differential equation for the intensity \( I^\omega \) in a single mode, we obtain

\[ I^\omega(z) = I^\omega(0)e^{\gamma(\omega)z} \]  

(3.27)

where

\[ \gamma(\omega) = \frac{(N_j - \frac{g_i}{g_j} N_i)3\pi^2 c^2}{n^2 \omega^2 \tau_{sp}} g(\omega) \]  

(3.28)

The parameter \( \gamma(\omega) \) is the gain coefficient and has the units of \([\text{length}]^{-1}\). The gain coefficient will have a positive value when \( N_j - \frac{g_i}{g_j} N_i \) is greater than zero. Such a situation occurs when the upper level population density is greater than the lower level, assuming that we do not consider any degeneracy effects. A situation where there is a greater population density in the upper rather than the lower energy level is referred to as a population inversion. When a population inversion exists in a laser medium, the rate of stimulated emission is greater than the rate of absorption and the intensity of the beam will increase as it travels through the medium. If the population density of the lower energy level is greater than that of the upper level, \( \gamma(\omega) \) is negative and the material experiences a net absorption. In this case, it is more convenient to define an absorption coefficient \( \beta(\omega) \) which is equal to the negative gain coefficient:

\[ \beta(\omega) = -\gamma(\omega) = \frac{(\frac{g_i}{g_j} N_i - N_j)3\pi^2 c^2}{n^2 \omega^2 \tau_{sp}} g(\omega) \]  

(3.29)

The two situations of net gain and net absorption are shown in figure 3.5.
Figure 3.5: The amplification and absorption of a monochromatic beam in a two level medium via the processes of stimulated emission and stimulated absorption.

3.3 Nonradiative Transitions

We have so far considered only the radiative transition processes that can occur in the atoms that make up a laser material. We now review the energy transitions that do not involve the absorption or emission of a photon. Such transitions are called non-radiative transitions. In this section, we will review non-radiative processes such as multiphonon lattice relaxation. We also consider in this section phonon-induced transitions and combined radiative-nonradiative processes such as vibronic processes.

3.3.1 Multiphonon Relaxation

Figure 3.6 shows a multiphonon relaxation process [43]. In such a process, an ion in an excited state given by level $|2>$ relaxes to level $|1>$ nonradiatively, with the energy lost by the ion being imparted to the host lattice in the form of two or more phonons of energy $\hbar\omega_i$. 

34
where

\[ E_2 - E_1 = \sum_i \hbar \omega_i \]  

(3.30)

In the above equation, \( i \) represents the number of phonons released and \( \omega_i \) represents the frequency of the lattice vibrations. The most generalized approach to this problem is the **Multiphonon Relaxation**

![Multiphonon RelaXation](image)

Figure 3.6: Multiphonon emission processes. Shown here is a three-phonon process from level \(|2\rangle\) to \(|1\rangle\), where \( \omega_i \) represents the frequency of the phonons emitted into the lattice.

configurational-coordinate model, developed by Struck and Fonger and others [44, 45]. We will consider this model later in this chapter. To gain a basic understanding of multiphonon processes, we will now consider a phenomenological model, first demonstrated by Riseberg and Moos [46]. This model has been shown to be valid in the case of weak electron-phonon coupling, as exhibited by rare earth materials, for example.

Riseberg and Moos begin their analysis with the assumption that the transition probability converges rapidly with the order of the transition process. This convergence can be
expressed in terms of a coupling constant $\xi$:

$$\frac{W^{(p)}}{W^{(p-1)}} = \xi, \quad \text{where } \xi \ll 1$$  \hspace{1cm} (3.31)

$W^{(p)}$ is the transition rate for a $p^{th}$-order process and $W^{(p-1)}$ is that for a $(p-1)^{th}$-order process. These authors assumed a single phonon frequency $\omega_p$ model for multiphonon relaxation across an energy gap $\Delta E$. In this case, they derive a relation known as the multiphonon emission formula for the non-radiative decay rate:

$$W_{nr} = W_o \xi^p (1 + < m >)^p$$  \hspace{1cm} (3.32)

where $W_o$ is a rate constant, $\xi$ is a coupling constant, $p$ is the number of phonons required to span the energy gap $\Delta E$ and

$$< m > = [\exp\left(\frac{\hbar \omega_p}{k_b T}\right) - 1]^{-1}$$  \hspace{1cm} (3.33)

is the thermal occupation factor for the phonons, $\omega_p$ being the phonon frequency.

Another phenomenological model leads to the derivation of what is termed the activation energy relation, which describes the nonradiative decay process by the relation

$$W_{nr} = W_o \exp\left(-\frac{E_x}{k_b T}\right)$$  \hspace{1cm} (3.34)

where $W_{nr}$ is the nonradiative decay rate, $W_o$ is a rate constant, $E_x$ is an activation energy, $k_b$ is Boltzmann's constant and $T$ is the temperature. This relation can be interpreted as the number of times per second that the excited atom tries to escape from a potential well multiplied by the probability that it will have sufficient energy to allow its escape [47].
3.3.2 Vibronic Processes

A vibronic energy transition is a radiative process where a portion of the energy is transferred nonradiatively to or from the host lattice [47]. Vibronic processes usually occur in systems involving magnetic ion-doped crystals. Magnetic ions in crystals often show spectral lines (in fluorescence or absorption) that are strongly dependent on temperature and whose frequencies do not correspond to any energy gap in the energy level scheme [48, 49]. These lines correspond to transitions that involve two simultaneous events: a change in the electronic state of the ion and a change in the excitation state of a vibrational crystal mode. Such transitions are called vibrational-electronic or vibronic.

Several lasers (such as Alexandrite lasers [31] and Titanium Sapphire lasers) take advantage of vibronic emission processes to obtain laser action, by obtaining a laser transition that decays to an upper vibrational level of the ground state which is not thermally populated at ambient temperatures. We will review vibronic processes in more detail later in this chapter, when we describe transition-metal solid-state lasers.

3.3.3 Raman Scattering

Another type of non-radiative relaxation occurs via Raman scattering processes, as shown in figure 3.7. A Raman scattering process consists of the absorption of a phonon and the emission of another phonon. In other words, it is a phonon-induced relaxation process [50]. One such possible Raman scattering process is Raman relaxation of an ion to a lower state. In such a process, the ion in its excited state absorbs a phonon of a certain frequency and re-emits a phonon of higher frequency. The difference between the two frequencies is equal to the frequency difference between the initial and final states. A special case of Raman scattering is known as an Orbach process, which occurs when scattering takes place in resonance with a real state. When the energy of the absorbed phonon is equal to the energy
difference between the initial level and an upper level, and the energy of the emitted phonon is equal to the difference in energy between this upper level and the final level of decay, the process taking place is known as an Orbach process [51, 52].

Figure 3.7: Raman (phonon-induced) relaxation and excitation processes.

Alternatively, one can have phonon-induced Raman excitation of an ion to a higher energy state. Such a process takes place when an ion in a certain state absorbs a phonon of a certain frequency and re-emits a phonon of a lower frequency. The difference between the two frequencies is equal to the energy difference between the initial and final states.

3.4 Concentration-Dependent Processes

We have so far reviewed only energy transition processes that involve one ionic centre. Such processes are independent of the doping ion concentration in the host material. There also are a few concentration dependent transition processes, which involve the migration of energy between centers, which we review below.
3.4.1 Ion-Ion Energy Transfer

There exists a class of transitions based on the transfer of energy among ions in a solid-state laser material [53]. Energy transfer processes between ions occur when an excitation or de-excitation in a particular ionic centre is accompanied by a corresponding transition in a neighbouring ionic centre. Such processes can be either radiative or nonradiative and can be either resonant or phonon assisted. Ion-ion energy transfer processes take place between an ion that is initially in the excited state (termed the sensitiser, S) and an ion (termed the activator) that is initially in the ground state. Four such processes are shown in figure 3.8 [53].

![Diagram of energy transfer processes](image)

**Figure 3.8:** Ion-ion energy transfer processes between two neighbouring ions.

**Resonant, radiative energy transfer:** In such a process, photons are emitted by the sensitiser ions and are then absorbed by an activator ion. The probability of such a transfer process occurring depends on three factors: the emission probability, the absorption probability and the distance between the two sites $R$. The transition probability is proportional to $R^{-2}$. 
Resonant nonradiative energy transfer: Consider the case of two ions, each having an excited state that is separated from the ground state by nearly equal amounts. If their is sufficient interaction between the two ions due to their close proximity, the excitation will jump from one ion to the other before one ion is able to emit a photon. Such a process was first treated by Forster [53], who considered this process to be a dipole-dipole interaction. He then derived the transfer probability, which he found to be proportional to the inverse sixth power of the interionic distance.

Phonon-assisted nonradiative energy transfer: Consider two ions with excited states of different energies. Energy transfer can take place between these two ions provided that overall energy conservation is maintained by the production or annihilation of phonons. For small energy mismatches on the order of 100 cm⁻¹, it has been shown that energy transfer assisted by one or two phonons can take place. In the case of rare earth materials, energy mismatches as high as several thousand cm⁻¹ are encountered. In such cases, multiphonon processes serve to maintain energy conservation. The probability of such a process occurring decreases exponentially with an increase in energy mismatch of the excited states of the two ions.

Fluorescence quenching: Consider two ions, one initially at a higher state than the other. If both ions possess an identical intermediate state, energy transfer can take place from the sensitizer to the activator. This presence of this ion-ion energy transfer process inhibits the luminescence emission from the sensitizer ion.

3.4.2 Cross-Relaxation and UpConversion Processes

Cross-relaxation refers to all types of ion-ion energy transfer processes occurring between identical ions. In such a case the same type of ion is both the sensitizer and activator [54].

Such processes are essentially similar to the ones described above with the exception of
the fact that in upconversion processes, both the sensitizer and the activator are in their excited states prior to the energy conversion. The probability of these processes are governed by the same factors as the processes described above.

3.5 Three and Four Level Lasers

The discussion so far has dealt with laser transitions based on the interaction of a monochromatic beam with a two-level atom. However, a "true" two-level system (not including some vibronic lasers which operate on two electronic levels but also make use of additional vibrational sublevels for laser action) will not be able to provide laser action [47]. The problem with two-level systems is their inability to maintain a population inversion. As soon as the population of the upper level becomes equal to that of the lower level, no further net absorption will take place, thereby inhibiting the establishment of a population inversion. Therefore, to achieve and maintain a population inversion, at least three energy levels must exist.

3.5.1 Three Level Lasers

A three level laser is one for which the atomic ground state is the lower laser level (designated by $|1>$). The upper laser level is designated as $|2>$. For optical pumping to work efficiently, it is desirable for level $|3>$ to consist of many closely spaced levels. In a three level system, atoms that are pumped to level $|3>$ quickly decay to the upper laser level $|2>$ in a characteristic decay time $\tau_{32}$. If the pumping rate is high enough, a population inversion is established between the upper and lower laser levels. To achieve population inversion, the lifetime of level $|2>$ must be long enough for stimulated emission to build up before all the stored energy is lost due to spontaneous emission or nonradiative emission [41].
Consider a three level scheme as shown in figure 3.9 [50]. In the figure shown, $W$ represents the transition rate, the subscripts $ij$ represent the initial and final state of the transition and the superscripts "st", "sp", and "nr" refer to stimulated, spontaneous and nonradiative transitions, respectively. The figure shows that atoms in the ground state are pumped to the pump bands represented by level $|3>$ at a rate $W_{13}^{st}$. At each of the two excited states, we assume that the atoms can de-excite via three mechanisms: spontaneous emission, stimulated emission and nonradiative transitions. Each of these processes has a decay rate associated with it.

![Three level laser system diagram](image)

Figure 3.9: Three level laser system. $W$ represents the transition rate, the subscripts $ij$ represent the initial and final state of the transition and the superscripts "st", "sp", and "nr" refer to stimulated, spontaneous and nonradiative transitions, respectively.

From the energy level diagram shown, we may write rate equation for the two upper levels designated by $|3>$ and $|2>$. For each level, we obtain a differential equation for the rate of change of population of that level, by considering all the processes that populate and
de-populate that particular level. For level $|3>$, we obtain

$$ \frac{dN_3}{dt} = W_{13}^{st}(N_1 - N_3) - (W_{31}^{st} + W_{31}^{nr} + W_{32}^{nr})N_3 $$ \hspace{1cm} (3.35)

The rate equation for level $|2>$ is

$$ \frac{dN_2}{dt} = W_{12}^{st}N_1 + W_{32}^{nr}N_3 - (W_{21}^{st} + W_{21}^{nr} + W_{21}^{nr})N_2 $$ \hspace{1cm} (3.36)

We also invoke the conservation equation

$$ N_1 + N_2 + N_3 = N_T $$ \hspace{1cm} (3.37)

where $N_T$ is the total population of atoms in the system. The following assumptions are valid for such a laser system:

1. The probability of nonradiative decay from level $|3>$ directly to the ground state $(W_{31}^{nr})$ is negligible due to the large energy difference between levels $|3>$ and $|1>$. As we discussed earlier, for multiphonon processes the probability of nonradiative processes decreases with increasing energy gap that must be traversed.

2. Radiative transitions from the pump bands to level $|2>$ are negligible compared to nonradiative transitions across the same energy levels.

3. The laser system operates at optical frequencies, implying that the ratio $\hbar \omega / k_b T \gg 1$ for all the transitions involved. The energy gap that corresponds to visible-frequency radiation is $\hbar \omega \approx 2eV$, as compared to $k_b T \approx 25meV$ at room temperature, so that $\hbar \omega / k_b T \approx 40$. In this limit, we can neglect all thermally-induced upwards transitions. Assuming that the pump radiation energy exceeds the energy of the upper laser level,
we can then neglect the upward rate $W^{u}_{12}$.

After invoking these assumptions into equations 3.35 and 3.36, we can rewrite these two rate equations. For level $|3>$,

$$\frac{dN_3}{dt} = W^{u}_{13}(N_1 - N_3) - \frac{N_3}{\tau_3}$$  \hspace{1cm} (3.38)

where

$$\frac{1}{\tau_3} = W^{u}_{31} + W^{sp}_{31} + W^{nr}_{32}$$  \hspace{1cm} (3.39)

and for level $|2>$,

$$\frac{dN_2}{dt} = \frac{N_3}{\tau_{32}} - \frac{N_2}{\tau_{21}}$$  \hspace{1cm} (3.40)

where

$$\frac{1}{\tau_{32}} = W^{nr}_{32}$$  \hspace{1cm} (3.41)

and

$$\frac{1}{\tau_{21}} = W^{u}_{21} + W^{sp}_{21} + W^{nr}_{21}$$  \hspace{1cm} (3.42)

We now define the fluorescence quantum efficiency $QE$ as the ratio of the emission on the laser transition to the total energy absorbed:

$$QE = \frac{\tau_3}{\tau_{32} \tau_{rad}(2 \rightarrow 1)}$$  \hspace{1cm} (3.43)

The relaxation time ratio representing the fraction of atoms excited to the pump bands that decay to the upper laser level is given by

$$\rho \equiv \frac{N_3}{N_2} = \frac{\tau_{32}}{\tau_{21}}$$  \hspace{1cm} (3.44)

Solving equations 3.40 and 3.38 and using the parameters $QE$ and $\rho$, we obtain the
steady-state population difference on the \( 2 \rightarrow 1 \) laser transition

\[
\frac{N_2 - N_1}{N_T} = \frac{(1 - \varrho)(QE)W_{p\text{rad}} - 1}{(1 + 2\varrho)(QE)W_{p\text{rad}} + 1}
\]

Population inversion can be obtained only if \( \varrho < 1 \) and the pumping rate exceeds a threshold value given by the expression

\[
W_{p\text{rad}} \geq \frac{1}{QE(1 - \varrho)}
\]

Therefore, the optimum situation occurs when

1. the relaxation from the pumping level \( |3> \) into the upper laser level \( |2> \) is very fast, such that \( \varrho \to 0 \).

2. the relaxation from the upper laser level \( |2> \) to the ground level \( |1> \) is purely radiative, such that \( QE \to 1 \).

### 3.5.2 Four Level Lasers

In a four-level laser system, the lower laser level is not the ground state. If the lower laser level corresponds to an energy that is much greater than the ground state energy by an amount \( k_bT \), then even a small population of the upper laser level will lead to a population inversion. Therefore, four-level lasers have the capability to be more efficient systems than lasers based on the three-level system.

Consider a four-level scheme shown in figure 3.10 [50]. As for the three level laser, \( W \) represents the transition rate, the subscripts \( ij \) represent the initial and final state of the transition and the superscripts "st", "sp", and "nr" refer to stimulated, spontaneous and nonradiative transitions, respectively. From the energy level diagram shown, we may write rate equations for each of the levels by considering all the processes that involve that
Figure 3.10: Four level laser system. $W$ represents the transition rate, the subscripts $ij$ represent the initial and final state of the transition and the superscripts "st", "sp", and "nr" refer to stimulated, spontaneous and nonradiative transitions, respectively.

particular energy level. For level $|3\rangle$, we obtain

$$\frac{dN_3}{dt} = W_{03}^{st}(N_0 - N_3) - (W_{32}^{nr} + W_{31}^{st} + W_{31}^{sp} + W_{30}^{nr}W_{30}^{sp} + W_{30}^{nr})N_3$$  \hspace{1cm} (3.47)$$

The rate equation for level $|2\rangle$ is

$$\frac{dN_2}{dt} = W_{12}^{st}(N_1 - N_2) - (W_{21}^{st} + W_{21}^{sp} + W_{20}^{nr} + W_{20}^{sp})N_2 + N_2W_{22}^{nr}$$  \hspace{1cm} (3.48)$$

and for level $|1\rangle$

$$\frac{dN_1}{dt} = N_0W_{01}^{sp} - (N_1 - N_2)W_{21}^{st} - N_1(W_{10}^{sp} + W_{10}^{nr}) + N_2(W_{21}^{sp} + W_{21}^{st} + W_{21}^{nr}) + N_3(W_{31}^{sp} + W_{31}^{nr})$$  \hspace{1cm} (3.49)$$
We also invoke the conservation equation

\[ N_0 + N_1 + N_2 + N_3 = N_T \]  \hspace{1cm} (3.50)

In the above equations, we have assumed that very fast nonradiative processes will dominate the de-population of the upper level \( |3 \rangle \). We also assume that the absorption processes involving the broad bands represented by level \( |3 \rangle \) will dominate all other absorption processes from the ground state to lower energy levels. In addition, we also invoke the three assumptions mentioned for the three level laser case. Defining \( W_{03}^{st} = W_p \), we can rewrite the rate equations in a simplified form. For level \( |3 \rangle \), we can rewrite equation 3.47 as

\[ \frac{dN_3}{dt} = W_p (N_0 - N_3) - \frac{N_3}{\tau_3} \]  \hspace{1cm} (3.51)

where the lifetime \( \tau_3 \) given by

\[ \frac{1}{\tau_3} = W_{32}^{nr} + W_{31}^{st} + W_{31}^{sp} + W_{30}^{sp} \]  \hspace{1cm} (3.52)

is the total lifetime for decay of level \( |3 \rangle \) to all lower levels. The steady-state population of level \( |3 \rangle \) (when \( dN_3/dt = 0 \)) is then given by

\[ N_3 = \frac{W_p \tau_3}{1 + W_p \tau_3} N_0 \]  \hspace{1cm} (3.53)

Assuming further that the probability of absorption from level \( |1 \rangle \) to \( |2 \rangle \) is low, we may rewrite the rate equation for level \( |2 \rangle \) given by equation 3.48 as

\[ \frac{dN_2}{dt} = \frac{N_3}{\tau_3} - \frac{N_2}{\tau_2} \]  \hspace{1cm} (3.54)
where the lifetime $\tau_{32}$ is given by

$$\frac{1}{\tau_{32}} \equiv W_{32}^{nr} \tag{3.55}$$

and the lifetime $\tau_2$ is given by

$$\frac{1}{\tau_2} \equiv W_{21}^{3t} + W_{21}^{np} + W_{21}^{nr} + W_{20}^{sp} \tag{3.56}$$

We can also rewrite the rate equation for level $|1>$ (equation 3.49) as

$$\frac{dN_1}{dt} = \frac{N_3}{\tau_{31}} + \frac{N_2}{\tau_{21}} - \frac{N_1}{\tau_{10}} \tag{3.57}$$

where

$$\frac{1}{\tau_{31}} \equiv W_{31}^{sp} \tag{3.58}$$

and

$$\frac{1}{\tau_{21}} \equiv W_{21}^{sp} + W_{21}^{np} + W_{21}^{nr} \tag{3.59}$$

and

$$\frac{1}{\tau_{10}} \equiv W_{10}^{sp} + W_{10}^{nr} \tag{3.60}$$

are the definitions for the lifetimes $\tau_{ij}$ relevant to this system. Under steady state conditions, equation 3.54 gives

$$N_2 = \frac{\tau_2}{\tau_{32}} N_3 \tag{3.61}$$

An optimum situation for a four-level scheme will involve a very fast $3 \rightarrow 2$ transition, in comparison to the relatively long lifetime of the upper laser level given by equation 3.56, such that $\tau_2 \gg \tau_{32}$, resulting in $N_2 \gg N_3$. Combining equations 3.61 and 3.57, we obtain
the steady state population of level $|1>$:

$$N_1 = \left( \frac{\tau_{10}}{\tau_{21}} + \frac{\tau_{32} \tau_{10}}{\tau_{31} \tau_2} \right) N_2 = \varrho N_2$$  \hspace{1cm} (3.62)

where we define the parameter $\varrho$ as

$$\varrho \equiv \frac{\tau_{10}}{\tau_{21}} + \frac{\tau_{32} \tau_{10}}{\tau_{31} \tau_2}$$  \hspace{1cm} (3.63)

$\varrho$ is a ratio of relaxation times that must be less than unity if a population inversion is to be established (ie: $N_2 > N_1$) on the $2 \rightarrow 1$ transition.

In the optimum situation for a four-level scheme, a very high percentage of the atoms excited to the pump bands represented by level $|3>$ must relax to the upper laser level $|2>$. This situation corresponds to a lifetime $\tau_{31} \rightarrow \infty$. If this condition holds, then population inversion can be established if the following relationship is true

$$\varrho \equiv \frac{N_1}{N_2} \approx \frac{\tau_{10}}{\tau_{21}} \ll 1$$  \hspace{1cm} (3.64)

The above equation implies that for a population inversion to be established, atoms should relax out of the lower laser levels much at a much faster rate than the rate at which atoms decay into the upper laser level from the pump bands. We also define the fluorescence quantum efficiency for a four level system as

$$QE = \frac{\tau_3}{\tau_{32} \tau_{\text{rad}(2 \rightarrow 1)}}$$  \hspace{1cm} (3.65)

where the ratio $\frac{\tau_3}{\tau_{32}}$ represents the fraction of atoms de-exciting from the pump bands into the upper laser level, instead of relaxing into lower levels. The ratio $\frac{\tau_2}{\tau_{\text{rad}(2 \rightarrow 1)}}$ represents the
fraction of the total decay from the upper laser level that is purely radiative on the laser transition \(2 \rightarrow 1\). Using equation 3.50 and the expressions for \(Q_E\) and \(\varphi\), we can solve for the population inversion in a four-level system:

\[
\frac{N_2 - N_1}{N_T} = \frac{(1 - \varphi)(Q_E)W_p\tau_{rad}(2 \rightarrow 1)}{1 + [1 + \varphi + \frac{2\tau_2}{\tau_{rad}(2 \rightarrow 1)}][Q_E]W_p\tau_{rad}(2 \rightarrow 1)}
\]  

(3.66)

As in the case of the three level laser, population inversion is maximized when the relaxation time ratio \(\varphi \to 0\) and the quantum efficiency \(Q_E \to 1\).

### 3.6 Solid State Lasers

Solid state lasers fall into two broad categories - transition metal lasers and lanthanide series lasers. The spectroscopic properties of these two classes of solid state lasers are quite different. The active material in transition metal lasers come from the fourth row of the periodic table, whereas the active atoms of the lanthanide series lasers come from the sixth row. The main difference between these two classes of solid state lasers has to do with tunability. Transition metal lasers usually exhibit a much wider tuning range than lanthanide series lasers, whose tuning range is relatively limited [55].

The reason that transition metal solid state laser exhibit a wide tuning range is due to the interaction between the active transition metal ion and the crystal field of the host laser material [47]. In transition metal lasers, the electrons that participate in the lasing process are the 3d electrons. In lanthanide series lasers, the electrons that participate in the lasing process are the 4f electrons. As a result of the electronic configuration, the 3d electrons have a strong interaction with the host crystal field, whereas the 4f electrons do not. This strong interaction of the 3d electrons with the crystal field is the reason why many transition metal lasers exhibit a wide tunability.
In transition metal atoms, the first two shells (consisting of the 1s, 2s and 2p subshells, where the number represents the radial quantum number and the letter represents the angular quantum number) are completely filled. Following this, the first two subshells of the third shell (3s and 3p) are filled. In an isolated transition metal atom, the next two electrons will be added to the 4s fourth subshell, after which the 3d subshell begins to fill. When the transition metal atoms are doped into the host crystal, the 4s electrons and possibly one or more of the 3d electrons will form chemical bonds with the host material. The remaining 3d electrons will therefore be exposed to the electric forces exerted by the surrounding host crystal, giving rise to the wide tunability exhibited in many transition metal lasers [56].

In lanthanide series atoms, all of the subshells of the first three shells (namely, 1s, 2s, 2p, 3s, 3p and 3d) are filled. In addition, the 4s, 4p and 4d subshells and the 5s and 5p subshells are filled. The next two electrons added will go into the 6s subshell before the 4f subshell begins to fill. When the lanthanide series atom is doped into a host laser material, three electrons (one from the 4f subshell and the two 6s electrons) will form bonds with the crystal lattice. Electrons from the 5s and 5p subshells form a shield for the 4f electrons from the crystal field. As a result, the crystal field does not have a strong interaction with the 4f electrons [57].

3.6.1 Energy Transitions in Solid State Lasers

A theory developed by Tanabe and Sugano in 1954 [58] has become the basic tool for deriving the energy levels associated with transition metal atoms doped into host laser materials. Tanabe and Sugano dealt with the case of transition metal atoms that are subjected to octahedral crystal fields. Examples of active atoms in octahedral sites include Cr:YAG and Cr:GSGG. Other combinations of active transition metals in laser hosts are often approximated as residing in octahedral sites. Laser materials such as Ruby and Titanium Sapphire
can be approximated as octahedral sites having a slight trigonal distortion. Energy levels of active atoms in other sites have also been calculated using the procedure outlined in the Tanabe and Sugano theory.

Tanabe and Sugano also considered selection rules, which indicate the strength of a particular transition between two different energy levels. Usually, the strongest interaction that allows a transition between levels with the emission of a photon is the electric dipole interaction. However, in the case of 3d electrons, all such transitions are forbidden due to the selection rules considered by Tanabe and Sugano. These researchers then considered the electric dipole transition coupled with a vibration, the electric quadrupole interaction, and the magnetic dipole interaction. Upon comparing the relative strengths of these interactions, these researchers found the electric dipole transition coupled with a vibration (referred to as a vibronic transition) was about two orders of magnitude higher than the next strongest interaction, the magnetic dipole interaction.

### 3.6.2 Vibronic Processes in Transition Metal Lasers

McCumber [59] analysed absorption and emission processes based on vibronic interactions of the transition metal Nickel. Upon measuring the emission spectra of \( \text{Ni} : \text{MgF}_2 \), McCumber observed sharp emission lines (which he attributed to electronic transitions) and broad emission spectra on the long wavelength side of the sharp lines (which he attributed to vibronic emission). Following this fundamental work by McCumber, a similar analysis has been used to relate the gain characteristics of an active atom to the absorption and emission spectra. Such an analysis is a very important tool because of the fact that the gain as a function of wavelength is a more difficult measurement than the absorption or emission.

McCumber considered a system consisting of an upper and lower manifold, where a manifold refers to a set of closely spaced energy levels. For such a system, he assumed that
each of the energy levels within a manifold can be approximated by simple harmonic motion of the active atom and its surrounding atoms. The position of the minimum of each of these simple harmonic potential wells may be spatially offset from each other due to the difference in size of the active atom in the ground level and the excited level. Another assumption in this analysis is that a single lattice temperature can describe the population densities of these manifolds. Levels within a manifold are separated by an energy $\hbar \omega$ which represents a quantum of vibrational energy associated with simple harmonic motion of the upper level. A single lattice temperature implies that the atoms in each manifold will be occupy the various vibrational levels of that manifold according to the Boltzmann distribution. It was also assumed that the time interval required for equilibrium population densities to be established in each of the manifolds is much shorter than the lifetime of the upper manifold. McCumber also assumed that nonradiative transitions are negligible compared to the absorption and emission transitions.

Based on these assumptions, McCumber derived an expression for the gain coefficient in terms of measurable parameters. Given the absorption coefficient $\beta(\omega)$ and emission coefficient $e(\omega)$, absorption and emission coefficients are defined as

$$\sigma_{\text{abs}}(\omega) = \frac{\beta(\omega)}{N_1}$$

and

$$\sigma_{\text{em}}(\omega) = \frac{e(\omega)}{N_2}$$

Using the principle of detailed balance, the absorption and emission cross section are related by the expression

$$\sigma_{\text{abs}}(\omega) = \sigma_{\text{em}}(\omega) \exp\left(\frac{\hbar(\omega - \nu)}{k_B T}\right)$$

In the above expression, $\hbar \nu$ is the energy required to excite one atom from the lower manifold.
to the upper manifold while maintaining the lattice temperature $T$. Using these relations, the gain coefficient $\gamma(\omega)$ as a function of frequency is given by

$$\gamma(\omega) = \sigma_{em}(\omega)[N_2 - N_1 \exp\left(\frac{\hbar(\omega - \omega_0)}{k_B T}\right)]$$  \hspace{1cm} (3.70)

McCumber suggests a method of deducing the emission cross section from the emission spectra. In doing so, he defines a function $f(\omega)$, which when multiplied by an incremental solid angle $d\Omega$ and unit frequency interval $d\omega$, represents the average intensity of emitted photons/second at frequency $\omega$. The function $f(\omega)$ is related to the radiative lifetime of the upper manifold via the relation

$$\frac{1}{\tau} = \int_0^{4\pi} d\Omega \int_0^{\infty} f(\omega) d\omega$$  \hspace{1cm} (3.71)

Using the function $f(\omega)$, the stimulated emission cross section is given by

$$\sigma_{em}(\omega) = f(\omega)\left(\frac{2\pi c}{\omega n}\right)^2$$  \hspace{1cm} (3.72)

where $c$ is the speed of light and $n$ is the refractive index. Combining these equations, McCumber derived an expression for the gain coefficient

$$\gamma(\omega) = [N_2 - N_1 \exp\left(\frac{\hbar(\omega - \omega_0)}{k_B T}\right)]$$  \hspace{1cm} (3.73)

in terms of measurable quantities related to the function $f(\omega)$. 

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3.6.3 Radiative Processes in Vibronic Lasers

The absorption and radiative emission processes can be visualized by looking at figure 3.11. If the crystal is at a low temperature, we assume that the optically active center resides in the lowest vibrational state of the lower potential curve at point A.

When a Ti$^{3+}$ ion undergoes optical excitation by photons of frequency $\nu_o$, the following four processes will occur if the Ti$^{3+}$ ion decays back to the ground state by emitting a photon [50]:

1. An upward transition induced by the absorption of a photon of energy $h\nu_o = E_B - E_A$ will excite the Ti$^{3+}$ ion to an excited state of the upper potential curve, given by point B.

2. From this vibrational state, the Ti$^{3+}$ ion undergoes non-radiative relaxation (by trans-
ferring energy to the lattice host material) to the lowest vibrational state of the upper curve (point C).

3. The ion then decays radiatively to an excited vibrational state of the lower curve (point D), emitting a photon of energy $E_C - E_D$.

4. Finally, the ion decays non-radiatively from D to A.

The purely electronic transitions ($A \rightarrow B$, $C \rightarrow D$) obey the Franck-Condon principle which states that atoms do not change their position (coordinate) during such a transition [50]. The configurational coordinate diagram also explains why the wavelength at which a laser emits radiation is longer than the wavelength at which its absorbs radiation: The ion in its excited state (B) does not decay radiatively back to the ground state but instead decays nonradiatively to the lowest vibrational energy level (C). From point C, the ion decays to a high vibrational state of the ground electronic state (D). Since the energy of the photon emitted during this radiative emission ($E_C - E_D$) is smaller than the energy of the photon absorbed ($E_C - E_D$), the wavelength of the emitted photon will be longer than the wavelength of the absorbed photon. In Ti: Sapphire, the $Ti^{3+}$ ion absorbs photon energy in the 340 - 650 nm range and emits photons in the 650 - 1100 nm range [60, 61].

3.6.4 Ion-Lattice Interactions: Non-Radiative Emission

Although McCumber’s analysis related the gain of a transition metal to the absorption and emission spectra, it neglected all nonradiative transition processes. Struck and Fonger presented a unified model of both the radiative and nonradiative decay processes in laser materials. They attempted in their model to reconcile the activation energy model of nonradiative decay and the multiphonon emission model of nonradiative decay using a single configurational coordinate model.
Struck and Fonger [44, 43] determined the total radiative and nonradiative transition rates by summing over all possible energy levels in the upper and lower manifolds. They assumed that the discrete vibrational energy levels in the upper and lower manifolds are equally spaced. Under this assumption, they calculated that the nonradiative transition rate in vibronic lasers for a phonon emission process of order $p$ is proportional to

$$W_{nr} = \frac{\exp(-S_0 < m >)}{p!} (S_0 < 1 + m >)^p \tag{3.74}$$

where the thermal occupation factor $< m >$ is

$$< m > = \frac{[\exp(-\frac{\hbar \nu}{k_b T}) - 1]^{-1}}{p!} \tag{3.75}$$

and $S_0$ is a parameter proportional to the offset in the configurational coordinate between the upper and lower manifold and $p$ is the number of phonons released by the upper manifold. Equation 3.74 implies that the nonradiative rate follows a Poisson distribution with respect to $p$.

Struck and Fonger also predicted that the radiative rate is also proportional to the right hand side of equation 3.74. The Poisson-distributed function also predicts that a greater thermal occupation factor $< m >$ and a greater configurational offset parameter $S_0$ will lead to transitions that are more broad-band than for a low thermal occupation or a small configurational offset. Struck and Fonger compared their theory of radiative and nonradiative transition rates to the activation energy model and the multiphonon model for nonradiative relaxation. These models can approximate the Struck and Fonger model in the case of small configurational offsets but are not valid for large configurational offsets.

In the previous section, we described the mechanism of a radiative transition using figure 3.11, which describes how an optically induced transition from the ground state (point
A) to an excited vibrational and electronic state (point B) will decay back to point A via three paths: from B to C by non-radiative emission into the lattice, from C to D by radiative photon emission and finally from D to A by non-radiative emission into the lattice. From the standpoint of establishing the conditions necessary for producing laser action, figure 3.11 represents the most favourable situation.

In some instances, it is possible that the decay of an optically excited ion from the excited state B to the ground state D can be entirely non-radiative. Figure 3.12 shows that there is a crossover energy $E_{nr}$ where the ground state and the excited state manifolds overlap. In this region of overlap, there is a finite probability that the ion will change both electronic and vibrational energy states without changing its energy. Such a transition is represented in figure 3.12 by the horizontal arrows. After the ion crosses over to an excited vibrational level of the ground electronic state, the ion will decay back to the lowest vibrational level of the ground state via non-radiative relaxation. If this entirely non-radiative decay process were to occur for every ion that is optically excited, no lasing action will be observed. There is another process by which all the energy transferred to the laser material is released non-radiatively. If all the optical energy is absorbed by defects present in the material (such as the voids and inclusions discussed in section 2.1.2), this energy will be entirely converted to non-radiative energy. Unlike the $Ti^{3+}$ ion which has the ability to de-excite from an excited state by emitting a photon, the defects present in the crystal will lose their absorbed energy by releasing heat into the lattice. The mechanism by which non-radiative energy is transferred from the ion (or the defects) to the lattice is by way of increased lattice vibrations known as phonon emission.
Figure 3.12: Configurational coordinate diagram of a dopant ion in a laser material ($Q$ is the configurational coordinate). The arrows pointing vertically downward represents non-radiative transitions of an ion in the same electronic state. The arrows pointing to the right represent non-radiative transitions of an ion from an excited electronic state to the ground state. The horizontal arrows pointing to the right indicate that this transition of both electronic and vibrational state can occur without a change in energy experienced by the ion.

3.7 Titanium Sapphire Lasers

The experiments described in this thesis were conducted on a laser material known as Titanium Sapphire. Although our work is aimed at being applicable to a broad class of solid state laser materials, in this section we focus on the properties of Titanium Sapphire lasers. Ti has only one 3$d$ electron exposed to the crystal field. In the presence of the crystal field, the 3$d$ level splits into two, into a lower energy three-fold degenerate $T_2$ level and a higher energy two-fold degenerate $E$ level. The presence of only two levels for a single 3$d$ electron implies that excited-state absorption effects are negligible in Titanium Sapphire.

In the strictest sense, a two level laser cannot lase because of the inability to obtain a
maintain a population inversion. However, because Titanium Sapphire lasers operate on a vibronic transition, it can operate much like a four level laser. A four level laser has a ground manifold and a pump manifold, along with upper and lower laser manifolds. Lasing occurs between a level in the upper laser manifold to a level in the lower laser manifold. For four level lasers, the lower laser level must be well above (in other words, separated by an energy much greater than $k_B T$ from) the ground manifold. This condition ensures that the lower laser level is virtually unpopulated, making population inversion easier to achieve. However, in the case of lasers operating on a vibronic transition (such as Ti: Sapphire), the lower laser level is actually a set of vibronic states (higher vibrational levels) of the lower electronic manifold, as shown in figure 3.13 [61, 63]. Radiative transitions occur to several of these vibrational levels. The laser transition corresponding to the luminescence peak is 14000 cm$^{-1}$ [61], implying that the vibrational level of the lower manifold to which this emission
line relaxes to is about 300 cm$^{-1}$ above the ground vibrational and electronic state. Since the value of $k_bT$ at room temperature is about 200 cm$^{-1}$, we make the approximation that there exists a terminal laser level (corresponding to a higher vibrational state of the lower electronic manifold) that is virtually unpopulated at room temperature. We also assume that the nonradiative relaxation processes that occur at higher vibrational levels of the excited state to the lowest vibrational level of the excited state can be assumed to be similar to a situation found typically in a four level laser, where the atoms excited to the pump bands decay very quickly to the upper laser level. On the basis of these assumptions, we can model the vibronic Ti: Sapphire laser as a four level system.

### 3.8 Experimentally Measurable Parameters

#### 3.8.1 Optical Absorption Coefficient Spectra

Consider a beam of light travelling through a semi-transparent material of thickness $\Delta x$, as shown in figure 3.14. Let $I_o$ be the intensity of the light incident on the material and $I'$ be the intensity emerging from the other end of the material. Assume that the material has zero reflection losses. As the beam passes through the material, a certain fraction of the light $\Delta I$ is lost due to absorption within the material:

$$I_o - I' = \Delta I \quad (3.76)$$

The magnitude of this loss is proportional to $I_o$, to the material thickness $\Delta x$ and to a constant of proportionality known as the absorption coefficient $\beta$:

$$I' - I_o = -\Delta I = I_o \beta \Delta x \quad (3.77)$$
Figure 3.14: Light of intensity $I_o$ entering a semi-transparent material of thickness $\Delta x$.

We now assume that this medium is made up of infinitesimally thin slices, each of thickness $dx$. In each slice, a constant fraction of light is lost and the above equation becomes

$$\frac{dI}{I_o} = -\beta dx$$  \hspace{1cm} (3.78)

Upon integrating this equation, we obtain the expression

$$I(x) = I_o e^{-\beta x}$$  \hspace{1cm} (3.79)

which describes the exponential decrease in intensity of an optical beam encountering a material with absorption coefficient $\beta$. This relationship is known as the Beer-Lambert law of optical attenuation by an absorbing medium. Based on this relationship, it is possible to measure experimentally the absorption coefficient by measuring the transmission of light through the material.

The absorption coefficient as described by equation 3.29 is due to the electronic absorption
only. However, in an experimental situation, the measured absorption coefficient is due to the sum of several absorptions, including the electronic absorption, the absorption due to defects in the bulk, and absorption due to defects in the surface. For an accurate estimate of the electronic absorption, it is important to account experimentally for the bulk defect- and surface defect-induced absorptions.

### 3.8.2 Fluorescence Radiative Lifetime

The lifetime \( \tau_j \) of an upper energy level can be measured by monitoring the fluorescent emission from an upper level \( E_j \) by irradiating the laser material with a pulse of optical energy and monitoring the subsequent time-dependent variation of the fluorescent emission that reaches an optical detector. The measured fluorescence intensity of a particular \( j \rightarrow i \) transition is proportional to the the total radiative decay rate \( W_{ji}^{sp} + W_{ji}^{at} \) on that particular transition and to the population of the upper level \( j \) as a function of time:

\[
I_{ft}(t) = \text{const}[W_{ji}^{sp} + W_{ji}^{at}]N_j(t)
\]  

(3.80)

The upper level population decays with an exponential decay rate equal to a total decay rate \( W_j \), the measured fluorescent emission will be

\[
I_{ft}(t) = \text{const}[N_j(t)] = \text{const}[e^{-t/\tau_j}]
\]  

(3.81)

In other words, a fluorescent lifetime measurement measures only the total lifetime \( \tau_j \) of the upper level \( E_j \), not the radiative lifetime. The total lifetime is given by

\[
\frac{1}{\tau_j} = \sum_i [W_{ji}^{sp} + W_{ji}^{at} + W_{ji}^{nr}]
\]  

(3.82)
where the summation over $i$ refers to all energy levels $E_i$ lower than $E_j$.

### 3.8.3 Fluorescence Quantum Efficiency

The precise determination of absolute fluorescence quantum yields by conventional luminescence has been shown to be very difficult. In a luminescence measurement, the number of quanta absorbed from a beam of monochromatic light has to be compared with the number of quanta emitted in the polychromatic fluorescent light, whose distribution in space may be geometrically complicated. To perform this measurement, a specific fraction of the fluorescent radiation must be measured. This measurement requires that various corrections (such as geometry, re-absorption, re-emission, polarization, refractive index) be taken into account [64].

### 3.8.4 Optical-to-Thermal Energy Conversion Efficiency

The optical-to-thermal non-radiative energy conversion efficiency $\eta_{NR}$ is defined as ratio of the amount of thermal energy released by a laser crystal to the amount of optical energy absorbed. This parameter can be measured by a technique known as photopyroelectric spectroscopy, described in chapter 4 of this thesis. This technique measures the total thermal energy released due to nonradiative de-excitations from all energy levels as well as the amount of optical energy absorbed by the sample. $\eta_{NR}$ is the ratio of these two quantities.

### 3.8.5 Heat Generation Rate

The heat generation rate in the bulk of a crystal $Q_b$ is defined as the amount of thermal energy generated per unit volume by nonradiative de-excitation processes from all energy levels in a laser crystal. The heat generation rate at the surface of a crystal $Q_s$ is defined as the amount of thermal energy generated at the surface of a crystal due to the presence of
nonradiative defects at the surface. These two parameters are measured using a technique known as photothermal radiometry, as described in chapter 5 of this thesis.

3.8.6 Slope Efficiency

The slope efficiency of a laser crystal is the slope of the variation of laser output power to input pump power when a laser material is aligned in a cavity. This standard method of characterizing laser materials is presented in chapter 6 of this thesis, in order to compare it with the two photothermal techniques (photopyroelectric spectroscopy and photothermal radiometry) described in chapters 4 and 5.

3.9 Determining Useful Parameters from the Measurable Parameters

3.9.1 Determining the Lifetime of the Laser Transition from the Fluorescence Lifetime

An important parameter to measure is the lifetime of the laser transition. In the example of the four level laser system presented earlier in this chapter, if we assume that all the atoms pumped into the absorption bands decay to the upper laser level, we can then obtain a simple relationship between the quantum efficiency $Q E$, the total lifetime of the upper laser level $\tau_2$ and the lifetime of the laser transition $\tau_{21}(rad)$:

$$\tau_{21}(rad) = \frac{\tau_2}{Q E} \quad (3.83)$$
3.9.2 Determining the Quantum Efficiency from the Optical-to-Thermal Energy Conversion Efficiency

Since a direct measurement of the quantum efficiency has been shown to be difficult due to the number of calibrations required, another method of obtaining the quantum efficiency is to first measure the optical-to-thermal energy conversion efficiency $\eta_{NR}$ (as will be shown in chapter 4 using photopyroelectric spectroscopy) and then obtain the quantum efficiency, assuming the energy levels and branching ratios of the various transitions are known. This process is described in chapter 7 for two different laser materials.

From the standpoint of laser crystal quality control for crystal growers, the total amount of heat generated in the material is a more useful parameter since it provides a measure of the number of defects in the material, thereby giving a measure of the overall quality of the growth process. As a result, the heat generation rate in the bulk of a crystal $Q_b$ and heat generation rate at the surface of a crystal $Q_s$ (as measured in chapter 5 using photothermal radiometry) are more useful parameters to a crystal grower than parameters such as the lifetime of the laser transition and the quantum efficiency, which are more useful from the standpoint of the basic physics of a laser material.

3.10 Scope and Limitations

We have made several assumptions with regard to the laser materials we evaluated and the techniques used to characterize these materials. Since the size of the smallest sample (0.1 cm) evaluated is much greater than the wavelength of the incident light, we assume that interference effects similar to that observed in thin-films are not produced in these samples. In the case of the photopyroelectric spectroscopy experiment, the Xenon lamp source that was used has a bandwidth of 4 nm, which in the visible range corresponds to
a coherence length of 62.5μm. In other words, the light emitted by the Xenon lamp can maintain its phase only over this coherence length. Any interference effects will only be visible for objects small enough to involve a path difference of the same order of magnitude as the coherence length. We also assume that in the case of photopyroelectric spectroscopy (chapter 4), the light source (a Xenon lamp) can be approximated by a plane wave. In the case of photothermal radiometry (chapter 5), the light source (a Ar-ion laser) can be approximated to be a gaussian beam. We also have ensured to irradiate the laser materials with a power that is not sufficient for nonlinear effects to become important. Finally, due to the low concentration of scattering centers in these laser materials, we assume that the energy lost due to scattering is negligible compared to the energy deposited in the sample due to absorption.

The work presented in this thesis is intended to be applicable to a broad class of solid state laser materials. We focus our experimental study on one such type of laser: the Ti: Sapphire laser. However, in chapter 7, we will speculate on how these techniques must be refined for other laser materials. Of the many radiative and nonradiative processes discussed earlier in this chapter, we only assume the presence of a few of these processes. Concentration-dependent processes involving ion-ion interactions are assumed to be negligible, based on the fact that we are working with lightly doped materials. As a result, we neglect processes such as cross-relaxation, upconversion and ion-ion energy transfer. Ion-ion energy transfer processes will be treated in chapter 7 when we speculate on how these techniques can be applied to other solid state laser materials. We also neglect the presence of excited-state absorption, which is valid for Ti: Sapphire as we discussed earlier in this chapter.

Although the Ti: Sapphire laser operates on a vibronic transition, it can be assumed to operate in a similar manner to a four level laser since the terminal level of the laser is an excited vibrational state of the ground electronic manifold. The validity of this assumption
depends on whether it can be assumed that this excited vibrational state that represents the lower laser level is virtually unpopulated. The energy of the vibrational state that serves as the terminal level of the transition corresponding to the fluorescence emission peak was found to be greater than (but of the same order as) $k_b T$ at room temperature [61]. Another assumption is that although Ti: Sapphire fluoresces to a number of vibronic levels within the same electronic state, we are assuming that these vibronic levels can be approximated by a single level (such that the four level laser system can be used to model this situation) corresponding to an energy equivalent to the average phonon energy released in the lower manifold following radiative transitions from the upper manifolds. Since the entire range of vibronic levels of the ground manifold that act as terminal levels in the lasing process will decay to the ground vibrational state instantaneously (with respect to the lifetime of radiative transitions from the upper manifold), our assumption that this range of vibrational levels can be approximated by a single level in the four level system is valid in that all the vibronic levels can be approximated by a single lifetime.

The photothermal methods used in this work allow the determination of the total amount of nonradiative energy released from all energy levels. No attempt is made in this work to measure specific nonradiative processes from individual levels. However, the techniques presented in this work, can be used as complementary information to information such as the fluorescence lifetime and the energy level diagram in order to obtain the quantum efficiency.
Chapter 4

A Study of Non-Radiative Processes in the Crystal Bulk Using Photopyroelectric Spectroscopy (PPES)

In this chapter, we describe our attempts to gain insight into the mechanisms causing nonradiative energy conversion in solid-state laser materials using photopyroelectric spectroscopy (PPES). To achieve this goal, we use PPES to measure two parameters that we defined in chapter 3: the optical absorption and nonradiative energy conversion efficiency of laser materials. Contrary to current thinking, our results show that the non-radiative processes at the surface may in many instances be the factor limiting the overall quality of a laser material.
4.1 Motivation for Using PPES Technique

Why should we use spectroscopy to study the properties of solid state laser materials? A particular laser material (such as Ti: Sapphire or Ruby) will have its own spectral characteristics. In other words, a particular material has its own distinct way of responding to or interacting with light [65]. How a material absorbs, reflects and transmits different wavelengths of light depends on the nature of the host material, the dopant ion and the defects in the material. Using different spectroscopic methods, we can obtain absorption, reflection and transmission characteristics of a particular material as a function of wavelength [65]. However, we are interested in the problem of non-radiative relaxation occurring in laser materials. We want to know the fluorescent quantum efficiency via the non-radiative decay characteristics of the material as a function of the excitation wavelength. As mentioned in Chapter 2, the problem with the existing spectroscopic techniques [29, 30, 34, 31] that have been used to measure non-radiative quantum efficiencies (such as Photoacoustic Spectroscopy) is that they have to be used in conjunction with an optical spectroscopic method that will measure the absorption coefficient. In order to perform these measurements self-consistently, it is very desirable to use a single technique in which both the optical absorption and the non-radiative energy release can be measured. A pyroelectric detector will produce a signal in response to either an optical excitation (by converting the optical energy to thermal energy) or a temperature change. We can exploit this dual characteristic of pyroelectric detectors to simultaneously measure both the optical absorption and the non-radiative energy using the same technique. Our primary motivation for attempting to use PPES to characterize laser materials is the capability of this technique to act as a dual-mode detector.
4.2 Objectives

The goals of the PPES research are:

1. to study the quality of Ti: Sapphire laser crystals of different figures of merit with regard to their suitability for use in laser cavities. To quantify this, we need to obtain high-resolution spectra of the optical to thermal energy conversion efficiency $\eta_{NR}$ of these crystals at the wavelength ranges of interest. These ranges include the visible range (350 - 700 nm) which coincides with the absorption spectrum of the Ti$^{3+}$ atom. This region is important because the laser material is usually pumped at a wavelength (460 - 500 nm) near its absorption peak. It is also important to study the near-infrared wavelength region (which coincides with the emission spectral range of Ti: Sapphire) in order to study the effects of “self-absorption” by the sample.

2. to separate the relative contributions made to the absorption and non-radiative energy generation by bulk crystal and the surface polish.

4.3 Introduction to PPES Technique

In this section, we discuss the principle of operation of a pyroelectric detector. We also summarize the current state of knowledge of the photopyroelectric spectroscopy (PPES) technique and state the various materials that have been characterized using this technique. Finally, we discuss the modifications we made to this technique which allow the determination of accurate, reproducible data from high-optical-quality laser materials.
Figure 4.1: Operating principle of a pyroelectric detector. The unpoled material in (a) can be aligned to give a net polarization within the material in (b), resulting in positive and negative charges aligning themselves on the electrodes of the material. A change in volume (due to a change in temperature) results in the flow of charge, $Q$.

### 4.3.1 Basic Principles of Pyroelectric Effect

A pyroelectric transducer is made from a thin film pyroelectric material with conducting electrodes on opposite surfaces as shown in figure 4.1 [66]. If a high electric field is applied across the film thickness, the molecular dipoles will preferentially align in the direction of the applied electric field. When the electric field is removed, the dipoles remain aligned due to the presence of the crystal field. This permanent alignment of dipoles gives rise to a net polarization inside the film, causing the charges at the surfaces of the two conducting electrodes to be aligned so as to compensate for this net polarization within the film. The charge density at the surface of the film is equal to the volume polarization, $P = (N\mu/V) <\cos(\theta)>$. In this equation, $N$ is the number of dipoles of moment $\mu$ inside the film volume $V$ and $<\cos(\theta)>$ is the average value of the cosine of the angle between the individual dipole direction and the net polarization direction [67].

A pyroelectric signal results from a change in the volume of the film. A change in temperature of the film results in a change in the volume of the film. This change in volume will change the net polarization in the material. As a result, there is an imbalance between the charges at the surface of the film and the net polarization within the film. Due to this
imbalance, a current is created under closed circuit conditions.

### 4.3.2 Other Relevant Work Done Using PPES

In 1984, Coufal [68] and Mandelis [69] developed a spectroscopic technique based on pyroelectric detection that is now known as photopyroelectric spectroscopy. By applying this technique to study thin films and powdered materials, these researchers showed that this technique is capable of detecting optical absorption and non-radiative energy conversion in condensed matter. In the recent past, researchers have used PPES to study absorption and non-radiative processes in semiconductors, photoelectrochemical cells, fluorescent dyes and photovoltaic cells [70]. In addition, other phenomena such as chemical reactions and photochemical effects in membranes have been monitored using this technique.

The most frequently used PPES experimental configuration is shown in figure 4.2, where the detector is in optical and thermal transmission mode [70]. In such a situation, the back surface of the sample (the side opposite to the one receiving the input radiation) is attached to the pyroelectric detector. The radiation incident on the sample is absorbed by the sample resulting in heat generated by the sample. In the case of an optically opaque
sample, the incoming light is absorbed at the surface, causing heat to be conducted into the solid and to the back surface of the sample. Since the back surface is in contact with the pyroelectric detector, there is heat conduction into the pyroelectric detector material. Due to a temperature-dependent change in polarization of the pyroelectric material, a voltage or current change is created and this voltage or current forms the pyroelectric signal.

4.3.3 The Need to Modify PPES to a Non-Contact Technique

One of the drawbacks of the PPES technique as applied previously is the fact that the pyroelectric detector is in contact with the sample. The problem with sample-detector contact is that the thermal resistance between the two media is unknown, difficult to model, and cannot be relied upon for reproducible data when the thermal signals are low (as is the case with weakly absorbing samples such as laser materials, which are highly transparent). The lack of reproducibility of data stems from the fact that it is virtually impossible to reproduce the same degree of thermal contact between the sample and detector on two successive occasions.

The existing PPES technique, when applied to optically transparent materials such as solid state laser crystals, suffers from another drawback. The light incident on the sample is transmitted through the sample and into the pyroelectric detector. This light is absorbed by the detector surface, thereby increasing the dc temperature of the pyroelectric material. These dc drifts in the pyroelectric signal can actually induce phase changes that are of the same order of magnitude as the sample-heating-induced phase change.

In order to improve the sensitivity of the PPES technique to a level that is required to accurately characterize transparent optical materials, we realized that the two deficiencies mentioned above must be overcome. Both the thermal contact resistance problem and the dc drift problem can be eliminated by making one important modification to the experiment.
We eliminated the need to contact the sample and the detector by incorporating an air gap between them [28]. The air gap thickness can be varied continuously by placing both the sample and the detector on micrometer translational stages, such that the detector and sample can be moved either closer to or away from each other. The modified arrangement of the PPES experiment is shown in figure 4.3. This modification also removes the dc drift problem, as explained in Section 4.4.2.

### 4.4 Generation of PPES Signal from Laser Materials

As mentioned earlier, pyroelectric detectors are sensitive to any optical or thermal perturbation. To understand the mechanisms by which the experimental PPES signal is generated, we will consider separately the optical and thermal components to the overall pyroelectric signal.

The top part of figure 4.4 shows the propagation of the optical beam through the sample and into the detector. The optical excitation beam impinges on the front surface of the laser crystal sample under test. The propagation of the optical beam through the crystal is governed by the Beer-Lambert law, where the transmitted light undergoes exponential
Figure 4.4: Propagation of optical beam (top figure) and thermal wave (bottom figure) through the experimental system. The dashed lines indicate individual thermal waves and the solid line is the summation of all individual thermal waves generated at every location along the crystal where optical absorption takes place.

attenuation due to crystal absorption. Upon leaving the back surface of the crystal, the light travels through the air gap and into the detector. The detector will absorb the incoming light and subsequently experience an increase in temperature, which will create a pyroelectric voltage or current signal.

We next consider the propagation of thermal waves through the sample, air gap and detector, as depicted in the lower part of figure 4.4. Part of the optical energy absorbed by the crystal will be converted to heat via non-radiative energy conversion processes. Because the optical beam is modulated, a modulated thermal wave is generated at every location within the sample. These thermal waves move through the crystal via heat conduction until they reach the back surface of the crystal. The amplitude of the sinusoidal thermal wave undergoes an exponential decay as it travels through the crystal. At the interface between
the back surface of the crystal and the air gap. The thermal wave suffers a high degree of
damping as it propagates into the air. The thermal wave then undergoes further exponential
decay in the air till it reaches the detector. The thickness of the air gap between the sample
and the detector - which in this modified version of PPES can be varied by the experimenter
- determines the strength of the thermal wave signal that is sensed by the detector. If the
air gap is very large, the thermal wave will have almost completely decayed before it reaches
the detector. If the air gap thickness is small, the thermal wave generated within the sample
undergoes negligible decay in the air gap and is almost entirely detected by the pyroelectric
sensor.

In this experiment, our primary goal is to obtain experimentally a measure of the thermal
energy generated in the crystal. The simplest way of doing so is to subtract the pyroelectric
signal with the sample in the optical transmission mode from the pyroelectric signal with
the sample in the mixed thermo-optical mode. The problem with this approach is that we
are subtracting one large number from another in order to obtain a small number. For
any optical excitation irradiating the detector, the ac pyroelectric signal generated will be
synchronous with the frequency at which the light is chopped. However, any thermally-
induced pyroelectric signal will be *delayed* relative to the chopping frequency. One reason
for this delay is the existence of the metastable state in Ti: Sapphire in which the material
relaxes nonradiatively after a specified delay time. The other reason for this delay (with
respect to the optical excitation frequency) is the additional time taken for the heat to
diffuse through the sample and into the detector. For a modulated optical excitation, the
thermally-induced pyroelectric signal will have a phase lag with respect to the optically-
induced pyroelectric signal. To detect such a phase lag, we require a *phase-sensitive detector*
such as a lock-in amplifier.
4.4.1 Two Modes of PPE Detection

We can exploit the fact that the origins of the pyroelectric signal are either thermal or optical, their relative magnitudes depending on the thickness of the air gap. When the air gap is large, the thermal wave generated in the crystal is heavily damped as it propagates through the air gap and is virtually undetectable by the time it reaches the detector. In this optical transmission mode of detection shown on the left side of figure 4.5, the pyroelectric signal is due to optical transmission only. In the mixed thermo-optical mode of detection shown on the right side of figure 4.5, the air gap thickness is very small and the pyroelectric signal is due to two sources: first, the signal due to optical transmission, which is exactly the same as the signal measured in the optical transmission mode; second, the signal due to the thermal wave generated in the crystal. These two components make up the detected signal in the mixed thermo-optical mode of detection. In this modified version of non-contact PPE spectroscopy, the pyroelectric signal must be measured for each required excitation wavelength with the detector in both the optical transmission and the mixed thermo-optical modes. When the
optical transmission mode signal is subtracted from the mixed thermo-optical mode signal. We obtain a purely thermal signal due to the thermal wave generated in the laser material. This subtraction also eliminates the dc drift problem. Since the dc drift is contained in the experimental signal in both modes of detection, subtracting the two signals removes the dc drift component.

4.4.2 Other Possible Contributions to the PPE Signal

We have assumed that the heat transfer between the laser material and the detector is only due to heat conduction through the air gap. It is important to determine whether a significant amount of heat can be transferred through the air gap due to convection or thermal radiation. Convection is a heat transfer process that occurs in fluids whereby heat is transferred by the movement of mass elements in the fluid. Since a mass of fluid at a certain temperature contains a certain amount of thermal energy, the transport of this mass simultaneously involves a transport of heat. If the motion of the fluid is a result of an imposed force (such as the blowing of a fan), the heat transfer process is known as forced convection. In the PPES experiment, the gap between the sample and the detector contains quiescent air, meaning that no heat transfer due to forced convection will take place. Another mechanism of heat convection - known as free or natural convection - takes place when temperature variations in a fluid give rise to density variation which in turn cause buoyancy forces due to the presence of a gravitational field. The buoyancy forces drive the fluid flow and consequently the transfer of heat. We need to find out whether natural convection plays a significant role in the transfer of heat within the air gap [71].

Consider two parallel vertical walls, where one wall represents the back surface of the sample (at a temperature $T_s$) and the other represents the front surface of the detector (at a temperature $T_d$). The enclosure between the two plates contains the air gap. The buoyancy
forces that drive the heat transfer process lead to an acceleration proportional to $gB\Delta T$. where $g$ is the acceleration due to gravity. $B$ is the coefficient of thermal expansion for the fluid (in $K^{-1}$, where for perfect gases $B = 1/T$, where $T$ is the absolute temperature), and $\Delta T = T_s - T_d$ the difference in temperature between the two walls. For natural convection processes, we can define a dimensionless parameter

$$Gr = \frac{gB\Delta T L^3}{\nu^2}$$

(4.1)

where $L$ is the horizontal distance between the two walls and $\nu$ is the viscosity of the fluid. The Grashof number represents the ratio of the buoyancy forces to the viscous forces in free convection. For enclosures between two parallel plates, free convection is suppressed for Grashof numbers below 2000, and heat transfer is due entirely to convection [71]. In the case of this PPES experiment, the two parallel plates are at a distance of 100 $\mu m$ apart.

Since we are working with low (10 mW) optical power input from a Xenon lamp and since we are testing high optical-quality laser crystals, the differences in temperature between the sample and the detector are quite small and on the order of one-hundredths of a degree Kelvin. Under these experimental conditions, the Grashof number is 0.01, meaning that natural convection does not play a significant role in the heat transfer process in the air gap.

Pyroelectric detectors are sensitive to a wide range of wavelengths of incident radiation, including infra-red radiation. Therefore, we must also determine whether thermal radiation plays a role in transferring heat from the sample to the detector via the air gap. Thermal radiation heat transfer between two bodies is governed by the difference in the temperatures of the two bodies, each temperature raised to the power of 4. Since we are using a source of low power (below 50 mW) and since Ti: Sapphire has a low absorption, we expect the temperature differences between the sample and the detector to be well below 1 Kelvin. For
such small temperature differences. the radiative transfer between the sample and detector is negligible.

4.5 Experimental PPES

In this section, we discuss the arrangement of the PPES experiment, followed by a description of the Ti: Sapphire samples that were tested using PPES. We also present experimental results from some preliminary absorption spectra measurements. These results establish the fact that surface absorption processes play a significant role in the non-radiative energy conversion problem in laser materials.

To conduct PPES experiments, we need the following components:

1. A source of light that can produce a wavelength-tunable output from 400 - 1000 nm.

2. A chopper or modulator of light that will generate modulated thermal waves in the material.

3. A phase-sensitive detector that can measure ac signals in-phase and out-of-phase with respect to a reference signal.

4.5.1 Experimental Layout and Procedure

Figure 4.6 shows the modified PPES experimental arrangement. The excitation source in this experiment is a Xenon lamp emitting broadband white light. The output from the Xe lamp is passed through a monochromometer, which will only allow a narrow band of wavelengths to pass through. The output from the monochromometer is collimated and then chopped by a mechanical chopper. The modulated, narrow-band light then impinges on the laser material, which is mounted on a sample holder that has three degrees of freedom via translational
Figure 4.6: Experimental layout of PPES apparatus, where IP and Q refer to the "in-phase" and "out-of-phase" channels of the lock-in amplifier.

micrometer stages. The light is transmitted through the laser material and into the pyroelectric detector. The pyroelectric detector is made up of a 50-micron thick polyvinylidene fluoride (PVDF) material [72]. The detector is mounted on an optical bench with three translational micrometer stages. This arrangement allows us to vary the thickness of the air gap by increments of 1 μm by moving either the sample or the detector.

We obtain optical absorption spectra and thermal energy generation spectra as follows. We first obtain a reference spectrum of the variation in intensity of the lamp output with respect to wavelength. This spectrum is obtained by directing the Xenon lamp output into the active area of the pyroelectric detector. The transparent laser material sample is then mounted on a three dimensional micrometer stage and aligned such that the light passes through the end faces of this cylindrical rod or disk and into the detector. With the sample and the detector "thermally isolated" from each other (separated by an air gap of thickness much greater than the thickness of the thermal diffusion length in air), the
detector will measure a signal corresponding to the transmission of the crystal. Once the signal is measured and stored, a stepper motor will move the sample to a location very close to - but not contacting - the detector (such that the air gap thickness is slightly less than the thermal diffusion length in air). When sufficient time is allowed to pass for the signal to stabilize due to the change in position of the sample, the pyroelectric signal will be due to two components: the direct optical transmission (which was also measured with the sample and detector far away from each other) and the thermal energy generated in the laser material. By obtaining the difference between the two signals, we can obtain a measure of the thermal energy generation. This "real time" subtraction of the optical transmission is crucial, since the pyroelectric detector signal could drift with time. By performing the subtraction immediately at each wavelength (as opposed to obtaining two complete spectra in the optical transmission and thermal mode and then subtracting), we are eliminating the problem of temporal drift.

The pyroelectric signal measured by a lock-in amplifier is digitized by an analog-to-digital (A/D) conversion board and read into the computer. At each wavelength, the number of sample points and their separation in time can be set and adjusted by the experimenter, with eight readings every one second apart being typical. After one experimental point is acquired and written to memory, the computer instructs the monochrometer controller to increment the wavelength by a specified amount via a stepper motor. The A/D board of the computer then receives another set of pyroelectric measured signals from the lock-in amplifier and the process is repeated until a specified wavelength is reached. We then have two data sets: optical transmission as a function of excitation wavelength and thermal energy generation as a function of excitation wavelength. These data sets, along with the reference spectrum, reflectance and air gap thickness, allow the determination of the optical absorption coefficient and the optical to thermal energy conversion efficiency spectra as described by
the theoretical model given in this chapter.

4.5.2 Sources of Error in the PPES Experiment

During the design of the PPE spectrometer, we encountered several difficulties which invariably led to experimental results that were not reproducible. Some of the difficulties we faced included the temporal drift of the Xenon lamp intensity, the accuracy of the air gap thickness measurement and the inaccuracy of the monochromometer stepper motor. We observed the Xe lamp to drift with time. The lamp required over an hour after start up to “thermalize” and maintain a steady output at a particular wavelength. Since it is very essential that at any wavelength the input signal is always the same, temporal drifts must be minimized and the experiment must be completed in as short a time as possible. An experiment to study the temporal variation in lamp output showed us that after thermalization, the lamp output still drifted at the rate of about 1% every hour. Since a wavelength scan takes about 20 minutes, we obtained a reference spectrum before and after each experiment and only accepted the data if the variation between the two reference spectra was below 0.5%.

The accuracy with which we know the value of the air gap thickness is very significant because of the exponential decay of the pyroelectric signal with air gap thickness. As we showed earlier, we have attempted to minimize this problem by comparing the experimental variation of the pyroelectric signal versus air gap thickness with the theoretical model, after which the amount by which the two signals are offset is added to the measured value of the air gap thickness when the detector is in the thermal mode. The most likely reason for the deviation from the expected 100% value of $\eta_{NR}$ in the case of the sooted silicon wafer is the error in the knowledge of the actual air gap thickness.

Another source of error involves the accuracy with which the monochromometer “steps” through the specified wavelength values in a wavelength scan. When a scan is repeated, we
noted that the stepper motor that drives the monochrometer begins to introduce a "lag", resulting in a 1 - 2 nm difference in the wavelength values scanned from experiment to experiment. Finally, another source of error deals with an assumption we made regarding the reflectivity (a nondimensional parameter) of light from thick and thin samples. We assumed that the reflectivity for a thick and thin sample polished in the same manner is the same. Our experiments have shown that two different bulk quality crystals having been polished in the same manner have reflectivity values that are different by 0.5 %. Since these samples were polished in a similar manner, we that the polishing process has a small degree of variability associated with it (from sample to sample).

4.5.3 Phase Sensitive Detection Using Lock-in Amplifier

To perform phase sensitive detection, we used a two-channel lock-in amplifier. A lock-in amplifier measures an ac signal and produces a dc output that is proportional to the fundamental fourier component of the ac signal [73]. This instrument is called a "lock-in amplifier" because it "locks into" a particular frequency and filters out input from all other frequencies. This property is very important to our PPES experiment, since the pyroelectric detector responds to all types of radiation including the laser light and other unwanted signals such as the 60 Hz light in the laboratory. By modulating the optical beam with a chopper at a specified frequency, the instrument removes all additional components of the signal that are not at this chopping frequency [65].

4.5.4 Description of Samples

We tested the following sets of samples (grown at Union Carbide) using PPES:

1. A pair of thick Ti: Sapphire cylindrical rods (length = 2 cm) of high and low figure of merit (FOM). The high figure of merit crystal was subjected to post growth annealing.
Figure 4.7: Xenon lamp output spectrum measured by pyroelectric spectroscopy. This spectrum serves as a reference spectrum that normalizes all optical transmission and thermal spectra.

2. A pair of thin Ti: Sapphire disks (thickness = 0.1 cm) of high and low figure of merit (FOM). The high figure of merit crystal was subjected to post growth annealing. These crystals were cut from the same location of the boule, ensuring that the concentration of Ti ions is the same. As a result, we may assume that the thick and thin crystals have the same bulk absorption coefficient.

4.5.5 Preliminary Experiments

The Xenon lamp has its own characteristic blackbody emission spectrum. The spectral behaviour of the output from the Xe lamp can be obtained by measuring the lamp output as a function of wavelength with the use of the pyroelectric detector. This can be accomplished by removing the sample out of the path of the beam, such that the measured signal corresponds to the output intensity of the lamp. A typical output curve for this Xe lamp is shown in figure 4.7. This blackbody spectrum serves as a reference for all optical transmission and thermal-wave measurements that are made. To obtain information about the samples’
response. we need to remove the blackbody spectrum variations by dividing the sample-related signal by the blackbody spectrum.

Optical transmission spectra can be obtained with the detector in the optical transmission mode. For a homogeneous medium, the intensity of the transmitted beam $I$ is given by

$$I = I_o e^{-\beta l}$$  \hspace{1cm} (4.2)

where $I_o$ is the intensity of the incident beam, $\beta$ is the absorption coefficient and $l$ is the thickness of the crystal. In the PPES experiment, $I$ represents the PPE transmission spectrum measured with the detector in the optical transmission mode and $I_o$ represents the blackbody spectrum of the lamp. We can thus obtain the optical absorption coefficient for the crystal by solving for $\beta$:

$$\beta = \frac{1}{l} \ln(I/I_o)$$  \hspace{1cm} (4.3)

We performed transmission measurements of the high and low figure-of-merit rods and disks. From the transmission spectra and the blackbody spectrum of the lamp, we obtained the optical absorption spectra for the four samples, as shown in figure 4.8. The figure shows that for a pair of crystals of a given figure of merit, the thin disk-shaped crystal has a higher absorption coefficient than the thick rod-shaped crystal. This result is unexpected, since the thin and thick samples (for a given figure-of-merit) were cut from the same location in the crystal boule. We therefore expect the two crystals to be very similar in $Ti^{3+}$ concentration and consequently to have very similar absorption coefficient spectra.

Since the thin crystal has a higher absorption coefficient than the thick crystal (for a given pair of similar figure-of-merit crystals), there is clearly an additional mechanism of absorption involved that seemingly has a greater influence on the thin crystals than the thick crystals. It is highly likely that there is a significant amount of optical absorption
Figure 4.8: Optical absorption spectra of FOM = 40 and FOM = 800 crystals of different thicknesses measured using PPES in the optical transmission mode. FOM = 40 Crystals: (triangle: $l = 0.0813$ cm; +: $l = 2.017$ cm). FOM = 800 Crystals: (x: $l = 0.130$ cm; box: $l = 2.013$ cm).

at the surfaces of the crystal [14]. This surface absorption would explain the fact that the thinner crystals have a higher calculated absorption coefficient than the thicker crystals.

4.5.6 The Need for a Theoretical Model

The pyroelectric detector measures the optical transmission and the ac temperature signal in the optically excited laser material. To relate these experimental signals to the properties of optical absorption and non-radiative energy conversion, we require a theoretical treatment that will model the experimental arrangement as well as all the relevant optical and thermal phenomena taking place in the material during the experiment. The model presented below is based on a generalized theoretical treatment given by Mandelis and Zver [74].
4.6 Theoretical Model

Before considering the thermal wave generation in laser materials in response to a modulated optical beam, we must consider the optical absorption profile in the material since it is the optical absorption that is the source of the non-radiative energy generated in the material. When an optical beam travels through an absorbing medium, there is a reduction in beam intensity due to optical absorption by the sample. It can be shown that at any location \( x \) along the sample, the intensity of the monochromatic beam (wavelength \( \lambda \)) is given by

\[
I(x, \lambda) = I_0 \exp(-\beta(\lambda)x)
\]

(Beer's Law), where \( I_0 \) is the incident intensity. This relation is valid as long as the material is not optically saturated. Since the source of radiation in this experiment is a wavelength-dispersed Xenon lamp, the material is being pumped at intensities on the order of 10 mW, which is much lower than the extremely high saturation intensity of Ti: Sapphire \((2.6 \times 10^6 W/m^2)\).

Figure 4.9 shows the one-dimensional theoretical geometry which is modeled after the pyroelectric experimental configuration. An optical beam modulated at angular frequency \( \omega_c \) and wavelength \( \lambda \) is incident on a transparent solid of thickness \( l \) with the following properties: optical-to-thermal energy conversion efficiency \( \eta_{NR} \), bulk optical absorption coefficient \( \beta_s \), and optical reflectance \( R_s(\lambda) \). At the surfaces of the solid \((x = 0, l)\), thin surface layers of absorptance \( A_s(\lambda) \) are present (due to cutting and mechanical polishing of the laser crystal surfaces). Behind the sample is an air-gap of variable thickness \( L \), interposed between the sample and the pyroelectric detector.

To obtain the functional form of the distributed heat source in this material, we need to describe the optical intensity at any location in the material, we must first develop an expression for the optical intensity distribution in the material. Consider a situation where the beam undergoes absorption at the surfaces, fractional absorption and transmission through the bulk of the solid and multiple reflections at the solid-air interfaces. Figure 4.10 shows
Figure 4.9: Theoretical geometry of PPES experiment showing the sample, air-gap and detector for a material of reflectance $R_s(\lambda)$, optical absorption coefficient $\beta(\lambda)$, surface absorptance $A_s$ and thickness $l$.

several inter-reflections and their intensity at depth $x$ in the solid. A summation of infinite inter-reflections at a depth $x$ in the crystal yields the optical intensity at any location $x$:

$$I(x) = I_o \frac{(1 - R_s)e^{-A_s}}{1 - R_s^2e^{-2(\beta_0l + 2A_s)}}[e^{\beta_0x} + R_se^{-2A_s} - \beta_0(2l-x)]$$  \hspace{1cm} (4.4)

where we define a parameter known as the surface absorptance which is a product of the absorption coefficient of the infinitesimal layer and the thickness of this layer:

$$A_s = \lim_{\epsilon \to 0} (\beta_0 \epsilon)$$  \hspace{1cm} (4.5)

From equation 4.4, we can also find the optical intensity that is transmitted out of the back
Figure 4.10: Absorption and reflection of light by a laser material of reflectance $R_s(\lambda)$, optical absorption coefficient $\beta(\lambda)$, surface absorptance $A_s$ and thickness $l$, showing contributions to the optical intensity at depth $x$ of the first three inter-reflections.

Having obtained the intensity distribution, we can now formulate the heat diffusion problem which will ultimately give us the temperature distribution in the air, laser material sample, and the pyroelectric detector. When modulated optical intensity $I_o(\omega_c; \lambda) = I_o(\lambda)e^{i\omega_ct}$ is incident on the crystal at $x = 0$, we assume that the temperature fields created in the sample, air-gap and detector have a harmonic dependence on time, given by

$$T_i(\omega_c, x; t) = T_i(\omega_c, x)e^{i\omega_ct}$$

where $\omega_c$ is the modulation frequency of the chopper. Note that this expression for the assumed harmonic temperature is *complex*. Upon solving the coupled differential equations
that describe the heat transfer in this system. We obtain a complex expression for the temperature signal in the pyroelectric detector. The real part of this expression represents the pyroelectric signal that is in phase with the optical modulation frequency $\omega_c$ and the imaginary component represents the pyroelectric signal that is out of phase with the optical modulation frequency.

To set up the heat conduction equations in the sample, air-gap and pyroelectric, we assume a harmonic temperature and take into account the heat generation sources (if present) in these three regions. In the gas (air), there are no thermal energy generation sources and the heat transfer is assumed to be only due to conduction, based on our earlier discussion of the possible effects of natural convection and radiation. Under these conditions, the thermal wave equation in the air (denoted by the subscript $g$) can be written as

$$\frac{d^2 T_g}{dx^2} - \sigma_g^2 T_g = 0, \quad x \leq 0 \text{ and } l \leq x \leq l + L$$

Similarly, in the pyroelectric material (denoted by the subscript $p$), the thermal wave equation can be written as

$$\frac{d^2 T_p}{dx^2} - \sigma_p^2 T_p = 0, \quad x \geq l + L$$

Within the sample, there is a heat generation source that is proportional to the product of the optical intensity $I$, the bulk optical absorption coefficient $\beta_b$, and the optical-to-thermal energy conversion efficiency $\eta_{NR}^{(b)}$. We can assume that the heat conduction in the sample is one-dimensional if the spot-size is much larger than the thermal diffusion length in the crystal sample. If we have a broad beam source, the heated area is much larger than in the case of a focused beam. As a result, broad-beam heating will result in temperature gradients in the lateral direction which will be much smaller than the temperature gradients in the axial direction. Since the transfer of heat is governed by temperature gradients, the
heat transfer for broad-beam heating will primarily be in the axial direction.

\[
\frac{d^2 T_s}{dx^2} - \sigma_t^2 T_s = -\eta_{NR}(\lambda)\beta_s(\lambda)(\frac{I(x; \lambda)}{2k_s}), \quad 0 \leq x \leq l
\]  

(4.10)

In the above three equations, we define \( \sigma_j \equiv (1 + i)\sqrt{\frac{\omega_c}{2\alpha_j}} \) as the complex thermal diffusion coefficient, where \( j \) represents the particular region we are considering (air, sample, or pyroelectric). \( k_s \) is the thermal conductivity of the crystal and \( I(x; \lambda) \) is given by equation 4.4.

To understand the physical meaning of \( \sigma_j \), we observe that the real part of this expression is related to the thermal diffusion length \( \mu_j = (2\alpha_j/\omega_c)^{1/2} \). This parameter represents the characteristic length at which the ac temperature decays to \( 1/e \) of its original value. Upon solving these equations, we obtain temperature solutions that contain integration constants which are coupled to the boundary conditions of this system. Because of the absence of interfacial thermal resistances, we assume that the temperature across each of the three interfaces is continuous. At \( x = 0 \) and \( x = l \) we also assume that the heat flux is discontinuous, due to the presence of infinitesimally thin absorbing surface layers. We express the conservation of heat flux at the two surface layers by rearranging the thermal wave equation 4.10 and integrating over a (infinitesimal) surface layer of thickness \( \epsilon \):

\[
k_s \int_0^\epsilon \frac{d^2 T_s(x)}{dx^2} dx - i\rho_s c_s \omega_c \int_0^\epsilon T_s(x) dx = -\frac{1}{2} \eta_{NR}(\lambda)\beta_s \int_0^\epsilon I(x; \lambda) dx
\]  

(4.11)

In this equation, \( \rho_s \) is the crystal density and \( c_s \) is the specific heat of the crystal. Upon integrating the above equation across the infinitesimal thickness \( \epsilon \) and taking \( \lim_{\epsilon \to 0} \) of both sides of equation 4.11 and incorporating equation 4.4, we obtain

\[
-k_s \left. \frac{dT_s(x)}{dx} \right|_{x=0} + k_s \left. \frac{dT_s(x)}{dx} \right|_{x=0} = \frac{I_0}{2} \eta_{NR} A_s \frac{(1 - R_s)(1 + R_s e^{-2A_s})}{1 - R_s e^{-2(\beta t + 2A_s)}}
\]  

(4.12)
where we define a parameter known as the surface nonradiative energy conversion efficiency:

\[ \eta_{NR}^{(0)} \equiv \lim_{\epsilon \to 0} \eta_{NR}^{(\epsilon)} \quad (4.13) \]

Equation 4.12 represents the conservation of heat flux boundary condition at the front surface of the laser crystal. Similarly, at the back surface of the crystal, if we integrate equation 4.10 between \( l - \epsilon \) and \( l \) and take the \( \lim_{\epsilon \to 0} \) of both sides, we obtain

\[ \begin{align*} 
   k_s \frac{dT_s(x)}{dx} \bigg|_{x=l} - k_g \frac{dT_g(x)}{dx} \bigg|_{x=l} &= \frac{I_0}{2} \eta_{NR}^{(0)} A_s \left( \frac{1 - R_s}{1 - R_s^2 e^{-2(\beta_0 l + 2A_s)}} \right) e^{\beta_0 l} 
\end{align*} \quad (4.14) \]

where we assume by symmetry that the surface absorptance is defined as

\[ \lim_{\epsilon \to l^-} [\beta_{l-\epsilon}(l - \epsilon)] = A_s \quad (4.15) \]

and the surface nonradiative energy conversion efficiency is defined as

\[ \lim_{\epsilon \to l^-} \eta_{NR}^{l-\epsilon} = \eta_{NR}^{(0)} \quad (4.16) \]

The final boundary condition is due to the heat flux discontinuity at \( x = l + L \), the air-pyroelectric interface. We can express the conservation of heat flux at this location as

\[ \begin{align*} 
   -k_p \frac{dT_p(x)}{dx} \bigg|_{x=l+L} + k_g \frac{dT_g(x)}{dx} \bigg|_{x=l+L} &= I_t(l) 
\end{align*} \quad (4.17) \]

By solving the coupled differential equations, we obtain the integration constant \( C(\omega_c; \lambda) \). We can then obtain an expression for the photopyroelectric voltage \( V(\omega_c) \),

\[ V(\omega_c; \lambda) = [S(\omega_c)/\sigma_p(\omega_c)] C(\omega_c; \lambda) \quad (4.18) \]
where $S(\omega_c)$ is an instrumental factor that can be normalized out experimentally when all the spectroscopy is performed at one modulation frequency $\omega_c = 2\pi f$. The factor $C(\omega_c; \lambda)$ contains all the thermal, optical and spectroscopic information about the sample:

$$ C(\omega_c; \lambda) = \frac{l_0}{k_p\sigma_p(1+b_{pp})} \left( \frac{1-R_s}{1-R_s e^{-2\sigma_s l}} \right) $$

$$ \left\{ (1 - R_s) \left( \frac{1-\gamma_{gs} Z e^{-2\sigma_g L}}{1-\gamma_{gs} \gamma_{gp} Z e^{-2\sigma_g L}} \right) e^{-(\beta_s l + 2\sigma_s l)} + \frac{b_{gs} e^{-(\sigma_s l + \theta_g L)}}{(1+b_{gs})(1-\gamma_{gs} \gamma_{gp} Z e^{-2\sigma_g L})} \right\} $$

$$ \left[ \frac{n_{R}^{(0)} \beta_g e^{-\theta_g}}{\sigma_s (r_{s}^2 - 1)} \left( \frac{2}{1+b_{gs}} [r_s (1 - R_s e^{-2(\beta_s l + \sigma_s l)}) + b_{gs} (1 + R_s e^{2(\beta_s l + \sigma_s l)})] ight) \right] $$

$$ - \left\{ [1 + R_s e^{-2\sigma_s l} + r_s (1 - R_s e^{-2\sigma_s l})] e^{\sigma_s l} - \gamma_{gs} [1 + R_s e^{-2\sigma_s l} - r_s (1 - R_s e^{-2\sigma_s l})] e^{-\sigma_s l} \right\} e^{-\beta_s l} $$

$$ + n_{NR}^{(0)} A_s \left( \frac{2}{1+b_{gs}} (1 + R_s e^{-2(\beta_s l + \sigma_s l)}) - (1 + R_s e^{-2\sigma_s l}) (e^{\sigma_s l} + \gamma_{gs} e^{-\sigma_s l}) \right) \} \right\} $$

(4.19)

This equation when substituted into equation 4.18 gives the General Pyroelectric Equation.

In the above equation, $b_{ij}$ is the thermal wave coupling coefficient at the interface $(i, j)$:

$$ b_{ij} \equiv \frac{k_i \sqrt{\alpha_j}}{k_j \sqrt{\alpha_i}} \quad (4.20) $$

and $\gamma_{ij}$, $r_s$ and $Z$ are defined for mathematical convenience as

$$ \gamma_{ij} \equiv \frac{1 - b_{ij}}{1 + b_{ij}} \quad (4.21) $$

and

$$ r_s \equiv \frac{\beta_s}{\sigma_s(\omega_c)} \quad (4.22) $$

and

$$ Z \equiv \frac{1 - e^{-2\sigma_s l}}{1 - \gamma_{gs}^2 e^{-2\sigma_s l}} \quad (4.23) $$

**Explanation of the General Photopyroelectric Equation**

To understand the physical meaning of the General Photopyroelectric Equation, we
 rewrite this equation as the summation of three functions $f_1$, $f_2$ and $f_3$:

$$V(\omega_c, \lambda) = f_1(\sigma_g, L, \beta_b, A_s, l, R_s, b_{g_2}, b_{g_2}) + f_2(\eta_{NR}^{(b)}, \beta_b, b_{g_2}, \alpha_g, l, L, R_s, \sigma_g, \sigma_s) + f_3(\eta_{NR}^{(0)}, \beta_b, A_s, l, R_s)$$

(4.24)

The left hand side of this equation is the experimental pyroelectric signal due to heating induced in the pyroelectric detector from three sources $f_1$, $f_2$ and $f_3$. $f_1$ represents the contribution to the overall signal due to direct optical heating by the light transmitted through the sample. $f_2$ represents the heating of the pyroelectric due to non-radiative energy generation processes in the crystal bulk. $f_3$ represents the heating of the pyroelectric due to non-radiative energy generation processes at the crystal surface. We use this expression to solve for the $\eta_{NR}^{(b)}$ contained in $f_2$. An explanation of the terms used in the general pyroelectric equation is given in Table 4.1.

**Special Cases of the General Photopyroelectric Equation**

The general pyroelectric equation can be reduced to simpler forms for certain special cases. In its original form, this equation models the experimental PPE signal when the sample and detector are in close thermal contact (as is the case in the mixed thermo-optical mode of detection). In the purely optical mode, the air gap thickness $L$ can be assumed to be infinite. In such a situation, the theoretical expression for the general pyroelectric signal
simplifies considerably to

\[ C_\infty(\omega_c; \lambda) = \frac{I_o}{k_p \sigma_p (1 + b_{gp})} \left( \frac{(1 - R_s)^2}{e^{-2(\beta_0 + 2A_s)}} \right) \] (4.25)

The above equation represents the optical transmission signal for a transparent optical material of reflectance \( R_s \) having a bulk absorption coefficient \( \beta_0 \) and a surface absorptance \( A_s \).

In the absence of a sample (which corresponds to a sample thickness \( l = 0 \)), the expression for the pyroelectric signal simplifies to

\[ C_R(\omega_c; \lambda) = \frac{I_o(\lambda)}{k_p \sigma_p (1 + b_{gp})} \] (4.26)

In the above equation, we note the explicit dependence of \( I_o \) on wavelength \( \lambda \). We use this equation to normalize any sample related measurements given by equation 4.19 (sample and detector in close contact) and equation 4.25 (sample detector distance is "infinite").

By combining equations 4.25 and 4.26, we obtain an expression for the total sample absorbance in terms of the normalized PPE signal \( V_\infty \):

\[ \beta_0 l + 2A_s = -\ln \left( \frac{(1 - R_s)^2}{2R_s V_\infty} \right) \left[ 1 + \left( \frac{2V_\infty R_s}{(1 - R_s)^2} \right)^{1/2} - 1 \right] \] (4.27)

where

\[ V_\infty(\lambda) \equiv C_\infty(\omega_c; \lambda)/C_R(\omega_c; \lambda) \] (4.28)

4.7 Experimental Results

Dr. Andreas Othonos (Ontario Laser and Lightwave Research Centre) obtained reflectance spectra for Ti: Sapphire crystals using Fourier Transform Infrared Spectroscopy. The re-
Figure 4.11: Reflectance Spectra of Ti: Sapphire using Fourier Transform Infrared Spectroscopy, for two disks of different figure of merit (FOM) with the same surface polish. The figure shows that the variability in reflectance between two crystals with similar surface polish is less than 0.2 %.

Reflectance spectra of figure 4.11 show that the surface reflection is almost constant across the 400 - 1000 nm spectral range.

### 4.7.1 Relative Magnitudes of In-Phase and Out-of-Phase Signals

The two channels in the lock-in amplifier measure different signals. The in-phase channel measures the pyroelectric signal that is in phase with the reference signal. The quadrature channel measures the pyroelectric signal that is out of phase with the reference signal. In other words, the in-phase channel measures the optical contribution to the pyroelectric signal and the quadrature channel measures the thermal contribution. To give an indication of the ability of this technique to measure lower thermal signals than previous attempts at PPES, we have shown the relative signal levels of the in phase and quadrature signals. In our experiments with Ti: Sapphire, the in phase (purely optical) component is 2 orders of magnitude stronger than the quadrature (purely thermal-wave) component. In comparison.
PPES experiments of $Nd_2O_3$ [68] thin powders yield in phase to quadrature signal ratios of about 60. The modified PPES technique allows us to measure the small thermal signals associated with high-quality optical materials such as Ti: Sapphire.

4.7.2 Optical Absorption Spectra

The preliminary absorption measurements showed that the crystal surfaces can absorb a significant amount of the input radiation. The presence of this surface absorption led us to deconvolute the total (measured) optical absorption coefficient into bulk and surface components. To perform this separation and calculate the bulk and surface absorption, we require a crystal that is cut into two pieces: a thick rod and a thin disk. By cutting a thick rod and a thin disk from the same cylindrical rod, we can ensure that the $Ti^{3+}$ concentrations in both crystals are very similar. Consequently, we can assume that the bulk properties of the thick and thin crystals are identical. The two crystals should also be treated with the same surface polish procedure, so that we may assume that they have identical surface absorptance.

Under the conditions of similar bulk and surface properties of a pair of crystals of different thickness $l_1$ and $l_2$, we can deconvolute the bulk absorption $\beta_b$ from the surface absorptance $A_s$ by using a system of two equations with two unknown parameters $\beta_b, A_s$ of the form

$$\beta_b l_1 + 2A_s = S_1$$
$$\beta_b l_2 + 2A_s = S_2$$

(4.29)

The left hand side of each equation above represents the summation of the bulk and surface absorptances for a given crystal of thickness $l_1$ (thick crystal) or $l_2$ (thin crystal). The right hand side of each equation is the experimentally measured total sample absorptance for each crystal, given by equation 4.27.
Figure 4.12: Bulk and Surface Optical absorptance spectra of Ti: Sapphire crystals obtained using PPES in the purely optical transmission mode at $f = 9$ Hz for a pair of figure of merit (FOM) = 40 crystals assumed to be having identical bulk and surface properties. For a description of how each point on this curve is obtained, please refer to Appendix A.

Figure 4.12 shows the results of the above deconvolution for a pair of FOM = 40 samples and figure 4.13 for a pair of FOM = 800 samples. The bulk absorptances are typical of the Ti: Sapphire system and consist of a broad peak centered around 470 nm with a red-shifted shoulder. The peak is due to the $2T_2g \rightarrow E_g$ transition broadened by phonons. Moulton [8] has attributed the presence of the red-shifted shoulder to the Jahn-Teller splitting of the $2E_g$ state. An important effect of the bulk and surface absorptance deconvolution is the observation that the bulk absorption spectrum of the FOM = 800 crystals becomes essentially zero above 640 nm and the surface absorption completely dominates the optical behaviour of these high figure of merit materials. For the FOM = 40 crystals, the overall bulk absorption is stronger than in the FOM = 800 samples. In particular, for wavelengths above 640 nm, bulk and surface absorptances of the thick crystal are of equal strengths, with the bulk absorptance of the FOM = 40 sample being considerably larger than that of the FOM = 800 sample in the same spectral region. On the other hand, the 400 -600 nm
range is almost completely dominated by bulk absorption in the thick crystals, while the thin crystals are dominated by surface effects throughout the entire visible range examined in this work. The high optical quality of the FOM = 800 crystal bulk is seriously affected due to the dominant surface absorptions for wavelengths above 620 nm. Since this region coincides with the fluorescence emission spectrum of Ti: Sapphire, figure 4.13 indicates that greater care of the surface polishing treatment of laser rods must be taken than in the current quality control technologies, which mainly focus on improvements of the bulk crystal quality.

Why do the FOM = 800 crystals have a lower overall bulk absorption coefficient $\beta_s$ than the FOM = 40 crystals? This behaviour is expected and is consistent with the improved optical quality of the high FOM crystals, which were subjected to an additional annealing (in a pure hydrogen environment at high temperatures). This additional annealing removes the bulk defects that are present in the crystal, such as inclusions and voids. As a result, the absorption of the FOM = 800 crystal can be assumed to be entirely due to the electronic
absorption by the $Ti^{3+}$ ion. The electronic component of absorption should in theory be the same for all samples and should effectively be zero at the lasing wavelengths (650 -1100 nm). We attribute the differences in the bulk absorption between the FOM = 40 and FOM = 800 crystals to a residual absorption due to the presence of bulk defects in the FOM = 40 crystal [15]. These bulk defects are responsible for absorption at the lasing wavelengths which hinders the laser output efficiency.

4.7.3 Non-Radiative Energy Conversion Efficiency

To calculate the non-radiative energy conversion efficiency spectra, we measure the out-of-phase PPE signal with the sample and detector in close thermal contact. By decreasing the airgap thickness $L$ to some predetermined value, we measure a stable, reproducible signal in the out-of-phase channel of the lock-in amplifier. In section 4.7.2, we measured the optical transmission signal (and subsequently the optical absorption coefficient) by measuring the in-phase signal of the lock-in with the sample and detector an “infinite” distance away from each other. In principle, the out-of-phase signal should read zero in this “purely optical” mode of detection. However, direct optical heating of the pyroelectric material can cause the out-of-phase signal to drift. To eliminate this drift, we store the out-of-phase signal measured when the sample and the detector are in close thermal contact. The result of this subtraction gives us an experimental signal that is due exclusively to the heat generated in the sample. This experimental signal represents the imaginary component of the left hand side of equation 4.18. To determine the non-radiative energy conversion efficiency $\eta_{NR}^{(b)}$ spectra, we need to consider the right hand side of this equation which is described by equation 4.19. To solve for $\eta_{NR}^{(b)}$ requires the knowledge of the optical reflectance of the laser material $R_s$, the bulk absorption coefficient $\beta_b(\lambda)$, the surface absorptance $A_s$, the thermal conductivity $k_i$ of each region (sample, air, pyroelectric), the thermal diffusivity
\( \alpha_i \) in each region and the air-gap thickness \( L \). We use the values of \( R_s \) obtained using FTIR spectroscopy shown in figure 4.11. We determine \( \beta_b(\lambda) \) and \( \lambda_i \), experimentally in the optical transmission mode as described in section 4.7.2. In other words \( \beta_b(\lambda) \) and \( \eta^{(b)}_{NR} \) are determined simultaneously at each wavelength by first measuring the optical transmission signal and then the mixed thermo-optical signal at each wavelength before the wavelength is incremented. \( k_i \) and \( \alpha_i \) are the only properties that we obtain from the literature. \( k \) and \( \alpha \) values for Ti: Sapphire are well established as are these values for the pyroelectric material and air. The final parameter whose numerical value must be known in order to solve for \( \eta^{(b)}_{NR} \) is the air gap thickness \( L \). Since both sample and detector are mounted on micrometer stages, it is possible to obtain the apparent distance between the sample and the detector. To determine the true air gap thickness, we measured the out-of-phase PPE signal (given by the imaginary part of equation 4.19) as a function of the apparent (measured) air gap thickness. This experimental variation of the PPE signal, when compared with the theoretical variation as shown in figure 4.14 is offset by a fixed distance. By calculating this offset and adding it to the value of the measured air gap thickness, we obtain the true air gap thickness.

### 4.7.4 Verifying the Accuracy of the PPES Technique

To determine the accuracy and reproducibility of the PPE instrument, we must evaluate a material which has a known value of \( \eta^{(b)}_{NR} \). Any opaque material which converts all the light it absorbs to heat will have an \( \eta^{(b)}_{NR} = 100 \% \). A silicon wafer is an example of such a material. A silicon wafer with a thin layer of soot deposited on the surface faces the optical beam. Under these conditions the PPE signal can be considerably simplified using only bulk absorption. Because the material is opaque, non-reflecting and has a \( \delta \) function absorption profile, the following assumptions are valid: \( e^{-\beta u} \approx 0 \), \( |r_s| \gg 1 \), \( A_s = 0 \) and \( R_s = 0 \). Under such conditions, the PPE signal can be simplified considerably. Using the relevant
Figure 4.14: Spatial decay profiles of the PPE signal as a function of air gap thickness. The solid line indicates the theoretical profile and the dotted line indicates the experimental profile. The arrows indicate the rigid shift that is required in the measured air gap thickness to obtain the true air gap thickness \( L \).

thermophysical parameters for silicon along with the out-of-phase experimental signal, we obtain the experimental \( \eta_{NR}^{(b)} \) spectra shown in figure 4.15. The figure shows spectra from two consecutive experiments, indicating that the values of \( \eta_{NR}^{(b)} \) are 100 % ± 3 % variance in reproducibility. For the silicon wafer, \( \eta_{NR}^{(b)} \) should be 100 % across the entire spectrum of wavelengths scanned. Figure 4.15 shows a ± 6 % deviation from 100 % across the 380 - 650 nm spectral range. These variances give an indication of the accuracy of the PPE instrument.

In the next section, we see that the spectral changes of \( \eta_{NR}^{(b)} \) of Ti: Sapphire are much greater than the instrumental spectral variations, implying that the instrumental effects of the PPE spectrometer have a negligible influence on \( \eta_{NR}^{(b)} \). Due to the dependence of \( \eta_{NR}^{(b)} \) on a number of different experimentally measured parameters, each having an uncertainty associated with it, the measure of variability we use in attaching an error estimate to the spectra shown in the next section is the 3 % variability that we obtained in this experiment.
Figure 4.13: Optical to thermal energy conversion efficiency spectrum of a sooted Silicon wafer using photopyroelectric spectroscopy. Figure shows data from two successive experiments (to check reproducibility) in the 380 - 650 nm range (to check the spectral constancy of the data and their deviations from the expected value of 100 % for Silicon (represented by the horizontal line), since all absorbed energy is converted to heat.

4.7.5 Non-Radiative Energy Conversion Efficiency of Ti: Sapphire

Figure 4.16 shows the $\eta_{NR}^{(b)}$ spectra for the two crystals of different bulk quality described in section 4.5.4. One crystal has an FOM = 800 and the other has an FOM = 40. This difference in bulk quality is borne out by the PPE experiment as seen in figure 4.16. At the Ti: Sapphire pump wavelength of 488 nm, we see that the FOM = 800 crystal has a lower $\eta_{NR}^{(b)}$ than the FOM = 40 crystal. In other words, the FOM = 800 crystal converts a lower fraction of its absorbed energy to heat, thereby having a greater fraction of the absorbed energy available for “useful” luminescent emission. The $\eta_{NR}^{(b)}$ spectra show a decrease with wavelength from 340 nm to 430 nm after which the spectrum flattens out until 540 nm. Theoretical quantum mechanical calculations by Grinberg and Mandelis [62, 75, 76] have shown that there is a crossover energy $E_{nr}$ at which the ground and excited state manifolds
Figure 4.16: Optical to thermal energy conversion efficiency spectra of the two pairs of Ti: Sapphire crystals for crystals of different figure of merit (FOM). Each curve is generated by using values of bulk and surface absorptance spectra measured using a pair of equal FOM crystals of different thicknesses. For a description of how each point on this graph is obtained, please refer to Appendix A.

overlap. For excitation wavelengths corresponding to energies greater than $E_{nr}$, there is a high probability that an electron in the excited state can change its electronic and vibrational states to the ground state without changing its energy. In other words, there is a high probability that the electron crosses over from the excited state to the ground state without emitting a photon (ie: nonradiatively) if the excitation energy is greater than $E_{nr}$. These authors have calculated for Ti: Sapphire that the crossover energy $E_{nr}$ is 430 nm [62]. As we go to progressively shorter wavelengths from 430 nm (ie: progressively greater energies from $E_{nr}$), figure 4.16 confirms the increase in nonradiative energy conversion. For wavelengths higher than 430 nm and less than 540 nm (ie: for energies less than $E_{nr}$) the $\eta_{NR}^{(b)}$ spectra are constant. Below the crossover energy the probability of radiative (and nonradiative)
relaxation is not dependent on excitation wavelength. For wavelengths greater than 540 nm, we observe a sharp increase in the $\eta^{(b)}_{NR}$ spectra which we attribute to residual absorptions in the crystal which are not related to the $Ti^{3+}$ electronic manifold. These residual absorptions are a direct result of the bulk defects that are present in the FOM = 40 crystal. The FOM = 800 crystal exhibits an even steeper increase at about 580 nm. This steep increase is attributed to the fact that the bulk absorption is almost zero for the FOM = 800 crystal at this wavelength. Since $\eta^{(b)}_{NR}$ is defined as the amount of heat released per photon absorbed, this parameter is only defined for crystals having a finite absorption. At such wavelengths the surface absorptance is the only factor that contributes to heat generated in the crystal.

4.8 Discussion

In comparing our results with other work reported in the literature, we note that our results agree with some of that work. Only one of the other groups that have considered this problem have obtained spectrally distributed values of $\eta^{(b)}_{NR}$ and their results are given only for a narrow range of wavelengths (460 - 510 nm) [27] compared to our results (340 - 700 nm). By obtaining values of $\eta^{(b)}_{NR}$ over a wide spectral range, we are in a better position to identify the causes of non-radiative relaxation in laser materials.

Albers et al. [77] used a resistive Wheatstone bridge circuit to measure the heat released by an optically excited Ti: Sapphire crystal in intimate contact with a positive-temperature coefficient (PTC) resistor. The heat generated in the sample affects the electrical characteristics of the PTC resistor, which these authors measured. From these measurements, they calculated radiative quantum efficiencies in the 315 - 325 K temperature range. The values obtained by Albers are consistent with the 24 % to 32 % range of $\eta^{(b)}_{NR}$ values we obtained. It is difficult to make a direct comparison between the two experiments because these authors
did not state the excitation wavelength that they used to perform this experiment. Byvik et al. [25] used a purely optical method using an integrating sphere to measure the luminescence from the crystal and subsequently measured a quantum efficiency of 70 % (implying that $\eta_{NR}^{(b)}$ is 30 %). This value of $\eta_{NR}^{(b)}$ is much higher than shown in figure 4.16. The reason for their higher value of $\eta_{NR}^{(b)}$ is due to the fact that the integrating sphere measures a spectrally integrated signal, meaning that their value of $\eta_{NR}^{(b)} = 30\%$ represents the thermal energy release over all wavelengths. Li et al. [27] used a dc thermal technique to measure the optical to thermal efficiency in Ti: Sapphire in the 460 - 510 nm range and about $\eta_{NR}^{(b)}$ in the 60 % range. These values are extremely high compared with our results. The most likely reason for these high values is the fact that these authors did not account for and separate out the surface absorption present in Ti: Sapphire. By not accounting for the surface absorption, this additional heat source has the effect of artificially raising the value bulk optical to thermal efficiency. Eilers et al [78] used pulsed photothermal beam deflection and calculated a 13.9 % $\eta_{NR}^{(b)}$ at 532 nm, which is in good agreement with our results.

4.9 Conclusions

In this chapter, we have used a technique known as photopyroelectric spectroscopy to quantify the problem of non-radiative energy conversion in laser materials. Our investigation of this problem is based on the need of crystal growers to be able to evaluate non-destructively and in a non-contact manner the quality of a laser material. Although our work focusses on this particular problem and not on the technique we use to study it, a useful by-product of our work is the modification of PPES to a non-contacting technique. By demonstrating the ability of PPES to perform non-contact measurements, we expect this technique to have a much wider application than before.
The experimental $\eta_{NR}^{(b)}$ spectra presented here are shown for a much wider range of wavelengths than previously measured. Upon observing the optical absorption spectra and the optical to thermal energy conversion efficiency spectra that we obtained, we can identify the two main mechanisms which inhibit the overall radiative efficiency of a laser material:

1. The presence of bulk defects in Ti: Sapphire gives rise to a residual absorption that is not related to the electronic absorption of the material. The presence of these defects is detrimental in two ways: first, the absorption by the defects of the pump light does not contribute to any radiative emission; second, the absorption by the defects of the lasing output light inhibits the useful output of the laser.

2. The presence of surface defects in Ti: Sapphire gives rise to a surface absorption that is also not related to the electronic absorption of the material. In high bulk quality crystals, we have shown that the surface absorptance is the limiting factor in the overall radiative efficiency of the laser. Like the residual defect absorption mentioned above, the presence of surface defects inhibits the useful output of a laser in the same two ways mentioned.

Several authors have already identified the first loss mechanism described above, leading industrial crystal growers to seek ways of removing these defects. One approach is the annealing of the laser material following growth, as performed to the FOM = 800 crystal. This approach has produced positive results in terms of lower losses (ie: lower $\eta_{NR}^{(b)}$), which our results confirm. However, the second loss mechanism mentioned above has not been considered previously. Our results show that in a high figure of merit crystal, the factors limiting laser output performance are surface absorption and surface heating. This unexpected result leads us to reconsider our overall approach to the problem of nonradiative energy conversion in laser materials.
4.9.1 Limitations of PPES Technique

Having identified surface absorption and surface heating as key limiting factors of the overall output efficiency of a laser material, we ask the following question: Is PPES the most suitable technique to accurately measure surface processes from the standpoint of doing industrial quality control? PPES is not suitable for two reasons:

1. PPES is a *back surface detection* technique, where the detector is placed on the side of the sample opposite to the optical irradiation. In other words, the front surface is heated and the back surface is monitored. This approach is not optimally sensitive to surface heating effects.

2. The separation of bulk and surface absorption requires a pair of samples of different thickness with the same surface treatment. This restriction is not a very practical one under industrial conditions, due to the additional time and cost of cutting and polishing two sets of samples for one measurement.

4.9.2 Recommendations

Although PPES is a useful technique to gain insight into the physics of nonradiative processes in laser materials, the above two limitations render this technique unsuitable from an industrial quality control point of view. To overcome the limitations mentioned above, a more suitable method would involve a combination of front surface heating with front surface detection. In addition, this method must be able to evaluate bulk and surface properties using one crystal. One approach to satisfying both these requirements is to irradiate the front surface of a laser material with laser light and detect the resulting infra-red radiation emitted from that same surface. Our attempts to simultaneously characterize surface and bulk nonradiative processes in laser materials is described in the following chapter.
Chapter 5

Evaluating Non-radiative Bulk and Surface Processes Simultaneously Using Photothermal Radiometry (PTR)

The dominant effect that surface non-radiative energy conversion has on the overall quality of a laser crystal is the key result that we have established by using the photopyroelectric spectroscopy technique in Chapter 4. Given this fact, we require a technique that is more sensitive to surface heating than photopyroelectric spectroscopy. We begin this chapter by describing the photothermal radiometry technique, the physical principles this technique is based on and the physical phenomena that are measured in this technique. We next describe the signal processing approaches that we attempted to use. Having selected a time-domain experimental approach, we use a time-domain theoretical model [79] to obtain key information about the nature of the IR radiation emission at various time ranges. The model predicts that surface and bulk non-radiative processes can be monitored by detecting the transient signal
at different time-ranges. However, the experimental transient IR radiation emission profiles show three distinct regions, as compared with the two (due to bulk and surface) predicted by the theoretical model. We determined that this additional component of the experimental IR emission signal is due to direct radiative emission (as opposed to thermal emission). Using a model [80] which accounts for this radiative emission, we conducted time-domain measurements of the IR emission signal from optically pumped laser materials. Our results show that phothermal radiometry can be used as a single technique to evaluate both the bulk and surface non-radiative energy conversion rates in a solid state laser material.

5.1 Photothermal Radiometry

The photothermal radiometric (PTR) method involves the detection of infrared emission from a sample that is irradiated by an optical source [81]. As described in section 5.2, the infrared emission is related to the sample temperature by the blackbody radiation law. This technique has been recognized as an important tool for the evaluation of surface properties [81] and solid samples [82, 83]. Several authors [84, 85] have presented theoretical treatments of this technique, relating the measured signal to some material parameter. To understand the signal generating mechanisms in this technique, we need consider in the next section the radiative exchange between the sample and its environment.

5.2 Planck's Law and Kirchhoff's Law

A body that is exposed to its surroundings will continually exchange radiation with those surroundings [86]. When radiation impinges on a body, some radiation may be transmitted through it, some may be reflected and a fraction of the radiation is absorbed by the body and transformed into heat, thereby raising the temperature of the body. It is convenient
to introduce the concept of a blackbody as a body which absorbs all the radiation incident on it. The photothermal radiometry (PTR) technique is based on the detection of excess blackbody radiation that is generated when a source of energy (such as a laser) interacts with the material being studied [86]. The emission of radiation by a body in thermal equilibrium with its surroundings at an absolute temperature \( T \) can be understood by following Planck’s treatment of radiative exchange, given in Chapter 3. Planck’s derivation of the energy density of blackbody radiation gives

\[
W_{bb}(\lambda, T) = \frac{2\pi \hbar c^2}{\lambda^5 \left[ \exp(\frac{\hbar c}{\lambda k_b T}) - 1 \right]},
\]

The function \( W_{bb} \) gives the spectral distribution of radiation exchanged between a blackbody at a given temperature \( T \) and its surroundings under the conditions of thermal equilibrium. The function \( W_{bb} \) predicts that a blackbody at room temperature will exchange radiation with its surroundings at wavelengths predominantly in the 8-14 \( \mu m \) range, as shown in figure 5.1.

For bodies which are not perfectly black such as a Ti: Sapphir crystal, the emission will be lower than for a blackbody by a factor of \( \varepsilon(\lambda, T) \), the spectral emissivity. The spectral emissive power radiated by the body will then be given by

\[
W_{\lambda}(\lambda, T) = \varepsilon(\lambda, T)W_{bb}(\lambda, T)
\]

**Kirchhoff’s Law:** For a radiating body in thermal equilibrium with its surroundings, Kirchhoff’s Law of heat radiation states that the emissivity of the body is equal to its absorptivity. Several researchers have discussed the issue of the validity of Kirchhoff’s law under nonequilibrium conditions such as an experiment involving laser irradiation of a sample. Weinstein [87], Bauer [88] and Baltes [89] argue that the condition of thermodynamic
Figure 5.1: Spectral variation of blackbody radiation emission by a body at a given temperature.

equilibrium is not required for Kirchhoff’s law to hold, given that absorption and emission are defined in a specific manner. Upon reviewing both Kirchhoff’s phenomenological theory and Einstein’s microscopic interpretation of radiative transfer, these authors concluded that the quantities *emissivity* and *absorptivity* referred to in Kirchoff’s law are the spontaneous emission and net absorption (defined as stimulated absorption minus stimulated emission) respectively. Since the emissivity is due to spontaneous emission only, the environment has no effect on the emission and hence on the validity of Kirchoff’s law. This definition of emissivity is consistent with the PTR experimental technique: since the experiment uses a broad-band detector, the signal generated is primarily due to spontaneous emission.

To derive an analytical expression for the amount of radiation collected by the detector, we must first consider how much radiation is generated within the sample. Consider the
radiation emitted by a thin section of the material shown in figure 5.2 of thickness \( dz \).

\[
\text{Figure 5.2: Radiation emission from a thin slice in the interior of a material of thickness } L.
\]

The amount of radiation emission from this section of material is

\[
dS_{em} = \epsilon(\lambda, T)W_{bb}(\lambda, T)dz
\]  

(5.3)

Due to self-absorption of infra-red radiation by the sample, the radiation emitted within the slice of material will attenuate exponentially according to the Beer-Lambert law as it propagates through the material. Some of the radiation arriving at the front surface is reflected by a surface of reflectance \( R \). The remaining radiation will be collected by the detector. For a detector with a bandwidth between \( \lambda_1 \) and \( \lambda_2 \), the total radiation seen by
the detector is

$$S_{em} = (1 - R) \int_{\lambda_1}^{\lambda_2} \left[ \int_0^L \epsilon(\lambda, T) e^{-\beta_{ir}(\lambda, T)L} W_{bb}(\lambda, T) dz \right] d\lambda$$

(5.4)

where $L$ is the sample thickness. Performing the integration over the sample thickness $L$ yields

$$S_{em} = (1 - R) \int_{\lambda_1}^{\lambda_2} \left[ \frac{\epsilon(\lambda, T)}{\beta_{ir}(\lambda, T)} W_{bb}(\lambda, T)(1 - e^{-\beta_{ir}(\lambda, T)L}) \right] d\lambda$$

(5.5)

By invoking Kirchhoff’s law and Planck’s radiation law, we obtain

$$S_{em} = (1 - R) \int_{\lambda_1}^{\lambda_2} \frac{2\pi hc^2(1 - e^{-\beta_{ir}(\lambda, T)L})}{\lambda_{em}^5 [\exp(\frac{hc}{\lambda_{em}k_B T}) - 1]} d\lambda$$

(5.6)

If we assume that the sample is opaque to infrared radiation within the detector bandwidth (i.e: $e^{-\beta_{ir}(\lambda, T)L} \to 0$), equation 5.6 reduces to

$$S_{em} = (1 - R) \int_{\lambda_1}^{\lambda_2} \frac{2\pi hc^2}{\lambda_{em}^5 [\exp(\frac{hc}{\lambda_{em}k_B T}) - 1]} d\lambda$$

(5.7)

By defining a dimensionless variable $\gamma = \frac{hc}{\lambda_{em}k_B T}$ and substituting in equation 5.7,

$$S_{em} = \frac{(1 - R)2\pi k_B^4 T^4}{h^3 c^2} \int_{\gamma_i}^{\gamma} \frac{\gamma^3}{\exp(\gamma) - 1} d\gamma$$

(5.8)

where $\gamma_i = \frac{hc}{\lambda_{em}k_B T_i}$. Carrying out the integration, we obtain

$$S_{em} = (1 - R)\psi \sigma T^4$$

(5.9)

where $\psi$ is the result of integration in equation 5.8 and $\sigma$ is the Stefan-Boltzmann constant. Equation 5.9 gives an expression for the infra-red radiation emission from a sample at
temperature $T$ that is opaque to the infra-red radiation that it emits. Because the PTR technique uses modulated laser excitation of the sample, the detector senses modulated infra-red emission from the sample. As a result, we are more interested in the change in infra-red emission than in the absolute emission. Assuming that the fluctuations in the infra-red emission signal are small compared to its absolute value, this fluctuation can be calculated using a first-order Taylor series expansion of equation 5.9:

$$\delta S_{em} \approx \frac{\partial S_{em}}{\partial T} \delta T \approx (1 - R) \psi \sigma T^3 \Delta T$$ (5.10)

Equation 5.10 implies that the PTR detection technique measures a signal $\delta S_{em}$ that is proportional to the change in sample temperature $\Delta T$, given that the sample is perfectly opaque to its own IR emission. By relating this temperature change to changes in some thermal and/or electronic property, it is possible to characterize the thermal and electronic properties of the material.

### 5.3 Generation of Radiometric Signal in Laser Materials

In this section, we consider the physical mechanisms responsible for generating the IR photons emitted by the sample which are subsequently collected by the IR detector. The detector we use in photothermal radiometry (PTR) experiments is a photon detector, which is sensitive to IR photon emission. Since we are interested in measuring the amount of non-radiative (thermal) energy generated in the laser crystal, we must ensure whether or not the IR photon emission by the sample is exclusively the direct result of the non-radiative energy generated in the sample.
The energy gained by the atoms during the absorption process causes their outer electrons to be pumped to excited energy states. This additional energy is dissipated in many forms.

1. Radiative decay via stimulated emission, emitting photons in the visible to near infra-red (700 - 1100 nm) range.

2. Radiative decay via spontaneous emission, emitting photons ranging from the visible to the far infra-red wavelength region.

3. Non-radiative decay via energy transfer between the ion and the host lattice. Energy is transferred to the lattice by the emission of one or more phonons which have energy sufficient to conserve the energy of the transition from the upper to the lower energy level.

The photon emission resulting from process 1 will not contribute to the PTR signal since the emission is outside the bandwidth of the detector. The emission process 2 can result in two possibilities, depending on the wavelength range of the emitted photons. The first possibility is that the emitted IR photons will be transmitted through and out of the sample and be collected by the detector. The other possibility is that the emitted IR photons will be reabsorbed by the sample. The energy due to the reabsorbed photons will then be dissipated via multiphonon processes whereby energy is transferred to the lattice. The non-radiative de-excitation process 3 results in multi-phonon emission into the host lattice [90, 77].

The phonon emission due to processes 2 and 3 can result in a number of different interactions [91]. Interactions between the lattice phonons and the Ti$^{3+}$ ions can cause some phonon energy to be transferred back to the ion, exciting the ion to a higher energy state [50]. The net amount of lattice vibrational (phonon) energy that is produced is dissipated through the crystal. As a result, there will be a greater number of phonon-induced processes that will result in the atoms at the surface being excited to higher energy levels. When these
atoms at the surface de-excite. They emit IR photons which are collected by the detector.

In light of the many processes taking place in the crystal, we summarize this section by asking the following question: What does the IR detector actually measure during a PTR experiment? The detector is sensitive to two processes:

1. The net amount of vibrational (phonon) energy generated in the host lattice crystal as a result of optical excitation and subsequent relaxation of the Ti$^{3+}$ ions embedded in the host.

2. The direct, radiative emission of IR photons by optically excited Ti$^{3+}$ ions, assuming that all the IR photon emission from the crystal bulk is not re-absorbed by the crystal itself. This radiative emission of IR photons is due to energy transitions to higher vibrational sublevels of the ground state manifold as compared to the fluorescence emission lines which decay to lower vibrational sublevels.

We must keep in mind that if Process 2 exists (in other words, if the crystal is not totally self-absorbing in the wavelength range of interest), it provides an additional component to the PTR signal, since it is not related to the non-radiative energy generation process in the crystal. In the ideal situation, we want the detector to sense Process 1 only.

5.4 Three Approaches to Processing Radiometric Signals

Having decided that photothermal radiometry (PTR) is the most optimal technique to monitor non-radiative processes in laser materials, we next describe the various signal processing methods that we attempted in order to obtain acceptable signal-to-noise ratios and reproducible data sets. The choice of signal processing method is extremely important in situations
such as photothermal radiometry of laser materials, where the radiative emission signals are relatively low and often buried in noise. To determine the most suitable signal detection and processing method for this particular problem, we considered and attempted three experimental approaches: time-domain detection, frequency-domain detection and the hybrid rate-window detection methods. The important factors to consider in selecting an experimental procedure include signal-to-noise (SNR) ratio, reproducibility, ease of interpretation of data and other practical considerations such as the amount of time required to run an experiment. We performed preliminary experiments using all three detection methods before selecting the most appropriate method.

5.4.1 Frequency Domain PTR Detection

This mode of detection involves a harmonically modulated laser beam irradiating the crystal and the resulting infra-red emission from the sample is collected by the detector. By modulating this PTR signal at several modulation frequencies, a PTR frequency scan is obtained. At low frequencies, frequency-scanned photothermal detection has a higher signal-to-noise ratio than time-domain detection. At higher frequencies, this advantage in SNR is minimised because of the decrease in photothermal signal amplitude with frequency increase. In a study involving the measurement of the quantum efficiency of ruby crystals, Mandelis et al. [92] derived an expression for the PTR emission signal of an optically transparent medium as a function of frequency \( f \). These authors predict that the PTR emission signal has a minimum occurring at a frequency \( f_{\text{min}}^{\text{PTR}} \), which is inversely related to \( \tau_{21} \), the metastable lifetime of the material. By locating the extremum of the frequency-scanned PTR emission signal, these authors calculated the radiative quantum efficiency of ruby crystals, which have a relatively long lifetime in the millisecond range. For the case of Ti:Sapphire, a lifetime in the microsecond range corresponds to a minimum in frequency in the kHz range. To detect
this extremum, the range of frequencies scanned must be between 50 - 100 kHz. At such high frequencies, we observed the photothermal signal to be too low to obtain reproducible data sets. As shown in figure 5.3, we were unable to detect an extremum in the PTR emission signal up to 100 kHz, which is the maximum frequency that the signal processing instrumentation (in this case, a lock-in amplifier) can operate at. The other significant problem

![Graph](image1.png)

**Figure 5.3:** Variation of Ti: Sapphire IR radiation emission with modulation frequency of the pump beam.

with this technique is the difficulty in interpreting the relative contributions of the bulk- and surface- originating components to the photothermal signal.

### 5.4.2 Rate Window PTR Detection

The rate-window PTR technique involves pulsed heating of the sample and subsequent detection of the infra-red emission using a lock-in amplifier. A *rate-window scan* can be performed
as follows: The duty cycle can be continuously varied either by varying the pulse duration for a given repetition period or by varying the period continuously for a given pulse duration. For each duty cycle, the lock-in amplifier detects the fundamental Fourier component of the transient signal generated due to the repetitive pulse [93]. Figure 5.4 describes how a rate window PTR scan is performed.

![Diagram of Excitation Pulse and Sample Temperature Response](image)

Figure 5.4: The rate window technique: the pulse duration is varied and the fundamental fourier coefficient of the resulting transient signal is measured at each pulse duration.

Munidasa and Mandelis [94] have shown experimentally that at high frequencies, the lock-in amplifier rate-window technique gives better SNR's than frequency-scanned detection. In applying this technique to laser materials, we experienced the following problem: since the pulse duration is scanned with the period held constant, the power input to the sample varies at each location of the scan. To obtain an appreciable radiometric signal level from laser materials, relatively high input power (3-5 W) is required. As a result, a change in the duty cycle of the input beam causes the thermal equilibrium of the sample to be disturbed significantly. We observed that at such high input power levels, re-establishing thermal equilibrium took about an hour. The long time required to allow the sample to thermalize
renders this approach impractical, since thermal equilibrium will be disturbed several times during a rate-window scan. The only way to get around this problem is to reduce the input laser power to the sample, which in turn diminishes the SNR.

As a result of conducting preliminary experiments using the frequency-scan method and the rate-window method, we concluded that obtaining high-resolution, reproducible data from laser materials requires:

1. modulating the input laser beam at a lower frequency.

2. Keeping the duty cycle of the modulated input beam constant (though not necessarily at 50% duty cycle).

5.4.3 Boxcar Integrator Time-Domain PTR Detection

To satisfy the two requirements mentioned above, we decided to use time-domain detection using a boxcar integrator. This instrument allows us to use both a low frequency to ensure a high SNR and a constant duty cycle to ensure thermalization. The key advantage of this method is that even at low modulation frequencies (corresponding to repetition periods on the order of milliseconds) we can use the boxcar to monitor the transient signal profile in the microsecond range.

A boxcar integrator is an instrument capable of processing analog signals with the use of a gated integrator. Consider a transient signal as shown in figure 5.5. The boxcar integrator can measure the average signal at any location of the transient by “opening a gate of a specified width” [95]. By this we mean that the integrator will monitor the signal for a specified time period that is usually much smaller than the repetition period of the signal. The trigger that opens the gate is set up such that the same location of the transient signal is sampled at every measurement cycle. During the time that the gate is opened, the signal
is monitored and used to charge a capacitor. A resistor placed across the capacitor allows the capacitor to discharge slightly. After monitoring several cycles, the capacitor potential reaches a steady state value that represents the value of the signal (at the particular location that the gate scans) averaged over several cycles.

How can boxcar integration or averaging be used to map out an entire transient signal? The time-difference between the beginning of the signal transient and the triggering of the gate is known as the gate delay, as shown in figure 5.5. A transient can be recorded by monitoring a given location of the transient over several cycles and then changing the gate delay, such that a different (adjacent) location of the transient signal is measured and averaged over several cycles. By changing the gate delay to monitor the averaged signal at several locations as shown in figure 5.6, the transient signal can be reconstructed.
Figure 5.6: Reconstructing a transient signal using a boxcar integrator.

5.5 The Need for a Model Conforming to Boxcar Time-Domain Detection

Upon selecting time-domain detection as the most suitable method for characterizing laser materials via IR radiation emission, our next task was to incorporate a mathematical treatment that would allow us to quantify our experimental data and relate it to physical parameters of the sample. As we have learned from photopyroelectric spectroscopy of Ti: Sapphire laser materials, there are several optical and thermal phenomena occurring in laser materials.
that any accurate model must account for:

1. Non-radiative energy conversion processes occurring simultaneously at both the crystal surface as well as in the bulk of the crystal.

2. The material having a finite excited-state lifetime.

3. The material having finite bulk and surface optical absorption.

4. The spot-size and gaussian nature of the pump laser beam.

In view of these requirements, we reviewed several existing theoretical models dealing with thermo-optical phenomena in materials. Many of these models account for only one of the four phenomena mentioned above. Foster and Osterink [96] and Koechner [97] first approached the problem of determining the temperature distribution in optically pumped laser materials by invoking the assumption of one-dimensional heat transfer due to an infinitely long rod. Buoncristiani et al. [98] extended this model to account for two-dimensional heat transfer, but also did not consider in detail the optical absorption processes that ultimately cause the heat generation in the laser rod. Bechtel [99] developed the most detailed model to date of the optically-induced temperature distribution, by considering separately the bulk- or surface-induced heat generation in optical materials. However, his model cannot be used for a comparative study of simultaneous surface and bulk non-radiative sources. Furthermore, his use of an adiabatic boundary condition at the laser-irradiated surface appears to be too restrictive based on our experimental results using Ti: Sapphire laser materials. Finally, his model ignores the generation of delayed heat due to the metastable state de-excitation in laser materials. To address the four concerns mentioned above as well as the deficiencies in the aforementioned models, Mandelis developed a theoretical model of non-radiative de-excitation and thermal-conduction transient evolution in solid-state laser materials sub-
jected to pulsed optical pumping. This model is consistent with the time-domain detection approach that we used experimentally.

5.6 Theoretical Model

This section presents a summary of Mandelis’ theoretical treatment of the non-radiative energy generation in optical materials due to intense optical pumping [79]. In the first part of this section, the excited-state decay of an intensely optically pumped unsaturated laser material is considered. The transient evolution of the excited-state population (which is proportional to the luminescence signal) is derived. Next, the thermal energy generation rate density is derived using the excited-state population as the source of non-radiative relaxations. Finally, the transient heat conduction problem in laser rods (accounting for the various phenomena listed above) is addressed.

5.6.1 De-excitation Dynamics of Intensely Pumped 4-level Laser System

Mandelis’ analysis of the heat conduction problem in laser materials requires the knowledge of the rate of thermal energy generation in the bulk of the material. Since one of the sources of non-radiative de-excitation is the metastable level, an expression for the transient population of this level is derived below, followed by a derivation of the thermal energy density rate.

To study the decay dynamics of a four-level laser medium, one needs to consider an energy level diagram as shown in figure 5.7. In such a situation, the material is pumped by an optical source to level 3 with a pumping rate $W_p(t)$ and the following is assumed about the pumping and decay processes:

1. Since intense pumping is usually required to overcome low signal levels in PTR, it
2. The instantaneous decay from the pump bands (represented by level $|3>\rangle$) is assumed to be entirely non-radiative. This assumption is valid since the atoms are pumped to excited vibrational levels of the excited state electronic manifold and will decay instantaneously (with respect to the lifetime of the upper laser level $|2>\rangle$) to the upper laser level which corresponds to the ground vibrational state of the excited state electronic manifold (as represented by level $|2>\rangle$).

3. The decay from the upper laser level $|2>\rangle$ is assumed to occur due to either radiative
or non-radiative relaxations with quantum efficiencies $\eta_R$ and $\eta_{NR}$, respectively. The radiative transitions from this level can occur to a number of different excited vibrational sublevels of the ground state manifold. We assume that these sublevels can be approximated by an "average" such that a single level representing the terminal level of the laser transition can be used. We also assume that radiative transitions from the upper laser level to the ground vibrational level of the ground electronic manifold can be neglected, due to the offset between the two electronic manifolds along the configurational coordinate. Therefore, it is assumed that all atoms residing in level $|2>$ will eventually de-excite to level $|1>$, implying that the lifetime of the laser transition $\tau_{21}$ is equal to the lifetime of the upper laser level $\tau_2$. A luminescence decay measurement which yields a value for the lifetime of the upper laser level $\tau_2$ can in this case be represented by the lifetime $\tau_{21}$.

**Rate Equations and Derivation of Luminescence Transient**

For the conditions mentioned above, the rate equation for level $|3>$ is

$$\frac{dN_3(t)}{dt} = W_p(t)N_0(t) - \frac{1}{\tau_{32}}N_3(t) \quad (5.11)$$

If we assume that the upper state is not occupied at the onset of laser pumping (ie: $N_3(0) = 0$) and that $\tau_{32}$ is much smaller than the earliest observation time, a Laplace inversion yields

$$N_3(t) \simeq \tau_{32}W_p(t)N_0(t) \quad (5.12)$$

Using Equation 5.12, the rate equation for level $|2>$ can be written as

$$\frac{dN_2(t)}{dt} = \frac{1}{\tau_{32}}N_3(t) - \frac{1}{\tau_{21}}N_2(t) \simeq W_p(t)N_0(t) - \frac{1}{\tau_{21}}N_2(t) \quad (5.13)$$
The rate equation for level $|1\rangle$ is

$$\frac{dN_1(t)}{dt} = \frac{1}{\tau_{21}} N_2(t) - \frac{1}{\tau_{10}} N_1(t)$$  \hspace{1cm} (5.14)$$

Assuming that level $|1\rangle$ is not occupied at the onset of pumping (ie: $N_1(0) = 0$) and Laplace transforming equation 5.14, we obtain

$$\hat{n}_1(s) = \hat{n}_2(s) \frac{\tau_{21}}{\tau_{10}(s + \tau_{10}^{-1})}$$  \hspace{1cm} (5.15)$$

where $\hat{n}$ denotes the Laplace transform of $N$ and $s$ is the variable in the Laplace domain. Assuming that $\tau_{10}$ is much smaller than both $\tau_{21}$ and the earliest observation time, we can simplify equation 5.15 to

$$\hat{n}_1(s) \approx \left(\frac{\tau_{10}}{\tau_{21}}\right) \hat{n}_2(s) \approx 0$$  \hspace{1cm} (5.16)$$

Assuming that the total population $N_T$ is constant in time, where

$$N_T = N_0(t) + N_1(t) + N_2(t) + N_3(t)$$  \hspace{1cm} (5.17)$$

from which a solution for $N_0(t)$ can be obtained. Substituting $N_0(t)$ in Equation 5.13 and accounting for low occupation of levels $|1\rangle$ and $|3\rangle$ at all times, we obtain

$$\frac{dN_2(t)}{dt} + \left[W_p(t) + \tau_{21}^{-1}\right] N_2(t) \approx W_p(t) N_T$$  \hspace{1cm} (5.18)$$
This equation can be solved once the functional form of $W_\rho$ is known. For a rectangular optical pulse of duration $\tau_p$

$$W_\rho(t) = \begin{cases} W_{\rho_0} & ; \text{if } t < \tau_p \\ 0 & ; \text{if } t > \tau_p, \end{cases} \quad (5.19)$$

Equation 5.18 has the solution

$$N_2(t) = W_{\rho_0} N_T \tau \begin{cases} 1 - e^{-t/\tau} & ; \text{if } t \leq \tau_p \\ (e^{\tau_p/\tau_{21}} - e^{-W_{\rho_0}\tau_p})e^{-t/\tau_{21}} & ; \text{if } t \geq \tau_p \end{cases} \quad (5.20)$$

where

$$\frac{1}{\tau} \equiv \frac{1}{\tau_{21}} + W_{\rho_0} \quad (5.21)$$

$N_2(t)$ describes the temporal behaviour of the luminescence signal from an optically pumped laser medium, since the rate of radiative emission is proportional to the population of the metastable level $|2>$ and to the radiative quantum efficiency.

**Derivation of Thermal Energy Density Rate**

Based on the energy level diagram shown in figure 5.7, the rate of generation of thermal energy per unit volume in an optically excited four-level laser medium is given by

$$\frac{dQ(t)}{dt} = \frac{E_{32}}{\tau_{32}} N_3(t) + \eta_{NR}\frac{E_{21}}{\tau_{21}} N_2(t) + \left(\frac{E_{10}}{\tau_{10}}\right) N_1(t) \quad [W/m^3] \quad (5.22)$$

Accounting for low occupation of levels $|1>$ and $|3>$, equation 5.22 becomes

$$N_T \simeq N_\sigma(t) + N_2(t) \quad (5.23)$$

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Equation 5.22 can be written using equation 5.12 as

\[
\frac{dQ(t)}{dt} = N_T E_{32} W_p(t) + \left[ \frac{E_{20}^{NR}}{\tau_{21}} - E_{32} W_p(t) \right] N_2(t)
\]  (5.24)

where

\[ E_{ij} \equiv E_i - E_j \]  (5.25)

and

\[ E_{20}^{NR} \equiv \eta_{NR} E_{21} + E_{10} \]  (5.26)

where \( E_{20}^{NR} \) accounts for the non-radiative portion of the total energy that is released from the metastable level \( |2> \). In equation 5.24, the pumping rate \( W_p(t) \) can also be written in terms of the incident optical intensity \( I_o(t) \) and the absorption coefficient \( \beta_{30}(\lambda) \) of the medium:

\[ W_p(t) = \frac{\sigma_{30}(\lambda)}{E_{30}} I_o(t) \]  (5.27)

We must now consider the behaviour of the absorption cross-section \( \sigma_{30} \) and the corresponding optical absorption coefficient \( \beta_{30} \) under the condition of intense optical pumping of the material. Under intense pumping, the populations of levels \( |0> \) and \( |2> \) vary significantly with time, resulting in a time-dependent optical absorption coefficient. By defining the population difference between \( |0> \) and \( |2> \) as

\[ \Delta N(t) \equiv N_0(t) - N_2(t) \]  (5.28)

Using Equation 5.23 to obtain a rate equation for \( N_0(t) \) and Equation 5.13 as the rate equation for population \( N_2(t) \), we then obtain a rate equation for the population difference
whose solution for a rectangular pulse $W_p(t)$ is

$$\Delta N(t) = N_T \begin{cases} 
\tau [(\tau_{21}^{-1} - W_p) + 2W_p \exp(-t/\tau)] & \text{if } t \leq \tau_p \\
1 - 2W_p \tau (1 - e^{-\tau_p/\tau}) e^{-t/\tau_{21}} & \text{if } t \geq \tau_p
\end{cases}$$

(5.30)

We may now relate this time-dependent expression for the population difference $\Delta N$ to the time-dependent absorption coefficient under saturation conditions by invoking the relationship between $\beta_{30}, \sigma_{30}$ and $\Delta N$:

$$\beta_{30}(t; \lambda) = \sigma_{30}(\lambda) \Delta N(t) \equiv \beta_m[\Delta N(t)/N_T]$$

(5.31)

and finally obtaining

$$\beta_{30}(t; \lambda) = \beta_m(\lambda) \begin{cases} 
\tau [(\tau_{21}^{-1} - W_p) + 2W_p \exp(-t/\tau)] & \text{if } t \leq \tau_p \\
1 - 2W_p \tau (1 - e^{-\tau_p/\tau}) e^{-t/\tau_{21}} & \text{if } t \geq \tau_p
\end{cases}$$

(5.32)

where $\beta_m(\lambda)$ is the maximum possible value of $\beta_{30}$ under completely unsaturated conditions.

For the rectangular optical pulse profile of equation 5.19, $N_2(t)$ is given by equation 5.20. In this case, the heating rate (equation 5.19) becomes

$$\frac{dQ(t)}{dt} = \frac{W_p N_T}{1 + W_p \tau_{21}} \begin{cases} 
E_{30}^{NR}(1 + be^{-t/\tau}) & \text{if } t < \tau_p \\
E_{20}^{NR}(e^{\tau_p/\tau_{21}} - e^{-W_p \tau_p})e^{-t/\tau_{21}} & \text{if } t > \tau_p
\end{cases}$$

(5.33)

where we define

$$E_{30}^{NR} \equiv E_{32} + \eta_{NR} E_{21} + E_{10}$$

(5.34)
in analogy with equation 5.26 and also

\[ b \equiv (\tau_{21} W_{po} E_{32} - E_{20}^{NR}) / E_{30}^{NR} \]  

(5.35)

In the above equation, \( b \) represents the total thermal energy \( E_{30}^{NR} \) released by the population in level |2> via metastable de-excitation into the ground state |0>.

5.6.2 Transient Heat Conduction in Laser Rods

In analyzing the transient heat conduction problem in laser rods, Mandelis used a Green’s function approach to obtain time-dependent temperature distributions in optically excited laser materials. This section deals with the derivation of a theoretical expression for the transient temperature at the surface of a laser rod in response to intense, modulated optical excitation. This expression accounts for the relative contributions of the non-radiative processes occurring in the surface and bulk of the laser rod to the total surface temperature.

Assume a semi-infinite cylindrical laser medium in both the axial and radial directions, corresponding to a thick and long laser rod. A pump laser beam is incident on the polished surface of the medium, with intensity profile

\[ I(r) = \frac{2P_o}{\pi R^2} e^{-\frac{r^2}{R^2}} \]  

(5.36)

where \( P_o \) is the incident optical power [W], \( r \) is the radial coordinate and \( R \) is the beam waist as shown in figure 5.8.

The spatial and temporal evolution of the temperature field in the laser medium can be described by the cylindrical coordinate Green’s function for this geometry:

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial G}{\partial r} \right) + \frac{\partial^2 G}{\partial z^2} - \frac{1}{\alpha} \frac{\partial G}{\partial t} = 134 \]
Figure 5.8: Geometry of optically pumped laser rod of radial dimension $D \gg R$ ($R$: pump beam waist). The polished surface absorptance is $\Gamma_s$. The rod length is much longer than all characteristic photothermal length parameters in the (mathematically semi-infinite) medium.

$$\frac{1}{2\pi kr_o} \delta(r - r_o) \delta(z - z_o) \delta(t - t_o); \quad 0 \leq r < \infty; \quad z \geq 0$$

where $\alpha$ is the thermal diffusivity, $k$ is the thermal conductivity and $(r, z, t), (r_o, z_o, t_o)$ are the observation and source coordinates respectively. The translated temperature field in the laser medium

$$\theta(r, z, t) \equiv T(r, z, t) - T_{\infty} \quad (T_{\infty}: \text{ambient temperature}) \quad (5.37)$$
satisfies the equation

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \theta}{\partial r} \right) + \frac{\partial^2 \theta}{\partial z^2} - \frac{1}{\alpha} \frac{\partial \theta}{\partial t} = -\frac{1}{k} \rho(r, z, t) \tag{5.38}
\]

subject to the initial and boundary conditions

\[
\theta(r, z, 0) = 0 \tag{5.39}
\]

\[
\theta(\infty, z, t) = 0 \tag{5.40}
\]

\[
\theta(r, \infty, 0) = 0 \tag{5.41}
\]

\[- k \frac{\partial}{\partial z} \theta(r, z, t) \big|_{z=0} = Q_o(r, t) - h\theta(r, 0, t) \tag{5.42}\]

In the above equations, \(Q_o(r, t)\) is the incident thermal flux on the surface of the laser medium and \(h\) is the heat transfer coefficient. Crowther and Padet [100] have measured the local convection coefficient in a photothermal radiometric experiment. Assuming both radiation and convection losses at the interface, they assume that \(h\) is the sum of a radiative (\(h_r\)) and a convective (\(h_c\)) coefficient. By linearizing the radiative heat transfer coefficient, they obtain numerical values of the heat transfer coefficient. The values they obtained indicate that convection losses will not occur in the microsecond and millisecond time-scales over which we will be conducting our experiments.

In view of the above boundary conditions, the Green's function must satisfy the homogeneous initial and boundary conditions including the homogeneous thermal flux boundary
condition in the source coordinate system:

$$-k \frac{\partial}{\partial z_0} G(r, z, t | r_o, z_0, t_o) |_{z_0=0} = hG(r, z, t | r_o, 0, t_o)$$  \hspace{1cm} (5.43)$$

The Green's function $G$ is separated into the product of a radial and axial function

$$G(r, z, t | r_o, z_0, t_o) = G_R(r, t | r_o, t_o)G_A(z, t | z_0, t_o)$$  \hspace{1cm} (5.44)$$

For the radial function which satisfies $G_R(r, t|r_o, 0) = G_R(r, t|\infty, t_o) = 0$, the corresponding Green's function is given in the literature [101] as

$$G_R(r, t | r_o, t_o) = \frac{1}{4\pi \alpha(t-t_o)} \exp\left[-\frac{(r^2 + r_o^2)}{4\pi \alpha(t-t_o)}\right] I_0\left[\frac{rr_o}{2\alpha(t-t_o)}\right]$$  \hspace{1cm} (5.45)$$

where $I_0(x)$ is the modified Bessel function of the first kind of order zero.

For the axial Green's function which satisfies the Green's function boundary condition $G_A(z, t|\infty, t_o) = G_A(z, t|z_0, 0) = 0$ and $k \frac{\partial}{\partial z_0} G_A(z, t|z_0, t_o)|_{z_0=0} = hG_A(z, t|0, t_o)$, the corresponding Green's function is given in the literature [101] as

$$G_A(z, t | z_0, t_o) = \frac{1}{\sqrt{4\pi \alpha(t-t_o)}}\{\exp\left[-\frac{(z-z_o)^2}{4\pi(t-t_o)}\right] + \exp\left[-\frac{(z+z_o)^2}{4\pi(t-t_o)}\right]\}$$

$$-\frac{1}{\sqrt{\alpha \tau_h}} \exp\left[-\frac{(z+z_o)^2}{4\pi \alpha(t-t_o)}\right] Y\left[\frac{z+z_o}{\sqrt{4\pi \alpha(t-t_o)}} + \frac{\sqrt{t-t_o}}{\tau_h}\right]$$

where

$$Y(z) \equiv e^{z^2} erf c(z)$$  \hspace{1cm} (5.46)$$

and $\tau_h$ is the characteristic thermal transfer time from the surface of the laser medium into
the surrounding air:

\[ \tau_h \equiv \frac{k^2}{\hbar^2 \alpha} \quad (5.47) \]

The translated temperature field in the medium is given in terms of integrals of Green’s function [102, 101]:

\[
\begin{align*}
\theta(r, z) &= \frac{a}{k} \int_0^t dt_0 \int \int V_0 G(r, z, t | r_o, z_o, t_o) \rho(r_o, z_o, t_o) dV_o \\
&\quad + \int_0^t dt_0 \int S_0 G(r, z, t | r_o, 0, t_o) Q_o(r_o, t_o) dS_o \\
&\quad + \int_0^t dt_0 \int S_0 G(r, z, t | r_o, 0, t_o) Q_o(r_o, t_o) dS_o
\end{align*}
\]

where \( V_0 \) is the source volume and \( S_0 \) is the surface defined by the plane \( z_0 = 0 \). \( \rho \) and \( Q_o \) are the volume and surface sources, which affect the temperature distribution in the medium.

Performing the integrations in cylindrical coordinates yields

\[
\frac{k}{2 \pi a} \theta(r, z, t) = \int_0^t dt_0 \int G_R(r, t, | r_o, t_o) r_o dr_o \int_0^\infty G_A(z, t | z_o, t_o) \rho(r_o, z_o, t_o) dz_o \\
+ \int_0^t dt_0 G_A(z, t | 0, t_o) \int G_R(r, t | r_o, t_o) Q_o(r_o, t_o) r_o dr_o
\]

The above equation contains the thermal energy generation sources \( \rho \) in the bulk and \( Q_o \) at the surface. To determine the functional form of \( \rho \), we must account for i) the net optical power density which is transmitted past the surface layer of absorptance \( \Gamma_\lambda(\lambda) \); ii) the optical absorption profile in the laser medium, including saturation phenomena and assumed to be homogeneous and obeying the Beer-Lambert law; iii) the spatial distribution of the incident Gaussian beam in radial coordinates, given by equation 5.36; and iv) the heat release density rate given by equation 5.33. Taking these four factors into consideration, the bulk thermal energy generation source \( \rho \) can be written in the source coordinates as

\[
\rho(r_o, z_o, t_o) = (1 - \Gamma_s) e^{-\frac{2z_o^2}{R^2}} e^{-\beta z_o} F(t_o)
\]

(5.50)
where

\[
F(t_o) \equiv \frac{2P_o \beta_{30}}{\pi R^2 E_{30}(1 + \bar{W}_{po} \tau_{21})} \begin{cases} 
E_{30}^{NR}(1 + be^{-\frac{\tau_p}{b}}) & \text{if } t < \tau_p \\
E_{20}^{NR}(e^{-\frac{\tau_p}{b}} - e^{-\bar{W}_{po} \tau_p})e^{-\frac{\tau_p}{b}} & \text{if } t > \tau_p,
\end{cases} 
\]  

(5.51)

The surface thermal source \(Q_0(r_0, t_0)\) is due to optical absorption within the surface layer of absorptance \(\Gamma_s\), and the subsequent 100 \% optical-to-thermal energy conversion efficiency in this layer. \(Q_0(r_0, t_0)\) can be described in the source coordinates by

\[
Q_0(r_0, t_0) = \Gamma_s(\lambda)e^{-\frac{2\tau_p^2}{R^2}} q_0(t_o)
\]

(5.52)

where

\[
q_0(t_o) \equiv \frac{2P_o}{\pi R^2} \begin{cases} 
1 & \text{if } t < \tau_p \\
0 & \text{if } t > \tau_p,
\end{cases}
\]

(5.53)

By substituting the above four equations into Equation 5.33, we obtain

\[
\frac{k}{2\pi c} \theta(r, 0, t) = 
(1 - \Gamma_s) \int_0^t F(t_o) K(r; t; t_o) H(t; t_o) dt_o \quad \text{(Volume contribution)}
\]

\[
+ \Gamma_s \int_0^t q_o(t_o) K(r; t; t_o) G_A(0, t \mid 0, t_o) dt_o \quad \text{(Surface contribution)}
\]

(5.54)

where the following integrals have been defined

\[
K(r; t; t_o) \equiv \int_0^\infty G_R(r, t \mid r_o, t_o)e^{-\frac{2\tau_p^2}{R^2} r_o} dr_o
\]

(5.55)

and

\[
H(t; t_o) \equiv \int_0^\infty G_A(0, t \mid z_o, t_o)e^{-\beta_{30} z_o} dz_o
\]

(5.56)

The details of the calculation of \(K\) and \(H\) in terms of tabulated functions is given in [79].
Once these parameters are determined, insertion into equation 5.54 gives the general expression for the laser-induced temperature change in the material:

$$\theta(r, 0, t) =$$

$$\frac{\alpha R^2}{k} \left\{ \frac{\gamma_s}{\sqrt{\alpha}} \left[ \frac{1}{\sqrt{\pi}} \int_0^{t_0} q_0(t_0) \exp \left[ -\frac{2t^2}{\beta(0-t_0)^2 + R^2} \right] dt_0 \right] - \frac{1}{\sqrt{\tau_h}} \int_0^t \frac{\gamma_s Y \left[ \sqrt{\frac{t-t_0}{\tau_h}} \right]}{8\alpha(0-t_0) + R^2} \exp \left[ -\frac{2t^2}{8\alpha(0-t_0) + R^2} \right] dt_0 \right\}$$

(5.57)

$$+ (1 - \gamma_s) \left\{ \int_0^t \frac{F(t_o) Y \left[ \sqrt{\frac{t-t_0}{\tau_h}} \right]}{1 - \sqrt{\frac{t}{\tau_h}}} \beta(0-t_0) + R^2 \right] \exp \left[ -\frac{2t^2}{8\alpha(0-t_0) + R^2} \right] dt_0$$

$$- \sqrt{\tau_h} \int_0^t \frac{F(t_o) Y \left[ \sqrt{\frac{t-t_0}{\tau_h}} \right]}{\tau_h(t_0) - \sqrt{\tau_h}} \beta(0-t_0) + R^2 \right] \exp \left[ -\frac{2t^2}{8\alpha(0-t_0) + R^2} \right] dt_0 \right\}$$

Since the detector aperture in the radiometry experiment is very narrow, we may assume that the measured signal is proportional to the temperature changes occurring at the center of the optically excited surface, $r = 0$. We now separate the laser-induced temperature change at the surface $\theta$ in equation 5.57 into two components: bulk-heating-induced temperature change $\theta_b$ and surface-heating-induced temperature change $\theta_s$. We may then represent the total temperature change $\theta$ as

$$\theta(0, 0, t) \equiv \theta_{s(\text{surface})}(0, 0, t) + \theta_{b(\text{bulk})}(0, 0, t)$$

(5.58)

where

$$\theta_s(0, 0, t) =$$

$$\frac{R^2}{k \sqrt{\pi}} \Gamma_s \left\{ \int_0^t q_0(t_0) \left[ \frac{dt_0}{8\alpha(0-t_0) + R^2 \sqrt{t-t_0}} \right] - \sqrt{\frac{\pi}{\tau_h}} \int_0^t q_0(t_0) \left[ \frac{Y(\sqrt{t-t_0})}{8\alpha(0-t_0) + R^2} \right] dt_0 \right\}$$

(5.59)
Solving equation 5.59 and 5.60 requires the knowledge of \( q_o(t_o) \) and \( F(t_o) \) which are given by equation 5.51 and 5.53 respectively.

**Physical Description of Equation 5.59 and 5.60**

Equation 5.59 represents the time-evolution of the surface temperature change due to non-radiative processes occurring at the surface only. The two terms on the right hand side of this equation represent a balance between the time evolution of the energy generated at the surface and the time evolution of the energy convected away from the surface and into the air. Equation 5.60 represents the time-evolution of the surface temperature change due to non-radiative processes occurring at the bulk only. The two terms on the right hand side of this equation represent a balance between the time evolution of the energy generated inside the bulk that is travelling towards the surface and the time evolution of the energy convected away from the surface and into the air.

How is this theoretical calculation of the laser-induced temperature change relevant to the photothermal radiometry experiment we discussed in section 5.2? As mentioned in that section and described by equation 5.10, the PTR experiment detects a signal that is proportional to the temperature change in the material (assuming that the material is opaque to its own IR emission). We can therefore relate the experimental data to this theoretical expression and obtain quantitative information about the nonradiative processes occurring in the bulk and surface of the laser crystal.
Table 5.1: Assumed Values in Numerical Modelling

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>thermal diffusivity, ( \alpha )</td>
<td>0.106 \text{ cm}^2/\text{s}</td>
<td>metastable lifetime, ( \tau_{21} )</td>
<td>3.5 \text{ \mu s}</td>
</tr>
<tr>
<td>thermal conductivity, ( k )</td>
<td>33 \text{ W/m.K}</td>
<td>pulse duration, ( \tau_p )</td>
<td>3.0 \text{ \mu s}</td>
</tr>
<tr>
<td>spot size, ( R )</td>
<td>100 \text{ \mu m}</td>
<td>thermal transfer time, ( \tau_h )</td>
<td>1 \text{ ms}</td>
</tr>
<tr>
<td>Surface Absorptance, ( \Gamma_s )</td>
<td>0.02</td>
<td>thermal transfer time, ( \tau_\beta )</td>
<td>9.43 \text{ s}</td>
</tr>
<tr>
<td>absorption coefficient, ( \beta_{30} )</td>
<td>1.0 \text{ cm}^{-1}</td>
<td>pumping rate, ( W_p )</td>
<td>3 \times 10^4 \text{ s}^{-1}</td>
</tr>
<tr>
<td>conversion efficiency, ( \eta_{NR} )</td>
<td>0.10</td>
<td>pump power, ( P_o )</td>
<td>3 \text{ W}</td>
</tr>
</tbody>
</table>

5.7 Numerical Simulations of Transient Surface Temperature

Following Mandelis' development of the theoretical model, we performed numerical simulations of the surface temperature and its components due to heat generation in the bulk and surface of the crystal (as represented by equation 5.59 and 5.60, using the Ti\(^{3+}\)Al\(_2\)O\(_3\) laser material as an example). The simulations serve three purposes: first, we are able to determine whether the model makes physical sense; next, we can obtain key information about the optimum conditions under which the experiments should be conducted; and finally, we can fit the theoretical curves to the experimental results and obtain fitting parameters that correspond to some physical property of the material.

The numerical simulations consisted of varying parameters (such as the characteristic thermal transfer times \( \tau_h \) and \( \tau_\beta \), the metastable lifetime \( \tau_{21} \), the spot size \( R \), and the surface absorptance \( \Gamma_s \)) and studying the corresponding transient temperature profiles for \( t \leq 50 \mu s \). Except for the parameter being varied in order to study its effect on the transient profiles, the remaining parameters were set to their default values for the Ti: Sapphire system (unless stated on the figures below), as shown in Table 5.1.
Figure 5.9: Theoretical prediction of the thermal energy generation rate density $dQ/dt$ using the Ti: Sapphire energy level diagram as an example. $\tau_{21} = 3.5\mu s$ $\tau_p = 50\mu s$.

5.7.1 Effect of Bulk Heating Rate and Luminescence on Bulk-Heating-Induced Temperature Change

To understand the dependence of the bulk-heating-induced temperature change on the dynamic parameters of the metastable state $| 2 >$, we must study the profile of the bulk thermal source $dQ/dt$ (given by equation 5.33) as shown in figure 5.9. The asymmetry in the rise- and decay-times is due to the dependence of $\tau$ on the pumping rate $W_p$ for high pumping rates. High pump rates of the excited state result in earlier saturation of the thermal flux per unit depth released in the crystal bulk, due to the high pumping out of the ground state. Once saturation is reached and the optical pulse is switched off, non-radiative decay controlled by the lifetime $\tau_{21}$ takes place. The time constants governing the evolution of $dQ/dt$ are the
Figure 5.10: Theoretical prediction of the transient luminescence signal (via the population of the metastable state \( N_2(t) \)) for various strong pumping rates \( W_{p_0} \) using the Ti: Sapphire energy level diagram as an example. \( \tau_{21} = 3.5 \mu s \) \( \tau_p = 50 \mu s \).

same as those governing the evolution of the metastable-state population \( N_2(t) \) (that is also proportional to the luminescence signal) as shown in figure 5.10. Therefore, it is more convenient to monitor the luminescence transient experimentally and deduce from the rise- and decay-times the constants \( \tau_{21} \) and \( \tau \). Thus, the superior SNR of the luminescence transient (which is several orders of magnitude stronger than the IR radiation emission signal) can be used as input data when analyzing the IR radiation emission profiles.
5.7.2 Effect of Convective Boundary Condition on Bulk-Heating-Induced Temperature Change

The nature of the boundary condition describing heat transfer at a solid-gas interface can greatly affect the temperature profile at the surface of the material. In this case, the convective boundary condition encompasses the two extreme limits of isothermal \( (h \to \infty) \) and adiabatic \( (h = 0) \) boundaries. By understanding the physical meaning of the parameter \( \tau_h \), we can see the importance of the effect of this parameter on the transient temperature of the laser crystal surface. \( \tau_h \) is the characteristic thermal transfer time for heat to be transferred from a solid of thermal conductivity \( k \) (in this case, the laser material) to a gas (in this case, the surrounding air) with a convection coefficient \( h \).

For conditions of three-dimensional heat flow within the sample (which occur when the pump-beam is highly focused), figure 5.11 shows the effect of the heat transfer rate \( h \) on the bulk-heating-induced temperature of the crystal, \( \theta_b \). As the convective heat transfer rate decreases, the thermal transfer time increases, implying that it takes longer for heat to be convected away from the surface of the laser material and into the surrounding air. As a result, the surface temperature decays slower with time as the thermal transfer time increases. At high values of \( \tau_h \), it is seen that the decay is not dependent on \( \tau_h \) because \( \tau_h \) is much greater than the detection time range.

Under one-dimensional heat flow conditions within the sample (which can be achieved by using an unfocused pump beam), figure 5.12 indicates that there is no decay of the bulk-heating-induced temperature profile \( \theta_b \) when \( \tau_h \geq 10^{-3} \text{s} \), due to fully adiabatic conditions and the fact that it is not possible for as much heat to be lost in the lateral direction due to broad-beam heating.
Figure 5.11: Theoretical prediction of the bulk-heating-induced surface temperature $\theta_b$ as a function of the thermal transfer time $\tau_h$ (in response to a focused optical pulse of duration 3 $\mu$s).

5.7.3 Effect of Beam Size on Bulk-Heating-Induced Temperature Change

Figure 5.13 shows the gradual transition from a one-dimensional to three-dimensional heat diffusion configuration, showing the very different behaviour of the transient profiles for these two cases. For pump beam sizes $R \geq 10^3 \mu m$ one-dimensional heat diffusion behaviour is observed. For spot-sizes less than 100 $\mu m$, the temperature profiles peak earlier, indicating that tight focusing can interfere with the measurement of the relaxation time of these temperature profiles. It is therefore necessary to accurately determine the spot-size $R$ in order to precisely measure the relaxation time of these temperature profiles, given that $R$ is less
Figure 5.12: Theoretical prediction of the bulk-heating-induced surface temperature $\theta_s$ as a function of the thermal transfer time $\tau_h$ (in response to an unfocused optical pulse of duration 3 $\mu$s).

than 100 $\mu$m.

5.7.4 Effect of Optical Absorption on Bulk-Heating-Induced Temperature Change

Another important parameter that can affect the temperature profile is the characteristic thermal transfer time $\tau_\beta$. $\tau_\beta$ is the characteristic thermal transfer time for heat to travel from a distance $\frac{1}{\beta \rho_0}$ within the material to the surface of the material. Figure 5.14 shows that an increasing value of $\tau_\beta$ will cause the heat from within the material to take longer to travel to the surface, resulting in the peak surface temperature being shifted to later and later times.
Figure 5.13: Theoretical prediction of the bulk-heating-induced surface temperature $\theta_b$ as a function of the pump beam spot size $R$ (in response to an optical pulse of duration $3 \, \mu s$).

For Ti: Sapphire, the value of $\tau_3$ is $10 \, s$, based on spectroscopic measurements of $\beta_{30}$ made in Chapter 4 and thermal measurements of the diffusivity $\alpha$ [103]. Figure 5.15 shows the effect that optical saturation can have on the transient temperature profile. When the material is optically saturated due to intense pumping, the optical absorption coefficient becomes time-dependant and decreases in magnitude. As a result, the transient temperature (given by equation 5.60 decreases in comparison with the fully unsaturated transient.

5.7.5 Effect of Metastable Lifetime on Bulk-Heating-Induced Temperature Change

Figure 5.16 shows how the metastable lifetime $\tau_{21}$ can affect the bulk-heating-induced temperature profile. For a given material, $\tau_{21}$ is a constant at a given temperature. However,
as the temperature increases, $\tau_{21}$ will decrease. The figure shows that an increase in $\tau_{21}$ has the effect of shifting the peak of the transient profile to progressively later times. Even after the pulse is cut off, the temperature continues to increase. This increase in temperature is attributed to the delayed heat generated due to the metastable lifetime of the material.

5.7.6 Effect of Surface Absorptance on Bulk- and Surface-Heating-Induced Temperature Changes

What is the role that the surface absorptance parameter $\Gamma_s$ plays in determining the evolution of the transient temperature? As seen by equation 5.59, the surface-heating-induced
Figure 5.15: Theoretical prediction of the bulk-heating-induced surface temperature $\theta_b$ for an optically saturated and unsaturated material.

Temperature change $\theta_s(0,0,t)$ is directly proportional to the surface absorptance $\Gamma_s$. For increasing $\Gamma_s$, the $\theta_s(0,0,t)$ transient shifts upwards although its shape remains unaffected. However, the shape of the overall transient $\theta$ will be affected by changes in $\Gamma_s$. Due to the instantaneous nature of the de-excitation from the surface layer following a rectangular optical pulse, the surface-heating-induced temperature change $\theta_s(0,0,t)$ shows instantaneous relaxation profiles similar to those obtained experimentally with opaque samples. In order to assess the relative strengths of the bulk and surface contributions to the surface temperature, the total surface temperature $\theta$ and its bulk and surface contributions $\theta_b$ and $\theta_s$ are shown in figure 5.17 on the $\mu$s and $ms$ scales respectively. On the $0 - 50 \mu s$ timescale, the surface term dominates the bulk term as shown in figure 5.17.

The relative signal strengths of the bulk and surface temperature components become
Figure 5.16: Theoretical prediction of the bulk-heating-induced surface temperature $\theta_b$ as a function of the metastable lifetime $\tau_{21}$ (in response to an optical pulse of duration $3 \mu s$).

comparable only for time $\geq 3 ms$, as shown in figure 5.18. The bulk component becomes larger as time progresses because delayed heat arrives at the rapidly cooled surface from inside the bulk at times much longer than the surface cooling time $\tau_h = 1 ms$.

Figures 5.17 and 5.18 thus give us the following information pertaining to optimum experimental conditions: To characterize the surface, we must probe the transient temperature response at very early times after the pulse is cut off; To characterize the bulk, we must monitor the response at very long times after the pulse is cut off.
Figure 5.17: A comparison of the bulk-induced ($\theta_b$) and surface-induced ($\theta_s$) contributions to the total surface temperature $\theta$ in the early time $\mu s$ range; Surface absorptance $\Gamma_s = 0.02$.

5.8 Preliminary Time-Domain Radiometric Measurements

5.8.1 Photothermal Radiometric Detection: Instrumentation and Procedure

The arrangement of the photothermal radiometry experiment is shown in figure 5.19. The continuous wave output from an Argon ion-laser is modulated at the required pulse repetition rate and duty cycle by an acousto-optic modulator before impinging on the sample.
Figure 5.18: A comparison of the bulk-induced ($\theta_b$) and surface-induced ($\theta_s$) contributions to the total surface temperature in the *late time ms* range: Surface absorptance $\Gamma_s = 0.02$.}

...
Figure 5.19: Experimental layout of a photothermal radiometric detection system.

which reconstructs the transient signal. I conducted the radiometry experiments in collaboration with Dr. Mahendra Munidasa of the Photothermal and Optoelectronic Diagnostics Laboratory.

We used the following approach to measure the transient IR emission profile of radiation emitted by the laser material in response to an optical excitation. The sample is irradiated by modulated Ar-ion laser light and allowed to re-establish thermal equilibrium with the surroundings. The drift in the IR emission signal (corresponding to the sample temperature) is monitored by a lock-in amplifier. After the lock-in signal becomes stable, the sample is aligned such that the beam waist is coincident with the front surface of the sample. This alignment is obtained by varying the sample along the optical beam axis and monitoring the lock-in signal, which will yield a maximum value when the beam waist irradiates the front surface of the sample. With the sample in this position, the detector is aligned such that the energy collected by the parabolic mirrors has a focal point at the surface of the detector.
active area.

A repetitive pulse of a given duration and period irradiates the detector. With the pulse duration and period fixed, the boxcar integrator is used to reconstruct the transient profile of the IR emission in response to this pulse. In a typical reconstruction, the boxcar integrator will open a gate of a specified width at a specified location along the transient and average the measured signal over 10,000 cycles. The gate will then move to the next location along the transient and obtain an average over the next 10,000 cycles. When every point along a transient has been averaged, the transient is reconstructed. To test whether instrumental effects are contributing to this transient emission, the transient instrumental response is also measured (by short circuiting the inputs to the boxcar integrator).

Infrared Detectors

There are two basic types of IR detectors in use today. Photon detectors rely on the interaction of individual photons with electrons in the detector material itself. An example of a photon detector is the MCT detector we use in the radiometry experiments. The other type of detector is a thermal detector, which measures the total energy absorbed by measuring a change in the detector temperature. An example of a thermal detector is a pyroelectric detector, which we used in the previous chapter to perform pyroelectric spectroscopy of laser materials.

In a photon detector, the photons irradiating the detector interact with the detector material by exciting electrons from the valence to the conduction band, as shown in figure 5.20 [105]. This excitation of electrons causes an increase in conductivity of the detector material, which is subsequently measured as a current or voltage. The problem with detecting broadband IR radiation is that as the wavelength of light to be detected gets longer, the energy gap in the semiconductor must become smaller. Mercury-Cadmium-Telluride is very suitable for
detecting broadband IR radiation because this material has a bandgap that can be varied to give a long-wavelength cutoff from 2 to 30 $\mu m$ [106]. The particular detector we used for the radiometry experiments has a bandwidth of 2 to 14 $\mu m$.

5.8.2 Sources of Error in Photothermal Radiometry

One possible source of error is the drift in the temperature of the sample with time. Over a long period of time during which the sample is exposed to modulated light, the infrared emission profile is made up of a slowly increasing temperature ("dc temperature") plus a rapidly varying modulated temperature ("ac temperature"). It is the ac temperature that we are interested in measuring. The boxcar integrator has a low frequency cutoff of 1 Hz. However, we found that in the case of an experiment where several thousand samples must be averaged at each point of the transient, the time taken for the experiment could be long.
enough that dc temperature changes can dominate the ac temperature changes. We therefore used a pre-amplifier with a dc (low frequency) cutoff to remove any dc components from the transient measurement.

Another possible problem with regard to reproducibility of the data is problem of irradiating the same region on the material on successive experiments. To minimize this problem, we ensured that we were working with a spot size that was much larger than the dimensions of the surface defects, ensuring that a significant number of nonradiative defects were being irradiated. The resulting IR emission signal will then represent an average value, ensuring that the variations from experiment to experiment are minimized.

A final important issue that must be considered is the polarization of the material, which in turn affects its absorption coefficient. To ensure that the material responds in the same manner (in terms of its absorption) from experiment to experiment, we found it necessary to rotate the material such that its absorption is maximized. Apart from the issue of repeatability, maximising the absorption also improves the signal to noise ratio since the material absorbs more energy.

We can get an idea of the level of reproducibility of this technique (in the case of the lowest possible signal to noise ratio, which occurs at high pulse repetition frequencies) by studying figure 5.32 later in this chapter. This figure shows two materials whose surfaces are processed in an identical manner.

5.8.3 Identification of Three Regimes of Thermal Emission

The transient temperature profile from the time of pulse cutoff to 10 ms later is shown in figure 5.21. These figures show clearly that there are three distinct regions of transient decay. Region I is a very steep decay in the 0 to 10 μs time range. Region II is a much slower decay in the 10 to 100 μs time range. Region III is a decay in the ms range. Contrary
Figure 5.21: Three regions of thermal emission: The transient IR radiation emission signal is shown in three distinct regions whose profiles are governed by direct IR emission (Region I), surface heat generation (Region II), and bulk heat generation (Region III). For a description of how each point on the graph is obtained, please refer to Appendix B.

to the experimental data, the numerical model described in section 5.6 (and depicted by figures 5.17 and 5.18) predicts that there are only two distinct regions of temperature decay, due to non-radiative energy conversion at the surface and bulk respectively. This disparity leads us to conclude that either one of the regions seen in the data is due to an experimental artifact or the model does not account for all the IR radiation generating processes that occur in the laser material. Since the instrumental effects have already been suppressed in relation to the signal level, we concluded that the additional decay region must be due to an effect not considered in the model. Going back to the original assumptions we made in the derivation of the PTR signal, we assumed that the sample was opaque to its own radiation, within the spectral range corresponding to the spectral bandwidth of the MCT detector.
Figure 5.22 shows an FTIR transmittance spectrum of a Ti: Sapphire crystal in the 2 $\mu m$ - 25 $\mu m$ range. From this figure, we see that the sample is not opaque in the 2 - 6 $\mu m$ range. It is therefore possible that any IR radiation in the 2 to 6 $\mu m$ range generated in the sample will not be re-absorbed by the sample and will therefore be collected by the detector.

Comparison of the experimental data and theoretical predictions lead us to conclude that Region II is due to surface heating effects and Region III is due to bulk heating effects, leaving Region I as the region in which the source of the signal is as yet unaccounted for. Our next task was to attempt to experimentally identify the origins of this IR emission in Region I.
5.8.4 Origins of Thermal Emission in 0 - 5 μs Range

To determine the origin of the IR emission shown in region I of figure 5.21 that we have not yet accounted for, we conducted two experiments. The first test was to extrapolate the slope of the curve in Region II all the way to the \( t = 0 \) location as shown in figure 5.23. By subtracting the extrapolated curve from the original curve in Region I, we obtain as

![Graph showing extrapolation of Region II decay curve back to Region I. Extrapolated curve in Region I shows that there is a difference between the total measured emission and the surface-heating induced emission which we must account for. Detector bandwidth = 2 to 14 μm. For a description of how each point on the graph is obtained, please refer to Appendix B.](image)

shown in figure 5.24 a measure of the additional component to the total radiative signal. By measuring the lifetime of the decay of this additional component (fitted to an exponential decay), we found the lifetime to be equal to 3.1 μs, which is very close to the lifetime of the upper laser level in Ti: Sapphire. This fact suggests that the signal could possibly be...
Figure 5.24: Subtraction of the two signals in the previous figure results in a plot of the additional component to the signal.

due to radiative emission from the upper laser level to higher vibrational sublevels of the ground state manifold than in the case of the fluorescence emission. Photons emitted in the 2 to 6 μm range will be transmitted through and out of the sample and collected by the detector and are responsible for the decay profile shown in Region I. To confirm that such excited-state carriers are indeed responsible for this direct emission, we performed an additional test by doing a photothermal radiometry experiment identical to the one described in section 5.8.1 with the exception of the pump laser source. Instead of the Argon-ion laser, we used an Nd: YAG laser at a 1.06 μm pump wavelength. At such a wavelength, there is not enough energy to excite the carriers to the excited state manifold [61], thereby ensuring that the carriers will all de-excite non-radiatively from the upper vibrational levels of the ground state manifold that they have been excited to by the Nd: YAG laser. As a result,
no infra-red photons will be emitted and the decay characteristic of Region I will be absent.

Figure 5.25 shows the PTR signal for a Nd:YAG pumped Ti: Sapphire laser material.

![Figure 5.25: A comparison of the radiation emission transient from a laser material in response to Ar-ion excitation and Nd:YAG excitation. The “fast” decay seen with Ar-ion laser excitation in the 0 - 10 $\mu$s range is not present with the Nd:YAG excitation. Detector bandwidth = 2 to 14 $\mu$m. For a description of how each point on the graph is obtained, please refer to Appendix B.](image)

The break in the transient profile at about 10 $\mu$m after pulse cutoff is not present in this curve. The above two tests confirm that the signal in region I is a radiative process from the upper laser level.

### 5.8.5 Implications of the Existence of Direct IR Emission

As a result of this additional component to the experimental signal that was not originally accounted for in the theoretical model of section 5.6, some modifications are required in order to incorporate the direct IR emission component into the theoretical expression for the
radiation emission signal. The next section presents a theoretical model of the PTR signal in the *early* times after pulse cutoff: a time range which is too short for any heating effects due to bulk non-radiative energy conversion to be felt at the front surface of the sample.

5.9 Early Time Theoretical Model

This section provides a summary of Mandelis’ theoretical treatment of the transient radiative emission signal response for short time periods after pulse cutoff. At such early (typically 0 to 100 μs) times after pulse cutoff, two contributions to the IR emission signal are present. The first contribution is the IR photon emission by stationary photo-excited Ti$^{3+}$ ions. The other contribution is due to the non-radiative processes occurring at the surface of the crystal. We ignore any contributions to the IR emission signal due to non-radiative processes occurring in the bulk of the crystal, since the time ranges in which this theory is valid are much shorter than the time required for heat to diffuse from the bulk towards the front surface of the crystal.

Consider a laser rod of length L with its front surface labelled by $z = 0$, as shown in figure 5.2. For harmonic excitation, the IR absorption coefficient of a Ti: Sapphire laser rod is

$$\beta_{IR}(z, t; \lambda) = \beta_{IR}^{(0)}(z; \lambda) + \Delta \beta_{IR}(z, t; \lambda)$$  \hspace{1cm} (5.61)

where $\beta_{IR}^{(0)}(z; \lambda)$ is the IR absorption coefficient in the absence of a pump laser beam and $\Delta \beta_{IR}(z, t; \lambda)$ is the time-dependent IR absorption coefficient due to spontaneous decay of stationary photo-excited Ti$^{3+}$ ions. In the above equation $(z, t, \lambda)$ are the depth coordinate, time coordinate and the IR wavelength respectively. Let $T_\infty$ be the ambient temperature and $\theta(0, z, t)$ be the time-dependent temperature change due to irradiation of the sample.
Planck's distribution function is given by

\[ W_P(\lambda, \theta_T; z) = \frac{2\pi h c^2 A}{\lambda^5 \left[ \exp \left( \frac{h c}{\lambda k_b \theta_T(0, z, t)} \right) - 1 \right]} \]  \hspace{1cm} (5.62)

where \( \theta_T(0, z, t) = T_\infty + \theta(0, z, t) \) is the absolute temperature of the sample, \( A \) is the emitting surface area, \( k_b \) is the Boltzmann constant, \( h \) is Planck's constant and \( c \) is the speed of light.

The change in Planck's distribution function \( W_P(\lambda, \theta_T, z) \) can be found by expanding this function around \( \theta_T = T_\infty \) using a Taylor series expansion:

\[ \Delta W_P(\lambda, \theta_T = T_\infty + \theta) \equiv W_P(\lambda, T_\infty) + \frac{\partial W_P}{\partial T_\infty} \theta \]  \hspace{1cm} (5.63)

Upon differentiating \( W_P \) and setting the product \( \theta \frac{\partial W_P}{\partial T_\infty} \) equal to a quantity \( \Delta W_P(\lambda, T_\infty) \):

\[ \Delta W_P(\lambda, T_\infty) \equiv \left( \frac{h c}{\lambda k_b T_\infty} \right) \frac{W_P(\lambda, T_\infty)}{\exp(h c/\lambda k_b T_\infty)} \left[ \frac{\theta(0, z, t)}{T_\infty} \right] \]  \hspace{1cm} (5.64)

We can now rewrite Planck's distribution function as

\[ W_P[\lambda, \theta_T(z, t)] \approx W_P[\lambda, T_\infty] + \Delta W_P(\lambda, T_\infty; z, t) \]  \hspace{1cm} (5.65)

To calculate the IR radiation that is incident on the MCT detector, the first step is to find the total IR radiation power (per unit wavelength) arriving at the surface of the material from the interior. This quantity, integrated over the spectral bandwidth of the detector and adjusted for reflection losses at the inner front surface of the crystal, will yield the power incident on the detector. The total IR radiation power (per unit wavelength) at the surface
of the material arriving from the interior of a laser rod of length \( L \) is

\[
P(\lambda, t) = \int_0^L \beta_{IR}(z, t; \lambda) \exp\left[-\int_0^z \beta_{IR}(z', t; \lambda') dz'\right] \Delta W_P[\lambda, \theta_T(z, t)] dz
\]  

(5.66)

Using equations 5.61 and 5.65, the above equation can be expanded to

\[
P(\lambda, t) = \int_0^L \left[ \beta_{IR}^{(0)}(z; \lambda) + \Delta \beta_{IR}(z, t; \lambda) \right] \left[ W_P(\lambda, T_\infty) + \Delta W_P(\lambda, T_\infty; z, t) \right] \exp\left[-\int_0^z \left[ \beta_{IR}^{(0)}(z'; \lambda) + \Delta \beta_{IR}(z', t; \lambda) \right] dz'\right] dz
\]

(5.67)

From the FTIR transmission spectrum shown in figure 5.22, we may set

\[
\int_0^z \beta_{IR}^{(0)}(z'; \lambda) dz' = \beta_{IR}^{(0)}(\lambda) z
\]

(5.68)

The rise in the IR absorption coefficient (which is equal to the IR emission coefficient by Kirchoff's law of detailed balance) is proportional to the density of the photo-excited \( \text{Ti}^{3+} \) ions. For typical doping concentrations of the host crystal of about 0.1 \%, the density of \( \text{Ti}^{3+} \) ions is negligible, implying

\[
\int_0^L \Delta \beta_{IR}(z, t; \lambda) dz' \ll 1
\]

(5.69)

As a result of the above two equations,

\[
\exp\left[-\int_0^L \left[ \beta_{IR}^{(0)}(z'; \lambda) + \Delta \beta_{IR}(z, t; \lambda) \right] dz'\right] \simeq e^{-\beta_{IR}^{(0)} z}
\]

(5.70)
We may now rewrite equation 5.67 as a summation of four integrals:

\[
P(\lambda, t) = \int_0^L \beta_{IR}^{(0)}(z; \lambda) W_P(\lambda, T_\infty) dz e^{-\beta_{IR}^{(0)} z} \\
+ \int_0^L \beta_{IR}^{(0)}(z; \lambda) \Delta W_P(\lambda, T_\infty; z, t) dz e^{-\beta_{IR}^{(0)} z} \\
+ \int_0^L \Delta \beta_{IR}(z, t; \lambda) W_P(\lambda, T_\infty) dz e^{-\beta_{IR}^{(0)} z} \\
+ \int_0^L \Delta \beta_{IR}(z, t; \lambda) \Delta W_P(\lambda, T_\infty; z, t) dz e^{-\beta_{IR}^{(0)} z}
\]  

(5.71)

In the above equation, the first term is independent of time and represents the background radiation level on which the pump laser induced radiometric transient is superposed. The last term includes the product of two small quantities \( \Delta W_P \) and \( \Delta \beta_{IR} \) and is therefore negligible compared to the second and third terms in the above equation. Because the boxcar filters out any dc components of the measured signal, we neglect the first (constant) term as well and rewrite the above equation as

\[
P(\lambda, t) \equiv \\
\int_0^L \beta_{IR}^{(0)}(z; \lambda) \Delta W_P(\lambda, T_\infty; z, t) dz e^{-\beta_{IR}^{(0)} z} \\
+ \int_0^L \Delta \beta_{IR}(z, t; \lambda) W_P(\lambda, T_\infty) dz e^{-\beta_{IR}^{(0)} z}
\]  

(5.72)

This equation gives us a clear indication that the measured experimental signal will be due to a change in \textit{thermal emission} \( \Delta W_p \) and a change in \textit{electronic emission} \( \Delta \beta_{IR} \). In the above equation, \( \Delta \beta_{IR} \) is proportional to the distribution of stationary IR photon emitting \( \text{Ti}^{3+} \) ions and is given by

\[
\Delta \beta_{IR}(z, t; \lambda) = \sigma_{IR} N_2(t) e^{-\beta_{vis} z} (1 - \Gamma_S)
\]  

(5.73)

where \( N_2(t) \) is the time-dependent population of the metastable state in Ti: Sapphire given by equation 5.20. \( \sigma_{IR} \) is the absorption cross-section, \( \beta_{vis} \) is the absorption coefficient of
the pump wavelength and $\Gamma$, is the surface absorptance. Noting that $I_{IR}^{(s)}$ is independent of the depth coordinate and substituting equations 5.73, 5.64, and 5.20 into equation 5.72 we obtain

$$P(\lambda, t) = W_P(\lambda, T_{\infty}) \left( \frac{h c \beta_{IR}^{(s)}}{\lambda k T_{\infty}^{2} \exp \left( \frac{h c \beta_{IR}^{(s)}}{k T_{\infty}} \right) - 1} \right) \int_0^L \theta(0, z, t) dz e^{-\beta_{IR}^{(s)} z}$$

$$+ \sigma_{IR} \int_0^L N_2(t) e^{-\beta_T z} dz$$

where $\beta_T = \beta_{\text{vis}} + \beta_{IR}^{(s)}$. For long crystal rods, we may assume $L \to \infty$ and rewrite equation 5.74 as

$$P(\lambda, t) = W_P(\lambda, T_{\infty}) \left[ a(\lambda) \int_0^\infty dz \theta(0, z, t) e^{-\beta_{IR}^{(s)} z} + b(\lambda) N_2(t) \right]$$

where $a(\lambda) = \frac{h c \beta_{IR}^{(s)}}{\lambda k T_{\infty}^{2} \exp \left( \frac{h c \beta_{IR}^{(s)}}{k T_{\infty}} \right) - 1}$ and $b(\lambda) = \frac{\sigma_{IR}}{\beta_T(\lambda_{\text{vis}})}$. We now have an expression for $P(\lambda, t)$, the total IR radiation power (per unit wavelength) arriving at the surface of the material from the interior. Using this expression for $P(\lambda, t)$, we can find an expression for the IR emission collected by the MCT detector by accounting for reflection losses and integrating over the bandwidth $\lambda_1 - \lambda_2$ of the detector:

$$S(t; \lambda_{\text{vis}}) = [1 - R(\lambda_{\text{vis}})] \int_{\lambda_1}^{\lambda_2} [1 - R(\lambda)] P(\lambda, t) d\lambda$$

Incorporating equation 5.75 into the above equation, we obtain

$$S(t; \lambda_{\text{vis}}) = A(\lambda_{\text{vis}})[\int_0^\infty dz \theta(0, z, t) e^{-\beta_{IR}^{(s)} z}] + B(\lambda_{\text{vis}}) N_2(t)(1 - \Gamma_S)$$

where $A(\lambda_{\text{vis}}) = [1 - R(\lambda_{\text{vis}})] \int_{\lambda_1}^{\lambda_2} [1 - R(\lambda)] W_P(\lambda, T_{\infty}) a(\lambda) d(\lambda)$ and $B(\lambda_{\text{vis}}) = [1 - R(\lambda_{\text{vis}})] \int_{\lambda_1}^{\lambda_2} [1 - R(\lambda)] W_P(\lambda, T_{\infty}) b(\lambda) d(\lambda)$. Under experimental conditions, the terms $A(\lambda_{\text{vis}})$ and $B(\lambda_{\text{vis}})$ can be considered as multiplying constants in equation 5.77. We must evaluate the integral $\int_0^\infty \theta(0, z, t)$, where $\theta(0, z, t)$ is the transient temperature fluctuation of the laser material due
to pump laser irradiation. \( \theta(0, z, t) \) can be obtained by applying equation 5.54 and 5.53 at very early times, where heat conduction from the volume sources (bulk) will be neglected. In addition, the characteristic thermal transfer time \( \tau_h \) is assumed to be much longer than the observation time interval and radial heat flow is considered to be negligible in the observation time interval. The integral \( \int_0^\infty \theta(0, z, t) \) can then be written explicitly (using equation 5.54 and 5.53) as

\[
I(t) = \begin{cases} 
\frac{2I_0 \Gamma \sigma_0}{\pi k} \left[ 2 \sqrt{\frac{\pi \chi_0}{\pi}} - \tau_{IR} [1 - Y(\sqrt{\frac{t}{\tau_{IR}}})] \right] & \text{if } t < \tau_p \\
2I_0 \Gamma S(\alpha / \pi k) \int_0^{\tau_p} Y(\beta_{IR}^{(0)} \sqrt{\alpha(t - t_0)} dt_0) & \text{if } t > \tau_p,
\end{cases}
\]

(5.78)

where \( \tau_{ir} \equiv \frac{1}{\beta_{IR}^{(0)^2}}, Y(x) \equiv \exp(x^2)erfc(x) \) \( \alpha \) is the thermal diffusivity and \( k \) is the thermal conductivity. Finally, equation 5.78 is substituted into equation 5.77, yielding the final expression for the IR emission collected by the detector:

\[
S(t > \tau_p; \lambda_{vis}) = (1 - \Gamma_s) B(T_\infty, \lambda_{vis}) W_{po} N_{TT} (e^{\tau_p / \tau_{21}} - e^{-W_{po} \tau_p}) e^{-t / \tau_{21}} \\
+ \frac{2A(T_\infty, \lambda_{vis}) I_0 \Gamma \sigma_0 \tau_{IR}}{\pi k} \left[ Y(\sqrt{\frac{t}{\tau_{IR}}}) - Y(\sqrt{\frac{t - \tau_p}{\tau_{IR}}} + \frac{2}{\sqrt{\pi \tau_{IR}}} (\sqrt{t} - \sqrt{t - \tau_p})) \right]
\]

(5.79)

Since we are looking at the decay of the transient profile, we are only interested in the \( t > \tau_p \) equation. The first term of the above equation represents the direct infra-red emission by stationary excited \( Ti^{3+} \) ions in the crystal. This term is responsible for the fast decay of the signal shown in Region I of figure 5.21 and has a similar functional form as the luminescence transient given by equation 5.20. The second term represents the IR radiation emission due to non-radiative processes occurring at the surface, represented by Region II of figure 5.21. In the above equation, \( A \) and \( B \) are independent of time but depend on temperature and on the spectral range of the detector. \( \tau_{IR} \) is a characteristic time based on the IR absorption coefficient of the sample. \( \Gamma_s \) is the important surface absorptance parameter that we seek to find by fitting this equation to the experimental data. The
parameters involved in equation 5.79 are shown in Table 5.2. A plot of the theoretical (predicted) transient IR emission collected by the detector given by equation 5.79 in the early time range is shown in figure 5.26, where the two distinct regions of emission can be seen.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method of Determination</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Absorptance, $\Gamma_S$</td>
<td>From Curve Fitting</td>
<td>To be obtained</td>
</tr>
<tr>
<td>Spectrally Integrated Constants $A, B$</td>
<td>$A, B$ same for all samples</td>
<td>Not required</td>
</tr>
<tr>
<td>Characteristic time, $\tau_{IR}$</td>
<td>FTIR absorption spectra</td>
<td>12 s</td>
</tr>
<tr>
<td>Thermal Conductivity, $k$</td>
<td>Literature (Schultz and Henion)</td>
<td>33 W/m$^\circ$K</td>
</tr>
<tr>
<td>$W_{po, N_T, \tau, \tau_2}$</td>
<td>From Luminescence Curve Fits</td>
<td>Sample Dependent</td>
</tr>
<tr>
<td>Thermal Diffusivity $\alpha$</td>
<td>Literature (Schultz and Henion)</td>
<td>0.106cm$^2$/s</td>
</tr>
</tbody>
</table>

Figure 5.26: A plot of the predicted transient IR emission in the early time range.
5.10 PTR Experimental Results

To characterize the bulk and surface quality of a laser material using time-domain PTR, we approached the problem in the following manner. For a given laser material, we first measured the transient luminescence signal, obtaining the value of the metastable lifetime $\tau_{21}$ by fitting the experimental data to equation 5.20. Next, we used the PTR technique to measure the transient IR emission signal in the first 100 $\mu$s after pulse cutoff. This early-time region yields information about surface non-radiative energy conversion as a result of fitting the early time PTR experimental data to equation 5.79 (which describe the transient evolution of the radiometric emission signal in the early times after pulse cutoff). From the curve fit, we obtain a fitting parameter which represents the non-radiative surface energy generation. Finally, we conducted a late time PTR experiment in which the transient radiometric emission signal is measured in the millisecond range. We then fitted this data to equation 5.58 (which describes the transient evolution of the radiometric emission signal in the late times after pulse cutoff) and obtained a fitting parameter that represents the non-radiative energy generation at the bulk. By completing these three experiments for a given sample, we were able to quantify the bulk and surface non-radiative energy conversion processes in the laser material.

5.10.1 Curve Fitting Procedure

We fitted the experimental data to the theoretical expressions by using a general linear least squares method. In such a situation, the fitting function is not a linear combination of 1 and $x$ (for example, $a + bx$), but instead a linear combination of any $M$ specified functions of $x$. 
The general form of this model is

$$y(x) = \sum_{k=1}^{M} \phi_k X_k(x)$$  \hspace{1cm} (5.80)

where $X_1(x), ..., X_M(x)$ are arbitrary functions of $x$ that can even be nonlinear in $x$. We wrote a curve fitting program based on the general linear least squares method to fit the theoretical expressions to the experimental data [107]. Given a set of experimental data points with individual standard deviations, we use $\chi^2$ minimization to determine the coefficients $\phi(1)$ to $\phi(M)$ of the fitting function given by equation 5.80. We solve the fitting equations using singular value decomposition. The program returns the value of the $M$ fitting parameters $\phi(1)$ to $\phi(M)$ and a value of the $\chi^2$ parameter, indicating the goodness-of-fit. We used the above curve fitting procedure to fit data from three different types of experiments: transient luminescence measurements, early-time radiometric emission measurements and late-time radiometric emission measurements. The data from these three types of experiments corresponds to equations 5.20, 5.57 and 5.79.

**Fitting the Early-time Data to Quantify Non-radiative Surface Energy Generation:** We rewrite the equation governing early-time IR radiation emission given by equation 5.79 in the form of equation 5.80:

$$S(t; \lambda_{\text{vis}}) = \phi_1 \tau (e^{\tau_p/\tau_2} - e^{-W_{\text{pol}}\tau_p})e^{-t/\tau_2}$$

$$+ \phi_2 [Y(\sqrt{\frac{t}{\tau_{IR}}}) - Y(\sqrt{\frac{t-\tau_p}{\tau_{IR}}}) + \frac{2}{\sqrt{\pi}\tau_{IR}}(\sqrt{t} - \sqrt{t - \tau_p})]$$  \hspace{1cm} (5.81)

where the two fitting parameters are

$$\phi_1 = (1 - \Gamma_s)B(T_\infty, \lambda_{\text{vis}})W_{\text{pol}}N_T$$  \hspace{1cm} (5.82)
and
\[ \phi_2 = \frac{2A(T_\infty, \lambda_{\text{vis}})I_0 \Gamma_s \sigma_{\text{IR}}}{\pi k} \] (5.83)

The curve fitting process for the early time data results in the determination of the two fitting parameters \( \phi_1 \) and \( \phi_2 \) for a given crystal. In the expressions for \( \phi_1 \) and \( \phi_2 \), the only quantity that varies from crystal to crystal is the surface absorptance, \( \Gamma_s \). The other quantities such as \( k \) (thermal conductivity), \( \alpha \) (thermal diffusivity), \( W_p \) (pumping rate), \( N_T \) (total population), \( I_o \) (optical intensity) can be assumed constant from sample to sample, given identical input pumping conditions. Also, \( A \) and \( B \) are constant from sample to sample, since these two parameters are multiplying constants that depend only on ambient temperature and the spectral range of the detector.

For a given crystal sample, the curve fitting routine returns values of \( \phi_1 \) and \( \phi_2 \). For a given crystal sample \( i \), we can rewrite equations 5.82 and 5.83 as \( \phi_1^{(i)} = K_1(1 - \Gamma_s^i) \) and \( \phi_2^{(i)} = K_2 \Gamma_s^i \), where \( K_1 \) and \( K_2 \) are the same for any crystal sample. If we evaluate 2 crystals, we can write 4 equations with 4 unknowns \((K_1, K_2, \Gamma_s(Crystal1), \Gamma_s(Crystal2))\) and then solve for the surface absorptance \( \Gamma_s \) of the two crystals. Finally, we define the surface non-radiative energy generation rate, \( Q_s \):

\[ Q_s = I_o \Gamma_s \quad [\text{W/m}^2] \] (5.84)

where \( I_o \) is the incident optical intensity and \( \Gamma_s \) is the surface absorptance. In the work to follow, we will characterize the surfaces of different crystals by the \( Q_s \) parameter, having first found \( \Gamma_s \) from the results of the curve fitting to experimental data.

**Fitting the Late-time Data to Quantify Non-radiative Bulk Energy Generation:** We rewrite the equation governing late-time IR radiation emission given by equa-
tion 5.57 in the form of equation 5.80:

\[
\theta(0,0,t) = \theta_s(0,0,t) + \phi_1 \left\{ \int_0^t \frac{f(t_o)Y(\frac{\sqrt{(t-t_o)}}{\tau_p})dt_o}{1-\sqrt{\tau_h/\tau_p(t_o)(8\alpha(t-t_o)+R^2)}} - \sqrt{\tau_h} \int_0^t \frac{f(t_o)Y(\frac{\sqrt{(t-t_o)}}{\tau_p(t_o)})dt_o}{(\sqrt{\tau_p(t_o)})-\sqrt{\tau_h}(8\alpha(t-t_o)+R^2)} \right\}
\]  

(5.85)

where the function \( f(t_o) \) is defined for times \( t \geq \tau_p \) as

\[
(e^{-\Gamma_{21}} - e^{-W_{po}\tau_p})e^{-\frac{\Gamma_{21}}{2}} \left[ 1 - 2W_{po}\tau(1 - e^{-\tau_p/\tau})e^{-\frac{\tau_p}{2}} \right]
\]  

(5.86)

and the fitting function \( \phi_1 \) is given by

\[
\phi_1 = \frac{2(1 - \Gamma_s)\sqrt{\alpha P_o \beta_{30}(E_{30}^{NR}/E_{30})}}{\pi k(1 + W_{po}\tau_{21})}
\]  

(5.87)

The curve fitting procedure for the late time data results in the determination of the fitting parameter \( \phi_1 \) for a given crystal. In the expression for \( \phi_1 \), the quantities \( \alpha \) (thermal diffusivity), \( k \) (thermal conductivity) and \( W_{po} \) (pumping rate) are constant from crystal to crystal and have known numerical values [28]. The quantities that vary from crystal to crystal are the input power \( P_o \), the surface absorptance \( \Gamma_s \), the optical absorption coefficient \( \beta_{30} \), the nonradiative energy released during a transition from the upper level to the ground state \( E_{30}^{NR} \), and the metastable state lifetime \( \tau_{21} \). The surface absorptance and the metastable state lifetime of a given crystal can be found by conducting early-time PTR experiments and luminescence measurements respectively. Substituting the known values of \( P_o, \tau_{21}, \Gamma_s, \alpha, k, W_{po} \) and the fitting parameter \( \phi_1 \) returned by the curve fitting routine into equation 5.87, we obtain a numerical value for the parameter \( \beta_{30}(E_{30}^{NR}/E_{30}) \). Finally, we define
the bulk non-radiative energy generation rate $Q_b$:

$$Q_b = I_o \beta_{30}(E_{30}^{NR}/E_{30}) \quad [W/m^3]$$ (5.88)

where $I_o$ is the input optical intensity. In the work to follow, we will characterize the nonradiative bulk properties of different crystals by the $Q_b$ parameter, having first found $\beta_{30}(E_{30}^{NR}/E_{30})$ from the results of the curve fitting to experimental data.

5.10.2 Description of Ti: Sapphire Samples Tested Using PTR

Ti: Sapphire Sample with an Unpolished Surface:

This sample is a Czochralski-grown crystal that has not been subjected to any surface polishing. This crystal is not of laser quality in that its surface is extremely rough. We use this crystal as a test case, to give some indication of the very small differences in surface quality of other, laser-quality crystals.

Samples of Different Bulk Quality but Identical Surface Quality:

This set of samples consists of a low bulk quality figure-of-merit (FOM = 40) and a high bulk quality figure-of-merit (FOM = 800). The difference in the optical quality of the bulk of these two samples is due to differences in the growth processes. The two crystals were grown in an identical manner using the Czochralski technique, following which the FOM = 800 sample was subjected to further annealing, thereby removing bulk defects present in the crystal [28]. As defined earlier, the FOM parameter represents the ratio of the absorption coefficient at the absorption peak to the absorption coefficient at the emission peak, $\beta_{488nm}/\beta_{800nm}$. A high FOM implies a high quality bulk, since the residual absorptions at the emission wavelength $\beta_{800nm}$ will be much lower for an annealed, high-bulk-quality crystal. The two samples were then subjected to the same surface treatment procedure. The
surface processing consisted of mechanical polishing using a diamond paste containing $5 \mu m$ size particulates.

**Samples of Identical Bulk Quality but Different Surface Quality:**

These two samples are both of high bulk quality figure-of-merit (implying that they have both been subjected to the same growth procedure and also to post-growth annealing) whose surfaces have been treated with two different polishes. One crystal was polished with the "best available" surface polish, consisting of mechanical polishing using a diamond paste containing $1 \mu m$ size particulates followed by mechanical polishing using $0.25 \mu m$ size diamond particulates. The other crystal was polished with a diamond paste containing $5 \mu m$ size particulates.

### 5.10.3 Measurement of Metastable Lifetime via Luminescence

The measurement of the luminescence lifetime can be accomplished independently of the PTR measurements, without having to adjust the sample or any other optical elements in the PTR experiment. In other words, the PTR and luminescence measurements can both be conducted in succession without any additional alignment. The only additional component required is a Silicon photodiode. Luminescent photon emission out of the front surface of the Ti: Sapphire laser material is filtered from reflected pump beam (Argon-ion laser) photons using a glass filter and collected by a fast risetime (ns) Si photodiode. The resulting photovoltage generated due to this luminescent emission is fed into the boxcar integrator such that the luminescence intensity is measured as a function of time.

**Effect of Absolute Crystal Temperature on Luminescence Lifetime:** Before conducting luminescence measurements on the test samples, we investigated the effect of the dc sample temperature on the metastable state luminescence lifetime. The relationship between sample temperature and metastable state lifetime of Ti: Sapphire has been investigated by
Moulton [8] and Albers et al [77]. These researchers found that at temperatures higher than 150 K, there is a decrease in lifetime with increasing temperature as shown in figure 5.27 [8]. These authors attribute this decrease in upper laser level lifetime to the greater influence of competing non-radiative processes at higher temperatures. The temperature dependent behaviour of the luminescence transient implies that the pump laser power will also affect the luminescence measurement. If the pump power into the sample increases, the optical energy absorbed by the laser material increases as well, resulting in an increase in the dc temperature of the sample. To quantify the effect of the pump power on metastable lifetime, we conducted luminescence measurements at two different pump powers. Figure 5.28 shows that the luminescence lifetime can change from 3.2 to 2.3 $\mu$s if the pump laser power is increased from 0.1 W to 3 W.

Due to this dependence of luminescence lifetime on sample temperature, it is imperative that the luminescence measurements and the thermal radiation emission (PTR) measurements be conducted in immediate succession. This step will ensure that both measurements...
Figure 5.28: Luminescence transients from a Ti: Sapphire laser material at two different pump powers. Dots: input power = 0.1 W; Squares: input power = 3 W. Detector measures luminescence emission below 1 \( \mu m \). For a description of how each point on the graph is obtained, please refer to Appendix B.

are taken with the sample at the same dc temperature.

Metastable Lifetime Measurements of Ti: Sapphire Crystals:

We conducted luminescence measurements and obtained the metastable state lifetimes of the samples mentioned in the previous section. We obtained a lifetime of 3.09 \( \mu s \) for the unpolished crystal rod of length (2.5 cm) shown in figure 5.29. For the two high bulk figure-of-merit crystal rods (of length 1 cm) with different surface treatments, we obtained lifetimes of 2.61 \( \mu s \) (0.25 \( \mu m \)-polished surface) and 2.56 \( \mu s \) (5 \( \mu m \)-polished surface) as shown in figure 5.30. The high and low bulk figure-of-merit crystal rods (of length 2 cm) have luminescence lifetimes of 2.99 \( \mu s \) (FOM = 800) and 3.01 \( \mu s \) (FOM = 40) as shown in figure 5.31.
Figure 5.29: Luminescence transient for the unpolished crystal. Detector measures luminescence emission below 1 μm. For a description of how each point on the graph is obtained, please refer to Appendix B.

The differences in lifetimes for different samples can be explained by the fact that these samples are of different sizes. Consider two samples of different sizes: the smaller sample will have a higher dc steady state temperature for the same amount of pump beam energy absorbed by the two samples. These experimentally determined values of $\tau_{21}$ are required as known input parameters when the PTR data is curve-fitted to the theoretical transient temperature distribution.
Figure 5.30: Luminescence transients for the two high bulk quality crystals with different surface polish. Detector measures luminescence emission below 1 μm. For a description of how each point on the graph is obtained, please refer to Appendix B.

5.10.4 Surface Characterization Using Early Time PTR Detection

To perform surface characterization, the Argon-ion pump laser is modulated at 500 Hz, with a pulse duration of 1 ms and pulse period of 2 ms. Using time-domain boxcar detection, we monitored the resulting transient radiometric emission signal from the Ti: Sapphire crystal in the first 100 μs after pulse cutoff. Using the curve-fitting routine mentioned earlier in this section, we fit the experimental data to the early-time theoretical expression for the IR radiation emission given by equation 5.81.
Figure 5.31: Luminescence transients for the high and low bulk quality crystals with the same surface polish. Detector measures luminescence emission below 1 μm. For a description of how each point on the graph is obtained, please refer to Appendix B.

**Evaluating Crystals of Different Bulk Quality Subjected to the Same Surface Treatment:**

The low (FOM = 40) and high (FOM = 800) bulk quality figure-of-merit crystals have surfaces that have been processed in exactly the same manner. The radiometric emission transient profiles of these two samples are shown in figure 5.32. As seen here, the transient evolution of the two crystals show almost overlapping behaviour. Region I shows a steep decay due to direct IR emission by Ti$^{3+}$ ions in the excited state. This decay is governed by the radiative lifetime of the crystal. The two curves overlap in Region I because their radiative lifetimes are very similar, as seen in figure 5.31. Region II shows two curves with a much slower decay governed by the IR photon emission by the sample due to non-radiative
Figure 5.32: IR radiation emission from a high FOM and low FOM crystal, measured in the early-time $\mu$s range where bulk effects are not felt and surface effects dominate. Detector bandwidth = 2 to 14 $\mu$m. For a description of how each point on the graph is obtained, please refer to Appendix B.

processes occurring at the crystal surface. We expect the non-radiative processes occurring at the crystal surface to be very similar for both samples, since both samples have been subjected to the same surface treatment. As a result, we also expect the transient profiles in Region II to be very similar for both samples.

To quantify the effects of the non-radiative processes occurring at the surfaces of the two materials, we fitted the experimental transient profiles to the theoretical expression for the early-time transient IR emission given by equation 5.81 and obtained the fitting parameters $\phi_1$ and $\phi_2$ (equations 5.82 and 5.83). From these fitting parameters, we can find the surface non-radiative energy generation rate $Q_s$. For these two samples, we obtain $Q_s = 0.234 I_o [W/cm^2]$ for the high FOM = 40 crystal and $Q_s = 0.229 I_o [W/cm^2]$, where $I_o$
is the input optical intensity in $W/cm^2$. Another way of expressing these results is to state that the FOM = 40 crystal has a surface that converts 23.4 % of the input optical energy to heat and the FOM = 800 crystal has a surface that converts 22.9 % of the input optical energy to heat.

**Evaluating Crystals of Same Bulk Quality Subjected to Different Surface Treatments:**

We next tested two crystals with similar bulk properties whose surfaces have been treated differently. Our aim was to see if the experimental time-domain PTR detection in the early-time ($\mu m$) range is sensitive enough to detect the differences in the non-radiative energy generation of these two crystal surfaces as a result of the differences in surface polishing. As described in section 5.10.2, one crystal has a 5 $\mu m$-polished surface and the other has a 0.25 $\mu m$-polished surface. Figure 5.33 shows the transient IR emission profile for the two crystals. In Region I, the two curves overlap since the two crystals have similar radiative lifetimes as seen in figure 5.30. In Region II, we observe that the crystal with the 5 $\mu m$-polished surface decays faster than the crystal with the 0.25 $\mu m$-polished surface.

To get an idea of the sensitivity of this technique and its ability to detect minute differences in surface quality, we compared the differences in the radiation emission signal of the 0.25 $\mu m$-polished crystal and the 5 $\mu m$-polished crystal shown in figure 5.33 with the emission signal for the unpolished crystal. This comparison is shown in figure 5.34, where we note that the differences in the 0.25 $\mu m$-polished crystal and the 5 $\mu m$-polished crystal are very small when compared to the unpolished crystal. This figure gives us an idea of how small (though significant) these changes in surface quality can be for two different surface-polished samples and an idea of how sensitive the detection technique should be in order to detect changes in different grades of industrial-quality polish processing techniques.
Figure 5.33: IR radiation emission from a 5 \( \mu m \)-polished surface and a 0.25 \( \mu m \)-polished, measured in the early-time \( \mu s \) range where bulk effects are not felt and surface effects dominate. Detector bandwidth = 2 to 14 \( \mu m \). For a description of how each point on the graph is obtained, please refer to Appendix B.

To quantify the differences in surface polish quality of these two crystals, we again use the fitting equation 5.81 and obtain the fitting parameters which ultimately yield the values of the surface non-radiative energy generation rate \( Q_s \). We obtained \( Q_s = 0.238I_o \) [W/cm\(^2\)] for the 5 \( \mu m \)-polished surface and \( Q_s = 0.180I_o \) [W/cm\(^2\)] for the 0.25 \( \mu m \)-polished surface. In other words, the lower-quality 5 \( \mu m \)-polished surface converts 23.8 % of the incident optical energy to heat, whereas the higher-quality 0.25 \( \mu m \) surface converts only 18.0 % of the optical energy to heat.
Figure 5.34: A comparison of IR radiation emission profiles of the two laser-quality polished samples with an unpolished crystal. Detector bandwidth = 2 to 14 μm. For a description of how each point on the graph is obtained, please refer to Appendix B.

5.10.5 Bulk Characterization Using Late Time PTR Detection

Following the early-time PTR detection of surface non-radiative effects, we conducted late-time PTR detection measurements of the same samples. For a given sample, the early-time and late-time measurements can be conducted in succession with no additional alignment required between the two experiments. The only changes we made were to change the modulation frequency and the boxcar detection range, which are controlled by the computer controlled data acquisition system. A repetitive optical pulse modulated at 33.3 Hz with a pulse duration of 15 ms and period of 30 ms irradiated the laser material. We then monitored the resulting IR emission from the crystal in the first 10 ms after pulse cutoff. We fitted this data to the theoretical expression for the total time-dependent temperature change in the
crystal due to both bulk and surface effects given by equation 5.85.

**Evaluating Crystals of Different Bulk Quality Subjected to the Same Surface Treatment**

The low (FOM = 40) and high (FOM = 800) bulk quality figure-of-merit crystals have identical surface properties but different bulk properties. When we monitored the radiation emission signal in the early time (0 to 50 $\mu$s) range for these two crystals (see figure 5.32), we did not observe any differences in the two transient profiles. This fact reinforced our earlier conclusion that the early time detection is not sensitive to any differences in bulk properties and is only sensitive to differences in surface properties. To quantify the differences between the bulk properties of the FOM = 40 and FOM = 800 crystals, we monitored the radiation emission signal in the 0 to 10 millisecond range after pulse cutoff. The resulting transient profiles are shown in figure 5.35. The figure shows that the low FOM = 40 crystal has a faster decay than the high FOM = 800 crystal, implying that there is more non-radiative energy generated in the low FOM = 40 crystal than in the high FOM = 800 crystal.

To quantify the effects of the non-radiative processes occurring within the bulk of the two materials, we fitted the experimental transient profiles to the theoretical expression for the late-time transient IR emission given by equation 5.85 and obtained the fitting parameters $\phi_1$ given by equation 5.87. From these fitting parameters, we can find the **bulk non-radiative energy generation rate** $Q_b$. For these two samples, we obtain $Q_b = 0.180I_o [W/cm^3]$ for the low FOM = 40 crystal and $Q_b = 0.105I_o [W/cm^3]$ for the FOM = 800 crystal, where $I_o$ is the input optical intensity in $W/cm^2$. In other words, the lower bulk quality FOM = 40 crystal has a bulk that converts 19.0 % of the input optical energy to heat and the higher bulk quality FOM = 800 crystal has a bulk that converts 10.5 % of the input optical energy to heat.
Figure 5.35: IR radiation emission from a high FOM and low FOM crystal, measured in the late-time ms range where surface effects are not felt and bulk effects dominate. Detector bandwidth = 2 to 14 μm. For a description of how each point on the graph is obtained, please refer to Appendix B.

Evaluating Crystals of the Same Bulk Quality Subjected to Different Surface Treatments:

Figure 5.36 shows the transient IR emission from the two crystals in the 0 to 10 ms range. The transient IR emission profiles for the two samples show almost identical behaviour in this range. The differences in the transient IR emission profiles of these two samples in the early time range shown in figure 5.33 are not present in the late time range.

To quantify the bulk heating processes in these two crystals, we fit the PTR emission data to the late-time transient IR emission equation 5.85 and subsequently obtain from the fitting parameter the values of the bulk non-radiative energy generation rate $Q_b$. We obtain almost
Figure 5.36: IR radiation emission from a 5 μm-polished surface and a 0.25 μm-polished surface, measured in the late-time ms range where surface effects are not felt and bulk effects dominate. Detector bandwidth = 2 to 14 μm. For a description of how each point on the graph is obtained, please refer to Appendix B.

identical values of $Q_b$ for the two samples: $Q_b = 0.141 I_o [W/cm^3]$ for the 5 μm-polished surface and $Q_b = 0.145 I_o [W/cm^3]$ for the 0.25 μm-polished surface.

5.11 Discussion

In the previous section, we obtained values for the bulk non-radiative energy generation rate $Q_b$ and the surface non-radiative energy generation rate $Q_s$ as a function of the input optical intensity, $I_o$. In assessing this data, our first task is to determine whether these values of $Q_b$ and $Q_s$ make sense in terms of both their absolute values as well as the relative magnitudes of these values for different samples.
The PTR experiments involved the use of an Ar-ion pump laser beam with a spot size of 100 \( \mu m \) and an input power of 3 W. These values correspond to an input pumping intensity \( I_0 \) of 9550 \( W/cm^2 \). For the high quality FOM = 800 crystal (a rod of 2 cm thickness), we calculate that the \( Q_b = 0.105I_0 \) \( [W/cm^3] \) we obtained corresponds to 0.63 W heat generation for the 3 W of optical pumping. This value is in the same order of magnitude as an estimate given by Schultz and Henion [103], who used a thermal lens method to calculate a heat generation rate of 4 W in a 2 cm-long Ti: Sapphire crystal (in response to a pump excitation of 10 W). However, their method does not account for any surface heating effects, which can play a significant role in the production of the total amount of heat in the crystal.

In both the early- and late-time PTR experiments, the lower quality surface or bulk exhibited a steeper transient decay than its better quality counterpart. This fact can be explained by the argument that the greater the amount of heat generation due to the optical excitation during the time when the pulse is on, the faster the decay of the IR emission signal must be in order to achieve equilibrium during the time that the pulse is turned off.

### 5.11.1 Surface Evaluation

The main purpose of polishing an optical surface is to reduce optical reflection and scattering losses by attempting to remove the small pores, crevasses, grooves, scratches and cracks present at the unpolished surface [23]. By polishing this surface, it is possible to reduce the characteristic length of such imperfections by an appropriate amount. However, polishing a surface also involves the deposition of impurity inclusions from the polish material to the optical surface. The surface imperfections and impurity inclusions are sites at which optical absorption and nonradiative energy conversion take place. As a result, surfaces with a high density of absorbing sites will exhibit a higher amount of heating [19]. Using the PPES technique in the previous chapter, we found that these absorbing sites are responsible for a
significant amount of absorption across the entire visible spectrum.

In evaluating the surface quality of the 0.25 $\mu m$-polished surface and the 5 $\mu m$-polished surface, we found that the surface non-radiative energy generation rate $Q_s$ is 32% higher for the 5 $\mu m$-polished surface. We expect this trend because the finer the grit-size of the polishing material, the lower the minimum size of the imperfections or defects that can be removed. In other words, the finer the grit-size of the polish, the greater the removal of the number of absorbing sites at the surface of the material. Therefore, the number of absorbing (and heat-producing) sites is greater in the 5 $\mu m$-polished surface than in the 0.25 $\mu m$-polished surface, resulting in a greater value of $Q_s$ for the 5 $\mu m$-polished surface. In evaluating the surface properties of the FOM = 40 and FOM = 800 crystals (both having 5 $\mu m$-polished surface), we determined $Q_s$ values that were within 2% of each other. This difference of 2% between the two identically processed surfaces is not significant because the difference falls within the value of the 5% error that the curve fitting routine returns. The early-time PTR technique can therefore confirm the fact that two surface have similar properties. Furthermore, the almost identical values of $Q_s$ for the two crystals of different bulk quality confirms that early-time PTR detection is entirely insensitive to any bulk differences.

5.11.2 Bulk Evaluation

In a perfectly grown Ti: Sapphire crystal, Ti$^{3+}$ ions doped into the sapphire host will be the only entity responsible for absorption of pump light. However, in real Ti: Sapphire crystals, several defects exist which also are responsible for absorption of pump light. Unlike the photon absorption by Ti$^{3+}$ ions (which can result in radiative emission), these defects are responsible for absorption of photons which will ultimately result in the generation of heat.

In evaluating the bulk quality of the FOM = 800 and FOM = 40 crystal, we found that the FOM = 40 crystal has a $Q_s$ value that is 70% greater than the FOM = 800. We attribute
this increase in bulk non-radiative energy conversion to the presence of additional defects which are not present in the FOM = 800 crystal due to annealing. Annealing has the effect of reducing the number of point defects in the crystal such as oxygen and aluminum vacancies and aluminum interstitials. The two crystals with the similar high FOM bulk properties but different surfaces showed very similar behaviour in the late-time detection range. This fact proves that in the late-time detection range, the PTR technique is insensitive to nonradiative processes occuring at the crystal surface.

To compare our investigations of bulk non-radiative processes using photopyroelectric spectroscopy (PPES) and PTR, we must clearly understand the differences in the parameters which are determined using each technique. Using PPES, we obtained separately dependent values of the bulk optical absorption coefficient $\beta_b$ and the optical-to-thermal energy conversion efficiency $\eta$. This $\eta$ value gives information about the amount of heat released per photon absorbed. Using PTR, we obtained the bulk non-radiative energy generation rate $Q_b$, which is proportional to the product of $\beta_b$ and $\eta$. This technique gives us a measure of the total heat released by the material due to the total number of photons absorbed. Since we conducted both the PTR and PPES experiments on the FOM = 40 and FOM = 800 crystals, we can compare numerical values of $Q_b$ using PPES by using the values of of $\eta$ and $\beta$ at the Ar-ion 488 nm wavelength. By multiplying these two independently determined values, we obtain $Q_b = 0.092I_o \ [W/cm^3]$ for the FOM = 800 crystal using PPES as compared to $Q_b = 0.105I_o \ [W/cm^3]$ using PTR. How can we explain the differences in numerical values of $Q_b$ using the two techniques? The most likely cause is the difference in spot-size of the two techniques. PPES uses a Xenon lamp source, which has a broad beam of 1 cm diameter, whereas the PTR technique uses a focussed beam of spot-size 100 $\mu m$. If the beam diameter is much less than the impurity (or defect) separation, the possibility of irradiating an area which does not contain an absorbing impurity center is very high. In such cases, we expect
that the $Q_b$ and $Q_s$ values will be highly dependent on the location that is irradiated.

5.12 Conclusions and Recommendations

The PTR time-domain boxcar detection technique can monitor nonradiative processes at laser material surfaces by detecting the IR emission from the material several microseconds after pulse cutoff. At these early times, we have also shown that this technique is totally insensitive to any changes in nonradiative bulk processes that might be occurring. PTR can also monitor nonradiative processes within the laser crystal bulk by detecting the IR emission from the crystal several milliseconds after pulse cutoff. At these late times, the heat generated in the bulk will dominate the total IR emission signal and therefore this technique is insensitive to any changes in nonradiative surface processes that might be occurring.

In the PTR technique, the front surface of the sample is irradiated, following which changes in the front surface are detected. Conversely, in the PPES technique, the front surface is excited whereas changes are detected at the back surface. This difference makes the PTR technique a more sensitive one than PPES, in addition to the fact that PPES requires two identical-quality samples of different sizes in order to deconvolute the bulk and surface contributions of the optical absorption. The PPES technique measures the optical absorption $\beta$ and the nonradiative energy conversion efficiency $\eta$ as a function of wavelength. This type of information could be useful for determining the types of defects that might be present in the crystal. However, to determine the total amount of nonradiative energy produced in the crystal, PTR is the more suitable technique. In terms of its applicability in an industrial setting, the PTR technique is a remote, non-intrusive technique that has the capability of evaluating laser material quality at any stage of the post growth process: after a boule is grown; after the boule is cut into smaller blocks; after the blocks are cut into laser
quality rods and are polished.

The best possible way to demonstrate the ability of the PTR technique to characterize nonradiative losses in laser crystals is to compare this technique with the standard method of evaluating laser crystal performance. The standard method involves testing the crystal in a laser cavity and measuring the output power as a function of input pumping power. In the next chapter, we describe the evaluation of laser materials using both these methods. We will show that there are several reasons why the PTR technique is superior to the standard method of laser crystal performance evaluation.
Chapter 6

Correlating PTR Data with Laser Cavity Performance

In this chapter, we evaluate the performance of solid-state laser materials using the standard method of laser crystal quality evaluation. We then compare this standard technique with the photothermal radiometry technique we used in the previous chapter, by evaluating the same samples using both techniques. We find a correlation in the results obtained using these two techniques. We also find that the photothermal radiometry technique has several advantages over the standard method of laser crystal evaluation.
The standard method used by laser crystal growers to evaluate laser crystal performance is to test the crystal in a laser resonator cavity and measure its output power for a given pump power. In the previous chapter, we proposed that the PTR technique can perform this very same function. By designing a laser cavity and evaluating the optical quality of the crystal using the standard method, we were able to verify the accuracy of the PTR data. We were also able to compare many aspects of the two techniques, such as experimental difficulty.

6.1 Objectives

The objectives of this work are

1. To correlate the PTR data (which gives a measure of the losses in the crystal) from Chapter 5 with laser cavity output performance, thereby verifying whether the PTR technique can be used as an alternative to the standard method of laser material performance evaluation.

2. To compare the relative difficulties of the PTR method with the standard method.

3. To demonstrate that PTR can be used to perform remote, in-situ testing of laser crystals with brewster surfaces.

6.2 Standard Method of Measuring Efficiency of Solid State Lasers

The standard method of measuring the efficiency of an optically pumped laser material in an operating laser cavity is to measure the slope efficiency. The slope efficiency is the slope of a
plot of the laser output power versus the input pumping power. We can write the following expression for the laser output power, $P_{out}$:

$$P_{out} = \eta_s(P_{in} - P_{th})$$  \hspace{1cm} (6.1)

where $P_{in}$ is the pumping power of the Ar-ion laser. $P_{th}$ is the threshold pumping power at which the gain exceeds the losses within the cavity and $\eta_s$ is a dimensionless proportionality constant relating the output power to the input power known as the slope efficiency.

Both $P_{th}$ and $\eta_s$ are used in traditional methods of laser performance characterization to quantify the performance of the laser. However, this approach has some drawbacks due to the very nature of the $P_{th}$ and $\eta_s$ parameters. Both these parameters give some indication as to the amount of "losses" in the system. The value of both $P_{th}$ and $\eta_s$ can be affected by both the losses in the material as well as the losses in the cavity. An overall analysis of the losses in a solid-state laser system shows [1] that

$$\eta_s = \eta_p \eta_c \eta_A (QE)$$  \hspace{1cm} (6.2)

where $\eta_p$ is the pumping efficiency, $\eta_c$ is the output coupling efficiency, $\eta_A$ is the mode cross-section efficiency and QE is the quantum efficiency. Of these four parameters, only $\eta_q$ depends on the laser material. The other efficiencies depend on how well the cavity is aligned. As a result, the slope efficiency may not be the best parameter to characterize crystal quality.
6.3 Design of Laser Cavity

In collaboration with Dr. Andreas Othonos (formerly of Ontario Laser and Lightwave Research Center), we designed and built a four mirror, folded cavity Ti: Saphire laser resonator to evaluate the laser output performance of Ti: Sapphire crystals. Figure 6.1 shows the layout of this laser cavity. We used an argon ion laser operating multiline (488 - 514 nm) as the pump source. Longitudinal (end) pumping is used to produce a region of uniform gain in the crystal.

This method of pumping is very efficient for solid state laser media because the pump beam and the lasing cavity mode are collinear over the entire length of crystal [108]. Due to the low absorption of Ti: Sapphire, it is necessary to provide a high pumping intensity into the Ti: Sapphire medium. Such pumping intensities can be achieved by tightly focusing...
the pump beam into the gain medium with the use of a pair of curved folding mirrors (radius of curvature = 10 cm). The brewster-cut laser rod introduces a significant amount of astigmatic distortion to the beam, which can severely affect the beam quality of the laser. To compensate for this astigmatism, the two curved folding mirrors used to concentrate the beam into the laser gain medium are tilted off-axis by an appropriate amount. The amount by which the mirrors are tilted depends on the length of the gain medium. The resonator is completed with a flat, 10 % transmission output coupler and high-reflecting flat mirror.

6.4 Laser Cavity and PTR Experiments

This section describes our attempts at correlating the photothermal radiometry data (which gives a measure of the thermal “losses” incurred in a laser material) with the traditional laser cavity data (which gives a measure of the optical “gain” or output in the laser material).

6.4.1 A Description of the Samples Tested

The primary difference between the laser crystal samples tested here and the samples evaluated in the previous chapter using photothermal radiometry is their geometry. The crystals evaluated in the previous chapter were cylindrical rods with flat, polished end faces. In their present geometry, these crystals cannot be used to produce a working laser. The end faces of crystals used in lasers must be cut at an angle known as Brewster’s angle. When light interacts with a material, some of the light will undergo reflection. The amount of light reflected varies with the angle of incidence of the light on the material. There is a critical angle known as Brewster’s angle at which the reflection losses are minimised. Since reflection losses can form a significant component of the total losses in a laser cavity, the laser rod must be cut and oriented in such a way that reflection losses are minimised.
We evaluated two brewster-cut laser rods, each having different surface and bulk properties in relation to the other. One of the crystals had a high bulk figure-of-merit and surfaces treated with the best available surface polish (polishing with 1 $\mu m$ diamond particulates followed by polishing with 0.25 $\mu m$ particulates). The other crystal had a lower bulk figure-of-merit and surfaces treated by polishing with 5 $\mu m$ diamond particulates.

### 6.4.2 Laser Cavity Experiments to Determine Slope Efficiency

We evaluated the performance of the two brewster-cut laser rods using the astigmatically compensated four mirror laser resonator described in section 6.3. For each crystal, we tuned the cavity to obtain lasing action after which we measured the power of the 650 - 1100 nm Ti: Sapphire laser output as a function of 488-514 nm Ar-ion input pump power. Figure 6.2 shows the input-output power curve for the two samples mentioned above. The figure shows that the slope efficiency of the crystal with the better quality bulk and the better quality surface is 28.0 % and the laser crystal has a threshold lasing power of 2.1 W, whereas the lower quality crystal has a slope efficiency of 12.1 % and a threshold lasing power of 2.7 W.

### 6.4.3 Radiometry Experiments to Determine Bulk and Surface Heating Losses

Following the laser cavity experiments which we used to measure the optical output of the crystals, we used photothermal radiometry to measure the thermal energy generated in the same two crystals, which contribute to the losses in the laser. For each crystal, we conducted both early-time and late-time radiometry experiments to characterize their surface and bulk properties. The transient early-time IR radiation emission is shown in figure 6.3, monitored in the 50 to 100 $\mu$s range.

The figure shows that the 5 $\mu m$-polished surface has a faster decay than the 0.25 $\mu m$
Figure 6.2: Output power versus input power for two brewster-cut laser rods, each having distinct surface and bulk properties.

polished surface. Upon fitting this data to the early-time theoretical model given by equation 5.81, we obtained the value of the surface non-radiative energy generation rate $Q_s$ from the fitting parameters, as described in section 5.10.1. For the high bulk figure-of-merit crystal with the 0.25 $\mu$m-polished surface, we obtained a $Q_s$ value of $0.175 I_o [W/cm^2]$ and the low bulk figure-of-merit crystal with the 5 $\mu$m-polished surface has a $Q_s$ of $0.221 I_o [W/cm^2]$. We have expressed these quantities as a function of the input optical intensity $I_o [W/cm^2]$.

To evaluate and compare the bulk heating properties of the two crystals, we conducted late-time measurements in the 0 to 10 ms range after pulse cutoff. Figure 6.4 shows the IR radiation emission profiles for the two samples: we observe a faster decay for the lower quality bulk.

Upon fitting these curves to the theoretical late-time expressions for the transient temperature evolution in the crystal given by equation 5.55, we obtain from the fitting parameters a value for the bulk non-radiative energy generation rate $Q_b$. For the high bulk figure-of-merit
Figure 6.3: IR radiation emission from a high bulk and surface quality laser rod and a low bulk and surface quality laser rod, measured in the early-time $\mu$s range where bulk effects are not felt and surface effects dominate. For a description of how each point on the graph is obtained, please refer to Appendix B.

crystal with the 0.25 $\mu$m-polished surface, we obtained $Q_s$ value of $0.11I_o$ [W/cm$^3$] and the low bulk figure-of-merit crystal with the 5 $\mu$m-polished surface has a $Q_s$ of $0.17I_o$ [W/cm$^3$]. We have expressed these quantities as a function of the input optical intensity $I_o$ [W/cm$^2$].

### 6.4.4 Evaluating the Effects of Surface Polish Improvements

Upon completing the entire set of measurements described in the two previous sections, the surface quality of the lower quality crystal was improved by polishing the crystal with the highest available grade of polishing (polishing with 1 $\mu$m diamond particulates followed by polishing with 0.25 $\mu$m particulates). We then conducted the laser cavity experiments and
Figure 6.4: IR radiation emission from a high bulk and surface quality laser rod and a low bulk and surface quality laser rod, measured in the late-time ms range where surface effects are not felt and bulk effects dominate. For a description of how each point on the graph is obtained, please refer to Appendix B.

The radiometry experiments with the new sample to study the effect of surface improvement in laser materials.

Figure 6.5 shows the output power as a function of input power for the crystal with the improved surface in comparison with itself before surface improvement and in comparison with the high quality crystal. Note that the improvement of the surface has improved the slope efficiency of the laser, but not to the point that the crystal is as good as the high bulk figure-of-merit crystal with the 28% slope efficiency. In other words, the crystal with the 28% slope efficiency has a better quality bulk and surface than the other crystal. Improvements in surface quality of the poorer crystal result in an improvement in slope efficiency to 17.5% from 12.1%. After this surface improvement, the difference between the crystal with
28% slope efficiency and the surface-improved crystal with 17.5% slope efficiency are due primarily to the differences in bulk quality.

We also conducted photothermal radiometry experiments of the crystal before and after surface polish improvements and compared these results with the laser cavity output data. Figure 6.6 shows the radiometric emission profiles for the low bulk figure-of-merit crystal before and after surface modification in the 50 to 100 µs time range. Upon curve fitting these results, we found that the surface energy generation rate $Q_s$ improved from $Q_s = 0.22I_o$ before surface treatment to $Q_s = 0.18I_o$ after surface treatment. This new value of $Q_s$ is very close to the value of $Q_s = 0.175I_o$ for the crystal that was originally polished with the highest quality process. Figure 6.7 shows the radiometric emission profiles for the low bulk figure-of-merit crystal before and after surface modification in the 0 to 10 ms range. Since
Figure 6.6: IR radiation emission from a low bulk quality laser rod before and after surface treatment, measured in the early-time $\mu$s range where bulk effects are not felt and surface effects dominate. For a description of how each point on the graph is obtained, please refer to Appendix B.

the bulk properties of the crystal do not change during the surface processing, we expect the bulk properties to remain unchanged. By curve fitting to obtain the bulk energy generation rate $Q_b$, we found that the $Q_b$ value after surface treatment is almost the same as the value before the surface was modified.

6.5 Discussion

The input-output power characteristics of the two laser crystals shown in figure 6.2 exhibit straight line behaviour except at higher powers, where the output power stops increasing linearly with input power. This deviation from linearity is due to the temperature dependence
Figure 6.7: IR radiation emission from a low bulk quality laser rod before and after surface treatment, measured in the late-time ms range where surface effects are not felt and bulk effects dominate. For a description of how each point on the graph is obtained, please refer to Appendix B.

of the radiative and nonradiative lifetimes, which we discussed in the previous chapter. At higher powers, the temperature of the crystal increases, promoting more nonradiative activity in the crystal. As a result, the laser output power ceases to increase linearly with input power.

Based on the experimental results described in the previous section, we are now in a position to compare the standard method of laser material characterization (i.e., the slope efficiency from laser cavity output measurements) with our alternative method of characterization via photothermal radiometry. There are three main reasons why PTR is a more suitable method of characterization:

1. In the standard method the measured parameter is the slope efficiency, which is an
“overall” efficiency parameter affected by the pumping efficiency, the output coupling efficiency, the mode cross-section efficiency and the material quantum efficiency. By comparison, photothermal radiometry gives a measure of the net nonradiative energy generated in the crystal, which is a more direct measure of the optical quality of the material as opposed to the overall efficiency of a laser resonator.

2. Given two crystals A and B, both the laser cavity output method and the photothermal radiometry method can tell us if A is “better” than B or vice versa. However, the laser cavity method cannot tell us why crystal A is better than crystal B. In particular, the laser cavity method cannot tell us if crystal A is better than B because it has a better quality surface, a better quality bulk, or both. Conversely, photothermal radiometry can evaluate the bulk and surface quality independent of each other from a single sample.

3. From the standpoint of laser material quality control, photothermal radiometry is a much more practical technique to use than the laser cavity approach. Having implemented both experimental systems in our laboratory, we observed the fact that the laser cavity is far more difficult to align and also far more sensitive to misalignment. We noted that there are about 10 different alignment knobs in the laser cavity to which the laser output is very sensitive. By comparison, the photothermal radiometry technique is only highly sensitive to one such alignment. Another practical issue relates to sample size. Using the laser cavity method, it is not very accurate to compare two samples of different sizes because the cavity parameters usually change. Conversely, we have applied the radiometry technique to samples of different sizes and their bulk and surface quality independent of their size.
Chapter 7

Application of Photothermal Techniques to Other Laser Materials

Having applied two photothermal techniques to study Ti: Sapphire laser materials, we now discuss how these techniques may be applied to other solid state laser materials. In particular we study two laser systems: the ruby laser (which is a transition metal atom) and the Nd$^{3+}$ laser (which is a lanthanide series atom). We then discuss the key issues involved in adapting these photothermal techniques to studying other laser materials.
Before speculating on how the photopyroelectric spectroscopy and photothermal radiometry techniques can be applied to other laser materials, we must briefly review the exact nature of the measurements we made using these two techniques.

A key point to note is that the nonradiative processes in a laser can be assumed to take place at two different time-scales. Relatively fast nonradiative processes take place when a higher vibrational state of the excited state manifold is reached, resulting in an increase in lattice vibrational energy that takes place on a time-scale much faster than the radiative lifetime. Relatively slower nonradiative processes take place when the atom is at the upper laser level. In Ti: Sapphire, the nonradiative emission that occurs at the upper laser level occurs on a time-scale estimated to be about 18 $\mu$s [8]. Such time scales are several orders of magnitude faster than the detection time scales involved in both photothermal radiometry (which detects thermal energy changes in the bulk of the laser material in the millisecond time range after the optical excitation) and photopyroelectric spectroscopy (which detects thermal energy changes in the material after modulated optical excitation at very low frequencies). As a result, both these techniques do not monitor specific nonradiative processes from specified energy levels. Instead, both techniques measure the total nonradiative energy released from all energy levels of the material. This measurement can ultimately yield the optical-to-thermal energy conversion efficiency $\eta_{NR}$ which can then yield the quantum efficiency $QE$ given the assumption that the energy level diagram and the branching ratios of transitions to various energy levels are well known. In the following two sections, we will speculate on how these two techniques can be used along with the energy level diagrams to obtain the quantum efficiency of the laser.
7.1 Nd:Glass Lasers

Consider the case of the rare-earth ion $Nd^{3+}$ doped into ED2 glass. ED2 glass is a lithium aluminum silicate glass [3]. Unlike the ruby and Ti: Sapphire lasers which have crystal hosts, the emission lines of ions in this laser are inherently inhomogeneously broadened due to the presence of the glass host. In an analysis of such a laser material, Quimby and Yen suggest that the energy-level structure of $Nd^{3+}$ is fairly independent of the host material [29]. The absorption bands shown in figure 7.1 [29] between levels $|5 >$ and $|6 >$ are optically excited by the pump laser.

Figure 7.1: Energy Levels in $Nd^{3+}$ ions doped into a ED2 glass host. The dashed lines indicate cross relaxation processes. The subscripts "r," "nr" and "x" indicate radiative, non-radiative and cross-relaxation processes respectively. $b_{ij}$ are branching ratios for transitions from $i$ to $j$.

These bands release energy via a nonradiative cascade down to the upper laser level $|5 >$. 208
The upper laser level fluoresces to the lower four levels with known branching ratios \( b_{54}, b_{53}, b_{52}, \) and \( b_{51} \). The upper laser level also decays nonradiatively by multiphonon processes with a transition rate \( W_{NR} \). At high Nd ion concentrations, there is another process involving the upper laser level \( |5\rangle \). This process is the cross-relaxation process as shown by the dashed lines in figure 7.1. Cross-relaxation involves two neighbouring ions, one initially in the excited state \( |5\rangle \) and the other in the ground state \( |1\rangle \). Cross-relaxation occurs when the ion in level \( |5\rangle \) drops down to the intermediate state \( |4\rangle \), while the other ion is simultaneously excited to level \( |4\rangle \). Once in this level, both ions will decay nonradiatively in a cascade to the ground state. The net result of such a cross-relaxation process is that the entire excitation energy of the excited ion has been converted to nonradiative energy. The decay rate for such a process \( W_X \) increases with concentration since ion-ion interaction processes increase with a decrease in the interionic distance.

We can use this energy level scheme to relate the quantum efficiency \( QE \) to the optical-to-thermal energy conversion efficiency \( \eta_{NR} \) (which we can measure for this material using photopyroelectric spectroscopy). Given the definition of \( \eta_{NR} \) as the ratio of the total amount of nonradiative energy generated per photon of energy absorbed, we can relate \( \eta_{NR} \) and \( QE \) for this material with the aid of figure 7.1. Due to the fact that the heat generating processes are dependent on concentration \( \mathcal{N} \), we define a concentration-dependent energy conversion efficiency

\[
\eta_{NR}(\mathcal{N}) = \frac{E_{55} + QE(\mathcal{N})[b_{54}E_{41} + b_{53}E_{31} + b_{52}E_{21}] + P_{NR}(\mathcal{N})E_{51} + P_X(\mathcal{N})E_{51}}{E_{61}} \quad (7.1)
\]

where \( E_{ij} \) is the energy gap between levels \( i \) and \( j \) and the radiative quantum efficiency is defined as

\[
QE(\mathcal{N}) \equiv \frac{W_R}{W_R + W_{NR} + W_X(\mathcal{N})} \quad (7.2)
\]
Also, the "nonradiative quantum efficiency" \( P_{NR} \) is given by

\[
P_{NR}(\mathfrak{N}) \equiv \frac{W_{NR}}{W_{R} + W_{NR} + W_{X}(\mathfrak{N})}
\] (7.3)

and the "cross-relaxation quantum efficiency" \( P_{X}(\mathfrak{N}) \) is given by

\[
P_{NR}(\mathfrak{N}) \equiv \frac{W_{X}(\mathfrak{N})}{W_{R} + W_{NR} + W_{X}(\mathfrak{N})}
\] (7.4)

The energy differences between levels \( E_{ij} \) and the branching ratios \( b_{kl} \) for the \( Nd^2^+ : ED2 \) glass system have been calculated by Krupke [29]. Using these values and equation 7.1, Quimby and Yen obtained a direct relation between \( \eta_{NR} \) and \( QE \):

\[
\eta_{NR}(\mathfrak{N}) = 1 - 0.52QE(\mathfrak{N})
\] (7.5)

Therefore, if we can obtain experimentally the parameter \( \eta_{NR} \) using either photopyroelectric spectroscopy or photothermal radiometry, we can then obtain the quantum efficiency by an analysis as shown above, making use of the particular energy level diagram of the particular ion-host system that makes up the laser material.

The lifetime of the upper laser level has been measured to be 300 \( \mu s \) [3]. The nonradiative lifetime is estimated to be 1.2 ms. The detection range to be used to monitor these processes using photothermal radiometry should then be on the order of 100 ms for this material. Conversely, using photopyroelectric spectroscopy at low (9 Hz) frequencies will also ensure that the nonradiative energy measured is due to a summation of nonradiative de-exitations from all energy levels.
7.2 Ruby Lasers

The Ruby laser is a transition metal solid state laser consisting of $Cr^{3+}$ ions doped into a sapphire host [109, 110]. A simplified energy level diagram of ruby is shown in figure 7.2 [33]. In a ruby laser, population inversion is obtained by optically pumping $Cr^{3+}$ ions from the ground state $|0 >$ to the broad pump bands represented in the diagram by the levels $|4 >$ and $|3 >$. The two pump bands are located in the green and the violet region of the spectrum and have extremely short lifetimes, compared to the lifetimes of levels $|2 >$ and $|1 >$.

![Energy Level Diagram](image)

Figure 7.2: Energy Levels in a Ruby laser. The superscripts "r" and "nr" refer to radiative and nonradiative components of the transition rate $W_{ij}$ from level $i$ to $j$.

The two transitions from these two levels to the ground level provide fluorescence but laser action only occurs on the $1 \rightarrow 0$ transition. We make the following assumptions about this system [33]:

1. All upward transitions are negligible compared to the downward transitions.

2. The decay out of level $|3 >$ is dominated by nonradiative decay to level $|2 >$. In heavily
doped ruby, it has been reported that $|3\rangle$ may indeed de-excite to the ground state directly. Therefore, this assumption is only valid for materials of low concentration.

3. The decay out of level $|2\rangle$ is dominated by nonradiative decay to level $|1\rangle$.

For the above assumptions, we may write an equation relating the optical-to-thermal energy conversion efficiency $\eta_{NR}$ to the quantum efficiency $QE$:

$$\eta_{NR} = \frac{b_{43}[E_{43} + E_{32}] + b_{42}E_{42} + E_{21} + (1 - QE)E_{10}}{E_{40}}$$  \hspace{1cm} (7.6)

where the quantum efficiency is

$$QE = \frac{W_{10}^r}{W_{10}^r + W_{10}^\tau}$$  \hspace{1cm} (7.7)

and the branching ratios are defined as

$$b_{43} = \frac{W_{43}}{W_{43} + W_{42}}$$  \hspace{1cm} (7.8)

and

$$b_{42} = \frac{W_{42}}{W_{43} + W_{42}}$$  \hspace{1cm} (7.9)

We can therefore use equation 7.6 to relate our measured value of $\eta_{NR}$ using either of the two photothermal techniques to the quantum efficiency. With regard to the timescales used in photothermal detection, we note that the radiative lifetime of ruby is $3\ ms$ and the nonradiative lifetime has been estimated to be on the order of $10\ ms$. In this situation, we expect that the detection of these processes can be accomplished by using a low frequency photopyroelectric detection or using photothermal radiometry in the $100\ ms$ to $1\ s$ range.
7.3 Key Issues to Consider When Evaluating Other Materials

Absorption Coefficient Spectra

For a given laser material, it is important to know the absorption spectra in the range of wavelengths associated with the optical pumping of the material. This data will allow the experimenter to select a pump laser wavelength to excite the laser crystal in the photothermal radiometry experiment.

Fluorescence Spectra

The spectral variation of the fluorescence emission must also be known. This information has to be obtained independently. In the photopyroelectric spectroscopy experiment, the spectral fluorescence emission range is important since the absorption spectra (due to both surface and bulk absorptions) must be measured in this range using PPES to determine if residual absorption in the fluorescence emission range is significant.

The fluorescence emission range is also a key issue in the photothermal radiometry experiment. If the fluorescence emission spectrum overlaps the spectral range of the infrared detector, the measured signal will then be due to a combination of radiative emission and phonon-induced thermal (IR) emission, thus complicating the analysis of the data obtained. This problem is most likely for materials exhibiting fluorescence in the near infrared range. It is advisable to work with a detector that has a low-wavelength cutoff of about 10 \( \mu m \).

Fluorescence Lifetime

The fluorescence lifetime of the material is an important parameter since it allows the determination of the lifetime of the laser transition, given that the quantum efficiency is also known. However, in terms of either the photothermal radiometry technique and the photopyroelectric technique, it is the magnitude of the nonradiative lifetime that affects the
time-scales over which the measurements are performed. For example, suppose we have a material with a fluorescence lifetime on the order of microseconds and another material with a lifetime on the order of milliseconds. In both cases, the factors that determine the time-scales over which the photothermal radiometry measurements are performed are: 1. the nonradiative lifetime of the slowest of all nonradiative transitions in that particular material. 2. the lattice energy diffusion time of the crystal. If the nonradiative processes are very fast compared to the detection time-scales, the time it takes for the thermal energy released within the crystal to diffuse to the surface becomes the primary determining factor of the time-scale involved in photothermal radiometric detection.

**Ion Concentration**

Although the experimental approach does not change for materials with a high ion concentration, the analysis and interpretation of the data is greatly complicated by the fact that ion-ion interaction processes occur. In general, we will be unable to compare two crystals of different concentration because of the fact that the competition between radiative and nonradiative processes will vary with ion concentration. In some simple cases, such as the \( \text{Nd}^{3+} \) ion doped into ED2 glass that we discussed above, we see that the cross relaxation process ultimately leads to a nonradiative de-excitation. In this case, Quimby and Yen dealt with this problem by simply looking at the net result of this process, which is that the ion in the excited state decays to the ground state nonradiatively. In the case of only one type of ion-ion interaction process, an accurate analysis is possible. But for materials with high ion concentration, independent information on the types of ion-ion interactions is needed to analyze the data obtained using the two photothermal experiments.

**Site Selection**

Another issue that will affect how the photothermal experiments are performed is whether or not the material is inhomogeneously broadened. If the active ions in the material are
distributed among sites which are subjected to varying degrees of perturbation from the surrounding crystal, the quantum efficiency of the ion will be dependent on the particular site it occupies. In the case of Nd$^{3+} : ED2$Glass which we discussed above. Quimby and Yen [29] discuss the fact that the quantum efficiency of an Nd ion depends on the particular type of site that it occupies in the glass and varies by about 35 % over all the sites. Thus, if most of the types of sites are excited, the measured $\eta_{NR}$ and subsequently the $QE$ will be an average over all the sites. If a narrow-band laser is used in the photothermal radiometry experiment on a inhomogeneously broadened material, some sites will be preferentially excited over others. In such cases, different excitation wavelengths will give rise to different combinations of excited sites and consequently to different measured values of $\eta_{NR}$. In the case of photopyroelectric spectroscopy, the problem of site selection can cause some difficulty when the spectral data is analyzed, since it will be difficult to interpret whether the changes in $\eta_{NR}$ are due to changes in one particular ion or due to the fact that ions in different types of sites are excited at different wavelengths.

**Excited-State Absorption**

An effect we have not considered is excited state absorption from the upper laser level to higher states. Although not present in Ti: Sapphire, these effects are present in materials such as heavily doped ruby and $Cr : LiCaAlF_6$ [29, 47]. Such effects limit the useful power emitted by the laser. To avoid having to include such effects in our analysis, it is important to ensure that optical intensities used in the photothermal experiments do not approach the nonlinear limit. This effect has been shown to be nonlinear in the incident light intensity, since it depends on the population of the upper laser level. One way of ensuring that such effects are not significant is to vary the input power and see if the resulting photothermal signal is linear with input power.
Chapter 8

Overall Conclusions

8.1 Thesis Summary

The three main sections of this project (namely, photopyroelectric spectroscopy (PPES), photothermal radiometry (PTR) and laser cavity experiments) have each played a key role in determining the approach that should be taken to monitor non-radiative processes in solid-state laser materials. The results of the PPES technique have clearly established the fact that surface non-radiative processes, which were previously thought to have a negligible effect on the overall crystal quality, may be (especially in the case of high bulk quality crystals) the key factor limiting the overall crystal quality.

The PTR technique has the capability of yielding the bulk non-radiative energy generation rate and the surface non-radiative energy generation rate in the same experimental configuration. Because of its remote, non-contact nature, the PTR technique is also capable of monitoring the quality of a laser crystal under the exact conditions that the laser material is intended to operate in. In other words, the pump source used in the PTR experiment can be changed to whatever source that the material is pumped by when it operates as a solid-state laser.
We have shown that the standard method of laser crystal quality evaluation (ie: the laser cavity experiments to determine slope efficiency) cannot give a measure of the losses due to the laser material *only*. Since the slope efficiency is dependent on the cavity arrangement, this technique is limited in that one cannot compare two laser crystals of different sizes, which may be being used in two different cavities. Furthermore, these techniques cannot give any insight into *why* a particular material is poorer than another one. While these techniques may provide adequate information to a person using a laser for some application, they are unable to provide laser crystal growers with enough information about the grown crystals. A key requirement for the improvement in crystal growth processes and the growth of better quality laser materials is the establishment of a technique such as PTR, which can give the crystal grower useful information about both the sources of non-radiative energy conversion and their relative contributions to the overall losses in a crystal.

One of the limitations of these two techniques is the fact that in their present form, they are unable to monitor nonradiative processes from a particular level that may be of interest. Instead, these techniques detect a signal proportional to the sum of all nonradiative processes occurring from all levels in the detection time-scale. To be able to make a conclusion about a specific transition rate from a single level using data obtained from these photothermal techniques, we require additional information in the form of luminescence spectra and lifetimes of relevant energy levels, along with details of the energy level diagram for that particular material.

A valuable extension of the photothermal radiometry work we have presented here would be to perform spectrally distributed measurements of the infra-red radiation emission from a laser crystal in response to a pulse of a given duration. If it were possible to perform a wavelength-scan of the infrared emission from a laser material in the 2 to 20 µm region and further to perform such a wavelength scan at short and long times after pulse cutoff, it would
be possible to obtain more information about the nature of the nonradiative processes that dominate in both the bulk and the surface. By performing IR wavelength-scans at various time-scales, it may also be possible see features in the IR emission spectra at particular time-scales that do not appear at other time-scales. It may then be possible to identify both the lifetime and the energy differences involved in specific nonradiative transitions.

8.2 Contributions of This Work

We have extended the photopyroelectric spectroscopy technique to a noncontact method. The advantage of this modification is two-fold. First, a noncontact measurement eliminates the need to account for thermal resistances and eliminates one of the most significant sources of uncertainty in conventional photopyroelectric spectroscopy in the contact mode. Second, the noncontact form of photopyroelectric spectroscopy allows detection in two modes (optical transmission mode and thermal mode) such that optical absorption and nonradiative de-excitation phenomena can be measured self-consistently using the same technique. The significance of this modification to noncontact form has been noted by Chirtoş et al [111] in a review of photopyroelectric detection.

The key result obtained using photopyroelectric spectroscopy is the variation of the nonradiative energy conversion efficiency \( \eta_{NR} \) with excitation wavelength. Although \( \eta_{NR} \) has been measured previously for Ti: Sapphire using other methods, most of the data have been obtained for either a single excitation wavelength or for three or four specific wavelengths. The experimental determination of \( \eta_{NR} \) has allowed researchers involved in developing quantum mechanical models of nonradiative processes in solid state lasers to fit their model to this data [62]. As opposed to the other techniques used to measure \( \eta_{NR} \) in solid state lasers which require additional independent information such as the optical absorption coefficient,
this technique measures both the optical absorption coefficient and the nonradiative energy conversion using the two modes of detection. Finally, the results obtained using photopyroelectric spectroscopy has shown that in any experiment related to the measurement of nonradiative de-excitation phenomena, the nonradiative processes at the surface must be accounted for.

Because of the significant contribution to the total nonradiative energy released by a solid state laser material, we have used the photothermal radiometry technique to detect surface and bulk nonradiative processes simultaneously by monitoring nonradiative processes occurring at different time-scales. We have shown that in some instances, the presence of heat-producing surface defects is the key factor limiting the maximum laser output that a material can provide.

8.3 Relevance of Parameters Measured in this Work

The photopyroelectric spectroscopy technique yields the optical-to-thermal energy conversion efficiency $\eta_{NR}$ of a solid state laser material. This parameter is a ratio of the total nonradiative energy released to the total optical energy absorbed. The total amount of heat released by a laser material is a useful parameter in that it gives a measure of the degree to which several temperature dependent effects (such as birefringence) are present in a particular material. From the standpoint of the lasing process, the quantum efficiency is clearly a more useful parameter than $\eta_{NR}$ since the quantum efficiency deals with the laser transition, whereas $\eta_{NR}$ takes into account all nonradiative de-excitations. However, as we have shown in chapter 7, the knowledge of $\eta_{NR}$ along with knowledge of the lifetime of the upper laser level and the energy level diagram of the particular laser material can allow the determination of the quantum efficiency.
The photothermal radiometry method allows the determination of the nonradiative surface and bulk energy generation rate using the same method. The results obtained using photothermal radiometry are more useful to crystal growers who want to know the defect concentration of materials they have grown than to researchers developing new lasers who require parameters such as the upper laser level lifetime and the quantum efficiency. The primary application of the photothermal radiometry method therefore is to determine the overall heat generation rate due to both the presence of growth defects as well as the nonradiative processes intrinsic to the particular laser material under study. This technique has the capability to be a quality control tool for crystal growers, allowing them to quantify the effects of varying different growth and processing parameters and thereby allowing the crystal grower to optimize the growth process.
Bibliography


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Appendix A: PPES Data Acquisition

In a photopyroelectric spectroscopy (PPES) experiment, each data point on a given spectra is obtained as follows. Each point on the $\beta(\lambda)$ and $A_{\tau}(\lambda)$ spectra correspond to a reading at a particular wavelength of the pyroelectric detector signal with the detector in either the optical transmission mode or the thermal mode. At each wavelength, the data acquisition system obtains eight readings of the pyroelectric detector signal via the lock-in amplifier’s in phase and out of phase channels. These eight readings are acquired one second apart. Each data point therefore represents an average value of the raw data, with the error bars representing the standard deviations.

In the case of the $\eta_{NR}^{(b)}$ spectra, each point represents the result of solving for the General Pyroelectric Equation given in chapter 4 for $\eta_{NR}^{(b)}$. The raw data used to calculate $\eta_{NR}^{(b)}$ at each point are the average values (averaged over eight readings at each wavelength) of the in phase and out of phase signals measured by the lock-in amplifier in the optical transmission and thermal mode. The error bars represent the reproducibility as measured using the sooted silicon wafer.
Appendix B: PTR Data Acquisition

In a photothermal radiometry experiment, each data point on a given transient infrared emission profile is obtained as follows. At a given time after pulse cutoff, each point on the graph represents the average value of the signal measured by the open gate over 10,000 cycles. The data acquisition program was written in such a manner that after a specified number of samples were obtained at one particular location in time, the averaging process will be repeated if the signal to noise ratio does not exceed a specified amount. In this case, the signal to noise ratio we specified was 100 for the early-time measurements. Therefore each point on the transient profile has been obtained with a signal to noise ratio of at least 100. The error bars represent standard deviation values that are 100 times smaller than the mean value.

The late time measurements do not have error bars because of their extremely high signal to noise ratios (typically, over 500). Such high ratios are due to both the high degree of sampling as well as the high PTR signals measured at the low frequencies use for late time measurements.